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Novel Techniques and Standards for X-ray Spectrometry and Tests of QED

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Submitted in total fulfilment of the
requirements for the degree of

Doctor of Philosophy

School of Physics
The University of Melbourne
Australia

September 21, 2016

THE UNIVERSITY OF MELBOURNE

Abstract

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This thesis advances the standards and techniques used in x-ray spectrometry for laboratory sources and advanced sources, such as Electron Beam Ion Traps (EBITs). This impacts upon popular fields including x-ray diffraction, x-ray absorption spectroscopy and advanced quantum mechanics. A new method of removing cosmic ray signals from CCD detectors in a low flux environment is presented. New characterizations of Ti $K\beta$ and V $K\beta$, to be used as calibration standards, are presented. Preliminary measurements of lines of He-like Cr lines were performed to test QED.

Different types of x-ray spectrometry are important in fields such as testing Quantum Electrodynamics (QED) in the x-ray regime and the study of the local environment of atoms in the solid state through X-ray Absorption Fine Structure (XAFS). Tests of QED require highly accurate and precise determination of x-ray energy from low flux sources, while advances in XAFS studies require the ability to properly determine the validity of results. This research develops techniques and standards in spectrometry for use in XAFS and tests of QED. Further, these techniques are used to test QED.

The previous standard method of fitting XAFS did not use measured uncertainties, thus they could not be propagated to the results. Fitting via the minimisation of the statistically valid χ_r^2 measure of goodness of fit enables error bars to be propagated. A statistically valid χ_r^2 measure of goodness of fit was applied to the previous standard method of XAFS fitting. This improvement also allowed for a more robust interpretation of XAFS fitting parameters and the testing of XAFS theory. This new fitting method was applied to the K-edge XAFS of molybdenum. It was found that the XAFS theory and experiment were inconsistent with each other. New theory is necessary.

CCD detectors in a low flux environment have been used for tests of QED. In such situations, distinguishing between signal caused by cosmic rays and a low flux of x-ray photons from the desired source would enable higher precision tests of QED. This work presents a new method of removing the signal caused by cosmic rays from x-ray CCD detector spectra.

A new method of calibrating a Johann curved crystal spectrometer is presented, and used to create new characterizations of Ti $K\beta$ and V $K\beta$. These characterizations can be used for the calibration of x-ray spectrometers employed for tests of QED. The V $K\beta$ peak energy was found to be 5426.962(15) eV. This is an improvement in uncertainty by a factor of 4.7 over prior work. The Ti $K\beta$ peak energy was found to be 4931.966(22) eV, an improvement in uncertainty by a factor of 2.6 over the previous best reported result. The limits of the calibration method were tested by measuring Cr $K\beta$, which was on the limit of the calibrated energy range.

Preliminary measurements of the w , x , y and z lines of He-like Cr were performed to test QED. The w line energy was measured to be 5682.049(30)(200) eV, a factor of just under two improvement over previous measurements. The energies of the x , y and z lines were found to be 5664.425(73)(200) eV, 5654.232(68)(200) eV and 5626.305(42)(200) eV respectively. These energies had not previously been measured.

I, Lucas Smale, declare the following statements.

- This thesis comprises original work of the author towards the Doctor of Philosophy except where indicated in the preface.
- Due acknowledgement has been made in the text to all other material used.
- This thesis is fewer than the maximum word limit in length, exclusive of tables, maps, bibliographies and appendices.

Signature:

Preface

This thesis improves standards and techniques used in x-ray spectrometry. It contains a description of four broad experimental studies involving detailed analysis and one analysis of previously existing data. Each experimental study entailed the collaboration of at least three people. The present author was responsible for analysis and interpretation of all data and also for various aspects of the experimentation itself. The overall program of research was implemented under the direction of Prof. Chris Chantler who also supervised the present thesis. The responsibility taken by the present author in respect of each of the experimental studies is evaluated below.

(a) The CCD cosmic ray removal data was taken at the NIST EBIT at Gaithersburg, Maryland in 2005. The present author contributed roughly 10% to the data collection. Conceptualisation, design and preparation of the data collection was undertaken by others.

(b) The experiment to determine the calibration of the clinometers was undertaken at the University of Melbourne School of Physics in 2006. Roughly 10% of the design, 90% of the preparation and 100% of the experiment was undertaken by the present author. Within the preparation, 95% of the software used to run the experiment was written by the present author. The balance of the work was done by others.

(c) The Backgammon detector performance experimental studies were undertaken at the University of Melbourne in 2006. Roughly 30% of the design, 90% of the preparation and 100% of the data collection for this experiment was undertaken by the present author. Within the preparation, 95% of the software used to run the experiment was written by the present author. The balance of the work was done by others.

(d) Data collection for the spectrometer characterization and $K\beta$ lines study was performed at the Oxford EBIT at the Clarendon Laboratory, Oxford University in 2007. Roughly 10% of the design, 30% of the preparation and 25% of the data collection for the this experiment was undertaken by the present author. Within

the preparation, 95% of the software used to run the experiment was written by the present author. The balance of the work was done by others.

The modification of the XAFS analysis package that allowed a more accurate analysis was the basis for the honours thesis of the present author in 2004. This modification was carried out prior to enrolment in the Doctor of Philosophy.

All figures were created by the present author. Figure 5.6 is based on Figure 2.1 of Ezekiel [1].

Acknowledgements

This thesis was completed with the support of many people. I would like to acknowledge the meaningful contributions of the following people:

- Professor Christopher Chantler, my supervisor, whose guidance and support have been instrumental.
- Associate Professor Roger Rassool and Professor Les Allen, the balance of my supervisory panel, whose advice and care gave some much needed perspective to the enterprise.
- Justin Kimpton, whose expertise and practical support was much needed in building and performing experiments, both in Melbourne and overseas.
- The students Andrew Payne, Alexis Illig and Mark Kinnane, who were all directly involved in many aspects of the experiments and helped me think through the research.
- David Crosby, who enabled and supported the experiment in Oxford.
- The team at the NIST EBIT experiment, especially Larry Hudson, who encouraged my involvement in CCD data analysis.
- My family and friends for moral support.

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Abbreviations

EM	E lectro M agnetic
QED	Q uantum E lectro D ynamics
XAFS	X -ray A bsorption F ine S tructure
XANES	X -ray A bsorption N ear E dge S tructure
EXAFS	E xtended XAFS
SRO	S hort R ange O der
LRO	L ong R ange O der
DAFS	D iffraction A nomalous F ine S tructure
SCF	S elf C onsistent F ield
CSF	C onfiguration S tate F unction
MCHF	M ulti C onfiguration H artree F ock
MCDF	M ulti C onfiguration D irac- F ock
CCD	C harge- C oupled D evice
LIVS	L ow- I nductance V acuum S park
XFEL	X -ray F ree E lectron L aser
ECRIS	E lectron- C yclotron R esonance I on S ource
EBIT	E lectron B eam I on T rap
FWHM	F ull W idth at H alf M aximum
NIST	N ational I nstitute of S tandards and T echnology
BC	B ase C linometer
CC	C rystal C linometer
DL	D etector L ower clinometer
DU	D etector U pper clinometer
PXSM	P ossible X -ray S ignal M ask
PCRM	P ossible C osmic R ay M ask

Summary

Advances in x-ray spectrometry are needed in many areas. Increases in the precision and accuracy of x-ray spectrometers enable better tests of Quantum Electrodynamics. Better spectroscopic measurements of characteristic radiation may lead to deeper understanding of relativistic atomic physics. Better analysis of X-ray Absorption Spectroscopy (XAS) data through X-ray Absorption Fine Structure (XAFS) fitting can produce robust structural information about many disorder quantum systems. This thesis presents a set of advances in x-ray spectrometry that impact on these areas.

Topics in x-ray spectrometry are introduced in Chapter 2. The theoretical development of diffraction crystallography is summarised. The standard method of XAFS is presented. Characteristic spectra are introduced and then examined as calibration spectra for x-ray spectroscopy. The removal of cosmic ray noise on x-ray CCD sensors as used in spectroscopic experiments is explored.

Chapter 3 examines the theoretical and experimental development in atomic physics and how x-ray spectroscopy has contributed to that effort. In particular, it shows the use of spectroscopy of hydrogen-like and helium-like ions as a test of QED and the development of spectroscopy of characteristic spectra.

Chapter 4 develops ideas in the previous chapters into research questions. It then introduces the studies that were done to explore these questions. There were four fields of enquiry. The first field was the improvement of XAFS analysis via the introduction of an accurate χ_r^2 measure of goodness of fit to IFEFFIT, the most popular XAFS analysis package. The second field was computational techniques to remove cosmic ray signals from low-flux x-ray spectroscopic data in order to increase the precision of such data. The third field was the modelling of dispersion of x-rays in an adjustable curved crystal spectrometer in order to produce a spectrometer calibration. This involved studies to calibrate the detector subsystem and the clinometry subsystem of the spectrometer as well as the creation of

better spectroscopic standards for V $K\beta$ and Ti $K\beta$ that can be used in spectrometer calibration. The fourth field was testing QED through spectroscopy of highly charged ions. This involved the measurement of the w , x , y and z lines of He-like Cr.

Chapter 5 describes the options for the equipment that could have been used in the four fields of enquiry. It then describes the equipment and experimental setups that were used in the studies that were undertaken. The study in the first field used high quality mass attenuation coefficient data from the literature and therefore no experimental setup was needed. The setup for the study in the second field was an EBIT (a low flux source) with spectrometer and CCD detector at NIST. For the study in the third field, detector calibration was done using a rotating anode source and a double flat crystal diffraction setup to produce a line of $K\beta$ radiation. The inclinometers were calibrated by rotating them on a goniometer and measuring their response. The dispersion of the spectrometer system was examined by measuring its response to a set of standard characteristic radiation spectra produced via an x-ray tube. The study in the fourth field used the spectrometer system that was characterised in the third study.

Chapter 6 presents a modification to the XAFS analysis package, IFEFFIT, to include a more accurate χ_r^2 measure of goodness of fit. This was then applied to the most accurate mass attenuation coefficient data in the literature.

In Chapter 7, a study of the robustness of a linear correlation method to discriminate cosmic ray events from x-ray events in x-ray CCD detectors for low flux sources was presented. The method is found to be useful in conjunction with a previous cluster filtering method.

The spectrometer system used to study spectrometer dispersion and measure Ti and V $K\beta$ spectra is a Backgammon detector. Chapter 8 presents an experimental study of the responses of the detector to x-ray intensity and x-ray position. A method of linearising the positional response is then presented.

Clinometers were used in the Oxford 2007 experiment. Chapter 9 presents a calibration of these clinometers.

Chapter 10 describes a method of calibrating the spectrometer system used at the Oxford 2007 experiment.

Chapter 11 presents the most accurate characterisation of the V $K\beta$ spectral line to date.

Chapter 12 presents the most accurate characterisation of the Ti $K\beta$ spectral line.

Chapter 13 studies the robustness of the dispersion analysis method leading to a spectrometer calibration by applying the method at the limits of the calibration. This involved characterising the collected Cr $K\beta$ spectral line which is at the expected limit of the spectrometer system calibration.

Chapter 14 presents a study of the w , x , y and z lines of He-like Cr leading to tests of QED. Preliminary results are reported.

Chapter 15 presents the conclusions of the research. It then suggests further work.

The Development of Standards for X-ray Science

Radiation may be defined as any general process involving the dispersion of concentrations of energy into surrounding space. It has been studied since the time of Aristotle, if not before [2, 3]. Radiation can be mediated through a range of substrates. Each substrate that can support radiation has local degrees of freedom with associated energy and a local coupling between the degrees of freedom. The electromagnetic (EM) field is a prototypical substrate for radiation. Maxwell's equations provide a theory of EM radiation for fields with high intensity. Quantum Electrodynamics (QED) is the current theory for describing EM radiation and its interaction with electric charge. QED develops the idea that the EM field is quantised. In QED, the EM field can be thought of as a set of harmonic oscillators, one for each wave vector and polarisation. This leads to the conception that quantum excitations of these oscillators are particles, that is to say, photons.

By convention, x-ray radiation is the set of EM waves with frequencies above about 10 PHz (below 3 nm wavelength) [4]. This means that x-ray photons have energy above about 400 eV. Standards in x-ray science are critical for the scientific method as applied to x-rays, and for the replication of results between x-ray labs, thus forming a basis upon which x-ray science can be advanced.

This chapter discusses standard techniques developed in x-ray science. It begins with a brief consideration of x-ray spectrometry and diffraction crystallography. The growth of X-ray Absorption Spectroscopy and X-ray Absorption Fine Structure is then discussed. This is followed by a review of the use of characteristic radiation as a source of energy standards for x-ray spectrometry, particularly as used in tests of QED. Finally, the need for filtering out cosmic ray signals from data taken from CCD detectors in low x-ray flux experiments, such as tests of QED, is examined.

2.1 X-ray Spectrometry

The spectrometry of x-rays concerns the study of the strength of x-ray processes across a continuous range of x-ray energies. Key processes of interest are emission, scattering and absorption of x-rays. The changing strengths of these processes with energy make the separation of the continuity of energies critical to this study. The separation allows the observation of continuous x-ray energy profiles of these processes. Observations such as these lead to characterisation of phenomena such as emission resonances localised in energy. The major technique for high precision and accuracy x-ray spectrometry is that of x-ray diffraction crystallography.

2.2 The Basic Principle of X-ray Diffraction Crystallography

X-ray diffraction provides an important way to examine crystal structures, since diffraction by a crystal strongly depends on its structure as well as the x-ray wavelength being diffracted. With a sharp diffraction resonance, a crystal can physically separate and measure a continuum of x-ray energies. Such a use of diffraction is the basis for x-ray spectrometry, where x-ray energy measurement is a major goal. It is useful to understand how this field developed from Bragg's law [5] to dynamical diffraction in perfect crystals, to dynamical theory applied to crystals with some disorder, and finally to curved crystals.

The macroscopic version of Maxwell's equations, first published in 1865 [6], are a useful starting point for understanding any linear optical phenomenon, including diffraction. These differential equations assume that the charge and current can be divided into a free component that is the result of macroscopic motion of charges, and a bound component that is the result of microscopic motion of charges [7]. This version of Maxwell's equations is:

$$\nabla \cdot \mathbf{D} = \rho_f \quad \nabla \cdot \mathbf{B} = 0 \quad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad \nabla \times \mathbf{H} = \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t} \quad (2.1)$$

where ρ_f is the free charge density, $\mathbf{J}_f$ is the free current, $\mathbf{E}$ is the electric field, $\mathbf{B}$ is the magnetic induction, $\mathbf{D}$ is the electric displacement and $\mathbf{H}$ is the magnetic field.

$\mathbf{D}$ and $\mathbf{H}$ are defined by

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \quad \mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M} \quad (2.2)$$

in terms of $\mathbf{P}$, the polarization field and $\mathbf{M}$, the magnetization field. $\mathbf{P}$ and $\mathbf{M}$ are defined by the bound charge ρ_b and bound current $\mathbf{J}_b$ with

$$\rho_b = -\nabla \cdot \mathbf{P} \quad \mathbf{J}_b = \nabla \times \mathbf{M} + \frac{\partial \mathbf{P}}{\partial t} \quad (2.3)$$

It is also useful to define the dielectric function ε , the permeability μ and the susceptibility χ by

$$\mathbf{D} = \varepsilon \mathbf{E} \quad \mathbf{H} = \frac{1}{\mu} \mathbf{B} \quad \varepsilon = \varepsilon_0(1 + \chi) \quad (2.4)$$

Diffraction of x-rays by regular arrays of atoms (crystals) can be understood in two ways. The first is through kinematic theory, where power is taken out of the incoming beam and transferred to the diffracted beam. The second is dynamical diffraction theory, where the power from the diffracted beam is transferred back into the mode of the incoming beam inside the crystal and back again. This forms a stable mode consisting of both the incoming and diffracted waves inside the crystal. Both of these types of theory predict an intense diffracted beam when radiation scattered off successive planes of atoms constructively interfere.

Kinematic theory can predict diffraction angles well, but does not predict the diffracted intensities or diffraction profile shapes. The most basic understanding of diffraction from kinematic theory is Bragg's Law [5]:

$$n\lambda = 2d \sin(\theta) \quad (2.5)$$

where n is the order of the diffraction, λ is the wavelength of the radiation, d is distance between atomic planes and θ is the angle between an atomic plane and the incident rays. The diffracted rays also make an angle of θ with an atomic plane, and they lie on the plane formed by the incident rays and the normal vector to the atomic planes. θ is otherwise known as the diffraction angle or the Bragg angle.

Dynamical diffraction theory started with Darwin [8, 9] in 1914 by considering diffraction to be an optical problem. It was assumed to be the result of radiation reflecting off each layer of atoms that make up the diffraction planes, and then allowing that any reflected intensity can be reflected again. Darwin found that for a small range of angles near the Bragg angle, the diffracted intensity was much greater than absorption. In this range, as the wavefield moved into the crystal, the intensity of the wavefield was reduced by diffraction much faster than it was reduced by absorption (which was thus neglected). The width of this angular range came to be known as the Darwin width, while the characteristic depth of the extinction of the wavefield came to be known as the extinction length. An important correction to Bragg's Law is due to the average refractive index of the crystal. This correction is often of the order of 100-160 parts-per-million (ppm) in λ [10].

Ewald [11] in 1916 and von Laue [12] in 1931, successfully developed another approach to diffraction that is now the basis for the most common forms of dynamical diffraction theory today. These forms of theory result from finding single frequency solutions to the macroscopic Maxwell's equations where the dielectric function has a frequency dependence and is periodic, or nearly periodic, in space and time [13]. Common assumptions are that the free current and magnetisation are negligible. This approach led to the basic equation in dynamical diffraction:

$$\nabla \times \nabla \times \left[\frac{\mathbf{D}}{\epsilon_r} \right] = -\frac{1}{c^2} \frac{\partial^2 \mathbf{D}}{\partial t^2} \quad (2.6)$$

where $\epsilon_r = \epsilon/\epsilon_0$ and $c = 1/\sqrt{\epsilon_0\mu_0}$ is the speed of light in a vacuum [14]. The dielectric function is created by assuming that the polarisation is caused by the electrons in the crystal, which form a continuous charge distribution. The charge density at each point is then assumed to follow a classical equation of motion involving the single frequency electric field. The resulting infinitesimal motion of the charge density leads to a bound current that is integrated to get the polarisation proportional to the electric field. From this, a derivation of the dielectric function is clear. The remaining choices in the theory are what equations of motion an infinitesimal point charge of charge density is assumed to obey. The simplest choice is that of a free charge. Anomalous dispersion is included by adding restoring forces with damping terms where the natural frequencies of the restoring forces are the frequencies of the allowed quantum mechanical transitions of the electrons (Zachariasen [14]). Zachariasen focused on diffraction by an absorbing periodic

crystal with finite thickness and infinite extent, though some of these assumptions about the crystal were dropped later.

Zachariasen [14] proceeded as follows. Ideal crystals have a periodic lattice structure. Thus the susceptibility must be a periodic function of space and could be represented by a Fourier series

$$\chi = \sum_H \chi_H e^{i2\pi \mathbf{B}_H \cdot \mathbf{r}} \quad (2.7)$$

where $H = (h_1, h_2, h_3)$ are Miller indices, χ_H is the Fourier amplitude, $\mathbf{B}_H$ is the reciprocal lattice vector associated with H , and $\mathbf{r}$ are the space coordinates. The ansatz to Equation 2.6 combined with Equations 2.4 and 2.7 is

$$\mathbf{D} = \sum_H \mathbf{D}_H e^{i\omega_0 t - i2\pi \boldsymbol{\beta}_H \cdot \mathbf{r}} \quad (2.8)$$

where $\boldsymbol{\beta}_H = \boldsymbol{\beta}_0 + \mathbf{B}_H$ and $\boldsymbol{\beta}_0$ represents the wave vector of the incoming wave in the crystal while $\omega_0 = 2\pi\nu_0$ where ν_0 is the frequency. This leads to a system of linear equations for $\mathbf{D}_H$:

$$\sum_L [\chi_{H-L}(\boldsymbol{\beta}_H \cdot \mathbf{D}_L) \boldsymbol{\beta}_H - \chi_{H-L} \beta_H^2 \mathbf{D}_L] = (k_0^2 - \beta_H^2) \mathbf{D}_H \quad (2.9)$$

where L are Miller indices, $H - L = (h_1 - L_1, h_2 - L_2, h_3 - L_3)$ and k_0 is the wavenumber of the incident wave in free space, $k_0 = c/\nu_0$.

In Zachariasen's two beam dynamical diffraction theory [14], an incoming plane wave and a diffracted plane wave were assumed to exist in the crystal medium, so that D is the sum of two waves. Imposing the correct boundary conditions on D at crystal surfaces gives formulae for the power ratio of an outgoing diffracted plane wave to an incoming plane wave impinging on the crystal [14]. The two ideal cases of interest for two beam theory are Bragg diffraction, where the diffracted wave exits the same surface as the incoming wave, and Laue diffraction, where the diffracted wave exits the crystal at the opposite surface. Since the boundary conditions are different for these cases, different formulae result.

Some of the formulae for the Bragg case are now presented, though it should be noted that a similar story can be told for the Laue case. The formulae for the power ratio are written in terms of y , the diffraction parameter. The power ratio written in terms of y allow a common mathematical expression for the profiles

across any crystal. For Bragg diffraction, y is given in terms of b and α :

$$b = \frac{\hat{\mathbf{n}} \cdot \mathbf{k}_0^e}{\hat{\mathbf{n}} \cdot (\mathbf{k}_0^e + \mathbf{B}_H)} \quad (2.10)$$

$$\alpha = \frac{B_H^2 + 2\mathbf{k}_0^e \cdot \mathbf{B}_H}{k_0^2} \quad (2.11)$$

where $\hat{\mathbf{n}}$ is the unit normal vector to the surface of the crystal and $\mathbf{k}_0^e$ is the wave vector of the incident wave outside the crystal. $\mathbf{k}_0^e$ is related to the wave vector of the incident wave in the crystal, β_0 , by

$$\beta_0 = \mathbf{k}_0^e + \frac{k_0^2 \delta_0}{\hat{\mathbf{n}} \cdot \mathbf{k}_0^e} \hat{\mathbf{n}} \quad (2.12)$$

where $1 + \delta_0$ is the refractive index of the crystal. Equations 2.10 and 2.11 were then approximated assuming the Bragg angle is not close to $\pi/2$ radians. y was then defined as:

$$y = \frac{\chi_0(1 - b) + \alpha b}{2|b|^{1/2}K|\chi_H|} \quad (2.13)$$

where K a factor depending on polarisation. The definition of y condensed diffraction curves for a large range of experimental conditions into a few equations. For Bragg diffraction, the equation predicts a high power ratio for $-1 < y < 1$ falling off quite steeply for $y < -1$ and $y > 1$.

Caticha et al. [15] removed the approximations made to Equations 2.10 and 2.11 so y was correct for Bragg angles close to $\pi/2$ radians. The paper then applied the new formula for y to thick crystals. This work found a wider diffraction peak than was previously predicted for Bragg angles close to $\pi/2$ radians.

An approach to dynamical diffraction in crystals with small deformations was proposed by Takagi [16, 17] and Taupin [18] in the 1960s. The deformation was modelled by a vector function $\mathbf{u}(\mathbf{r})$ which represents the displacement of the charge density at $\mathbf{r}$ caused by the deformation. This work solved 2.6, where χ is approximated to the un-deformed susceptibility χ' , by

$$\chi(\mathbf{r}) = \chi'(\mathbf{r} - \mathbf{u}(\mathbf{r}_0)) \quad (2.14)$$

where $\mathbf{r}_0$ is the point where the charge density which is displaced to $\mathbf{r}$ by the deformation is originally situated. This approximation is only good when the deformation of each unit cell can be well approximated by a rigid rotation and translation. Other deformations would represent a change in total electron charge

per unit cell or a sheering of electron orbitals without considering quantum mechanics. The simplifications of 2.6 leading to a solution also rely on the condition of small deformation: $\partial \mathbf{u}(\mathbf{r})/\partial r_i \ll 1$. This approach allows the modelling diffraction in crystals with arbitrary small deformations, including singly curved crystals, doubly curved crystals and monochromator crystals under heat loads at synchrotrons.

The Takagi-Taupin approach was developed for large scale deformations that can be represented by macroscopic strain caused by stress. Kato [19] generalised the Takagi-Taupin approach to cover microscopic deformations with a random character. Kato's approach can be properly applied to crystalline or mosaic solids made of small crystals (crystalites) with randomised orientations in 1980. Kato found equations for the mean of $\mathbf{D}$ over a statistical ensemble of crystals, with small deformations that represent the mosaicity of a crystal. The mean of $\mathbf{D}$ was called the coherent wavefield while the expected deviations to this were the incoherent wavefield. It was found that power is transferred from the coherent wavefield to the incoherent wavefield, a process that is known as diffuse scattering. Kato treated the effect of the mosaicity of a crystal on diffraction by characterising a static Debye-Waller factor and a correlation length. Such an approach is also applicable to the dynamic disorder of a crystal caused by a non-zero temperature, as well as to static disorder caused by atomic substitutions or vacancies.

In a series of papers from 1978 to 1987, imperfect crystal diffraction was examined by Chukhovskii [20–22], using a Green's function [23] method. Chukhovskii also found an analytical solution to the Takagi-Taupin equations for a flat thick crystal where the lattice spacing varies monotonically with distance from the crystal surface. Punegov et al. [24] extended this work with the statistical approach to apply to such crystals with ions implantations.

The 1987 work of Caciuffo et al., in [25], found the diffraction pattern of a curved crystal by first representing a slice of the incoming plane wave as a localised ray characterised by a one dimensional path that is in the centre of the ray. The path the ray took through the crystal then had a definite angle to the lattice planes at each depth into the crystal. Upon such an assumption, a (different) y value can be calculated for each depth of the ray. A key approximation in Caciuffo et al. [25] was that the curved crystal could be broken up into layers of flat crystal, with different crystal plane orientations. Each crystal layer had a depth of $\Delta y = 2$ in the y coordinate, and the y value for each layer was the y value

at the centre of the crystal layer. Each layer had a transmission and diffraction coefficient taken from the thick crystal limit of the absorbing flat crystal theory of Zachariasen [14]. Diffracted rays were assumed to have y values far from zero that make diffraction negligible, so absorption was the only process modelled for these rays. This approach presented a method of calculating the power ratio between the incoming ray and the sum of outgoing power from each layer. This means that it did not trace where the diffracted rays exited the crystal or their directions having left the crystal.

In 1992 Chantler [26] took the work of Caciuffo et al. [25] and proposed improvements of the diffraction modelling inside the curved crystal, and also traced the full path of a set of rays from an inhomogeneous and monochromatic source to a detector. The main improvements in crystal diffraction modelling were (a) the use of the full absorbing flat crystal theory [14], (b) a segmentation of the layers that allowed a fuller accounting for the interference effects inside a given layer and accentuated the incoherence of diffracted beams between layers, (c) a segmentation of each layer into sub-layers that each have the correct y value, with a diffracted ray coming from each sub-layer, and (d) a better estimate of the physical path length of a ray, from crystal entry to crystal exit. External to the crystal, Chantler [26] proposed tracing a set of rays from a grid of points on the source to the crystal surface. At each grid point on the source, the set of rays emitted had a range of angles. The diffracted rays were then traced from the crystal surface to the detector. This allowed for a simulation of the x-ray light transport in an arbitrary two dimensional planar source, curved crystal and detector geometry. The Fortran program that implemented this simulation is called Mosplate (originally called Moscurve, but modified by Paterson et al. [27] to apply to flat plate detectors). Mosplate also includes a method for modelling mosaic curved crystals [28].

Following the Takagi-Taupin approach, a method to solve the Takagi-Taupin equations using finite element analysis was presented in 1997 by del Rio et al. [29]. It was integrated into Shadow-XOP x-ray ray tracing system [30–32] as an option. However, the manual for this system recommends using the layered calculation similar to that of Caciuffo et al. [25], as the Takagi-Taupin implementation is experimental [33]. It should be noted that the implementation details are unknown to the literature as of 2015 [34]. Another possible numerical implementation of the

Takagi-Taupin equations for curved crystals is a finite difference method. However, as their paper pointed out [29], this imposes a regular grid that would not adequately capture the deformations of the crystal.

As computational power and methods improve, the calculation of diffraction from curved crystals may become more accurate since more details are included and less assumptions are made. Such details may include second order effects that are neglected by the approaches taken by Takagi-Taupin, Caciuffo, or even Chantler.

The advances in the understanding of x-ray diffraction have enabled the creation of a number of fields of study. Three such fields are x-ray absorption spectroscopy, atomic physics of characteristic radiation, and tests of QED using the spectra of highly ionised, medium atomic number (Z) atoms.

2.3 X-ray Absorption Spectroscopy and XAFS

The ability to physically separate and measure x-ray energies through crystallographic techniques enabled the development of X-ray Absorption Spectroscopy. This is the study of the strength of x-ray absorption processes within a material as a function of x-ray energy. Assuming the linearity of absorption and homogeneity of absorption per atom with position inside the material, the strength of the absorption for a given x-ray energy can be measured by the mass attenuation coefficient. The mass attenuation coefficient, $[\mu/\rho](E)$, for a material is a function of x-ray energy, E , is implicitly given by the Beer-Lambert formula

$$I = I_0 e^{-[\mu/\rho](E)\rho t} \quad (2.15)$$

where I_0 is the incident intensity of x-rays with a given momentum vector, I is the transmitted intensity of x-rays an unchanged momentum vector, ρ is the density of the material and t is the thickness that the x-ray beam traverses through the material. Thus $[\mu/\rho](E)$ captures the total probability of elastic scattering, inelastic scattering and absorption together as a function of energy. Its values are conventionally quoted in cm^2/g .

The major contribution to attenuation in the x-ray regime is photo-ionisation, where there is enough energy in an x-ray photon to eject an electron from an inner shell (typically) when it is absorbed. For a given electron state in an atom, there

is a threshold x-ray energy for this process to occur. The $[\mu/\rho]$ spectrum rapidly increases as this threshold is crossed. As such, this jump is called an edge. The edges are labelled via the electron shell involved, so the highest energy edge is the K-edge.

2.3.1 XAFS Theory

Above an absorption edge, there is oscillatory structure in the mass attenuation coefficient called X-ray Absorption Fine Structure (XAFS). This structure is generally divided into two energy regions. Near the edge (within a few eV), there are sharp oscillations. This region is generally called X-ray Absorption Near Edge Structure (XANES). The oscillations in the region of XANES below the ionisation energy (pre-edge) are caused by bound-bound transitions. Oscillations that appear a few eV to hundreds of eV past the edge are called Extended XAFS (EXAFS). XAFS was first reported in 1919, in W. Stenström's thesis. Oscillations were seen above the M absorption edge of Uranium and Thorium [35].

The theoretical development of XAFS began in 1920 with Kossel [36]. By 1932 Kronig had developed two detailed theories of Extended XAFS (EXAFS), namely a Short Range Order (SRO) theory [37] for molecules, and a Long Range Order (LRO) theory [38] for solids. The SRO approach forms the basis of XAFS theory today. The approach aimed at calculating the fractional excursion of the absorption from an isolated atom to that of an atom in its molecular or solid state environment. This quantity is now called the XAFS spectrum and is denoted by $\chi(k)$. $\chi(k)$ is related to $[\mu/\rho](E)$ by

$$\chi(k) = \frac{[\mu/\rho](E) - [\mu_0/\rho](E)}{[\mu_0/\rho](E)} \quad (2.16)$$

$$E = \frac{h^2}{8m_e\pi^2}k^2 + E_0 \quad (2.17)$$

where k is the effective wavenumber of the photoelectron, μ_0 is a smooth atom-like background and E_0 is the energy of the edge.

The SRO theory was developed further by Peterson [39–41], who derived a formula for the XAFS spectra that forms the basis of the modern XAFS equation (Equation 2.18), still to come. Peterson recognised that the absorption is proportional to the electric dipole matrix element between the initial state of the electron in its

shell and the final state of the photoelectron. This led to the insight that XAFS oscillations are the result of how the scattering of a photoelectron off nearby atoms modulates the final state wavefunction at the centre of the atom as a function of x-ray energy. This can be thought of as self-interference of the photoelectron's wavefunction near the core of the absorbing atom. Thus the core of the XAFS problem could be solved by finding solutions (or approximate solutions) to the Schrödinger equation for the photoelectron. The initial formulation neglected thermal effects and the inelastic scattering of the photoelectron. Kostarev realised in 1941 [42] that the SRO theory was applicable for solids as well as molecules [35]. Sayers et al. [43] formulated and developed the modern theory of EXAFS, as well as the technique of Fourier transforming XAFS data [44, 45], in the first half of the 1970s. Further refinements and clarifications appeared in Ashley et al. [46] and Lee et al. [47], both in 1975. Ashley et al. [46] added the effect of the electron inelastic mean free path in the solid. Lee et al. [47] added shift of phase of the photoelectron caused by electron-atom scattering, as well as adding multiple-scattering paths.

This XAFS equation as developed by 1975 [46, 47] describes $\chi(k)$ as a sum over multiple scattering path types:

$$\chi_{th}(k) = \sum_j N_j S_0^2 F_j(k) \frac{\sin[2kr_j + \phi_j(k)]}{kr_j^2} \times e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda(k)} \quad (2.18)$$

where subscript j indexes the j^{th} path type, N_j is the number of paths of that type or the degeneracy, S_0^2 is the many body reduction factor, $F_j(k)$ is the backscattering amplitude function, $r_j = (1 + \alpha)r_{0,j}$ is half the path length, $r_{0,j}$ is the same quantity at a reference temperature, $\phi_j(k)$ is a total phase shift function, σ_j is a Debye-Waller factor and $\lambda(k)$ is the photo-electron inelastic mean free path function.

The basic XAFS equation has survived since 1975, but there have been major developments in the calculations of the terms of the equation. These include an understanding of shake-up, shake-off effects [48], a curved-wave approximation [49] replacing the earlier plane wave approximation to determine the phase shift, and multiple scattering from centres of electron density [50].

XAFS analysis packages (based on this work) have become very popular in determining the local microscopic structures of a wide variety of materials. The

packages are used to analyse XAFS data to solve for material structures routinely, and produce thousands of publications per annum. However, limitations in theoretical predictions and in XAFS analytical frameworks lead to significant uncertainty in results. This impairs structural predictions and prevents *ab initio* determination.

2.3.2 XAFS and Diffraction Anomalous Fine Structure

It is interesting to note the link between diffraction and XAFS via Diffraction Anomalous Fine Structure (DAFS). DAFS is the oscillatory part of diffracted power within a diffraction peak above an absorption edge. It is linked to XAFS in that they are both effects of anomalous dispersion. As with XAFS, the specific structure of the DAFS oscillations are dependent on the local environment of the absorbing atom.

The scattering power for a unit cell of a crystal is described by the structure factor $F(\mathbf{k}, \mathbf{k}', E)$. This describes both the diffraction and absorption for a crystal. It is parametrised by the wavenumber of the incoming radiation $\mathbf{k}$, the wavenumber of the scattered radiation $\mathbf{k}'$ and the energy of the incoming radiation E .

The structure factor can be written in terms of the atomic form factor, f , as:

$$F(\mathbf{k}, \mathbf{k}', E) = \sum_j f_j(\mathbf{k}, \mathbf{k}', E) e^{i2\pi(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}_j} \quad (2.19)$$

where j labels atoms in the unit cell and f_j is the atomic form factor of the j^{th} atom that is at position $\mathbf{r}_j$. The atomic form factor can be written as

$$f(\mathbf{k}, \mathbf{k}', E) = f_0(\mathbf{k} - \mathbf{k}') + f'(\mathbf{k}, \mathbf{k}', E) + if''(\mathbf{k}, \mathbf{k}', E) \quad (2.20)$$

where f_0 is the Thomson scattering component that is independent of energy, while f' and f'' are the energy-dependent real and imaginary parts of the anomalous correction to the scattering amplitude. f' is proportional to scattering power while the f'' is proportional to absorption.

As a result of causality, $f(\mathbf{k}, \mathbf{k}', E)$ is an analytic function in the upper half of the complex frequency plane [7, Chapter 7]. This means that $f(\mathbf{k}, \mathbf{k}', E)$ satisfies the Cauchy-Riemann conditions [51] and f' and f'' are causally related. Thus fine

structure in f'' implies a very similar fine structure in f' . This leads to XAFS having a very similar structure to DAFS for a given material and vice versa.

2.3.3 Issues in Standard XAFS Analysis

Standard XAFS analysis has three steps: (1) calculate the XAFS spectrum from measured mass attenuation coefficients; (2) generate a parametric model of XAFS spectra; and (3) fit the model to the data using least squares fitting. Steps (1) and (3) entail problems.

A problem arises in step (1) as follows. In Equations 2.17, there is currently no rigorous determination of the atom-like smooth baseline μ_0 or of the energy E_0 for general edges. Two of the most useful theoretical atomic baselines are due to Chantler [52, 53] and Mihelic [54]. Recently, limitations of both of these contemporary approaches have been shown to obscure the direct interpretation of XAFS. These limitations include the discrepancy between the observed and calculated baselines known as the triangle effect [55–58]. This is a systematic (roughly) triangular-shaped discrepancy between theory and experiment above the K-edge. More standard approaches simply draw a smooth line or curve (a spline) through the oscillatory amplitude and normalise empirically to this. Such an approach is ultimately unsatisfactory as a way of understanding the XAFS of a material as there is little reason to think that a fitted spline represents any material's atomic baseline correctly.

Steps (2) and (3) are usually done in an XAFS analysis package. One of the best current XAFS analysis packages is IFEFFIT [59], an interactive shell for the FEFF code [50] which uses the XAFS equation 2.18. For step (2), FEFF is given an input local structure, e.g. a crystal structure at some temperature. It then outputs N_j , $r_{0,j}$, $F_j(k)$, $\phi_j(k)$ and $\lambda(k)$ for the most dominant photoelectron scattering paths. That leaves S_0^2 , σ_j and α_j undetermined for each scattering path. Thus they may be determined through a refinement process to fit Equation 2.18 to experimental data.

To good accuracy all α_j 's are equal to a single parameter α (e.g. due to isotropic thermal expansion). The σ_j 's are modelled by the correlated Debye model with

the Debye temperature θ_D as a free parameter:

$$\sigma_j^2 = \frac{1}{4} \sum_{ij} \left\langle (\mathbf{u}_i - \mathbf{u}_{i+1}) \cdot \hat{\mathbf{R}}_{i,i+1} (\mathbf{u}_j - \mathbf{u}_{j+1}) \cdot \hat{\mathbf{R}}_{j,j+1} \right\rangle \quad (2.21)$$

where $\mathbf{u}_i$ is the fluctuation in position of the i^{th} atom in the path and $\mathbf{R}_{i,j}$ is the displacement from the i^{th} atom to the j^{th} atom in the path. This can be cast in terms of the correlation between the k^{th} component of the $\mathbf{u}_i$ vector and the l^{th} component of $\mathbf{u}_j$:

$$\langle u_{i,k} u_{i,l} \rangle = \frac{\hbar^2}{k_B \theta_D \sqrt{M_i M_j}} \int_0^1 dw \frac{\sin(w R_{ij} k_D)}{R_{ij} k_D} \coth \left(\frac{w \theta_D}{2T} \right) \quad (2.22)$$

where k_B is Boltzmann's constant, $k_D = (6\pi^2 N/V)^{1/3}$, N/V is the number density of the crystal, T is the absolute temperature of the crystal and M_i is the mass of the i^{th} atom in the path [50].

For each path $N_j S_0^2$ is a constant, so the roles of N_j and S_0^2 are not separable. A separate parameter $S_{0,j}^2$ for each path models the variation of the product.

Step (3) is done in IFEFFIT, given the fully specified and parametrised model generated by FEFF. There are a number of options for using IFEFFIT that are reported in the literature: k weighting and windowing. The non-linear least squares fitting procedure used in IFEFFIT is defined in terms of the deviations between an interpolation of the $\chi(k)$ data onto a uniform grid and the theory. The i^{th} such residual will be called $r_{F,i}$ with a k value of $k_{F,i}$. The procedure minimises χ_F^2 :

$$\chi_F^2 = \frac{N_{Fidp}}{N_{Fpts} \epsilon^2} \sum_{i=1}^{N_{Fpts}} [W(k_{F,i}) k_{F,i}^n r_{F,i}]^2 \quad (2.23)$$

where N_{Fpts} is the number of interpolated data points in the grid, ϵ is some estimated uniform measurement uncertainty, N_{Fidp} is the estimated number of independent data points, $W(k)$ is a windowing function that selects the region of k to be fit and n is the so called k weight. The k weight, n enters Equation 2.23 in the factor $k_{F,i}^n$ multiplying the i^{th} residual. The k weighing is usually $n \in (0, 1, 2, 3)$. For $n > 0$ residuals for higher k are given more importance through a larger weights in the fitting. This is equivalent to assuming the uncertainty for $r_{F,i}$ to be proportional is $k_{F,i}^{-n}$ during fitting. Thus k weighing (for $n \neq 0$) is an unprincipled way of representing a decreasing theoretical or experimental uncertainty

with k . This could be due to the atomic baseline being less certain at low values of k or assumptions of the theory breaking down near the edge. The essential problem of step (3) is as follows. This fitting procedure does not propagate measured uncertainties into parameter uncertainties as it does not use any measured uncertainties.

The reported measure of goodness of fit, χ_{Fr}^2 , is defined as:

$$\chi_{Fr}^2 = \frac{\chi_F^2}{N_{pts} - N_{var}} \quad (2.24)$$

where N_{var} is the number of free parameters of the fit. If χ_F^2 is distributed as a χ^2 distribution with $N_{pts} - N_{var}$ degrees of freedom, a χ_{Fr}^2 of about 1 would indicate a good fit. It is clear then, that a uniform estimation of uncertainties, and using a k weighting of anything other than $n = 0$, means that χ_F^2 is not distributed as a χ^2 distribution, and thus its value is not a good indicator of goodness of fit.

2.4 Characteristic Atomic Spectra

As well as facilitating the investigation of x-ray absorption phenomena, diffraction crystallographic techniques have made possible the high precision study of x-ray spectroscopy of elements. X-ray transitions of singly ionised atoms are usually called characteristic radiation, as the transition energies are characteristic of the element of the atom. In particular, the energies depend on the allowed energy state of the system of electrons in the nuclear field. Characteristic radiation is the result of a decay of an atom from an excited state, where there is a hole in an inner shell, to a state where that hole is filled. Theoretical modelling of characteristic radiation profile shape is dominated by diagram lines, where an electron from a higher n shell fills the inner shell hole and the atom ends in the an ionized state with an outer shell hole. Additional components, theoretically and empirically, are contributed by satellite lines caused by shake-up and shake-off effects. This set of transitions is complex, especially for elements with open sub-shells such as the transition metals.

The structure is properly modelled through the relativistic quantum theory of the atom, which has seen recent dramatic improvement [60]. A concerted effort to experimentally summarise experimental energies of characteristic radiation was

undertaken and compiled by Bearden via a 1964 internal report for the U.S. Atomic Energy Commission [61] and then publicly in 1967 [10]. This was complemented by theoretical computations by Desclaux [62] in 1973 and further experimental and theoretical compilation by Indelicato et al. [63] in 2003. That sequence of review work reported the energy of the dominant transition (diagram lines) without regard for the shifts and change of shape of the spectra due to satellite lines or profile asymmetry. Relativistic Many Body Perturbation Theory (RMBPT) has shown success by including correlations to high-order of the Auger shift. Quantum mechanics predicts a shift and a broadening when a state is degenerate with a continuum [64, 65]. Since 1970, significant advances in theory have been based on the relativistic approach of Grant [66], further developed by Parpia et al. [67] and Fischer et al. [68]. Literature to date has revealed that the comparison of advances in theory with high accuracy experiment has remained particularly challenging.

2.5 Standards for Energy Measurement in X-ray Spectroscopy

X-ray diffraction standards allow x-ray scientists to have a reliable way to measure x-ray wavelength and energy. Such standards have generally involved either a diffraction crystal, where the distance between diffracting lattice planes have been accurately measured, or a reproducible x-ray spectrum with well defined sharp features that has been accurately measured.

In relation to the first method, a standard diffraction crystal can be obtained with the combination of the X-Ray and Optical Interferometer (XROI) method from Deslattes et al. [69] and the delta-d method of Kessler et al. [70]. XROI uses a combined (simultaneous) x-ray and optical interferometer. It measured the distance between diffracting lattice planes in wavelengths of visible light, and thus constitutes an absolute measurement tied to the definition of a meter. It used a stabilised He-Ne laser for the standard visible light wavelength and compares that to an x-ray interferometric measurement of the distance between (110) lattice planes of silicon. The ratio then of these lengths calibrated x-ray wavelengths and silicon lattice spacing to the wavelength of the He-Ne laser. The XROI technique is one of the most complex and challenging in physics and has only been able to be performed at a few national standards laboratories (NIST in USA [69], PTB in

Germany [71], NRLM in Japan [72], and INRIM in Italy [73]). In order to enable wider experimentation, a separate method to transfer this accuracy to another crystal was needed. To carry-over this silicon (110) standard to another crystal, the delta-d procedure was developed by Kessler et al. [70]. Delta-d determined the difference between the lattice spacing of two crystals via measuring the diffraction of each crystal separately in a double-crystal Laue spectrometer. This resulted in the calibration of crystals with sets of planes that can be used as standards.

With a standard diffraction crystal and an accurate measurement of the geometry of an experimental setup, it is possible to define a theoretical calibration between the measured position of x-rays on a detector and the energy of the said x-rays. This method is possible for a flat crystal geometry. For curved crystal geometry, or flat crystal geometry involving a non-standard diffraction crystal, another approach is required. In this case, standard sharp featured x-ray spectra allow for an experimental calibration between detector position and x-ray energy.

Characteristic radiation profiles, such as the $K\alpha$ and the $K\beta$ profiles, are often used as calibration standards, as the profiles are sharp, stable and simple to produce. Other characteristic radiation profiles such as the $K\gamma$ profiles or the L series profiles have the same advantages but have a lot less intensity, thus they have generally not been used as standards. Excitation processes that produce characteristic radiation include electron bombardment, x-ray absorption and inelastic x-ray scattering. These processes all involve an energetic incoming particle ionising the atom, and can be subject to sensitive chemical shifts and solid state effects. When the incoming particle has an energy just above threshold, the excited states and the shape of the characteristic energy profile sensitively depend upon the energy of the incoming particle [74–76]. For electron bombardment, when the energy of the electron is at least 2.5 to 3 times the threshold energy of the dominant transition, the excited state and profile shape of the characteristic radiation stabilise [77]. This stability makes it possible to characterise the profile of $K\alpha$ and $K\beta$ radiation, robust to incoming electron energy variation. Standard x-ray sources include fixed anodes, rotating anodes, synchrotron excitation and others. Simple fixed source excitation following the standard technique of many past researchers is of great interest. A key question for all these standards is, what is the stable profile from such a source, and how can it be robustly used, fitted and modelled in secondary and critical experiments?

Experimental spectral profiles for the characteristic radiation of transition metals are represented by semi-empirical fitting of multiple components, using typically 5 or 7 peaks for $K\alpha$ spectra [78, 79]. Recent work has demonstrated that new approaches can yield a more robust standard [80–82]. Empirical modelling using fitting functions for a sum of a small number of Lorentzian, Gaussian, Voigt or instrumental functions fails to reveal the theoretical complexity of the many satellite transitions.

Efforts to find good empirical models of spectral radiation have built upon the work of Schweppe et al. [83], Deutsch et al. [78] and Hölzer et al. [79] in the 1990s and early 2000s [84, 85]. Deslattes et al. [63] includes a summary of these efforts, some of which is presented in Table 2.1 with experimental energies and uncertainties for $K\alpha$ characteristic peaks for Z from 22 to 26. Table 2.1 also includes $K\alpha$ energies from Chantler et al. [86]. The uncertainties for the $K\alpha$ energies in this range are on the order of 1 to 2 parts per million (ppm). However, the quoted uncertainty of the titanium $K\beta$ peak energy [10] (Table 2.1) is an order of magnitude larger at 12 ppm, limiting accuracy and calibration in this region of energy. This is driven both by the weakness of $K\beta$ compared to $K\alpha$, and the difficulty of calibration with suitable flux at low energies.

In particular, although a nearby $K\alpha$ spectrum can calibrate some experiments, $K\beta$ spectra are less easily affected by vignetting and produce a more precise calibration as they are sharper than $K\alpha$ profiles. A challenge in using $K\beta$ profiles in this way is that disentangling instrumental broadening and the ratio of energy difference to length on the detector is less precise. This is because these effects are more strongly correlated in the singly peaked $K\beta$ profiles than doubly peaked $K\alpha$ profiles.

The inclusion of $K\beta$ lines in calibration therefore represents both a challenge and an opportunity for sharper and much more constrained and accurate calibration of energy. Ideally, a maximal set of standard spectral profiles, including both $K\alpha$ and $K\beta$ characteristic lines could be used in calibration. However, until now, the accuracy of the determination of $K\beta$ transitions generally precluded their utility for such purposes.

X-ray spectroscopic experimental methods have often used a single flat crystal spectrometer employing the Bond method [78, 79], or a curved crystal spectrometer [84]. In the experimental work reported in Deutsch et al. [78], raw spectra were deconvolved with a measured, fitted or simulated instrumental broadening, and

each deconvolved spectrum was fitted empirically. The peak location of each empirical fit was taken to be the measure of each peak energy. The deconvolution of spectra limits the understanding of error propagation. It is not immediately clear how to use these characterisations as standards for experiments with different instrumental broadening. Chantler et al. [86] addressed this concern by providing a consistent set of empirical fit functions for a range of elements ($21 \leq Z \leq 25$) including an approach to allow for instrumental broadening effects.

A large volume of research has investigated $K\beta/K\alpha$ x-ray intensity ratios [87]. Some 40 papers on this are found in *Physical Review*, with hundreds appearing in other journals [88–90]. Most of these publications rely upon low resolution solid state detectors measuring the gross intensity of the lines, so can neither resolve the detailed shape of the $K\beta$ spectra nor provide high-accuracy energies. Of course, by being particularly low-resolution, the value returned from energy calibration is an effective weighted mean of the profile, and is a very different energy compared with the medium-resolution peak energy.

A full set of high quality characteristic radiation standards for spectrometry has been a purpose of a range of investigators at major laboratories. The existence of such a set would enable researchers to choose an appropriate subset for their particular needs. However, there are gaps in the literature in high accuracy characterisations of V $K\beta$ and Ti $K\beta$ as evidenced in Table 2.1. Also, high accuracy measurements of the Cr $K\beta$ profile suffer from a number of problems such as error bars having weak justification. What follows now is further review of the literature relating to V $K\beta$, Ti $K\beta$ and Cr $K\beta$.

Profiles of chemical energy shifts of the V $K\beta$ spectrum of compounds of vanadium compared with that of pure vanadium also have been conducted using sensitive instruments [91]. This work has focused on changes in peak separation, perhaps with uniform instrumental broadening, and thus does not report detailed line shapes on an absolute energy scale. An interesting recent paper on this area [92] discussed the components of $K\beta$ transitions and satellites, but not for vanadium. Indeed, there were no absolute energy measurements reported therein; they were calibrated by Bearden [10].

Three measurements of the characteristic V $K\beta$ line on an absolute energy scale were made between 1922 and 1935 [93–95]. The papers did not include explicit

error bars. These measurements were averaged by Bearden [10, 61] with the variance providing an uncertainty. Bearden reported the peak energy as 5427.320(71) eV after recalibration by Deslattes et al. [63]. Information about how instrumental broadening was dealt with could not be found in the original papers. Noting that V K β is an asymmetric line, it is likely that this literature value was significantly affected by different shifts caused by different amounts of instrumental broadening in the original papers. A theoretical calculation of the energy of the peak of V K β was 5430.00(94) eV [63]. The 3.4 standard error discrepancy between theory and experiment that was evident was unlikely to be explained by statistical fluctuation, and points to a problem in either theory or experiment. A new experimental measurement may be useful to resolve this discrepancy and to provide a rigorous standard for use in calibration.

There has been some interest in the shape of the Ti K β profile since the 1970s [92, 96–99]. Much of this work related to efforts in calibration, discussed above. In addition, the characteristic signature provides valuable information about atomic structure, molecular effects and solid-state effects. These include valence, ionisation state, and Fermi levels, as well as electron correlations, excitation dynamics and relaxation processes. Interest has been raised in the identification of radiative Auger energies, KM₁ quadrupole decay, K β^{III} and K β^{IV} double ionisation processes and other processes sometimes labelled K β' and K β_5 . Additionally, X-ray astronomy has observed numerous K spectra of transition metals arising from plasmas of different types, and characterisation of the profile can yield clues as to the nature of the plasma. This work has all been relative to the peak reported by Bearden [10], regarded in this thesis as problematic in that the resolution and broadening shift was not calibrated.

A theoretical calculation of the peak energy for the diagram line of Ti K β has been found to be 4930.86(85) eV [63], consistent with the experimental result reported. However, the relatively high uncertainty in the Ti K β peak energy compared to those of K α makes Ti K β a good candidate for improved characterization.

The shape of the Cr K β profile has been perhaps the most carefully studied of the K β spectra [92, 96–99]. The energy calibrations in this work were all related to the problematic peak energy reported in Bearden [10]. Hölzer et al. [79] reported an experimental line shape and peak energy (listed in Table 2.1). The line shape was reported as a fitted deconvolved spectrum. Because the uncertainty of the raw spectrum did not appear to be propagated through the deconvolution, the

Spectral Profile Peak	Reference Peak Energy (eV)	Peak Energy (ppm)	Uncertainty
Titanium $K\alpha_2$	4504.920 [63]		2.09
Titanium $K\alpha_1$	4510.899 [63]		2.08
Vanadium $K\alpha_2$	4944.651 [86]		2.22
Vanadium $K\alpha_1$	4952.131 [86]		1.21
Chromium $K\alpha_2$	5405.538 [63]		1.31
Chromium $K\alpha_1$	5414.804 [63]		1.31
Manganese $K\alpha_2$	5887.685 [63]		1.43
Manganese $K\alpha_1$	5898.801 [63]		1.42
Iron $K\alpha_2$	6391.03 [79]		1.5
Iron $K\alpha_1$	6404.01 [79]		1.5
Vanadium $K\beta_1$	5427.32 [63]		13.0
Titanium $K\beta_1$	4931.83 [63]		12.0
Chromium $K\beta_1$	5946.82 [79]		1.7

Table 2.1: Characteristic radiation peak energy data from the literature. The V $K\alpha$ data is from Chantler et al. [86]; the Fe $K\alpha$ and Cr $K\beta$ data is from Hölzer et al. [79]; the rest of the data is from Deslattes et al. [63]. The peak energy of the V and Ti $K\beta$ radiation has a larger uncertainty than for $K\alpha$ radiation by an order of magnitude.

reported uncertainties were not fully justified and hid systematic errors in the fitting process. A theoretical calculation of the peak energy for the diagram line of Cr $K\beta$ was 5947.1(10) eV [63] is in good agreement with older theory and the experimental value, but had a much larger uncertainty than the experimental result.

Review of the research on characteristic radiation standards has thus revealed that there are weaknesses in the measurements of V $K\beta$, Ti $K\beta$ and Cr $K\beta$, and that these spectral profiles are good targets for reinvestigation. New standards for these lines would expand the capability of researchers to calibrate x-ray spectrometers, particularly those interested in testing QED.

In aiming to use x-ray spectrometry in the particular area of QED testing, it was found that very clear lines relevant to tests of QED were produced for study by Electron Beam Ion Trap (EBIT) technology [100, 101]. However, EBITs generate relatively low intensity lines, meaning that cosmic ray noise must be filtered out if the most precise measurements are to be achieved. Standards for such filtering have been developed for a particular type of x-ray detector, namely the Charge-Coupled Device (CCD) introduced by Boyle et al. [102]. The next section discusses how cosmic ray noise presents difficulties in x-ray measurements and

reviews various approaches that could be proposed to solve this problem.

2.6 Cosmic Ray Noise in CCD Detectors

X-ray CCD detectors are important in a wide range of spectroscopic experiments from x-ray astronomy to atomic physics. Extracting significant information from x-ray CCD images is therefore a general and important problem. Cosmic ray tracks are a significant source of noise in x-ray CCD images with long integration times. The source of almost all cosmic ray tracks in laboratory experiments have been relativistic muons produced by secondary meson decay, although numerous other sources have been identified [103].

In atomic physics, reducing the noise from cosmic rays has been an important step in the analysis of polarisation data for measuring the Lamb shift of He-like Ti at an EBIT [104]. More generally, cosmic ray filtering is important in performing any test of QED at an EBIT, as the lines that are used in such tests are weak.

It is also extremely important in particle and nuclear physics to characterise these cosmic-ray processes and thus to isolate the critical processes of interest. In a number of these cases, extremely expensive and time-consuming experiments and detectors have been employed, rather than typical detectors available for more conventional synchrotron, EBIT or anode experiments.

Weak Rydberg lines generated by an EBIT source may be used in the future as calibration lines for EBIT experiments. Absolute calibration for spectroscopy of EBIT sources requires either a precise direct measurement of the spectrometer with an excellent understanding of dynamical diffraction or the use of calibration lines that have already been measured on an absolute scale. The source of the calibration lines have not typically been co-located with the EBIT trap, causing some uncertainty. The use of an array of Rydberg lines generated in the EBIT as calibration lines would reduce this uncertainty greatly and reduce the complexity of the experimental setup by removing the separate calibration source. However, because Rydberg lines are a particularly weak signal, it is particularly important to filter out cosmic ray tracks from Rydberg line data.

Thus, filtering background cosmic-ray events from low flux experimental x-ray spectroscopic data taken by pixelated detectors (especially CCDs) is an important

and generic problem. How can such filtering strengthen conclusions based arising from this type of data?

Various methods have been developed for removing cosmic ray noise. Van Dokkum [105] proposed a popular method based on Laplacian edge detection that is useful when the cosmic ray tracks are sharp compared to the x-ray data. Pych [106] reported a method based on a cosmic ray pixel intensity being an outlier within a small region of slowly varying x-ray intensity, thus relying on relative sharpness of cosmic ray tracks. These methods are not appropriate, however, for low flux EBIT sources, as the x-ray events are clearly just as sharp as the cosmic ray tracks.

Median filtering is another technique that has been used to remove cosmic rays [107]. This method is also based on the idea that cosmic ray pixel intensities are outliers in some local intensity distribution. However, for a low flux x-ray source, x-ray event pixel intensities are also outliers, making this method inappropriate for such sources.

For x-ray CCD images with weak x-ray signal, a method of cosmic ray identification based on cluster intensity filtering has been proposed [108]. This method does not capture parts of cosmic ray tracks disconnected from the main cluster, however, and therefore does not successfully filter out all comic ray noise.

Thus the problem of how to robustly identify all elements of cosmic ray tracks in CCD detectors is unsolved in reported research to date. A novel technique is required. A possible way to meet the challenge of reducing the noise of cosmic rays in weak lines for CCD detectors may lie in machine vision research. The machine vision community has developed a number of methods for identifying lines in images. The basis of these methods is the Hough transform [109], first developed by Hough in 1962 [110] to recognise bubble chamber tracks. In 1972, Duda et al. [111] modified the method to its current form, for use in general image processing. In this elegant method, the image space is transformed into the so-called Hough space. The location of a pixel in the Hough space represents a single line in the image space. A pixel intensity in the Hough space is a sum of all the intensities on the represented line in the image space. Thus pixels in the image space ‘vote’ for the lines they are a part of in the Hough space. The axes of the Hough space are the angle of the line and the shortest distance from the line to the origin. An approximately straight line can then be recognised by a peak in the Hough space image. Hough back-projection allows the lines recognised in a Hough

space image to be projected back into image space. The value of the Hough back-projected image at a particular pixel is calculated from the group of points in the Hough transform whose corresponding lines go through that particular pixel. The value of the image is the sum of intensities of this group. Using back-projection, the pixels that most contribute to the recognised lines can be identified. Thus, thin lines of high intensity pixels can be identified using this method.

In the present research, it was considered that a method based on the Hough transform may be useful in filtering cosmic ray tracks from low flux x-ray CCD data. This could be applied to the low flux x-ray CCD data from EBIT sources such as that of weak Rydberg lines that could be used for calibration or spectra of medium Z ions used for tests of QED. Such a strategy would strengthen tests of QED.

Atomic Theory and Experiment

The energies of spectral lines of atoms have been of fundamental importance to the development of quantum theory. This development went from old quantum theory, to non-relativistic quantum mechanics, to relativistic quantum mechanics, and finally to the quantum field theoretic quantum electrodynamics (QED). The general technique for testing these theories through spectroscopy involved finding the energies of the allowed states of the electron(s) in the relevant field of the nucleus and electrons, calculating correction terms, and then matching up differences in the energies of allowed states to spectral lines. Atomic hydrogen provides the simplest system to test theory with experiment, as it has only one electron in the field of the nucleus. Two extensions to the spectroscopy of hydrogen are firstly, the spectroscopy of hydrogen-like ions, and secondly, the spectroscopy of higher atomic number elements (with their systems of electrons). Emission lines of inner shell excitations of these atoms and ions are generally found in the x-ray regime.

This chapter discusses this line of development in quantum theory. It goes on to an extensive review of experiments to test H-like QED and then discusses the state of He-like tests of QED. Finally, it explores the history of characteristic radiation experiments and then focuses on $K\alpha$ and $K\beta$ lines of elements between Sc and Zn.

3.1 Old Quantum Theory

Old quantum theory assumed electrons moved in stable classical Newtonian orbits around nuclei, without emitting the radiation that Maxwell's equations were known to predict. It was assumed that the existence of spectral lines and the stability of atoms indicated that only a discrete subset of this continuum of stable orbits were physically realisable. Planck and Einstein's quanta of radiation would be emitted or absorbed via a discontinuous jump between the orbits, a radical

shift away from the continuity of Maxwell's equations and Newton's laws of motion. The energy of those orbits would have to have specific values, such that the wave-number of the photon emitted would conform to Rydberg's formula [112], itself a generalisation of Balmer's formula [113]. The challenge to old quantum theory was to find quantities that characterised the allowed orbits such that the quantity could only have an integer multiple of a fundamental value. The Bohr model [114] of 1913 limited angular momentum to integer multiples of $\hbar$, Planck's constant and also limited the orbits to circles.

The Sommerfeld model [115, 116] generalised this. It imposed a condition that the action variable of one period of a periodic motion is a multiple of Planck's Constant, and it therefore provides justification for the n and l quantum numbers of non-relativistic quantum mechanics.

3.2 Non-Relativistic Quantum Mechanics

After De Broglie [117] gave a wave interpretation of the Sommerfeld model, Schrödinger looked for a wave equation for the electron and found the Schrödinger equation [118, 119] in 1926. He applied this equation to the hydrogen atom assuming the potential energy of the electron was the Coulomb field of a point-like nucleus. The equation with the Coulomb potential is:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left[\frac{-\hbar^2}{2\mu} \nabla^2 + V(\mathbf{r}, t) \right] \Psi(\mathbf{r}, t) \quad (3.1)$$

$$V(\mathbf{r}, t) = -\frac{e^2}{4\pi\epsilon_0 r} \quad (3.2)$$

where $\Psi(\mathbf{r}, t)$ is the wave function for the electron, $\hbar$ is the reduced Planck's constant, μ is the reduced mass of the electron, $V(\mathbf{r}, t)$ is the potential energy function and e is the charge on the electron.

Assuming a steady state wave function, the above equation can be transformed into the time-independent Schrödinger equation:

$$E\Psi(\mathbf{r}) = \left[\frac{-\hbar^2}{2\mu} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) \quad (3.3)$$

or

$$E\Psi(\mathbf{r}) = \hat{H}\Psi(\mathbf{r}) \quad (3.4)$$

where $\hat{H}$ is the Hamiltonian operator and E is the energy of the state. Solutions to this equation were labelled by the principal, orbital and magnetic quantum numbers, n , l and m . The energies of the states depended only on the principal quantum number and not on the orbital or magnetic quantum numbers.

The resulting states reproduced Rydberg's formula and thus Schrödinger's equation was a triumphant success. However, it was not immediately clear how to apply it to systems of electrons or how to modify it to be consistent with special relativity.

3.2.1 Systems of Electrons

The emission lines of more complex atoms than hydrogen could not be summarised by such a simple idea as Rydberg's formula. This indicated that many electrons interacting in a nuclear field needed a more complex calculational technique. The developments in these techniques began with the Hartree method, progressed to the Hartree-Fock method, and finally resulted in the Multiconfiguration Hartree-Fock method. These methods and their progression are briefly outlined below.

For a system of electrons, a natural way to extend Schrödinger's equation is to (1) extend the wave function by making it a function of the positions and spins of the electrons and (2) use a multi electron Hamiltonian, that is the sum of single particle Hamiltonians and interaction terms between the electrons. This causes the complexity of solving a Schrödinger's equation to be exponentially hard. Electrons can be correlated with each other in an arbitrary fashion, including ways that violate the Pauli exclusion principle.

Hartree suggested a method of finding an approximation to the ground state wave function of a many electron Schrödinger equation via the variational principle [120]. The wave function was assumed to be a symmetrised product of single particle wave functions. This Hartree method was iterative. The first iteration assumed a wave function guess. An equation for each single particle wave function was created by assuming that the potential the electron represented by the wave function is given by the total charge distribution of the rest of the single particle wave functions. Solving these coupled single particle equations yielded a new wave function. This process was iterated until the total wave function converges, that is until the potentials created by the electrons support the state of the electrons. As

such, the explosion of complexity in the wave function was curtailed to make the problem tractable. The Hartree method has been called a Self Consistent Field (SCF) approach. The symmetrised product wave function always violates the Pauli exclusion principle and thus is appropriate for modelling indistinguishable Bosons and not Fermions such as electrons.

The Hartree-Fock method [121, 122] modified the Hartree SCF method by assuming that the wave function was an anti-symmetrised product of single particle wave functions (a Fock state). Another name for such a function is a Slater determinant. This form of wave function satisfied the Pauli exclusion principle by design and thus was a starting point for calculating atomic (electronic) structure. A major weakness was that many forms of correlation between electrons could not be represented in the wave function. Another weakness was that it only worked well for atoms with closed sub-shells as a single Slater determinant is not an eigenfunction of total angular momentum operators [123] for atoms with an open sub-shell.

These weaknesses were overcome with the MultiConfiguration Hartree-Fock (MCHF) method. In this method, the wave function was represented by a linear combination of orthonormal Configuration State Functions (CSFs) where the squares of the real-valued coefficients add to one. A single CSF was a sum of Slater determinants such that the CSF was an eigenfunction of total angular momentum operators. For any two Slater determinates that contribute to a single CSF, the number of single particle wave functions in each sub-shell must match up. The sub-shell of a single particle wave function is identified by the number of nodes in the radial part of the function. The CSF terms appropriate to a particular calculation were calculated one at a time using the variational principle and enforcing that the CSFs are orthogonal to each other. In the limit of an infinite number of CSFs, a representation of multi-electron wave functions this way should ideally define a space of solutions that is only restricted by the Pauli exclusion principle. The greater the number of CSFs calculated, the better the approximation to the solution to the multi-electron Schrödinger equation. Fischer implemented this method [124–126] successfully in the early seventies.

Because the method of dealing with complex atoms described so far depends on the variational principle, it approximates only the ground state of a system. To find transition energies and probabilities that correspond to emission lines, excited states must also be approximated. However, the MCHF method can also be used to find these approximations by following the above procedure and requiring the

wave function be orthogonal to the ground state and any other excited state wave functions that have been found. This produces an approximation for the next lowest energy excited state.

None of these approaches are relativistic since they are based on direct extensions of Schrödinger's equation. Fischer added relativistic effects as perturbations.

3.3 Relativistic Quantum Mechanics

The challenge of finding relativistic wave equation for a single electron in a central field was met by Dirac in 1928 [127]. The Dirac equation for a free electron is:

$$[i\hbar\gamma^\mu\partial_\mu - mc]\psi = 0 \quad (3.5)$$

where μ goes from 0 to 3, the Einstein summation convention applies, and ψ is a four component wave function of the electron and γ^μ satisfy the following equations:

$$\gamma^\mu\gamma^\nu + \gamma^\nu\gamma^\mu = 2\eta^{\mu\nu}I_4 \quad (3.6)$$

where $\eta^{\mu\nu}$ is the Minkowski metric with signature $(+ - - -)$ and I_4 is the 4×4 identity matrix. There are four independent plane wave solutions to this equation with a common wave number. These allow for the representation of the intrinsic spin of the electron and predicted the positron with its intrinsic spin.

The Dirac equation for an electron with electric charge q in the presence of an electromagnetic field with 4-potential $A_\mu = (\phi, A_1, A_2, A_3)$ [127] is:

$$\left[\gamma^\mu \left(i\hbar\partial_\mu - \frac{q}{c}A_\mu \right) - mc \right] \psi = 0 \quad (3.7)$$

Converting this equation to the Schrödinger form results in

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}_D\psi \quad (3.8)$$

where $\hat{H}_D$ is the Dirac Hamiltonian operator:

$$\hat{H}_D = -i\hbar c \sum_{i=1}^3 \alpha_i \frac{\partial}{\partial x^i} + q\phi + q \sum_{i=1}^3 \alpha_i A_i + \beta mc^2 \quad (3.9)$$

where $\alpha_i = \gamma^0 \gamma^i$ for i in $\{1, 2, 3\}$, $\beta = \gamma^0$ and $\phi = A_0$ is the electric potential.

If a steady state is assumed, the equation turns into the time-independent Dirac equation in Schrödinger form:

$$E\psi = \hat{H}_D\psi \quad (3.10)$$

where E is the energy of the state.

Eigenvalues of this equation with a nuclear potential have been labelled with the principal (n), total angular momentum (j), magnetic (m_j) and component of spin in the direction of the total angular momentum (k) quantum numbers [128]. The energies of these states depend only on n and k , leading to splitting of the n levels compared to the Schrödinger theory. This splitting of energy levels leads to splitting of emission lines is called fine structure and is caused by spin-orbit coupling. It should be noted that the Dirac equation predicted that the $2^2P_{1/2}$ and $2^1S_{1/2}$ levels of H had the same energy (i.e. are degenerate).

3.3.1 Systems of Electrons

In 1935, Swirles [129] showed that the Dirac equation could be derived from a variational principle and he extended this principle to a system of electrons. The Dirac-Fock method [129] resulted from using this insight with the SCF approach of the Hartree-Fock method. This gave a relativistic Hartree-Fock method.

The MultiConfiguration Dirac-Fock (MCDF) method extended the Dirac-Fock method in the same way as the MCHF method extended the Hartree-Fock method in that MCDF finds approximations to solutions of the a multi-electron Dirac equation assuming that such approximations are linear combinations of CSFs. This MCDF method will be examined in Section 3.7 as applied to characteristic radiation.

3.4 QED

Quantum Electrodynamics (QED) was first introduced by Dirac [130], treating solutions to the Dirac equation as degrees of freedom of a field to be quantised. It also quantised the wave solutions of the electromagnetic field and posits a point-like

interaction between the quantised fields. This produced infinities for measurable quantities and thus was not regarded as self-consistent. The techniques of regularisation and renormalisation were developed and allowed those infinities to be additively cancelled by other infinities to produce finite results. However, it was not clear that all infinities could be eliminated [131]. These results were for initial and final states being plane waves. They were therefore an idealised model for scattering processes.

Before the theory of QED was settled, an important experimental result that guided the development of the theory was the measurement of the energy difference between the $2^2P_{1/2}$ and $2^1S_{1/2}$ levels of H by Lamb et al. [132] in 1947. This measurement proved that the Dirac equation was not sufficient to understand H. In honour of Lamb, spectroscopic energy shifts and atomic energy level shifts away from relativistic quantum mechanical theory have been called Lamb shifts [133–135].

The basics of QED theory was settled in the following few years. By putting the equations of QED in a covariant form, Tomonaga [136], Schwinger [131, 137, 138], and Feynman [139, 140] showed that mass and charge renormalisation were all that was necessary to make finite predictions from the theory. Schwinger [131] developed covariance by using the interaction representation, where the state vector of free particle states and their combinations are constant and where field operators vary in a covariant way.

In 1951, Salpeter and Bethe introduced a fully covariant equation that described bound states in two body QED [141, 142]. The Bethe-Salpeter equation was found using Feynman's approach [140] and was then rigorously derived from covariant field theory by Gell-Mann et al. [143]. This equation is an integro-differential equation for a two particle wave-function. It has proven useful for finding the properties of the bound states of positronium [144, 145]. A generalisation has been made to apply to two bodies in a classical external field. This generalisation has been used in finding the properties of helium.

Furry [146] developed the bound state picture of QED in 1951. In this picture, the electromagnetic field was approximated as a classical external field plus a quantum field. The electron-positron field was solved for one electron states in the presence of the classical field via the Dirac equation in an electromagnetic field. The electron-positron field operator was then built out of these solutions. The state

vector and observables were affected by a time-dependent unitary transformation, keeping the one-electron field vector constant in time. This was similar to the interaction representation [131], but with free electron-positron fields replaced with electrons effected by the classical external field. The interaction term between the electron-positron field and the quantum electromagnetic field is then added as a perturbation. Thus the Hamiltonian operator in the bound state picture was the zeroth order Hamiltonian plus the interaction term that has a coupling constant factor, describing the strength of the perturbation.

On this basis, the method of calculating the spectrum of the full Hamiltonian was developed from the bound state picture by Gell-Mann et al. [143] in 1951. This method was put on a covariant footing by Sucher [147] in 1957 by using the S-matrix and thus allowing a more rigorous regularisation and re-normalisation. This line of development started with identifying eigenstates and eigenvalues of the zeroth order Hamiltonian, and formally shifting these in continuity with the coupling constant of the interaction term. This shift in energy was what is calculated in the method and did not rely on finding the eigenstates of the full Hamiltonian.

An opportunity for testing QED has been developed in the field of x-ray spectroscopy. This has begun through the study of the x-ray spectra of the simplest systems possible, namely, hydrogen-like and helium-like ions. This field of study is discussed in the following Sections 3.5 and 3.6.

3.5 Hydrogen-Like Atomic Spectra

Using the above theoretical approach, in 1983 Mohr [148] produced a comprehensive tabulation of energy levels of H-like ions with Z (nuclear charge) between 10 and 40. The calculation is customarily divided into seven components: the energy predicted by the Dirac equation with a Coulomb field, the mass corrections, the self-energy correction, the vacuum polarisation correction, high-order radiative corrections, nuclear size effect and the relativistic recoil correction. The need for the mass corrections, nuclear size effect and the relativistic recoil correction are due to the fact that the nucleus is not an infinity heavy classical point charge.

The self-energy correction, the vacuum polarisation correction and the high-order radiative corrections are the result of the QED effects that are the interaction of

the electron-positron field and the quantised part of electromagnetic field in the bound state picture. The sum of these three corrections are a power series in α , the fine structure constant, that can be represented by a set of increasingly complex Feynman diagrams. The power of α represents the number of loops in the Feynman diagram (and hence the order of the correction). Dyson [149] pointed out that there is reason to believe that such series seem to converge for many terms but are ultimately divergent. This leads to the conclusion that a full QED may not be complete and consistent within its domain. To make contact with experiment, such a series would need to be cut off while it is still seeming to converge. This is convenient as the high-order radiative corrections become unmanageable to compute as the Feynman diagrams get more complex. Mohr [148] cut the calculation off at the second order.

Johnson and Soff [150] tabulated H-like energy levels and 2S-2P transition energies for elements with nuclear charge between 1 and 110. They define the Lamb Shift to be the difference between the experimentally determined energy and the energy predicted by the Dirac equation with a Coulomb field and with the reduced mass corrections. This work agreed with Mohr [148] for those elements that were covered by Mohr.

Experimental tests of this body of theory for medium Z elements ($11 < Z < 32$) have been developed since 1983 [151–170]. The results in these papers and the computation of Johnson and Soff [150] are presented in Table 3.1 on page 46.

There have been three sources of hydrogenic ions in these experiments. The first source is a particle accelerator that produces a beam of bare ions of the elements of interest and directs them to a foil where the collisions with the foil. A percentage of the ions gain an electron that is left in an excited state as a result of the interaction. This can be a beam-foil or a beam-gas experiment. A major source of uncertainty in the results of this type of experiment is the Doppler shift as the ion beam travels at a large percentage of the speed of light. The second source is a tokamak, where a plasma is confined inside a toroidal magnetic field. Such a device can produce a hot plasma so the resulting radiation may be Doppler broadened. Satellite lines are also always an issue with a tokamak source.

The third source used to generate hydrogenic ions is an EBIT. This device produces a relatively cold and stationary collection of ions and thus does not have Doppler shifts or a large Doppler broadening. Satellite contamination can be minimised in

many studies. A disadvantage here is that an EBIT is a relatively weak source of x-rays. Electron-Cyclotron Resonance Ion Sources (ECRISs) have been used for spectroscopy of highly charged ions though no hydrogenic ions have been studied so far [171]. The advantage of an ECRIS as a highly charged ion x-ray source is that it creates high flux from a large plasma (cm scale), thus a reference line free double flat crystal spectrometer may be used [172].

There are three types of tests of the theory in these papers. The first is an absolute measurement of the energy of the radiation resulting from a transition. Such results are made using characteristic radiation to calibrate the spectrometer involved. In principle, a good measurement of the geometry of the experiment including the lattice spacing of the crystal, along with advanced dynamical diffraction theory would negate the need for calibration lines. Any such calibration-line-free method would need to be validated against lines of known energy to investigate unknown systematic errors. The second type of test is to perform a differential measurement. For example, the energy difference between a Lyman α line and a Balmer β line. In this type of study, energy differences are reported. The third type of test is a relative measurement. This is done by measuring a transition energy predicted by the theory using a spectrometer calibrated with the theoretical values of other transitions predicted by the theory. The calibration transitions may be one of the Lyman α lines or the Balmer β series. All three types of tests are valuable, but it must be kept in mind that the second and third types are much weaker tests, and include additional assumptions.

Two papers are notable for their small quoted uncertainties: Beyer et al. [151] and Kubicek et al. [162]. For emphasis, these studies are presented below in advance of the rest of the body of research.

The work of Beyer et al. [151] from 1985 consisted of a measurement of Lyman α_1 and α_2 for Ar^{17+} with an uncertainty of 5 ppm. The hydrogenic ions were created by bombarding an Ar filled chamber with a beam of U^{66+} from an accelerator. This ‘recoil’ process produced Ar ions with small speeds, minimising the Doppler shift systematic error in beam-foil experiments. The wavelength determination was performed with a Johann curved crystal spectrometer calibrated with the K $K\alpha$ radiation peaks. Most of the uncertainty was claimed to arise from the fitting of the spectrum as it was contaminated by range of (weak) satellite transitions.

In 2014, Kubicek et al. [162] reported 4 ppm and 8 ppm measurement of Lyman α_1 for Ar^{17+} and S^{15+} respectively. This was achieved using the technique, first presented in [173] and later refined in [174], that used a ‘Bond’ spectrometer [175] generalised to use two detectors with a laser-assisted reference method designed to accurately measure the geometry of the EBIT source in relation to the crystal. Such a method may be able to determine the diffraction angle to a high accuracy, but, tests of this have not been presented. It is unclear if there were unaccounted-for systematic errors in the measurement of the geometry. It is also unclear which diffraction theory was used to convert the geometric measurements into wavelength. Further, the method has not been used to measure the wavelength of a well characterised source as a test of the method. These three factors make it difficult to have confidence in the quoted uncertainties.

The rest of this body of work is composed of four Cl^{16+} , four Ar^{17+} , three Fe^{25+} and two Ge^{31+} measurements along with a measurement each for Mg^{11+} , Si^{13+} , S^{15+} , Ti^{21+} , Ni^{27+} , Ge^{31+} and Kr^{35+} . These measurements are discussed below. They are presented in chronological order as best as can be determined on the basis of where the measurements first appeared.

In 1983 Briand et al. [153] reported measurements of the Fe^{25+} Lyman α lines in a beam-foil experiment using the Bond method with a single flat crystal calibrated with Co $K\alpha$ lines. The paper claimed that foil composition and thickness were able to be controlled so to remove satellite contamination to the Lyman α lines, though details were not provided. The work produced a 90 ppm uncertainty. An explicit error budget was not given but it seems that the two major sources of uncertainty were the Doppler shift correction and the crystal calibration uncertainty. The Doppler shift correction uncertainty of the Lyman α lines was produced by uncertainty in the velocity of the ions that emitted those lines. The crystal calibration uncertainty was caused by uncertainty in the peak locations of the Co $K\alpha$ lines, although it was unclear how these were transferred to the calibration. The energy of the lines were consistent with the Mohr [148] theory. However, since some of the sources of error were correlated between the lines, the uncertainty of the difference in the energies was small enough to show an inconsistency with theory of 1.75 times the experimental uncertainty. This disagreement was not able to be explained.

The first measurement of the Ar^{17+} Lyman α lines are in Briand et al. [154] in 1983. Using a beam-foil design with a K $K\alpha$ calibrated single flat crystal

spectrometer, this study finds results of with an uncertainty of 150 ppm. The uncertainty was divided into two sources estimated with equal weight. The first was Doppler shift uncertainty caused by uncertainties in speed and direction of the ion beam. The second was the combined spectrometer calibration uncertainty and statistical uncertainty of the lines. There was also satellite line contamination that appeared to be uncharacterised in the study. The energy of the lines were consistent with the Mohr [148] theory. He-like line energies measured from the same beam were also reported.

The 1984 paper of Källne et al. [161] contained measurements of the Lyman α lines of Cl^{16+} . Using a single flat crystal analyser calibrated by Ar $K\alpha$ at a tokamak, 34 ppm measurements were reported. There was strong satellite contamination that contributed to the final uncertainty. Most of the uncertainty was due to an observed shift of the Lyman α lines with line intensity. This shift was attributed firstly to a rate dependence in the detector electronics, and secondly to different excitation conditions in the tokamak, producing different ratios of the Lyman α line's strengths to the unresolved satellite line strengths. The rate dependence of the electronics was characterised afterwards, and compensated for as well as possible. The different excitation conditions would accentuate asymmetry of the peak, leading to a shift in peak position that could not be systematically compensated for.

34 ppm and 41 ppm measurements of the Lyman α transition energies of Cl^{16+} were reported in Richard et al. [165] in 1984. This was done using a Johann curved crystal spectrometer with a beam-foil setup calibrated with the Ar $K\alpha$ lines. Satellite contamination of the Lyman α lines was observed and fitted along with the Lyman α lines. The major sources of uncertainty were the calibration and the Doppler shift. The Doppler shift was determined by observing the peak energies for multiple ion beam speeds, fitting a model to the results and extrapolating the model to zero speed. This parameter of the fit model that was constrained was the angle the ion beam made with the slits that defined the x-ray beam.

In 1985, Tavernier et al. [168] reported a measurement of the Kr^{35+} Lyman α_1 energy. This paper described a 37 ppm result using a beam-foil design incorporating a single flat crystal spectrometer using a 'Bond' method. The work was calibrated by Cr $K\alpha$ radiation. The Lyman α line was measured using second order diffraction while the Cr $K\alpha$ was measured using first order diffraction to make the angles of diffraction close. Darwin dynamical theory was used in the

calibration method to calculate the resulting difference in dynamical angle shifts between the two spectra. No reference to the theory was provided, so it is difficult to assess the accuracy of this aspect of the calibration. The detector was mounted on a circular track with the angular position controlled by a precise stepper motor. The crystal was rotated by another stepper motor. The paper reported just one of the Lyman α line energies as the method could only calibrate one energy. It was thought the linearity of the stepper motor was better than that of the detector. Thus the energy of the Lyman α_1 line was measured by rotating the detector to an angle where its peak appeared in the same detector channel as the calibrating $K\alpha$ radiation peak (but at a different angle). This unique arrangement did not seem to constrain the calibration uncertainty any better than previous methods, as it has not been repeated.

Deslattes et al. [158] found measurements of the Lyman α line energies of Cl^{16+} in 1985. Results with an uncertainty of 42 ppm and 51 ppm were achieved using a beam-foil approach, and with a Johann curved crystal spectrometer calibrated by the two lines in Ar $K\alpha$ radiation. The Doppler shift was compensated for by measuring the Lyman α lines for multiple beam speeds and by using a similar analysis to Richard et al. [165]. The calibration appears to be compromised by the poor fit of a two Voigt function model to the Ar $K\alpha$ profile. However, a discussion of the sources of uncertainty was missing from the paper, so it is difficult to assess the validity of the error bars.

The energies of the Ar^{17+} Lyman α lines were again measured in Marmar et al. [164] in 1986. These 11 ppm and 19 ppm measurements were taken with a tokamak in a continuation of the work in Källne et al. [161]. This experiment used the two peaks of K $K\alpha$ as a calibration. The Lyman α profile peaks were contaminated by satellite lines that were fitted along with the Lyman α peaks. The main source of uncertainty was the calibration, caused both by uncertainty of the K $K\alpha$ peaks and the extrapolation of the calibration to the Lyman α peaks.

Measurements of the Lyman α transition energies of Fe^{25+} were reported in Silver et al. [166] in 1987. This work used a beam-foil light source and two complementary Johann curved crystal spectrometers, producing a 107 ppm result. The dual spectrometer setup reduced the Doppler shift uncertainty by quantifying the effect of the misalignment of the ion beam with the spectrometers. The detectors used were long sheets of x-ray film curved around the Roland circles of each of the

crystals. The Balmer β lines of Fe^{25+} (measured in fourth order) were used as calibration. The calibration used Bragg's Law with an index of refraction correction and the Doppler shift correction as a dispersion model. It should be noted that this model excluded dynamical diffraction effects, such as depth penetration, that may be important. The model was fitted using the Balmer β lines. The energies of the Balmer β lines were taken from the theory of Erickson et al. [176], so this work was more of a consistency check for the QED theory than an absolute test of the theory.

Laming et al. [163] used a beam-foil method to generate the excited Ge^{31+} ions in 1988. The resulting Lyman α x-ray energies was measured used a dual curved crystal setup of the same type as Silver et al. [166], however the crystals had a small radius of curvature. Again, the Balmer β lines for the ion under investigations was used for relative measurement calibration. The result was three sets of two measurements each with a quoted uncertainty of between 13 and 17 ppm. The results disagree with theory (Johnson and Soff [150]) by 83 ± 14 ppm for Lyman α_1 and 66 ± 13 ppm for Lyman α_2 . Such a strong disagreement suggests either incompleteness of the theory, an unestimated systematic error in the measurement, or an uncertainty estimate that is too small. The diffraction model used in the calibration was the same as that of Silver et al. [166]. This model excluded all dynamical diffraction effects except the index of refraction correction. The other dynamical diffraction effects are needed to (accurately) interpolate between the widely spaced calibration lines used when the radius of curvature is small. It is likely that this systematic error accounted for much of the disagreement and thus this result should be excluded as evidence relevant to the validity of the theory. As a further test, the spectrometers were calibrated using Ga $K\alpha$ and S $K\alpha$, yielding similar discrepancies.

In 1991, Beyer et al. [152] reported the Ni^{27+} Lyman α_1 line energy. A Johann type curved crystal spectrometer was used at a beam-foil source to produce a 13 ppm result. The spectrometer was calibrated using Cu $K\alpha$ radiation and possibly Lyman α_2 . The uncertainties were due to spectator transitions.

The 2007 paper, Chantler et al. [156] and the 1992 Chantler PhD thesis [170] found the Fe^{25+} Lyman α line energies. Results with 32 ppm and 34 ppm uncertainty were achieved using a beam-foil source and a similar double curved crystal spectrometer technique as in Silver et al. [166]. This measurement used 78 H-like

and He-like Fe transitions also emitted from the ion beam with energies from theory as a calibration. These lines included seven Fe^{25+} Balmer β transitions. The Lyman α line energies are measurements of quantities predicted by theory calibrated by theory. Also reported in this paper is an absolute measurement of the $2p_{3/2} - 2p_{1/2}$ fine structure calculated by finding the difference of the energies of the Lyman α lines. This fine structure measurement had an absolute uncertainty 10 times smaller than the Lyman α line energies as major errors in the Lyman α line energies were correlated and thus they cancelled on subtraction.

The 2009 paper, Chantler et al. [157] and the Chantler PhD thesis [170] from 1992 measured Ge^{31+} Lyman α transition energies. A technique similar to [156] and [166] produced a 15 ppm result. The Lyman α energy measurements were relative to the theoretical Ge^{31+} Balmer β transition energies. The work also included a differential measurement of Lyman α energies minus Balmer β energies. This additional measurement constitutes the most stringent differential measurement and self-consistency check on the theory yet produced. An absolute measurement of the $2p_{3/2} - 2p_{1/2}$ fine structure was also reported.

In 1998, Hölzer et al. [160] found the Mg^{11+} Lyman α transition energies. This report quoted 24 ppm and 47 ppm measurements using an EBIT source. It used two parallel but separated flat crystal plates cut from a monolithic crystal. Each crystal plane produced its own image of a line on the detector. These two images were displaced in relation to each other. The diffraction angle of a line was determined by knowing the displacement between the two images and the distance between the diffracting crystal surfaces. The work was calibration-line free, incorporated the refractive index correction, and corrected for temperature variation. However, it assumed a well-defined stress-free lattice spacing, and a very good measurement of the geometry of the setup.

In 2002, Tschischgale et al. [169] reported measurements of the Si^{13+} Lyman α energies. This EBIT experiment used the same technique as Hölzer et al. [160] to produce 71 ppm and 107 ppm measurements. The dominant uncertainty was the measurement of the displacement between the images of the lines, which is in turn dominated by statistical uncertainty of the line fits, and by the sensitivity of flat crystal measurements to lateral displacements of the source or image.

The Lyman α_1 energy of Ti^{21+} was reported in Tarbutt et al. [167] in 2002. This 28 ppm result was produced using an EBIT and Johann type curved crystal

spectrometer. V $K\alpha$ radiation was used to calibrate the spectrometer. It appears that Lyman α_2 was used as part of the calibration as well. Lyman α_2 energy was taken from the QED theory. Thus the Lyman α_1 energy result was not a good test of the theory at the level presented.

Bruhns et al. [155] reported the energy of Cl^{16+} Lyman α_1 in 2007. This study used an EBIT and the single flat crystal with laser reference technique used in [162]. The uncertainty in the measurement was quoted as 10 ppm. The spectrometer system was calibrated with the theoretical value of the Ar^{17+} Lyman α_1 line. Thus the result was a consistency check rather than a measurement of energy. It could have been phrased as a differential measurement but this was not reported.

Measurements of the V^{22+} Lyman α line energies were reported in Gillaspy et al. [159] in 2010 by the group of Chantler. Results of 46 ppm for these lines were produced using an EBIT source and an adjustable Johann-type curved crystal spectrometer. The spectrometer was calibrated by the $K\alpha$ radiation of Ti, V, Cr and Mn. The work presented by the present author in this thesis used a similar but much improved technique.

Table 3.1 and Figure 3.1 below were created by the present author to summarise the results of the above body of research and how it compares to the theory of the Lamb Shift. These tests of QED show good agreement between theory and experiment for H-like systems down to as low as 4 ppm, excluding the Ge^{31+} measurement of Laming et al. [163]. There is reason to exclude it as the diffraction model used in the calibration excluded depth penetration effects (or any dynamical diffraction) that are needed to interpolate between the widely spaced calibration lines used when the radius of curvature is small. The fact that all these measurements with different experimental techniques taken as a whole produce agreement with theory results in some confidence that researchers have a good grasp of the precision and accuracy of their respective approaches to testing the theory.

QED effects in atoms are strongest when a particle is in a strong field. This can be achieved using a highly charged nucleus attracting an electron as in the above work. It can also be achieved with muonic hydrogen and deuterium, where the muon stays close to the nucleus because of its large mass. A discrepancy between the QED theory and an experiment in the 2S-2P transition of muonic hydrogen has recently been reported [177]. A similar discrepancy was also measured with muonic deuterium [178]. In these experiments, highly excited muonic atoms was

created via muons impacting a hydrogen or deuterium gas target. A small proportion of the highly excited μp decayed to the 2S state. A tunable laser excited these atoms to the 2P states. The closer the energy of the laser photons to the transition energy, the higher the proportion of the 2S atoms were excited to 2P. This relative proportion was measured by the strength of the x-ray transitions from 2P to 1S. Thus the transition energies could be measured by fitting the x-ray strength versus laser frequency graphs and finding the peak frequencies. The results cast some doubt on the estimation of uncertainty of theory, QED high-order radiative corrections and perhaps the proton and deuterium charge radii. However, any error of the proton radius and deuterium radius is not observed in other experimental types including scattering. Further work on more precise experiments in the medium Z hydrogenic ion measurements would be helpful in establishing a cause for this discrepancy.

Transition	Measured (eV)	Reference	Year	Theory (eV) [150]
Mg ¹¹⁺ Lyman α_1	1472.671(35)	[160]	1998	1472.63608(13)
Mg ¹¹⁺ Lyman α_2	1471.622(70)	[160]	1998	1471.69048(12)
Si ¹³⁺ Lyman α_1	2006.06(14)	[169]	2002	2006.07833(26)
Si ¹³⁺ Lyman α_2	2004.41(21)	[169]	2002	2004.32346(25)
S ¹⁵⁺ Lyman α_1	2622.704(20)	[162]	2014	2622.69887(52)
Cl ¹⁶⁺ Lyman α_1	2962.46(10)	[161]	1984	2962.35239(66)
Cl ¹⁶⁺ Lyman α_2	2958.62(10)	[161]	1984	2958.52525(62)
Cl ¹⁶⁺ Lyman α_1	2962.47(12)	[165]	1984	2962.35239(66)
Cl ¹⁶⁺ Lyman α_2	2958.59(10)	[165]	1984	2958.52525(62)
Cl ¹⁶⁺ Lyman α_1	2962.49(12)	[158]	1985	2962.35239(66)
Cl ¹⁶⁺ Lyman α_2	2958.68(15)	[158]	1985	2958.52525(62)
Cl ¹⁶⁺ Lyman α_1	2962.344(30)	[155]	2007	2962.35239(66)
Ar ¹⁷⁺ Lyman α_1	3323.20(50)	[154]	1983	3322.99188(78)
Ar ¹⁷⁺ Lyman α_2	3318.10(50)	[154]	1983	3318.17598(74)
Ar ¹⁷⁺ Lyman α_1	3322.988(17)	[151]	1985	3322.99188(78)
Ar ¹⁷⁺ Lyman α_2	3318.171(17)	[151]	1985	3318.17598(74)
Ar ¹⁷⁺ Lyman α_1	3322.956(62)	[164]	1986	3322.99188(78)
Ar ¹⁷⁺ Lyman α_2	3318.178(36)	[164]	1986	3318.17598(74)
Ar ¹⁷⁺ Lyman α_1	3322.993(14)	[162]	2014	3322.99188(78)
Ti ²¹⁺ Lyman α_1	4976.86(14)	[167]	2002	4976.8909(13)
V ²²⁺ Lyman α_1	5443.95(25)	[159]	2010	5443.6263(14)

Table 3.1 – Continued on next page

Table 3.1 – continued from previous page

Transition	Measured (eV)	Reference	Year	Theory (eV) [150]
V ²²⁺ Lyman α_2	5431.10(25)	[159]	2010	5430.6997(12)
Fe ²⁵⁺ Lyman α_1	6973.80(60)	[153]	1983	6973.1751(26)
Fe ²⁵⁺ Lyman α_2	6951.90(70)	[153]	1983	6951.9609(25)
Fe ²⁵⁺ Lyman α_1	6972.65(75)	[166]	1987	6973.1751(26)
Fe ²⁵⁺ Lyman α_2	6951.19(74)	[166]	1987	6951.9609(25)
Fe ²⁵⁺ Lyman α_1	6972.73(24)	[156, 170]	1992	6973.1751(26)
Fe ²⁵⁺ Lyman α_2	6951.49(23)	[156, 170]	1992	6951.9609(25)
Ni ²⁷⁺ Lyman α_1	8101.76(11)	[152]	1991	8101.7406(40)
Ge ³¹⁺ Lyman α_1	10625.47(15)	[163]	1988	10624.5174(78)
Ge ³¹⁺ Lyman α_1	10625.51(15)	[163]	1988	10624.5174(78)
Ge ³¹⁺ Lyman α_1	10625.26(15)	[163]	1988	10624.5174(78)
Ge ³¹⁺ Lyman α_2	10575.91(14)	[163]	1988	10575.2575(74)
Ge ³¹⁺ Lyman α_2	10576.18(18)	[163]	1988	10575.2575(74)
Ge ³¹⁺ Lyman α_2	10575.91(14)	[163]	1988	10575.2575(74)
Ge ³¹⁺ Lyman α_1	10624.24(16)	[157, 170]	1992	10624.5174(78)
Ge ³¹⁺ Lyman α_2	10574.94(16)	[157, 170]	1992	10575.2575(74)
Kr ³⁵⁺ Lyman α_1	13508.95(50)	[168]	1985	13508.932(13)

Table 3.1: Experimental H-like energies along with the theory of Johnson and Soff [150]. The theoretical uncertainties range from 0.084 ppm to 0.96 ppm and increase with atomic number due to increasing nuclear charge distribution uncertainty. The quoted experimental uncertainties claim to be at least 17 times larger than the quoted theoretical uncertainties. This means that all measurements thus far made do not test the theory at its currently estimated limits. Therefore, more accurate and precise x-ray spectrometry would be valuable in testing QED.

3.6 Helium-Like Atomic Spectra

Two electron ionic systems have also been of interest in testing QED. The lowest energy lines resulting from transitions to the ground state for He-like atoms are the w , x , y and z lines. These names originated in Gabriel [179]. The corresponding transitions are: $1s2s(^3S_1) \rightarrow 1s^2(^1S_0)$ for the z line, $1s2p(^3P_1) \rightarrow 1s^2(^1S_0)$ for the y line, $1s2p(^3P_2) \rightarrow 1s^2(^1S_0)$ for the x line and $1s2p(^1P_1) \rightarrow 1s^2(^1S_0)$ for the w line.

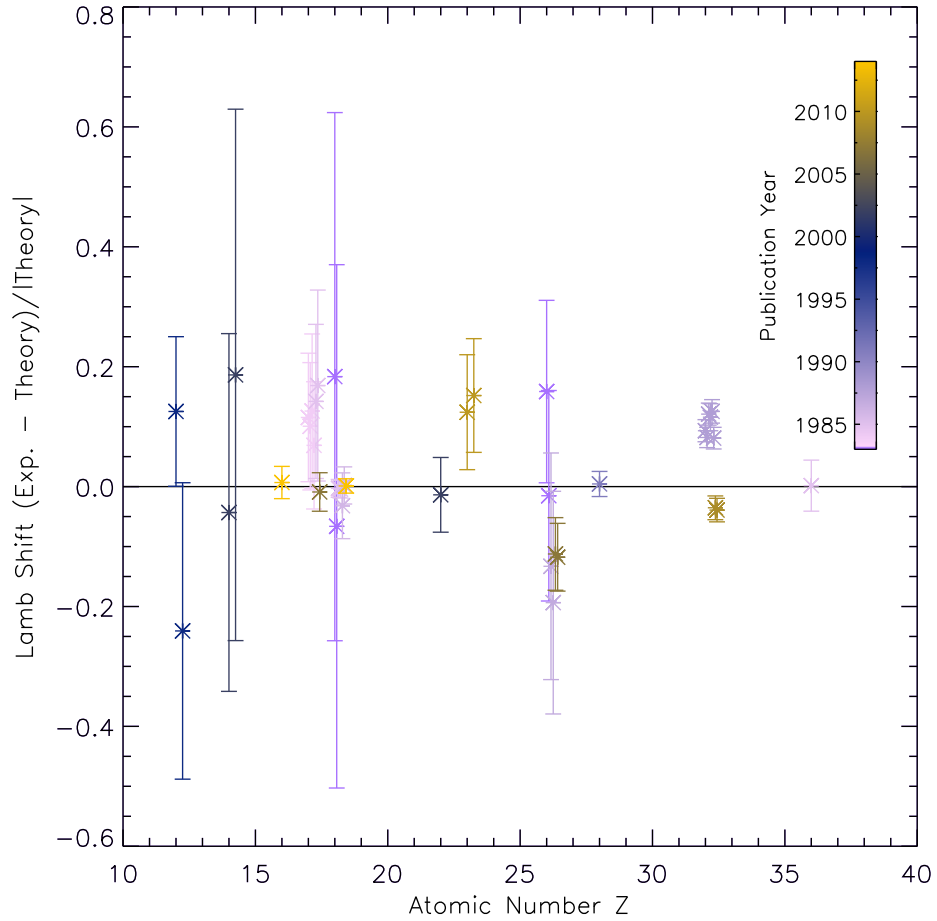


Figure 3.1: Comparison between theory and experiment for the 1S-2P Lamb Shift. The theoretical calculations are from Johnson and Soff [150] while the experimental measurements are from [151–169]. The range of uncertainties of transition energies in these experimental results is from 150 ppm to 4 ppm. The χ_r^2 for this data set is 5.1. Excluding the $Z=32$ measurements in [163] leads to a χ_r^2 of 0.99. Thus the theoretical and experimental transition energies seem to agree down to approximately 4 ppm, however there are not many results with uncertainties less than 10 ppm.

Important theoretical tabulations of the energies of the states underlying these transitions levels have included Drake [180], Plante et al. [181], Cheng et al. [182], Artemyev et al. [183]. Previous to this body of work, approximations introduced in the calculation of the energies of states meant that these calculations were tuned to be accurate for either low atomic number or high atomic number. Medium atomic number ions were not well served. In 1988, Drake [180] used a method of calculation that provided results over the entire range of atomic number. Newer calculations have built on this success, including higher orders of QED corrections.

The most recent tabulation, Artemyev et al. [183], is the one of the most complete treatments to date and includes two-electron QED corrections.

Numerous measurements of He-like transitions from medium atomic number ions have been made from the early 1970s [155, 174, 184–205]. However, no reports of the x , y or z lines of He-like Cr exist in this literature. There have been two measurements of the w line of He-like Cr reported in the literature to date.

In 1988, Aglitsky et al. [193] reported a 92 ppm measurement of the w line. This work used a Johann curved crystal spectrometer calibrated by unspecified characteristic radiation. The He-like Cr source was a Low-Inductive Vacuum Spark (LIVS) source. The dominant uncertainty was caused by unresolved satellites contaminating the spectrum.

Beiersdorfer et al. [195] produced a 70 ppm of the w line in 1989. A Johann curved crystal spectrometer calibrated to hydrogenic theory was used. The source was the Princeton Large Torus tokamak. The sources of the largest uncertainties were Doppler broadening and unresolved satellites contamination, as expected for a tokamak experiment.

Recently, there has been controversy over the lines of He-like ions [203, 205–208]. Chantler et al. [203] reported the measurement of the w line of He-like Ti, as well as a meta-analysis of all the preceding He-like lines compared to theory [183] for elements with an atomic number between 16 and 36. It was observed that there is a systematic discrepancy (ΔE) between theory and experimental findings. If put into the form of αZ^3 , the discrepancy had a high degree of significance. The fitted result was: $\Delta E = 1.000(197) \times 10^{-5} Z^3 eV$ with a χ_r^2 of 1.28.

A comment by Epp [206], on Chantler et al. [203] stated that the Kubicek et al. [174] measurement of the w line of He-like Ar was not included in the meta-analysis. This measurement had a remarkable claimed accuracy of 1.5 ppm (the best in the region by an order of magnitude). With the Kubicek et al. measurement included in the meta-analysis, a result of a Z^0 fit was claimed - $\Delta E = 0.0017(48) eV$ with a χ_r^2 of 3.7. This result is consistent with $\Delta E = 0$ but the χ_r^2 indicates that the model does not fit the data. It was claimed that this uncertainty in the fitted parameter and the higher χ_r^2 led to the conclusion that the fit is inconclusive with regard to the claim that there is a Z^3 dependence. Inclusion of this measurement also leads to the Z^3 fit of $\Delta E = 1.4(8) Z^3 eV$ with a χ_r^2 of 3.4. Therefore, the Z^3 model fits the data slightly better. This issue should be experimentally investigated further.

The reply by Chantler et al. [207] to the comment by Epp [206] on the original paper [203] pointed out that the best fit for $\Delta E = pZ^n eV$ with the Kubicek et al. [174] measurement included was for $n = 5$ with a χ_r^2 of 2.4. Hence there continues to be some Z^n dependence of the discrepancy between theory and experiment that should be investigated further, both experimentally and theoretically.

Payne et al. [205] reported the energies of the x , y and z lines of He-like Ti. It was found that the ΔE from theory [183] of these x , y and z line results was positive with a discrepancy of 3.2 standard errors. This was consistent with a Z dependence of the ΔE and showed inconsistency between theory and experiment. It was hypothesised that the uncertainty of [174] is underestimated by a factor of 2-4.

Chantler et al. [208] added the Payne et al. [205] results to the meta-analysis of [203, 206, 207] and all the x , y , z measurements. This paper commented on the consistency of Kubicek et al. [174] with the rest of the experimental data. It concluded that Kubicek et al. [174] was a very clear outlier in the distribution of discrepancies between theory and data. It was thus justified that the result was excluded from the meta-analysis.

The surveys and meta-analysis of Chantler et al. present the only robust and accurate statistical analysis of the claimed experimental uncertainties in the literature to date. The clear conclusion concerning the disagreement evident in the literature is that more He-like measurements should be made. Further investigation of He-like measurements would build a more conclusive base of evidence for the existence or absence of a discrepancy.

3.7 Characteristic Radiation

Research on characteristic radiation ($K\alpha$ and $K\beta$ lines) provide standards for calibrating QED experiments with H-like and He-like ions and also has the advantage of providing an evidence base for relativistic atomic theory. This section will describe early history of characteristic radiation and then go on to focus on the $K\alpha$ and $K\beta$ lines of elements between Sc and Zn.

The history of characteristic radiation spectroscopy started with Friedrich, Knipping and Laue [209] in 1913, through the idea that x-rays display interference,

and that this property could be used to create diffraction patterns with a crystal. Friedrich, Knipping and Laue observed spots around a central image when x-rays from an x-ray tube with a platinum anticathode passed through a crystal. To explain this pattern, they postulated that the observed x-ray radiation consisted of a number of monochromatic waves.

In 1913, Moseley and Darwin [210] were the first to study the spectrum of a platinum anticathode-based x-ray tube. They found a consistent sets of lines using Bragg diffraction from four different crystals, demonstrating that the lines were a product of the source and not the crystal. Moseley [211] extended this work to study the spectra of Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn. He identified and named $K\alpha$ and $K\beta$ radiation for each element studied. Moseley then studied the $K\alpha$ and $K\beta$ spectra of elements with Z in the following set: (13-14, 17, 19-20, 22-30, 39-42, 44, 46-47) [212]. This work demonstrated that the frequency of the radiation in a series was proportional to Z^2 . From this pattern it was predicted that elements with $Z = 43$, $Z = 61$, $Z = 75$ had yet to be found.

In a series of papers from 1916 to 1919 [213–217], Siegbahn, Friman and Leide focused on two priorities. The first paper reported measuring characteristic radiation of high Z elements to identify the missing elements. The second paper reported a refinement of the spectrometry technique to reduce instrumental broadening, achieving a 100 fold increase in accuracy. This priority resulted in the observation that $K\alpha$ radiation consisted of two very closely spaced wavelengths. Siegbahn compared the results obtained for copper $K\alpha$ to the early quantum theory of Sommerfeld [115, 218] and found them to be in agreement.

In 1927, Larsson [219] reported a precision measurement of the K-series of molybdenum and iron using an improved spectrometer.

The work measuring characteristic x-ray wavelengths until 1967 was summarised by Bearden [10], putting the best measurements into a single framework of the $\text{\AA}^*$ unit for x-ray wavelength first proposed in 1965 [220]. The $\text{\AA}^*$ unit was defined by setting the wavelength of peak of the relatively symmetrical W $K\alpha$ line to 0.20901 $\text{\AA}^*$, because there was no direct calibration of x-ray wavelengths to the meter at the time.

This review now moves on to the $K\alpha$ and $K\beta$ lines of the transition metals. A clear theme of a lot of this past work is the effect of the chemical environment of an element on the radiation.

In 1970, Koster et al. [96, 221] studied $K\beta$ spectra of Ca, Ti, Cr, Mn and Fe and their oxides [96] as well as non-oxide compounds [221]. The commercial powder diffractometer used was calibrated with lines from Bearden [10]. These papers found that a shift in the $K\beta$ peak energy from metal to compound depended on oxidation state of the target element in the compound. The energy was found to increase with increasing oxidation number.

Using a simultaneous x-ray and optical interferometry method called XROI in 1973, Deslattes and Henins [69] were the first to report any x-ray wavelengths using the standard optical definition of the meter as a basis. XROI allowed measurement of the lattice spacing of the (111) planes of a boule of Si crystal to 0.30 ppm. A double flat crystal spectrometer was constructed using Si(111) from that boule. Diffraction angle was measured by a digital angle generator with an angle interferometer. The angle was then converted to wavelength by Bragg's Law with the index of refraction correction. Deslattes and Henins reported the Cu and Mo $K\alpha_1$ peak wavelength at 1 ppm uncertainty.

In 1979, LaVilla [222] reported the shape of the Cu $K\beta$ spectrum. The measurement used the double flat crystal spectrometer employed in [69], although the energy scale was relative to the peak position. The line had a central and distinct asymmetry that was evident in the top half of the spectrum while both the tails had low intensity peak structure. This shape was then compared to theoretical calculations of satellite transition energies and strengths using the non-relativistic Hartree-Fock approach of Fischer [125]. It was found that the central asymmetry was due to a doublet of single vacancy transitions (as was expected) and the structure in the tails roughly lined up with theoretical double-vacancy transitions. Therefore, there was a qualitative (though not quantitative) agreement between theory and experiment.

In 1982, Deutsch et al. [223] showed the line shape of Cu $K\alpha_1$ and reported the peak wavelength to a claimed accuracy of 0.85 ppm. This work used a double flat crystal spectrometer.

In 1986, as part of the CODATA adjustments of physical constants [224], the wavelengths of the W, Cu and Mo $K\alpha_1$ peaks were adjusted. This was done to provide a more consistent definition of x-ray wavelengths.

Kawai et al. [225] measured $K\alpha$ and $K\beta$ profiles for Sc and its compounds in 1990 using a double flat crystal spectrometer. The data was smoothed and then

deconvolved before being further analysed. Consequently, experimental uncertainties in the spectra were not propagated through the analysis. This means that the reported peak shifts and full width half maximas remain very difficult to interpret.

The Cu $K\alpha_1$ wavelength was measured by Härtwig et al. [226] in 1991. The spectrometer used was a single flat crystal design using the Bond method. The lattice parameter of the Si crystal used was measured with simultaneous x-ray and optical interferometry method, the second experimental set up of its kind. This method produced a result with a claimed uncertainty of 0.3 ppm. This work was extended in Härtwig et al. [227] from 1994 to report the line shapes of Cu $K\alpha$ and Cu $K\beta$. It represented the profile shapes as a sum of Lorentz functions.

Kawai et al. [228] measured $K\alpha$ profiles for Ti and its compounds in 1994 using a double flat crystal spectrometer. The aim of the paper was to find the magnitude and direction of shifts in empirical parameters that characterised the spectra due to chemical effects. These shifts were reported as differences in energy, thus absolute energy calibration was not necessary for the purposes of the paper. This paper found a correlation between the energy shifts of $K\alpha_1$ and $K\alpha_2$ from Ti compounds from Ti metal with 3d electron density from atomic calculations. This can be interpreted as a correlation between energy shift and oxidation number.

In 1994, Schweppe et al. [83] performed a measurement of Mg and Al $K\alpha$ profiles. This work used a vacuum double flat crystal spectrometer with the Bond method being used with the second crystal. It was calibrated by Cu $K\alpha_1$ radiation and fitted these profiles with two Voigt functions. The final uncertainties on the absolute peak energies were between 6.2 ppm and 10.3 ppm. The major contributing sources of uncertainty were considered to be an index of refraction correction, the lattice spacing of the crystals used and uncertainty in the fitting of the Voigt functions.

The Cu $K\alpha$ and Cu $K\beta$ line shapes were again measured in 1995 by Deutsch et al. [78]. The peak energies were measured using the Bond method with a single flat crystal spectrometer, while the relative line shapes were measured with a commercial double flat crystal spectrometer. The absolute measurement of peak energies were used to calibrate the line shape measurements. The instrumental broadening function was modelled by the method described in [229]. This enabled a deconvolution of the instrumental broadening function from the spectra. The spectra were then fitted by a sum of Lorentzians. The uncertainties in the energies

of the dominant component of these fits were about 0.8 ppm. This work also included comparisons to new relativistic Dirac-Fock and non-relativistic Hartree-Fock calculations. The detailed comparisons indicate that the $K\alpha$ spectrum can be explained by diagram lines plus 3d spectator transitions to the 1% level. There was a discrepancy with the $K\beta$ spectrum. It was proposed that this discrepancy could be accounted for by the absence of exchange interaction and plasma excitations from the theory.

Hölzer et al. [79] used the Bond method to measure the Cr, Mn, Fe, Co, Ni, and Cu $K\alpha$ and $K\beta$ profiles on an absolute scale in 1997. The profiles were deconvolved assuming the instrumental broadening function in [229]. These profiles were then fitted with a sum of Lorentzians. Uncertainties of 0.002 eV and 0.003 to 0.005 eV for the dominant Lorentzian of the $K\alpha_1$'s and $K\alpha_2$'s were quoted. Uncertainties of 0.001 eV to 0.009 eV for the dominant Lorentzian of the $K\beta$'s were quoted. This led to uncertainties down to 0.25 ppm for the higher energy $K\alpha$ lines and 0.12 ppm for higher energy $K\beta$ lines. As the method to propagate uncertainties through a deconvolution was not stated, it is difficult to assess the validity of these fits, and thus the reported uncertainties of fitted energies.

Anagnostopoulos et al. [84] reported the profile shape of the $K\alpha$ and $K\beta$ spectra of Sc in 1999. This study used a spherically bent Johann-type reflection crystal spectrometer with a CCD detector. This was a relative measurement, where the peak energies of the spectra were set to those reported in Bearden [10]. Both the $K\alpha$ and $K\beta$ profiles were fitted with a sum of six Voigt functions. The difference between the $K\alpha_1$ peak energy and the $K\alpha_2$ peak energy was reported, with an uncertainty of 0.008 eV. MCDF calculations were made and compared to the measurement. It was found that the $K\alpha$ spectrum was best explained with the inclusion of 3d and 3p spectator transitions. The $K\beta$ spectrum could not be explained as well by the MCDF calculations. It was proposed that the isolated atom approximation was the cause of the extra disagreement, and that transitions that include solid Sc's band structure may be needed.

In 2003, Deslattes et al. [63] evaluated x-ray transition energies in a comprehensive manner, updating the work in Bearden [10]. While Bearden used the $\text{\AA}^*$ unit, Deslattes was able to use $\text{\AA}$, due to the development of x-ray optical interferometry. The paper compared the experimental work to new calculations using the MCDF theory of Indelicato [64]. It should be noted that this theory did not calculate satellite lines, thus the shape of the profiles were not taken into account. In general,

peak shifts should be expected from the satellite lines, thus the experimental numbers are required for use as standards for spectrometry.

In that same year, 2003, Anagnostopoulos et al. [85] used Ti $K\alpha$ to validate QED calculations of Hydrogen-like π Ne lines measured at an ECRIS. The measurements were done with a Johann spectrometer as with the Sc measurements in [84]. Once validated, the suggestion was to use these lines as a standard. The uncertainties of the Ti $K\alpha$ peak locations were about 5 ppm and 9 ppm.

Also in 2003 Ursic et al. [98] reported a study of second order radiative contributions in the $K\beta$ x-ray spectra of Ca, Ti and Cr. The spectral dependence on the chemical state was investigated using the measurement of Cr $K\beta$ in Cr compounds. This study used a high resolution crystal spectrometer of unknown type, with image plate detector. These measurements found the shape of the profiles on a relative energy scale.

In 2006, Fazinić et al. [91] studied chemical dependence of second-order radiative contributions in the $K\beta$ x-ray spectra of vanadium and its compounds using a single flat crystal spectrometer. As in [98], this study was concerned with profile shape without regard for absolute energy. Mandić et al. [99] followed this work up by measuring the same things for titanium and some of its compounds.

In 2006, Chantler et al. [86] reported a new profile for V $K\alpha$ and a refit of the $K\alpha$ spectral fits of Sc, Ti, Cr and Mn taken from [79, 84, 85, 228]. V $K\alpha$ was measured using a Johann curved crystal spectrometer calibrated by the Sc, Ti, Cr and Mn $K\alpha$ lines. This work reported these $K\alpha$ lines with a consistent sum of six Voigt functions to study the progression of these components through the series of elements.

In 2010, Limandri et al. [92] measured $K\beta$ satellite and forbidden transitions in elements with $12 \leq Z \leq 30$, induced by electron impact. They used an off-the-shelf Jahansson curved crystal spectrometer calibrated by lines from Bearden. The calibration lines were Sc, Ti, Cr, Fe, Ni, and Zn $K\beta$ and Mg, Al, and Si $K\alpha_1$.

As has emerged from the review of past literature presented in Chapters 2 and 3 above, and especially as evident in Table 2.1, there is opportunity to perform more accurate measurements the $K\beta$ profiles of V and Ti. Such measurements would be useful for two purposes. The first purpose would be to test relativistic atomic theory. A second purpose is that these measurements could lead to new standards

that constrain the calibration of x-ray spectrometers, especially as used in tests of QED.

It is such considerations that led to the rationale and aims of the research presented in this thesis, as described in the next chapter.

Rationale and Aims of This Research

The research reviewed in Chapters 2 and 3 revealed attempts to improve the reliability and validity of conclusions that can be drawn from experiments in x-ray spectrometry. Such improvements, in some cases, have led to better tests of QED. But the fact that there remains significant levels of uncertainty in the measurements that constitute these tests means that further work has been called for.

Improvements in spectrometry may be wrought by expanding data collection itself, by adjusting the apparatus used for data collection, or by modifying the usage of the apparatus. Another method of improving reliability and validity in spectrometry, that adopted in the research reported here, is to decrease the systematic and random errors in both data collection and data analysis and, where possible, to estimate the size of these errors with greater validity.

The fundamental aim of the present research was, then, to increase the accuracy and thus validity of spectrometry by reducing or elucidating errors in measurement and data analysis, as part of the wider aim of better examining QED and its predictions.

Four distinct areas of investigation emerge from the research reviews in Chapters 2 and 3, generating four basic research questions, which have been taken up in the research reported in this thesis.

4.1 Research Questions

Firstly, in XAFS as set out in Section 2.3, experimental uncertainties have not been adequately represented in fitting procedures leading to error bars on physical parameters being estimated incorrectly. This has been caused by an incorrect

measure of χ^2 . This gave rise to the question – what is the effect of a more accurate measure of χ^2 being introduced into XAFS analysis?

Secondly, as outlined in Section 2.6, in the spectrometry of atomic systems at low flux EBITs used in tests of QED, cosmic ray background appeared to affect the CCD detectors used in data collection. There was no cosmic ray filtering method that can recognise small disconnected parts of cosmic ray tracks. However, Hough transform methods exist that may be able to recognise these disconnected parts. This gave rise to the question – could tests of QED using an EBIT source in conjunction with a spectrometer system that includes a CCD detector be improved by employing a Hough transform method to remove the cosmic ray background?

Thirdly, in spectrometry itself, the robustness of spectrometer calibration has rarely been investigated. This gave rise to the question – can a method of analysing the dispersion of calibration spectra be validated? As shown in Section 2.5, the use of V $K\beta$ and Ti $K\beta$ lines as standards for spectrometer calibration may be useful in tests of QED, but there has been a deficit in the literature regarding these spectra. These spectra have not been measured with the accuracy or precision of other $K\alpha$ and $K\beta$ lines in the same region of Z . Ergo, can improved measurements of V $K\beta$ and Ti $K\beta$ spectra produce new standards for x-ray spectrometry useful for tests of QED?

Fourthly, QED can be tested through the measurement of the Lamb shift of H-like and He-like medium- Z ions. Recently, there has been disagreement within the literature about whether the preponderance of evidence from He-like ions shows a disagreement with leading QED calculations. The w line of He-like Cr is the most poorly determined in this class of system and the x , y and z lines have not been reported. This gave rise the question – do the w , x , y and z lines of He-like Cr agree with the leading QED calculations?

4.2 Aims

These research questions in turn gave rise to four areas of enquiry, indeed a set or series of studies, and aims in respect of each. Hence, considering the above research questions, the aims of the research reported in this thesis can be laid out as follows.

4.2.1 Aim 1: To Improve Accuracy in XAFS Data Analysis

The most accurate mass attenuation coefficient data in the literature (the Mo K-edge) would be analysed using the standard technique and the more accurate χ^2 technique in order to assess the effects on the results. The Mo K-edge mass attenuation coefficient data used to pursue this aim existed before the present research was begun. They were collected by members of The University of Melbourne School of Physics and reported in de Jonge et al. [56].

4.2.2 Aim 2: To Improve Cosmic Ray Filters for CCD Detectors

A study of three techniques to remove cosmic ray background using data collected from a QED experiment at NIST EBIT in 2005. The efficiency and robustness of the techniques are examined.

4.2.3 Aim 3: To Improve X-ray Spectrometer Dispersion Function Analysis

The third question led to the development of the analysis of the dispersion function of a Johann type curved crystal spectrometer. This work was done using the calibration data from the Oxford EBIT experiment in 2007, conducted in the Clarendon Laboratory. Part of this development involved characterising the responses of the Backgammon detector and the clinometers that subsystems of the spectrometer system used at Oxford. These subsystem calibrations were done at the University of Melbourne x-ray optics laboratory in 2006.

Using data generated by the Oxford EBIT experiment in 2007, the V $K\beta$ and Ti $K\beta$ lines were measured and characterised, in analysis conducted subsequent to 2007 at the University of Melbourne. These characterisations were created for use as energy standards for x-ray spectroscopy calibration, in tests of QED. The characterisations would also be more widely useful for comparisons to future atomic physics calculations.

4.2.4 Aim 4: To Test QED by Measuring the Energies of He-like Cr Lines

To test QED, the energies of the w , x , y and z lines of He-like Cr were measured. This was also done at the Oxford EBIT in 2007 using the same Johann curved crystal spectrometer.

4.3 Pursuing the Research Aims

In each study, data were first collected by the present author or others in the University of Melbourne Optics Group in The School of Physics. This was followed by the main thrust of the present author's work, a complex, investigative data analysis, generally using software systems developed by the present author.

The above aims were pursued in a series of studies conducted between 2005 and 2015. These studies are reported in the chapters below in sequence. First, however, the next chapter describes the apparatus employed to generate the data in these experiments, within the context of a discussion of developments in x-ray spectrometry.

Apparatus

Aims 2, 3, and 4 of the present research involved the collection of spectrometry data. The data used in relation to Aim 1 had been gathered earlier.

Any high accuracy x-ray spectrometry relies on (a) the source of the x-rays, (b) an analysing crystal, and (c) a position-sensitive x-ray detector arranged in one of a number of geometries. This chapter firstly gives an overview of types of x-ray sources. Secondly, it outlines the different spectrometer geometries that have been developed over time. Thirdly, it presents an overview of different types of position sensitive x-ray detector. Finally, it describes the apparatus used in the experiments that related to Aims 2, 3, and 4.

5.1 X-ray Source Types

There have been many different sources of x-rays developed since they were first discovered by Wilhelm Röntgen [230]. They can be used in experiments as either broad spectrum sources or narrow spectrum line sources. Most development has focused upon increasing the flux or the brilliance of these sources. The types of x-ray source that are relevant to this thesis are the x-ray tube (including the rotating anode), the EBIT and the synchrotron. Other important x-ray sources are the ECRIS, the LIVS, the tokamak, and the X-ray Free Electron Laser (XFEL), though these are beyond the scope of the present work.

5.1.1 X-ray Tubes

X-ray tubes were the first x-ray sources and continue to be the dominant technology in producing x-rays. The general concept of these sources is to fire high energy electrons through an evacuated space (usually a tube) at a target. The electrons

interact with atoms in the target to produce x-rays via two types of inelastic scattering process. In the first type, as an incoming electron is accelerated by the electric field of an atom, it emits EM radiation. When the incoming electron's energy is high enough, the EM radiation is in the x-ray range. This resulting radiation is called Bremsstrahlung or braking radiation. X-ray photons generated with this mechanism have a broad range of energies. In a second type of process, energy may also be transferred from the incoming electron to the internal structure of the atom. In this case, an inner shell electron becomes excited to a high energy bound state or to a state in the continuum. Then, another electron from a higher energy level jumps into the vacated inner shell, losing energy, which is then transferred to an emitted x-ray photon. This fluorescence process generates x-ray photons that are called characteristic radiation. Characteristic radiation has a narrow energy range as it is caused by a transition between distinct energy levels.

X-ray tubes were developed from the Geissler vacuum tube to the Crookes tube (an evacuated tube) [231]. These tubes ionised the gas remaining in the tube for the source of free electrons to accelerate. A beam of electrons so produced was called a cathode ray. In 1896, Röntgen [230] noticed x-rays for the first time, finding them to be emitted from the part of the a Crookes tube where the cathode ray hit glass. It was also found that a cathode ray hitting aluminium produced x-rays. The Coolidge tube was developed in 1912 [232]. This boiled electrons off a metal filament to produce an electron beam while the target was made of tungsten, allowing for higher power sources with more reliability.

Heat management has been a major focus of developments of x-ray tubes. The issue is that most of the energy in the electron beam turns into heat in the anode. The temperature of the electron impact spot on the anode builds up very quickly until the anode material is damaged. Water cooling of the anode was introduced to convect heat away. Rotation of the anode was also introduced to spread the heat load. Water cooled rotating anode sources became widely available in the 1960s [233].

There is an advantage to having a point-like or line-like x-ray source for many applications of x-ray tubes such as medical imaging or x-ray spectrometry. The advantage is that in many cases, the smaller the dimensions of the source, the more spatial resolution there is for the imaging system. However, for a given source power, there is a trade-off between the heat load that must be dissipated, and the smallness of the area of the anode that produces x-rays. It has been found

that this trade-off can be circumvented by using x-rays from a large area of anode that are emitted at a large angle from the normal direction to the anode surface [234]. This reduces the effective cross sectional area of the x-ray beam produced in one direction, thus increasing available resolution. Having an adjustable so-called take-off angle allows for the investigation and optimisation of this trade-off for any particular experiment.

Stability of x-ray power can be an important quality in a rotating anode source. It depends on the kinematics of the geometry electron beam spot on the anode though a rotation and also on the stability of the voltage that drives the electron beam current. A higher frequency of rotation blurs the effect of any wobbling geometric shift in a short exposure.

5.1.2 EBIT Technology

The Electron Beam Ion Trap (EBIT) was introduced in 1988 [100] to be a source for the spectroscopy of highly charged ions. It followed the failure of the Electron Beam Ion Source (EBIS) due to the amplifications of longitudinal plasma instabilities. In the EBIT, x-rays produced are from the excited highly charged ions in an electromagnetic trap. It consists of a high current electron beam that multiply ionises atoms and also acts as a major part of the radial trap for the ions. Superconducting magnets also compress the radial part of the trap. The ions are trapped axially by electrical potential barriers. Atoms of the element of interest are injected into the trap by one of three methods, (a) vapour phase injection via the Metal Ions from Volatile Organic Compounds (MEVOC) technique [235], (b) the use of a MEtal Vacuum Vapour Arc (MEVVA) [236, 237] or (c) the sputtering of atoms off a coated wire by the electron beam [238].

The plasma of ions must be cooled to stay in the trap. This is done by injecting a lighter cooling gas. For a given temperature, the cooling gas ions will be travelling faster. This means that the proportion of the ions that escape the trap that are cooling gas ions will be greater than that proportion for the ions in the trap. This evaporation cools the plasma and leaves a greater number of the ions of interest in the trap than without the cooling gas.

The spectra of all ions up to bare uranium are able to be produced using EBIT technology with low satellite contamination [239]. However the low density of ions in the trapping region means that an EBIT source has a very low flux.

The other major use of EBIT technology has been to create beams of highly charged ions that have been used in a variety of ways. An important application of EBITs to create such beams in the last decade has been to inject such beams into accelerators for highly charged ions. This is because the EBIT has been considered to be more efficient than earlier technologies for this use.

5.1.3 The Synchrotron

Synchrotron radiation is radiation from moving charged particles that are changing direction. There have been four generations of synchrotron radiation sources [240]. The first generation parasitically used the radiation from the bending magnets of particle and nuclear physics accelerators in the 1960s. However, the motion of the accelerating particles was not optimised for generating x-rays. The second generation of the synchrotron saw the dedicated storage ring facilities of the 1970s and 1980s, still using bending magnet radiation. The third generation of sources were larger and produced more brilliant beams via insertion devices in straight sections such as undulators and wigglers. These were being built from the 90s. Some define a fourth generation to include X-ray Free Electron Lasers or XFELs (linear accelerators with undulators).

The performance of a synchrotron source is generally summarised in a brilliance versus photon energy graph. The brilliance of a beam at a nominal x-ray energy is the number of photons with energy within 0.1% of the nominal energy per second, per source area, per solid angle of beam divergence in the beam. Thus performance can increase via a higher flux, a smaller beam size or a smaller divergence. Generally, a synchrotron beamline can be optimised for bandwidth or tunable peak brilliance. Because of the high brilliance, a synchrotron source allows for a range of experiments. Experiments can be highly time-resolved for samples which photo-degrade or degrade for other reasons. Sub-micron position resolution permits elemental maps of a sample [241]. Angular or orientational resolution can be used for diffraction of complex systems, for example. Extensive investigation of absorption spectroscopy producing high accuracy mass attenuation coefficient data has also been performed [56].

5.2 Spectrometer Geometries

The second issue facing x-ray spectrometry concerns the analysing crystal. Indeed, a fundamental problem in spectrometry is how to measure the angle of diffraction. Another major problem is how to increase resolving power. There are a number of geometric arrangements of source, crystal and detector that allow these issues to be traded off or solved. These arrangements may be divided into flat crystal and curved crystal geometries, discussed below.

5.2.1 Flat Crystal geometries

Flat crystal geometries have generally been used when the flux of x-rays is high. They have instrumental broadening due to the finite width of the x-ray beam. The higher flux can compensate for the lower resolving power. Due to dynamical diffraction, there is asymmetry in the broadening in the single flat crystal case. Flat crystal systems need to control source and detector alignment to the sub-micron scale, as significant systematics have been found to arise from very small shifts of image and source position.

5.2.1.1 Double Flat

A double flat crystal spectrometer uses two flat crystals. The incoming x-rays diffract off the first crystal onto the second, and are then diffracted a second time. Proper arrangement of the crystals can significantly reduce asymmetry of a monochromatic source due to the dynamical diffraction effects of single crystal diffraction. The asymmetry of the profile and location of the source and detector yields large systematics which must be carefully accounted for. None the less, the asymmetry itself can be modelled. Slightly different incoming angles of x-rays for the two crystals, called detuning, can also sharpen the diffraction profile of a single wavelength, to create lower instrumental broadening. A disadvantage of this type of spectrometer is that it reduces the intensity of the diffracted x-rays so it may not be suitable for low flux sources.

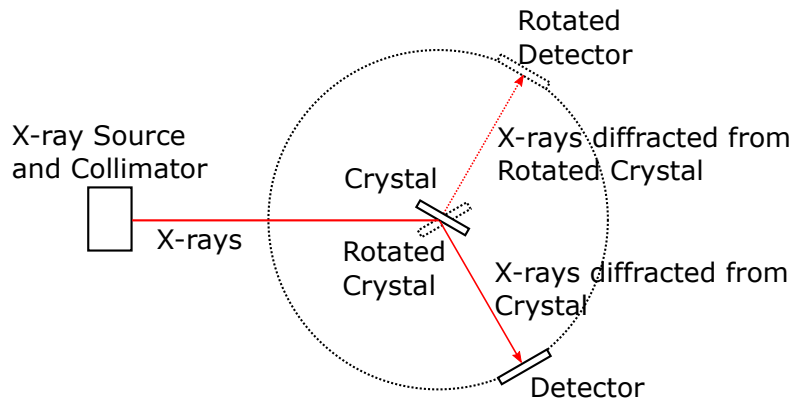


Figure 5.1: The geometry used in the simplest application of Bond's method. The single flat crystal and the detector both rotate around a single axis as shown. There are two configurations shown. The solid line configuration and the rotated configuration shown with dotted lines. The Bragg angle is half the difference in crystal angle between the two configurations. This calculation leads a cancellation of the error of the zero position in the angle measurement. Thus a major systematic error is eliminated with this method. However, the profiles and circle of confusion on the rotational axis need to be carefully studied. The incident beam should also be monochromatic.

5.2.1.2 Bond's Method

This method uses a collimated beam of x-rays with a rotatable crystal and a rotatable detector with the same axis of rotation for both [175]. A schematic of the setup is shown in Figure 5.1. Ideally, this setup would have no circle of confusion. Its advantage is that it eliminates the zero angle offset error. A variation to this setup has been to use two detectors, one on each side, where the angle between the detectors must be able to be precisely measured [174]. If successfully implemented, this has advantages of faster shifting between sides and the possibility of a smaller packaging of the experiment.

Bond's method has been used in conjunction with other techniques. One such technique has been to use Bond's method in conjunction with a double flat crystal method, where the second crystal is setup in the earlier arrangement. This gives the advantages of a double crystal technique as outlined in Section 5.2.1.1 as well as the superior angle measurement of Bond's method. This is the current standard realisation of Bond's method as, for example, represented by Schweppe et al. [83] at the National Institute of Standards and Technology (NIST).

A major difficulty in using flat crystal geometries at an EBIT source is measuring the position of the source accurately. An interesting approach that may address

this problem is using visible laser lines as fiducial markers [174]. In this method, the EBIT is configured to produce visible light. A half silvered mirror is placed between the EBIT and the crystal. A laser source is then pointed at the half silvered mirror such that the laser light reflects off the mirror onto the crystal. Using the interference between the laser light and the EBIT light, the laser source is placed into a position such that if the geometry of laser source was reflected in the plane of the half silvered mirror, the laser source and the EBIT source would be in the same position. Measuring the location of the EBIT source is then reduced to measuring the position of the laser source, which is a less challenging problem.

5.2.2 Curved Crystal Geometries

Geometries where the crystal planes are curved into a sections of cylinders offer the advantage of x-rays being focused towards the detector. This yields higher flux at the detector as well as higher resolution. This is especially important for low flux sources such as EBITs.

5.2.2.1 Von Hámos Geometry

In a von Hámos geometry [242, 243], the crystal is curved in such a way as to focus the flux of x-rays onto a line as shown in Figure 5.2. It does not improve the broadening that is due to the finite size of the source, but does increase the flux on the detector and hence efficiency. Unfortunately there can often be additional broadening or systematics from imperfect focusing.

5.2.2.2 Johansson Geometry

A crystal whose planes are curved to radius R and whose surface is machined to be curved to radius $R/2$ is the basis of Johansson geometry [244]. The circle that completes the arc of the surface of the crystal with radius $R/2$ is called the Roland circle. Such a crystal will focus x-rays from one point on the Rowland circle to another point on the Rowland circle, where each pair of points corresponds to an x-ray wavelength. A physical x-ray source does not need to be on the Roland circle, as for each wavelength, the source acts like a virtual source on the Roland circle. A perfect realisation of this geometry removes the broadening due to the

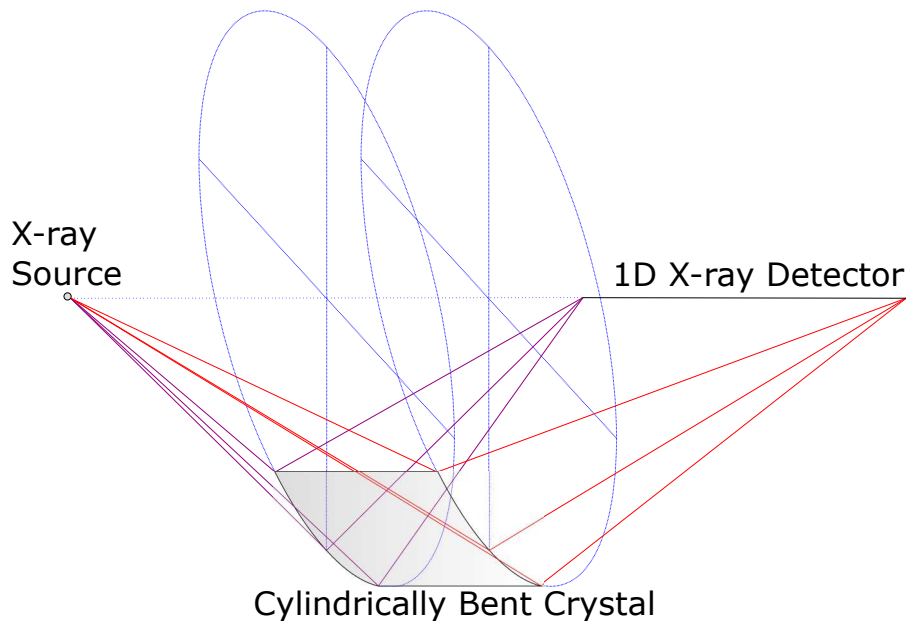


Figure 5.2: Schematic of the von Hámós geometry. The blue circles with crosses represent the completion of the cylinder defined by the crystal and the dotted line going through the centre of those circles is the axis of rotation of that cylinder. X-rays emitted from the axis of rotation are diffracted to other points of the axis as shown. The purple lines represent the paths of lower energy x-rays while the red paths represent higher energy x-rays. Both sets of paths converge to different points on the axis. An x-ray detector with one dimension of positional resolution is then able to discriminate x-ray wavelengths diffracted from the whole crystal.

finite source size and markedly reduces the dependence of a measured spectrum at the Roland circle on the exact location of the source. Such a geometry is, however, very difficult to realise in practice. Critically, a theoretical model of the Johansson geometry based on dynamical diffraction theory has not yet been completed, so systematic profile shifts may be large.

5.2.2.3 Johann Geometry

The Johann geometry [245] has the crystal planes and the surface of the crystal both curved to the same radius R through bending a flat-faced crystal. The idea of a Roland Circle with radius $R/2$ touching the middle of the surface of the crystal is relevant, as for a small arc of crystal, x-rays will be focused from and to the circle with some small circle of confusion. The smaller the arc of the crystal, the better the Roland Circle approximation. It is possible to theoretically predict the dynamical diffraction profiles including resolution and shifts of such crystals, thanks to Mosplate [26, 28].

5.3 Position Sensitive X-ray Detector Types

The third principal issue faced in x-ray spectrometry relates to the detector used. X-ray spectroscopy based on x-ray diffraction must rely a capacity to localise x-rays in space. This could be done by having a small area detector that is movable, or a detector that is sensitive to the position of the detected x-ray photons.

A range of position sensitive x-ray detectors have been developed [246]. They are usually classified as linear detectors or as area detectors depending on whether they have appreciable resolution in either one or two dimensions. If an area detector has much lower resolution in one dimension it may be called 1.5 dimensional. As many as six different position sensitive detector types have been developed for use in this field: Microstrip, Image Plate, CCD, PILATUS, Backgammon, and Photographic Plate. The work reported in this thesis has directly involved selection of the CCD, Backgammon, and PILATUS detectors.

5.3.1 Image Plate

Image Plates are area detectors that use electron-hole pairs generated by the deposition of x-ray energy into phosphor atoms in a plate. As this is a local phenomenon, position sensitivity in two dimensions is achieved. Photostimulated luminescence is used to readout the device [247]. The plates can have good quantum efficiency [248]. Their large size makes them ideal for medical imaging and x-ray crystallography studies. They are relatively heavy and take a long time to readout, so they are only useful when they do not need to be systematically moved in an experiment and a long integration time is called for. An ideal usage is in powder diffraction.

5.3.2 CCD

X-ray CCD detectors are pixelated solid state area detectors that integrate charge liberated by photo-absorption events over a given exposure time. The readout process is that each pixel's charge is sequentially moved to an Analog-to-Digital Converter (ADC). Pixels can be very small, however each pixel has a narrow range of linear response to x-ray intensity.

5.3.3 PILATUS

The PILATUS detector is a pixelated solid state area detector that leverages the ongoing miniaturisation in the silicon chip industry to provide a set of acquisition and counting electronics for each pixel [249]. Advantages of this approach are good linearity of response in intensity and position as well as an ability to filter out photon energies higher than a set cut-off. The main disadvantage is low resolution due to large pixel size as the electronics for each pixel approximates the area of the pixel. More recent developments along this line include the EIGER [250, 251], MYTHEN [252], and the Maia [253] microprobe detectors.

5.3.4 Backgammon

A Backgammon detector is a gas filled multi-wire proportional counter originally developed in France. The position of the avalanche in one dimension is encoded by charge division between two halves of a segmented anode board [254, 255]. The two segments have interlocking triangular teeth that make a pattern similar to that of a backgammon board. The position sensitivity is analogue, resulting in potentially better resolution than pixelated detectors. Some sensitivity to the position in the second dimension is achieved through resistive charge division on the threaded back and forth anode wire by researchers at NIST [256]. It provides real time acquisition of x-ray absorption events. The dead time is negligible for low count rate signals.

Further development of the technology has been made in the last ten years in Australia by The University of Melbourne Optics Group. A study of the correction of non-linearities in position has been done [257]. A study of the efficiency and linearity has been conducted [258]. Data acquisition has been improved [259]. Finally, the design of the detector has been improved to increase the intrinsic resolution of the device. [260, 261].

5.4 Experimental Apparatus Used

The various methods described above can be discriminated in terms of their specific use. The challenge to the researcher is to identify the method appropriate to the

aim of the study.

For the experiment that generated the data relating to Aim 1 of this research, namely improving XAFS data analysis, the apparatus that had been involved included the Advanced Photon Source synchrotron at the Argonne National Laboratory.

The data collected relating to Aims 2, 3 and 4 were derived from work at three laboratories. The cosmic-ray filtering study relied on data taken in Gaithersburg, Maryland at the National Institute of Standards and Technology (NIST) EBIT. The characterisation of $K\beta$ lines and the test of QED was undertaken at the Oxford University Clarendon Laboratory. The calibration of clinometers and the backgammon detector used at the Oxford experiment was undertaken at The University of Melbourne School of Physics.

The experimental apparatus that was used in each of these locations for these experiments is now described.

5.4.1 NIST Experimental Setup

At the EBIT at NIST, two experiments were performed sequentially with a shared experimental setup. The first had the aim of measuring the Lyman α lines of H-like Ti as a test of QED. The second had the aim to measure the Rydberg lines of H-like Ti as a way to contribute to the understanding of QED and plasma physics. In the experimental setup [200], there were two Johann geometry spectrometers [262, 263] attached to perpendicular ports of the NIST EBIT.

This is illustrated by Figure 5.3. The main spectrometer had a vertical configuration with a backgammon type multi-wire proportional counter as the detector. This was an absolutely calibratable spectrometer. The secondary had a horizontal configuration with an x-ray CCD detector. An absolute calibration was not possible for this spectrometer. It was set up to study polarisation of the Lyman α lines in conjunction with the primary spectrometer and also collected the Rydberg lines. Since it used a CCD detector, it was effected by cosmic ray tracks. Techniques for cosmic ray removal in CCD x-ray detectors were studied using this CCD data. The study using this setup is reported in Chapter 7.

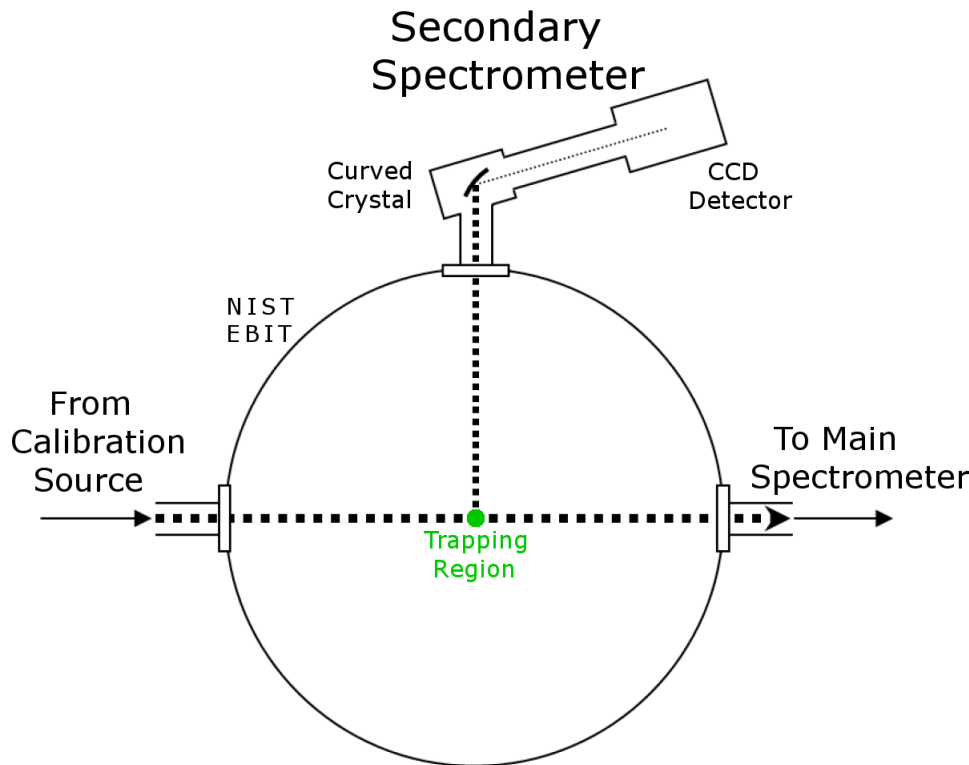


Figure 5.3: Schematic of the NIST experimental setup. Note the horizontal configuration of the secondary spectrometer with x-ray CCD detector attached.

5.4.2 Oxford Experimental Setup

This experiment employed a Johann geometry curved crystal spectrometer at the Oxford EBIT [264] in the Clarendon Laboratory. It has two aims. The first aim was to use a fluorescence source to characterise the V, Ti and Cr $K\beta$ lines, in order to define standards for x-ray spectroscopy that may be used in tests of QED. The second aim was to use the EBIT in a test of QED by measuring the w , x , y , and z lines of He-like Cr. An unexpected constriction in the availability of liquid He needed to run the EBIT resulted in a very short running time for the EBIT, so a limited amount of EBIT data was collected. Figure 5.4 shows the arrangement of the two x-ray sources, the diffracting crystal and the detector while Figure 5.5 shows the corresponding labelled photo of the setup.

5.4.2.1 Fluorescence Source

The fluorescence source, also known as the calibration source, was an x-ray tube that produced the V, Ti and Cr $K\beta$ lines as well as the $K\alpha$ radiation used for

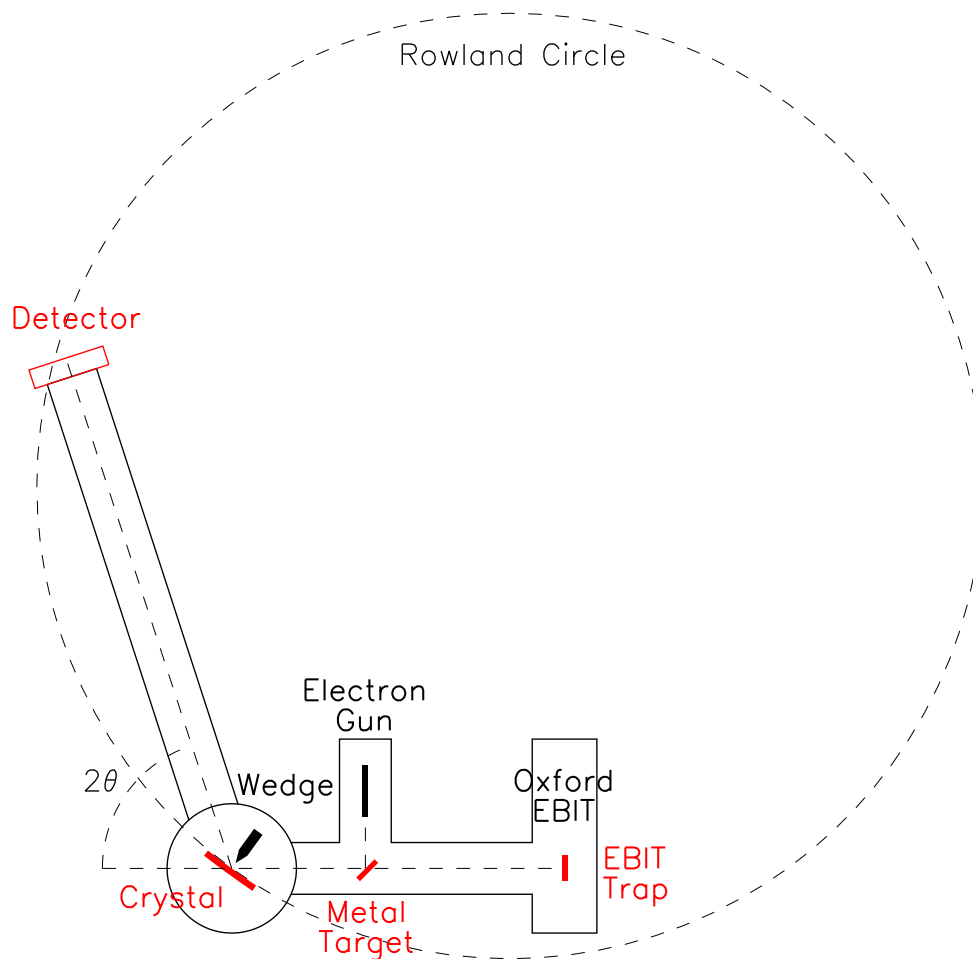


Figure 5.4: Schematic diagram of the Oxford experimental setup. The Electron Gun and Metal Target make up the Calibration Source, which is the source of the $K\alpha$ radiation used in calibration, and of the $K\beta$ radiation. The EBIT Trap is the region of the Oxford EBIT where He-like Cr x-ray lines are emitted. It should be noted that the Electron Gun and Metal Target should be rotated 90 degrees into the page together, so that the Electron Gun sits behind the Metal Target. Details of the setup can be found in Section 5.4.2. A photo of this setup is shown in Figure 5.5.

calibration. It consisted of an electron gun firing 20 keV electrons at a collection of metal targets ($Z=22$ to 26), each of which was placed in the electron beam separately via the movement of a linear stage. The electron gun was a Kimball Physics EMG-12 backed by an EGPS-12 electron gun power supply. The electron beam incident on the transition metal target results in the emission of the characteristic x-ray radiation.

The electron gun was normal to both the path of the x-rays from the target to the crystal and to the path of the x-rays from the crystal to the detector. Transition

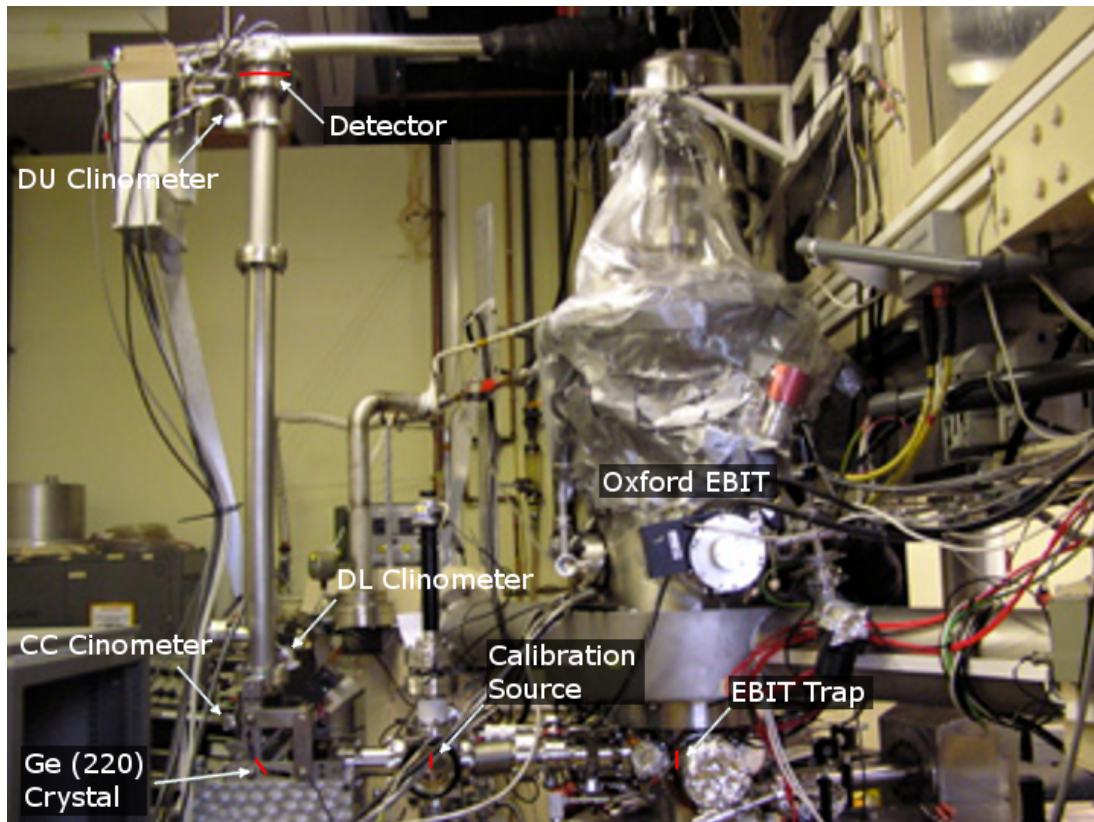


Figure 5.5: Photo of the Oxford experimental setup. The Calibration Source is the source of the $K\alpha$ radiation used in calibration and the $K\beta$ radiation. A schematic of this setup is shown in Figure 5.4. The DU and DL clinometers measure the inclination of the spectrometer arm while the CC Clinometer is mounted on the housing of the crystal and measures the inclination of the crystal. The base plate of the spectrometer is not shown. The inclination of the base is measured by the BC Clinometer. Details of the setup can be found in Section 5.4.2.

metal targets were mounted at 45 degrees to both the electron beam and the path from the selected target to the crystal. The radius of the spot size of the electron beam on the selected target was 5(1) mm. The distance from the target position to the crystal was 350(3) mm.

5.4.2.2 EBIT Source

Figure 5.6 shows components of the Oxford EBIT that control the electron beam. The electrical potential the electron beam sees on its path from the cathode to the collector (and thus the beam energy) is controlled by biasing a number of components of the EBIT. In order, these are (1) the anode, (2) the snout, (3) the transition, (4) DT1, (5) DT2, (6) DT3, (7) the suppressor, (8) the collector. The DT1 and DT3 biases are usually measured relative to DT2 since these voltages

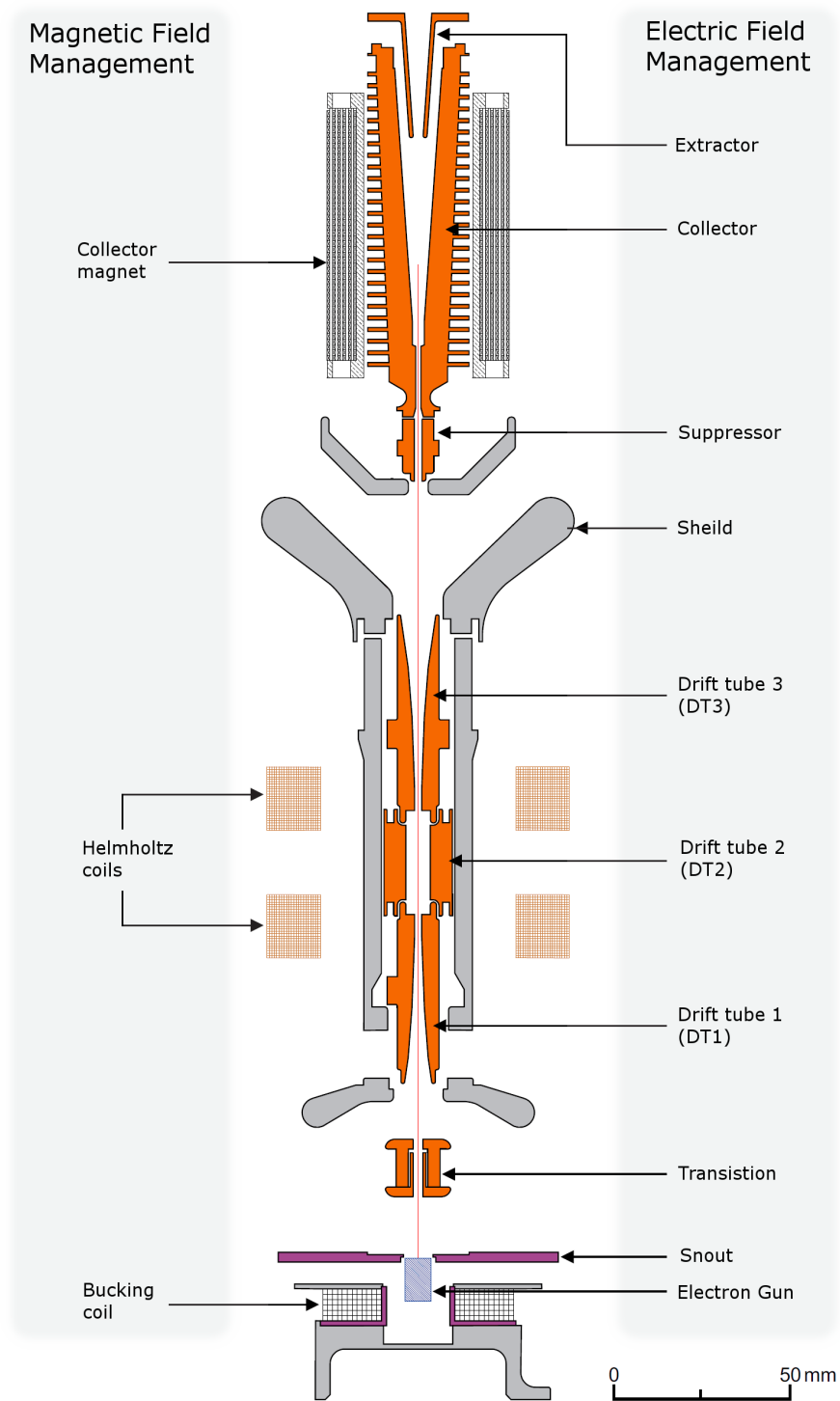


Figure 5.6: Cross section of the Oxford EBIT. This diagram based on Figure 2.1 of [1]. The major components that have an effect on the magnetic and electric fields that the electron beam (shown in red) is exposed to from its journey from the electron gun to the collector are shown here. The voltages and currents for these components that were tuned for He-like Cr are shown in Table 5.1. The ions are trapped in the DT2 region. There are apertures in DT2 and the shield to enable x-rays from the trapped ions to leave the EBIT.

Setting	Value	Setting	Value
Snout	3.77 kV	Anode	3.99 kV
Transition	5.800 kV	Focus	0 V
DT1	500 V	Filament	6.000 V
DT2 ionisation	8.0000 kV	Shield	-200 V
DT3 trap	200 V	Bucking coil	12.15 A
DT3 dump	-200 V	Superconducting Helmholtz coils	142.0 A
Suppressor	500 V	Collector magnet	5.000 A
Collector	860 V		

Table 5.1: EBIT conditions tuned to maximise He-like Cr line count rate at the detector. The anode, focus and filament are all part of the electron gun. Figure 5.6 shows how these components are arranged in the EBIT.

define the height of the trap on both sides. The magnetic field electron beam sees on its path controls the beam radius. The magnetic field is controlled by the currents in the bucking coil, the superconducting Helmholtz coils and the collector magnet. The bucking coil is designed to zero the magnetic field at the electron gun, the superconducting Helmholtz coils radially confine the beam and the ions in the trap, and collector magnet zeros the field at the collector so the beam diverges onto it. The snout passively reduces the magnetic field at the electron gun so the bucking coil need not do so much work. These voltages and currents used for the He-like Cr run are shown in Table 5.1 as well as the voltages of the anode, focus, filament and shield. The anode, focus and filament are parts of the electron gun. The shield voltage reduces the possibility of stray electrons becoming trapped. [265]. The magnetic field in the trap was 2.7 T.

The vapour injection method was used to introduce Cr atoms into the trap. The volatile compound of Cr used in this method was chromocene ($\text{Cr}(\text{C}_5\text{H}_5)_2$). The distance from the EBIT trap, where the He-like x-rays are emitted, to the center of the crystal was 965(3) mm.

5.4.2.3 Analysing Crystal

The germanium (220) crystal used in the spectrometer was manufactured and calibrated by NIST (prior to curvature) and was a near-perfect single crystal. In other words, there was no mosaic spread in the crystal. The crystal was triangular. Thermal (Debye-Waller) parameters are important and are included for the estimated temperature on an isotropic basis, as is normal for symmetric and

monatomic solids. The value of σ^2 used was $0.5661(26)\text{\AA}^2$ for a temperature of 293 K, with a linear expansion coefficient of $5.7 \times 10^{-6} K^{-1}$ [266].

The crystal was curved so it had a radius of curvature of 2742(20) mm. Thus, the radius of the Roland circle was 1371(10) mm. The two x-ray sources were in an off-focus position away from the Roland Circle, to increase the accuracy and to reduce the sensitivity of the resulting spectra to the spacial intensity distribution of the source. The aim was to image the wavelength intensity distribution of a source, not its spacial intensity distribution.

5.4.2.4 Spectrometer Angle Control and Crystal Housing

The detector arm could be set at an angle of 2θ , where θ is a nominal Bragg angle. The detector arm angle was fully adjustable, with low hysteresis on the gearing and high reproducibility. The housing for the crystal was mechanically linked to the detector arm, such that the normal vector to the crystal surface bisected the angle between the source and detector arm. Thus the crystal angle (θ) was half the detector arm angle. The source arm will be at some small angle, ϕ , to the horizontal plane.

An adjustable ‘Seemann wedge’ mounted in the crystal housing limited the diffracting region of illumination of the germanium (220) Bragg crystal. The Seemann wedge permitted adjustment of the band-pass of radiation through the crystal and controlled the major source of instrumental broadening. By varying the wedge position, the crystal curvature perfection and the consistency of prediction from dynamical diffraction theory could be investigated.

5.4.2.5 Clinometers

The crystal and detector arm angles were measured by gravity referenced electronic clinometers, each outputting a raw voltage, V . The clinometer voltages were calibrated to clinometer angle, γ , in a clinometer calibration experiment prior to the Oxford 2007 experiment. This calibration was modified to calibrate V to θ in the dispersion function analysis.

Four clinometers were installed on the spectrometer. The Base Clinometer (BC) was mounted mounted on the base of the spectrometer, the Crystal Clinometer

(CC) was mounted on the crystal holder housing, the Detector Lower clinometer (DL) was mounted at the base of the detector arm, and the Detector Upper clinometer (DU) was mounted at the top of the detector arm. DL and DU needed to measure a large range of angles. Jewell Instruments LSRP-90 clinometers were used, as could measure -90 to $+90$ degrees. BC and CC were the Jewell Instruments LSRP-30 that measured -30 to $+30$ degrees. These clinometers work by measuring the force it takes to keep a test mass in place in one direction against whatever acceleration the clinometer is undergoing. By the principle of equivalence, when the clinometer is stationary with respect to the earth, it is moving with an acceleration equal and opposite to the local gravitational acceleration vector (with respect to an inertial frame). The force is translated into an output voltage between -5 and 5 V corresponding to the limits of their respective angular ranges. Thus it is expected that the output voltage would be sinusoidal with angle with small corrections. It is also expected that the output voltage for angles close to zero degrees may be effected by hysteresis. Therefore, the DU and DL clinometers were mounted at a -20 degree angle to the spectrometer arm, while the CC was mounted at 45 degrees to the crystal housing, to avoid a zero degree angle. These mountings can be seen in Figure 5.5. The BC is just out of frame, on the left below the picture. It should be noted that after the initial calibration experiment, the mountings of the clinometers imply the specific relationships between the crystal angle, θ , the source arm offset angle, ϕ , and the calibrated clinometer angle γ . These relationships were as follows. For BC:

$$\phi = -\gamma \quad (5.1)$$

For CC:

$$\theta = 90^\circ - [\gamma + 45^\circ + \phi] \quad (5.2)$$

For DU and DL:

$$\theta = \frac{90^\circ - [\gamma - 20^\circ + \phi]}{2} \quad (5.3)$$

5.4.2.6 Detector

A multi-wire gas proportional counter with a backgammon configuration was used to detect x-rays. The detector had an active area of 40 by 40 mm. The distance from the crystal to the active region of the detector was $1500(5)$ mm. It provided good resolution in the dispersion axis of the detector, thus enabling the collection

of position data for each x-ray detection event. The outputs of the detector were four voltage signals, two from the cathode board and two from the anode wire. On the output, an x-ray detection looked like a simultaneous rapid increase in all the signals followed by exponential decays. The size of the rapid increase in voltage was proportional to the charge collected in that channel. The maximum rate of change of the voltage within the period of the rapid increase was proportional to the size of the increase.

5.4.2.7 Data Acquisition System

The signals generated from the spectrometer had to be acquired to form the raw data of the experiment. The four voltage signals from the detector, the four clinometer voltages and the temperature signal were processed and recorded by the data acquisition system, illustrated in Figure 5.7. The amplifiers output the first derivative of the detector signals. The quad single channel analyser was set to suppress signals with peak voltages less than 0.5 V and greater than 9.5 V in order to filter out noise at the low end and cosmic rays at the high end. The linear gate and stretchers identified the maximum rate of change within a period that was triggered by a universal coincidence module that was fed by the quad single channel analyser. Once a linear gate and stretcher identified this maximum, its output was held at the maximum for a specified period of time. The NI-6132 16 bit digitiser was also triggered by an appropriately delayed signal from the coincidence module. The digitiser then sampled the four linear gate and stretcher outputs as they were being held to their maximums. The digital signals were read into the computer by a custom program written in LabVIEW. This program also acquired the digitised voltages from the clinometers and the temperature sensor. The development of this data acquisition system was presented in Kimpton et al. [259].

For the calibration of the spectrometer, crystal alignment and detector scale, a series of calibration spectra was collected in successive diffracting positions, in order to assess systematics and evaluate the dispersion function. The method of the study employing the Oxford 2007 apparatus is placed in Chapter 10.

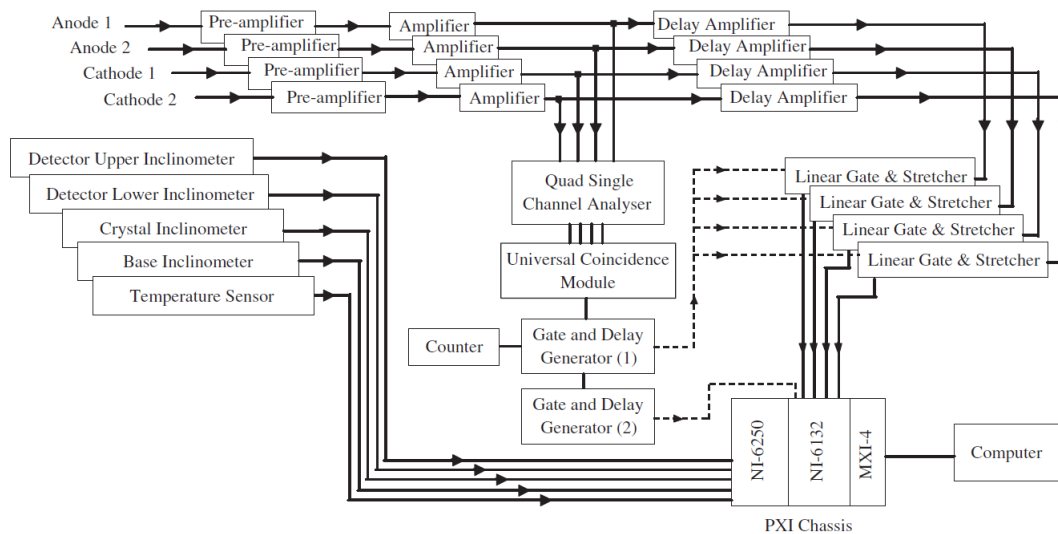


Figure 5.7: Schematic of the data acquisition system used at the Oxford 2007 experiment. The dotted lines denote the trigger lines.

5.4.3 The University of Melbourne Experimental Setups

Subsystems of the spectrometer system used at the Oxford experiment were investigated and calibrated via experiments at the University of Melbourne. These experiments investigated the linearity of the intensity response of the backgammon detector, the calibration of the backgammon detector's positional response and the calibration of the clinometers.

5.4.3.1 Backgammon Detector Intensity Response

To study the position and intensity response linearity of the Backgammon detector used at the Oxford experiment, calibration experiments were performed at The University of Melbourne with a monochromated x-ray beam generated by a MAC Science SRA M18XH1 water cooled rotating anode source. The monochromator was a channel cut Si (111) crystal set to monochromate the x-ray beam to a small range of energies around $\text{Cu K}\alpha$. The source typically has a standard deviation in x-ray intensity of 6% due to drift. This drift was assessed using a PILATUS detector.

The intensity response linearity was tested by performing an attenuation experiment. The attenuator used was a flat pack of Al foil. The thickness of the attenuator was varied by varying the number of foils in the pack. The thickness

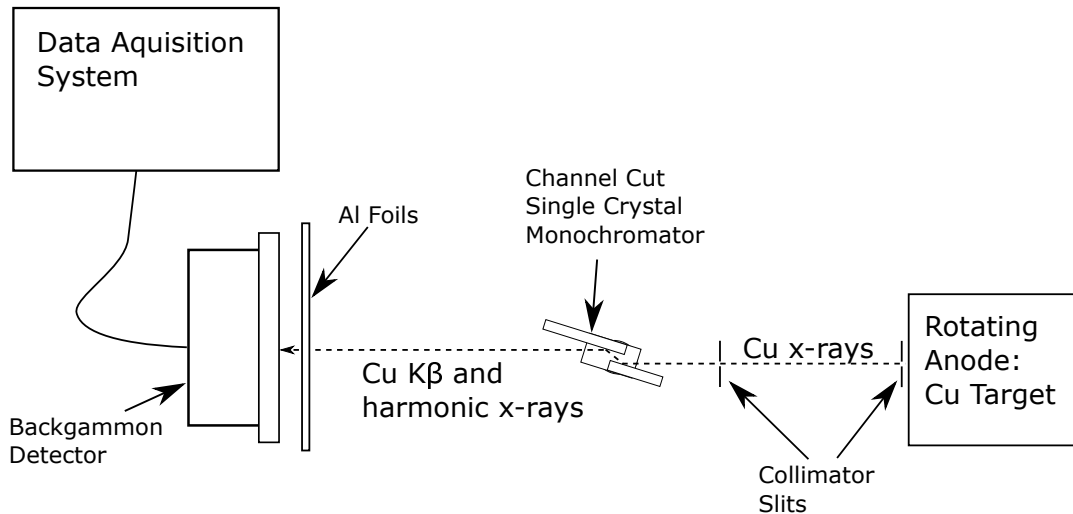


Figure 5.8: Schematic of the detector intensity linearity setup. The major components of the setup were a rotating anode source and monochromator tuned to Cu K β , an attenuator consisting of foil holder which would accept a number of Al foils and the backgammon detector.

of the foil was measured to be $10(5) \mu\text{m}$ with a micrometer. A schematic of the experimental set up is shown in Figure 5.8.

5.4.3.2 Backgammon Detector Positional Response Calibration

The position response calibration of the Backgammon detector was determined in a spatial linearity correction experiment. The MAC Science SRA M18XH1 rotating anode with a monochromator tuned to Cu K β was again used to produce a line source. The detector was mounted onto a linear stage that could move the line source across the face of the detector. The direction of the motion was the same as that of the x-ray dispersion in the Oxford experiment. A schematic of the setup is shown in Figure 5.9. A custom LabView program was written to integrate linear stage control and data acquisition.

5.4.3.3 Clinometer Calibration

Before being installed on the spectrometer in Oxford, all the clinometers has been calibrated in a calibration experiment in Melbourne. The clinometers were calibrated against a Heidenhain ROD 800 interferometric encoder with a Heidenhain ND 261 readout using a Huber 410 goniometer with a Huber SMC 9000 step-per motor controller to provide angular motion. A small stage was fastened to

Top View

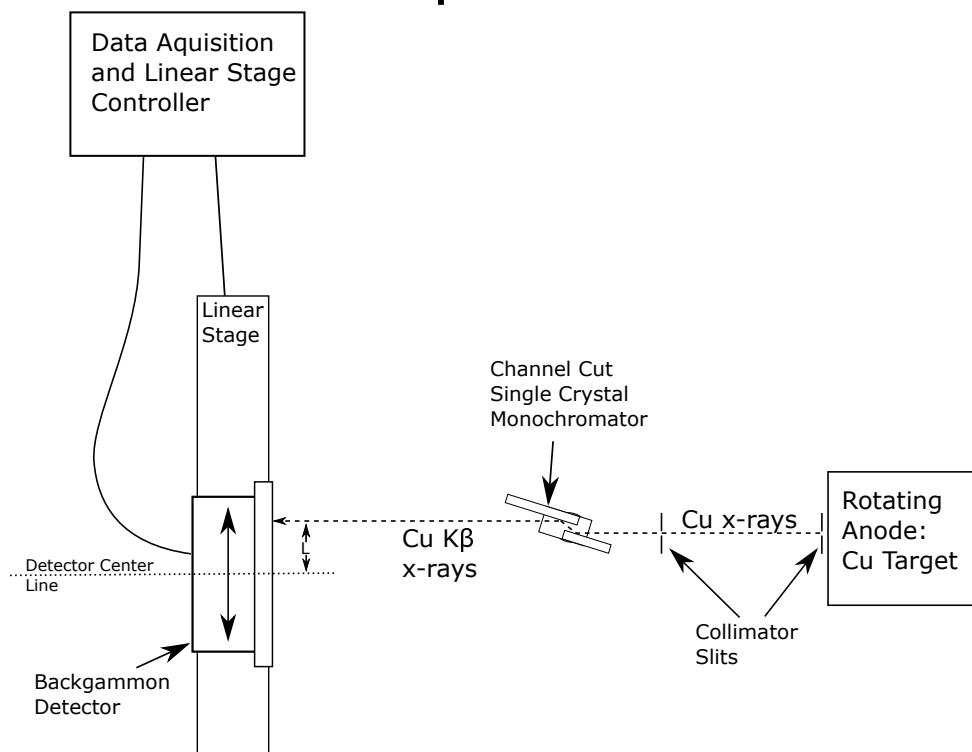


Figure 5.9: Schematic of the detector spatial linearity calibration setup. The major components of the setup were a rotating anode source and monochromator tuned to Cu K β and a linear stage with the backgammon detector mounted on it. The stage allowed for a computer to control the horizontal location of the vertical K β line on the face of the detector, measured by L . The detector data acquisition system and the linear stage were integrated with a custom LabVIEW program.

the rotatable part of the goniometer. The clinometers and a spirit level were attached to the stage. The Heidenhain readout was set to read zero when the spirit level showed the stage was level. With this setting, the Heidenhain measured the angle between the normal vector of the stage and the local gravitational acceleration vector. This angle was called θ . The experiment was controlled by a data acquisition PC. The stepper motor controller and the angle readout were both connected to the PC via RS232 connections. The clinometer voltages were sampled by National Instruments equipment and sent to the PC. A schematic of the experimental setup is shown in Figure 5.10. A custom LabVIEW program was written to integrate goniometer control and data acquisition.

The relevant studies using The University of Melbourne apparatus are described in Chapters 8 and 9.

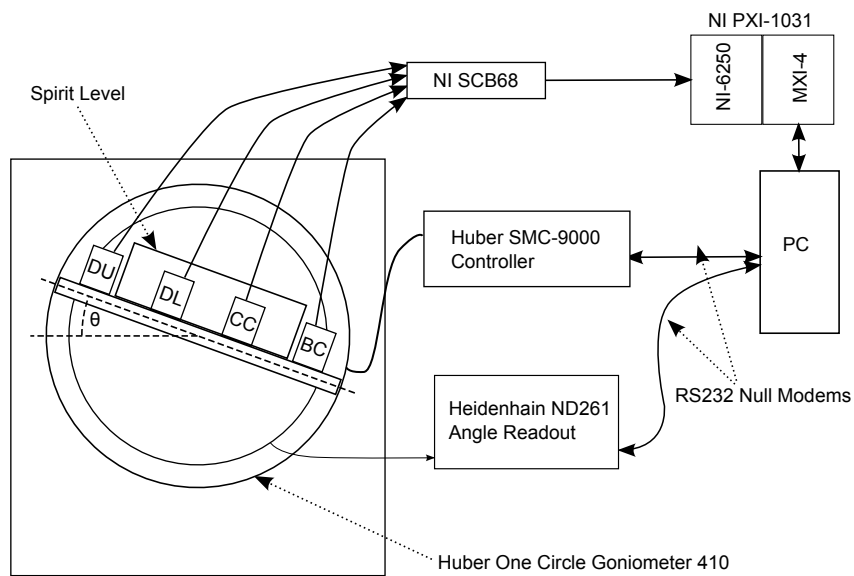


Figure 5.10: Schematic of the clinometer calibration setup. The four clinometers and the spirit level are rotated by the goniometer which is controlled by the PC. The goniometer angle and the four clinometer voltages are also acquired by the PC.

Improvement in XAFS Data Analysis

The first aim of the present research series outlined in Chapter 4 was to improve XAFS data analysis. Accordingly, this chapter presents the first error analysis of XAFS using absolute x-ray mass attenuation coefficients, through the introduction of a true χ_r^2 .

Summary

X-ray absorption spectroscopy has uncovered oscillations of the absorption above an absorption edge. These oscillations, called X-ray Absorption Fine Structure (XAFS) have been found to depend on the arrangement of atoms a short distance away from the absorbing atom. Standard techniques of XAFS analysis have been used to determine the local environment of an element in a solid or molecule. In the simplest case, this has included finding a detailed crystal structure that is consistent with the XAFS spectrum of the crystal. However, the analysis of XAFS using standard techniques has a number of problems. The first and most important problem is that XAFS fitting has not used a valid definition of χ_r^2 , the measure of goodness of fit optimised in the fitting process. This means that the quality of the fit is difficult to determine and that fitting parameters are distorted. Thus, XAFS analysis to date had been a qualitative tool to provide evidence for one structure over another when the proposed structures are sufficiently different, although there had been no way to quantify that sufficiency condition. Implementation of a definition of χ_r^2 based on experimental data would give an accurate quantitative picture of the weaknesses of the standard XAFS analysis process, enabling further improvement to that process and more reliable results. In this chapter, the modification of XAFS technique to implement an accurate χ_r^2 fitting procedure is detailed. This was then applied to the highest accuracy experimental data to date (metallic molybdenum [56]) obtained using the XERT [267, 268] to analyse the local dynamic structure of metallic molybdenum. This allowed a new

focus on propagating accurate experimental errors through a direct windowed k space fitting, to give the most direct and transparent test of the XAFS procedure. Thus the quantitative aspects of XAFS analysis have been made more reliable and thus now valid, enabling a new range of studies to be undertaken.

Key Achievements

- Implemented an accurate χ_r^2 measure for XAFS fitting, enabling the first accurate analysis of error propagation for XAFS.
- An unwindowed fit of Mo XAFS constrained so as to represent the crystal structure produced an accurate χ_r^2 of 3,000, indicating a dramatic disagreement between theory and experiment, proving that the theory needs significant development.
- A windowed fit of Mo XAFS that excluded the XANES region produced an accurate χ_r^2 of 96, indicating that most of the disagreement between theory and experiment is in the XANES region. This is expected from the current practice but is the first clear quantification of goodness of fit and theoretical limitations.
- Unconstrained models, using 16 independent path coefficients, produce unphysical model parameters with both the current analysis technique and χ_r^2 fitting technique, due in particular to the correlations between parameters.
- The more accurate error propagation has driven use of XAFS data in later research.

Publications

- LF Smale, CT Chantler, MD de Jonge, Z Barnea, and CQ Tran. Analysis of X-ray absorption fine structure using absolute X-ray mass attenuation coefficients: Application to molybdenum. *Radiation Physics and Chemistry*, 75(11):1559–1563, 2006

6.1 The Propagation of Uncertainties

The propagation of experimental uncertainties to results in XAFS analysis would be fundamental to the advancement of the field as it would allow the analysis to become reliable enough to identify deficiencies in XAFS theory. It will also permit much greater insight into the identification of local structure.

The propagation of experimental uncertainties to results involves using those uncertainties in fitting. This means defining the χ_r^2 to relate to experiment.

6.2 Improvement of χ_r^2 Fitting

The standard method of χ_r^2 fitting of XAFS spectra as outlined in Section 2.3 can be improved by an accurate χ_r^2 in the fitting procedure. The accurate χ_r^2 for XAFS spectrum ($\chi(k)$) data is

$$\chi^2 = \sum_{i=1}^{N_{pts}} \left(\frac{\chi_{data}(k_i) - \chi_{th}(k_i)}{\sigma(k_i)} \right)^2 \quad (6.1)$$

where $(k_i, \chi_{data}(k_i))$ is the i^{th} data point and $\sigma(k_i)$ is the measurement uncertainty of the of $\chi_{data}(k_i)$ [270]. The reduced χ_r^2 [270] is then

$$\chi_r^2 = \frac{\chi^2}{N_{pts} - N_{var}} \quad (6.2)$$

The interpretation of χ_r^2 relies on the idea that for every k_i , $\chi_{data}(k_i)$ is a sample of $\chi(k_i)$ drawn from a normal distribution with a mean of $\chi_{th}(k_i)$ and a standard deviation of $\sigma(k_i)$. In this case, the χ^2 defined by Equation 6.1 has a χ^2 distribution with $(N_{pts} - N_{var})$ degrees of freedom. χ_r^2 then has a distribution with a mean of 1 and a standard deviation of $\sqrt{2/(N_{pts} - N_{var})}$ [271, p. 943]. A χ_r^2 of much greater than one may come about in the following ways: (1) the theory, $\chi_{th}(k)$, may not model the XAFS spectrum correctly, (2) the experimental uncertainties may be underestimated, (3) the deviates may not be normally distributed, (4) the totality of the $\chi_{data}(k_i)$ values may be outliers by chance. With regard to (4), the probability of the data producing a χ_r^2 greater than q , when there are df degrees

of freedom, given that the statistical model of the data is correct, is defined by:

$$Pr(\chi_r^2 > q|df) = \frac{\Gamma(dfq/2, df/2)}{\Gamma(dfq/2)} \quad (6.3)$$

where $\Gamma(x)$ is the gamma function and $\Gamma(x, y)$ is the upper incomplete gamma function [271, p. 940].

χ^2 fitting and the χ_r^2 measure was implemented in the core of the IFFEFIT code by the present author, defining a new IFFEFIT-like code. Fits generated by the standard procedure and the χ^2 fitting procedure were evaluate with χ_r^2 to determine the accurate goodness of fit for both types of fits of the specific test case of metallic molybdenum XAFS.

6.3 Metallic Molybdenum: An Ideal Test Case for the XAFS Technique

The mass attenuation coefficient data for metallic molybdenum has been determined to unprecedented accuracy within the range from 13.5 keV to 41.5 keV by de Jonge et al. [56]. Accuracy was within 0.02%-0.4% and 0.1% over most of the energy range. This range included the K edge for molybdenum. These data, represented in Figure 6.1, were calibrated on absolute scales for both the mass attenuation and X-ray energy axes. The accuracy of the energy determinations of each datum was typically 1 eV – 3 eV. This accuracy was obtained using the X-ray Extended-Range Technique (XERT) [267, 268]. The XERT tests for many potential experimental systematic errors over a large energy range, and hence offers an unprecedented opportunity to critically examine and improve the standard XAFS analysis technique and theory. These measurements obtained from molybdenum yielded the most accurately determined form factor in the literature for any element or substance. Therefore, these data constituted an ideal medium for testing the validity of XAFS theory through the improved χ^2 fitting procedure described in the above section.

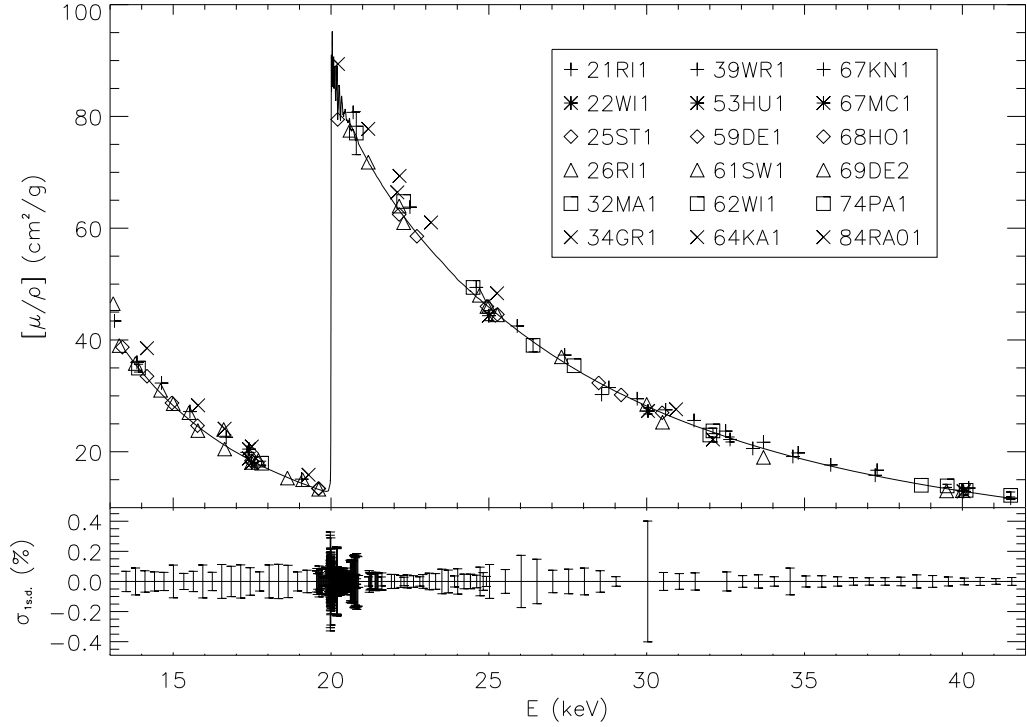


Figure 6.1: $[\mu/\rho](E)$ versus E for molybdenum from de Jonge et al. [56], compared with previous measurements sourced from the compilation of [272] (legends as given therein). The error bars for previous measurements are between 2% and 4% or approximately 10-200 times that of the best data set. The solid line is the recent data. The bottom section shows σ_{1sd} in the new data as a percentage of the data ranging from 0.02% to 0.4%, and generally 0.1% or approximately 10 to 200 times better than that of the next best data set. This quality of data is uniquely suited to test XAFS theory.

6.4 Investigations and Results

Variation of two parameters of the standard procedure were investigated, namely the windowing region and the parametrisation of the paths $S_{0,j}^2$ for the molybdenum model. Fits with the following three window regions were examined: $3.7 \text{ \AA}^{-1}$ to $13.0 \text{ \AA}^{-1}$ (7 peak window), $2.0 \text{ \AA}^{-1}$ to $13.0 \text{ \AA}^{-1}$ (8 peak window) and a range covering all the data (un-windowed). The model for molybdenum included 16 scattering paths, as the theory converged after the inclusion of these 16 paths. All 16 of the $S_{0,j}^2$'s were set equal to the one model parameter S_0^2 . Figure 6.2 shows that the windowed fits were of very high quality and in good qualitative agreement with the peaks and troughs of the data. No k-weighting was employed as this would distort experimental uncertainties (as described in Section 2.3.3). This

result is a confirmation of the modified χ_r^2 technique as well as of the experimental data.

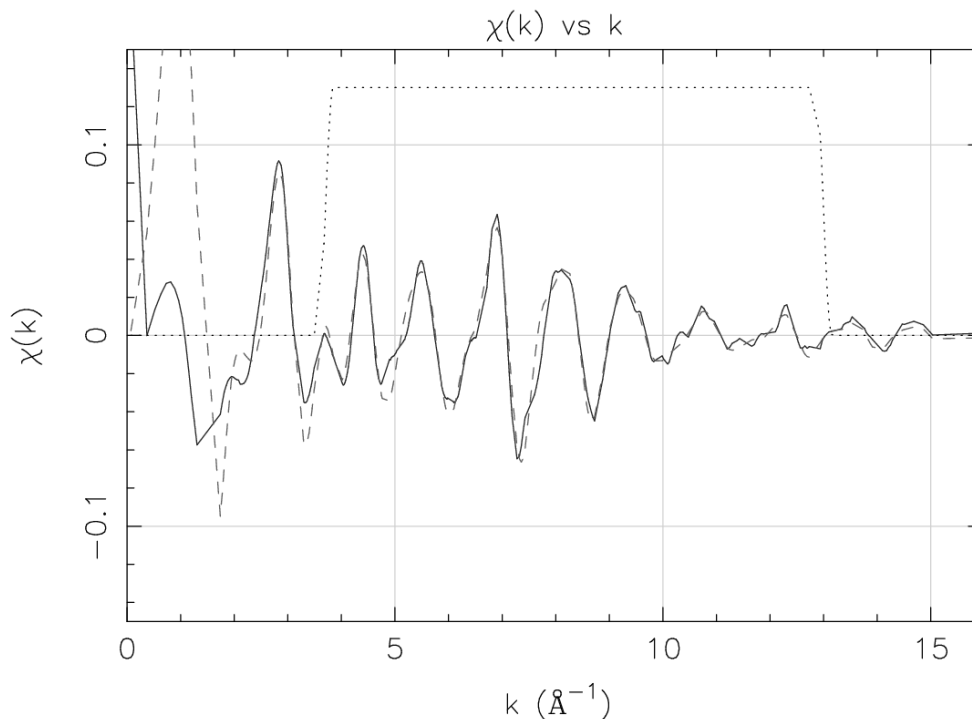


Figure 6.2: The $\chi(k)$ data (solid line) and the windowed χ_r^2 fit using the reduced set of parameters (dashed line). The k space window function (dotted line) represents the 7 peak window. $\chi_r^2 = 96$. The fit is qualitatively consistent with the data in the windowed region, matching peak locations and heights. However the χ_r^2 indicates a continued significant disagreement between theory and the high accuracy experimental data. Further theoretical work is needed.

The model curves for the 7 and 8 peak windowed fits followed the experimental data with peak locations and heights being roughly consistent. However, the χ_r^2 was consistently between 63 and 180 for all fits, indicating a model failure revealed by the high accuracy of the data.

The unwindowed fits had χ_r^2 exceeding 2500, an order of magnitude greater than the windowed fits. All parameter values for the unwindowed fits were unphysical and dominated by failure in the XANES region. This is the traditional justification within the XAFS community of windowing; peaks in the XANES region may not be well represented by an XAFS analysis. The upper limit of the window prevents the noise level far from the edge from being too significant, especially if traditional

	Improved fit(7 peaks)			standard fit (8 peaks)	literature value
	value	σ	$\sigma\sqrt{\chi_r^2}$		
χ^2	24000			38000	
χ_r^2	96			130	
$E_0(eV)$	1996.88	0.03	0.33	1996.21	?
α	.00183	9×10^{-5}	.00086	-.0003(5)	$0 \pm 6 \times 10^{-5}$
θ_D (K)	360	2	16	344(9)	385(7)
S_0^2	1.153	0.006	0.055	1.11(3)	0.9

Table 6.1: The parameters and uncertainties from a 7 peak window fit (windowed from $3.7 \text{ \AA}^{-1}$ to $13.0 \text{ \AA}^{-1}$). Two estimates, σ and $\sigma\sqrt{\chi_r^2}$, give lower and upper bounds for one standard deviation uncertainty. The fit is consistent with established values to within 2-3 standard deviations. The model gives meaningful parameters with a particularly restricted window. The unit cell length is between $3.1470 \text{ \AA}$ and $3.1474 \text{ \AA}$, [273–275], based on x-ray crystallography carried out between 18°C and 25°C . With this model parameter, an expected expansion coefficient of $(1 + \alpha)$, $\alpha=0.00000(6)$ follows. The Debye temperature for molybdenum is $385(7) \text{ K}$ from powder neutron diffraction [276].

k^3 scaling is used. Such k weighting distorts uncertainties at high k by artificially lowering the nominal uncertainties in this region.

Parameter values for the 8 peak window fits were either unphysical or poorly determined. Generally the values for the Debye temperature were slightly too low, and the values for the path amplitudes, the $S_{0,j}^2$ parameters, were too high. This was correlated with a higher χ_r^2 , although the 8 peak window fits were obviously poor in a range where the model assumptions are not adequate. Perhaps surprisingly, the first 4 peaks were already removed by windowing, so naively one might expect the model to work well. In fact, by the conventional treatment, one might argue that it works well, as it does in a qualitative (relative) sense.

Windowed fits that allowed all 16 $S_{0,j}^2$ parameters to vary independently, yielded high correlations. Although the extra parameters gave a reduction in χ_r^2 , the corresponding path amplitudes were often unphysical, implying that the amplitudes were not determined, even for such an ideal model system as pure molybdenum.

In all fits, the development of the accurate χ_r^2 fitting procedure including error propagation showed improvement of the XAFS determinations by between 5% and 70%. The 7 peak windowed fit yielded parameter values corresponding closely to physical quantities. Other results, while still useful for some applications, were likely to lead to significant uncertainty in determined parameters.

It is important to note why other options were excluded. Standard procedures for fitting the FEFF model to an experimental XAFS spectrum are based on a least squares fit of some linear transformation of the residues of the data interpolated onto a $0.05 \text{ \AA}^{-1}$ spaced grid. Options include fits on three different axes (original or ‘ R or Q space’) with k^2 or k^3 or k^n scaling (suppressing near-edge and magnifying far-edge structure), and with a variable fitting window in k space. However, these transformations of the residues do not propagate experimental uncertainties, and thus distort the accuracies and uncertainties of the original data set. Therefore, such significantly flawed options were not used in this investigation.

6.5 Significance

The χ_r^2 for every fit is over 90, clearly indicating a disagreement between theory and experiment. The probability that the experimental data was generated by processes that were correctly modelled by the fitted theory was, in every case, many orders of magnitude less than 10^{-17} . Hypothetically, the experimental error bars could be too low by a factor of 9. However the structured pattern of the residuals is inconsistent with a random noise signature, confirming the quality and error bars of the data to within a factor of two, and highlighting that the theoretical issue raised and limitations of the model and theory are the dominant cause of the failure.

The χ_r^2 for the unwindowed fit using the current analysis techniques was 3000. Improved theory for the whole range of data should therefore improve agreement with experimental structure by a further factor of $\sqrt{3,000} \simeq 55$.

This finding has had major further impact in the field. The new χ_r^2 fitting and error propagation of this chapter has been crucial in a number of ongoing studies. It allowed an incisive stereochemical analysis of ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, using XAFS data from 10 mM solutions of the compound to be performed in a rigorous way [277]. The analysis was able to distinguish, for the first time, between the subtly different ‘staggered’ and ‘eclipsed’ conformations of ferrocene. The method has also allowed the identification of a discrepancy between FEFF and the XAFS of the K edge of silver [58]. This discrepancy was attributed to a variation of effective thermal contributions across the XAFS spectrum.

Cosmic Ray Removal in CCD Detectors

Summary

The second research aim proposed in Chapter 4 concerned the removal of cosmic ray noise from low flux x-ray data collected with CCD detectors. Low flux sources of x-rays relevant to test QED such as EBITs, combined with spectrometry based on CCD detectors, provide a challenge. The relatively large noise, especially from cosmic rays, limits the signal-to-noise ratio and hence the physical information content and therefore the significance of critical tests and measurements. Thus filtering out cosmic ray events from the CCD images of spectra in a robust manner, so as to remove background noise from the spectra themselves without changing the significant aspects of the spectra, would improve these critical tests and measurements. Rydberg series and Lyman α spectra from H-like Ti were collected at the National Institute of Standards and Technology (NIST) EBIT in 2005. These data provided a test bed on which to develop and assess cosmic ray removal techniques for x-ray CCD detectors used in low flux environments. In this chapter, the procedures of this study are set out, followed by the results, and then the conclusions that can be drawn concerning the improved accuracy of measurement.

Key Achievements

- Implemented three cosmic ray event filters for x-ray CCD detectors: a cluster method, a linear correlation method using Hough transforms and a combination filter.
- Found that the new combined filter method was the strongest filter and that the method was robust.

- Presented a characterisation of the Rydberg series spectrum from H-like Ti using the combined filter method for cosmic ray filtering.

Publications

- LF Smale, CT Chantler, and LT Hudson. The effects of cosmic ray filtering on low intensity X-ray CCD data. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 619(1):150–153, 2010

7.1 Low Flux EBIT Spectral Data

CCD detectors are sometimes used in x-ray spectroscopic tests of QED at low-flux EBIT sources. In such cases, the detectors are affected by cosmic ray noise. Since the spectra of interest in these experiments are so weak, the cosmic ray noise can significantly affect the sensitivity of the test of QED. This is because the noise introduces a variable background to a spectrum that makes the physically significant fitting parameters less certain by an increase in signal-to-noise or signal-to-background ratio. The need for novel methods to differentiate cosmic ray background tracks from x-ray signals in x-ray CCD detectors is clear, especially in the context of weak signals such as spectrometry of EBIT sources.

Distortions of the characteristics of a spectral profile such as peak centroid and relative integrated peak intensities must be kept to a minimum with cosmic ray filtering methods, or potential accuracy and physical insight will be lost. An ideal method would minimise broadening and uncertainty of final centroid determination and of relative intensities, consistent with the distribution for the unfiltered data.

Three methods for cosmic ray filtering were compared in the present study. A cluster method based on that of Hudson et al. [108], a linear correlation method using Hough transforms, and a method that combined both of these methods were examined. They were compared in relation to the Rydberg series x-rays of H-like Ti collected at the NIST EBIT in 2005.

Spectra from He-like Ti and H-like Ti were observed. Specifically, a spectrum that included a very low intensity Rydberg series of H-like Ti was collected with the CCD. In the CCD detector, cosmic rays constituted a significant source of noise. The CCD used had background levels, defined as a fixed-pattern noise on top of a thermal pedestal, partially due to typical radiation damage accumulated in the detector over time. To correct for these effects, the background had to be characterised and then removed from each data image. A typical CCD image is shown in Figure 7.1 on page 96. Note that many such images must be processed, and the results aggregated through addition to create a spectrum with significant statistics.

7.2 Removal of the Effects of Radiation Damage

7.2.1 Mean Background Determination

Each data image from the CCD needed to be partitioned into three computational masks (pixel intensity patterns), representing the regions and nature of the constituent pixel signal. The first mask represents the background or electronic noise or damage signal of the CCD detector itself, the second represents the cosmic ray events at play (to be excluded from the signal), and the third mask represents the ‘true’ x-ray signals of interest. Ten exposures of the background were taken during the experiment. All the background images intensities were normalised to the brightest background image through linear intensity histogram matching.

The intensity histograms of every CCD image examined in the experiment had two disjoint (bimodal) peaks. Therefore, to scale each background image to the brightest background image, both peaks for both images were found. The intensity of each pixel in the background image was linearly transformed such that the means of the two peaks of each background matched those of the brightest background. This transformation corrected for variations in dead-time, temperature drifts, or integration times and avoided secondary distortion.

At this stage, for each pixel location there was a set of samples of intensities (grey level) taken from normalised background images. An accurate measure of the background was taken to be the mean of this set, excluding elements that represent cosmic-ray intensities. These cosmic ray events were outliers in the

sample distribution. The mean and standard deviation of the remaining grey level distribution were then considered to define the background distribution.

In order to detect outlier sample intensities within the set of normalised background image intensities, the set was divided into two new subsets: the set of intensities above the midpoint between the mean and maximum of the set, and the set of intensities below that midpoint. If a t-test for the consistency of these subsets shows they are *inconsistent*, we take the second subset to represent the background, otherwise we take the original set to be a sample of the background distribution.

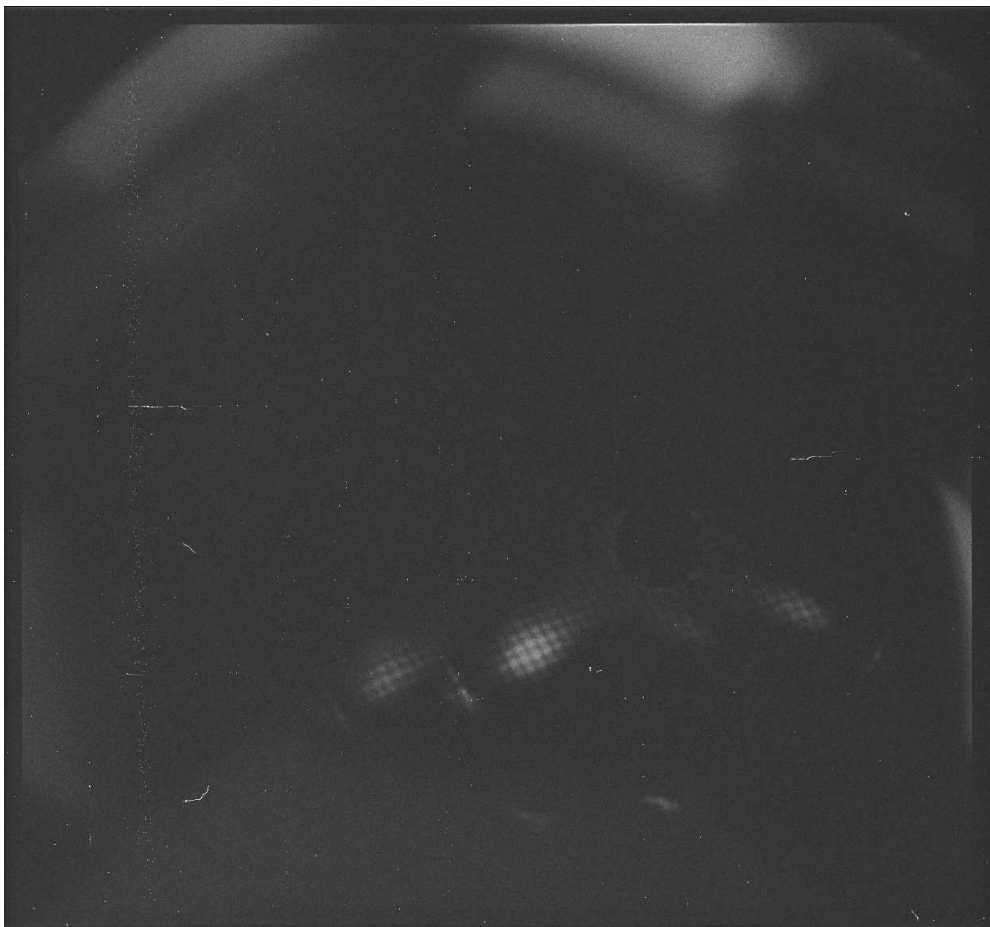


Figure 7.1: Raw image data of He-like Ti, showing the background pattern as well as cosmic rays and the x-ray signal. The need for an effective background subtraction is evident as the x-ray and cosmic ray signals are almost impossible to see. This is because the x-ray and cosmic ray signals have a much lower magnitude than the variation in the background and the image has a resolution of 1242 pixels by 1152 pixels.

7.2.2 Background Subtraction

To subtract the mean background from a raw CCD image, the mean background was normalised to the image through a scaling of intensity. The intensity scaling was necessary due to effects such as laboratory temperature drift.

For each image, a difference image was created by subtracting the normalised background image from the image. The grey level distribution of the difference image is peaked around 0 but is not precisely 0 because of thermal noise. The pixels corresponding to this peak around 0 show an absence of cosmic rays and x-rays. That is, they appear to be due to thermal noise or background patterning. A cutoff value greater than the noise but less than the signal was therefore chosen to define a background distribution mask. All pixels that had an intensity above the cutoff were kept in a ‘Possible X-ray Signal Mask’ (PXSM). Figure 7.2 shows the sum of the PXSMs of all He-like Ti data images. The intensity of each pixel marked by the PXSM in the difference image is assumed to be proportional to the energy deposited (by x-rays or cosmic rays) in that CCD pixel in the collection time of the image.

7.3 Cosmic Ray Filters

As stated above, three filters were examined and thus four classification methods were set up for the data, namely the unfiltered method, a cluster method, a linear correlation method using Hough transforms and a combination of the latter two. An example of how these filters applied to a small section of an image is shown in Figure 7.3.

In the cluster method, continuous clusters of pixel signals in the PXSM, whose combined energy deposition was greater than a chosen cutoff, were marked as cosmic ray events and filtered out. The cutoff was chosen through an examination of x-ray events identified by eye in a few images. The linear correlation method identified linear tracks in the PXSM that need not be continuous clusters. It used Hough transforms and Hough back-projection, as detailed below.

There were linear correlations of pixels in the PXSM other than cosmic rays, most importantly, the spectral lines (the positional-dependent x-rays of the signal).

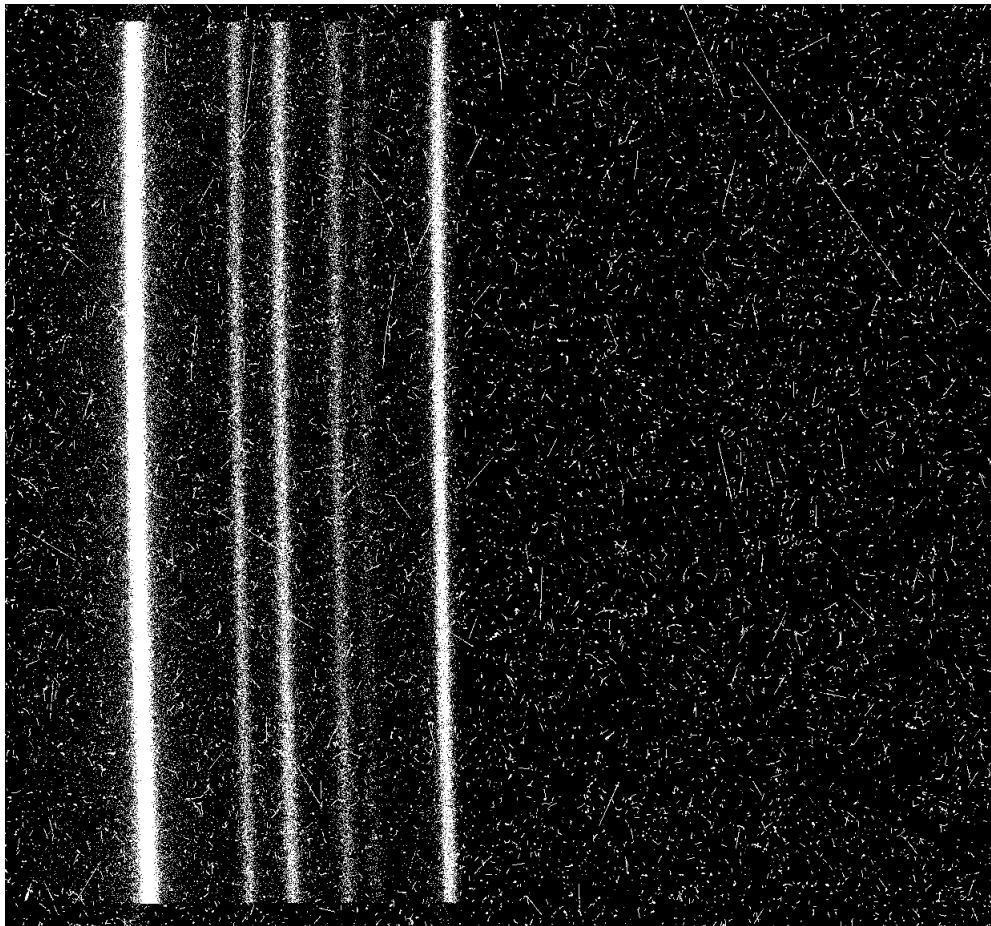


Figure 7.2: The image shows the sum of the Possible X-ray Signal Masks (PXSMs) generated from each of the He-like Ti raw data images. This represents the unfiltered data. Notice the large number of thin streaks and blotches that represent cosmic ray tracks. These must be removed to increase the sensitivity of any tests of QED that may result from these lines.

Spectral line x-ray points are normally isolated from each other (i.e. they are not usually overlapping clusters), due to the low intensity of the spectral lines. Thus, these isolated points can be recognised as x-ray events and removed from their identification as possible cosmic rays. Isolated points in the PXSM were defined to be points with less than 3 possible x-ray signal pixels in the surrounding 5 by 5 sub-mask. The remaining loosely clustered points were included in the ‘Possible Cosmic Ray Mask’ (PCRM).

The PCRM was Hough transformed, and the pixels of the Hough image which were less than a cutoff (chosen to be five) were zeroed. This meant that there must have been five pixels in a discontinuous line in the PCRM for such a collection of points to be recognised as a line. This cut Hough transform image was then Hough

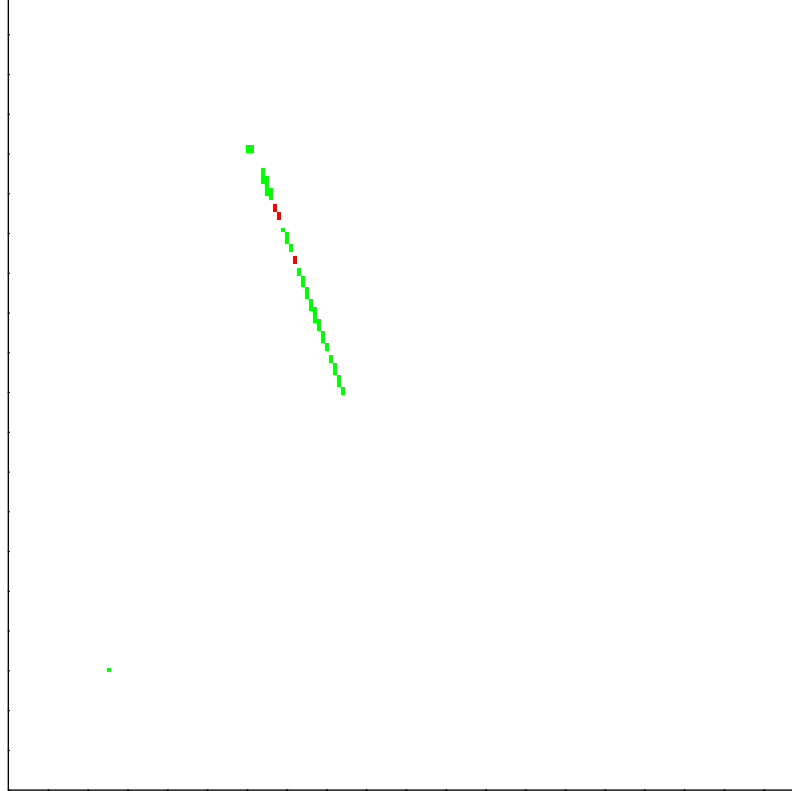


Figure 7.3: Different filter methods are sensitive to different parts of a disjointed cosmic ray track. This is an example of cosmic ray filters applied to a 200 by 200 section of a PXSM. The green pixels were identified as part of a cosmic ray by both the cluster filter and the linear correlation filter. The red pixels are identified by the linear correlation filter only, as the signal strengths are reasonable for x-ray events, but they are also part of a larger linear correlation.

back-projected into the original image space. Areas of high intensity represented pixels in approximately collinear (confined) patterns in the original PCRM.

All pixels with a Hough back-projection intensity below a cutoff, and that were also marked by the PCRM, were marked as linearly correlated cosmic rays and filtered out as cosmic ray events. The cutoff was chosen to be 150, robust within a wide range. This cutoff was a good balance between identifying confined linear correlations and correlations between very isolated clusters. Figure 7.4 shows the sum of the results of the linear correlation method applied to each He-like Ti data image.

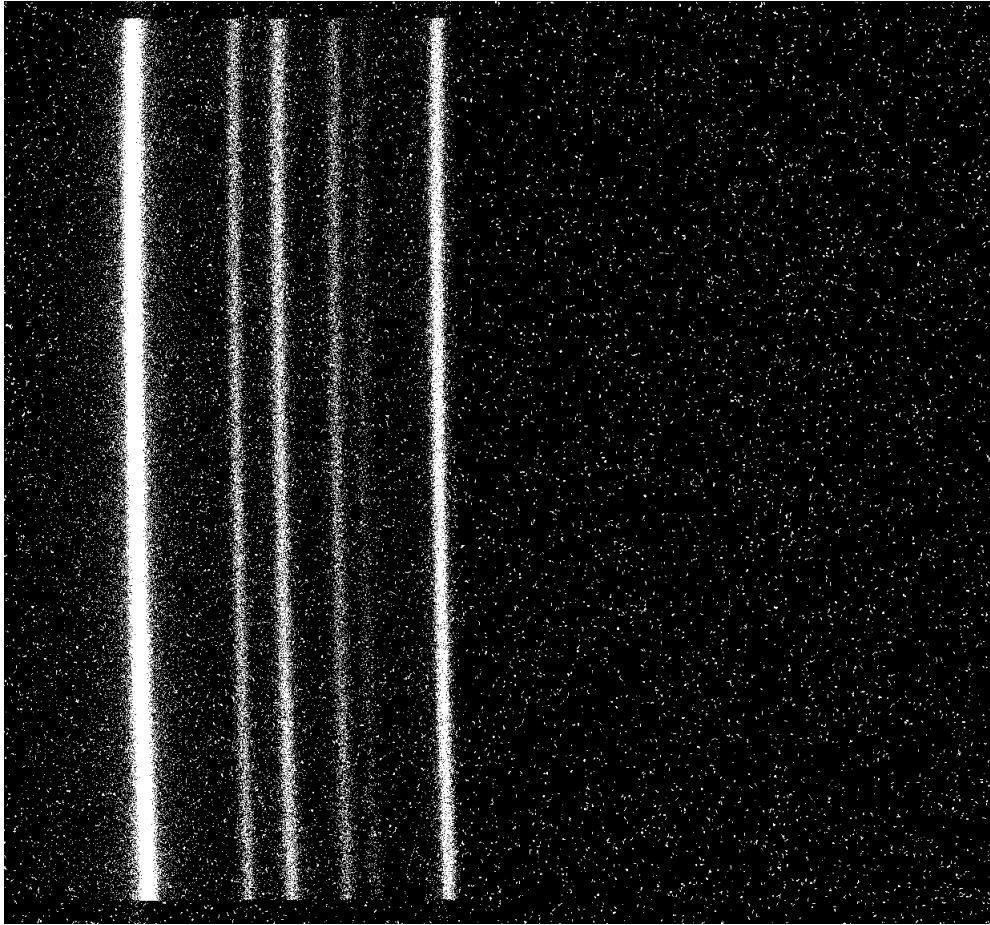


Figure 7.4: The sum of the events that were identified as x-rays after applying the linear correlation filter method to each He-like Ti data image. Notice that all cosmic ray tracks that have a linear correlation in them have been removed. There remains, however, a background of events that were not identified as cosmic rays.

7.4 CCD Misalignment: Problem and Solution

The spectral lines were not perfectly vertical on the CCD image due to the difficulty of rotating the CCD camera once the spectrometer is evacuated. To sum the spectra and see the signal after a column sum, the image was rotated in order to minimise the width of the strongest peak in the spectrum. Robustness of this simple rotation optimisation was tested by shifts in angular rotation from the final result by 0.25 degrees.

7.5 Results

Four sets of results from the Rydberg series of H-like Ti data, corresponding to the four classification methods, were generated for comparison: no cosmic-ray filtering (Set A); Linear Correlation filtering (Set B); Cluster filtering (Set C); and combined Linear Correlation and Cluster filtering (Set D). Each set of results was created through event identification, spectrum creation (through a rotation and column sum of all the event images), and spectrum fitting (the fit function was a sum of eight Voigt functions with a common Gaussian width and a constant background for the noise). The i^{th} Voigt function was defined to be:

$$V(x; A_i, C_i, W_i, \sigma_G) = A_i \int_{-\infty}^{\infty} \left(\frac{e^{-x'^2/(2\sigma_G^2)}}{\sigma_G \sqrt{2\pi}} \right) \frac{W_i/2}{\pi[(x - C_i - x')^2 + (W_i/2)^2]} dx' \quad (7.1)$$

where A_i is the integrated area of the Lorentzian profile, C_i is the centroid of the profile, W_i is the Lorentzian full width at half maximum (FWHM) and σ_G is the Gaussian broadening standard deviation. The Gaussian broadening FWHM is $2\sqrt{2 \ln 2} \sigma_G \approx 2.35\sigma_G$. Thus the histograms were modelled with:

$$\begin{aligned} P(x; b, \sigma_G, A_1, A_2, \dots, A_8, C_1, C_2, \dots, C_8, W_1, W_2, \dots, W_8) \\ = B + \sum_{i=1}^8 V(x; A_i, C_i, W_i, \sigma_G) \end{aligned} \quad (7.2)$$

Figure 7.5 shows the identified events for each filter. Figure 7.6 shows the fits of the corresponding histograms. Table 7.1 shows the parameter sets of equation 7.2 generated by those fits A to D. Note that the peak locations, Lorentzian widths and integrated areas from these parameter sets are characterisations of the Rydberg series spectrum of H-like Ti on a column channel axis that is linearly related to energy.

To assess the effectiveness and robustness of the filter methods, a number of measures were inspected. These were the signal-to-noise ratio for each peak, the full width half maximum of each peak, and the peak position and intensity relative to the strongest peak. Table 7.2 shows the signal-to-noise ratio for each peak in each filtering method, A to D. The signal-to-noise ratio for the i^{th} peak is here defined to be the dimensionless number $A_i/(F_i b)$, where F_i is the FWHM of the peak. The noise estimate per channel was given by the constant background level from the fit. This ratio measures the strength of the filter. The combination filter, (D),

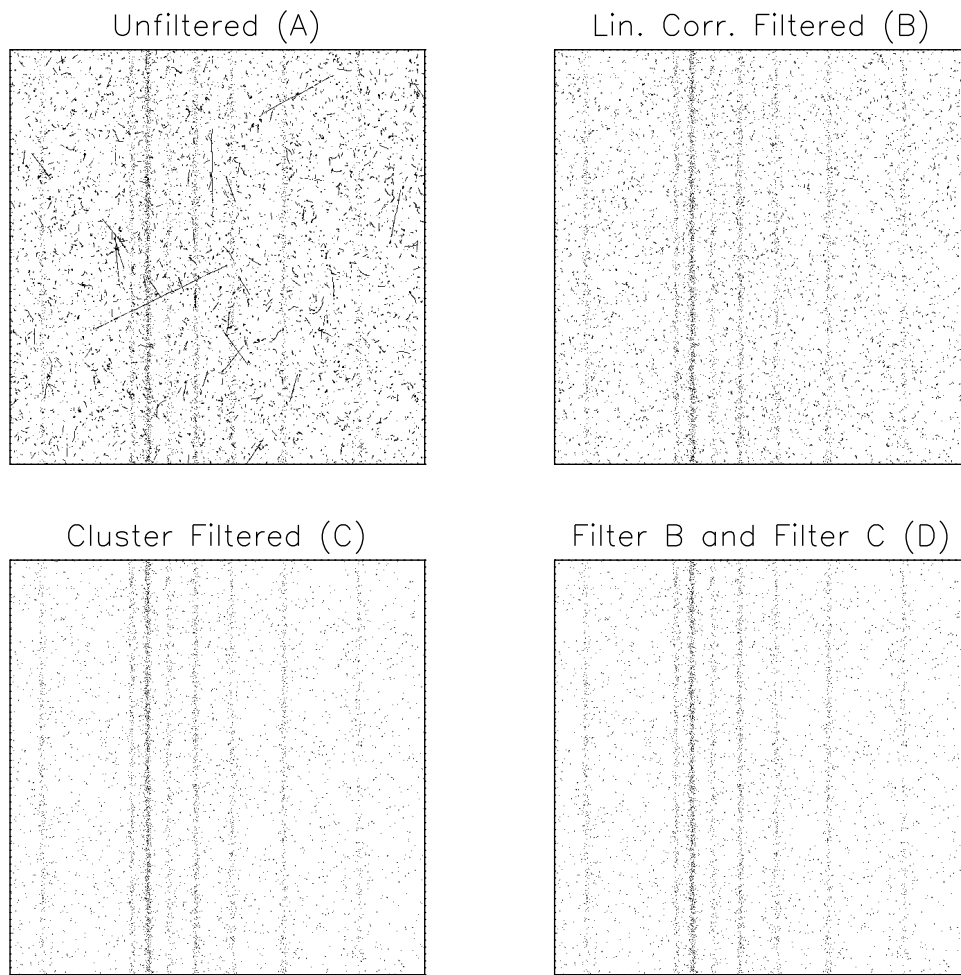


Figure 7.5: The x-ray events by the four different filtering methods after image rotation. The unfiltered image (A) clearly shows long streaks corresponding to cosmic rays. The Linear Correlation Filtering Method (B) removed these streaks. As the streaks are usually connected in one or two clusters, the Cluster Filtering Method (C) also removed most of the streaks. However it is clear that it also removed additional clusters. The Combination Filtering Method (D) allowed each sub-filter to make up for the weaknesses of the other sub-filter, removing the most cosmic ray events. Figure 7.6 shows fits of the histograms of these data sets.

was stronger than either sub-filter. Hence, as was expected, the sub-filters were found to filter out different components of the cosmic ray noise and/or the x-ray signal. Table 7.2 demonstrates that all methods yielded dramatic improvement in separating real (x-ray) signal from noise or correlated components, by factors of up to between 7 and 9.

Table 7.3 illustrates the dependence of the peak FWHM on the filtering method. The fitted centroid and width of the strongest peak (peak 3) is stable under all methods of filtering A to D (Table 7.1), supporting the idea that for strong lines

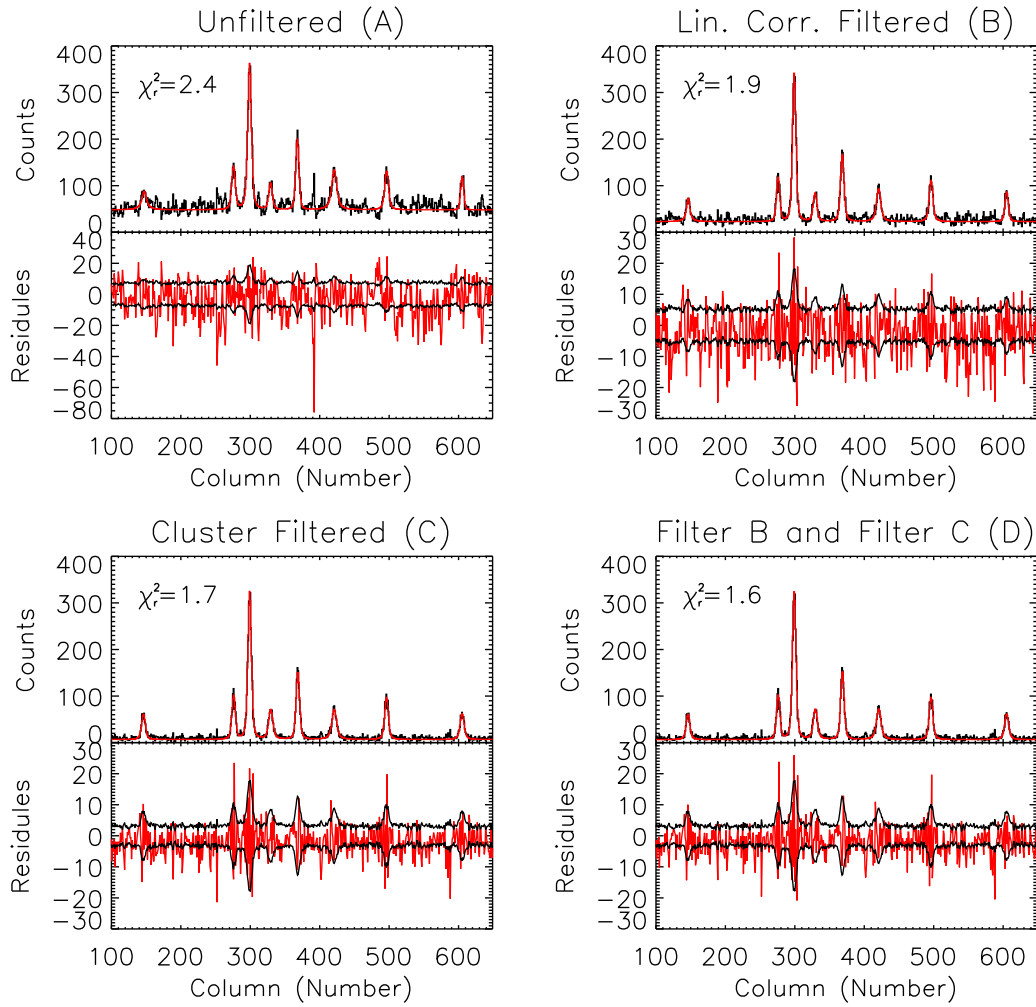


Figure 7.6: This figure shows fits of the histograms generated by of the four different filtering methods. The fitted background, b , of the histograms in counts per channel were as follows: (A) 48.07(22), (B) 22.79(15), (C) 6.730(82) and (D) 6.484(81). Note that the background is lower in each subsequent fit, showing the increasing effectiveness of the cosmic ray filtering methods.

each of these approaches has a valid construction. The peak fits of the raw rotated image (Set A) may be broadened by artificial (poor) definitions of the background, by the noise or cosmic rays themselves, and by poor definitions of the lines due to statistics. However, filtered data should be stable in FWHM if all processing has avoided distortion. Conversely, FWHMs should always be larger if the processing has involved distortion and loss of definition of peaks. The results here suggested that the weakest components (1, 4 and 8) increase their apparent FWHM from set B to C to D. This further suggested that weak peaks are distorted and that Set B minimises this effect.

Table 7.4 gives the relative peak position and relative intensity as measures of peak

distortion. Relative integrated intensities are normalised to the strongest peak in this table. The distortions of intensity generally increase with the strength of the filter, in support of the observations relating to the FWHM. The second strongest peak (the fourth peak) shifts by circa $2-3 \sigma$ in relative intensity with filter (B), with the shift doubling with the energy cluster filtering (C). Peaks 4, 5 and 6 in particular show strong dependencies with filtering, both with integrated relative intensities and with centroid location. Of course, both of these measures are the primary outputs for calibration of scientific results using a CCD detector.

The stability and robustness of filtering cosmic-ray noise from low intensity x-ray data from CCD cameras is an important problem. Four filtering methods were compared using fits of the Rydberg series spectrum of H-like Ti. A characterisation of this spectrum from each of the filter methods has been presented. The FWHM of the spectral line was found to be the most stable (most narrow) with the Hough transform (B). Perhaps cluster methods (C) increased noise and widths on weak lines. The cluster method was a strong filter compared to the linear correlation filter, but can distort centroids and relative intensities. The linear correlation method appeared to distort less. The strongest filtering was achieved by combining both filters (D) in which case the distortions are typically enhanced further. All methods appear moderately robust under test conditions on real data.

7.6 Conclusion

The tentative conclusion of this study was that the linear correlation filter is the preferred filter for removing cosmic ray noise from CCD data with weak signals such as those arising from tests of QED at EBITs. This is because it appeared to reduce fit parameter uncertainties while minimising distortions. A reduction in the uncertainty of fit parameters would lead to stronger tests of QED. More work would clearly be needed both to optimise and investigate these and further alternate methods in the presence of important but weak signals, for CCD investigations or indeed for any pixel-based imaging. Specifically, a careful implementation of the filter method of Hudson et al. [108] should be compared to the methods presented in this thesis. Also, in future methods, identified pixel clusters in each filtered image should be replaced by single pixels at the average locations of the clusters in order to more accurately represent single x-ray events. The characterization of

the Rydberg series spectrum of H-like Ti generated using the linear correlation filter may be useful to compare to theory in a relative sense.

Parameter	Histogram Wide Parameters			
	Set A	Set B	Set C	Set D
b	48.07(22)	22.79(15)	6.730(82)	6.484(81)
σ_G	1.98(29)	1.940(51)	2.01(14)	1.975(58)
Peak #	Integrated Area A_i (Counts)			
	Set A	Set B	Set C	Set D
1	500(57)	447(38)	443(25)	447(26)
2	702(44)	641(35)	681(30)	674(30)
3	2510(64)	2320(56)	2360(52)	2359(52)
4	424(39)	485(34)	593(30)	598(30)
5	1042(43)	1097(42)	1077(36)	1076(36)
6	1041(50)	707(40)	701(33)	699(32)
7	710(46)	727(37)	712(31)	720(31)
8	430(35)	456(31)	488(27)	490(27)
Peak #	Peak Position C_i (Column Channels)			
	Set A	Set B	Set C	Set D
1	147.28(48)	146.42(28)	146.16(19)	146.18(19)
2	275.90(20)	275.95(16)	276.05(14)	276.08(14)
3	299.010(84)	299.116(74)	299.108(69)	299.108(69)
4	329.22(29)	329.20(23)	329.55(19)	329.54(19)
5	367.84(13)	368.28(12)	368.51(10)	368.51(10)
6	420.88(25)	420.71(22)	420.87(20)	420.87(20)
7	496.36(22)	496.21(17)	496.17(14)	496.17(14)
8	605.17(21)	605.11(21)	605.13(21)	605.08(21)
Peak #	Lorentzian Width W_i (Column Channels)			
	Set A	Set B	Set C	Set D
1	7.00(50)	5.37(39)	2.42(13)	2.48(13)
2	2.15(14)	1.68(11)	1.886(90)	1.874(89)
3	2.377(59)	1.992(49)	1.992(44)	2.043(45)
4	2.06(21)	2.43(16)	2.99(12)	3.00(12)
5	1.638(27)	2.167(85)	1.967(31)	1.945(69)
6	3.898(97)	3.31(14)	3.58(11)	3.51(11)
7	2.65(15)	2.53(12)	2.268(95)	2.350(94)
8	0.91(11)	1.90(14)	2.78(13)	2.86(13)

Table 7.1: The fitted parameter sets of the histogram fits shown in Figure 7.6. There is one set of parameters for each cosmic ray filter method. The fit function is the sum of Voigt peaks with a constant background specified in Equation 7.2. The background, b , is in counts per channel while the Gaussian broadening, σ_G , is in channels.

Peak #	Peak Signal To Noise			
	Set A	Set B	Set C	Set D
1	1.31(17)	3.48(26)	10.36(60)	10.81(62)
2	2.41(13)	5.04(26)	17.13(79)	17.86(82)
3	8.33(21)	17.45(43)	58.6(15)	61.1(16)
4	1.47(12)	3.41(22)	12.60(65)	13.26(68)
5	3.84(16)	8.03(30)	26.85(98)	28.2(10)
6	2.52(15)	4.21(22)	13.18(64)	13.89(67)
7	2.26(13)	5.03(24)	17.00(76)	17.83(80)
8	1.73(13)	3.48(22)	10.78(60)	11.15(62)

Table 7.2: The signal-to-noise ratio of each peak increases with filtering from A (raw data with background normalisation and rotation) to B (Hough transform with background normalisation and rotation) to C (cluster method with background normalisation and rotation) to D (B and C combined). The signal for a peak is given by the integrated area divided by the full width half maximum of the fitted Voigt that represents the peak (these numbers are presented in Tables 7.1 and 7.3). The noise level is given by the fitted constant background coefficient as presented in Table 7.1.

Peak #	FWHM (Column Channels)			
	Set A	Set B	Set C	Set D
1	7.9(13)	5.64(17)	6.36(20)	6.39(19)
2	6.07(62)	5.58(12)	5.91(25)	5.83(16)
3	6.27(64)	5.835(47)	5.98(34)	5.956(50)
4	5.98(66)	6.26(21)	7.00(21)	6.96(23)
5	5.65(67)	5.997(66)	5.97(32)	5.88(15)
6	8.60(79)	7.38(43)	7.91(12)	7.66(23)
7	6.55(67)	6.34(17)	6.23(35)	6.23(10)
8	5.17(57)	5.76(10)	6.74(35)	6.77(11)

Table 7.3: The full width half maximum and the dependence on filtering method. The FWHM is most stable with Linear Correlation filtering (set B).

Peak #	Relative Peak Position (Column Channels)			
	Set A	Set B	Set C	Set D
1	-151.7(5)	-152.6(3)	-153.0(2)	-152.9(2)
2	-23.1(2)	-23.2(2)	-23.1(2)	-23.0(2)
4	30.2(3)	30.1(2)	30.5(2)	30.4(2)
5	68.8(1)	69.2(2)	69.4(1)	69.4(1)
6	121.9(3)	121.6(2)	121.8(2)	121.8(2)
7	197.4(2)	197.1(2)	197.1(2)	197.1(2)
8	306.1(2)	306.0(2)	306.0(2)	306.0(2)

Peak #	Relative Peak Intensity			
	Set A	Set B	Set C	Set D
1	0.20(2)	0.20(2)	0.19(1)	0.19(1)
2	0.28(2)	0.28(2)	0.29(1)	0.29(2)
4	0.17(2)	0.21(2)	0.25(1)	0.25(1)
5	0.41(2)	0.47(2)	0.46(2)	0.46(2)
6	0.41(3)	0.30(2)	0.30(2)	0.30(2)
7	0.28(2)	0.31(2)	0.30(2)	0.31(1)
8	0.17(1)	0.20(1)	0.20(1)	0.21(1)

Table 7.4: This table shows the peak position and intensity of each peak across all filtering methods relative to the strongest peak (the third peak). The dimensionless relative intensity is the integrated area of a peak relative to that of the strongest peak. The relative peak position measures the consistency within errors of the relative centroid locations and hence of the calibration. The second strongest (peak 5) shifts by circa 2-3 σ in position, doubling with Cluster Filtering. Peaks 4, 5 and 6 in particular show strong dependencies with filtering.

Characterization of The University of Melbourne Backgammon Detector

The third aim of this thesis research was to improve x-ray spectrometry, while the fourth aim was to perform a test of QED with an EBIT. It was planned to conduct an EBIT study at Oxford's Clarendon Laboratory to achieve these aims. Before this could be done, preliminary studies were necessary. These studies were to characterise the responses of two subsystems that formed part of the apparatus; the first subsystem was the Backgammon detector, and the second subsystem consisted of the clinometers, both relying on the data acquisition system. These preliminary studies were conducted at The University of Melbourne School of Physics. The first one is the subject of the present Chapter 8, while the second is described in Chapter 9. The Oxford work itself is laid out in Chapters 10 to 14.

Summary

It was considered that, in order to confidently use the Backgammon detector in a high precision experiment such as that planned for Oxford 2007, its responses to x-rays had to be characterised to enable the minimisation of systematic errors in the analysis of the data produced. The two major responses important here were the intensity response and the spatial response. Ideally these responses would be linear. If not, a characterisation of the response could be used to linearise the response. In this preparatory study, the intensity response was tested using an x-ray absorption experiment, while the spatial response was characterised by subjecting the Backgammon detector to a thin line of x-rays at a set of controlled positions on the detector. This experimental setup is given in Section 5.4.2 of Chapter 5.

Key Achievements

- The Backgammon detector was demonstrated to have a linear response to x-ray intensity up to a count rate of at least 17 kHz.
- A combined hardware/software system was designed and built by the author to construct a spatial calibration map for a backgammon detector which maps raw output of the detector to a physical length scale in dispersive axis of the detector, using the a characterisation of the spatial response. This spatial linearity calibration system can be applied to any Backgammon detector with little modification.
- The spatial linearity calibration system was used to construct a spatial calibration map for the Backgammon detector.
- This map was used in the research reported in Chapters 10 to 14 below to linearise the detector for use in the curved crystal spectrometer system.

8.1 Intensity Response Linearity

To test the linearity of the x-ray intensity response of the detector, an x-ray attenuation experiment with the rotating anode source with a Cu target was performed. The setup for this experiment is described in Section 5.4.3.1 above. For each attenuator thickness, the number of x-ray detection events of the attenuated x-rays was measured for a period of 10 seconds. The thickness of the attenuator was recorded in terms of the number of foils in the flat pack. Thirteen thicknesses between 16 and 192 foils were examined.

The count rate for each thickness was calculated to be the number of detection events divided by 10 s. The uncertainty in count rate had two components that were added in quadrature. The first was the uncertainty due to the Poisson distribution of event counting. This is the square root of the number of events divided by 10 s. The second source of uncertainty was the variability of the source intensity. This was calculated to be the fractional standard deviation in x-ray intensity times the count rate. The source variability dominated the uncertainty at high

count rate, while the counting statistics dominated at low count rate. An ungraded experiment would use a monitor to measure this. The thirteen count rates measured were between 7 Hz and 17 kHz.

To fit these attenuation data, a model was built with two assumptions: (1) that the detector count rate responded linearly to x-ray intensity, and (2) that the x-ray intensity entering the detector consisted of three components. The first component was assumed to be Cu K α x-rays attenuated by the foils. The second component was Bremsstrahlung with energy at twice that of Cu K α from second order diffraction. The third component was dark current in the detector.

The model of count rate versus thickness was

$$y = a_0(1 - a_2)e^{-\mu_1 a_1 x} + a_0 a_2 e^{-\mu_2 a_1 x} + a_3 \quad (8.1)$$

where x is the number of Al foil sheets, y is the count rate recorded by the detector in Hz, a_0 to a_4 are the fitting parameters, and μ_1 and μ_2 are the linear attenuation coefficients of Al for the energy of Cu K α and its first harmonic respectively. The fitting parameters have the following meanings: a_0 is the incident count rate which is the x-ray intensity times the detector efficiency, a_2 is the fraction of the incident count rate due to the harmonic component of the beam, a_1 is the thickness of the Al foils used, and a_3 is the dark current count rate.

In the fit, a_3 was constrained to be not less than zero. The fit that was found is shown in Figure 8.1, and the fitted parameters in Table 8.1. A χ_r^2 of 1.3 indicates a good fit (there is a probability of 0.23 that an experiment would produce data with a larger χ_r^2), while all fit parameters were plausible. Such a good fit up to 17 kHz implied that both elements of the model were supported. The detector had a linear response to x-ray intensity up to at least 17 kHz and the x-ray beam at the detector had a Cu K α component and a harmonic component.

8.2 Spatial Linearity Correction

Non-linearities in the spatial response in the energy dispersive direction in an x-ray detector used would lead to systematic errors in the energy calibration of the spectrometer system. It is important to calibrate any detector used in this way to minimise such non-linearities.

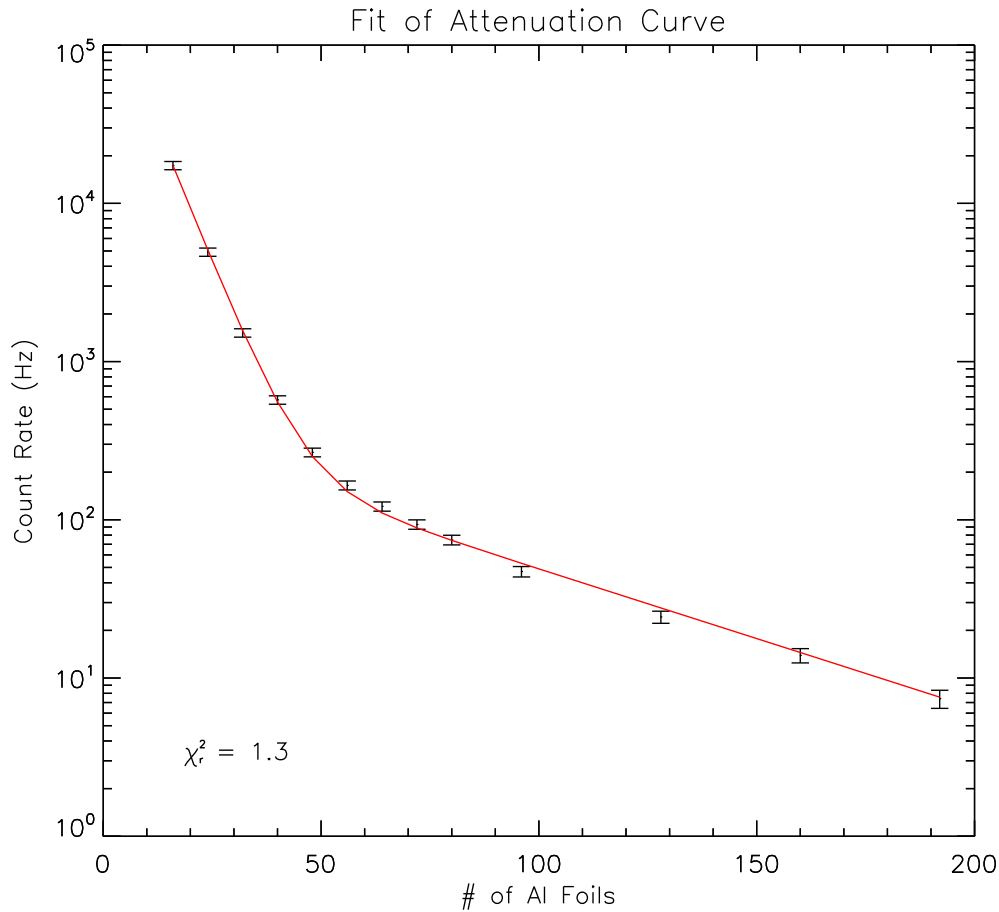


Figure 8.1: This log-linear plot of the fit of the attenuation curve in the intensity linearity experiment shows a clear signature of two energy components being attenuated by different amounts. There are two straight sections that blend together. The first section reflects the high attenuation component (Cu $K\alpha$), while the second reflects the low attenuation component (the harmonic).

Parameter	Value
a_0	213000(21000) Hz
a_1	12.07(29) μm
a_2	0.00175(11)
a_3	0 Hz

Table 8.1: Fitted parameters of Equation 8.1 for Count Rate verses the number of Al foils. a_3 hit the zero constraint so was set to zero without uncertainty. The χ^2_r of 1.3 indicates a good fit. That is, assuming the model fits the data, there would a probability of 0.22 that a new experiment data set would generate a higher χ^2_r . The foil thickness of 12.07(29) μm is consistent with the independently measured value of 10(5) μm .

The experimental setup that was used to achieve this is described in Section 5.4.3.2 of Chapter 5. The output of the detector electronics are four digitised voltages for each x-ray detection event, being two from the Cathode Board (the C and D voltages) and two from the Anode Wire (the A and B voltages). The detector calibration maps these four outputs to a position in mm of the energy dispersive axis (x -position) of the detector and a rough position in the other axis (y -position).

The naive approach to produce locations for x-ray events is with the following equations:

$$x = C/(C + D) \quad (8.2)$$

$$y = A/(A + B) \quad (8.3)$$

As shown in Figure 8.2, this produced a bimodal distribution in x for a line source. The pattern is due to the locations of the wire segments in relation to the teeth of the backgammon board and the shape of the charge cloud collected by each half of the board. This non-linearity could be reduced by modifying the design and construction of the detector [261]. However, even for a modified detector some non-linearity would remain, so a calibration experiment would still be necessary.

It should be noted that, in all the data, and as seen in Figure 8.2, there were two wire segments that appear to produce no x-ray events. These wire segments were located at about $0.34 < y < 0.37$ and $0.55 < y < 0.59$. The voltages that the x-ray events on these wire segments produced were filtered out by the quad single channel analyser in the early stages of data acquisition, as they were too high.

A calibration was defined to be a map from x location to position on the detector. This map will be dependent on y .

To calibrate the spatial response of the detector, it was mounted on a linear stage in front of a single energy x-ray source with a vertical line distribution. The experiment was done using The University of Melbourne Rotating Anode source. The monochromator was a channel cut Si (111) crystal while the Rotating Anode target was Cu. A schematic of the experiment is presented in Figure 5.9 of Chapter 5 above. At each stage position, the line of x-rays illuminated a different vertical slice of the detector. The response of the detector to a line of x-rays at each position across the face of the detector could be mapped in this way.

The centre of the detector in the energy dispersive axis was aligned to the vertical line distribution of x-rays. This was done by attaching a vertical slit mask on to

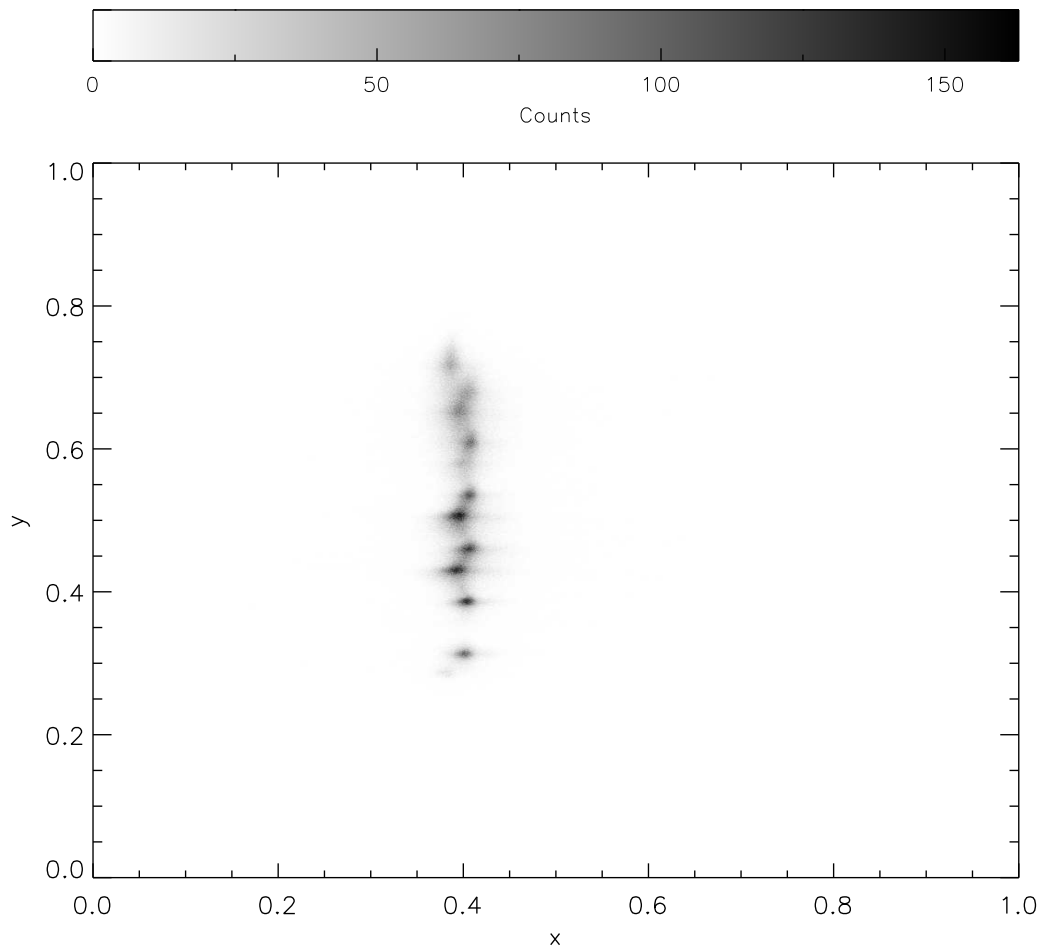


Figure 8.2: This is the image of the two dimensional histogram (or image) of the raw data for a typical Cu $K\beta$ line taken as part of linearity calibration. The image has 500 pixels in the y direction and 1000 pixels in the x direction. Thus there are 500 rows and 1000 channels. These data were taken when the linear stage was at -5.000 mm. Each lobe in this image represents the response of a particular wire segment to the incoming x-rays. The x positions of the lobes do not align, though every second lobe seems to align well. This bimodal distribution is one of the non-linearities that must be corrected.

the face of the detector then moving the linear stage to find the maximum count rate. This position on the linear stage position (L) was then called 0 mm. The mask was then removed.

A LabVIEW program was written to automate the rest of the experiment. Data were collected from $L = -20.00$ mm to $L = +20.00$ mm, and then $L = +19.08$ mm to $L = -20.00$ mm every 0.02 mm. This led to 4001 data files covering the whole active region of the detector twice. Each spectrum recorded was identified with its corresponding calibrated position L .

For each data file, a 2D histogram (an image) was made with the x and y directions being the basis. The x axis was split into 1000 columns from 0 to 1 and the y axis was split into 500 rows from 0 to 1. A histogram of this type can be shown as an image, an example of which is in Figure 8.2. Some rows, especially at the top and bottom of the y range, never display a meaningful response to x-rays, manifesting a very low number of counts in those rows. In this analysis, for each row with enough data, a Gaussian was fitted. The fit was χ^2 fit where the uncertainty for I_i , the count in the i^{th} column, was assumed to be $\sqrt{I_i}$ (Poissonian) when $I_i > 0$ and 1 when $I_i = 0$. The position of the Gaussian was taken to be a measure of the output x position response of the detector for the given row, to x-ray radiation falling at physical position L . An example of such a fit found by this analysis (actually for Row 268) is shown in Figure 8.3. The resulting positions determined by these row fits for a single data file are presented in Figure 8.4.

Thus, taking all the data files together, for each row on the detector, an association of x to L was found. To map out the non-linearities of the detector, the L vs x data for each row was fitted with a polynomial. Polynomials from degree 2 to degree 20 were tried. A typical fit for a row is shown in Figure 8.5.

It was found that the map of degree 11 captured the present non-linearities without over-fitting. The fits were extended past the limits of the captured data by linear extrapolation. Taken together, these degree 11 polynomial fits each associated with a row, defined the calibration of the detector response to x-ray position L in the x axis. This constituted the calibration map of the detector. The effect of the map on the calibration data can be seen in Figure 8.6.

To then test the calibration, a central tendency of each calibrated data file was produced and compared to the Linear Stage Position at which it was taken. A successful calibration would have small deviations compared to the physical extent of the calibration.

To produce a central tendency for a calibrated data file, a four step process was undertaken. The first step was to put the raw data through the calibration map. A typical image of data put through the calibration is shown in Figure 8.7. The second step was to produce a histogram of the calibrated data. The third step was to fit the histogram with a sum of two Lorentz functions plus a constant background. The fourth step was to calculate a central tendency of the fitted function. The measure of central tendency selected was the center of mass of the

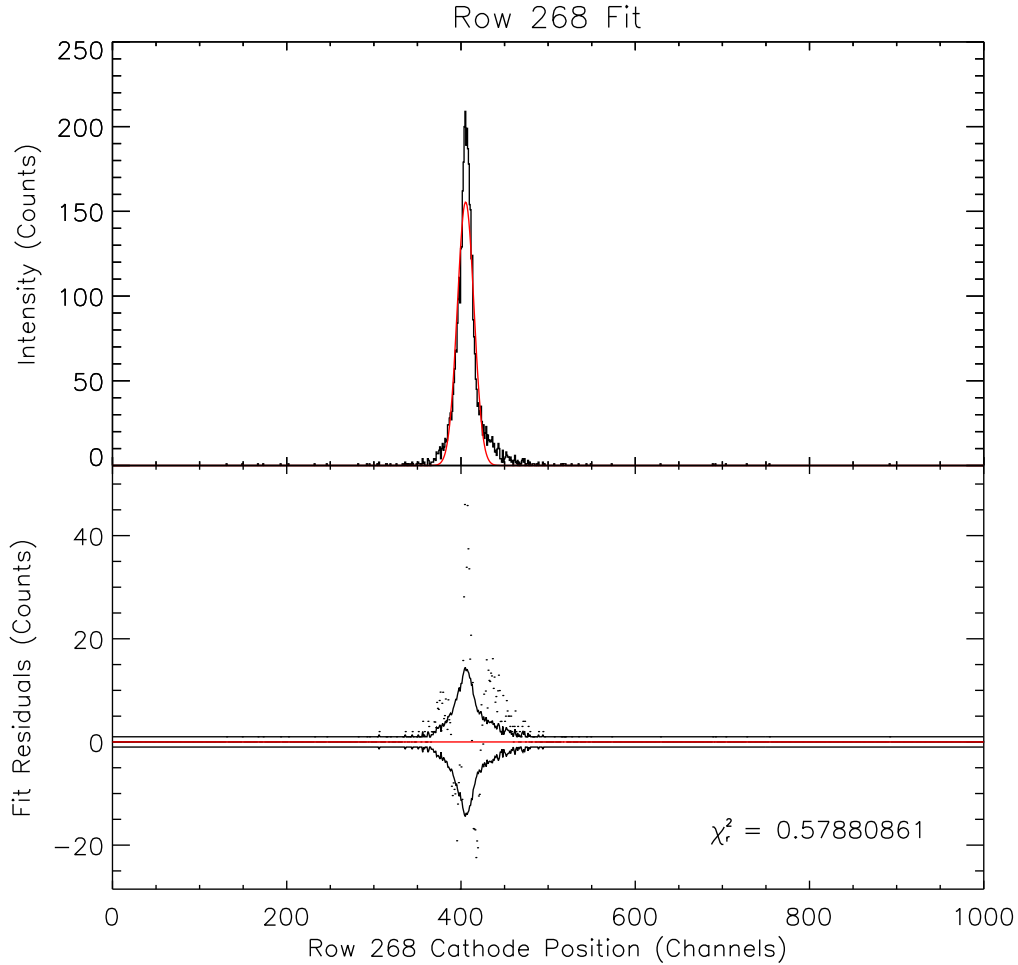


Figure 8.3: This is a fit and residual of an example row (row 268) of the image shown in Figure 8.2. The fitting function was a Gaussian. The uncertainty envelope is shown in the residues. It was assumed that the peak of the fit was a reasonable measure of the central tendency of the spectrum on the row. The peak position was found to be 145.3 ± 3.4 channels for this row. The intensity away from the peak was zero counts for almost all the channels. The low χ_r^2 of 0.58 is unexpected at first glance because of the large residuals at the peak compared to the uncertainties. This can be resolved by recognising that the tails of this spectrum is almost all zero counts and the model function is a Gaussian which approaches zero quickly away from the peak. Thus χ^2 fitting with a Gaussian fits the tails too well, leading to a χ_r^2 that does not represent the quality of the fit at the peak.

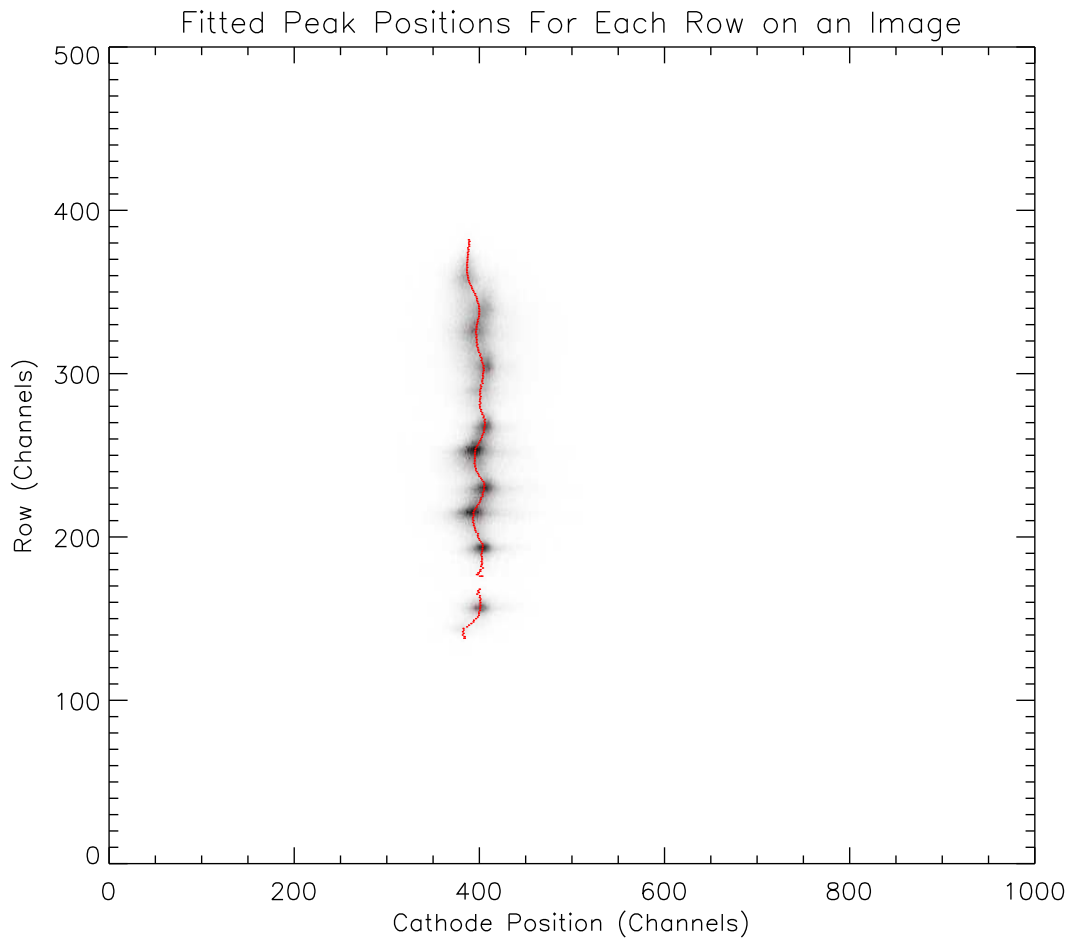


Figure 8.4: The fitted row positions of the data shown in Figure 8.2. These data were taken at a linear stage position of 5.000 mm. Note that the histogram and fit of row 268 is shown in 8.3.

fitted function, taken between two limits. These limits were located where the function crossed 20% of the height of the maximum. This corresponded, of course, to using the function where its value was within 80% of the maximum.

The residuals of a straight line fit of the central tendency versus linear stage position is presented in Figure 8.8. The maximum fractional excursion of the residuals in the fit indicated that the detector response can be made linear in the energy dispersive axis to 160 microns across the central 22 mm of the detector. Almost all the residuals were within 100 microns. Thus the non-linearity was now at most 0.073%.

In this way, through a calibration of the spatial response of the Backgammon detector, a high degree of linearity was achieved. Linearity to within 0.073% was

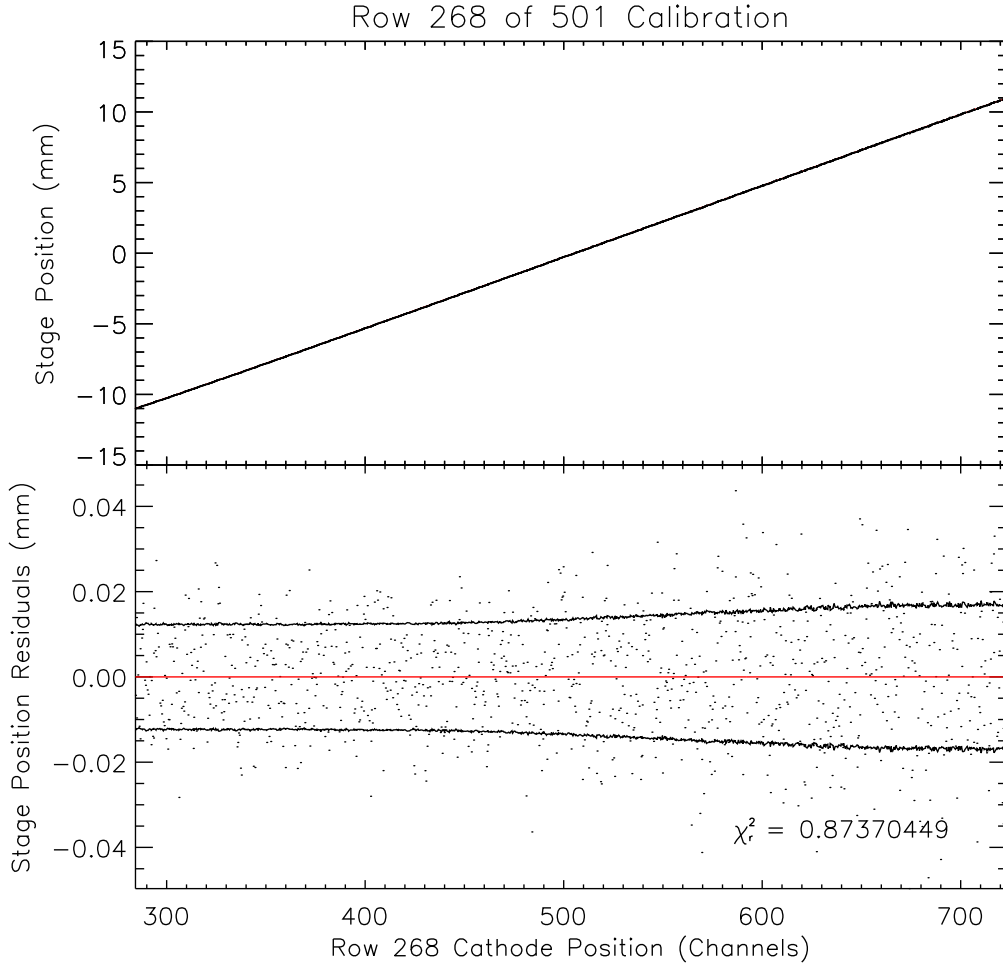


Figure 8.5: This figure shows a fit with corresponding residues of the response of the backgammon detector in an typical example row (row 268). The x axis is the position of the fitted maxima of the 268th row of each calibration image in channels. The fitting function was an 11th order polynomial. Assuming the model fits the data, the χ_r^2 of 0.87 implies that there is a probability of 0.001 that χ_r^2 would be below this value. This indicated that the uncertainties in peak position were likely underestimated.

found for the central 22 mm of the detector.

8.3 Conclusions

This chapter has reported that the University of Melbourne Backgammon detector achieved a linear response to x-ray intensity up to a count rate of at least 17 kHz. The construction of a spatial calibration map for the detector which maps the raw output of the detector to a physical length scale in cathode board axis

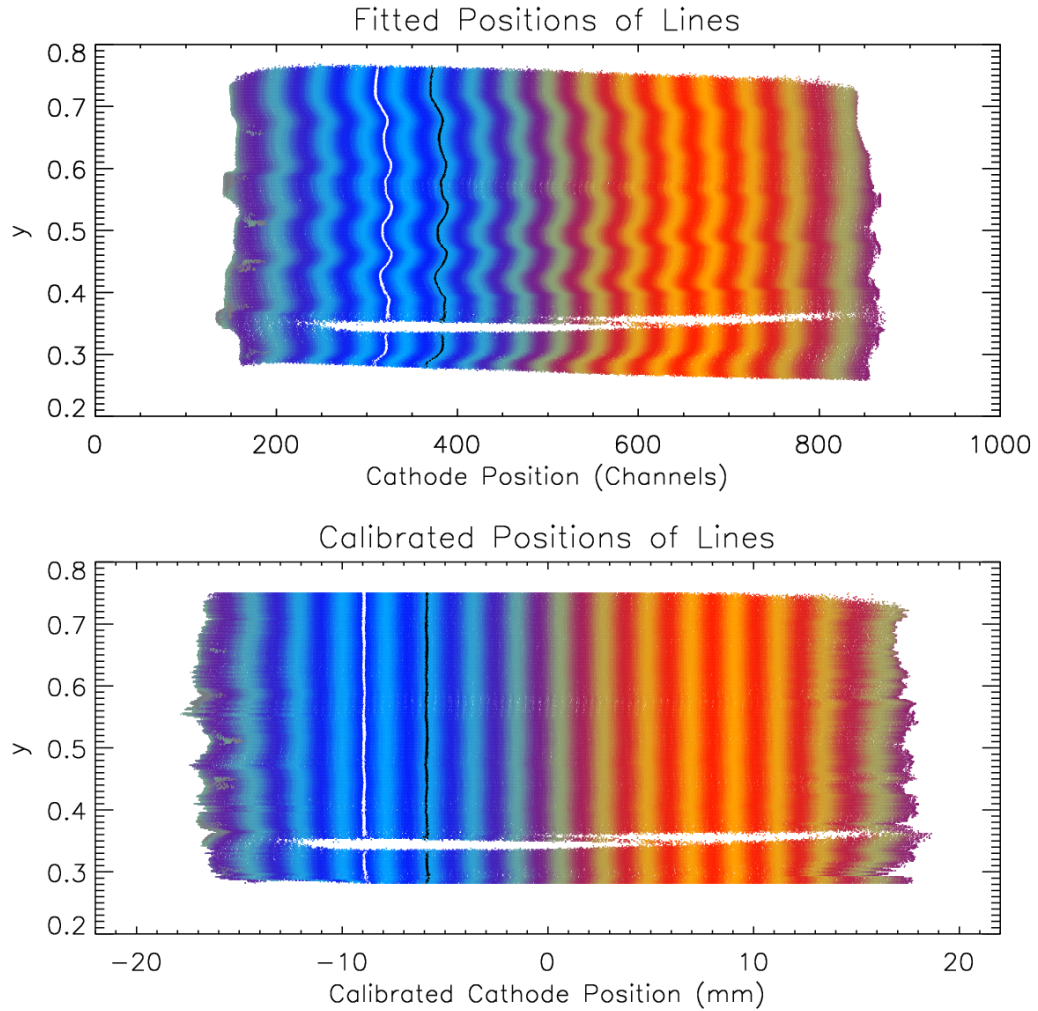


Figure 8.6: This figure visualises the effect of the calibration. The top image shows the fitted Gaussian peak positions of all the rows in all the calibration data files. The bottom image shows these positions after calibration. Each peak position is colored by Linear Stage Position. The fact that the waves of color are regular and flat between -11 mm and 11 mm show some measure of success of the calibration. The calibration gets worse outside this range, as expected.

was demonstrated. This work prepared the detector for use in the Oxford 2007 experiment measuring the spectral profiles of V $K\beta$, Ti $K\beta$, Cr $K\beta$ and He-like Cr that is a major focus of this thesis, detailed in Chapters 11 to 14.

There are implications here for further research. Whenever this particular Backgammon detector is used (for instance, in other tests of QED), the raw data collected should, as a first step, be put through the calibration map developed here, as was done in the case of the Oxford 2007 experiment. As the detector was used in the NIST 2005 QED experiment, so the map will be used for a forthcoming analysis. In short, this Backgammon detector and accompanying calibration map can be

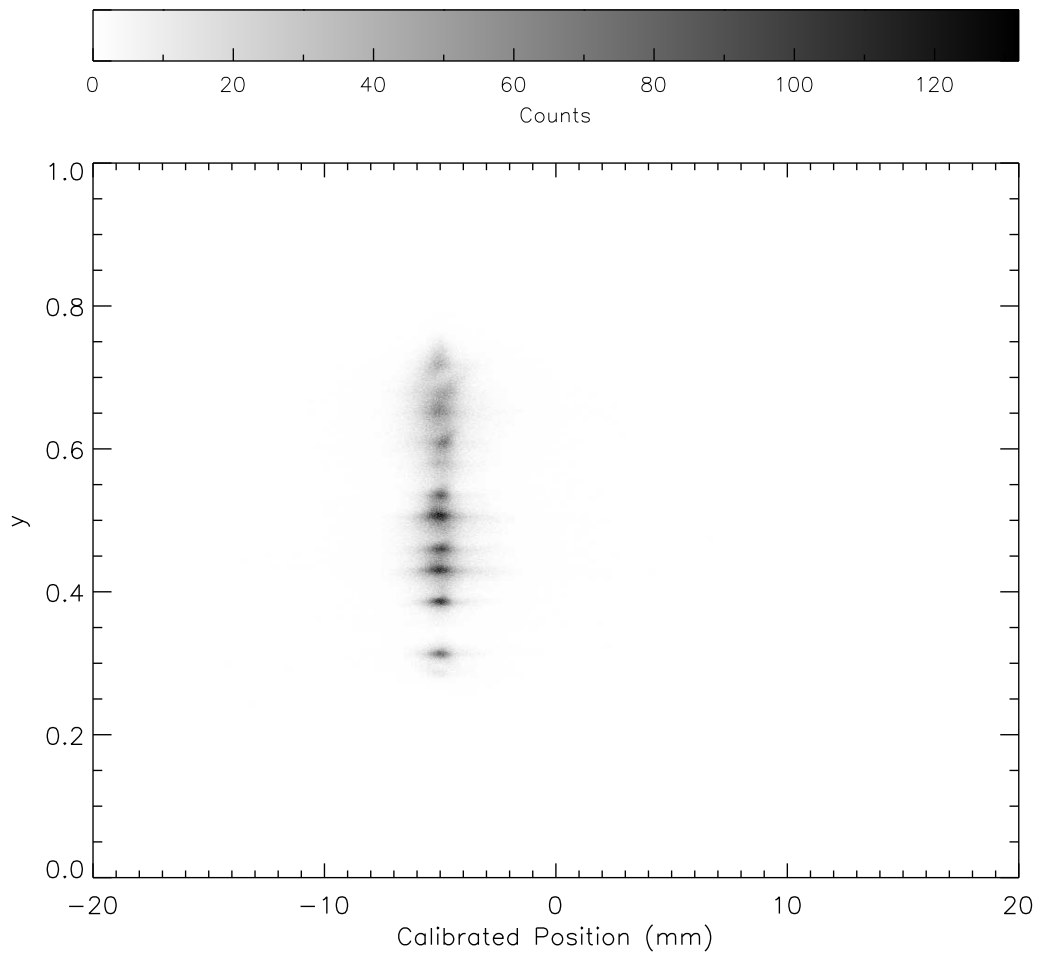


Figure 8.7: This is the image of the two dimensional histogram of the calibrated data for a typical Cu $K\beta$ line taken as part of linearity calibration. This is the same data as in Figure 8.2. The lobes corresponding to the wire segments are now lined up vertically and the x axis is now in mm. This data was taken when the linear stage was at -5.000 mm. The calibration puts the data around -5.000 mm as expected.

used in upcoming QED experiments, as well as other measurements of $K\alpha$ and $K\beta$ profiles.

The software/hardware system that the present author designed and built as described in this thesis, enabling the construction of the spatial calibration map of the above chapter, can be applied to other Backgammon detectors. In fact, the system was successfully applied to the detector described in Payne et al. [261] after that paper was published.

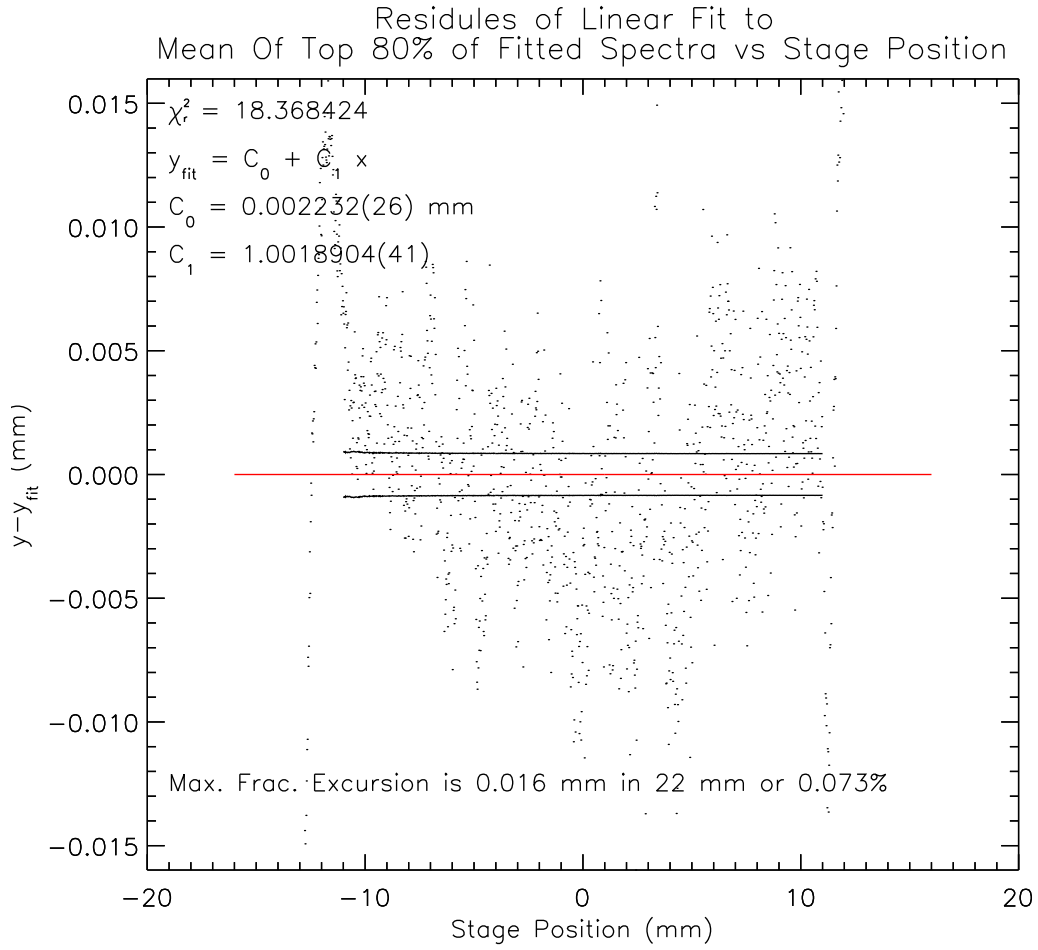


Figure 8.8: The residuals of a straight line fit of central tendency of the fitted spectra to the linear stage position are shown. The black lines are the uncertainty envelope of the central tendency.

Clinometer Calibration

A further preparation for the 2007 Oxford EBIT studies was the calibration of the four clinometers to be installed on the spectrometer, as described in Section 5.4.2 of Chapter 5. The present chapter describes this work and development.

Summary

Angle measurement is a basic requirement of all x-ray diffraction techniques used in spectrometry as it is one of the major variables of Bragg's Law. Two major ways have been used to measure angle, namely with an encoder and with a clinometer. An interferometric encoder measures angle between two vectors in a fixed plane while a clinometer is an accelerometer that measures angle with reference to the local gravitational acceleration vector. In the present research, four clinometers were to be installed on the spectrometer to measure angles, and these were calibrated through a calibration experiment that matched an interferometric encoder measurement of clinometer angle γ to clinometer output voltage V .

Key Achievements

- The four clinometers used in the Oxford 2007 experiment were calibrated with an angle to clinometer output voltage function.

9.1 Clinometer Calibration Method

As set out in Chapter 5, four clinometers were to be installed. These were the Base Clinometer (BC), the Crystal Clinometer (CC), the Detector Lower clinometer (DL) and the Detector Upper clinometer (DU). The four clinometers were calibrated in a single experiment.

The data collection for this calibration was broken into four legs, in order to understand possible hysteretic effects. These were the two forwards legs (-85 to 85 degrees) and the two backwards legs (85 to -85 degrees). These legs were interleaved, since leg 1 was forwards, leg 2 was backwards, leg 3 was forwards and leg 4 was backwards. A single leg consisted of moving the rotational stage from the start angle to the end angle in 0.5 degree steps. At each angle, the setup was allowed to settle for 30 seconds then the Heidenhain angle and the clinometer voltages were sampled for 216 seconds. 2,160,000 clinometer samples were taken at 10 kHz and 2,160 Heidenhain samples were taken at 10 Hz. A LabVIEW program was written to automate this process.

For each angle of each leg, the mean Heidenhain angle γ was calculated, as was the mean voltage V for each clinometer. The uncertainties in each were taken to be the standard error. Thus a V_{data} vs γ_{data} dataset was produced for each leg for each of the four clinometers. The γ to V mapping for each leg for each clinometer was found with a four stage process.

Firstly, the V_{data} versus γ_{data} dataset for each leg of each clinometer were fitted with

$$V_1(\gamma; \mathbf{a}) = a_0 \sin(\gamma + a_1) + a_2 \quad (9.1)$$

where $\mathbf{a}$ was a vector of three fitting parameters.

Secondly, the residues of these first stage fits were then fitted with polynomials of order eight. Therefore, second stage model of the γ to V mapping for a particular leg and clinometer was

$$V_2(\gamma; \mathbf{a}) = a_0 \sin(\gamma + a_1) + a_2 + \sum_{i=3}^{11} a_i \gamma^{(i-3)} \quad (9.2)$$

where $\mathbf{a}$ is a vector of length twelve and a_0 to a_2 were refined by the first stage fit and a_3 to a_{11} were refined by the second stage fit.

Param.	CC Leg 1 Value	CC Leg 2 Value	CC Leg 3 Value	CC Leg 4 Value
a_0	-10.0194272(23)	-10.0194474(22)	-10.0194004(22)	-10.0194711(22)
a_1	-0.083999(91)	-0.082693(87)	-0.084122(89)	-0.084870(89)
a_2	-0.004860(15)	-0.004533(14)	-0.004653(14)	-0.004692(14)
a_3	$6.8(16) \times 10^{-6}$	$-0.6(15) \times 10^{-6}$	$-3.17(16) \times 10^{-5}$	$-2.57(16) \times 10^{-5}$
a_4	$-9.80(25) \times 10^{-6}$	$-6.67(23) \times 10^{-6}$	$-9.18(24) \times 10^{-6}$	$-8.84(24) \times 10^{-6}$
a_5	$-2.21(33) \times 10^{-7}$	$1.4(32) \times 10^{-8}$	$7.28(32) \times 10^{-7}$	$5.78(33) \times 10^{-7}$
a_6	$3.05(18) \times 10^{-8}$	$7.9(17) \times 10^{-9}$	$2.79(17) \times 10^{-8}$	$2.20(18) \times 10^{-8}$
a_7	$8.1(16) \times 10^{-10}$	$-2.8(16) \times 10^{-10}$	$-2.82(16) \times 10^{-9}$	$-2.25(16) \times 10^{-9}$
a_8	$-3.70(40) \times 10^{-11}$	$2.5(37) \times 10^{-12}$	$-3.40(38) \times 10^{-11}$	$-1.60(38) \times 10^{-11}$
a_9	$-8.5(28) \times 10^{-13}$	$7.7(26) \times 10^{-13}$	$3.75(28) \times 10^{-12}$	$3.09(28) \times 10^{-12}$
a_{10}	$2.30(25) \times 10^{-14}$	$2.9(22) \times 10^{-15}$	$2.22(24) \times 10^{-14}$	$8.5(24) \times 10^{-15}$
a_{11}	$2.7(15) \times 10^{-16}$	$-4.9(14) \times 10^{-16}$	$-1.65(15) \times 10^{-15}$	$-1.42(15) \times 10^{-15}$

Table 9.1: The partial fit characterisation of the Crystal Clinometer (CC) for the four calibration legs. The parameters (a_1 to a_{11}) in this table are for use in Eqn 9.2. a_0 to a_2 are the fit parameters of the sin function that is fit first. a_3 to a_{11} are coefficients of an eight order polynomial that refined in the second round of fitting. The smallness of a_3 to a_{11} indicate that the polynomial correction to the sin function is small. The Crystal Clinometer was used as the basis for the spectrometer calibration analysis described in Chapter 10.

Thirdly, the structure of the residues of the second stage fits were modelled with a function $f_3(\gamma; \mathbf{a}; V_{data}, \gamma_{data})$ that linearly interpolated the boxcar averaged residuals. The boxcar average for the i^{th} residual averaged it with the next three residuals of lower γ and the next three residuals of higher γ . The map for a single leg of a single clinometer was then:

$$V_3(\gamma; \mathbf{a}) = a_0 \sin(\gamma + a_1) + a_2 + \sum_{i=0}^8 a_{i+3} \gamma^i + f_3(\gamma; \mathbf{a}; V_{data}, \gamma_{data}) \quad (9.3)$$

The final γ to V map for a clinometer was an weighted mean of all the third stage functions for four legs of a clinometer.

9.2 Calibration Results

The calibration results in respect of each of the four legs are presented for the Crystal Clinometer (CC). These demonstrate the application of the calibration method in relation to all four clinometers. Only results for the CC calibration were subsequently used in the Oxford 2007 experiment for reasons set out in Section 10.3.6 of the next chapter, Chapter 10.

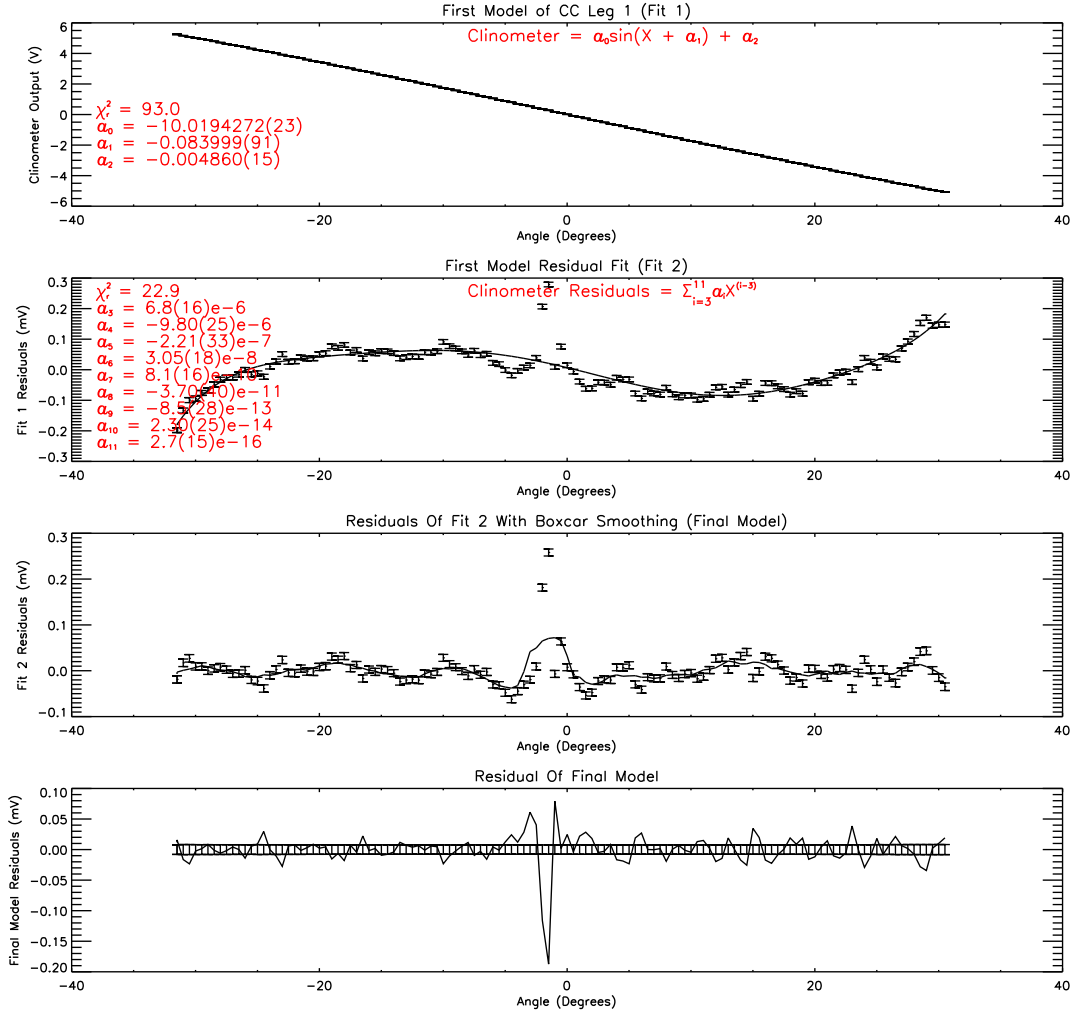


Figure 9.1: The four stages of creating a map for Leg 1 for the CC are shown here.

Maps for CC in the four legs are shown in Figures 9.1 to 9.4. Note that the crystal clinometer calibrations have what appears to be a discontinuity around zero degrees. Presented in Table 9.1 are the fitted parameters of equation 9.3 for the crystal clinometer.

These CC results were used as a basis for the spectrometer calibrations created with the method described in Chapter 10 and used in Chapters 11, 12, 13 and 14.

Section 10.3.6 of Chapter 10 describes the inversion of this calibration presented here as a first step in spectrometer calibration. That is, V to γ functions were created from the γ to V calibration functions presented in this chapter. Given the necessity of this inversion in the spectrometer calibration method, in future research involving these clinometers, the clinometer calibration data itself should

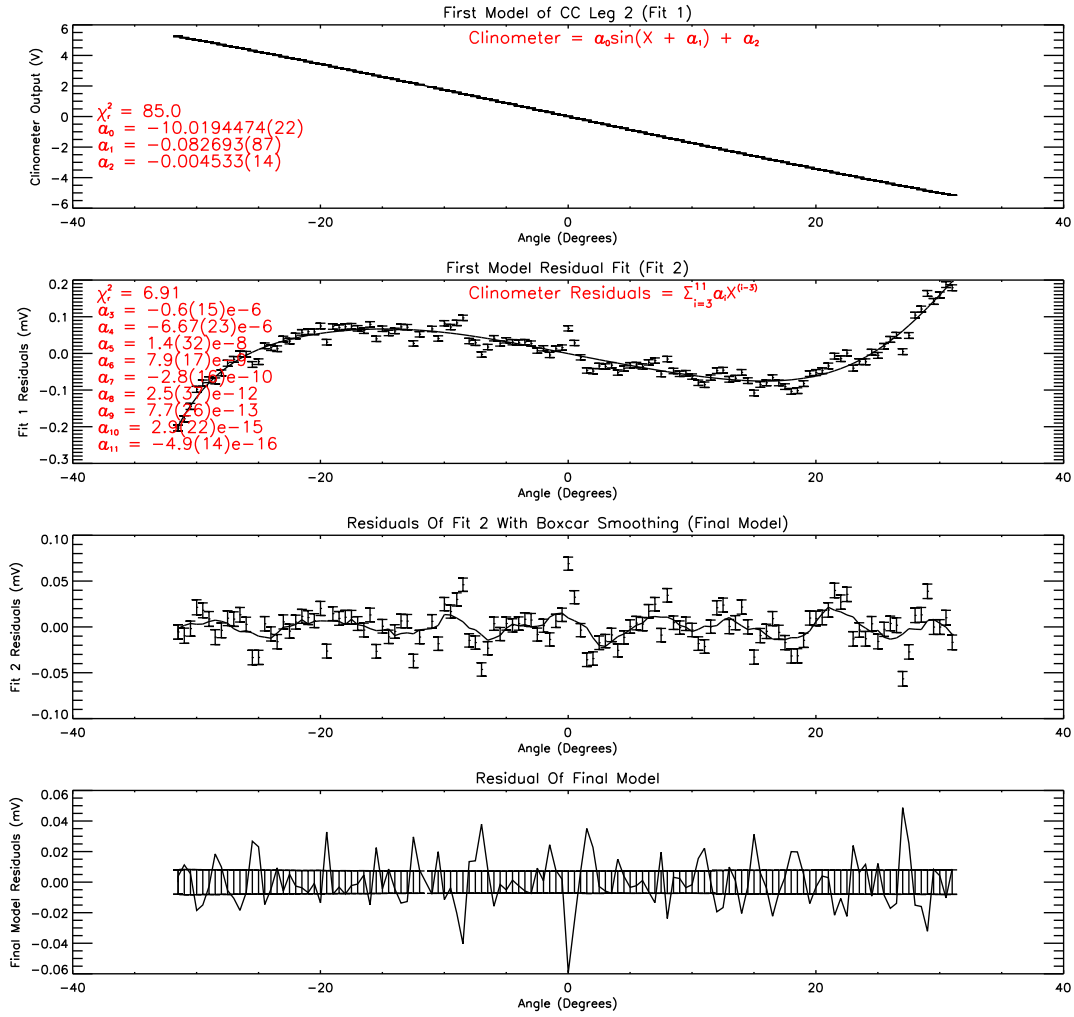


Figure 9.2: The four stages of creating a map for Leg 2 for the CC are shown here.

be inverted, then refitted to directly create a V to γ calibration function. This would create a more reliable V to γ clinometer calibration.

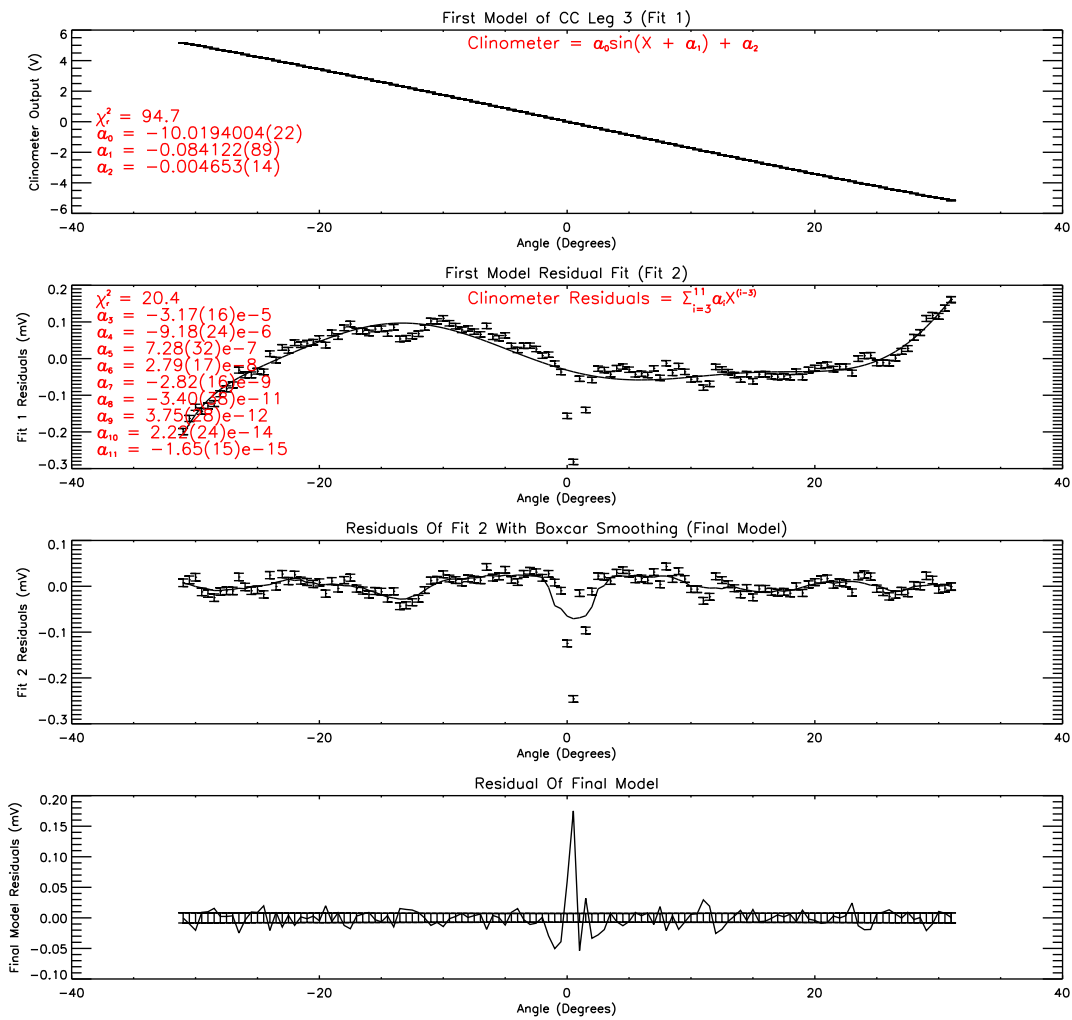


Figure 9.3: The four stages of creating a map for Leg 3 for the CC are shown here.

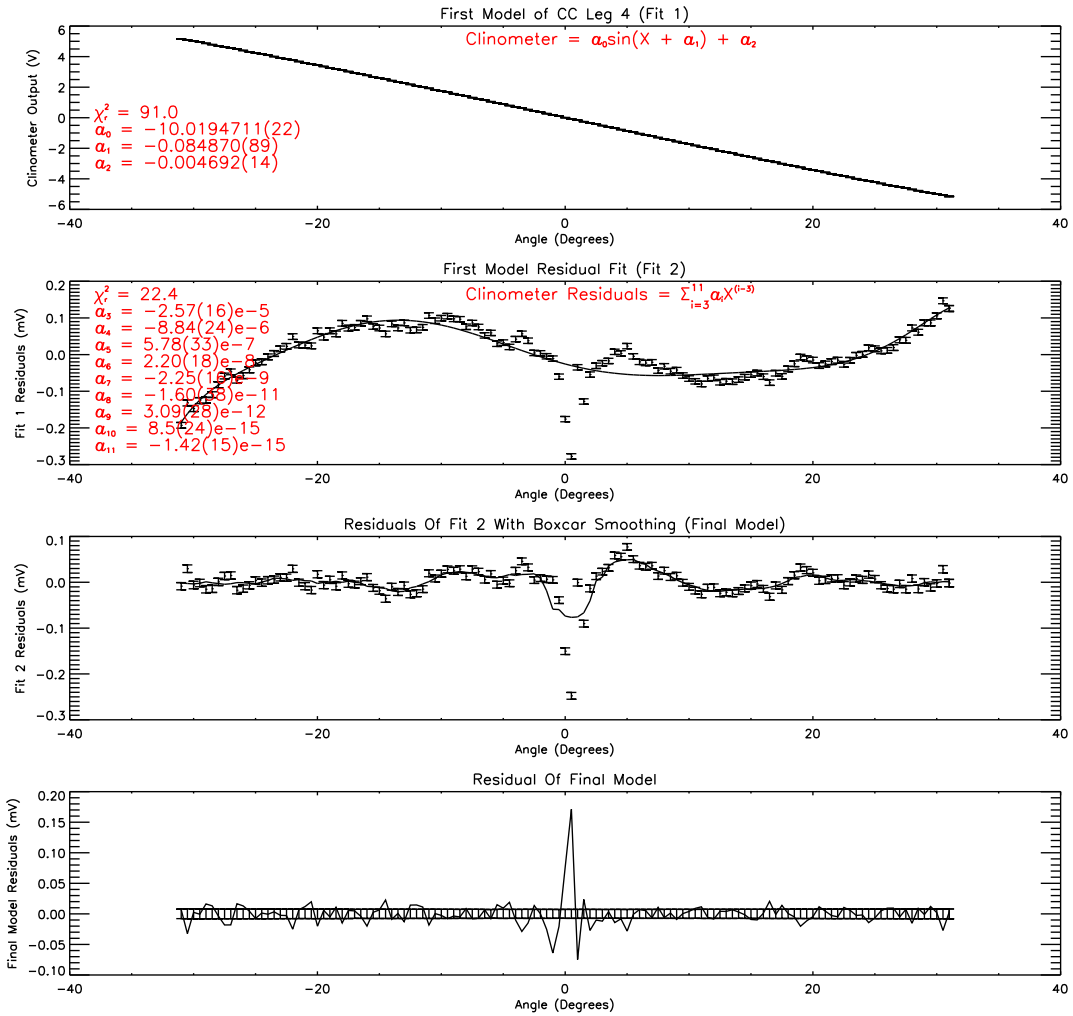


Figure 9.4: The four stages of creating a map for Leg 4 for the CC are shown here.

High Accuracy Spectrometry Method

In this chapter, the overall method employed in calibrating the spectrometer system for the Oxford 2007 experiment, conducted at the Clarendon Laboratory, is presented. This work sought high accuracy in measuring the spectral profiles of Ti $K\beta$, V $K\beta$, Cr $K\beta$, and the w , x , y and z transitions of He-like Cr. The spectrometer system was described in Chapter 5.

Summary

A high accuracy method of using a curved crystal spectrometer system with a linked crystal angle and detector arm angle is presented. This method was created for the Oxford 2007 experiment to measure and characterize the V, Ti, and Cr $K\beta$ spectral profiles, and to test QED by measuring the w , x , y and z lines of He-like Cr. The method involves the collection of a range of standard spectral profiles that are used to create spectrometer system calibrations ($K\alpha$ profiles in this case) and the profiles of interest ($K\beta$ profiles in this case). These profiles are collected in an extended range of spectrometer geometries in order to characterise the spectrometer system as fully as possible. The spectrometer system was then theoretically modelled by the dynamical diffraction code, Mosplate [26–28], for the set of standard energies identified from the standard spectral profiles (energies of $K\alpha$ profile peaks in this case). The theoretical model data and the experimental calibration data were then linked via a fitting of the calibration functions of the spectrometer components. Modelling of the shapes of the profiles of interest must be performed. To create x-ray standards, identification of a standard feature of the profiles of interest must be made ($K\beta$ profile peaks in this case). This allows the standard feature to be given an energy through the spectrometer calibration. Refinement of the calibration functions of the spectrometer components is done through refitting, this time including the consistency of the energy of the standard

feature as part of the fitting optimisation process. Variations in this process are explained.

Using a large range of lines to calibrate a Johann spectrometer system at an EBIT has a history. QED lines of H-like and He-like V were measured [27, 159, 200] in the late 1990s and QED lines of He-like Ti along with V $K\alpha$ were also measured in the mid 2000s [86, 203, 205]. These experiments were performed at the NIST EBIT using the same x-ray tube as a source of calibrating characteristic radiation, the same crystal housing and the same mechanism for ensuring the θ to 2θ crystal angle to detector arm angle ratio. There were a number of problematic issues that had been found in the previous experiments. The first issue was that, as the EBIT was positioned between the x-ray tube and the crystal, the spectrometer had a small bandpass for the characteristic radiation due to vignetting. This meant that only a fraction of the detector could be used for calibration. This was overcome in the present research by placing the x-ray tube between the EBIT and the crystal, increasing the bandpass for the characteristic radiation. The second issue was a paucity of statistical evidence for the clinometer voltages due to by a low sample rate. The largest source of uncertainty in these experiments was caused by uncertainty in the detector arm angle which was the direct result of this issue. This was improved in the present research by increasing the sample rate for the clinometers. The third issue was that the backgammon detector used had a circular window, causing a profile distortion. This was improved by the construction of a detector with a square window (The University of Melbourne Backgammon Detector). These improvements to the setup and running of the spectrometer system enabled a more careful data analysis to be undertaken.

Key Achievements

- A method of dealing with the physical line curvature observed on the detector was proposed and implemented.
- A method of calibrating the spectrometer system was proposed and implemented.
- A method of optimising for the consistency of the spectrometer system calibration in regions of interest was found.

10.1 The Oxford 2007 Experiment

In order to characterize the V, Ti, and Cr $K\beta$ spectral profiles for use as standards for x-ray spectrometry and to test QED through the spectral profile of He-like Cr, these profiles must be measured with a calibrated spectrometer system. These profiles were measured at the Oxford 2007 experiment using the apparatus described in Section 5.4.2. The clinometer and detector subsystems were calibrated in independent experiments performed at the University of Melbourne as described in Chapters 8 and 9. Thus, the spectrometer system, as it was set up in Oxford, had to be calibrated. This was done using previously characterised $K\alpha$ spectra as calibration standards.

The method of calibration presented in this chapter and method of characterisation of $K\beta$ lines represent a new high accuracy method for x-ray spectrometry with variations that can be used to examine remaining systematic errors and assess their size. Thus, the robustness of the method could be tested by checking for the consistency of the results, when the method is optimised for a small variance in results. The method involves data collection, spectrometer calibration fitting, spectral profile modelling and spectral profile energy uncertainty estimation.

10.2 Data Collection at Oxford

Seven series of characteristic radiation data were collected at the Clarendon Laboratory. The series were grouped into three data collection runs named *prerun*, *prerun2*, and *postrun*. The spectrometer was opened up between *prerun* and *prerun2* with adjustments made to the mechanism that moved the wedge. Between *prerun2* and *postrun*, high charge state Cr EBIT data was collected. The EBIT was tuned to produce He-like Cr. 38 hours of EBIT Cr data were collected. Within each run, each series used a different wedge position. This meant that the diffraction theoretical modelling used in this method had to make accurate independent predictions of the geometry of each position. Within each series, $K\alpha$ and $K\beta$ spectral profiles from $Z=22$ to 26 were collected. The $K\alpha$'s were collected to form the basis of the calibrations of the spectrometer that were used to calculate the $K\beta$ and EBIT Cr line energies from detector positions.

Series		Spectra Collected				
Run	Wedge Pos. (mm)	Ti $K\alpha$	V $K\alpha$	Cr $K\alpha$	Mn $K\alpha$	Fe $K\alpha$
<i>prerun</i>	2.28	5	5	7	6	5
<i>prerun</i>	4.64	6	5	5	5	5
<i>prerun</i>	18.66	5	5	5	5	5
<i>prerun2</i>	6.44	4	3	3	4	3
<i>prerun2</i>	8.63	3	3	3	3	3
<i>prerun2</i>	16.40	5	3	4	3	3
<i>postrun</i>	16.40	4	4	4	3	3

Table 10.1: The number of $K\alpha$ spectra collected at Oxford for each series of data.

Series		Spectra Collected				
Run	Wedge Pos. (mm)	Ti $K\beta$	V $K\beta$	Cr $K\beta$	Mn $K\beta$	Fe $K\beta$
<i>prerun</i>	2.28	5	5	5	5	11
<i>prerun</i>	4.64	5	5	5	6	5
<i>prerun</i>	18.66	5	5	5	5	5
<i>prerun2</i>	6.44	3	3	3	3	3
<i>prerun2</i>	8.63	5	3	3	3	3
<i>prerun2</i>	16.40	8	3	3	5	3
<i>postrun</i>	16.40	4	5	4	3	3

Table 10.2: The number of $K\beta$ spectra collected at Oxford for each series of data.

Custom LabVIEW software was written by the present author to acquire x-ray, clinometer and temperature data, and show a realtime view of the data as they were collected. The software featured important diagnostic displays that enabled real-time troubleshooting. The data were acquired in pseudo-event mode, so each x-ray absorption event was independently recorded. The spectral profile of each type of characteristic radiation was collected at a minimum of three detector arm angles, to sample profiles at different positions on the detector and investigate the dispersion function and the detector response function accordingly. The numbers of $K\alpha$ and $K\beta$ spectra collected for each series are shown in Tables 10.1 and 10.2 respectively. The brightness of the fluorescence source was manually adjusted before the data was collected for each profile to keep the count rate at the detector at around 1 kHz, to minimise the broadening that was observed in the detector for count rates above 1 kHz. Vignetting of the profiles was an issue for some $K\alpha$ profiles at extreme positions on the detector.

10.3 Spectrometer Calibration

The calibration of the spectrometer is the analytical method used to link the spectrometer system output data to an absolutely calibrated energy scale tied to the meter. It thus required theoretical modelling of the experiment and a link between the experimental data and that modelling.

10.3.1 Theoretical Modelling: Mosplate Diffraction Theory

The experimental process was modelled theoretically by the dynamical diffraction code, Mosplate [26–28]. Other systems, such as XOP [32], do not include some important dynamical diffraction effects. Mosplate predicts and models diffraction phenomena that have an effect on energy determination up to the order of hundreds to thousands of ppm, and characterises these to an accuracy below 1 ppm. These diffraction phenomena include lateral shifts in position due to x-rays penetrating the crystal to some depth and refractive index corrections. The refractive index shift, of order 100 ppm, as calculated by Mosplate for the Oxford 2007 experiment, is shown in Figure 10.1. Lateral shifts in curved crystal spectrometry can be of a similar order of magnitude. Corrections for asymmetry and polarisation are typically responsible for another 30 ppm. Depth penetration of the dynamical wavefield can dominate in curved crystal spectrometry, but can be even more significant for flat crystal spectrometry. At the Oxford 2007 experiment, the depth penetration shift was roughly an order of magnitude greater than the other shifts as calculated by Mosplate. A plot of this calculation of the sum of all these shifts can be seen in Figure 10.2.

Mosplate calculates the x-ray intensity spectrum expected to be seen on a detector for a particular x-ray energy, E , and crystal angle, θ . The incident wavefield at the crystal is computed by ray tracing, performed from a point grid at the source to a point grid on the cylindrically curved crystal. It should be noted that for computational efficiency, the traced rays are all in a two dimensional plane. The wavefield is then propagated through the crystal to find the diffracted wavefield at the exit surface of the crystal. Mosplate includes any scale of mosaicity in the code and computation, but as the crystal was perfect in this instance, none was

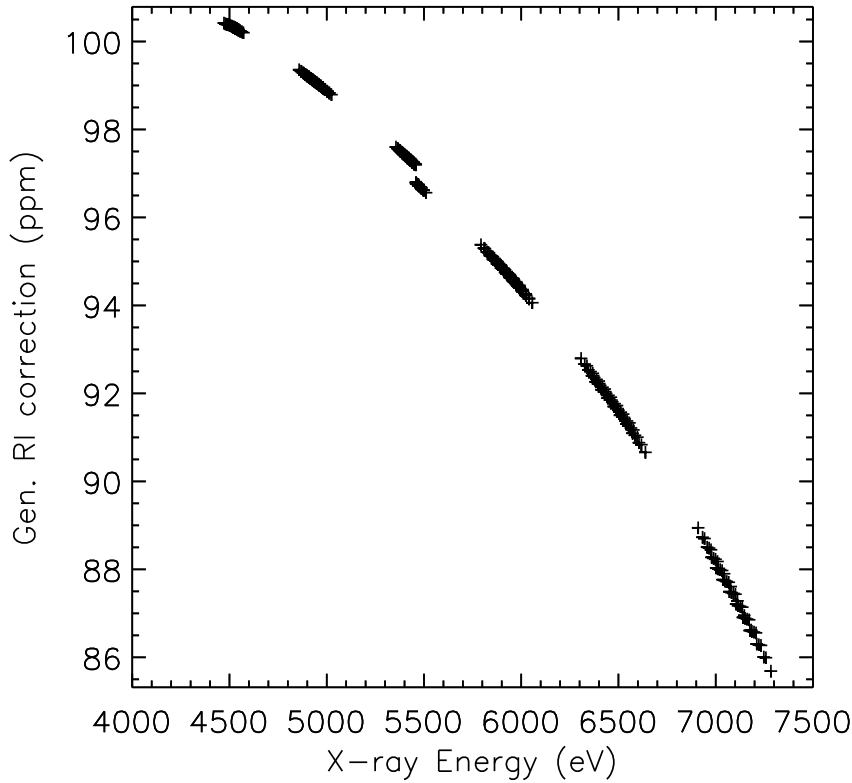


Figure 10.1: This figure shows the refractive index correction calculated by Mosplate for the ranges of x-ray energy that fell on the detector at the Oxford 2007 experiment while taking characteristic radiation data. Note that the correction is between 85 and 105 ppm and it varies with energy and therefore must be taken into account for accurate modelling used for calibration. The 0.8 ppm discontinuity at about 5459 eV leads to an uncertainty of about 0.4 ppm for this calculation. This discontinuity arose from the stable convergence criteria of the calculations being computationally expressed differently between the two continuous sections.

included. The diffracted field distributions in position and angle at the crystal surface are then used as a source to ray trace to the detector. These rays are again traced in the same two dimensional plane. Mosplate outputs the calculated spectrum by specifying the x-ray intensity, I , as a function of detector position, x , on a uniform grid of points $\{x_i\}$ with a grid spacing of less than a micron. The raw calculated intensity at the point x_i is $I_{raw,i}$.

To model the Oxford 2007 experiment, two sets of calculations were done. Both sets assumed a wedge position of 16.40 mm. The first set was for the wavelengths that were defined by the peaks of the standard $K\alpha$ spectra that were used for calibration. For each wavelength, a range of spectra were calculated at different

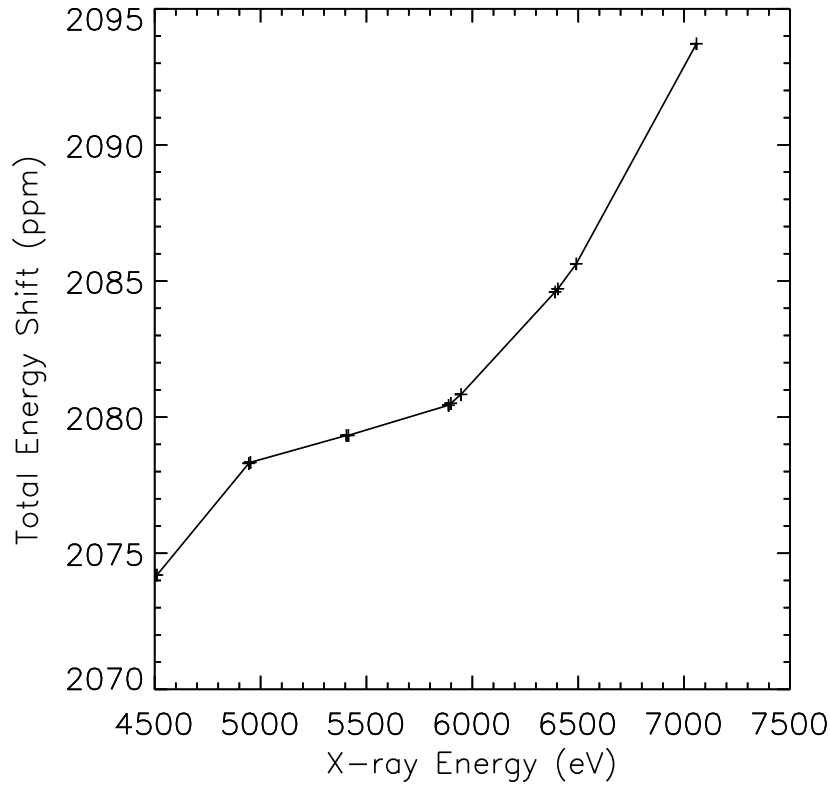


Figure 10.2: The total energy shift from Bragg's Law predicted by Mosplate. The shift was dominated by depth penetration of the wavefield. This figure is similar to Figure 3 in [81] but shows the magnitude of the shift as well as the general shape.

crystal angles. The second set was for defined crystal angles that covered the $K\beta$ lines of interest. For each crystal angle, a range of spectra were calculated for the ranges of wavelengths that covered the detector at those angles.

Some of the calculated spectra had a high spatial frequency oscillatory component that was due to some of the grid spacings in the calculations used to generate rays being too large for the grid spacing of the detector. This would result in a density of rays hitting the each bin of the detector that is not as representative of a continuity of rays as would be possible with finer grid spacings for ray generation. In order to uniformly remove this computational artefact, every spectrum was convolved with a top hat 100 channels wide, this width corresponding to a distance of less than 0.1 mm. The convolved intensity at the point x_i is denoted I_i . Figure 10.3 shows an example of a raw spectrum, together with the resulting convolved spectrum; the high frequency artefact is clearly removed.

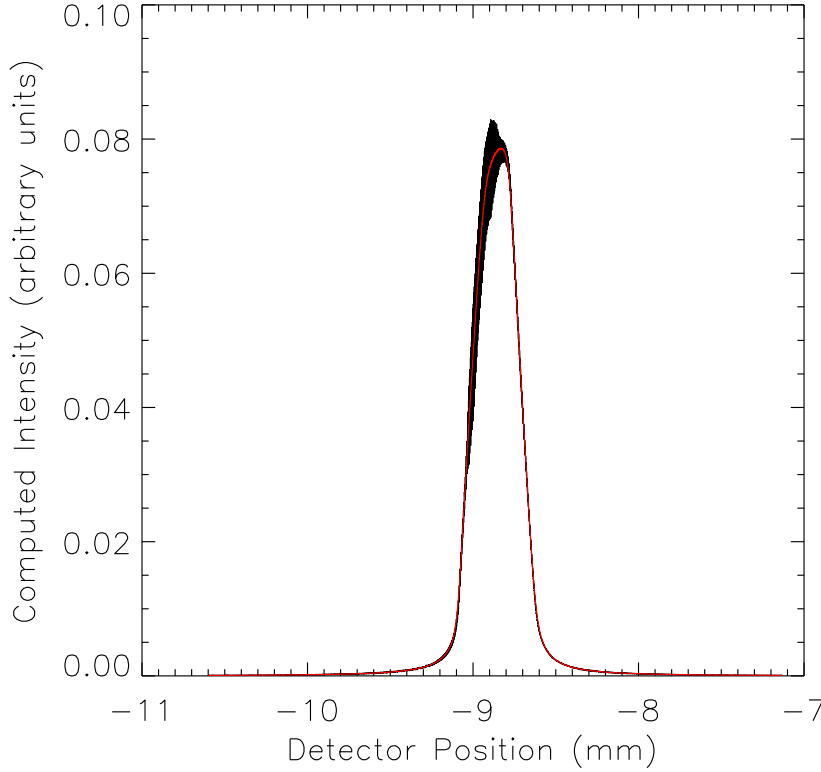


Figure 10.3: The spectrum calculated by Mosplate for the Cr $K\alpha_2$ wavelength at an crystal angle, θ , of 35.318958 degrees. The black line is the raw spectrum. It has a high spacial frequency component that is an artefact of the calculation. This artefact was eliminated with by convolving the raw spectrum with a top hat. The convolved spectrum is shown in red. The peak position, D , was calculated to be -8.8565178 mm for this spectrum.

For each spectrum calculated in both sets, a peak position, D , was then computed. D was defined to be an estimate of the a mean position of photons hitting the detector ignoring some of the tails:

$$D = \frac{\sum_{i=i_0}^{i_1} x_i I_i}{\sum_{i=i_0}^{i_1} I_i} \quad (10.1)$$

where i_0 and i_1 are defined such that $(x_{i_1} - x_{i_0})$ is maximised under the constraint that for every i between those limits, I_i is greater than 1% of the largest intensity.

These calculations of theoretical peak position sampled the Mosplate model function for the peak position D and profile as a function of peak energy E and crystal angle θ :

$$D = D_{mos}(E, \theta) \quad (10.2)$$

This model also implicitly defines functions that calculate E and θ from the remaining variables:

$$\theta = \theta_{mos}(D, E) \quad (10.3)$$

$$E = E_{mos}(D, \theta) \quad (10.4)$$

For computational implementation, Equation 10.3 was approximated by an interpolation between the calculated values in the first set of calculations, while Equation 10.2 was approximated by an interpolation between the calculated values in the second set of calculations. Interpolation uncertainty was negligible, being well below 1 ppm.

10.3.2 Line Curvature Removal

Mosplate's ray tracing is in two dimensions, as if the experiment exists in a two dimensional plane. Extruding the results of the calculation into the third dimension leads to a single energy of x-rays falling on a straight line on the detector. However, the directions of propagation of the photons in a real experiment are not restricted to a two dimensional plane. The main effect of the three dimensional nature of the experiment that is not modelled by Mosplate is that x-ray photons with a particular energy fall on the detector with some curvature instead of in a straight line. This is due to the fact that if the path of an x-ray hitting the cylindrically curved crystal is not perpendicular to the axis of rotational symmetry of the cylinder, the x-ray interacts with an arc of an ellipse instead of the arc of a circle. In particular, the radius of curvature of the arc with which it interacts will be larger. This causes curvature of the line in the direction perpendicular to the dispersive direction.

This effect must be addressed in order to make a link between any experimental data and the theory. Here, it was considered that the simplest method to address this effect was to remove the line curvature in the experimental data. A sequence of two detector maps were created to removed this curvature. The aim of the first map was to produce linearity in the y direction as far as possible. This is referred to here as the wire segment map. The aim of the second map was to then to remove line curvature. This was done by dividing the detector into rows, then finding a straight line map for each row that caused a set of $K\beta$ lines to be

straightened; this was a similar process to the one used to create spatial linearity in the detector. The creation of the two maps is now examined in detail.

The need for a wire segment map is demonstrated by looking at a typical example of a $K\beta$ line, as is shown in Figure 10.4. There is background intensity in a zigzag pattern in this figure. This zigzag pattern arises from the fact that the y value is proportional to the length along the anode wire, that the liberated charge cascade was collected. This length allows the identification of the wire segment giving a coarse measure of the y location of the x-ray event but, within a wire segment, the length is correlated to the x location. This causes a slope for each wire segment. Thus there is a changing non-linearity in the spatial response of the detector in the y direction with changing x . In order to characterise and remove the line curvature effect, this non-linearity first had to be removed as far as possible. Therefore a function was created that ensured the same non-linearity in y for each x location. This constituted the wire segment map.

The wire segment map was created by dealing with each wire segment separately. The first task was to programmatically extract bounding boxes for wire segments from the data shown in Figure 10.4. This six stage process was as follows. First, peak locations for each column of image were identified by fitting a sum of Lorentzians. Second, locations from each column belonging to the same wire segment were grouped by wire. Third, peak locations for each wire were fitted with a straight line. Fourth, missing wire segments were identified and a guess of the line for each of these segment was made. Fifth, intersections of the lines that represented adjacent segments were found. Sixth, wire segment bounding boxes were identified by assuming that the diagonal of each box was the corresponding line from intersection to intersection. The results of this process are shown in Figure 10.5. This process had to omit the top and bottom wire as the process could not identify the extreme ends of those wires segments through intersections of lines, as was required in stage six. Future work would benefit from the inclusion of data from those wire segments, with a modified process to identify the bounding boxes associated with those wire segments.

For each wire segment bounding box, consistent non-linearity in y was created treating 5 different regions of the box differently. The regions for one of the boxes along with their transformations are presented in Figure 10.6. Note that the transformation for each region did not change the x axis and was a linear function for each x value. The most important region for each wire, is the central region as

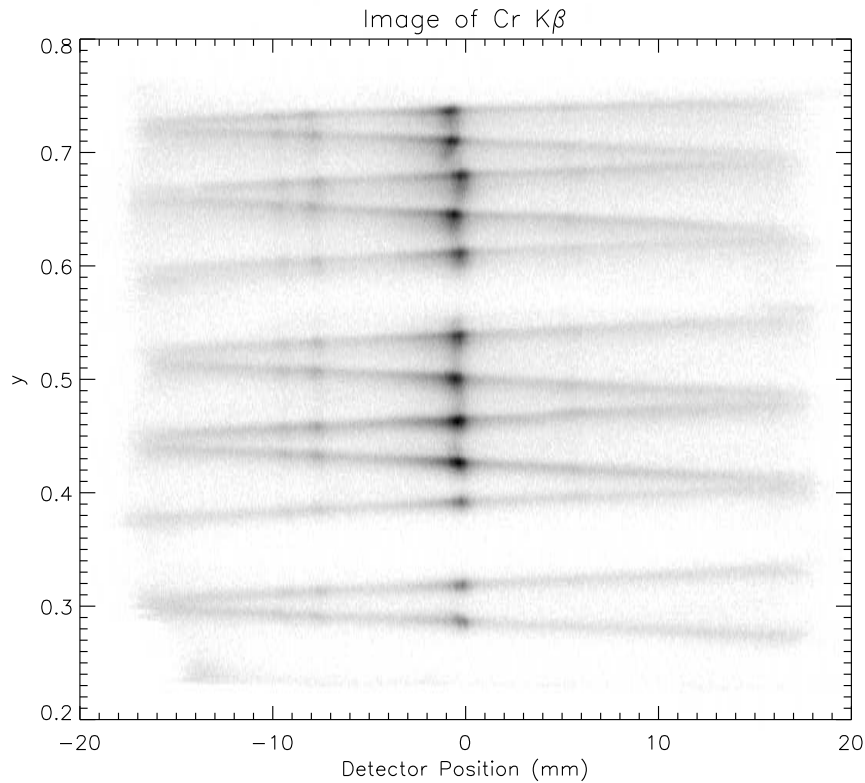


Figure 10.4: This image was used to identify the regions of the detector space that corresponded to the wire segments of the detector. It contains a large Cr $K\beta$ peak in the center, some Mn $K\alpha$ signal off to the left and a background signal. Twelve wire segment regions are clearly visible. This image is presented with the intensity of the black being proportional to the square root of the counts in the pixels, in order to bring out the background.

it contains almost all the data. The transformation for this region was found to be very well represented as a direct shear. The result of applying the wire segment map to a typical $K\beta$ line is shown in Figure 10.7. Note that the non-linearity in y seems to be highly reproducible across the detector, so the x-ray intensity response in each row (in the central region of x) is constant, enabling a fit of a row.

The second stage of removing the curvature of the lines was to find a mapping of the detector that produced a set of $K\beta$ lines that were straight. The line set used consisted of eight Ti $K\beta$ lines taken at relatively even positions on the face of the detector. The mapping was made with the following process. First, for each $K\beta$ line, the peak location for each row was found by taking the location parameter of a fit of that row with a Lorentzian plus a constant background. Second, the set of rows for which there were reasonable fits for all lines was found. Third, each line was given a corrected position, which was the weighted mean of the row

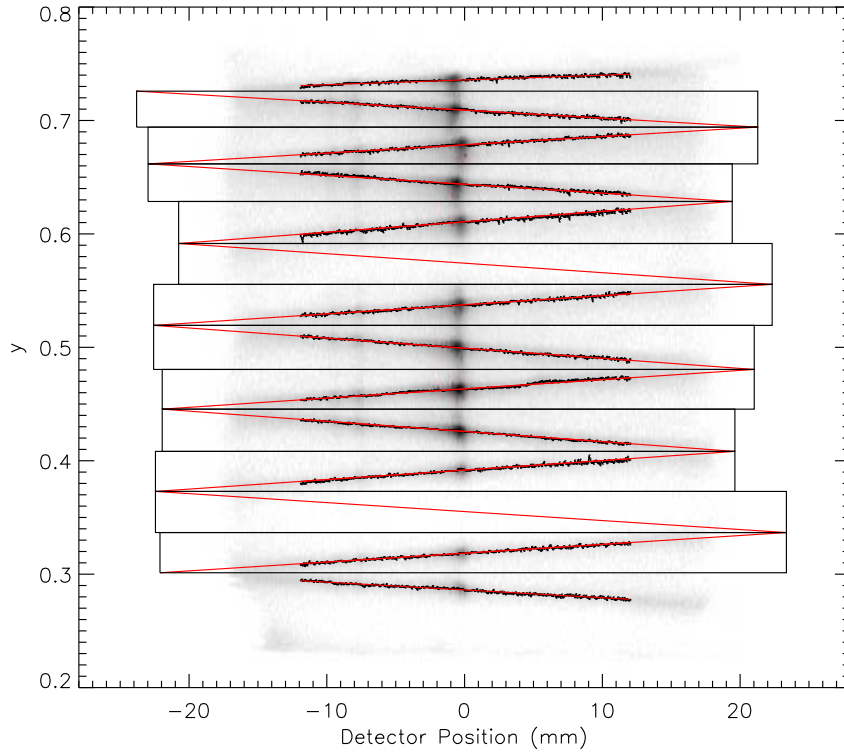


Figure 10.5: The wire bounding boxes created for use in the wire segment map. The image data is the same as that in Figure 10.4. The noisy black lines near the maximas of the wire signals are the peak locations for each column of the image. The red lines are fits of the peak locations and estimates for the two missing wire segments (located at about $0.34 < y < 0.37$ and $0.55 < y < 0.59$). The top and bottom wire segments do not have bounding boxes, thus data from these segments were filtered out by the wire segment map.

peak locations of the line taken from the rows generated in the second stage where $0.25 < y' < 0.5$ was also satisfied. An uncertainty for each corrected position was generated. Figure 10.8 shows the row peak locations for the eight lines, along with the corrected positions that were calculated. Fourth, for each row, a straight line fit was made from the row peak locations from all lines to the corrected positions of all lines. A typical fit is shown in Figure 10.9. This set of fits, one for each row, defined the line curvature correction map. Figure 10.10 presents the results of the curvature correction map.

To link the three dimensional experiment to the two dimensional Mosplate calculations, the raw (x, y) data points were taken through the three maps in sequence to end up in with the corrected position of each data point. The corrected positions raw data were put through the linearity calibration map then the wire segment

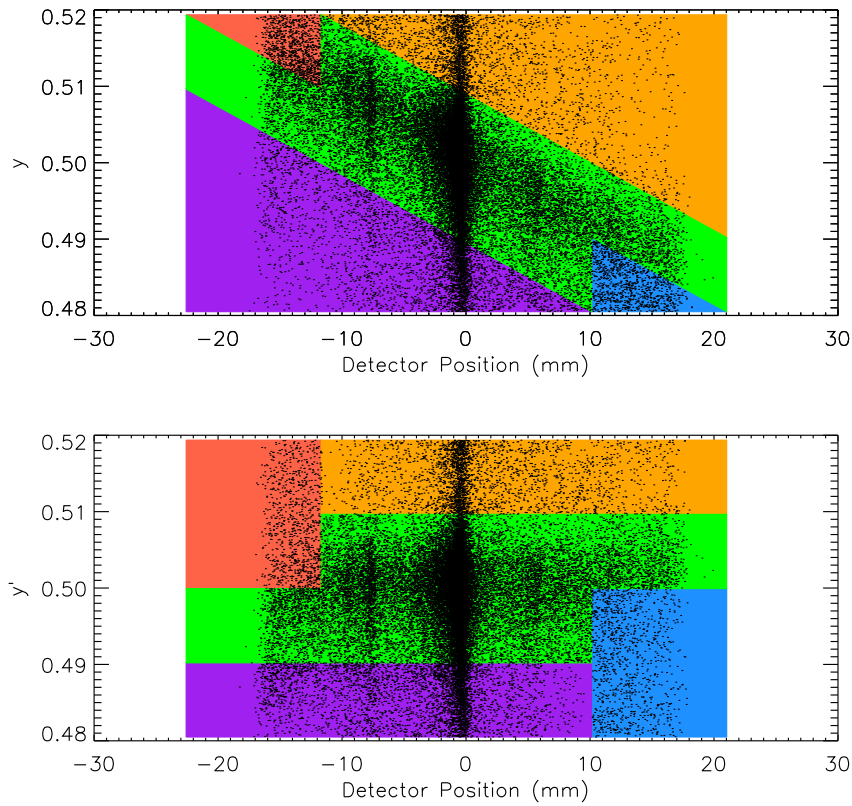


Figure 10.6: The wire bounding boxes regions (top) and their transformations (bottom) used as part of the wire segment map. The black data points are a random sample of the data represented in Figure 10.4 to show how the wire segment map applies to real data. Each region has a different color. The region in the upper figure maps onto the corresponding region in the lower figure.

map, and then the curvature correction map. They were then binned on the energy dispersive axis of the detector, leading to a reduction of a two dimensional detector to the one dimensional detector of Mosplate. The resulting histogram is labelled the detector profile.

10.3.3 $K\alpha$ Profile Modelling

Using characterisations of $K\alpha$ lines as standards in this experiment meant modelling the measured detector profiles of these lines with mathematical functions derived from the literature. Some such measured profiles were found to be affected by vignetting. Hence a method to identify and deal with those profiles was developed by the present author, and this is outlined below.

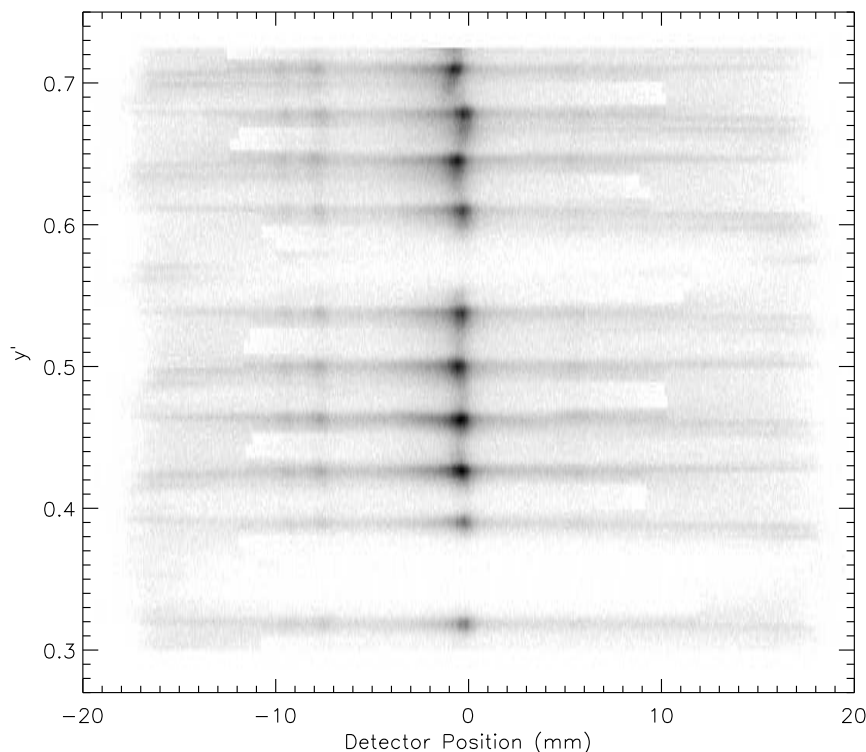


Figure 10.7: This shows the results of the wire segment map having been applied to the data in Figure 10.4. The map transforms y into y' . As demonstrated in this figure, wire segments were largely flattened by the map.

10.3.3.1 $K\alpha$ Profile Models Used

$K\alpha$ profiles of the elements with $Z=22$ to 26 were collected. For $Z=22$ to 25, $K\alpha$ profiles were fitted as functions of energy as defined by Chantler et al. [86]. Each of these functions is a sum of six Voigt profiles with a common Gaussian width to model the instrumental broadening, and maps x-ray energy to x-ray intensity. The energy offsets, Lorentzian widths, and relative amplitudes of the Voigt profiles were defined by Chantler et al. [86]. For the $Z=26$ Fe $K\alpha$ profiles, the same type of data for a sum of Voigt profiles were given by [79]. Each of the $K\alpha$ detector profiles were measured on the detector position axis rather than directly on an energy axis. Therefore, the profiles were refined by fitting five parameters: (i) a detector scale that represented the energy difference per detector position difference across the detector, (ii) a detector offset to map the a mean energy of the profile to a detector position, (iii) an intensity scale to model the overall intensity of the profile, (iv) a constant intensity background, and (v) a common Gaussian broadening width.

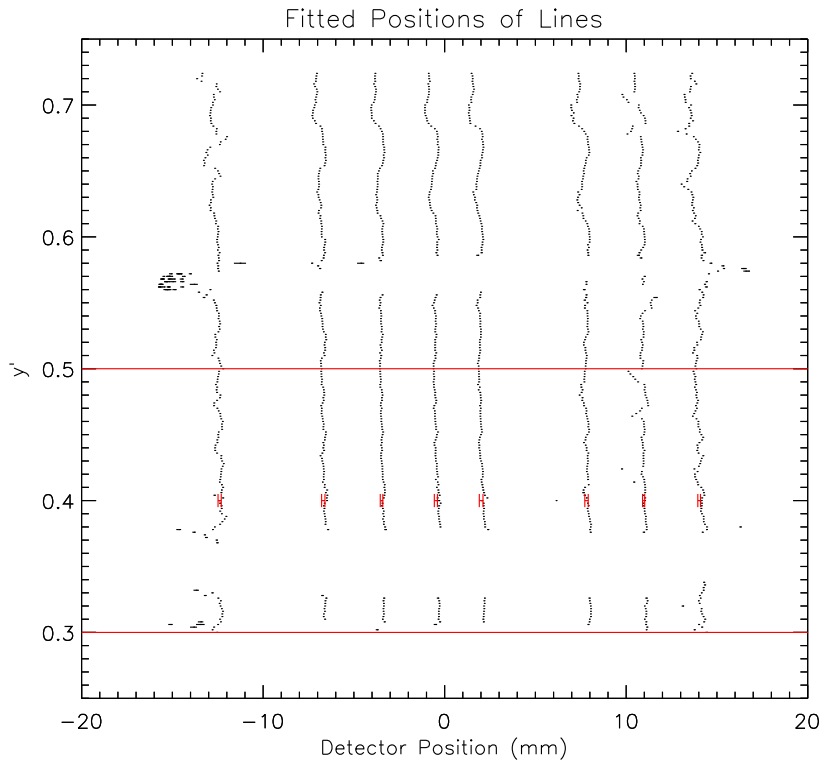


Figure 10.8: Peak locations for the Ti $K\beta$ lines used for the curvature correction map along with the corrected positions for each line in red. The two horizontal red lines show the limits of the data that was averaged to create each corrected position. The main curvature that appears in this data is due to the fact that the detector's cathode board axis (the detector position), was misaligned to the energy dispersive axis of the spectrometer, creating a slight slant to the data. There appears to be additional non-linearity in the spacial response of the detector above about $y' = 0.6$ (a 'wobble' in the lines) that could be due to a change in the characteristics of the wire segments in this region of the detector.

10.3.3.2 Vignetting

Some of the $K\alpha$ spectra were affected by vignetting (Figure 10.11). When vignetting occurred, it affected either the peak $K\alpha_1$ or the $K\alpha_2$ peak by reducing the intensity of one peak or the other. Vignetting was automatically detected by comparing the values of two functionals of the observed spectrum with those values of the functionals of the fitted function. The two functionals were (i) the ratio of peak areas, and (ii) the skewness (a technical term defined below). For each functional, the comparison measure used to identify vignetting was the ratio of the functional of the observed spectrum to the functional of the fitted function.

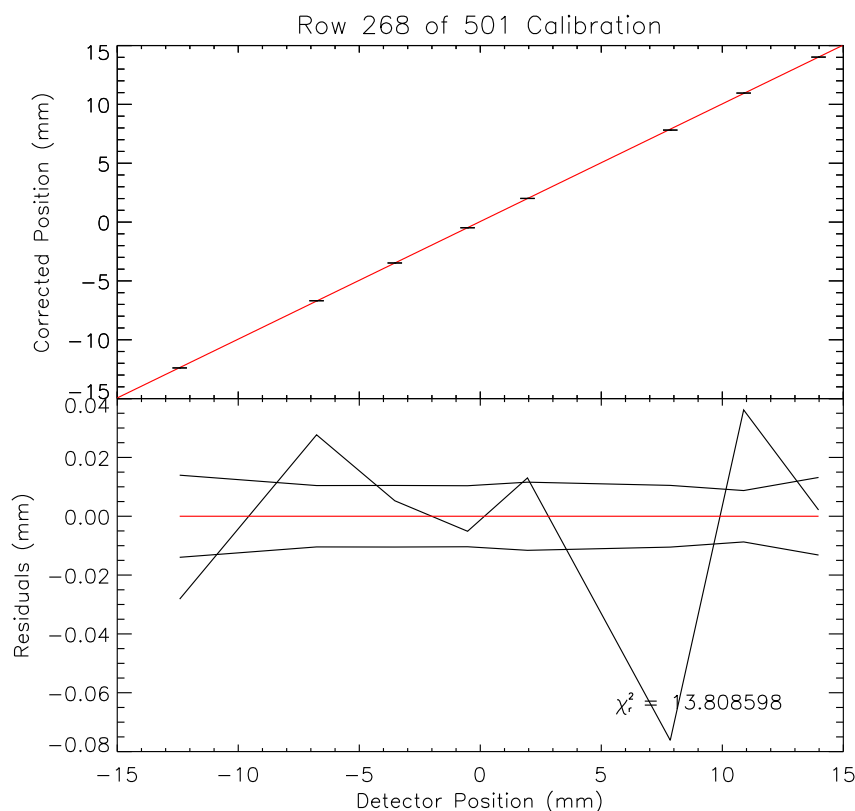


Figure 10.9: Straight line fit that maps a set of Ti $K\beta$ centroids within a row to average positions for the lines. This row is typical for the curvature correction map.

To calculate the ratio of peak areas, the area of each peak had to be identified. This required a consistent definition of the area of each peak in terms of the background level, the shared limit of each peak in between the peaks and the outer limits of the peaks. The background level was identified as the fitted background from the spectrum and it was thus subtracted from the spectrum. The shared limit that divided the peaks was defined as the halfway point of the two highest local maxima in the spectrum (the peak positions). The outer limit of each peak was defined to be a distance of the half width half maximum away from the peak position, in the direction opposite to the shared limit. The area of each peak was then calculated as the sum of the counts in the defined peaks.

The skewness was calculated on the spectrum minus the fitted background within some limits. If this histogram data is represented as n bins the i^{th} bin having

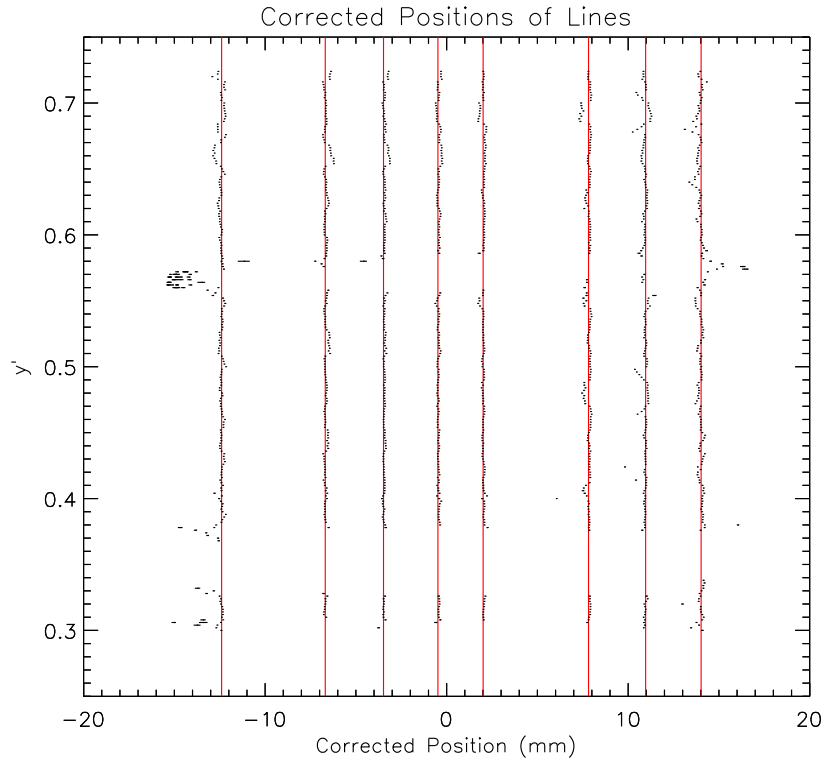


Figure 10.10: This figure shows the effect of the curvature correction map on the peak locations of the Ti K β lines shown in Figure 10.8. The red lines show the corrected positions of those lines. The map handles the lines within -11 mm and 11 mm as the lines outside this region are significantly distorted.

location x_i with h_i counts, then skewness, g_1 , was defined [279] as

$$g_1 = \frac{\sum_{i=1}^n h_i (x_i - \mu)^3}{\left[\sum_{i=1}^n h_i (x_i - \mu)^2 \right]^{3/2}} \quad (10.5)$$

where the mean location, μ , is

$$\mu = \frac{\sum_{i=1}^n h_i x_i}{\sum_{i=1}^n h_i} \quad (10.6)$$

The background subtracted spectrum was limited from both directions at the point at which its height crossed a quarter of the maximum height.

These measures are sensitive to a reduction in the intensity of one or other of

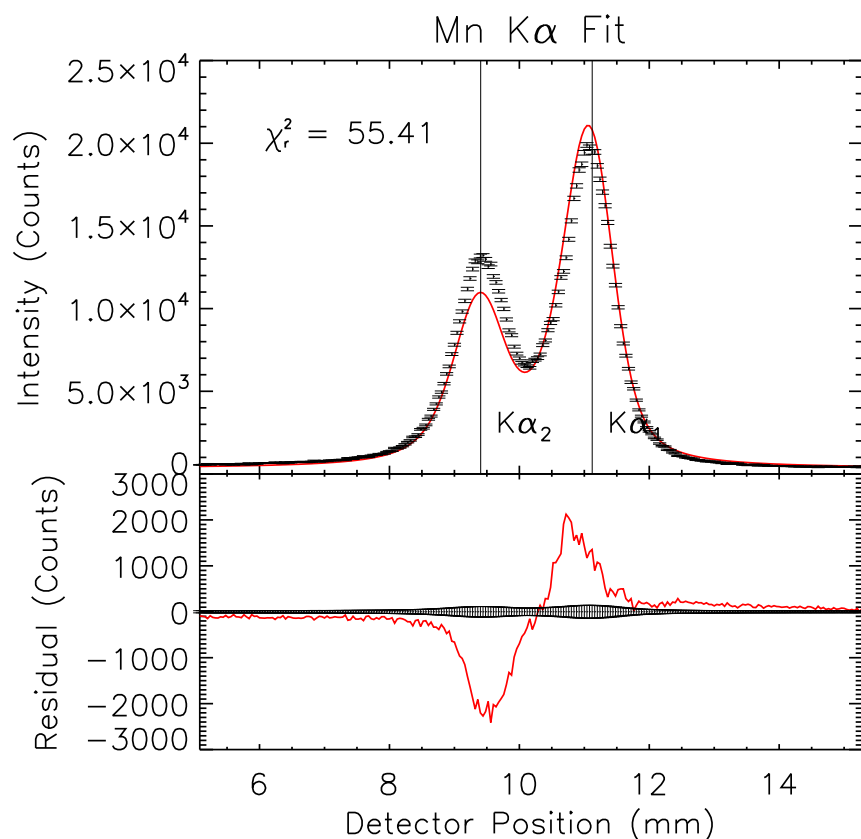


Figure 10.11: A vignettted Mn $K\alpha$ spectrum. The measured spectrum is shown in black while the best fit id in red. $K\alpha_1$ was vignettted in this spectrum as it was at the edge of the bandpass of the spectrometer at this detector arm angle. The area ratio comparison measure was 1.31, indicating that the ratio of peak areas of the fit was greater than that of the data. The skewness comparison measure was 1.61, indicating that the skewness of the fit was greater than that of the data. Both these measures indicate that $K\alpha_1$ was vignettted as expected.

the peaks of the observed spectrum in comparison to the characterisations from the literature. If the fitted function was a good model for the observed spectrum, the ratios of each of the functionals should be around one. Various limits for the classification of vignettted spectra were examined; making the limits too narrow, combined with noise in the measure would produce false positives for vignetting. By inspection, a good criterion for the identification of vignetting was an area ratio comparison measure below 0.92 or above 1.08, or the skewness comparison measure below 0.92 or above 1.10. Note that since each comparison measure is a ratio of functionals of the observed spectrum to the fitted function, a comparison measure of 1 would indicate that the functionals of observed spectrum and the fitted function are equal. This would mean they had the same peak area ratios or skewness.

For each spectrum that was affected by vignetting, an independent refit was done on a part of the profile that was not affected by vignetting. The initial guess parameters for the refit were taken from previous fitted parameters. The part of the profile that was refitted was the unvignetted peak, while the peak affected by vignetting was discarded. The dividing limit between the peaks was taken to be the position the minimum intensity between the two peaks, assuming an instrumental broadening of 0. This was estimated from the whole spectrum fit function, modified by setting the Gaussian broadening width to 0. This process produced a subset of $K\alpha$ profile fits that were unaffected by vignetting.

10.3.3.3 $K\alpha$ Radiation Lines as Standards for Spectrometer Calibration

These fits of highly accurate $K\alpha$ characterisations to unvignetted detector profiles allowed the assignment of $K\alpha_1$ and/or $K\alpha_2$ peak energies to the detector positions of each measured profile. Since each profile also had a different detector arm angle and thus clinometer voltage, each peak position and energy derived from a $K\alpha$ profile defined a calibration point. Figures 10.12, 10.13 and 10.14 below illustrate how three fits of three different $K\alpha$ lines led to six calibration points. The residuals show a small structure which is well-centred on the main component peaks and which contains noise within one standard deviation.

Two separate rounds of $K\alpha$ fitting were performed that led to spectrometer calibrations used in certain published papers. In the first round, the fits were of a narrow range of the measured $K\alpha$ spectra. These narrow fits cut off the tails of the spectra and were employed to produce the calibration that was used in the measurement of V $K\beta$ reported in Smale et al. [80]. An example fit from this round can be seen in Figure 10.12. In the second round, the range of the fits was improved to include a much larger part of the tails of the $K\alpha$ spectra. An example fit from this round can be seen in Figures 10.13 and 10.14. This round of fitting was used to produce the calibrations used in a redefinition of the V $K\beta$ profile and a measurement of Ti $K\beta$ in Chantler et al. [81], as well as the examination of calibration methodology in Smale et al. [280].

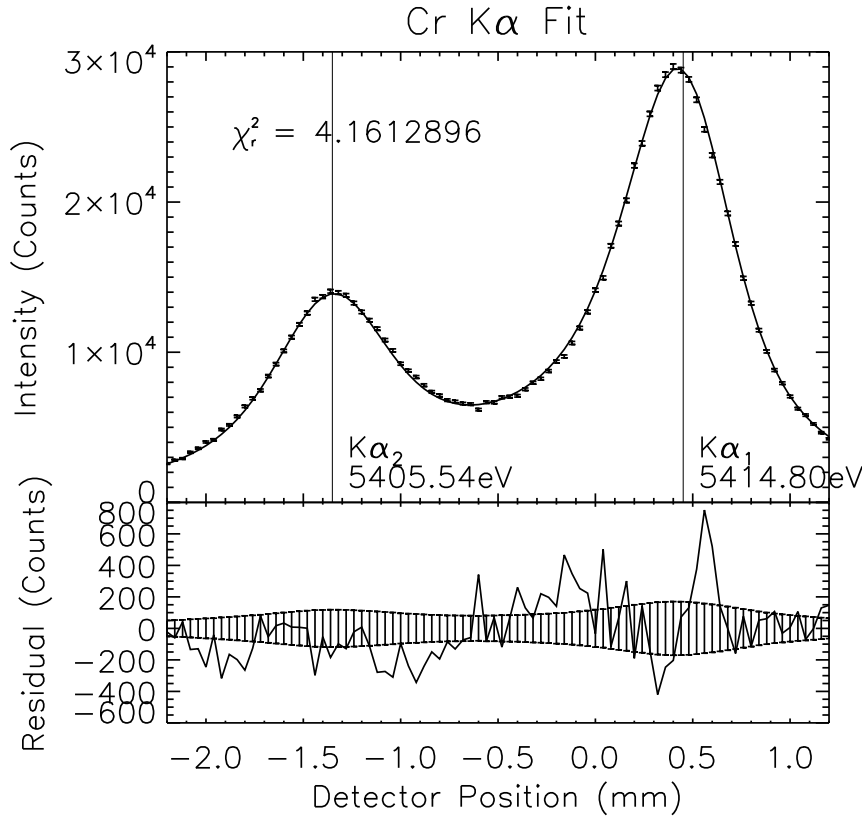


Figure 10.12: Typical fit of Cr $K\alpha$ spectrum, yielding two calibration points (Cr $K\alpha_1$ and Cr $K\alpha_2$), constraining the spectrometer dispersion (calibration) function. The fit has a χ^2_r of 4.2. The $K\alpha_1$ peak has an energy 5414.8045(71) eV and Detector Position 0.4510(12) mm. The $K\alpha_2$ peak has an energy 5405.5384(71) eV and Detector Position -1.3507(21) mm. The Crystal Clinometer voltage was -1.705582(11) V.

10.3.4 Spectrometer Calibration Functions

The aim was to link the Mosplate theory data to the experimental calibration data. These links were obtained from the spectrometer calibration functions.

Two spectrometer calibration functions were required to map the dispersion function $E_{mos}(D, \theta)$ and detector profile to an absolute energy axis. The clinometer calibration function, $I(V; P_I)$, maps the clinometer voltage V to the offset clinometer angle I . For CC, I was related the dispersion crystal angle, θ , by $\theta = -I$ while for DL and DU, the relationship was $\theta = -I/2$. Thus, according to Equations 5.2 and 5.3, for a particular clinometer, I was related to the calibrated clinometer angle γ by an offset that included the small source arm offset angle, ϕ , and the angular offset caused by the clinometer mount.

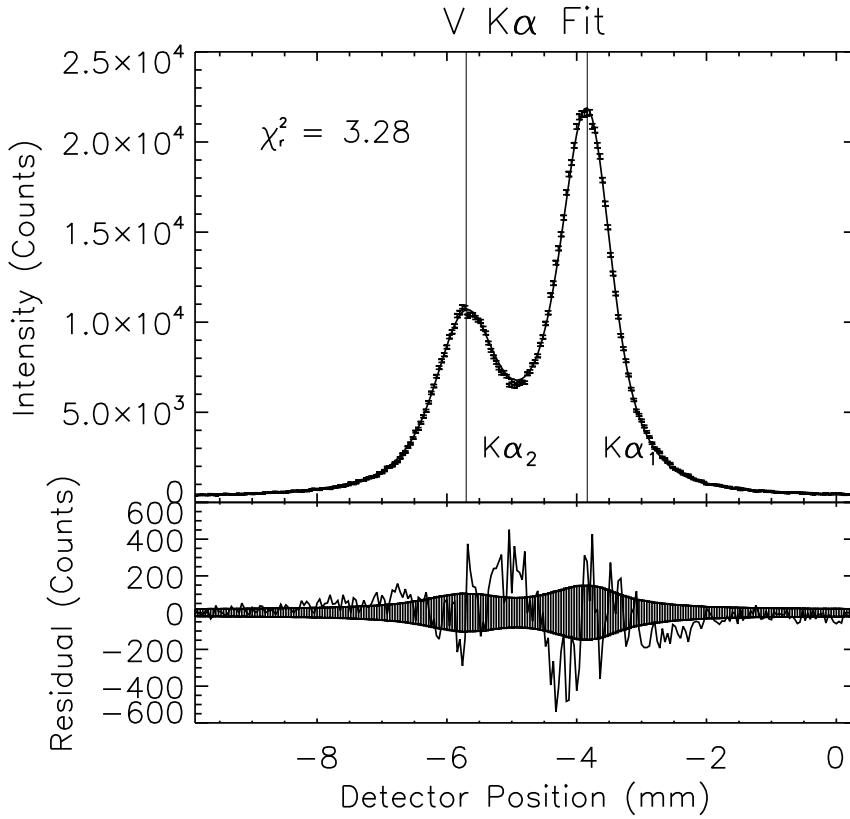


Figure 10.13: Typical fit of V $K\alpha$ spectrum using only five scaling parameters, yielding two calibration points (V $K\alpha_1$ and V $K\alpha_2$ which constrain the spectrometer dispersion function). The fit has a χ_r^2 of 3.28. The $K\alpha_1$ peak has an energy 4952.131(6) eV and Detector Position -3.8157(14) mm. The $K\alpha_2$ peak has an energy 4944.651(11) eV and Detector Position -5.6973(26) mm. The Crystal Clinometer voltage was -1.0749865(99) V.

The clinometer calibration function $I(V; P_I)$, that models the offset clinometer angle I , is defined to be:

$$I(V; P_I) = \arcsin\left(\frac{V - P_{I,2}}{P_{I,0}}\right) - P_{I,1} + \sum_{i=0}^n P_{I,(i+3)}(V - P_{I,2})^i \quad (10.7)$$

where P_I is the vector of fitting parameters and n is the degree of the polynomial represented by the third term of the equation.

A second calibration function, the detector dispersion calibration function $D_2(x; P_D)$, was considered to map the recorded detector profile position x in mm to the theoretical detector position D in mm. The map from x to D was defined by:

$$D_2(x; P_D) = \sum_{i=0}^1 P_{D,i} x^i \quad (10.8)$$

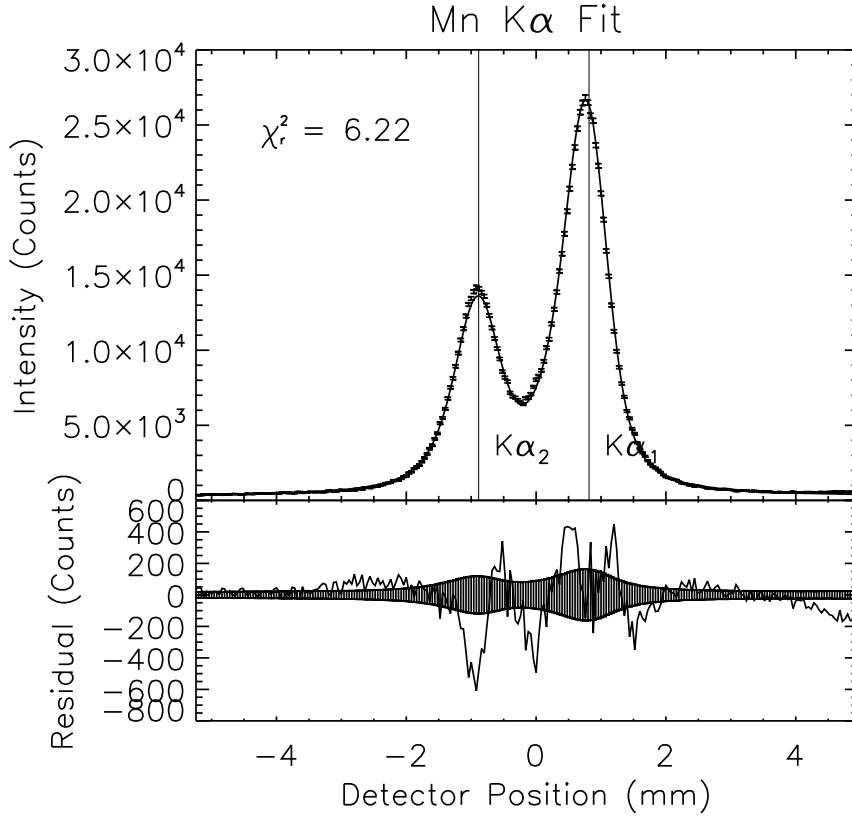


Figure 10.14: Typical fit of Mn $K\alpha$ spectrum, yielding two calibration points (Mn $K\alpha_1$ and Mn $K\alpha_2$) which constrain the spectrometer dispersion function. This particular fit has a χ_r^2 of 6.2. The $K\alpha_1$ peak has an energy of 5898.8010(84) eV and Detector Position of 0.8154(16) mm. The $K\alpha_2$ peak has an energy of 5887.6859(84) eV and Detector Position of -0.8850(25) mm. The Crystal Clinometer voltage was -2.2499502(79) V.

where P_D is the vector of fitting parameters. This linear function takes account of the shift introduced by the curvature correction map and any misalignment of the detector with the energy dispersive axis of the spectrometer.

Using this calibration, an energy can be assigned for any detector position x and any clinometer voltage V :

$$E(x, V; P_D, P_I) = E_{mos}(D_2(x; P_D), -I(V; P_I)) \quad (10.9)$$

Since Equations 10.2, 10.3 and 10.4 were only calculated for a wedge position of 16.40 mm, a limitation in the form of a known systematic error in the theoretical modelling for the calibration of the data series with another wedge position was introduced. It is assumed that this systematic error can be compensated for, to

the first order, by the fitting parameters P_I and P_D of Equations 10.7 and 10.8, provided there is a separate calibration fitting for each experimental configuration with a different wedge position. This assumption is supported by the flexibility of the polynomial part of Equation 10.7. Thus, with the above mentioned limitation in the set of theoretical calculations involved in the modelling, it was expected that each wedge position would produce a different set of fitting parameters, compensating for this limitation. This would produce separate and reasonable calibration functions for each wedge position.

10.3.5 The Use of a Dispersion Function

Equations 10.7 and 10.8 define the calibration of an experimental configuration. The calibration determination process was reduced to simultaneously finding the P_I and P_D fitting parameters that best fitted the $K\alpha$ data generated by the methods of Section 10.3.3, possibly combined with a minimization of the variance of another interesting line's measured peak energy at the same time (in this experiment: Ti $K\beta$, V $K\beta$ or Cr $K\beta$). This process optimised the statistical information for the determination of a $K\beta$ profile peak energy and the dispersion function.

Evidence of the $K\beta$ data was used to define a minimum-variance solution for parametrization of the dispersion function. In one sense, this is a variant of a least-squares hypothesis, used widely in all statistical fitting, but here it was used to directly assess the variance of the final measured energies.

10.3.6 Calibration Function Fitting With $K\alpha$ Peak Data

As an initial pass at finding good values for P_I and P_D , those values were optimised using only the $K\alpha$ peak data as found in Section 10.3.3.3, combined with the corresponding $K\alpha$ peak locations found by the methods of Section 10.3.3. The fitting parameters P_I and P_D for each calibration were determined following two steps of refinement, these being the clinometer calibration first estimate and then the six stage calibration fitting.

First, then, an estimate of the clinometer voltage to angle calibration function was constructed by generating data with the use of the angle to voltage calibration function (Equation 9.3), inverting those data, and then fitting those inverted data

(γ versus V) with $I(V; P_I)$ (Equation 10.7), where the order of the polynomial was set to $n = 3$. The fit was good for the clinometer mounted on the crystal mount holder (CC). Thus, the process continued using this clinometer only. It is noted here that including data from the other three clinometers would enable the investigation of systematic errors such as spectrometer base movement with arm position. A method to incorporate these data should be developed and investigated in future work, in order to reduce or eliminate any such systematics. At the end of this step, there was a fit of how the crystal clinometer functioned in the calibration experiment, as represented by the P_I fitting parameters.

In the second step of refinement, calibration fitting proceeded with a six stage process, beginning with P_I from the first step and an estimate of P_D . Each stage made a refinement of either P_I or P_D through one round of fitting.

The first stage of the calibration fitting was to fit the $I(V; P_I)$ function to I_{data} versus V , where I_{data} is a set of calculated data predicting the expected offset clinometer angle for each peak based on the energy and detector position:

$$I_{data} = -\theta_{mos}(D(x, P_D), E) \quad (10.10)$$

It has uncertainty ΔI_{data} :

$$\Delta I_{data}^2 = \left(\frac{\partial \theta_{mos}}{\partial E} \Delta E \right)^2 + \left(\frac{\partial \theta_{mos}}{\partial D} \right)^2 \left[\sum_{ij} \frac{\partial D}{\partial P_{D,i}} \frac{\partial D}{\partial P_{D,j}} C_{D,ij} + \left(\frac{\partial D}{\partial x} \Delta x \right)^2 \right] \quad (10.11)$$

This first fit only allowed the refinement of $P_{I,1}$, the overall angle offset to $I(V; P_I)$. It should be noted that the polynomial order of $I(V; P_I)$ was increased from $n = 3$ to $n = 4$ at this stage, thus adding one element, $P_{I,7}$ (which was set to zero), to P_I . This offset estimates the offset implied by Equation 5.2.

The second stage of the calibration fitting was a refit of I_{data} versus V with $I(V; P_I)$ using the P_I from fit 1 as a estimate, this time only allowing the refinement of $P_{I,4}$ through $P_{I,7}$, fitting the fine details and secondary functional parameters of $I(V; P_I)$.

The third stage was to fit $D(x; P_D)$ to D_{data} versus x where D_{data} is a set of calculated data that provides the expected theoretical detector position for each

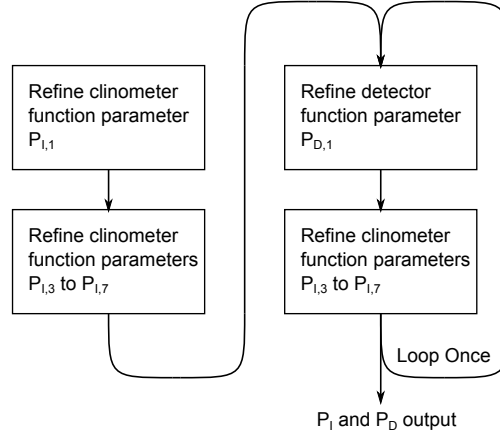


Figure 10.15: Schematic of calibration fitting stages. Each stage is a round of refitting.

peak based on the energy and crystal angle:

$$D_{data} = D_{mos}(E, -I(V; P_I)) \quad (10.12)$$

It has uncertainty ΔD_{data} :

$$\Delta D_{data}^2 = \left(\frac{\partial D_{mos}}{\partial E} \Delta E \right)^2 + \left(\frac{\partial D_{mos}}{\partial \theta} \right)^2 \left[\sum_{ij} \frac{\partial I}{\partial P_{I,i}} \frac{\partial I}{\partial P_{I,j}} C_{I,ij} + \left(\frac{\partial I}{\partial V} \Delta V \right)^2 \right] \quad (10.13)$$

Both P_D parameters were free in this fit.

In the fourth stage of the calibration fitting, results from the third stage were then used to refit I_{data} versus V using $I(V; P_I)$, allowing the refinement of $P_{I,4}$ through $P_{I,7}$, as in the second fit.

The last two stages were a repeat of the third and fourth stages, using results from the fourth stage as input to the fifth stage. This method generated the P_I and P_D parameters, along with associated covariance error matrices C_I from the sixth fit and C_D from the fifth fit.

These six stages of this third step are diagrammed in Figure 10.15.

At the end of this six stage step, the fitted P_I parameters characterised how the clinometers functioned in the setup. To sum up, the interlinked $K\alpha$ peak energy, peak position, and clinometer voltage data were used to refine the calibration of the spectrometer via a sequence of optimisations.

10.3.7 Calibration Function Refitting With $K\alpha$ and $K\beta$ Peak Data

A second pass at finding good spectrometer calibrations took account of the consistency of the $K\beta$ peak energies that those calibrations produced. A second pass was necessary as there was a systematic error in the first calibration pass conducted. This systematic error appeared as a slope in the energy vs angle plots for the $K\beta$ peak energies. The slope depended on which $K\beta$ line (or range of detector arm angles) was examined. The slope was negative for high arm angles, positive for low arm angles, and was monotonically changing with detector arm angle in between. One possible cause of this error was the possibility that the angle of the detector arm may influence the source arm offset angle, ϕ , as the detector arm is very heavy. See Figure 5.5 for the physical arrangement when the arm had a 2θ angle of about 90 degrees. Small changes in detector arm angle from this position would not affect the physical configuration of the base very much. However this weight would have more effect for smaller detector arm angles, with the same changes in angle leading to larger changes in ϕ . The relationship between detector arm angle and position on the detector of a particular energy should be almost linear for a small range of detector arm angles with the same constant of proportionality for all energies. However, if the weight of the detector arm affects the angle of the base, and affects it at an increasing rate as the detector arm angle decreases, this would cause the constant of proportionality to change with energy. Since the calibration analysis assumed a constant of proportionality that does not change with energy, this effect would appear as the calibrated energy vs angle curve for a single real energy (which should be constant) having a slope that depends on arm angle. The size of the systematic error found could be partially controlled locally for one energy by varying the detector scale ($P_{D,1}$) according to some optimisation criteria.

A key question on robustness of calibration fitting was whether the optimisation criteria selected could distort the analysis, variance and result. If robust and consistent, the optimised result should minimise variance and preserve a consistent peak energy determination. Hence, the present author investigated the self-consistency of a series of alternate optimisations, minimising five different measures of the quality of the calibration fitting. Optimisation of each measure was a three step process: (1) for a range of detector scales, there was a fit of I_{data}

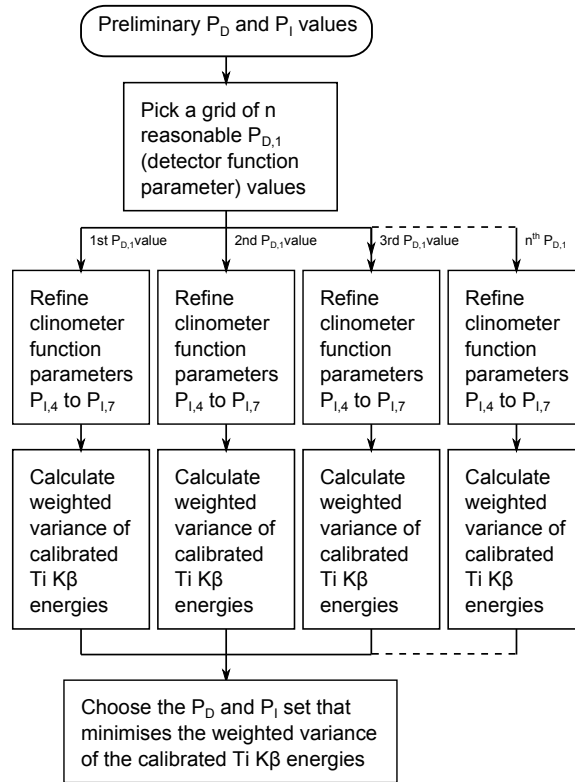


Figure 10.16: Schematic of the refitting process.

versus V using the $K\alpha$ lines, which refined the clinometer calibration function in the context of that detector scale; (2) for each detector scale, a calculation of the measure to be minimised was made; and (3) the detector scale and clinometer calibration function that minimised the measure was then selected. This process constituted a grid search for the detector scale ($P_{D,1}$) and calibration fit that produced the minimum value of the measure. For clarity, Figure 10.16 shows a schematic summary of the refinement process.

The five optimisations minimised the following measures for each of the seven series of characteristic radiation data:

- (a) The χ_r^2 value of the Ti $K\beta$ peak energy measurements.
- (b) The sum of two values - (1) the χ_r^2 value of the Ti $K\beta$ peak energy measurements, and (2) the χ_r^2 value of the V $K\beta$ peak energy measurements.
- (c) The χ_r^2 value of the V $K\beta$ peak energy measurements.
- (d) The sum of four values - (1) the χ_r^2 value of the Ti $K\beta$ peak energy measurements, (2) the χ_r^2 value of the V $K\beta$ peak energy measurements, (3) the χ_r^2

value of the Cr $K\beta$ peak energy measurements, and (4) the χ_r^2 value of the clinometer calibration function fit which is a measure of the spread of the $K\alpha$ data around the literature values.

(e) The χ_r^2 value of the Cr $K\beta$ peak energy measurements.

For each $K\beta$ line, it was to be expected that the uncertainty in the region of interest is minimised by optimising the measure most closely associated with that line. Note that optimisation using measures (a), (c), and (e) only locally minimises the systematic error, evident as a slope in the $K\beta$ energy versus detector arm angle graph, around each of the $K\beta$ detector arm angles. In other words, for other energies, the slope systematic would be visible.

10.4 $K\beta$ and EBIT Cr Profile Modelling Function

As well as the standard reference calibration $K\alpha$ spectra, $K\beta$ spectra and a EBIT Cr spectrum were also collected. These spectra were put into detector profile form and then fitted with line shape functions.

To define characteristic $K\beta$ line shape functions, each of the $K\beta$ detector profiles were fitted using a sum of four Voigt functions with a common Gaussian width, σ , with a constant intensity background, B . Past literature, such as [79], has often used a sum of a small number of Lorentzians or Gaussians. Though these components do not represent component (diagram and satellite) transitions directly, they can adequately represent the sum of these transitions. Profile decomposition can be made in principle with arbitrary functions. However, it is preferred that each component, even if semi-empirical in nature, should have a broadening representative of a real diagram line. The number of components is partially limited, or fixed, by the information content.

The i^{th} Voigt function in the sum of four functions used to characterize a $K\beta$ line was defined to be:

$$V(x; A_i, C_i, W_i, \sigma_i) = A_i \int_{-\infty}^{\infty} \left(\frac{e^{-x'^2/(2\sigma_i^2)}}{\sigma_i \sqrt{2\pi}} \right) \frac{W_i/2}{\pi[(x - C_i - x')^2 + (W_i/2)^2]} dx' \quad (10.14)$$

where A_i is the integrated area of the Lorentzian profile, C_i is the centroid of the profile, W_i is the Lorentzian Full Width at Half Maximum (FWHM) and σ_i is the Gaussian broadening standard deviation. The Gaussian broadening FWHM is $2\sqrt{2\ln 2}\sigma_i \approx 2.35\sigma_i$. Thus the spectra containing a $K\beta$ spectral profile was modelled with:

$$\begin{aligned} P(x; b, \sigma, A_1, A_2, \dots, A_n, C_1, C_2, \dots, C_n, W_1, W_2, \dots, W_n) \\ = B + \sum_{i=1}^n V(x; A_i, C_i, W_i, \sigma_i = \sigma) \end{aligned} \quad (10.15)$$

where n is the number of Voigt components. This function (with n equals 4) was found to capture enough of the structure of the $K\beta$ lines to be useful.

Equation 10.15 was also used to model the EBIT Cr spectral profile. Since it had six peaks, n was set to six for this spectrum.

10.5 Energy Uncertainties for a Single Spectrum

For the peaks the $K\beta$ detector profiles, and the peaks in the EBIT Cr detector profile, a peak location was calculated. Since each peak had an associated clinometer voltage, each clinometer voltage and peak location pair was converted to a peak energy using Equation 10.9. Following this equation, the uncertainty in the energy assigned to a detector position measurement, ΔE , was due to four sources of uncertainty: (i) the statistical precision of the determination of the peak of the spectral fit (Δx_{fit}), (ii) the uncertainty due to the detector dispersion fit, (iii) the noise in clinometer voltage (ΔV), and (iv) the clinometer calibration function fitting uncertainties. The following equation for ΔE is a sum of the four terms representing these uncertainty components:

$$\Delta E^2 = \left(\frac{\partial E}{\partial x} \Delta x_{fit} \right)^2 + \sum_{ij} \frac{\partial E}{\partial P_{D,i}} \frac{\partial E}{\partial P_{D,j}} C_{D,ij} + \left(\frac{\partial E}{\partial V} \Delta V \right)^2 + \sum_{ij} \frac{\partial E}{\partial P_{I,i}} \frac{\partial E}{\partial P_{I,j}} C_{I,ij} \quad (10.16)$$

where $C_{D,ij}$ is the i,j^{th} element of the covariance error matrix from the detector dispersion function fit. Likewise, $C_{I,ij}$ is the i,j^{th} element of the covariance error matrix from the clinometer calibration function fit.

The clinometer calibration function covariance included all uncertainties from the clinometer fitting. These include clinometer non-linearity, $K\alpha$ peak position uncertainty due to fitting and diffraction theory uncertainty. While the $K\alpha$ peak position uncertainties are as detailed in Table 2.1 in Chapter 2 above, the uncertainties of the refractive index correction and temperature variation were approximately 1 ppm. Indeed, any temperature uncertainty primarily cancelled in the modelling. The impact of uncertainty of the source position upon the diffraction computations was almost negligible. Further, the correlated uncertainty of more complex diffraction estimates cancelled to first order.

The effect of systematic errors within a single spectrum peak energy measurement caused by deficiencies in calibration analysis must be approached in different ways for $K\beta$ lines and the EBIT Cr spectrum. This is because the $K\beta$ lines were measured a number of times in different circumstances while the EBIT spectrum was measured once.

10.6 $K\beta$ Energy Uncertainty Estimation

Since each $K\beta$ profile type was measured a number of times at different positions of the detector with a number of calibrations based on different calibration runs, there were many measurements of peak energy. To estimate the uncertainty of a peak energy, firstly, the calibrated energy and energy uncertainty of each single spectrum was calculated using Equation 10.16. Secondly, these values were combined.

10.6.1 Combining Single Spectrum Energy Measurements

It was expected that systematic errors within a single spectrum peak energy measurement caused by deficiencies in calibration analysis would appear as inconsistencies within the set of measurements. Since the calibration spectra went over the same range of detector positions as the $K\beta$ measurements, it seemed reasonable to assume that the systematic errors would be zero on average. Thus a final value for $K\beta$ peak energy was calculated via a weighted mean:

$$E = \frac{\sum_{i=1}^N E_i / (\Delta E_i)^2}{\sum_{i=1}^N 1 / (\Delta E_i)^2} \quad (10.17)$$

where there were N measurements of energy. The i^{th} energy measurement was E_i while its uncertainty was ΔE_i . The corresponding uncertainty was calculated via the standard error:

$$\sigma_E = \sqrt{\frac{\sum_{i=1}^N (E - E_i)^2 / (\Delta E_i)^2}{(N - 1) \sum_{i=1}^N 1 / (\Delta E_i)^2}} \quad (10.18)$$

The effect of the systematic error on a single spectrum could be thought of as the deviation of the single energy from this mean value. Therefore it is reasonable to estimate the uncertainty associated with the unresolved systematic errors of a single measured energy as the standard deviation of all the energies.

10.7 EBIT Cr Energy Uncertainty Estimation

The fact that only a single EBIT Cr profile was measured necessitated a method for estimating the uncertainty associated with the systematic errors. One way to do this is to estimate the standard deviation of a hypothetical set of EBIT line energies taken with a similar set of wedges and detector positions as was collected with the $K\beta$ lines. This can be done by interpolating the standard deviation from surrounding $K\beta$ lines. This is further discussed in Chapter 14.

10.8 Spectrometer Calibration Variations

The calibration fitting process described above has four dimensions in which variations were investigated. These dimensions are (A) the profile ranges of the $K\alpha$ spectral profiles fit that were used to create calibration points, (B) the selection of $K\alpha$ lines used to create calibration points, (C) the method of partitioning the data series into calibrations, and (D) the measure of quality of the calibration fitting used in refits. The variations in each dimension are described in what follows.

(A) As described in Section 10.3.3.3, there were two sizes of profile range of the $K\alpha$ detector profiles that were fitted. These were the profiles that excluded the tails, and the profiles that included the tails.

(B) There were two selections of $K\alpha$ profiles that were used to create calibration points. These selections were:

- Ti $K\alpha$, V $K\alpha$, Cr $K\alpha$ and Mn $K\alpha$.
- Ti $K\alpha$, V $K\alpha$, Cr $K\alpha$, Mn $K\alpha$, Fe $K\alpha$.

The addition of Fe $K\alpha$ in the second selection allowed for larger energy range to be calibrated. This was necessary for the examination of Cr $K\beta$, which has an energy between that of Mn $K\alpha$ and Fe $K\alpha$.

(C) Partitioning the seven data series into separate calibration data sets was achieved in two ways, namely:

- The seven data series have their own calibrations.
- The six wedge positions each have their own calibrations. This means that *prerun2* and *postrun* data series with a wedge position of 16.40 mm shared calibrations.

These partitioning methods ensured the best accuracy and precision of the calibrations, as each partition method ensured that wedge positions did not mix in a calibration. Mixing wedge positions would not allow the fitting parameters to compensate for the fact that Mosplate calculations were done for the one wedge position. This would lead to large systematic disagreements between results from different wedge positions, compromising accuracy and precision.

(D) As described in Section 10.3.7, there were five measures of quality of the calibration fitting used in refits. The five measures were the sum of χ_r^2 values of different sets of the $K\beta$ peak energies resulting from the calibrations. One of these measures also added the χ_r^2 value of the clinometer calibration function fit using the $K\alpha$ peak energy data. Thus, the five measures allowed the investigation and minimisation of systematic error observed in the $K\beta$ peak energies.

Every combination of the last three dimensions, (B) to (D), was tried through the research using calibration points coming from the $K\alpha$ profiles that included the tails. This led to twenty sets of calibrations. The use of the $K\alpha$ profiles that cut off the tails was abandoned at an early stage as it provided poor self-consistency.

10.9 Application of Method to $K\beta$ Lines and EBIT Cr Lines

The high accuracy method of spectrometry described in this chapter was applied to the measurement of a number of $K\beta$ profiles taken in the Oxford 2007 experiment. It was also applied to the measurement of the EBIT Cr spectrum collected at the same experiment. Chapter 11 describes the results of the method applied to V $K\beta$, Chapter 12 the results of the method applied to Ti $K\beta$, and Chapter 13 describes the results of the method applied to Cr $K\beta$. Chapter 13 includes a special focus on the robustness of the method. Chapter 14 describes the results of the method applied to the EBIT Cr lines.

10.10 Future Work

The work presented in this chapter leads to further opportunities to improve the spectrometer method. The CC was the only clinometer data used in the current calibration function fitting, limiting the ability to cross check results between clinometers. Calibrations based on DL and DU would allow detailed cross checking. For example, the angle of the source arm of the spectrometer may depend on the angle of the detector arm due to mechanical instability, leading the calibration fitting to compensate for this effect. This can be investigated by fitting the differences of calibrated clinometer angles to the experimental calibration θ data. The relevant angle differences are CC - BC, DU - CC, DL - CC, (DU - BC)/2, and (DL - BC)/2. In this work, one wedge position was used in the theoretical Mosplate curved crystal calculations to model the spectrometer system, even when the wedge position of the experiment did not match. It was assumed that the spectrometer calibration functions were flexible enough to compensate for this mismatch. In future work, the correct wedge position in all theoretical Mosplate curved crystal calculations should be used with some allowance for experimental calculation in order to do a combined fit for separate wedge positions. Future work would benefit from the inclusion of data from the two end wire segments, with a modified process to identify the bounding boxes associated with those wire segments. The calibration function fitting process could also be simplified by fitting in energy space rather than an angle space.

The Characterization of the $K\beta$ Spectral Profile for Vanadium

This chapter moves on to outline the application of the high accuracy spectrometer method, detailed in Chapter 10 above, to the characterization of vanadium $K\beta$, based on the data collected in the experiment carried out in the Clarendon Laboratory in Oxford in 2007. The subsequent analyses, presented here, were conducted at The University of Melbourne School of Physics.

Summary

Reports of high precision characterization of the vanadium $K\beta$ spectral profile have been lacking. Such a characterization would be useful as a calibration standard for use in tests of QED and other x-ray spectrometry experiments. This chapter presents a completely new measurement of the vanadium $K\beta$ spectral profile produced by electron bombardment far above the threshold energy. It also presents a transferable characterization of the profile, leading onto to a measurement of the energy of vanadium $K\beta$ peak. The results presented are for two sets of spectrometer calibrations. The first is based on fitting a narrow range of the $K\alpha$ spectra. The second is based on the larger range of the $K\alpha$ spectra. The inclusion of broadening effects in the $K\beta$ fitting method enables the results to be transferable to a large range of experimental conditions. Specifically, the characterization can be used in a straight-forward manner in experiments where the level of instrumental broadening is difficult to determine. This characterization of the vanadium $K\beta$ spectral profile is useful as a calibration standard for x-ray spectrometry, and in particular, for use in tests of QED.

Key Achievements

- A characterization of the spectral profile of V $K\beta$ was created that could be used as a new standard for x-ray spectrometry.
- The V $K\beta$ peak energy was found to be 5426.962(15) eV. This is an improvement in uncertainty by a factor of 4.7 over prior work.

Publications

- LF Smale, CT Chantler, JA Kimpton, DN Crosby, and MN Kinnane. Characterization of $K\beta$ spectral profile for vanadium. *Physical Review A*, 87: 022512–1–7, 2013
- CT Chantler, LF Smale, JA Kimpton, DN Crosby, MN Kinnane, and AJ Illig. Characterization of Titanium $K\beta$ spectral profile. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 46:145601–1–10, 2013

11.1 Vanadium $K\beta$ Profile Modelling

All the samples of the V $K\beta$ profile were independently measured and fitted with Equation 10.15. The fits were done with a sum of four Voigt functions with the amplitude parameters constrained to be positive. The fitting procedure drove the fits to a sum of three Voigt functions with the fourth amplitude hitting the zero limit. The information content of the measured profiles was such that for a sum of three Voigt functions, the remaining residuals shown in Figure 11.1 were within the one standard error band.

For the three best fitted profiles as measured by χ_r^2 , the relative intensities, positions and widths of the Voigt functions of the fits were consistent with one another. That is, the determined parametrization from one representative profile was found to be within the uncertainty of other profiles and their independent parametrizations. Further, each representative determination was able to be used as a calibration functional for the other profiles. Hence minimum uncertainty results are reported here. The characteristic parameters of these fits are shown in

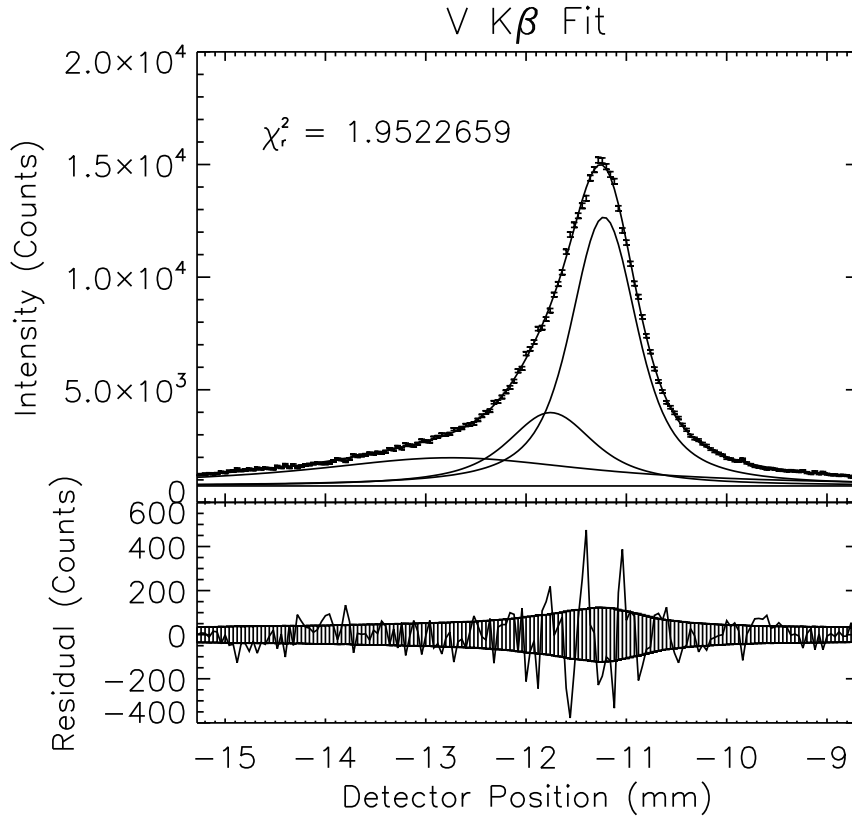


Figure 11.1: Typical fit of a V $K\beta$ spectrum. The Crystal Clinometer voltage was $-1.781742(11)$ V and the Detector Position was $-11.234(1)$ mm. The $K\beta$ peak has an energy $5427.104(61)$ eV.

Table 11.1, with positions converted to energies. Figure 11.1 shows a typical fit for one of the Vanadium $K\beta$ spectra.

The characteristic parameters of the profile of the best fit of the measured V $K\beta$ spectrum defined the shape of the V $K\beta$ without reference to an energy scale. All V $K\beta$ profiles were then refitted under the constraints of these characteristic parameters. Each refit had free parameters characterizing the overall intensity, position, detector position to energy scale conversion, instrumental broadening and background of the spectral profile in the specific geometry of the measurement. As each refit had a slightly different instrumental broadening due to geometry changes, the transferable reference position of the peak of each profile was the position of the maximum of the fit function with the Gaussian width set to zero. All refits were reliable and consistent with the original fits as discussed above. Therefore, this characterization allows for a consistent transferable standard both in this measurement, in the calibration of the dispersion function, and for any subsequent independent measurement. This enabled a consistent measurement

Proportion of Area $A_i / \sum_{i=1}^3 A_i$	Integrated Area A_i (counts)	Centroid C_i (eV)	Width W_i (eV)
0.258(21)	160280(12941)	5418.20(35)	18.86(83)
0.236(18)	146750(11207)	5424.50(11)	5.48(21)
0.507(14)	315345(8472)	5426.998(13)	2.498(69)

Table 11.1: The full characterization of the V $K\beta$ spectral profile on an absolute energy scale. The parameters in this table are used in Equation 10.15. Amplitudes A_i , centroids C_i and widths W_i of individual components were obtained from a fit on the intensity versus detector position axis. The detector position axis was transformed to an absolute energy scale via the calibration procedure. The Gaussian width σ was 0.804(25) eV. The background was 749(24) counts.

of peak position on any V $K\beta$ profile, taking account of any local instrumental broadening.

11.2 Choice of Spectrometer Calibration

As discussed in Section 10.3.3.3, two rounds of fitting of the $K\alpha$ profiles was conducted. This led to two sets of calibrations for each series of data. Set 1 depended on the fits of a narrow central range of the $K\alpha$ profiles. Set 2 depended on the fits of $K\alpha$ profiles that included the tails, and also included uncertainty from the diffraction theory of Mosplate added into the calibration fitting. The narrow-range $K\alpha$ fits should give less robust and reliable estimates of the positions of $K\alpha_1$ and $K\alpha_2$ on the detector, leading to less robust and reliable calibrations. However, the changes in the calibrations did not lead to inconsistent results between the two calibration sets.

The results of these sets of calibrations are set out below.

11.3 Calibration Set 1: V $K\beta$ Peak Energy

Fits of the V $K\beta$ spectra provided relatively independent measurements of the peak energy of V $K\beta$. The peak energies calibrated from the first set of calibrations are shown in Figure 11.2. Table 11.2 shows average values of the four contributions to ΔE for a single V $K\beta$ spectrum outlined in Section 10.5. There is a systematic functional in the dispersion of measured energies with the crystal

Uncertainty Source	Average contribution to energy uncertainty for an individual V $K\beta$ spectrum (ppm)
V $K\beta$ Spectrum Fit ($\frac{\partial E}{\partial x} \Delta x_{fit}$)	0.98
Detector Dispersion Function Fit ($\sqrt{\sum_{ij} \frac{\partial E}{\partial P_{D,i}} \frac{\partial E}{\partial P_{D,j}} C_{D,ij}}$)	0.021
Clinometer Noise ($\frac{\partial E}{\partial V} \Delta V$)	1.3
Clinometer Calibration Fit ($\sqrt{\sum_{ij} \frac{\partial E}{\partial P_{I,i}} \frac{\partial E}{\partial P_{I,j}} C_{I,ij}}$)	0.12
Total Uncertainty	1.6

Table 11.2: Error budget for the peak energy of the three spectral profiles of V $K\beta$ that go into the final energy determination. Since the three determined energies are consistent, the final energy measurement has a smaller uncertainty. The value of $\sqrt{\chi_r^2}$ for the clinometer calibration fit was 8.3 while its value for the detector dispersion function fit was 18.6.

angle θ . These data were pooled with their weighted mean, reflecting the total uncertainty, including the remnant systematic error.

Combining these data using a weighted mean defined in Equation 10.17 resulted in a measurement of the V $K\beta$ profile peak energy of 5426.962(15) eV (2.7 ppm uncertainty). This result was reported in Smale et al. [80], reproduced in Appendix B.

11.4 Calibration Set 2: Definition of Vanadium $K\beta$ Standard

A characterization of vanadium $K\beta$ reported in this section uses the second set of calibrations conducted. Applying these calibrations resulted in a characterization of the V $K\beta$ profile in Table 11.3. The weighted mean peak energy (as defined by Equation 10.17), was found to be 5426.956(18) eV (3.4 ppm uncertainty) as shown in Figure 11.3. This represented a shift of 0.006 eV (0.4 of a sigma) from the Calibration Set 1 result. This very small shift indicated that the two results were consistent with each other as expected. Nevertheless, the higher uncertainty in this result reflects a larger spread of energies in Figure 11.3 compared to Figure 11.2. In other words, the systematic errors in the calibration method were more fully explored using the second set of calibrations. Therefore, the characterization

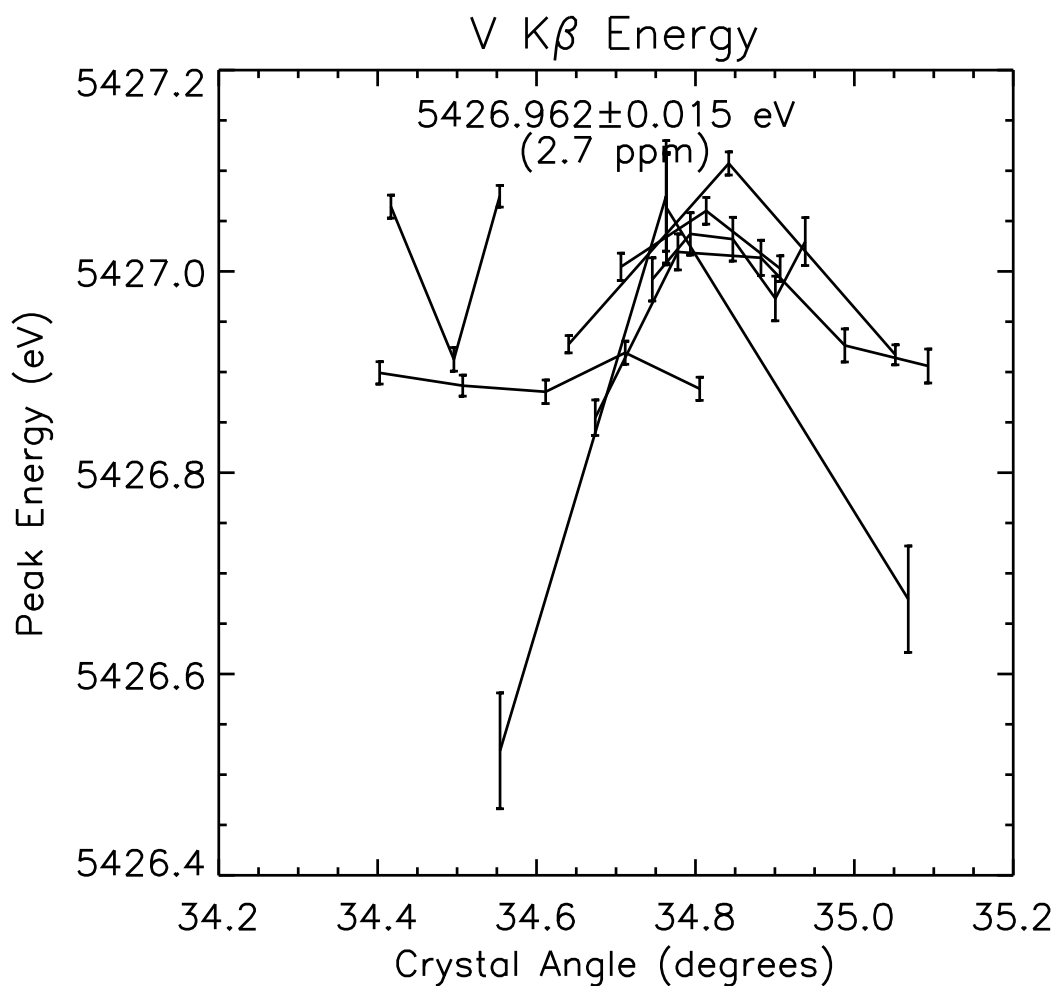


Figure 11.2: The peak energies of the fits of individual V $K\beta$ energy spectra. Each of the 7 series represents a subset of the data corresponds to a different configuration of the spectrometer. Hence each series must be modelled with a different prediction of the dynamical diffraction code suited to the geometry. Within each subset consecutive points correspond to a methodical stepping of arm position (θ) so that each profile falls on a different part of the detector area. The variance observed is a sign of limitations and systematics of the whole procedure. Therefore the pooled variance correctly represents the robustness of the final determination of profile and energy.

Proportion of Area $A_i / \sum_{i=1}^3 A_i$	Integrated Area A_i (counts)	Centroid C_i (eV)	Width W_i (eV)
0.258(21)	160000(13000)	5418.19(35)	18.86(83)
0.236(18)	147000(11000)	5424.50(11)	5.48(21)
0.507(14)	315300(8500)	5426.992(13)	2.499(69)

Table 11.3: The full characterization of the V $K\beta$ spectral profile on an absolute energy scale. The parameters in this table are used in Equation 10.15. Amplitudes A_i , centroids C_i and widths W_i of individual components were obtained from a fit on the intensity versus detector position axis. The detector position axis was transformed to an absolute energy scale via the calibration procedure. The Gaussian width σ was 0.805(25) eV. The background was 749(24) counts.

of vanadium $K\beta$ resulting from the second set of calibrations was considered to be more robust and reliable, and was taken to define a new standard for Vanadium $K\beta$. This result was reported in Chantler et al. [81].

This measurement of vanadium $K\beta$ peak energy was inconsistent with the theoretical value of 5430.00(94) eV [63]. The 3.044 eV discrepancy is just over 3.2 standard deviations. This discrepancy was interpreted as reflective of theoretical inaccuracy and imprecision.

The uncertainty of this measurement was a factor of 3.8 improvement over the experimental literature value of 5427.320(71) eV (13 ppm uncertainty) [10]. The 0.364 eV discrepancy was just over 5.1 standard deviations of the previous work. Such a large discrepancy was therefore unlikely to be the result of a statistical fluctuation, but was likely evidence of error in one of the two experimental values, possibly due to inconsistency of instrumental broadening in the prior work or a discrepancy in the characterization of the shape (and thus the peak energy) of the spectrum. Since an account of instrumental broadening was not provided for in the prior work, the discrepancy may well be attributable to instrumental broadening therein. Although a peak energy uncertainty of 3.4 ppm was larger than the earlier 2.7 ppm uncertainty, this is a more complete and robust standard. The vanadium $K\beta$ profile deserves more study, possibly in standards laboratories such as NIST in the USA, and The National Metrology Institute of Germany (PTB).

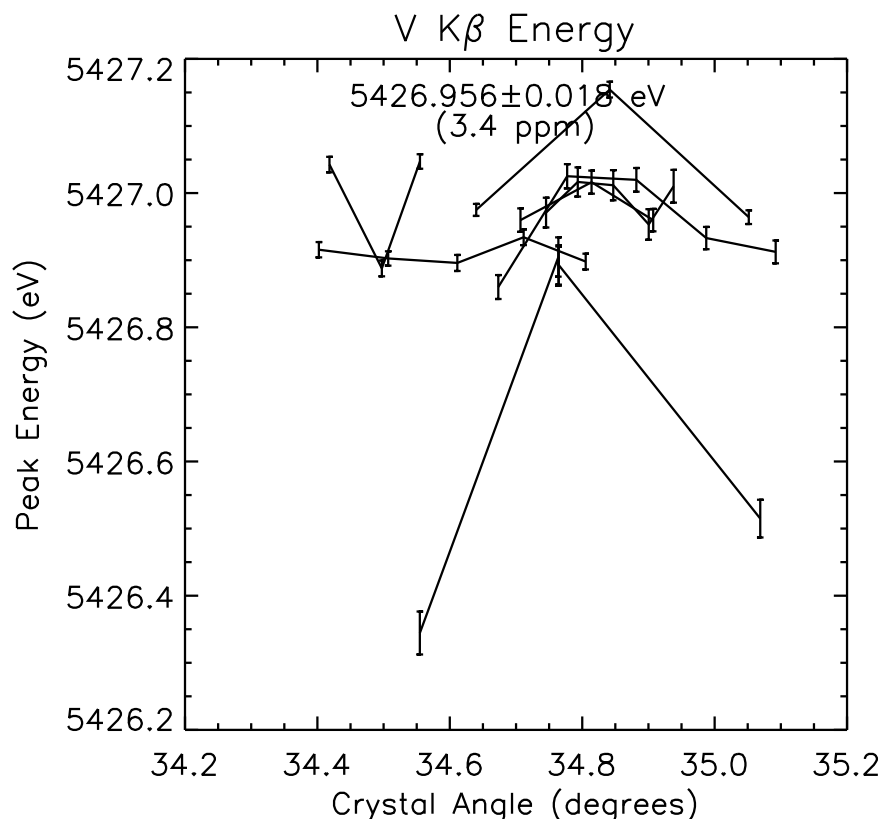


Figure 11.3: The peak energies of the fits of individual measured V $K\beta$ spectra. Each of the 7 lines represents an independently measured set of results from the full calibration series, derived by methodical stepping of the spectrometer arm length so that the profile stepped across the detector area. The variance is (much) larger than the point precision, indicating sources of systematics. The characterization function drifts off towards the edges of the detector, where vignetting or other loss of efficiency may affect the calibration. Further, some of the linked series have offsets, whether from minor hysteresis or e.g. temperature variations. The overall consistency and hence robustness of the independent measurements yields an excellent final pooled uncertainty of 3.4 ppm.

11.5 Use of the Vanadium $K\beta$ Standard

The last section presented a transferable characterization of V $K\beta$ in terms of a sum of Voigt functions with a common instrumental (Gaussian) broadening (Table 11.3) for a standard in x-ray spectrometry. For an arbitrary spectrometry experiment, the instrumental broadening should be refitted to the relevant profile, while the relevant contributions and widths of each component should remain the same. Fitting of an overall amplitude, the energy scale and background to the

experimental data should be all that is required to maintain the accuracy of the transfer.

Specifically, measuring the V K β profile and fitting it with:

$$\begin{aligned}
 P_{fit}(X; B, \sigma, A, X_1, X_2) \\
 = P(X; B, \sigma, A, X_1, \Delta W_1, \\
 AA_2/A_1, X_2, \Delta W_2, \\
 AA_3/A_1, \Delta(C_3 - C_1) + X_1, \Delta W_3) \quad (11.1)
 \end{aligned}$$

where the A_i 's, C_i 's and W_i 's come from Table 11.3 and the X_i parameters are the positions of the first 2 Voigt peaks, A is the area of the first peak, σ is the Gaussian width of all the Voigt functions, B is the background height, and $\Delta = \frac{X_2 - X_1}{C_2 - C_1}$.

This characterization of V K β can be usefully transferred to other experiments to generate calibration points for high accuracy x-ray experiments. The absolute value of the determined peak, free from instrumental broadening, should then correspond to the result reported here, together with the given uncertainty.

11.6 Conclusion

The spectral profile of V K β was measured and characterized in a transferable way. The characterization involved modelling the profile with four Lorentzian peaks convolved with an overall Gaussian. The Gaussian is recommended as a reasonable approximation for modelling additional instrumental broadening. The individual widths, positions, and relative intensities for each Lorentzian component were described and tabulated. The V K β peak energy was found to be 5426.956(18) eV (3.4 ppm uncertainty). This is an improvement in uncertainty by a factor of 3.8 over prior work.

This better characterization may serve to enable a reduction in experimental complexity of calibration of some experiments, by reducing the need for different elements to produce characteristic radiation. This result may also make calibration more accurate by enabling a fuller analysis with which to diagnose and correct systematic errors in calibration. This standard may also serve as a useful test for characteristic radiation theory as it improves.

Characterization of the Titanium $K\beta$ Spectral Profile

The second application of the high accuracy spectrometer method outlined in Chapter 10 above, is presented by this chapter. Again, data collected in the Oxford 2007 experiment, this time relating to titanium $K\beta$, were analysed at The University of Melbourne.

Summary

As with vanadium $K\beta$, a high precision characterization of the titanium $K\beta$ spectral profile has not been found to be reported in the literature to date. Such a characterization is useful as a calibration standard for use in tests of QED. This chapter presents a new measurement of the titanium $K\beta$ spectral profile produced by electron bombardment far above the threshold energy, and a transferable characterization of the profile leading to a measurement of the energy of titanium $K\beta$ peak. The inclusion of broadening effects in the fitting method enables the results to be transferable to a large range of experimental conditions. Specifically, the characterization can be used in a straight-forward manner in experiments where the level of instrumental broadening is difficult to determine. Like the characterization of vanadium $K\beta$, this characterization of the titanium $K\beta$ spectral profile is considered to be useful as a calibration standard for x-ray spectrometry, and in particular, for use in tests of QED.

Key Achievements

- A characterization of the spectral profile of Ti $K\beta$ was created that could be used as a new standard for x-ray spectrometry.

- The Ti $K\beta$ peak energy was found to be 4931.966(22) eV, an improvement in uncertainty by a factor of 2.6 over the previous best reported result.

Publications

- CT Chantler, LF Smale, JA Kimpton, DN Crosby, MN Kinnane, and AJ Illig. Characterization of Titanium $K\beta$ spectral profile. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 46:145601–1–10, 2013

12.1 Titanium $K\beta$ Profile Fitting

Ti $K\beta$ profiles were collected and characterized on intensity and detector profile position axes. A large collection of independent measurements of Ti $K\beta$ profiles were fitted with Equation 10.15. The information content of the measured profiles was such that when a sum of three Voigts was attempted, there was a strong residual signature indicating proof of the requirement of a fourth component. Equally, it is seen from Table 12.1 that the area involved in the fourth peak is minor and that remaining residuals from Figure 12.1 are within the one standard error band. Hence there was no significant evidence for a fifth peak in the data themselves. The relative intensities, positions and widths of the Voigt functions were consistent in all fits (to better than one standard error of the scaled fitting parameters), so the minimum uncertainty results are reported here. The characteristic parameters of these fits are shown in Table 12.1, with the position axis converted to energy. Figure 12.1 shows a typical fit for one of the Ti $K\beta$ spectra.

These optimum parameters were then used to constrain refits of all of the Ti $K\beta$ profiles. Each refit had free parameters characterizing the overall intensity, position, detector position to energy scale conversion, instrumental broadening and background of the spectral profile in the specific geometry of the measurement. As each refit had a slightly different instrumental broadening due to geometry changes, the transferable reference position of the peak of each profile was again taken to be the position of the maximum of the fit function with the Gaussian width set to zero. All refits were reliable and consistent with the original fits (to within one standard error of scaled parameter values). This enabled a consistent

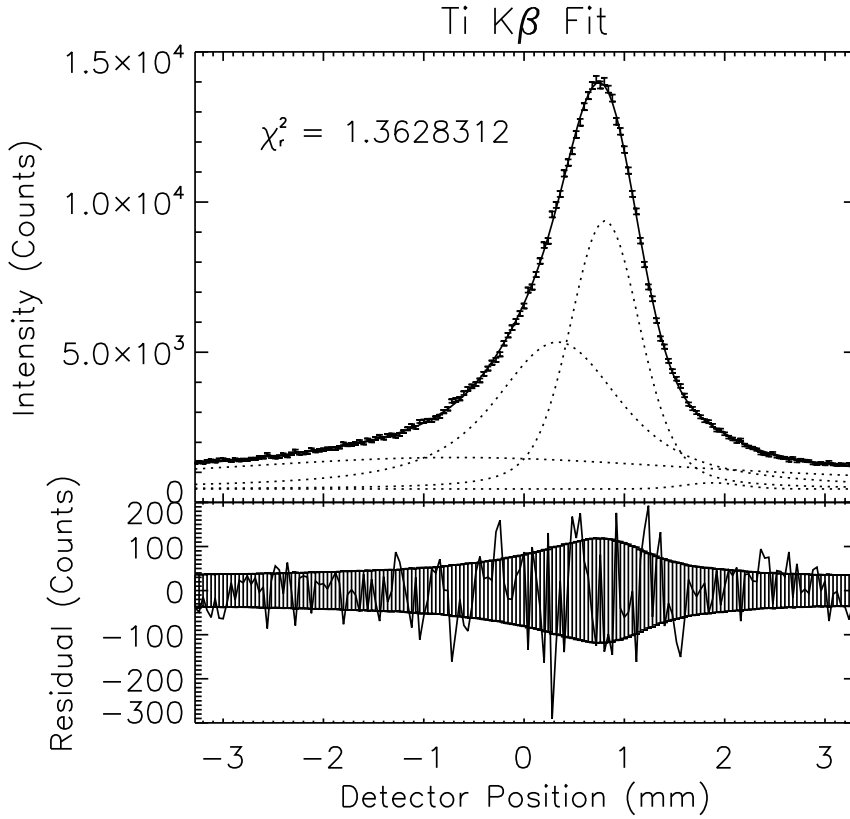


Figure 12.1: Typical fit of a Ti K β spectrum. The Crystal Clinometer voltage was -1.0129597(74) V and the peak detector position was 0.8089(14) mm. Fitting parameters are provided in Table 12.1.

measurement of peak position on any Ti K β profile for any local instrumental broadening.

12.2 Ti K β Peak Energy

The transformation of peak positions to peak energies through Equation 10.9, for the fits of the Ti K β spectra, provided independent measures of the peak energy of Ti K β , as shown in Figure 12.2. Table 12.2 presents average values of the four contributions to ΔE for a single Ti K β spectrum outlined in Section 10.5. A systematic functional in the dispersion of measured energies with Crystal Angle was revealed. These data were pooled with their weighted mean reflecting the total uncertainty including the remnant systematic error.

The resulting measurement of the Ti K β profile peak energy was 4931.966(22) eV. The previous theoretical reference value was 4930.86(85) eV [63]. The 1.106 eV or

Proportion of Area $A_i / \sum_{i=1}^4 A_i$	Integrated Area A_i (counts)	Centroid C_i (eV)	Width W_i (eV)
0.199(24)	120700(14700)	4925.37(50)	16.3(10)
0.455(23)	276000(13700)	4930.096(75)	4.25(19)
0.326(22)	197700(13200)	4931.967(16)	0.42(22)
0.0192(54)	11660(3250)	4935.59(16)	0.47(44)

Table 12.1: Characterization of the Ti $K\beta$ spectral profile. The profile is fully characterized on an absolute energy scale through a sum of component Lorentzians convolved with a Gaussian instrumental broadening. Integrated areas A_i , centroids C_i and FWHMs W_i of individual components were obtained from a fit of intensity against detector position. The detector position axis was transformed to an absolute energy scale via the calibration procedure. The Gaussian width $\sigma = 1.244(41)$ eV. The background was $B = 831(26)$ counts. The second and third components are dominant, contributing more than three quarters of the intensity of the spectrum while the fourth component is very weak. The third and fourth component widths are dominated by the Gaussian instrumental width. The first component is very broad relative to the entire $K\beta$ spectrum.

Uncertainty Source	Average Contribution to Energy Uncertainty For An Individual Ti $K\beta$ Spectrum (ppm)
Ti $K\beta$ Spectrum Fit ($\frac{\partial E}{\partial x} \Delta x_{fit}$)	0.98
Detector Dispersion Function Fit ($\sqrt{\sum_{ij} \frac{\partial E}{\partial P_{D,i}} \frac{\partial E}{\partial P_{D,j}} C_{D,ij}}$)	0.021
Clinometer Noise ($\frac{\partial E}{\partial V} \Delta V$)	1.3
Clinometer Calibration Fit ($\sqrt{\sum_{ij} \frac{\partial E}{\partial P_{I,i}} \frac{\partial E}{\partial P_{I,j}} C_{I,ij}}$)	0.14
Total Uncertainty	1.6

Table 12.2: Error budget for the peak energy of all the spectral profiles of Ti $K\beta$ that go into the final energy determination. Since the energies show evidence of an unknown variance, the final energy determination has a larger uncertainty than this ideal 1.6 ppm for the individual spectrum.

1.3 standard deviation discrepancy that emerged is considered to be reflective of the imprecision of the theoretical value in the literature.

The new measurement represents a factor of 2.6 improvement in the uncertainty compared with the prior experimental value of 4931.827(59) eV, which had a 12 ppm uncertainty [10]. The discrepancy is 0.139 eV or about 2.4 standard deviations. As in the case of the V $K\beta$ analysis, since an account of instrumental broadening was not given in the earlier experimental measurement, the 0.139 eV

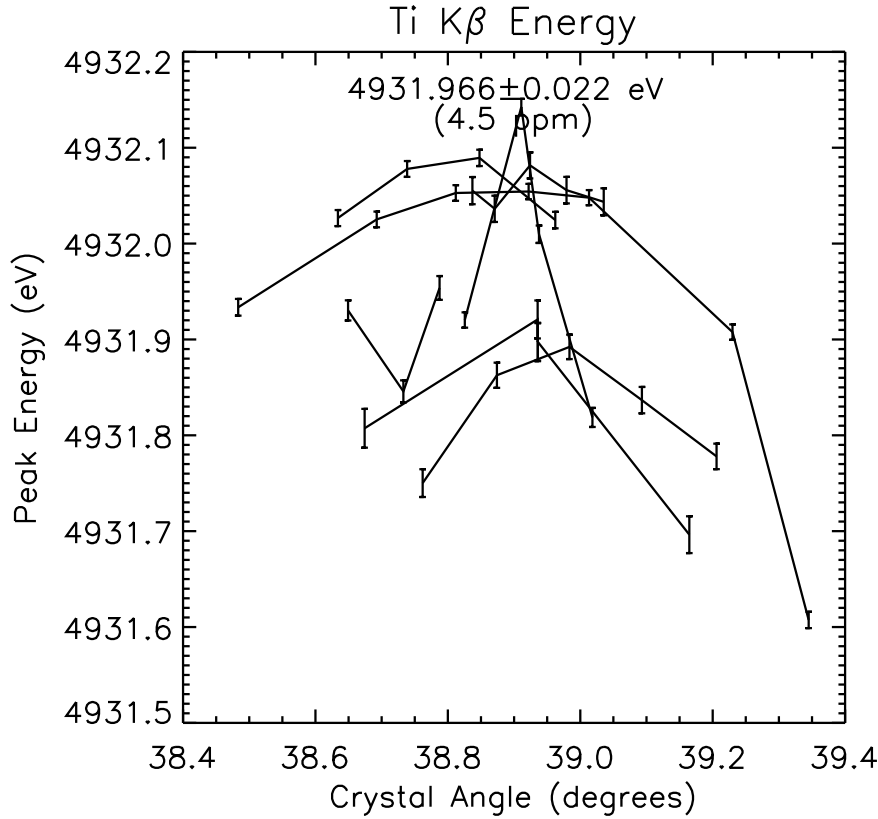


Figure 12.2: The peak energies of the fits of individual measured Ti $K\beta$ spectra. Each of the 7 lines represents an independently measured set of results from the full calibration series, derived by methodical stepping of the spectrometer arm length so that the profile stepped across the detector area. The variance is larger than the point precision, indicating sources of systematics. The characterization function drifts off towards the edges of the detector, where vignetting or other loss of efficiency may affect the calibration. Further, some of the linked series have offsets, whether from minor hysteresis or e.g. temperature variations. The overall consistency and hence robustness of the independent measurements yields a final pooled uncertainty of 4.5 ppm.

discrepancy is likely to be attributable to instrumental broadening. The relationship between peak energy and instrumental broadening is shown in Fig.12.3. The asymmetry of the peak means that the greater the broadening, the more the peak energy is shifted to lower values. Hence any instrumental broadening would shift the peak energy significantly. Therefore, the instrumental-independent location and parametrization is presented, so that the characterization can be used with a general experimental methodology in situations with higher or lower resolution, in order to maintain an accurate calibration and energy transfer.

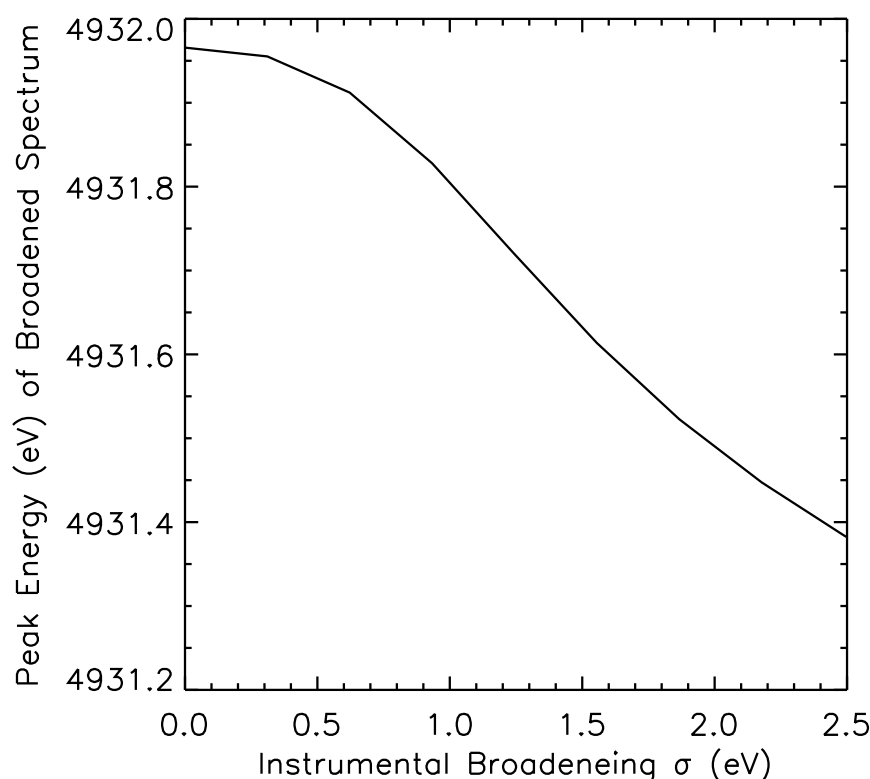


Figure 12.3: The peak energy of the fitted model function of the Ti $K\beta$ spectra as a function of the instrumental broadening. The measured broadening of the spectrum of 1.24(4) eV and the asymmetry of the peak leads to a shift of peak position of 0.25 eV or 50 ppm.

12.3 Use of the Characterization of Titanium $K\beta$

The analyses outlined above offer a transferable characterization of Ti $K\beta$ in terms of a sum of Voigt functions with a common instrumental (Gaussian) broadening, presented in Table 12.1. This characterization can function as a standard reference for use in arbitrary experimental environments, where the instrumental broadening will be different. The instrumental broadening should be fitted to the relevant profile, while the percentage contributions and eV widths of each component should remain unchanged. Fitting of an overall amplitude coefficient, the energy scale, and background to the experimental data should be all that is required to maintain the accuracy of the transfer. The simplest improvement over previously reported work is that a user may measure the Ti $K\beta$ profile, remove the instrumental broadening, locate the peak position, and finally use the above determination to calibrate the spectrum.

On the basis of the present work, a more accurate and transferable methodology could be to measure a Ti $K\beta$ line as part of the calibration, and then fit it with

$$P_{fit}(X; B, \sigma, A, X_1, X_2) = P(X; B, \sigma, A, X_1, W_1 \frac{X_2 - X_1}{C_2 - C_1}, \frac{AA_2}{A_1}, X_2, W_2 \frac{X_2 - X_1}{C_2 - C_1}, \frac{AA_3}{A_1}, (C_3 - C_1) \frac{X_2 - X_1}{C_2 - C_1} + X_1, W_3 \frac{X_2 - X_1}{C_2 - C_1}, \frac{AA_4}{A_1}, (C_4 - C_1) \frac{X_2 - X_1}{C_2 - C_1} + X_1, W_4 \frac{X_2 - X_1}{C_2 - C_1}) \quad (12.1)$$

where the A_i 's, C_i 's and W_i 's come from Table 12.1, the X_i parameters are the positions of the first 2 Voigt peaks, A is the area of the first peak, σ is the Gaussian width of all the Voigt profile components, and B is the background height. This characterization of Ti $K\beta$ can be directly transferred to other experiments to generate calibration points for high accuracy x-ray experiments.

12.4 Conclusion

The spectral profile of Ti $K\beta$ was measured and characterized in a transferable methodology. The characterization involved modelling the profile with four Lorentzian peaks convolved with an overall Gaussian. For future work, the Gaussian is recommended to model additional (instrumental) broadening, provided significant profile vignetting is not involved, that is, provided the profiles are complete $K\beta$ profiles and not truncated by the source size or slit width. In fact, this method revealed the significance of any such vignetting by returning a high χ_r^2 value for the fits, and by being strongly dependent on crystal or diffracting angle with a clear asymmetry of the fit.

The individual widths for each Lorentzian component were described and tabulated. The Ti $K\beta$ peak energy was found to be 4931.966(22) eV. This was an improvement in uncertainty by a factor of 2.6 over the previous best reported result. It must be remembered that unlike the present work, the previous tabulated value had not resolved the issue of instrumental broadening as a significant source of peak shift. This characterization can be used as a calibration standard for future x-ray spectrometry experiments, especially for tests of QED. It will be used in the construction and analysis of the calibrations used for existing QED experimental data coming from the NIST 2005 experiment. It would be interesting to compare this characterization to future MCDF calculations as those calculations improve.

Robustness of the Methodology for the Characterization of Characteristic Spectral Profiles, Applied to Chromium $K\beta$

The third application of the high accuracy spectrometer method set out in Chapter 10 to the characterization of the chromium $K\beta$ spectral profile is presented. After describing this analytic work, this chapter focuses on a novel test of the robustness of the overall methodology by reference to the chromium $K\beta$ region of the spectrometer range. Once more, the data were generated by the Oxford 2007 experiment, and analysed at The University of Melbourne School of Physics.

Summary

The robustness of a measurement method is a key area that should be investigated. The high accuracy spectrometry method outlined in Chapter 10 includes a method to estimate the size of systematic errors. The robustness of the spectrometry method was examined by applying it to the chromium $K\beta$ spectra measured at the Oxford 2007 experiment. This was done by using calibrations resulting from variations of the method to the chromium $K\beta$ spectra. Robustness of method would be shown by the consistency of the identified chromium $K\beta$ peak energy between variations, implying that the systematic errors were properly accounted for. Cr $K\beta$ was a good choice to test the robustness of the method as it was on the edge of the calibratable range of the spectrometer system as it was used at the Oxford 2007 experiment. A key challenge and problem here is that the earlier methodologies would have led to extrapolation in the case of chromium $K\beta$, and, in any case, the spectrum is near the end of the spectrometer calibration range as

set up. This chapter presents as much a study of systematic error in the dispersion function, as an investigation of the chromium $K\beta$ spectral profile itself.

Key Achievements

- Consistency of major variations of the method were demonstrated, showing robustness in challenging circumstances.

Publications

- LF Smale, CT Chantler, and JA Kimpton. Methodology for the characterisation of characteristic spectral profiles, applied to chromium $K\beta$. *X-Ray Spectrometry*, 44(2):54–62, 2015

13.1 Test of Robustness of Measurement

A method of creating a spectrometer calibration was shown in Chapter 10. This method was used to analyse and optimise the calibration for the V and Ti $K\beta$ profiles in Chapters 11 and 12. The limits of this method should be explored. One important limit for the method is detector arm angles that are near the edge of the calibration range. Systematic errors should have larger effects at this limit. For the Oxford experiment, this limit appears near the angles where chromium $K\beta$ was observed. Thus a good test of the use the method with different optimisations to create different calibrations what can be applied to chromium $K\beta$. If the optimisations produce self-consistent results as well as results that are consistent with previous experiments and theory, then the method would be shown to produce robust and accurate calibrations in challenging situations. This chapter explores the methodology used in Chapters 11 and 12 in the creation of a chromium $K\beta$ standard.

Proportion of Area $A_i / \sum_{i=1}^4 A_i$	Integrated Area A_i (counts)	Centroid C_i (eV)	Width W_i (eV)
0.333(20)	219011(13177)	5937.00(31)	19.84(60)
0.209(18)	137415(11971)	5943.70(16)	5.74(32)
0.458(15)	300778(9767)	5946.705(24)	2.37(11)

Table 13.1: Characterization of the Cr $K\beta$ spectral profile. The profile is characterised on an absolute energy scale using a sum of component Lorentzians convolved with a common Gaussian instrumental broadening. Integrated areas (A_i), centroids (C_i) and FWHMs (W_i) of individual components were obtained from a series of fits of intensity against detector position. The detector position axis was then transformed to an absolute energy scale using the calibration procedure. The Gaussian width $\sigma = 1.517(32)$ eV. The background was $B = 629(23)$ counts. The third component dominates the height of the profile, while the first and second components fill out the low energy profile asymmetry.

13.2 Chromium $K\beta$ Profile Modelling

At the Oxford 2007 experiment at the Clarendon Laboratory, 27 Cr $K\beta$ profiles were collected. Subsequently, all measured Cr $K\beta$ detector profiles were separately fitted with Equation 10.15. The information content of the measured profiles was such that when a sum of three Voigt functions was attempted, the remaining residuals, shown in Figure 13.1, were within the one standard error band. The relative intensities, positions and width parameters of the Voigt functions were consistent with one another, so the minimum uncertainty functionals are reported. The fits were done with a sum of four Voigt functions, although one of the Voigt function intensities hit the fitting constraint that enforced a non-negative Voigt function intensity. This means that three Voigt functions were sufficient to represent Cr $K\beta$ as measured. The characteristic parameters of these fits are shown in Table 13.1, with the position axis converted to energy. Figure 13.1 shows a typical fit for one of the Cr $K\beta$ spectra.

These characteristic parameters were then used to constrain refits of all of the Cr $K\beta$ profiles. Each refit had free parameters characterising the overall intensity, position, detector position to energy scale conversion, instrumental broadening and background of the spectral profile in the specific geometry of the measurement. As each refit had a slightly different instrumental broadening due to geometry changes, the transferable reference position of each profile peak was taken to be the position of the maximum of the fit function with the Gaussian width set to zero. All refits were reliable, and consistent with the original fits.

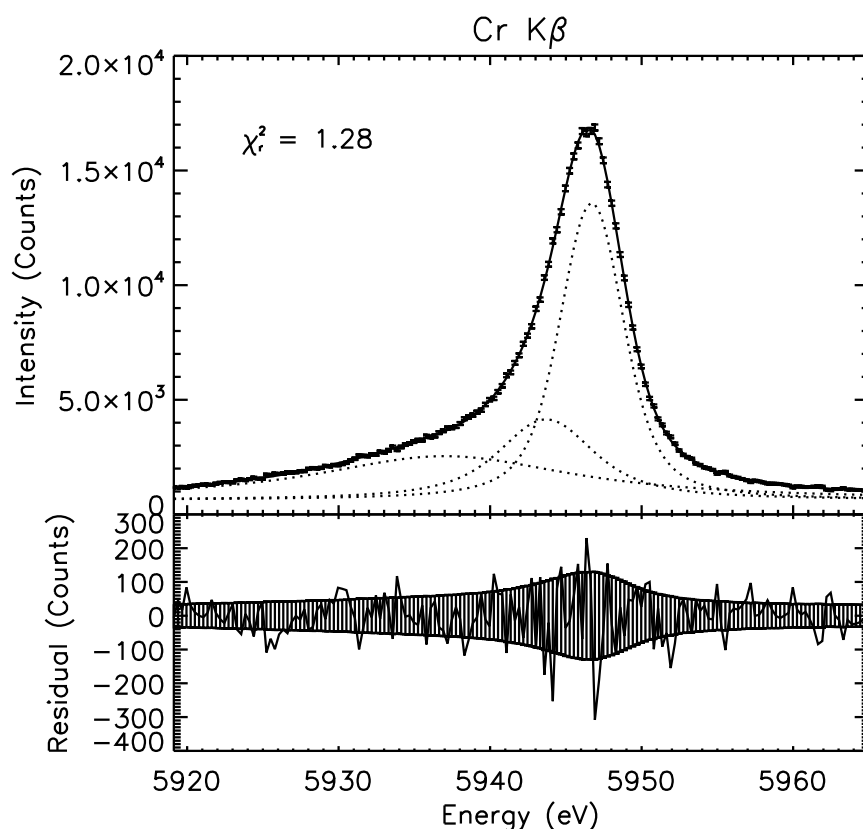


Figure 13.1: Typical fit of a Cr $K\beta$ spectrum. The points with error bars are the experimental data, the solid line is the fitted sum of Voigt functions and the three dotted lines are the three individual Voigt components with the background offset. The corresponding fitting parameters are provided in Table 13.1.

The characterization, described above, allowed for a consistent transferable standard in this measurement, in the calibration of the dispersion function, and allows for any subsequent independent measurement by other authors. This enables a consistent measurement of peak position of Cr $K\beta$ spectra for any particular instrumental broadening where the spectra are not significantly vignettted by the effects of source size or a slit width. Fitting spectra with this method would reveal the significance of any such vignetting by returning a high χ^2_r value for the fits. In the current situation, the method enabled a more consistent use of experimental and theoretical standards discussed to date in the literature.

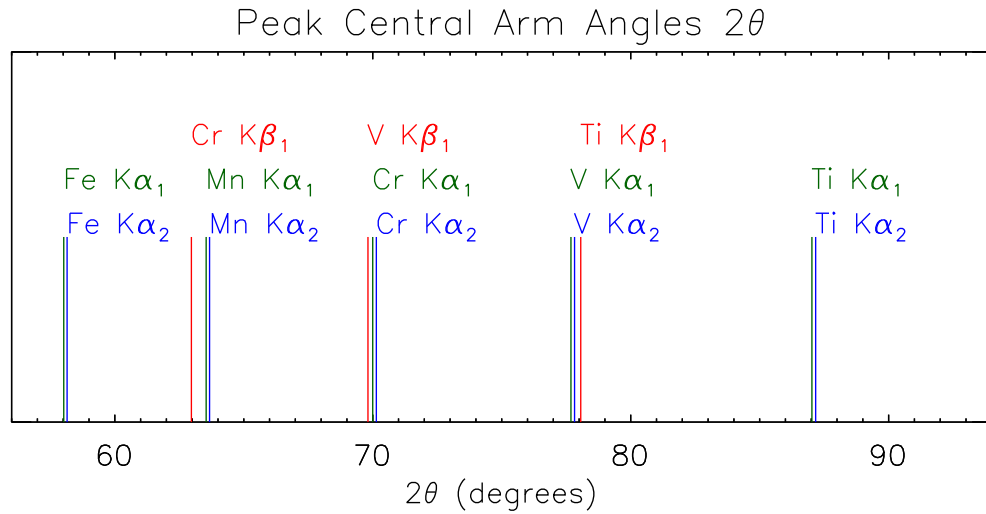
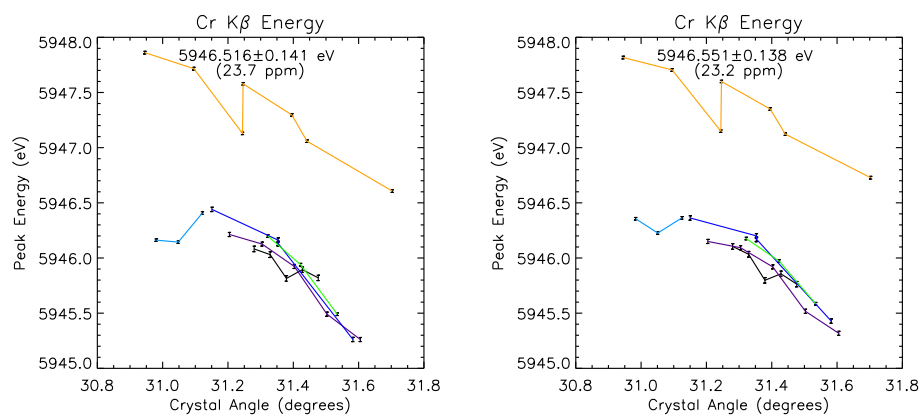


Figure 13.2: The detector arm angle for each characteristic radiation peak where the peak is centred on the detector. The Fe $K\alpha$ peaks were included in the creation of the calibration for this Cr $K\beta$ measurement to constrain the dispersion fitting in this region. It also results in the transfer of the calibration to the angular range of Cr $K\beta$ being an interpolation instead of an extrapolation.

13.3 Optimisation of the Dispersion Function

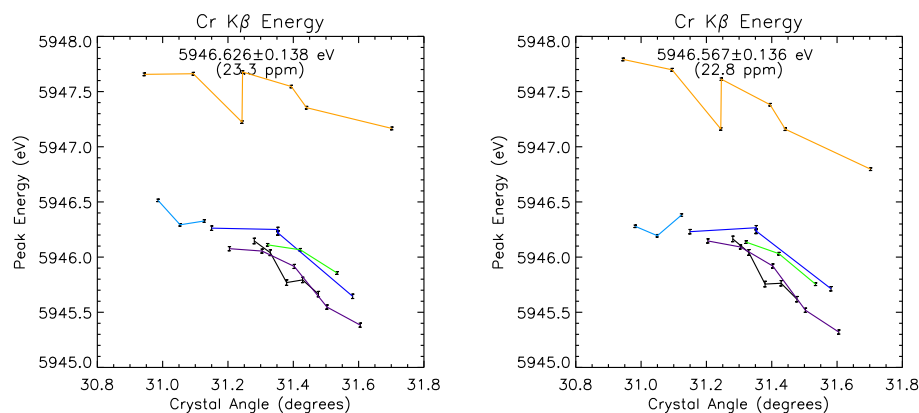
The dispersion function was optimised in this study using a slightly different method than that of the V and Ti $K\beta$ studies in Chapters 11 and 12. The differences in method were the inclusion of the Fe $K\alpha_1$ and Fe $K\alpha_2$ data in the calibration fitting, and the pooling of all $K\alpha$ data for a given wedge position into the same fit rather than separating them by wedge and collection time. The uncertainties near Cr $K\beta$ were large, due to Cr $K\beta$ being on the edge of the range of 2θ (detector arm angles) included in the dispersion fitting procedure. This meant that the addition of the Fe $K\alpha$ data was able to much better constrain the dispersion fits in the Cr $K\beta$ detector arm angle range. The relationships between the detector arm angles are shown in Figure 13.2. The pooling of calibration data by wedge position also led to a better distribution of good data and therefore less variance in the Cr $K\beta$ peak energy.

Critical questions regarding robustness, are whether the optimisation criteria used distort the analysis, the variance and the result. If robust and consistent, the optimised result should minimise variance and preserve a consistent central energy determination. Hence, in a novel test of robustness, the self-consistency of a series of alternate optimisations, each minimising a different measure of quality of the



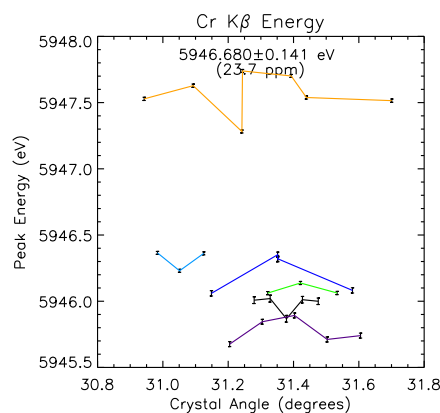
(a) The spread of Ti K β peak energy (only) is minimised.

(b) The spread of V K β and Ti K β peak energies are minimised.



(c) The spread of V K β peak energy (only) is minimised.

(d) The spread of V K β , Ti K β , Cr K β and all the K α peak energies are minimised.



(e) The spread of Cr K β peak energy (only) is minimised.

Figure 13.3: The Cr K β peak energies of individual measured spectra. Each of the 6 lines in each sub-figure are energies from a single wedge position. Each sub-figure [(a) to (e)] is the result of a different χ_r^2 measure [(a) to (e)] that has been optimised. The systematic slopes in these sub-figures indicate an incorrect optimisation of detector scale parameter. The optimisation of measure (e) minimises this systematic in the energy region of Cr K β , thus accurately determining of the detector scale parameter.

calibration fitting was investigated. These are measures (a) through (e) described in Section 10.3.7. As described in Section 10.3.7, each optimisation involved a three step process: (1) for a range of detector scales, there was a fit of I_{data} versus V , which refined the clinometer calibration function in the context of that detector scale; (2) for each detector scale, a calculation of the measure to be minimised was made; and (3) the detector scale and clinometer calibration function that minimised the measure was then selected. The first and third optimisations have been used in past analyses to determine the energy and profile of Ti $K\beta$ and V $K\beta$. Following these past results, the range of energy of interest in this study was that of Cr $K\beta$. The others are provided to both prove that they are consistent and to reveal difficulties of the minimisation. Figures 13.3a to 13.3e provide the resulting distributions of Cr $K\beta$ peak energies for each of the optimisations.

The resulting calibrated Cr $K\beta$ peak energies derived from the optimisation of measure (a) are shown in Figure 13.3a. This reveals that in this optimisation of the set of independent measurements of the Cr $K\beta$ peak energy, there was a clear slope in the results for each calibration series that represents a possible systematic error in $P_{D,1}$, the detector scale parameter. This was a result of $P_{D,1}$ being optimised only for crystal angles where the Ti $K\beta$ line was measured. It should be noted that the optimisation of this measure was used for the Ti $K\beta$ study of Chapter 12.

The resulting calibrated Cr $K\beta$ peak energies derived from the optimisation of measure (b) are shown in Figure 13.3b.

The resulting calibrated Cr $K\beta$ peak energies derived from the optimisation of measure (c) are shown in Figure 13.3c. It should be noted that the optimisation of this measure was used for the V $K\beta$ study of Chapter 11.

The resulting calibrated Cr $K\beta$ peak energies derived from the optimisation of measure (d) are shown in Figure 13.3d.

The resulting calibrated Cr $K\beta$ peak energies emerging from the optimisation of measure (e) are shown in Figure 13.3e. It is to be expected that the uncertainty in the region of interest was minimised by this approach, and that the result was likely to be optimal using this last method. By definition, the systematic error reflected in the slope of each calibration was minimised. Note that this optimisation only locally minimises this systematic around the Cr $K\beta$ detector arm angles, away from this range, the systematic is visible.

What insight emerges from the comparisons in Figure 13.3? They principally demonstrate that each wedge settings is not uniformly well-defined, and that while the uncertainty of each point from the statistical fitting was very well-defined, on the order of 2-3 ppm, the systematic uncertainties clearly dominated the data, being some ten times this value. Earlier studies of Ti $K\beta$ and V $K\beta$ used data from Sc $K\alpha$ through Mn $K\alpha$, but neglected Fe $K\alpha$. The divergence of constraint at Cr $K\beta$ energies demanded the inclusion of analysis of Fe $K\alpha$ profiles, so that the dispersion function was interpolated rather than extrapolated to the region of interest. Nonetheless, the constraint was not uniformly effective because the quantity and quality of the individual peak profiles varied from one wedge setting to another. Hence, the collection of profiles for each wedge setting will not in general be equally well-defined. Perhaps more importantly, this study demonstrated that any sensible optimisation system yields a similar agreement and pattern of discrepancy, and a similar final uncertainty. We investigated a more extensive set but these illustrate the general principle that under normal circumstances this methodology is robust.

The remaining error (scatter) between the calibration runs reflected the known fact that Cr $K\beta$ was at the far edge of the calibrated region of the crystal angle range, so that the variance observed was deliberately maximised in this study. It should be emphasised that effectively the same dispersion function and optimisation as presented in measure (a) yielded no large systematic in the energy regime of Ti $K\beta$, and yielded a final consistency at the $\sigma = 4.5$ ppm level or ± 0.022 eV, while that presented in measure (c) yielded no large systematic in the energy regime of V $K\beta$ and yielded a final consistency at the $\sigma = 2.7$ ppm level or ± 0.015 eV. Indeed, in the latter measurement and characterization, the individual point uncertainties were 1.6 ppm. The point is that divergences due to limited accuracy of subsets with different wedge settings near the edge of the interpolation region were expected and they were indeed observed.

Figure 13.4 presents the weighted mean values of the peak energy for each optimisation [measures (a) to (e)] in comparison to the peak energy reported in Hölzer et al. [79]. The energies reported here are all consistent with each other and are all within 1.5 sigma of Hölzer et al. [79]. Optimising the calibrations to minimise the slope systematic error for the Cr $K\beta$ profile peak energy led to a value for that energy to be within one σ of Hölzer et al. [79]. This shows the ability of this calibration method to be tuned to different energies within the same data set, through

Uncertainty Source	Average Contribution to Energy Uncertainty for an Individual Cr K β Spectrum (ppm)
Cr K β Spectrum Fit ($\frac{\partial E}{\partial x} \Delta x_{fit}$)	1.0
Detector Dispersion Function Fit ($\sqrt{\sum_{ij} \frac{\partial E}{\partial P_{D,i}} \frac{\partial E}{\partial P_{D,j}} C_{D,ij}}$)	0.21
Clinometer Noise ($\frac{\partial E}{\partial V} \Delta V$)	1.3
Clinometer Calibration Fit ($\sqrt{\sum_{ij} \frac{\partial E}{\partial P_{I,i}} \frac{\partial E}{\partial P_{I,j}} C_{I,ij}}$)	0.93
Total Uncertainty	1.9

Table 13.2: Typical uncertainty budget for the peak energy of each of the spectral profiles of Cr K β in the final plots and which contribute to the energy determination. The energy measurements show evidence of an unknown variance, likely involved in the experimental and geometrical parametrisation, including any error from diffraction theory for known and estimated wedge positions. Therefore the final energy determination has a larger uncertainty than this ideal 1.9 ppm for the individual spectrum, as required and determined by the observed variance. The independent self-consistency shown in this work is invaluable in uncovering sources of systematic uncertainty that might otherwise go unnoticed and remain unanalysed.

the minimisation of the systematic error at those energies. Table 13.2 shows the averages of these various contributions to energy uncertainty for a single Cr K β spectrum as outlined in Section 10.5.

13.4 Cr K β Peak Energy

All five calibrations based on minimising measures (a) to (e) were found to be consistent. It is therefore reasonable to report any of these results. By definition, the calibration that worked best was based on measure (e), the calibration that minimises the χ_r^2 value of the Cr K β peak energy measurements (Figure 13.3e). Therefore, it was this dispersion function calibration that was used for the remainder of the analysis.

The weighted mean resulted in a measurement of the Cr K β profile peak energy of 5946.68(14) eV. This 24 ppm uncertainty was larger than that for an individual fit given in Table 13.2, and was understandably a result of the remaining systematic error between wedge positions and within each wedge position across the angular range used. Comparing this value to the prior theoretical literature value of

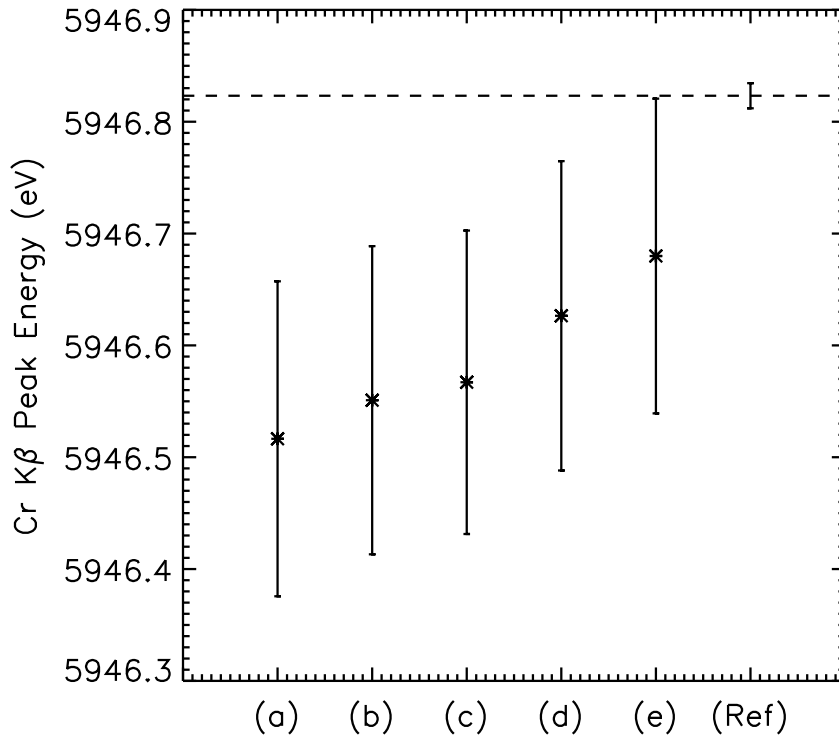


Figure 13.4: The mean peak energies of the fits of individually measured Cr $K\beta$ spectra for each optimisation method compared to the literature value. Note that all of these, despite different ansatz, yield results consistent with one another to within one standard error. Further, the optimised method focussing on the region of interest gives the highest accuracy and lies within one standard error of the best literature value for the peak energy [79].

5947.1(10) eV [63], the 0.42 eV discrepancy was just over 0.42 standard deviations and is proposed to be a reflection of the theoretical imprecision. Further, this was an improved result compared to current theory [63].

Conversely, the prior experimental value of 5946.823(11) eV (1.7 ppm uncertainty) in the literature [10, 79] was a more accurate determination of the peak energy for that specific experimental configuration. The discrepancy was 0.143 eV, or about 1.01 standard deviations, so was in excellent agreement, even in this difficult arrangement (at the edge of the calibration series).

An advantage of the characterization presented in this chapter, however, is that the error bars on the characterization allowed for profile and geometry-dependent variation. More particularly, it proved the methodology presented in this thesis (in Chapters 8, 9 and 10) and used in this chapter as well as in Chapters 11 and

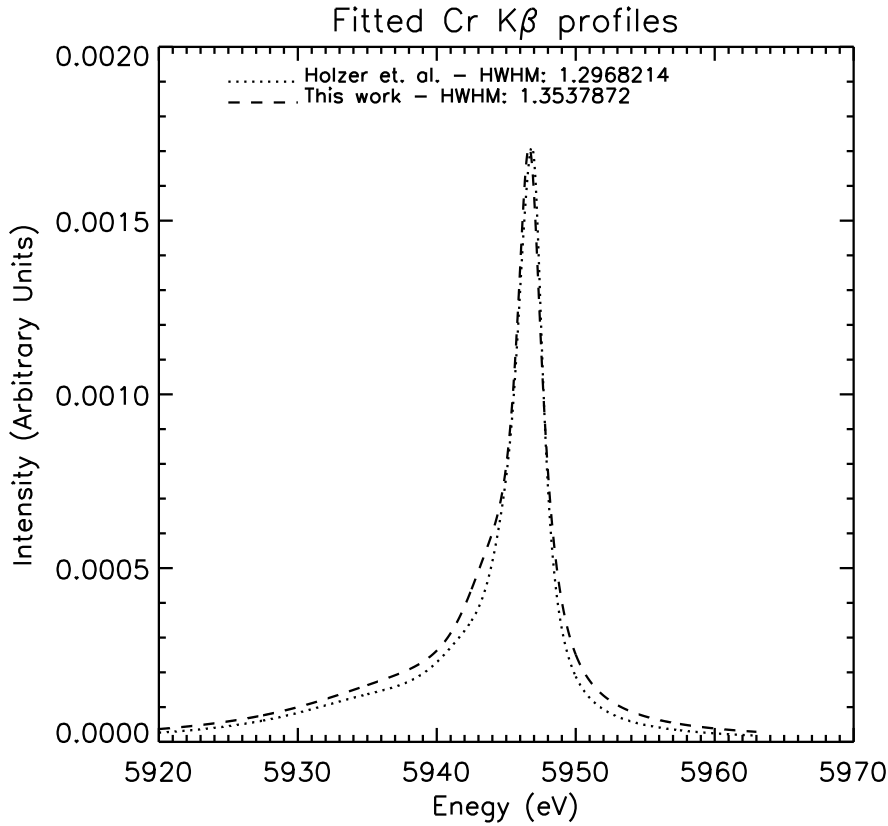


Figure 13.5: The spectral profile of Cr $K\beta$ measured in this work (dashed line) compared to that reported in Hölzer et al. [79] (dotted line). As presented here, the dashed line is a sum of three Lorentzians with parameters given in Table 13.1. This corresponds to setting the Gaussian width that represents instrumental broadening to 0 eV. The resolution and half width at half maxima (HWHMs) of the two results are in agreement to within 4%. Being a sum of six Lorentzians, the characterization in [79] is smoother. This is expected as the 1.4 eV instrumental broadening obtained in the current work smooths out the spectrum so that [79] can capture some higher resolution information. It should be noted that [79] deconvolved the $K\beta$ spectrum before fitting with an unreported broadening.

12, down to a valuable limit. A comparison of the profile fit in [79] and the present work is presented in Figure 13.5.

13.5 Conclusion

The spectral profile of Cr $K\beta$ was measured and characterised in a way that makes it transferable to experiments with different instrumental broadening. The characterization involved modelling the profile with four Lorentzian peaks convolved

with a common Gaussian. A Gaussian is recommended to model additional (instrumental) broadening, provided significant profile vignetting is not involved, that is, provided that the profiles are complete $K\beta$ profiles not truncated by the source size or a slit width. This method will reveal the significance of any such vignetting by returning a high χ_r^2 value for the fits, and by being strongly dependent on crystal or diffracting angle. The individual widths and component parametrisation are given explicitly for each component. The Cr $K\beta$ peak energy was found to be 5946.68(14) eV. This is a 24 ppm result. This demonstrated that the component modelling is reliable and a recommended standard methodology for future x-ray calibration. Most importantly, this study demonstrated that even near the edge of a calibrated region, with strong variance of results from systematics, the computed final uncertainties accurately reflect the uncertainty of the measurement, even when modelled by a range of distinct optimisations.

The calibration methodology was thus demonstrated to be robust and gives reason for confidence in using the optimisation methods used to create the standards for V $K\beta$ and Cr $K\beta$ in Chapters 11 and 12. The results also strengthens confidence in the use of the calibration method in experiments to measure the energy of Lyman α lines of He-like medium atomic number ions at an EBIT that could be used to test QED.

Further work on in this Cr $K\beta$ data would be useful. Priorities for such work include a reanalysis of the data that enables further investigation of remaining systematics. This may be done via a separate of Mosplate theory calculation for each wedge position, enabling consistent fitting parameters for the calibration between wedge positions. Further, all wedge positions could be put in a single fit.

He-like Cr QED Lines

Finally, after the high accuracy spectrometer method outlined in Chapter 10 was validated in Chapter 13, it was applied to the He-like Cr data collected in the Oxford 2007 experiment. Again, these data were analysed at The University of Melbourne.

Summary

X-ray spectroscopic tests of QED using highly charged medium-Z ions have a history dating back to the early 1980s. Tests of QED with He-like ions have used the w , x , y and z lines of medium-Z elements. Analysis of the He-like literature showed disagreement as to whether there exists a significant discrepancy between the QED theoretical calculations and existing measurements. Within the w line measurements of the medium-Z ions, the He-like Cr w line was the most poorly determined. In order to provide further evidence for or against such a discrepancy, the w , x , y and z lines of He-like Cr were measured. This chapter presents an examination of these measurements and discusses preliminary estimates of the systematic errors that remain in the analysis. It then goes on to discuss the significance of the findings to current QED calculations.

Key Achievements

- The energy of the w line of He-like Cr was measured to be 5682.049(30)(200) eV, a factor of just under two improvement over previous measurements.
- The energies of the x , y and z lines of He-like Cr were measured for the first time. The energies were found to be 5664.425(73)(200) eV, 5654.232(68)(200) eV and 5626.305(42)(200) eV respectively.

Line	Peak # i	Integrated Area A_i (Counts)	Peak Position C_i (mm)	Lorentzian Width W_i (mm)
z	1	2175(63)	-6.3942(72)	0.151(26)
r	2	308(41)	-3.944(26)	-0.079(86)
q	3	1068(62)	-2.879(12)	0.167(49)
y	4	1194(56)	-1.549(12)	-0.220(42)
x	5	1030(48)	0.205(12)	-0.229(40)
w	6	3192(74)	3.2189(50)	-0.085(22)

Table 14.1: The fit parameters for the peaks of the EBIT Cr profile shown in Figure 14.1. The fit function was a sum of six Voigts with a shared Gaussian broadening and a constant background. The fitted background was $b = 3.82(41)$ counts, while the fitted Gaussian broadening was $\sigma = 0.2240(82)$ mm.

14.1 EBIT Cr Profile Modelling

Highly charged Cr ions were created with the EBIT in the Oxford 2007 experiment. In a 40 hour period, the EBIT was turned to maximise the flux of the He-like Cr w , x , y and z lines, while the spectrometer crystal angle, θ , was set to observe those lines. The wedge position was 16.40 mm. The data collected in this period were transformed into detector profile form.

The resulting profile was then fitted. The fit function was a sum of six Voigts with a common Gaussian width to model instrumental broadening, and a constant background. This function was defined by Equation 10.15. The detector profile, along with the fit and residuals, is shown in Figure 14.1. The resulting fitting parameters are shown in Table 14.1. The residuals indicated that the fit function modelled the structure of the data fairly well, though there was some structure not captured by the fit. The χ_r^2 of the fit was 1.3 with 318 degrees of freedom, implying if the model fit the data perfectly, the probability a new measurement of the spectrum with a subsequent fit with using same conditions, producing a higher χ_r^2 would be 0.00007. This is in accordance with the evident structure of the residuals and the high number of degrees of freedom of the fit.

In Figure 14.1, the peaks are labelled z , r , q , y , x and w . The z , y , x and w lines are transitions of He-like Cr, while the q and r lines are Li-like Cr transitions. The presence of Li-like ions the trap as well as He-like ions was expected.

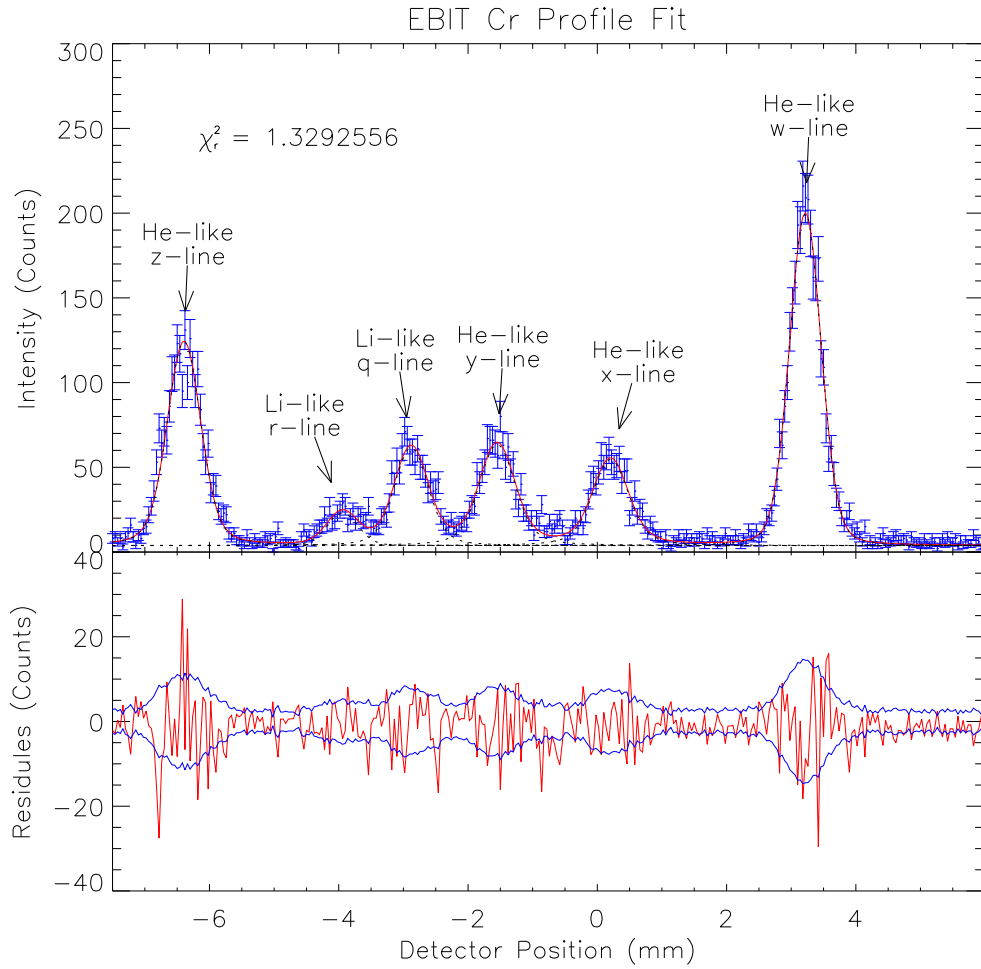


Figure 14.1: The fit of the spectral profile of highly ionised Cr trapped in the Oxford EBIT and the residuals of the fit. The blue curves on the residuals are the envelope of measurement uncertainties. The fit function was a sum of six Voigts with a shared Gaussian broadening and a constant background. The fit parameters are shown in Table 14.1. The χ_r^2 of 1.3 indicates this is a good fit though there is some structure in the residuals. The fitted background seems to be systematically low around the *w* line. Fits with linear and quadratic backgrounds were tried but they produced unphysical results with the background negative around the *z* line in both cases. The clinometer voltage was -2.00345747(90) V.

14.2 Dispersion Functions Used

Since the wedge was 16.40 mm from the crystal when the EBIT Cr spectrum was taken, calibrations based on only two series of characteristic radiation could be applied to the EBIT spectrum. These are the series with the same wedge position as the EBIT spectrum. These series were derived from the *prerun2* and *postrun* runs and were not pooled together.

The five optimised dispersion functions described in Section 13.3 were applied to the peak positions and clinometer voltage of the lines in the spectrum. One more optimisation measure was defined and also used, to try to tune the calibrations to the θ where the data were collected. The six optimisations, then, minimised the following measures:

- (a) The χ_r^2 value of the Ti K β peak energy measurements.
- (b) The sum of two values - (1) the χ_r^2 value of the Ti K β peak energy measurements, and (2) the χ_r^2 value of the V K β peak energy measurements.
- (c) The χ_r^2 value of the V K β peak energy measurements.
- (d) The sum of four values - (1) the χ_r^2 value of the Ti K β peak energy measurements, (2) the χ_r^2 value of the V K β peak energy measurements, (3) the χ_r^2 value of the Cr K β peak energy measurements, and (4) the χ_r^2 value of the clinometer calibration function fit which is a measure of the spread of the K α data around the literature values.
- (e) The sum of two values - (1) the χ_r^2 value of the V K β peak energy measurements, and (2) the χ_r^2 value of the Cr K β peak energy measurements.
- (f) The χ_r^2 value of the Cr K β peak energy measurements.

Optimisations of measures (a)-(d) and (f) were described in Section 13.3. Since the EBIT Cr spectrum was measured at only one detector arm angle, an optimisation based on the energy region of the EBIT Cr spectrum could not be performed. Measure (e) was defined to try to optimise the slope systematic for the EBIT Cr spectrum. The justification for this measure is that this spectrum has an energy half way between V K β and Cr K β . This measure minimising the combined variances of V K β and Cr K β may be appropriate.

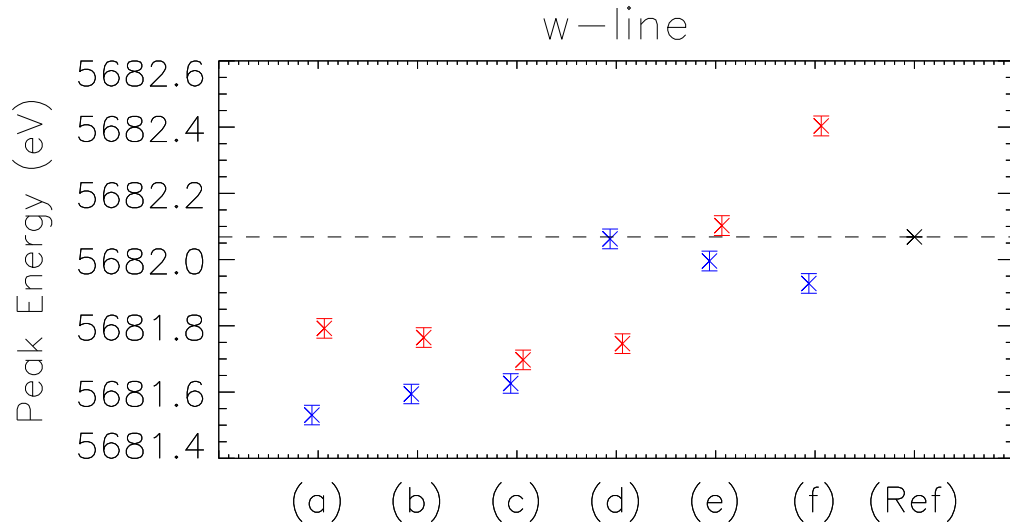


Figure 14.2: A He-like Cr w line energy comparison. The six calibration optimisations, (a)-(f), as defined in Section 14.2 and the literature value of Artemyev et al. [183], (Ref), are shown. Each optimisation has two points. The blue point is from the *prerun2* calibration while the red point is from the *postrun* calibration.

The six optimisations produced two relevant calibrations each, a *prerun2* calibration and a *postrun* calibration, for a total of twelve calibrations. Thus, for each peak of the EBIT spectrum, twelve energies were calculated.

14.3 He-like Cr Line Energies

The twelve calibrations were applied to the He-like Cr lines. The energy calculated from each of the calibrations, (a) to (f), for each of these lines, is shown in Figures 14.2 to 14.5. These figures also show the theory of Artemyev et al. [183] for comparison. Optimisation (e) was expected to produce the energy least affected by the slope systematic.

Table 14.2 shows theoretical energies of the He-like lines as well as the experimental energies generated from the two calibrations from optimisation (e). Six sources of uncertainty had to be assessed. These were (1) clinometer voltage error, (2) clinometer calibration function fit uncertainty, (3) the uncertainty in the peak position due to the spectrum fit, (4) the detector calibration function fit uncertainty, (5) the uncertainty in the distance from the EBIT trapping region to the crystal and (6) the systematic errors in the calibrations. The first five of these sources

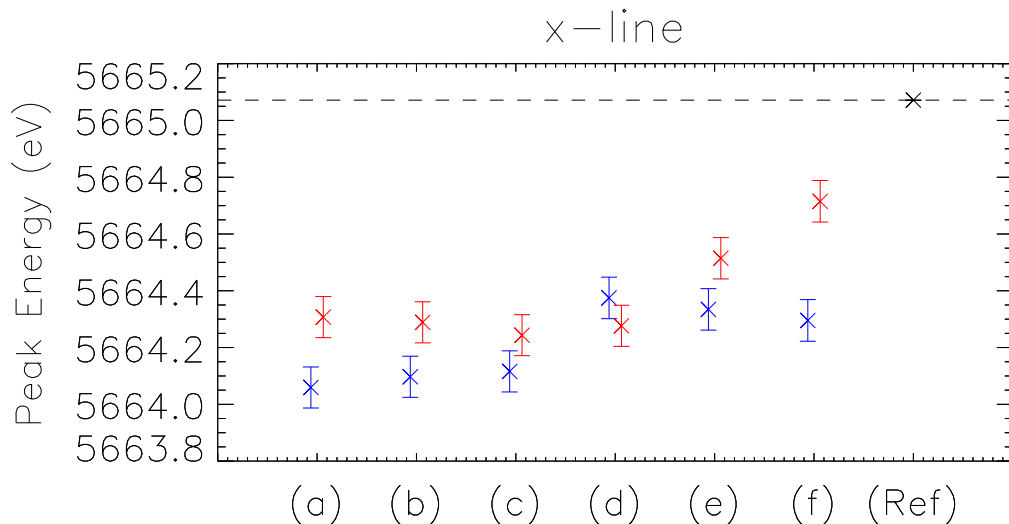


Figure 14.3: A He-like Cr x line energy comparison. The six calibration optimisations, (a)-(f), as defined in Section 14.2 and the literature value of Artemyev et al. [183], (Ref), are shown. Each optimisation has two points. The blue point is from the *prerun2* calibration while the red point is from the *postrun* calibration.

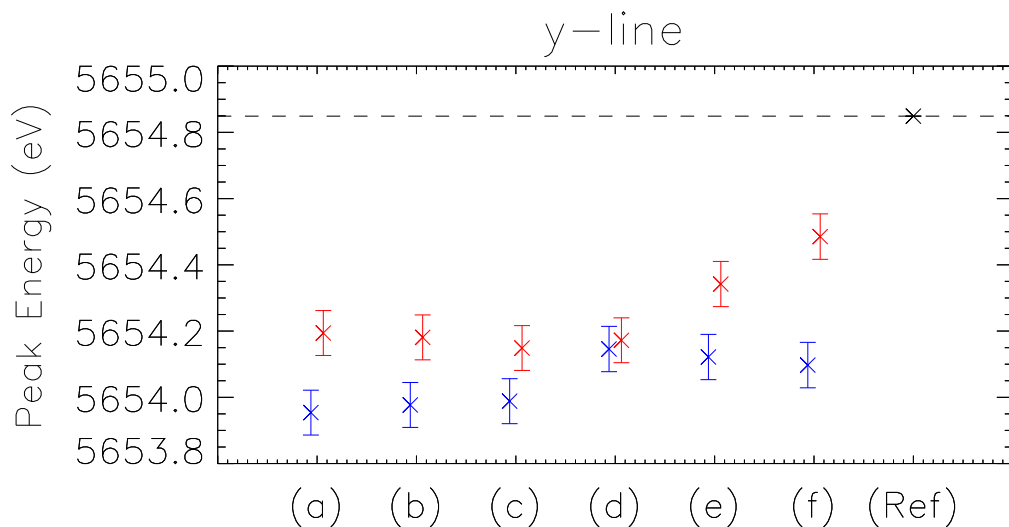


Figure 14.4: A He-like Cr y line energy comparison. The six calibration optimisations, (a)-(f), as defined in Section 14.2 and the literature value of Artemyev et al. [183], (Ref), are shown. Each optimisation has two points. The blue point is from the *prerun2* calibration while the red point is from the *postrun* calibration.

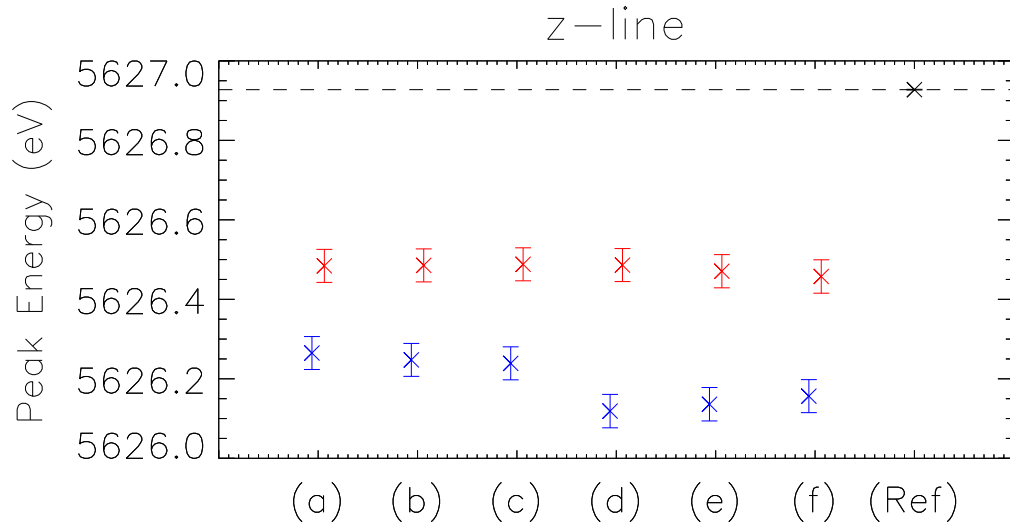


Figure 14.5: A He-like Cr z line energy comparison. The six calibration optimisations, (a)-(f), as defined in Section 14.2 and the literature value of Artemyev et al. [183], (Ref), are shown. Each optimisation has two points. The blue point is from the *prerun2* calibration while the red point is from the *postrun* calibration.

have a statistical basis. The sizes of the statistical uncertainties are shown in Table 14.3 for each of the He-like lines.

The systematic errors in the calibration were evident in Chapters 11 and 13 by the spread of energies. The standard deviation in energy being 0.17 eV for V $K\beta$ and 0.70 eV for Cr $K\beta$. These were the estimates for the systematic error uncertainties for a single spectrum. However, the associated energy uncertainty for the corpus of spectra was explicitly estimated by taking the standard error of the weighted mean energy for measurements (defined by Equation 10.18). This method is not possible for these EBIT data because only one profile was taken at one detector arm angle and wedge position.

In a preliminary sense, systematic estimates may be obtained in the following two ways. The first is to interpolate the systematic uncertainty for a single spectrum of the EBIT lines from nearby energies. The Cr EBIT spectrum is halfway between V $K\beta$ and Cr $K\beta$ in energy. This would result in a systematic uncertainty that is about halfway between 0.17 eV and 0.70 eV or about 0.435 eV. However, it could be as low as 0.17 eV. Alternately, one could assume that the spread of two energies within an optimisation about the mean represents a sample of the size of the systematic uncertainty. Thus for each line, the average spread of the optimisations would represent the systematic uncertainty. This method resulted

	Theoretical Line Energies			
	z	y	x	w
Theory [180] (eV)	5626.905	5654.829	5665.047	5682.046
Theory [181] (eV)	5626.983	5654.903	5665.126	5682.125
Theory [182] (eV)	5626.942	5654.869	5665.093	5682.080
Theory [183] (eV)	5626.928	5654.849	5665.071	5682.068
	<i>prerun2</i> Experimental Line Energies			
	z	y	x	w
Exp. Value (eV)	5626.136(42)	5654.122(68)	5664.334(73)	5681.996(30)
Exp. σ (ppm)	7.5	12	12	5.2
	<i>postrun</i> Experimental Line Energies			
	z	y	x	w
Exp. Value (eV)	5626.471(42)	5654.342(68)	5664.515(73)	5682.103(30)
Exp. σ (ppm)	7.4	12	12	5.2

Table 14.2: He-like Cr line energies. The theoretical values of Drake [180], Plante et al. [181], Cheng et al. [182] and Artemyev et al. [183] are presented. Two sets of experimental values are presented. They are both calculated from the peak positions from Table 14.1 and the clinometer voltage of -2.00345747(90) V. Equation 10.9 was applied to these values to calculate energy. The two sets come from two calibrations, one from the calibration series from the *prerun2* run with wedge position 16.40 mm, the second from the calibration series from the *postrun* run with wedge position 16.40 mm. These calibrations were optimised minimising measure (e) as defined in Section 14.2.

Uncertainty Source	Line Uncertainties (ppm)			
	z	y	x	w
Clinometer Voltage	0.18	0.12	0.12	0.14
Clinometer Calibration Fit	1.2	0.76	0.77	0.93
Spectrum Fit	7.4	12	12	5.1
Detector Function Fit	0.29	0.25	0.27	0.34
EBIT Distance	0.013	0.0088	0.0063	0.0038
Total	7.5	12	12	5.2

Table 14.3: He-like Cr lines energy error budget for the *prerun2* calibration. The total uncertainty for each line is the sum in quadrature of the sources since they are assumed to be independent. It is clear that the uncertainty from the spectrum fit dominates the other uncertainties. These uncertainties are the representation of the uncertainties in C_i in Table 14.1. This set of uncertainties is also representative of the *postrun* calibration.

Line	Energy (eV)	Energy Uncertainties			
		Statistical		Systematic	
		(eV)	(ppm)	(eV)	(ppm)
<i>w</i>	5682.049	0.030	5.2	0.200	35
<i>x</i>	5664.425	0.073	13	0.200	35
<i>y</i>	5654.232	0.068	12	0.200	35
<i>z</i>	5626.305	0.042	7.5	0.200	35

Table 14.4: The systematic uncertainties are of order 0.2 eV based on preliminary estimates.

in estimates of the following systematic uncertainties: 0.17 eV for the *w* line, 0.15 for the *x* line, 0.15 eV for the *y* line and 0.20 eV for the *z* line.

Since the first method resulted in systematic uncertainty estimates of 0.17 to 0.44 eV and the second method resulted in estimates of 0.15 to 0.20 eV, a consistent range of estimates would be approximately 0.17 eV to 0.20 eV. Therefore, the author currently estimates a 0.20 eV uncertainty to be associated with the systematic errors in the calibration (the high end of the consistent range of estimates). It is noted by the present author that further analysis of this is important.

The energies of the He-like Cr lines were taken to be the weighted mean of the two energies generated from optimisation method (e). These energies and associated uncertainty estimates are shown in Table 14.4. These constitute the first measurements of the *x*, *y* and *z* lines of He-like Cr.

The energy of the *w* line of He-like Cr was measured to be 5682.049(30)(200) eV. This is the best measurement of this line by a factor of just under two. The previous measurements of the *w* line energy were by Beiersdorfer et al. [195], with an energy of 5682.32(40) eV, and Aglitsky et al. [193] with an energy to 5682.66(52) eV. The theoretical value of Artemyev et al. [183] was 5682.068 eV. The measurement reported here and these other measurements and calculations are all consistent with each other to within one standard deviation.

The measured energies of the *x*, *y* and *z* lines were all between 2.9 and 3.2 standard deviations away from theory [180–183]. In particular, the disagreement with Artemyev [183] for these lines were 0.646 eV, 0.617 eV, 0.623 eV respectively. These correspond to 3.0, 2.9 and 3.0 standard deviation differences. These disagreements may be due to underestimates of systematic error, incomplete calculations, or of course, a problem with QED itself.

The pattern of discrepancies within these four lines (one agreement and three disagreements of similar size) makes it unlikely that the these disagreements can be explained by a simple linear error in the calibration from detector position to energy. Any calibration error would most likely have to be non-linear to explain the pattern of discrepancies. The present author is not aware at the time of writing of any experimental error that would produce such non-linearity. Thus, this pattern of discrepancy is regarded as evidence of incomplete calculations or a problem with QED itself.

14.4 Further Work

The work presented in this chapter is preliminary in the sense that the uncertainties in peak energy are dominated by systematic errors in the spectrometer calibration that should be able to be removed by reanalysis of the calibration data using modified processing. Such modifications would consist of those suggested in section 10.10 of Chapter 10. Restated and summarised, there modifications are: (1) the creation of calibrations based on DL and DU, to allow detailed cross checking of results, (2) the fitting of the angles, CC - BC, DU - CC, DL - CC, $(DU - BC)/2$, and $(DL - BC)/2$, to the experimental calibration θ data derived from peak position and energy, (3) the use of the correct wedge position in all theoretical Mosplate curved crystal calculations, (4) the inclusion of data from the two end wire segments of the detector, with a modified process to identify the bounding boxes associated with those wire segments, and (5) the simplification of the calibration function fitting process by fitting in energy space rather than an angle space. Refitting the Cr spectrum with a higher degree polynomial to model the background would also lead to a better fit.

The H-like Ti data taken with from the primary spectrometer of the NIST 2005 experiment would lead to another test of QED. As shown in Appendix A, there appears to be an adequate amount of data for such a purpose.

Conclusions and Further Work

Novel techniques and standards for x-ray spectrometry in three areas have been presented, followed by an x-ray spectroscopic test of QED, in accordance with the aims formulated for this research, as set out in Chapter 4. Conclusions arising from each of these studies and the implications of their results for further work have been discussed in respect of each study in the course of this thesis. The conclusions and implications for further research are now summarised.

15.1 Improvement of Accuracy in XAFS Data Analysis

In previous research, the standard technique of the analysis of X-ray Absorption Fine Structure (XAFS), used to determine the local structure of a material around an absorbing atom, has not taken experimental error bars into account. This means that the error bars that result from the previous analyses cannot be considered statistically valid.

A new method of XAFS analysis, which was implemented for the first time, was based on statistically valid χ_r^2 fitting that correctly propagates experimental error bars. To investigate current XAFS theory as well as the new method, the standard method and the new method were used to analyse XAFS derived from extremely high accuracy absolute mass attenuation data for molybdenum.

Models using 16 independent path coefficients, $S_{0,j}^2$, produced unphysical model parameters with both the standard analysis technique and χ_r^2 fitting technique, due in particular to the correlations between parameters. The simpler model with a single common path amplitude produced parameters in reasonable agreement with literature values when the fit was windowed to 7 peaks. This appears to constitute a more serious constraint upon the range of validity of the model than

previously believed, especially since this is the XAFS spectrum of a monatomic solid.

The χ_r^2 for every fit was over 90, clearly indicating a disagreement between theory and experiment. The pattern of residuals highlighted that the theoretical issue raised and limitations of the model are the dominant cause of the failure. The χ_r^2 for the unwindowed fit using the current analysis techniques was 3000. Subsequently to this work, the new χ_r^2 fitting and error propagation has been crucial in a number of ongoing studies. It enabled an rigorous and incisive stereochemical analysis of ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, using XAFS data [277]. The method has also allowed the identification of a discrepancy between FEFF and the XAFS of the K edge of silver [58].

15.2 Improvement of Cosmic Ray Filters for CCD Detectors

The second area explored in this set of studies was the analysis of pixelated detectors such as CCD detectors used in low count rate x-ray spectroscopic experiments, particularly, tests of QED at EBITs. In low count rate experiments, cosmic rays can be a strong signal compared to the QED signals of interest. Filtering out cosmic ray signals from such data would improve the precision of these experiments.

A cluster based method of filtering cosmic rays suitable for such data existed but did not reliably identify parts of cosmic ray tracks that were disconnected from the main track. A method based on linear correlation was proposed in this thesis. The method was compared and contrasted with the existing cluster based method as well as with a combination of both, using low flux Rydberg lines collected with a CCD detector at the NIST EBIT.

It was found that the new combined filter method was the strongest filter, and that the method was robust. A characterisation of the Rydberg series spectrum from H-like Ti was presented, using the combined filter method for cosmic ray filtering.

15.3 Improvement of X-ray Spectrometer Dispersion Function Analysis

The third area investigated in this research series was the definition and use of calibration standards for x-ray spectrometry, particularly with a view to spectroscopic QED experiments. Spectral profiles of characteristic radiation, such as $K\alpha$ and $K\beta$ profiles, are a good choice for use as calibration standards, as they are simple to produce and sharp. However, no high accuracy characterisations of V $K\beta$ and Ti $K\beta$ existed that could be used as standards. Therefore, high accuracy characterisations of V $K\beta$ and Ti $K\beta$ were sought.

Measurements of the profiles of V $K\beta$ and Ti $K\beta$ were made using a Johann curved crystal spectrometer with an adjustable detector arm angle and calibrated with $K\alpha$ radiation from elements with atomic numbers 22 through 26. A Backgammon detector was used for the collection of the profiles, while clinometers were used to measure detector arm angle. The calibration analysis of the spectrometer system involved independent calibrations of the Backgammon detector and clinometers. Variations of the calibration method were examined to assess and minimise systematic errors.

New high accuracy characterisations of the V $K\beta$ and Ti $K\beta$ spectral profiles were presented. These characterisations are transferable to other spectrometer systems and thus define new standards for x-ray spectroscopy.

The peak energy of V $K\beta$ was found to be 5426.962(15) eV. This is an improvement in uncertainty by a factor of 4.7 over prior work. The peak energy of Ti $K\beta$ was found to be 4931.966(22) eV, an improvement in uncertainty by a factor of 2.6 over the previous best reported result. Analysis of the variations of the calibration method as applied to Cr $K\beta$ show that this method produces robust results, validating the error bars for V $K\beta$ and Ti $K\beta$.

15.4 Test QED by Measuring the Energies of He-like Cr Lines

The final area that was examined in the course of this research was the testing of QED through measurement of the Lamb shift of medium atomic number H-like and He-like ions. Recently, there has been disagreement within the literature about whether the preponderance of evidence from He-like ions demonstrates a disagreement with leading QED calculations. The w line of He-like Cr has been the most poorly determined in this class of system, while the x , y and z lines of He-like Cr have not been reported at all. The w , x , y and z lines of He-like Cr were measured in order to test QED.

A Measurement of the profiles of the x , y and z lines of He-like Cr was made using a Johann curved crystal spectrometer with an adjustable detector arm angle and calibrated with $K\alpha$ radiation from elements with atomic numbers 22 through 26. This was performed in the same experiment as the V $K\beta$ and Ti $K\beta$ characterizations.

New measurements of the w , x , y and z lines of He-like Cr were presented. These measurements are the most precise results for these lines to date.

The energy of the w line of He-like Cr was measured to be 5682.049(30)(200) eV, a factor of just under two improvement over previous measurements. The energies of the x , y and z lines were found to be 5664.425(73)(200) eV, 5654.232(68)(200) eV and 5626.305(42)(200) eV respectively. The w line was in agreement with QED theory. However the x , y and z line measurements disagree with theory by about 3.0σ .

15.5 Further Work

This thesis suggests a number of areas of future study. These areas will now be discussed.

For x-ray spectrometry of emission processes, further improvements to the method of analysis can be made in the future. (1) The slope systematic was a major cause of uncertainty in the Oxford 2007 results in this work. Its cause is currently

unknown. The use of more than one clinometer in the spectrometer calibration function fitting can investigate this. (2) In this work, one wedge position was used in the theoretical Mosplate curved crystal calculations to model the spectrometer system, even when the wedge position of the experiment did not match. It was assumed that the spectrometer calibration functions were flexible enough to compensate for this mismatch. In future work, the correct wedge position in all theoretical Mosplate curved crystal calculations can be used in order to do a combined fit for separate wedge positions. These improvements would allow the further examination of causes of the variances between wedge positions evident in the $K\beta$ measurements. (3) Further investigation of the accuracy of Mosplate is advisable via a study of how Mosplate calculations convergence with decreases in the grid step sizes that define the sampling of the rays emitted from the source and then diffracted by the crystal. (4) In particular, an investigation detailing the accuracy and efficacy of Mosplate as seen in this thesis and earlier is quite important.

These improvements could be applied to a number of existing data sets to further test QED. (5) The investigation and elimination of the systematic errors evident in the calibration of the Oxford 2007 experiment through reanalysis would be useful. (6) The analysis of the H-like Ti data collected at the NIST NIST 2005 experiment would also produce a test of QED (see Appendix A for a description of the extent of this data). The new calibration standards defined in this work can be employed in the calibration of the NIST EBIT 2005 data. This calibration will use a calibration analysis method based on this thesis. (7) Additional tests of QED through the spectroscopy of H-like and He-like lines are required to probe the theory at a deeper level. (8) Further theoretical work will be necessary to investigate current discrepancies between theory and experiment.

(9) Further analysis of the characterisation of the H-like Ti Rydberg lines could be performed in the future using plasma physics theory. (10) The combined filter method of cosmic ray filtering could also be applied to other data from the NIST 2005 experiment, in order to study polarisation in the Lyman α lines of H-like Ti. (11) It is recommended that future work using low-flux x-ray sources with CCD detectors should use a method of filtering out cosmic rays that includes the identification of cosmic rays through a linear correlation, in order to identify parts of cosmic ray tracks that are disconnected from the main track.

(12) In XAFS, improved theory for the whole range of Mo data has the potential to improve agreement with experimental structure by a further factor of $\sqrt{3,000} \simeq 55$. (13) More generally, the new method of XAFS analysis should be used in any case where the XAFS data has measured uncertainties.

Study (5), which includes studies (1) to (4) as antecedents, should be the first priority. Study (6) should follow, then studies (9) and (10). In the longer term, studies (7), (8), and (11) to (13) would further the fields of x-ray spectrometry and tests of QED a great deal.

Bibliography

- [1] TZ Ezekiel. *Determining The 1s Lamb Shift In Medium-Z Highly Charged Ions*. PhD thesis, University of Oxford, 2007.
- [2] M von Laue. *History of physics*. Academic Press Inc., 1950.
- [3] G Waldman. *Introduction to light: The physics of light, vision, and color*. Courier Corporation, 2002.
- [4] FH Allen, O Kennard, DG Watson, L Brammer, AG Orpen, and R Taylor. *International Tables for Crystallography, Vol. C, edited by AJC Wilson*. Dordrecht: Kluwer Academic Publishers, 1995.
- [5] WH Bragg and WL Bragg. The reflection of X-rays by crystals. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, pages 428–438, 1913.
- [6] JC Maxwell. A dynamical theory of the electromagnetic field. *Philosophical Transactions of the Royal Society of London*, pages 459–512, 1865.
- [7] JD Jackson. *Classical electrodynamics 2nd edition*. John Wiley & Sons, Ind, 1975.
- [8] CG Darwin. XXXIV. The theory of X-ray reflexion. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 27(158):315–333, 1914.
- [9] CG Darwin. LXXVIII. The theory of X-ray reflexion. Part II. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 27(160):675–690, 1914.
- [10] JA Bearden. X-ray wavelengths. *Reviews of Modern Physics*, 39(1):78, 1967.
- [11] PP Ewald. Zur Begründung der Kristalloptik. *Annalen der Physik*, 354(1): 1–38, 1916.
- [12] M von Laue. Die dynamische Theorie der Röntgenstrahlinterferenzen in neuer Form. In *Ergebnisse der Exakten Naturwissenschaften*, pages 133–158. Springer, 1931.

- [13] BW Batterman and H Cole. Dynamical diffraction of X rays by perfect crystals. *Reviews of Modern Physics*, 36(3):681, 1964.
- [14] WH Zachariasen. *Theory of X-Ray Diffraction in Crystals*. John Wiley and Sons, New York, 1945.
- [15] A Caticha and S Caticha-Ellis. Dynamical theory of x-ray diffraction at Bragg angles near $\pi/2$. *Physical Review B*, 25(2):971, 1982.
- [16] S Takagi. Dynamical theory of diffraction applicable to crystals with any kind of small distortion. *Acta Crystallographica*, 15(12):1311–1312, 1962.
- [17] S Takagi. A dynamical theory of diffraction for a distorted crystal. *Journal of the Physical Society of Japan*, 26(5):1239–1253, 1969.
- [18] D Taupin. Théorie dynamique de la diffraction des rayons X par les cristaux déformés. *Bulletin De La Societe Francaise Mineralogie Et De Cristallographie*, 87(4):469, 1964.
- [19] N Kato. Statistical dynamical theory of crystal diffraction. I. General formulation. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, 36(5):763–769, 1980.
- [20] FN Chukhovskii, KT Gabrielyan, and PV Petrashen. The dynamical theory of X-ray Bragg diffraction from a crystal with a uniform strain gradient. The Green–Riemann functions. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, 34(4):610–621, 1978.
- [21] FN Chukhovskii, KT Gabrielyan, EN Kislovskii, and IV Prokopenko. Experimental and Theoretical Study of the Elastic Bending Effect on (111) Bragg Diffraction in Silicon Crystals. *physica status solidi (a)*, 103(2):381–387, 1987.
- [22] FN Chukhovskii and C Malgrange. Theoretical study of X-ray diffraction in homogeneously bent crystals—the Bragg case. *Acta Crystallographica Section A: Foundations of Crystallography*, 45(10):732–738, 1989.
- [23] G Green. *An Essay on the Application of Mathematical Analysis to the Theories of Electricity and Magnetism*. Self Published, 1828.

- [24] VI Punegov, AP Petrakov, and NA Tikhonov. X-Ray Diffraction on Laser Disturbed Near-Surface Crystal Layers. *physica status solidi (a)*, 122(2): 449–458, 1990.
- [25] R Caciuffo, S Melone, F Rustichelli, and A Boeuf. Monochromators for x-ray synchrotron radiation. *Physics Reports*, 152(1):1–71, 1987.
- [26] CT Chantler. X-ray diffraction of bent crystals in Bragg geometry. I. Perfect-crystal modelling. *Journal of Applied Crystallography*, 25(6):674–693, 1992.
- [27] D Paterson, CT Chantler, CQ Tran, LT Hudson, FG Serpa, and RD Deslattes. Absolute calibration of an x-ray spectrometer on the NIST electron-beam ion trap: control, design and systematics. *Physica Scripta*, 1997(T73): 400, 1997.
- [28] CT Chantler. X-ray diffraction of bent crystals in Bragg geometry. II. Non-ideally imperfect crystals, modelling and results. *Journal of Applied Crystallography*, 25(6):694–713, 1992.
- [29] M Sanchez del Rio, C Ferrero, and V Mocella. Computer simulation of bent perfect crystal diffraction profiles. In *SPIE's International Symposium on Optical Science, Engineering, and Instrumentation*, volume 3151, pages 312–323, 1997.
- [30] MS del Rio and RJ Dejus. XOP: a multiplatform graphical user interface for synchrotron radiation spectral and optics calculations. In *Optical Science, Engineering and Instrumentation'97*, pages 148–157. International Society for Optics and Photonics, 1997.
- [31] MS del Rio and RJ Dejus. XOP: Recent developments. In *SPIE's International Symposium on Optical Science, Engineering, and Instrumentation*, pages 340–345. International Society for Optics and Photonics, 1998.
- [32] MS del Río and RJ Dejus. XOP v2. 4: recent developments of the x-ray optics software toolkit. In *SPIE Optical Engineering + Applications*, pages 814115–814115. International Society for Optics and Photonics, 2011.
- [33] Xop 2.3: X-ray Optics. http://ftp.esrf.eu/scisoft/xop2.3/doc/WebHelp/functions/x_ray_optics.htm.

- [34] M Sanchez del Rio, N Perez-Bocanegra, X Shi, V Honkimäki, and L Zhang. Simulation of X-ray diffraction profiles for bent anisotropic crystals. *Journal of Applied Crystallography*, 48(2):477–491, 2015.
- [35] RS von Bordwehr. A history of X-ray absorption fine structure. In *Annales de Physique*, volume 14, pages 377–465. Les Editions de Physique, 1989.
- [36] W Kossel. Zum Bau der Röntgenspektren. *Zeitschrift für Physik A Hadrons and Nuclei*, 1(1):119–134, 1920.
- [37] R de L Kronig. Zur Theorie der Feinstruktur in den Röntgenabsorptionsspektren. III. *Zeitschrift für Physik A Hadrons and Nuclei*, 75(7):468–475, 1932.
- [38] R de L Kronig. Zur Theorie der Feinstruktur in den Röntgenabsorptionsspektren. II. *Zeitschrift für Physik*, 75(3-4):191–210, 1932.
- [39] H Petersen. Zur Theorie der Röntgenabsorption molekularer Gase. *Zeitschrift für Physik*, 76(11-12):768–776, 1932.
- [40] H Petersen. Zur Theorie der Röntgenabsorption molekularer Gase. II. *Zeitschrift für Physik*, 80(3-4):258–266, 1933.
- [41] H Petersen. *La structure fine de l'absorption des rayons X par les gaz moléculaires*. PhD thesis, University of Groningen, 1933.
- [42] AI Kostarev. Zhur. eksptl. teoret. *Fiz. SSSR*, 11(60):19, 1941.
- [43] DE Sayers, FW Lytle, and EA Stern. Point scattering theory of X-ray K-absorption fine structure. *Advances in X-Ray Analysis*, 13:248–271, 1970.
- [44] DE Sayers, EA Stern, and FW Lytle. New technique for investigating non-crystalline structures: Fourier analysis of the extended X-rayabsorption fine structure. *Physical Review Letters*, 27(18):1204, 1971.
- [45] EA Stern. Theory of the extended x-ray-absorption fine structure. *Physical Review B*, 10(8):3027–3037, 1974.
- [46] CA Ashley and S Doniach. Theory of extended X-ray absorption edge fine structure (EXAFS) in crystalline solids. *Physical Review B*, 11:1279–1288, 1975.

- [47] PA Lee. Theory of the extended X-ray absorption fine structure. *Physical Review B*, 11:2795–2811, 1975.
- [48] JJ Rehr, EA Stern, RL Martin, and ER Davidson. Extended x-ray-absorption fine-structure amplitudes Wave-function relaxation and chemical effects. *Physical Review B*, 17(2):560, 1978.
- [49] JJ Rehr, J Mustre de Leon, SI Zabinsky, and RC Albers. Theoretical X-ray absorption fine structure standards. *Journal of the American Chemical Society*, 113(14):5135–5140, 1991.
- [50] SI Zabinsky, JJ Rehr, A Ankudinov, RC Albers, and MJ Eller. Multiple-scattering calculations of X-ray-absorption spectra. *Physical Review B*, 52(4):2995–3009, 1995.
- [51] HK Wagenfeld. The angular dependence of X-ray dispersion corrections. *Zeitschrift für Physik B Condensed Matter*, 65(4):437–441, 1987.
- [52] CT Chantler. Theoretical form factor, attenuation, and scattering tabulation for $Z = 1$ –92 from $E = 1$ –10 eV to $E = 0.4$ –1.0 MeV. *Journal of Physical and Chemical Reference Data*, 24(1):71–643, 1995.
- [53] CT Chantler. Detailed tabulation of atomic form factors, photoelectric absorption and scattering cross section, and mass attenuation coefficients in the vicinity of absorption edges in the soft X-ray ($Z = 30$ –36, $Z = 60$ –89, $E = 0.1$ keV–10 keV), addressing convergence issues of earlier work. *Journal of Physical and Chemical Reference Data*, 29(4):597–1056, 2000.
- [54] A Mihelic, A Kodre, I Arcon, and JP Gomilsek. High-resolution X-ray absorption spectrometry of atomic vapors. *Acta Chimica Slovenica*, 51:33–38, 2004.
- [55] CQ Tran, CT Chantler, Z Barnea, MD De Jonge, BB Dhal, CTY Chung, D Paterson, and J Wang. Measurement of the x-ray mass attenuation coefficient of silver using the x-ray-extended range technique. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 38(1):89, 2004.
- [56] MD de Jonge, CQ Tran, CT Chantler, Z Barnea, BB Dhal, DJ Cookson, WK Lee, and A Mashayekhiand. Measurement of the x-ray mass attenuation coefficient and determination of the imaginary component of the atomic

- form-factor of molybdenum over the energy range of 13.5–41.5 keV. *Physical Review A*, 71:032702, 2005.
- [57] MD de Jonge, CQ Tran, CT Chantler, Z Barnea, BB Dhal, D Paterson, EP Kanter, SH Southworth, L Young, MA Beno, et al. Measurement of the x-ray mass attenuation coefficient and determination of the imaginary component of the atomic form factor of tin over the energy range of 29–60 keV. *Physical Review A*, 75(3):032702, 2007.
- [58] LJ Tantau, CT Chantler, JD Bourke, MT Islam, AT Payne, NA Rae, and CQ Tran. Structure determination from XAFS using high-accuracy measurements of x-ray mass attenuation coefficients of silver, 11 keV–28 keV, and development of an all-energies approach to local dynamical analysis of bond length, revealing variation of effective thermal contributions across the XAFS spectrum. *Journal of Physics: Condensed Matter*, 27(26):266301, 2015.
- [59] M Newville. IFEFFIT: interactive EXAFS analysis and FEFF fitting. *Journal of Synchrotron Radiation*, 8:322–324, 2001.
- [60] CT Chantler, JA Lowe, and IP Grant. Multiconfiguration Dirac-Fock calculations in open-shell atoms: Convergence methods and satellite spectra of the copper K α photoemission spectrum. *Physical Review A*, 82(5):052505, 2010.
- [61] JA Bearden. *X-Ray Wavelengths*. US Atomic Energy Commission, Division of Technical Information Extension, 1964.
- [62] JP Desclaux. Relativistic Dirac-Fock expectation values for atoms with $Z=1$ to $Z=120$. *Atomic Data and Nuclear Data Tables*, 12(4):311–406, 1973.
- [63] RD Deslattes, EG Kessler, P Indelicato, L de Billy, E Lindroth, and J Anton. X-ray transition energies: new approach to a comprehensive evaluation. *Reviews of Modern Physics*, 75(1):35–99, 2003.
- [64] P Indelicato, S Boucard, and E Lindroth. Relativistic and many-body effects in K, L, and M shell ionization energy for elements with the determination of the 1s Lamb shift for heavy elements. *The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics*, 3(1):29–41, 1998.

- [65] T Mooney, E Lindroth, P Indelicato, EG Kessler Jr, and RD Deslattes. Precision measurements of K and L transitions in xenon: Experiment and theory for the K, L, and M levels. *Physical Review A*, 45(3):1531, 1992.
- [66] IP Grant. Relativistic calculation of atomic structures. *Advances in Physics*, 19(82):747–811, 1970.
- [67] FA Parpia, CF Fischer, and IP Grant. GRASP92: A package for large-scale relativistic atomic structure calculations. *Computer Physics Communications*, 94(2):249–271, 1996.
- [68] CF Fischer, G Gaigalas, and Y Ralchenko. Some corrections to GRASP92. *Computer physics communications*, 175(11):738–744, 2006.
- [69] RD Deslattes and A Henins. X-ray to visible wavelength ratios. *Physical Review Letters*, 31(16):972, 1973.
- [70] EG Kessler, A Henins, L Nielsen, RD Deslattes, and M Arif. Precision comparison of the lattice parameters of silicon monocrystals. *Journal of research of the National Institute of Standards and Technology*, 99(1), 1994.
- [71] P Becker, K Dorenwendt, G Ebeling, R Lauer, W Lucas, R Probst, HJ Rademacher, G Reim, P Seyfried, and H Siegert. Absolute measurement of the (220) lattice plane spacing in a silicon crystal. *Physical Review Letters*, 46(23):1540, 1981.
- [72] K Nakayama, H Fujimoto, M Tanaka, and K Kuroda. Silicon lattice measurement with an improved X-ray/optical interferometer. *IEEE transactions on instrumentation and measurement*, 42(2):401–404, 1993.
- [73] E Massa, G Mana, U Kuetgens, and L Ferroglio. Measurement of the $\{2\ 2\ 0\}$ lattice-plane spacing of a ^{28}Si x-ray interferometer. *Metrologia*, 48(2):S37, 2011.
- [74] S Galambosi, H Sutinen, A Mattila, K Hämäläinen, R Sharon, CC Kao, and M Deutsch. Near-threshold multielectronic effects in the Cu $K\alpha_{1,2}$ x-ray spectrum. *Physical Review A*, 67(2):022510, 2003.
- [75] M Fritsch, CC Kao, K Hämäläinen, O Gang, E Förster, and M Deutsch. Evolution of the Cu $K\alpha_{3,4}$ satellites from threshold to saturation. *Physical Review A*, 57(3):1686, 1998.

- [76] M Deutsch, O Gang, K Hämäläinen, and CC Kao. Onset and Near Threshold Evolution of the Cu $K\alpha$ X-Ray Satellites. *Physical Review Letters*, 76(14): 2424–2427, 1996.
- [77] CT Chantler, JA Lowe, and IP Grant. High-accuracy reconstruction of titanium x-ray photoemission spectra, including relative intensities, asymmetry and satellites, and ab initio determination of shake magnitudes for transition metals. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 46: 015002, 2012.
- [78] M Deutsch, G Hölzer, J Härtwig, J Wolf, M Fritsch, and E Förster. $K\alpha$ and $K\beta$ x-ray emission spectra of copper. *Physical Review A*, 51(1):283–296, 1995.
- [79] G Hölzer, M Fritsch, M Deutsch, J Härtwig, and E Förster. $K\alpha_{1,2}$ and $K\beta_{1,3}$ x-ray emission lines of the 3d transition metals. *Physical Review A*, 56(6): 4554–4568, 1997.
- [80] LF Smale, CT Chantler, JA Kimpton, DN Crosby, and MN Kinnane. Characterization of $K\beta$ spectral profile for vanadium. *Physical Review A*, 87: 022512–1–7, 2013.
- [81] CT Chantler, LF Smale, JA Kimpton, DN Crosby, MN Kinnane, and AJ Illig. Characterization of Titanium $K\beta$ spectral profile. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 46:145601–1–10, 2013.
- [82] AJ Illig, CT Chantler, and AT Payne. Voigt Profile Characterisation of Copper $K\alpha$. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 46:235001–1–11, 2013.
- [83] J Schweppe, RD Deslattes, T Mooney, and CJ Powell. Accurate measurement of Mg and Al $K\alpha$ 1, 2 X-ray energy profiles. *Journal of Electron Spectroscopy and Related Phenomena*, 67(3):463–478, 1994.
- [84] DF Anagnostopoulos, R Sharon, D Gotta, and M Deutsch. $K\alpha$ and $K\beta$ x-ray emission spectra of metallic scandium. *Physical Review A*, 60(3):2018–2033, 1999.
- [85] DF Anagnostopoulos, D Gotta, P Indelicato, and LM Simons. Low-Energy X-Ray Standards from Hydrogenlike Pionic Atoms. *Physical Review Letters*, 91(24):240801, 2003.

- [86] CT Chantler, MN Kinnane, CH Su, and JA Kimpton. Characterization of $K\alpha$ spectral profiles for vanadium, component redetermination for scandium, titanium, chromium, and manganese, and development of satellite structure for $Z = 21$ to $Z = 25$. *Physical Review A*, 73(1):012508, 2006.
- [87] S Raj, HC Padhi, P Palit, DK Basa, M Polasik, and F Pawłowski. Relative K x-ray intensity studies of the valence electronic structure of 3d transition metals. *Physical Review B*, 65(19):193105, 2002.
- [88] O Sogut, E Büyükkasap, and H Erdoğan. Chemical-effect variation of $K\beta/K\alpha$ X-ray intensity ratios in 3d elements. *Radiation Physics and Chemistry*, 64(5):343–348, 2002.
- [89] S Raj, HC Padhi, DK Basa, M Polasik, and Pawowski F. $K\beta$ -to- $K\alpha$ X-ray intensity ratio studies on the changes of valence electronic structures of Ti, V, Cr, and Co in their disilicide compounds. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 152(4):417 – 424, 1999.
- [90] HC Padhi, CR Bhuinya, and BB Dhal. Influence of solid-state effects on the $K\beta/K\alpha$ intensity ratios of Ti and V in TiB_2 , VB_2 and VN. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 26(23):4465, 1993.
- [91] S Fazinić, M Jakšić, L Mandić, and J Dobrinić. Chemical dependence of second-order radiative contributions in the $K\beta$ x-ray spectra of vanadium and its compounds. *Physical Review A*, 74(6):062501, 2006.
- [92] SP Limandri, AC Carreras, RD Bonetto, and JC Trincavelli. $K\beta$ satellite and forbidden transitions in elements with $12 \leq Z \leq 30$ induced by electron impact. *Physical Review A*, 81:012504, 2010.
- [93] M Siegbahn and V Dolejšek. Erhöhung der Meßgenauigkeit innerhalb der Röntgenspektren. II. *Zeitschrift für Physik A Hadrons and Nuclei*, 10(1):159–168, 1922.
- [94] S von Friesen. Präzisionsmessungen in der K-Serie der Elemente Titan und Vanadium. *Zeitschrift für Physik*, 58(11-12):781–793, 1929.
- [95] JA Bearden and CH Shaw. Shapes and wavelengths of K series lines of elements ti 22 to Ge 32. *Physical Review*, 48(1):18, 1935.

- [96] AS Koster and H Mendel. X-ray $K\beta$ emission spectra and energy levels of compounds of 3D-transition metalsI: oxides. *Journal of Physics and Chemistry of Solids*, 31(11):2511–2522, 1970.
- [97] S Morita and J Fujita. $K\beta$ x-ray transition energies of M-shell-ionized ions of Ti through Ni in a plasma. *Physical Review A*, 31(5):3299, 1985.
- [98] M Ursic, M Kavcic, and M Budnar. Second order radiative contributions in the $K\beta_{1,3}$ X-ray spectra of 3d transition metals and their dependence on the chemical state of the element. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 211(1):7–14, 2003.
- [99] L Mandić, S Fazinić, and M Jakšić. Chemical effects on the $K\beta$ and $K\beta_2$, 5 x-ray lines of titanium and its compounds. *Physical Review A*, 80(4):042519, 2009.
- [100] MA Levine, RE Marrs, JR Henderson, DA Knapp, and MB Schneider. The electron beam ion trap: A new instrument for atomic physics measurements. *Physica Scripta*, 1988(T22):157, 1988.
- [101] MA Levine, RE Marrs, JN Bardsley, P Beiersdorfer, CL Bennett, MH Chen, T Cowan, D Dietrich, JR Henderson, DA Knapp, et al. The use of an electron beam ion trap in the study of highly charged ions. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 43(3):431–440, 1989.
- [102] WS Boyle and GE Smith. Charge coupled semiconductor devices. *Bell System Technical Journal*, 49(4):587–593, 1970.
- [103] D Groom. Cosmic rays and other nonsense in astronomical CCD imagers. *Experimental Astronomy*, 14(1):45–55, 2002.
- [104] CT Chantler. Discrepancies in quantum electro-dynamics. *Radiation Physics and Chemistry*, 71:611–617, 2004.
- [105] PG Van Dokkum. Cosmic-ray rejection by Laplacian edge detection. *Publications of the Astronomical Society of the Pacific*, 113(789):1420, 2001.
- [106] W Pych. A fast algorithm for cosmic-ray removal from single images. *Publications of the Astronomical Society of the Pacific*, 116(816):148, 2004.

- [107] M Donahue, CA Scharf, J Mack, YP Lee, M Postman, P Rosati, M Dickinson, GM Voit, and JT Stocke. Distant Cluster Hunting. II. A Comparison of X-Ray and Optical Cluster Detection Techniques and Catalogs from the ROSAT Optical X-Ray Survey. *The Astrophysical Journal*, 569:689–719, 2002.
- [108] LT Hudson, JD Gillaspy, JM Pomeroy, CI Szabo, JN Tan, B Radics, E Takacs, CT Chantler, JA Kimpton, MN Kinnane, and LF Smale. Detection of faint X-ray spectral features using wavelength, energy, and spatial discrimination techniques. *Nuclear Instruments and Methods in Physics Research A*, 580:33–36, 2007.
- [109] ER Davies. *Machine vision: theory, algorithms, practicalities*. Elsevier, 2004.
- [110] PVC Hough. Method and means for recognizing complex patterns. U.S. Patent 3,069,654, 1962.
- [111] RO Duda and PE Hart. Use of the Hough transformation to detect lines and curves in pictures. *Communications of the ACM*, 15(1):11–15, 1972. ISSN 0001-0782.
- [112] JR Rydberg. The New Series in the Spectrum of Hydrogen. *The Astrophysical Journal*, 6:233, 1897.
- [113] JJ Balmer. Notiz über die Spectrallinien des Wasserstoffs. *Annalen der Physik*, 261(5):80–87, 1885.
- [114] N Bohr. I. On the constitution of atoms and molecules. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 26(151):1–25, 1913.
- [115] A Sommerfeld. Zur quantentheorie der spektrallinien. *Annalen der Physik*, 356(17):1–94, 1916.
- [116] W Wilson. LXXXIII. The quantum-theory of radiation and line spectra. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 29(174):795–802, 1915.
- [117] L De Broglie. *Thèses. Recherches sur la théorie des quanta*. PhD thesis, Universit de Paris, 1924.

- [118] E Schrödinger. Quantisierung als eigenwertproblem. *Annalen der Physik*, 385(13):437–490, 1926.
- [119] E Schrödinger. Quantization as an eigenvalue problem. *Annalen der Physik*, 79(4):361–376, 1926.
- [120] DR Hartree. The wave mechanics of an atom with a non-Coulomb central field. Part I. Theory and methods. In *Mathematical Proceedings of the Cambridge Philosophical Society*, volume 24, pages 89–110. Cambridge Univ Press, 1928.
- [121] V Fock. Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems. *Zeitschrift für Physik*, 61(1-2):126–148, 1930.
- [122] JC Slater. Note on Hartree’s method. *Physical Review*, 35(2):210, 1930.
- [123] C Froese-Fischer and T Brage. *Computational atomic structure: an MCHF approach*. CRC Press, 1997.
- [124] CF Fischer. A multi-configuration Hartree-Fock program. *Computer Physics Communications*, 1(3):151–166, 1970.
- [125] CF Fischer. A multi-configuration Hartree-Fock program with improved stability. *Computer Physics Communications*, 4(1):107–116, 1972.
- [126] CF Fischer. Average-energy-of-configuration Hartree-Fock results for the atoms helium to radon charlotte froese fischer. *Atomic Data and Nuclear Data Tables*, 4:301–399, 1972.
- [127] PAM Dirac. The quantum theory of the electron. In *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, volume 117, pages 610–624. The Royal Society, 1928.
- [128] W Gordon. Die Energieniveaus des Wasserstoffatoms nach der Diracschen Quantentheorie des Elektrons. *Zeitschrift für Physik A Hadrons and Nuclei*, 48(1):11–14, 1928.
- [129] B Swirles. The relativistic self-consistent field. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 152(877): 625–649, 1935.

- [130] PAM Dirac. The quantum theory of the emission and absorption of radiation. In *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, volume 114, pages 243–265. The Royal Society, 1927.
- [131] J Schwinger. Quantum electrodynamics. I. A covariant formulation. *Physical Review*, 74(10):1439, 1948.
- [132] WE Lamb Jr and RC Retherford. Fine structure of the hydrogen atom by a microwave method. *Physical Review*, 72(3):241, 1947.
- [133] Charles Schwartz. Lamb shift in the helium atom. *Physical Review*, 123(5):1700, 1961.
- [134] PJ Mohr. Lamb shift in a strong Coulomb potential. *Physical Review Letters*, 34(16):1050, 1975.
- [135] J Schweppe, A Belkacem, L Blumenfeld, Nelson Claytor, B Feinberg, Harvey Gould, VE Kostroun, L Levy, S Misawa, JR Mowat, et al. Measurement of the Lamb shift in lithiumlike uranium ($U\ 8\ 9+$). *Physical Review Letters*, 66(11):1434, 1991.
- [136] S Tomonaga. On a relativistically invariant formulation of the quantum theory of wave fields. *Progress of Theoretical Physics*, 1(2):27–42, 1946.
- [137] J Schwinger. Quantum electrodynamics. II. Vacuum polarization and self-energy. *Physical Review*, 75(4):651, 1949.
- [138] J Schwinger. Quantum electrodynamics. III. The electromagnetic properties of the electronradiative corrections to scattering. *Physical Review*, 76(6):790, 1949.
- [139] RP Feynman. Space-time approach to quantum electrodynamics. *Physical Review*, 76(6):769, 1949.
- [140] RP Feynman. The theory of positrons. *Physical Review*, 76(6):749, 1949.
- [141] HA Bethe and EE Salpeter. A relativistic equation for bound state problems. In *Physical Review*, volume 82, pages 309–310, 1951.
- [142] EE Salpeter and HA Bethe. A relativistic equation for bound-state problems. *Physical Review*, 84(6):1232, 1951.

- [143] M Gell-Mann and F Low. Bound states in quantum field theory. *Physical Review*, 84(2):350, 1951.
- [144] R Karplus and A Klein. Electrodynamic displacement of atomic energy levels. III. The hyperfine structure of positronium. *Physical Review*, 87(5):848, 1952.
- [145] R Barbieri and E Remiddi. Solving the Bethe-Salpeter equation for positronium. *Nuclear Physics B*, 141(4):413–422, 1978.
- [146] WH Furry. On bound states and scattering in positron theory. *Physical Review*, 81(1):115, 1951.
- [147] J Sucher. S-matrix formalism for level-shift calculations. *Physical Review*, 107(5):1448, 1957.
- [148] PJ Mohr. Energy levels of hydrogen-like atoms predicted by quantum electrodynamics, $10 \leq Z \leq 40$. *Atomic Data and Nuclear Data Tables*, 29(3):453–466, 1983.
- [149] FJ Dyson. Divergence of perturbation theory in quantum electrodynamics. *Physical Review*, 85(4):631, 1952.
- [150] WR Johnson and G Soff. The lamb shift in hydrogen-like atoms, $1 \leq Z \leq 110$. *Atomic Data and Nuclear Data Tables*, 33(3):405–446, 1985.
- [151] HF Beyer, RD Deslattes, F Folkmann, and RE LaVilla. Determination of the 1s Lamb shift in one-electron argon recoil ions. *Journal of Physics B: Atomic and Molecular Physics*, 18(2):207, 1985.
- [152] HF Beyer, P Indelicato, KD Finlayson, D Liesen, and RD Deslattes. Measurement of the 1s Lamb shift in hydrogenlike nickel. *Physical Review A*, 43(1):223, 1991.
- [153] JP Briand, M Tavernier, P Indelicato, R Marrus, and H Gould. High-Precision Spectroscopic Studies of Lyman α Lines of Hydrogenlike Iron: A Measurement of the 1 s Lamb Shift. *Physical Review Letters*, 50(11):832, 1983.
- [154] JP Briand, JP Mosse, P Indelicato, P Chevallier, D Girard-Vernhet, A Chetoui, MT Ramos, and JP Desclaux. Spectroscopy of hydrogenlike and heliumlike argon. *Physical Review A*, 28(3):1413, 1983.

- [155] H Bruhns, J Braun, K Kubicek, JRC López-Urrutia, and J Ullrich. Testing QED screening and two-loop contributions with he-like ions. *Physical Review Letters*, 99(11):113001, 2007.
- [156] CT Chantler, JM Laming, DD Dietrich, WA Hallett, R McDonald, and JD Silver. Hydrogenic Lamb shift in iron Fe 25+ and fine-structure Lamb shift. *Physical Review A*, 76(4):042116, 2007.
- [157] CT Chantler, JM Laming, JD Silver, DD Dietrich, PH Mokler, EC Finch, and SD Rosner. Hydrogenic Lamb shift in Ge 31+ and the fine-structure Lamb shift. *Physical Review A*, 80(2):022508, 2009.
- [158] RD Deslattes, R Schuch, and E Justiniano. Application of decelerated bare nuclei to precision spectroscopy of one-electron ions. *Physical Review A*, 32(3):1911, 1985.
- [159] JD Gillaspy, CT Chantler, D Paterson, LT Hudson, FG Serpa, and E Takacs. First measurement of Lyman alpha x-ray lines in hydrogen-like vanadium: results and implications for precision wavelength metrology and tests of QED. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 43(7):074021, 2010.
- [160] G Hölzer, E Förster, D Klöpfel, P Beiersdorfer, GV Brown, JRC López-Urrutia, and K Widmann. Absolute wavelength measurement of the Lyman- α transitions of hydrogenic Mg 1 1+. *Physical Review A*, 57(2):945, 1998.
- [161] E Kallne, J Kallne, P Richard, and M Stockli. Precision measurement of the H-like x-ray spectrum of Cl and the 1s Lamb shift. *Journal of Physics B: Atomic and Molecular Physics*, 17(5):L115, 1984.
- [162] K Kubicek, PH Mokler, V Mäkel, J Ullrich, and JRC López-Urrutia. Transition energy measurements in hydrogenlike and heliumlike ions strongly supporting bound-state QED calculations. *Physical Review A*, 90(3):032508, 2014.
- [163] JM Laming, CT Chantler, JD Silver, DD Dietrich, EC Finch, PH Mokle, and SD Rosner. A differential measurement of the ground state Lamb shift in hydrogenic germanium, Ge 31+. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 31(1):21–23, 1988.

- [164] ES Marmar, JE Rice, K Kallne, J Kallne, and RE LaVilla. Precision measurement of the 1s Lamb shift in hydrogenlike argon. *Physical Review A*, 33(1):774, 1986.
- [165] P Richard, M Stockli, RD Deslattes, P Cowan, RE La Villa, B Johnson, K Jones, M Meron, R Mann, and K Schartner. Measurement of the 1 s Lamb shift in hydrogenlike chlorine. *Physical Review A*, 29(5):2939, 1984.
- [166] JD Silver, AF McClelland, JM Laming, SD Rosner, GC Chandler, DD Dietrich, and PO Egan. Simultaneous observation of Lyman- α and Balmer- β transitions in hydrogenic iron, Fe 2 5+: A novel technique for 1 s Lamb-shift measurement. *Physical Review A*, 36(3):1515, 1987.
- [167] MR Tarbutt and JD Silver. Measurement of the ground-state Lamb shift of hydrogen-like Ti21+. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 35(6):1467, 2002.
- [168] M Tavernier, JP Briand, P Indelicato, D Liesen, and P Richard. Measurement of the (1s) Lamb shift of hydrogen-like krypton. *Journal of Physics B: Atomic and Molecular Physics*, 18(11):L327, 1985.
- [169] J Tschischgale, D Klöpfel, P Beiersdorfer, GV Brown, E Förster, H Schultes-Schrepping, and SB Utter. Absolute wavelength measurement of the Lyman- α transition of hydrogen-like silicon. *Canadian Journal of Physics*, 80(8): 867–874, 2002.
- [170] CT Chantler. *Beam-foil spectroscopy of highly-ionized atoms, precision measurements of hydrogenic Lamb shifts and x-ray diffraction of curved crystals*. PhD thesis, Oxford University, 1992.
- [171] P Indelicato, S Boucard, DS Covita, D Gotta, A Gruber, A Hirtl, H Fuhrmann, EO Le Bigot, S Schlessner, JMF Dos Santos, et al. Highly charged ion X-rays from Electron–Cyclotron Resonance Ion Sources. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 580(1):8–13, 2007.
- [172] P Amaro, CI Szabo, S Schlessner, A Gumberidze, EG Kessler, A Henins, EO Le Bigot, M Trassinelli, JM Isac, P Travers, et al. A vacuum double-crystal spectrometer for reference-free X-ray spectroscopy of highly charged ions. *Radiation Physics and Chemistry*, 98:132–149, 2014.

- [173] J Braun, H Bruhns, M Trinczek, JRC López-Urrutia, and J Ullrich. Novel technique for high-precision Bragg-angle determination in crystal x-ray spectroscopy. *Review of Scientific Instruments*, 76(7):073105, 2005.
- [174] K Kubicek, J Braun, H Bruhns, JRC López-Urrutia, PH Mokler, and J Ullrich. High-precision laser-assisted absolute determination of x-ray diffraction angles. *Review of Scientific Instruments*, 83(1):013102, 2012.
- [175] WL Bond. Precision lattice constant determination. *Acta Crystallographica*, 13(10):814–818, 1960.
- [176] GW Erickson. Energy levels of one-electron atoms. *Journal of Physical and Chemical Reference Data*, 6(3):831–870, 1977.
- [177] A Antognini, F Nez, K Schuhmann, FD Amaro, F Biraben, JMR Cardoso, DS Covita, A Dax, S Dhawan, M Diepold, LMP Fernandes, A Giesen, AL Gouvea, T Graf, TW Hansch, P Indelicato, L Julien, CY Kao, P Knowles, F Kottmann, EO Le Bigot, YW Liu, JAM Lopes, L Ludhova, CMB Monteiro, F Mulhauser, T Nebel, P Rabinowitz, JMF dos Santos, LA Schaller, C Schwob, D Taqqu, JFCA Veloso, J Vogelsang, and R Pohl. Proton structure from the measurement of 2S-2P transition frequencies of muonic hydrogen. *Science*, 339(6118):417–420, 2013.
- [178] R Pohl, F Nez, LMP Fernandes, FD Amaro, F Biraben, JMR Cardoso, DS Covita, A Dax, S Dhawan, M Diepold, et al. Laser spectroscopy of muonic deuterium. *Science*, 353(6300):669–673, 2016.
- [179] AH Gabriel. Dielectronic satellite spectra for highly-charged helium-like ion lines. *Monthly Notices of the Royal Astronomical Society*, 160(1):99–119, 1972.
- [180] GW Drake. Theoretical energies for the $n=1$ and $n=2$ states of the helium isoelectronic sequence up to $Z=100$. *Canadian Journal of Physics*, 66(7):586–611, 1988.
- [181] DR Plante, WR Johnson, and J Sapirstein. Relativistic all-order many-body calculations of the $n=1$ and $n=2$ states of heliumlike ions. *Physical Review A*, 49(5):3519, 1994.
- [182] KT Cheng and MH Chen. Energy levels of the low-lying states of mid- Z heliumlike ions. *Physical Review A*, 61(4):044503, 2000.

- [183] AN Artemyev, VM Shabaev, VA Yerokhin, G Plunien, and G Soff. QED calculation of the $n=1$ and $n=2$ energy levels in He-like ions. *Physical Review A*, 71(6):062104, 2005.
- [184] WM Neupert. Satellite lines in the solar x-ray spectrum. *Solar Physics*, 18(3):474–488, 1971.
- [185] EV Aglitskii, VA Boiko, SM Zakharov, Sergei Alexandrovich Pikuz, and A Ya Faenov. Observation in laser plasmas and identification of dielectron satellites of spectral lines of hydrogen-and helium-like ions of elements in the Na–V range. *Soviet Journal of Quantum Electronics*, 4(4):500, 1974.
- [186] CL Cocke, B Curnutte, and R Randall. X-ray emission from foil-exited sulphur beams. *Physical Review A*, 9(5):1823, 1974.
- [187] HD Dohmann and R Mann. Measurement of the lifetime of the $3P_{2,1}$ and $4P_{5/2}$ states in Ar^{16+} and Ar^{15+} . *Zeitschrift für Physik A Atoms and Nuclei*, 291(1):15–22, 1979.
- [188] L Schleinkofer, F Bell, HD Betz, G Trollmann, and J Rothermel. Precision Wavelength Determination of $21P_{1-11S_0}$ and $23P_{1-11S_0}$ Transitions in Helium-Like Sulfur Ions. *Physica Scripta*, 25(6B):917, 1982.
- [189] JP Briand, P Indelicato, M Tavernier, O Gorceix, D Liesen, HF Beyer, B Liu, A Warczak, and JP Desclaux. Observation of hydrogenlike and heliumlike krypton spectra. *Zeitschrift für Physik A Atoms and Nuclei*, 318(1):1–5, 1984.
- [190] RD Deslattes, HF Beyer, and F Folkmann. Precision X-ray wavelength measurements in helium-like argon recoil ions. *Journal of Physics B: Atomic and Molecular Physics*, 17(21):L689, 1984.
- [191] JP Briand, M Tavernier, R Marrus, and JP Desclaux. High-precision spectroscopic study of heliumlike iron. *Physical Review A*, 29(6):3143, 1984.
- [192] P Indelicato, JP Briand, M Tavernier, and D Liesen. Experimental study of relativistic correlations and QED effects in heliumlike krypton ions. *Zeitschrift für Physik D Atoms, Molecules and Clusters*, 2(3):249–250, 1986.
- [193] EV Aglitsky, PS Antsiferov, SL Mandelstam, AM Panin, UI Safronova, SA Ulitin, and LA Vainshtein. Comparison of calculated and measured

- wavelengths of resonance transitions in He-like ions for $Z = 16-39$. *Physica Scripta*, 38(2):136, 1988.
- [194] JP Briand, P Indelicato, A Simionovici, V San Vicente, D Liesen, and D Dietrich. Spectroscopic study of hydrogenlike and heliumlike xenon ions. *EPL (Europhysics Letters)*, 9(3):225, 1989.
- [195] P Beiersdorfer, M Bitter, S Von Goeler, and KW Hill. Experimental study of the x-ray transitions in the heliumlike isoelectronic sequence. *Physical Review A*, 40(1):150, 1989.
- [196] JP Briand, P Chevallier, P Indelicato, KP Ziock, and DD Dietrich. Observation and measurement of $n = 2 \rightarrow n = 1$ transitions of hydrogenlike and heliumlike uranium. *Physical Review Letters*, 65(22):2761, 1990.
- [197] S MacLaren, P Beiersdorfer, DA Vogel, D Knapp, RE Marrs, K Wong, and R Zasadzinski. Precision measurement of the $K\alpha$ transitions in heliumlike Ge $30+$. *Physical Review A*, 45(1):329, 1992.
- [198] K Widmann, P Beiersdorfer, and V Decaux. Wavelength measurements of the He-like krypton K-shell spectrum. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 98(1):45–47, 1995.
- [199] K Widmann, P Beiersdorfer, V Decaux, and M Bitter. Measurements of the $K\alpha$ transition energies of heliumlike krypton. *Physical Review A*, 53(4):2200, 1996.
- [200] CT Chantler, D Paterson, LT Hudson, FG Serpa, JD Gillaspay, and E Takács. Absolute measurement of the resonance lines in heliumlike vanadium on an electron-beam ion trap. *Physical Review A*, 62(4):042501–+, 2000.
- [201] CT Chantler, JM Laming, JD Silver, DD Dietrich, PH Mokler, EC Finch, and SD Rosner. Hydrogenic Lamb shift in Ge[$31+$] and the fine-structure Lamb shift. *Physical Review A (Atomic, Molecular, and Optical Physics)*, 80(2):022508, 2009. URL <http://link.aps.org/abstract/PRA/v80/e022508>.
- [202] K Kubicek, H Bruhns, J Braun, JR Crespo López-Urrutia, and J Ullrich. Two-loop QED contributions tests with mid-Z He-like ions. In *Journal of Physics: Conference Series*, volume 163, page 012007. IOP Publishing, 2009.

- [203] CT Chantler, MN Kinnane, JD Gillaspy, LT Hudson, AT Payne, LF Smale, A Henins, JM Pomeroy, JN Tan, JA Kimpton, E Takacs, and K Makonyi. Testing Three-body Quantum Electrodynamics with Trapped Ti^{20+} Ions: Evidence for a Z-Dependent Divergence between Experiment and Calculation. *Physical Review Letters*, 109:153001–1–5, 2012.
- [204] P Amaro, S Schlessler, M Guerra, EO Le Bigot, JM Isac, P Travers, JP Santos, CI Szabo, A Gumberidze, and P Indelicato. Absolute measurement of the relativistic magnetic dipole transition energy in heliumlike argon. *Physical Review Letters*, 109(4):043005, 2012.
- [205] AT Payne, CT Chantler, MN Kinnane, JD Gillaspy, LT Hudson, LF Smale, A Henins, JA Kimpton, and E Takacs. Helium-like titanium x-ray spectrum as a probe of QED computation. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 47(18):185001, 2014.
- [206] SW Epp. Testing Three-body Quantum Electrodynamics with Trapped Ti^{20+} Ions: Evidence for a Z-Dependent Divergence between Experiment and Calculation, Comment. *Physical Review Letters*, 110:159302, 2013.
- [207] CT Chantler, MN Kinnane, JD Gillaspy, LT Hudson, AT Payne, LF Smale, A Henins, JM Pomeroy, JA Kimpton, E Takacs, and K Makonyi. Testing Three-body Quantum Electrodynamics with Trapped Ti^{20+} Ions: Evidence for a Z-Dependent Divergence between Experiment and Calculation, Reply. *Physical Review Letters*, 110:159302, 2013.
- [208] CT Chantler, AT Payne, JD Gillaspy, LT Hudson, LF Smale, A Henins, JA Kimpton, and E Takacs. X-ray measurements in helium-like atoms increased discrepancy between experiment and theoretical QED. *New Journal of Physics*, 16(12):123037, 2014.
- [209] W Friedrich, P Knipping, and M Laue. Interferenzerscheinungen bei roentgenstrahlen. *Annalen der Physik*, 346(10):971–988, 1913.
- [210] HGJ Moseley and CG Darwin. XIV. The reflexion of the X-rays. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 26(151):210–232, 1913.
- [211] HGJ Moseley. XCIII. The high-frequency spectra of the elements. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 26(156):1024–1034, 1913.

- [212] HG J Moseley. LXXX. The high-frequency spectra of the elements. Part II. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 27(160):703–713, 1914.
- [213] M Siegbahn and E Friman. XLVII. On the high frequency spectra of the elements gold-uranium. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 31(184):403–406, 1916.
- [214] M Siegbahn and E Friman. IV. On the high-frequency spectra (L-series) of the elements tantalum-uranium. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 32(187):39–49, 1916.
- [215] M Siegbahn. LVIII. Precision-measurements in the X-ray spectra. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 37(222):601–612, 1919.
- [216] M Siegbahn. LXIII. Precision-measurements in the X-ray spectra. Part II. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 38(227):639–646, 1919.
- [217] M Siegbahn and AB Leide. LXIV. Precision-measurements in the X-ray spectra. Part III. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 38(227):647–651, 1919.
- [218] A Sommerfeld. Atombau und Röntgenspektren. *Physikalische Zeitschrift*, 19:297–307, 1918.
- [219] A Larsson. CX. Precision measurement of the K-series of molybdenum and iron. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 3(18):1136–1160, 1927.
- [220] JA Bearden. Selection of W K α 1 as the X-Ray Wavelength Standard. *Physical Review*, 137(2B):B455, 1965.
- [221] AS Koster and H Mendel. X-ray K β emission spectra and energy levels of compounds of 3D-transition metals-II: Non-oxidic compounds. *Journal of Physics and Chemistry of Solids*, 31(11):2523–2530, 1970.
- [222] RE LaVilla. Double-vacancy transitions in the copper K β 1, 3 emission spectrum. *Physical Review A*, 19(2):717, 1979.

- [223] M Deutsch and M Hart. Wavelength, energy shape, and structure of the Cu K α 1 x-ray emission line. *Physical Review B*, 26(10):5558, 1982.
- [224] ER Cohen and BN Taylor. The 1986 adjustment of the fundamental physical constants. *Reviews of Modern Physics*, 59(4):1121, 1987.
- [225] J Kawai, E Nakamura, Y Nihei, K Fujisawa, and Y Gohshi. Sc K α , and K β X-ray fluorescence spectra. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 45(4-5):463–479, 1990.
- [226] J Härtwig, S Grosswig, P Becker, and D Windisch. Remeasurement of the CuK α 1 Emission X-Ray Wavelength in the Metrical System (Present Stage). *physica status solidi (a)*, 125(1):79–89, 1991.
- [227] J Härtwig, G Hölzer, E Förster, K Goetz, K Wokulska, and J Wolf. Remeasurement of characteristic X-ray emission lines and their application to line profile analysis and lattice parameter determination. *physica status solidi (a)*, 143(1):23–34, 1994.
- [228] J Kawai, T Konishi, A Shimohara, and Y Gohshi. High resolution titanium K α x-ray fluorescence spectra. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 49(7):725–738, 1994.
- [229] J Härtwig, G Hölzer, J Wolf, and E Förster. Remeasurement of the profile of the characteristic Cu K α emission line with high precision and accuracy. *Journal of applied crystallography*, 26(4):539–548, 1993.
- [230] WC Röntgen. On a new kind of rays. *Science*, pages 227–231, 1896.
- [231] RW Henry. The X-Ray, A Potent Factor in Determining Important Decisions. *Journal of the National Medical Association*, 12(1):11, 1920.
- [232] W Coolidge. Some Applications of Wrought Tungsten and Molybdenum. *Industrial & Engineering Chemistry*, 4(1):2–4, 1912.
- [233] J Als-Nielsen and D McMorro. *Elements of Modern X-ray Physics*. John Wiley & Sons, 2011.
- [234] GS Knapp, H Chen, and TE Klippert. Development of a laboratory EXAFS facility. *Review of Scientific Instruments*, 49(12):1658–1666, 1978.

- [235] H Waldmann and B Martin. Highly charged metal ion beams produced from organometallic compounds. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 98(1): 532–535, 1995.
- [236] Ian G Brown, James E Galvin, and Robert A MacGill. High current ion source. *Applied Physics Letters*, 47(4):358–360, 1985.
- [237] Sun Biehe, Hu Shangbin, Chen Qin, and Shui Yongqin. Development of mevva ion source. *Review of scientific instruments*, 65(4):1266–1268, 1994.
- [238] SL An and YF He. Study of Gas Injection System for EBIT Facilities. In *Advanced Materials Research*, volume 291, pages 2809–2813. Trans Tech Publ, 2011.
- [239] RE Marrs, SR Elliott, and DA Knapp. Production and trapping of hydrogenlike and bare uranium ions in an electron beam ion trap. *Physical Review Letters*, 72(26):4082, 1994.
- [240] S Khan. Free-electron lasers. *Journal of Modern Optics*, 55(21):3469–3512, 2008.
- [241] D Paterson, MD De Jonge, DL Howard, W Lewis, J McKinlay, A Starritt, M Kusel, CG Ryan, R Kirkham, and G Moorhead. The X-ray Fluorescence Microscopy Beamline at the Australian Synchrotron. In *THE 10TH INTERNATIONAL CONFERENCE ON X-RAY MICROSCOPY*, volume 1365, pages 219–222. AIP Publishing, 2011.
- [242] L von Hámos. Röntgenspektroskopie und Abbildung mittels gekrümmter Kristallreflektoren. *Naturwissenschaften*, 20(38):705–706, 1932.
- [243] L von Hámos. X-ray micro-analyser. *Journal of Scientific Instruments*, 15(3):87, 1938.
- [244] T Johansson. Über ein neuartiges, genau fokussierendes Röntgenspektrometer. *Zeitschrift für Physik*, 82(7-8):507–528, 1933.
- [245] HH Johann. Die erzeugung lichtstarker röntgenspektren mit hilfe von konkavkristallen. *Zeitschrift für Physik*, 69(3-4):185–206, 1931.
- [246] L Brügemann and EKE Gerndt. Detectors for X-ray diffraction and scattering: a user’s overview. *Nuclear Instruments and Methods in Physics*

- Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 531(1):292–301, 2004.
- [247] W Hillen, U Schiebel, and T Zaengel. Imaging performance of a digital storage phosphor system. *Medical Physics*, 14(5):744–751, 1987.
- [248] M Thoms. The quantum efficiency of radiographic imaging with image plates. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 378(3):598–611, 1996.
- [249] C Broennimann, EF Eikenberry, B Henrich, R Horisberger, G Huelsen, E Pohl, B Schmitt, C Schulze-Briesse, M Suzuki, T Tomizaki, et al. The PILATUS 1M detector. *Journal of Synchrotron Radiation*, 13(2):120–130, 2006.
- [250] R Dinapoli, A Bergamaschi, B Henrich, R Horisberger, I Johnson, A Mozzanica, E Schmid, B Schmitt, A Schreiber, X Shi, et al. EIGER: Next generation single photon counting detector for X-ray applications. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 650(1):79–83, 2011.
- [251] I Johnson, A Bergamaschi, H Billich, S Cartier, R Dinapoli, D Greiffenberg, M Guizar-Sicairos, B Henrich, J Jungmann, D Mezza, et al. Eiger: a single-photon counting x-ray detector. *Journal of Instrumentation*, 9(05):C05032, 2014.
- [252] A Bergamaschi, A Cervellino, R Dinapoli, F Gozzo, B Henrich, I Johnson, P Kraft, A Mozzanica, B Schmitt, and X Shi. The MYTHEN detector for X-ray powder diffraction experiments at the Swiss Light Source. *Journal of Synchrotron Radiation*, 17(5):653–668, 2010.
- [253] R Kirkham, D Siddons, PA Dunn, AJ Kuczewski, R Dodanwela, GF Moorhead, CG Ryan, G De Geronimo, R Beuttenmuller, D Pinelli, et al. The Maia spectroscopy detector system: engineering for integrated pulse capture, low-latency scanning and real-time processing. In *American Institute of Physics Conference Proceedings*, volume 1234. Brookhaven National Laboratory (BNL) National Synchrotron Light Source, 2010.
- [254] R Allemand and G Thomas. Nouveau détecteur de localisation: Le dispositif à? jeu de jacquet? *Nuclear Instruments and Methods*, 137(1):141–149, 1976.

- [255] BP Duval, J Barth, RD Deslattes, A Henins, and GG Luther. Position-sensitive X-ray detector. *Nuclear Instruments and Methods in Physics Research*, 222(1):274–278, 1984.
- [256] GG Luther, PL Cowan, A Henins, and S Brennan. New two dimensional position sensitive proportional detectors using charge division. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 246(1):537–540, 1986.
- [257] MN Kinnane, JA Kimpton, MD de Jonge, K Makonyi, and CT Chantler. The correction of systematic image deformations inherent to two-dimensional proportional counters. *Measurement Science and Technology*, 16(11):2280, 2005.
- [258] JA Kimpton, MN Kinnane, and CT Chantler. Development of backgammon-type multiwire proportional counters for the detection of x rays. *Review of Scientific Instruments*, 77(8):083102, 2006.
- [259] JA Kimpton, MN Kinnane, LF Smale, CT Chantler, LT Hudson, A Henins, CI Szabo, JD Gillaspay, JN Tan, JM Pomeroy, et al. Data acquisition system development for the detection of X-ray photons in multi-wire gas proportional counters. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 580(1):246–249, 2007.
- [260] AT Payne, JA Kimpton, MN Kinnane, and CT Chantler. Simulation and minimization of nonlinear effects in backgammon-type multi-wire gas proportional counters. *Measurement Science and Technology*, 20(2):025601, 2009.
- [261] AT Payne, JA Kimpton, LF Smale, and CT Chantler. Optimisation of the spatial linearity in backgammon-type multi-wire gas proportional counters—The relevance of charge cloud distribution. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 619(1):190–197, 2010.
- [262] A Henins. Variable radius curved crystal mount. *Review of Scientific Instruments*, 58:1173–1176, 1987.

- [263] S Brennan, PL Cowan, RD Deslattes, A Henins, DW Lindle, and BA Karlin. Performance of a tuneable secondary x-ray spectrometer. *Review of Scientific Instruments*, 60:2243–2246, 1989.
- [264] JD Silver, AJ Varney, HS Margolis, PEG Baird, IP Grant, PD Groves, WA Hallett, AT Handford, PJ Hirst, AR Holmes, DJH Howie, RA Hunt, KA Nobbs, M Roberts, W Studholme, JS Wark, MT Williams, MA Levine, DD Dietrich, WG Graham, ID Williams, R O’Neil, and SJ Rose. The Oxford electron-beam ion trap: A device for spectroscopy of highly charged ions. *Review of Scientific Instruments*, 65(4):1072–1074, 1994.
- [265] JD Gillaspay. First results from the EBIT at NIST. *Physica Scripta*, 1997 (T71):99, 1997.
- [266] M Deutsch, M Hart, and E Cummings. High-accuracy structure-factor measurements in germanium. *Physical Review B*, 42(2):1248, 1990.
- [267] CT Chantler, CQ Tran, Z Barnea, D Paterson, DJ Cookson, and DX Balaic. Measurement of the x-ray mass attenuation coefficient of copper using 8.85–20KeV synchrotron radiation. *Physical Review A*, 64:062506, 2001.
- [268] CQ Tran, CT Chantler, and Z Barnea. X-Ray Mass Attenuation Coefficient of Silicon: Theory versus Experiment. *Physical Review Letters*, 90(25):257401, 2003.
- [269] LF Smale, CT Chantler, MD de Jonge, Z Barnea, and CQ Tran. Analysis of X-ray absorption fine structure using absolute X-ray mass attenuation coefficients: Application to molybdenum. *Radiation Physics and Chemistry*, 75(11):1559–1563, 2006.
- [270] PR Bevington and DK Robinson. *Data Reduction and Error Analysis for the Physical Sciences*. McGraw-Hill, 2003.
- [271] M Abramowitz and IA Stegun. *Handbook of Mathematical Functions: with Formulas, Graphs, and Mathematical Tables*, volume 55. Courier Corporation, 1964.
- [272] JH Hubbell. Bibliography of Photon Total Cross Section (Attenuation Coefficient) measurements 10 eV to 13.5 GeV, 1907-1993. *NISTIR*, 5437, 1994.

- [273] JW Edwards, R Speiser, and HL Johnston. High temperature structure and thermal expansion of some metals as determined by x-ray diffraction data .1. platinum, tantalum, niobium, and molybdenum. *Journal of Applied Physics*, 22(4):424–428, 1951.
- [274] RWG Wyckoff. *Crystal Structures*, volume 3, page 16. John Wiley & Sons, 1963.
- [275] A Taylor, NJ Doyle, and BJ Kagle. The constitution diagram of the molybdenum-hafnium binary system. *Journal of the Less Common Metals*, 3(4):265–280, 1961.
- [276] J Bashir, NM Butt, MN Khan, QH Khan, B Zhang, N Yang, Y Ding, and C Ye. Determination of the Debye-Waller factor of molybdenum by powder neutron diffraction. *Journal of Applied Crystallography*, 25(6):797–799, 1992.
- [277] CT Chantler, NA Rae, MT Islam, SP Best, J Yeo, LF Smale, J Hester, N Mohammadi, and F Wang. Stereochemical analysis of ferrocene and the uncertainty of fluorescence XAFS data. *Journal of Synchrotron Radiation*, 19(2):145–158, 2012.
- [278] LF Smale, CT Chantler, and LT Hudson. The effects of cosmic ray filtering on low intensity X-ray CCD data. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 619(1):150–153, 2010.
- [279] DN Joanes and CA Gill. Comparing measures of sample skewness and kurtosis. *Journal of the Royal Statistical Society: Series D (The Statistician)*, 47(1):183–189, 1998.
- [280] LF Smale, CT Chantler, and JA Kimpton. Methodology for the characterisation of characteristic spectral profiles, applied to chromium $K\beta$. *X-Ray Spectrometry*, 44(2):54–62, 2015.

A

Extent of NIST 2005 Primary Spectrometer Data

Section 5.4.1 of Chapter 5 mentions that the experiment at NIST in 2005 had two aims. The first aim was to measure lines of H-like Ti and He-like Ti on an absolute scale to test QED. As shown in Figure 5.3, there was a calibration source and a primary spectrometer attached to the EBIT on opposite ports. The calibration source emitted $K\alpha$ and $K\beta$ lines of Sc, Ti, V, Cr and Mn in order to calibrate the primary spectrometer. This appendix is a profile of the extent of the data collected that related to this aim and that used this part of the setup.

Eight calibration series and six EBIT series were collected. These series were collected in the following order; (1) four *preruncal* calibration series, (2) three *Leg1* H-like Ti EBIT series, (3) one *midruncal* calibration series, (4) one *Leg2* H-like Ti EBIT series, (5) three *pstruncal* calibration series, (6) one *Leg3a* H-like Ti EBIT series, (7) one *pstruncal* calibration series, (8) one *Leg3b* He-like Cr and He-like Ti EBIT series. Table A.1 presents the numbers of $K\alpha$ profiles that were collected in the calibration series. The numbers of $K\beta$ profiles that were collected in the calibration series are presented in Table A.2. Table A.3 presents the numbers of EBIT profiles that were collected in the EBIT series.

The 95 spectra of H-like Ti were collected in 9 days 11 hours (227 hours). The spectra contain about 378,000 counts. The test case spectrum of He-like Cr was collected for 12 minutes and contained 300 counts. The He-like Ti data were separated into 27 spectra collected in 2 days 7 hours (55 hours). These data contain about 116,000 counts. It should be possible to analyse this data using the methods outlined in Chapter 10 or developments thereof.

Series		Spectra Collected				
Run	Wedge Pos. (mm)	Sc $K\alpha$	Ti $K\alpha$	V $K\alpha$	Cr $K\alpha$	Mn $K\alpha$
<i>preruncal</i>	17.17	6	5	5	5	6
<i>preruncal</i>	17.96	5	5	5	5	6
<i>preruncal</i>	9.53	4	4	4	4	1
<i>midruncal</i>	16.15	11	5	5	5	7
<i>pstruncal</i>	9.53	5	5	5	5	0
<i>pstruncal</i>	17.96	0	5	5	5	5
<i>pstruncal</i>	17.17	5	5	5	5	5
<i>pstruncal</i>	16.15	5	5	5	5	5

Table A.1: The number of $K\alpha$ spectra collected at NIST for each series of data. Total of 193 files. An average of 6 minutes each at 2800 Hz for 1,018,000 counts. Total of 19 hours 28 minutes.

Series		Spectra Collected				
Run	Wedge Pos. (mm)	Sc $K\beta$	Ti $K\beta$	V $K\beta$	Cr $K\beta$	Mn $K\beta$
<i>preruncal</i>	17.17	5	5	5	6	2
<i>preruncal</i>	17.96	5	5	5	6	0
<i>preruncal</i>	9.53	4	4	4	4	0
<i>midruncal</i>	16.15	5	5	5	7	6
<i>pstruncal</i>	9.53	5	5	5	0	0
<i>pstruncal</i>	17.96	5	5	5	5	2
<i>pstruncal</i>	17.17	5	5	5	5	0
<i>pstruncal</i>	16.15	5	5	5	5	2

Table A.2: The number of $K\beta$ spectra collected at NIST for each series of data. Total of 167 files. An average of 6 minutes each at 2200 Hz for 780,000 counts. Total of 16 hours 10 minutes.

Series		Spectra Collected		
Run	Wedge Pos. (mm)	H-like Ti	He-like Ti	He-like Cr
<i>Leg1</i>	9.53	38	0	0
<i>Leg1</i>	17.17	1	0	0
<i>Leg1</i>	16.15	20	0	0
<i>Leg2</i>	16.15	22	0	0
<i>Leg3a</i>	16.15	14	0	0
<i>Leg3b</i>	16.15	0	27	1

Table A.3: The number of EBIT spectra collected at NIST for each series of data.

B

Publications

The following publications are a direct result of the work presented in this thesis. The vast majority of the content of these papers was produced by present author, and the papers were written by the present author with help and contributions from Professor Chris Chantler. They are reprinted in full in this appendix.

- LF Smale, CT Chantler, MD de Jonge, Z Barnea, and CQ Tran. Analysis of X-ray absorption fine structure using absolute X-ray mass attenuation coefficients: Application to molybdenum. *Radiation Physics and Chemistry*, 75(11):1559–1563, 2006
- LF Smale, CT Chantler, and LT Hudson. The effects of cosmic ray filtering on low intensity X-ray CCD data. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 619(1):150–153, 2010
- LF Smale, CT Chantler, JA Kimpton, DN Crosby, and MN Kinnane. Characterization of $K\beta$ spectral profile for vanadium. *Physical Review A*, 87:022512–1–7, 2013
- CT Chantler, LF Smale, JA Kimpton, DN Crosby, MN Kinnane, and AJ Illig. Characterization of Titanium $K\beta$ spectral profile. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 46:145601–1–10, 2013
- LF Smale, CT Chantler, and JA Kimpton. Methodology for the characterisation of characteristic spectral profiles, applied to chromium $K\beta$. *X-Ray Spectrometry*, 44(2):54–62, 2015

Analysis of X-ray absorption fine structure using absolute X-ray mass attenuation coefficients: Application to molybdenum

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Accepted 9 July 2005

Abstract

XAFS structures are solved routinely and hundreds of publications appear per annum. Limitations in theoretical predictions and XAFS analytical frameworks lead to significant uncertainty in results. This impairs structural predictions and prevents *ab initio* determination. The highest accuracy experimental data have been obtained using the XERT and the most popular technique to analyse the structure. We apply an accurate χ^2 fitting procedure to the molybdenum attenuation data including error propagation and improve the XAFS determinations by between 5% and 70%.

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PACS: 78.70.Dm; 61.10.Ht; 32.80.Fb

Keywords: X-ray absorption; XAFS; XANES; Molybdenum

1. Metallic molybdenum: an ideal test case for the XAFS technique

The mass attenuation coefficient data for metallic molybdenum have recently been determined to unprecedented accuracy within the range from 13.5 to 41.5 keV. Accuracy is within 0.02–0.4% and 0.1% over most of the energy range. This range includes the K edge for molybdenum (de Jonge et al., 2005). The data (Fig. 1) are on absolute scales for both the mass attenuation and X-ray energy axes. The accuracy of the energy determinations of each datum is typically 1–3 eV. This accuracy was obtained using the X-ray

extended-range technique (XERT) (Chantler et al., 2001; Tran et al., 2003). The XERT tests for many potential experimental systematic errors over a large energy range, and hence offers an unprecedented opportunity to critically examine and improve the standard XAFS analysis technique and theory. These measurements obtained from molybdenum yield the most accurately determined form factor in the literature for any element or substance.

2. Issues in current XAFS analysis

The mass attenuation coefficient $[\mu/\rho]$ for a material is a function of X-ray energy given by the Beer–Lambert formula

$$I = I_0 e^{-[\mu/\rho]\rho t}. \quad (1)$$

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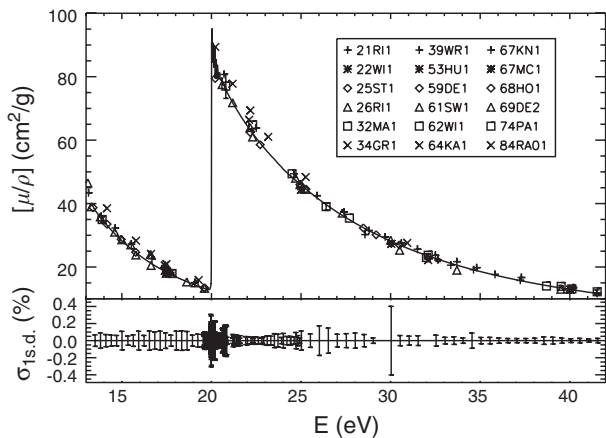


Fig. 1. $[\mu/\rho](E)$ versus E for molybdenum, compared with previous measurements sourced from the compilation of Hubbell (1994) (legends as given therein). The error bars for previous measurements are between 2% and 4%. The solid line is the recent data. The bottom section shows $\sigma_{1s.d.}$ in the new data as a percentage of the data ranging from 0.02% to 0.4%, and generally 0.1%. This quality of data is uniquely suited to test XAFS theory.

The normalised offset XAFS spectrum, fitted by standard techniques, called $\chi(k)$, is the oscillatory part of the mass attenuation above an absorption edge as a function of the photo-electron wave number k . $\chi(k)$ is related to $[\mu/\rho](E)$ by

$$\chi(k) = \frac{[\mu/\rho](E) - [\mu_0/\rho](E)}{[\mu_0/\rho](E)}, \quad (2)$$

$$E = \frac{h^2}{8m_e\pi^2} k^2 + E_0, \quad (3)$$

where μ_0 is a smooth atom-like background and E_0 is the energy of the edge. There is currently no rigorous determination of the atom-like smooth baseline μ_0 or of the effective energy E_0 for general edges. More standard approaches simply draw a smooth line or curve through the oscillatory amplitude and normalise empirically to this. Two of the most useful atomic baselines for XAFS are Chantler (1995, 2000) and Mihelic et al. (2004). Recently, limitations of both contemporary theoretical approaches have been shown to obscure the direct interpretation of XAFS.

The XAFS equation describes this $\chi(k)$ as a sum over multiple scattering paths:

$$\chi_{th}(k) = \sum_j N_j S_0^2 F_j(k) \frac{\sin[2kr_j + \phi_j(k)]}{kr_j^2} \times e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda(k)}, \quad (4)$$

where subscript j indexes the j th path, N_j is the degeneracy, S_0^2 is the many-body reduction factor, $F_j(k)$ is the backscattering amplitude function, $r_j =$

$(1 + \alpha)r_{0,j}$ is half the path length, $r_{0,j}$ is the same quantity at a reference temperature, $\phi_j(k)$ is a total phase shift function, σ_j is a Debye-Waller factor and $\lambda(k)$ is the photo-electron mean free path function.

XAFS analysis techniques use Eq. (4) as a model for XAFS. One of the best current analysis packages is IFEFFIT, an interactive shell for the FEFF code (Newville, 2001). Given an input local structure (a crystal structure at some temperature), FEFF will output N_j , $r_{0,j}$, $F_j(k)$, $\phi_j(k)$ and $\lambda(k)$ for the most dominant photoelectron scattering paths. That leaves S_0^2 , σ_j and α_j undetermined for each scattering path.

This leaves freedom to model these path parameters. To good accuracy all α_j 's are equal to a single parameter α . The σ_j 's are modelled by the correlated Debye model with the Debye temperature θ_D as a free parameter:

$$\sigma_j^2 = \frac{1}{4} \sum_{ij} \langle (\mathbf{u}_i - \mathbf{u}_{i+1}) \cdot \hat{\mathbf{R}}_{i,i+1} (\mathbf{u}_j - \mathbf{u}_{j+1}) \cdot \hat{\mathbf{R}}_{j,j+1} \rangle, \quad (5)$$

where $\mathbf{u}_i$ is the fluctuation in position of the i th atom in the path and $\hat{\mathbf{R}}_{ij}$ is the displacement from the i th atom to the j th atom in the path. This can be cast in terms of the correlation between the k th component of the $\mathbf{u}_i$ vector and the l th component of $\mathbf{u}_j$:

$$\langle u_{i,k} u_{j,l} \rangle = \frac{\hbar^2}{k_B \theta_D \sqrt{M_i M_j}} \int_0^1 dw \frac{\sin(w R_{ij} k_D)}{R_{ij} k_D} \coth\left(\frac{w \theta_D}{2T}\right), \quad (6)$$

where k_B is Boltzmann's constant, $k_D = (6\pi^2 N/V)^{1/3}$, N/V is the number density of the crystal, T is the absolute temperature of the crystal and M_i is the mass of the i th atom in the path (Zabinski et al., 1995).

For each path $N_j S_0^2$ is a constant, so the roles of N_j and S_0^2 are not separable. A separate parameter $S_{0,j}^2$ for each path models the variation of the product. The analysis of this work focuses on propagating accurate experimental errors through a direct windowed k space fitting as this gives the most direct and transparent test of the procedure.

The accurate χ^2 (chi-squared) for χ (chi) data is

$$\chi^2 = \sum_{i=1}^{N_{pts}} \left(\frac{\chi_{data}(k_i) - \chi_{th}(k_i)}{\sigma(k_i)} \right)^2, \quad (7)$$

where $(k_i, \chi_{data}(k_i))$ is the i th data point and $\sigma(k_i)$ is the measurement uncertainty of the $\chi_{data}(k_i)$. The reduced χ^2 is

$$\chi_r^2 = \frac{\chi^2}{N_{pts} - N_{var}}. \quad (8)$$

We can evaluate fits generated by the standard procedure with χ_r^2 to determine the accurate goodness of fit. χ_r^2 was implemented in the core of the computation code so we fit with respect to χ^2 and evaluate the standard fits with χ_r^2 .

3. Investigations and results

We report here variation of two parameters of the standard procedure: the windowing region and the parametrisation of the paths $S_{0,j}^2$ for the molybdenum model. We examined fits with the following window regions: 3.7–13.0 Å⁻¹ (7 peak window), 2.0–13.0 Å⁻¹ (8 peak window) and a range covering all the data (unwindowed). The model for molybdenum includes 16 scattering paths, the theory converging after the inclu-

sion of these 16 paths. All 16 of the $S_{0,j}^2$'s were set equal to the one model parameter S_0^2 . The figure shows that the windowed fits are of very high quality and in good qualitative agreement with the peaks and troughs of the data. No k -weighting was employed. This is a confirmation of the modified technique and of the experimental data.

The model curves for the 7 and 8 peak windowed fits followed the experimental data with peak locations and heights being roughly consistent. However, the χ_r^2 was consistently between 63 and 180 for all fits, indicating a model failure revealed by the high accuracy of the data (Fig. 2, Table 1).

The unwindowed fits had χ_r^2 exceeding 2500, an order of magnitude greater than the windowed fits. All parameter values for the unwindowed fits were unphysical. Hence the model is unable to fit the XANES region. This is the traditional justification within the XAFS community of windowing: peaks in the XANES region may not be well represented by an XAFS analysis. The upper limit of the window prevents the noise level far from the edge from being too significant, especially if traditional k^3 scaling is used.

Parameter values for the 8 peak window fits were either unphysical or poorly determined. Generally the values for the Debye temperature were too low, and the values for the path amplitudes were too high. This is correlated with a higher χ_r^2 , although the 8 peak window fits are obviously poor in a range where the model assumptions are not adequate. Perhaps surprisingly, we have already removed the first 4 peaks by windowing, so naively one might expect the model to work well (and it does in a qualitative sense).

Windowed fits allowing all 16 $S_{0,j}^2$'s to vary independently yielded high correlations. Although the extra

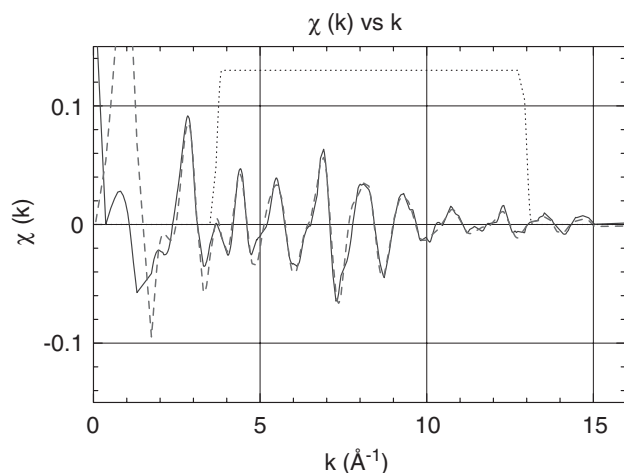


Fig. 2. The $\chi(k)$ data (solid line) and the windowed χ^2 fit using the reduced set of parameters (dashed line). The k space window function (dotted line) represents the 7 peak window. $\chi_r^2 = 96$. The fit is qualitatively consistent with the data in the windowed region, matching peak locations and heights. However, the χ_r^2 indicates a significant disagreement between theory and the high-accuracy experimental data. Further theoretical work is needed.

Table 1

The parameters and uncertainties from a 7 peak window fit (windowed from 3.7 to 13.0 Å⁻¹)

	Improved fit (7 peaks)			Standard fit (8 peaks)	Literature value
	Value	σ	$\sigma\sqrt{\chi_r^2}$		
χ^2	24 000			38 000	
χ_r^2	96			130	
E_0 (eV)	19996.88	0.03	0.33	19996.21	
α	0.00183	9×10^{-5}	0.00086	-0.0003(5)	$0 \pm 6 \times 10^{-5}$
θ_D (K)	360	2	16	344(9)	385(7)
S_0^2	1.153	0.006	0.055	1.11(3)	0.9

Two estimates, σ and $\sigma\sqrt{\chi_r^2}$, give lower and upper bounds for one standard deviation uncertainty. The fit is consistent with established values to within 2–3 standard deviations. The model gives meaningful parameters with a particularly restricted window. The unit cell length is between 3.1470 and 3.1474 Å (Edwards et al., 1951; Wyckoff, 1963; Taylor et al., 1961), based on X-ray crystallography carried out between 18 and 25 °C. With the model parameter 3.1474 Å., an expected expansion coefficient of $(1 + \alpha)$, $\alpha = 0.00000(6)$ follows. The Debye temperature for molybdenum is 385(7) K from powder neutron diffraction (Bashir et al., 1992).

parameters always gave an expected reduction in χ_r^2 , the corresponding path amplitudes were often unphysical, implying that the amplitudes were not determined, even for such an ideal model system as pure molybdenum.

In all fits, the development of the accurate χ^2 fitting procedure including error propagation showed improvement of the XAFS determinations by between 5% and 70%. The 7 peak windowed fit yields parameter values corresponding to physical quantities. Other results, while still useful for some applications, were likely to lead to significant uncertainty in determined parameters.

Standard procedures for fitting the FEFF model to an experimental XAFS spectrum are based on a least-squares fit of some linear transformation of the residues of the data interpolated onto a $0.05 \text{ \AA}^{-1}$ spaced grid. Options include fits on three different axes (original or 'R or Q space') with k^2 or k^3 or k^n scaling (suppressing near-edge and magnifying far-edge structure), and with a variable fitting window in k space. These transformations of the residues do not propagate experimental uncertainties, distorting the accuracies and uncertainties of the original data set. Therefore, such options are significantly flawed and were not used in this investigation.

4. Significance

To investigate current XAFS theory, this work used newly available absolute mass attenuation data for molybdenum of extremely high accuracy. This was made possible by the implementation of a systematic propagation of errors through least-squares analysis. The current analysis techniques were improved by the implementation of a χ_r^2 fitting technique.

Models using 16 independent path coefficients produce unphysical model parameters with both the current analysis technique and χ_r^2 fitting technique, due in particular to the correlations between parameters. The use of k^3 scaling is not recommended from this work because unphysical scaling of error bars is common, distorting the meaning of the fitted parameters.

The simpler model with a single common path amplitude produced parameters in reasonable agreement with literature values when the fit was windowed to 7 peaks. This appears to constitute a more serious constraint upon the range of validity of the model than previously believed, especially since this is the XAFS spectrum of a monoatomic solid.

The χ_r^2 for every fit is over 60, clearly indicating a disagreement between theory and experiment. In the abstract, the experimental error bars could simply be too low by a factor of 7. However, the structured pattern of the residuals is inconsistent with a random noise

signature, confirming in fact the quality and error bars of the data (to within a factor of two), and highlighting the theoretical issue raised.

The χ_r^2 for the unwindowed fit using the current analysis techniques was 3000. Improved theory for the whole range of data should therefore improve agreement with experimental structure by a further factor of $\sqrt{3000} \simeq 55$.

Acknowledgements

The authors acknowledge the experimental team as well as funding from the ASRP and ARC for this work. We acknowledge the assistance of our collaborators at the Advanced Photon Source including David Paterson and the staff of SRI-CAT and BESSRC-CAT.

References

- Bashir, J., Butt, N., Khan, M., Khan, Q., Zhang, B., Yang, N., Ding, Y., Ye, C., 1992. Determination of the Debye–Waller factor of molybdenum by powder neutron diffraction. *J. Appl. Crystallogr.* 25 (6), 797–799.
- Chantler, C., 1995. Theoretical form-factor, attenuation and scattering tabulation for $z = 1-92$ from $e = 1-10 \text{ eV}$ to $e = 0.4-1.0 \text{ MeV}$. *J. Phys. Chem. Ref. Data* 24 (1), 71–591.
- Chantler, C., 2000. Detailed tabulation of atomic form factors, photoelectric absorption and scattering cross section, and mass attenuation coefficients in the vicinity of absorption edges in the soft X-ray ($Z = 30-36$, $Z = 60-89$, $E = 0.1-10 \text{ keV}$), addressing convergence issues of earlier work. *J. Phys. Chem. Ref. Data* 29 (4), 597–1048 (<http://physics.nist.gov/PhysRefData/FFast/Text/cover.html>).
- Chantler, C., Tran, C., Barnea, Z., Paterson, D., Cookson, D., Balaic, D., 2001. Measurement of the X-ray mass attenuation coefficient of copper using 8.85–20 keV synchrotron radiation. *Phys. Rev. A* 64, 062506.
- de Jonge, M., Tran, C., Chantler, C., Barnea, Z., Dhal, B., Cookson, D., Lee, W., Mashayekhi, A., 2005. Measurement of the X-ray mass attenuation coefficient and determination of the imaginary component of the atomic form-factor of molybdenum over the energy range of 13.5–41.5 keV. *Phys. Rev. A* 71, 032702.
- Edwards, J., Speiser, R., Johnston, H., 1951. High temperature structure and thermal expansion of some metals as determined by X-ray diffraction data. 1. platinum, tantalum, niobium, and molybdenum. *J. Appl. Phys.* 22 (4), 424–428.
- Hubbell, J., 1994. Bibliography of photon total cross section (attenuation coefficient) measurements 10 eV to 13.5 GeV, 1907–1993. NISTIR 5437.
- Mihelic, A., Kodre, A., Arcon, I., Gomilsek, J., 2004. High-resolution X-ray absorption spectrometry of atomic vapors. *Acta Chimica Slovenica* 51 (1), 22–28.
- Newville, M., 2001. Ifeffit: interactive exafs analysis and feff fitting. *J. Synchrotron Radiat.* 8, 322–324.

- Taylor, A., et al., 1961. The constitution diagram of the molybdenum–hafnium binary system. *J. Less Common Metals* 3, 265–280.
- Tran, C., Chantler, C., Barnea, Z., 2003. X-ray mass attenuation coefficient of silicon: theory versus experiment. *Phys. Rev. Lett.* 90 (25), 257401.
- Wyckoff, R., 1963. *Crystal Structures*. vol. 3. Wiley, New York, p. 16.
- Zabinski, S., Rehr, J., Ankudinov, A., Albers, R., Eller, M., 1995. Multiple-scattering calculations of X-ray-absorption spectra. *Phys. Rev. B* 52 (4), 2995–3009.



The effects of cosmic ray filtering on low intensity X-ray CCD data

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ARTICLE INFO

Available online 14 January 2010

Keywords:
X-ray detectors
Cosmic rays

ABSTRACT

Various methods exist to filter cosmic rays from X-ray CCD images with weak X-ray spectra. Distortions of the characteristics of a spectral profile such as peak centroid and relative integrated peak intensities must be kept to a minimum. Optimum methods are those minimising error bars and widths on the final centroid determination and on relative intensities which remain consistent with the widths for unfiltered data. A cluster method, a linear correlation method and a combination of both were examined using H-like Ti collected at the NIST EBIT. The cluster method is a strong filter but appears to distort centroids and relative intensities. The linear correlation method filters less and distorts less. The strongest filtering is to use both yielding the highest signal-to-noise while enhancing apparent distortions. All methods appear fairly robust. Strong cosmic-ray filters with minimal distortion of X-ray spectra can increase the precision of X-ray CCD measurements and enhance the resulting physical insight.

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1. Introduction

X-ray CCD images of weak X-ray spectra can be analysed to remove significant noise signals such as from cosmic rays [1–3]. Distortions of the characteristics of a spectral profile such as peak centroid and relative integrated peak intensities must be kept to a minimum with these methods, or potential accuracy and physical insight will be lost. An ideal method will minimise broadening and uncertainty of final centroid determination and of relative intensities consistent with the distribution for the unfiltered data. A cluster method, a linear correlation method and a combination of both were examined using H-like Ti X-rays collected at the NIST EBIT.

X-ray CCD sensors are important in a wide range of experiments from X-ray astronomy to atomic physics. Extracting significant information from X-ray CCD images is therefore quite a general and important problem. Cosmic ray tracks are a significant source of noise in X-ray CCD images with significant integration times. Automated techniques to differentiate these background tracks from X-ray signals of direct interest in a particular investigation need further development.

Reducing the noise from cosmic rays has been an important step in the analysis of polarisation data for measuring the Lamb shift of He-like Ti [4]. Lamb shift and general high-accuracy experiments require detailed characterisation of systematics and detector performance [5,6]. In the experimental setup [7], there

were two Johann geometry spectrometers [8,9] attached to perpendicular ports of the NIST EBIT (Fig. 1). The main spectrometer had a vertical configuration with a backgammon type multi-wire proportional counter as the detector and the secondary had a horizontal configuration with an X-ray CCD detector. Spectra observed include He-like Ti and a very low intensity H-like Ti source. Therefore, in the CCD detector, cosmic rays were a significant source of noise. The CCD used had background levels, defined as a fixed-pattern noise on top of a thermal pedestal, partially due to typical radiation damage accumulated in the detector over time. To correct for these effects, we need to characterise the background and remove it. A typical raw data CCD image is shown in Fig. 2. Note that many such images must be processed and the results added to create a spectrum with significant statistics.

2. Mean background determination

Each data image from the CCD needs to be separated into three computational masks, representing the regions and nature of constituent pixel signals. We are searching for a mask (a pixel intensity pattern) which represents the background or electronic noise or damage signal of the CCD detector, a mask which represents the cosmic ray events for exclusion from the signal, and a mask of the 'true' X-ray signals of interest. Ten exposures of the background were taken during the experiment. All the background images were normalised to the brightest background image through linear intensity histogram matching.

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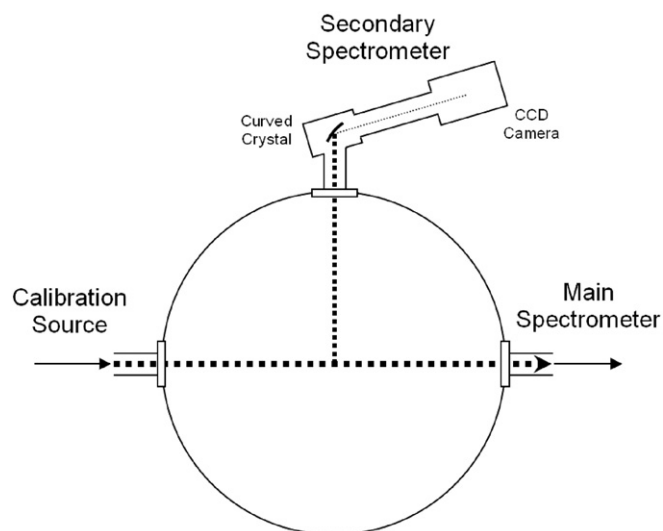


Fig. 1. The experimental setup showing the horizontal configuration of the secondary spectrometer with X-ray CCD detector attached.

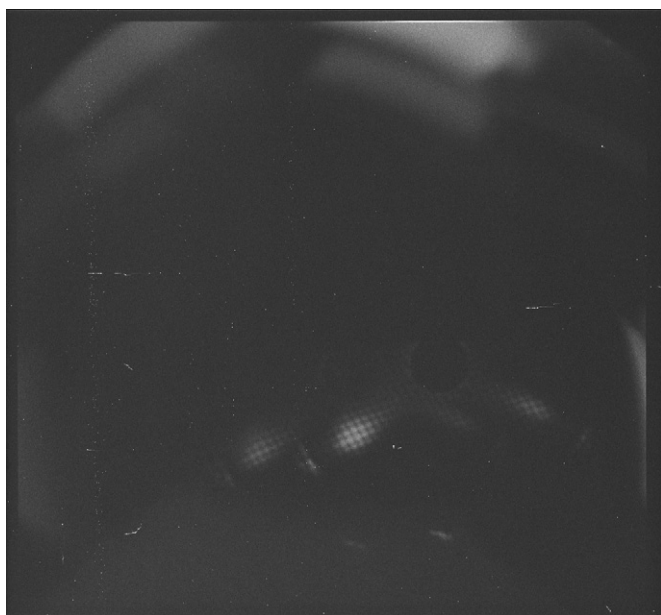


Fig. 2. Raw image data of He-like Ti, showing the background pattern as well as cosmic rays and the X-ray signal.

The intensity histograms of every CCD image examined in the experiment had two disjoint (bimodal) peaks. Therefore, to scale each background image to the brightest background image, the means of each of these two peaks for both images were found. The intensity of each background was linearly transformed such that the means of the two peaks of each background matched those of the brightest background. This will correct for variations in dead-time, temperature drifts or integration times and will hopefully avoid secondary distortion.

Therefore, for each pixel location there is a set of samples of intensities (grey level) taken from normalised background images. An accurate measure of the background was taken to be the mean of this set, excluding elements that represent cosmic-ray intensities. These cosmic ray events are outliers in the sample distribution. Therefore, for each pixel, outliers were removed. The mean and standard deviation of the remaining grey level distribution then defined the background distribution, and the

scale was normalised to the background level mean and standard deviation of the distribution.

To detect outlier sample intensities within the set of normalised background image intensities, the set was divided into two new subsets: the set of intensities above the midpoint between the mean and maximum of the set and the set of intensities below that midpoint. If a *t*-test for the consistency of these subsets shows they are *inconsistent*, we take the second set to represent the background, otherwise we take the original set to be a sample of the background distribution.

3. Background subtraction

Typically, there will be a background average image, and a series of data-containing images. However, these backgrounds do not have the same brightness (grey-scale) because of drift in laboratory temperature for example. To subtract the mean background from a raw CCD image, the mean background was normalised to the image through a scaling of intensity.

For each image, a difference image was created by subtracting the normalised background image from the image. The grey level distribution of the difference image is peaked around 0 but is not precisely 0 because of noise in the component images. The pixels corresponding to this peak around 0 show an absence of cosmic rays and X-rays. That is, they appear to be due to thermal noise or background patterning. A cutoff value greater than the noise but less than the signal was therefore chosen to define a background distribution mask. All pixels that had an intensity above the cutoff were kept in a 'Possible X-ray Signal Mask' PXSM (Fig. 3 shows the sum of the PXSMs of all He-like Ti data images). The intensity of each pixel marked by the PXSM in the difference image is assumed to be proportional to the energy deposited (by X-rays or cosmic rays) in that CCD pixel in the collection time of the image.

4. Cosmic ray filters

Three filters were examined: a cluster method, a linear correlation method using Hough transforms and a combination of

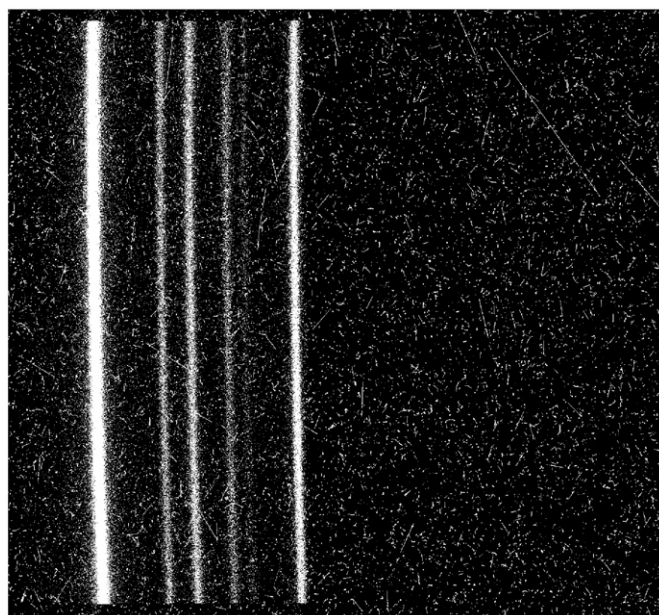


Fig. 3. The sum of the Possible X-ray Signal Masks (PXSMs) for the He-like Ti data. This represents the unfiltered data.

both. In the cluster method, continuous clusters of pixel signals in the PXSM whose combined energy deposition is greater than a chosen cutoff are marked as cosmic ray events and filtered out. The cutoff is chosen through an examination of X-ray events identified by eye in a few images. The linear correlation method identifies linear tracks in the PXSM that need not be continuous clusters. It uses Hough transforms and Hough back-projection.

4.1. Hough transform

The Hough transform [10] is a robust line recognition technique. The set of all straight lines possible in the image is parameterised by a set of two numbers. Each axis of a Hough space image represents a parametrisation of the line. Therefore each 2D point in the Hough space represents a particular (distinct) line in the image. The value of the Hough transformed image at a particular point (parameter set) is the number of non-zero pixels in the source image that are elements of the line represented by that parameter set. An approximately straight line can then be recognised by a peak in the Hough image.

The value of the Hough back-projected image at a particular pixel is calculated from the group of points in the Hough transform whose corresponding lines go through that particular pixel. The value of the image is the sum of intensities of this group.

4.2. Linear correlation method

There are linear correlations of pixels in the PXSM other than cosmic rays—most importantly the spectral lines of the positional-dependent X-rays of the signal. These points can be recognised and removed from misidentification as cosmic rays because they are normally isolated from each other (i.e. they are not usually overlapping clusters) due to the low intensity of the spectral lines. Isolated points in the PXSM are points with less than 3 on-pixels in the surrounding 5×5 sub-mask. The remaining loosely clustered points are included in the 'Possible Cosmic Ray Mask' PCRM.

We Hough transform the resulting PCRM, zero the pixels of the Hough image which are less than a cutoff (chosen to be five). This means that there must be five pixels in a discontinuous line on the PCRM for such a collection of points to be recognised as a line. We then Hough back-project this cut Hough transform image into the original image space. Areas of high intensity represent pixels in approximately collinear (confined) patterns in the original PCRM.

All pixels with a Hough back-projection intensity below a cutoff (chosen to be 150 but robust within a wide range, a good balance between identifying confined linear correlations and correlations between very isolated clusters) that are marked by the PCRM are marked as linearly correlated cosmic rays and filtered out as cosmic ray events. Fig. 4 shows the sum of the results of the linear correlation method applied to each He-like Ti data image.

The spectral lines were not perfectly vertical on the CCD image due to the difficulty of rotating the CCD camera once the spectrometer is evacuated. To sum the spectra and see the signal after a column sum, the image was rotated in order to minimise the width of the strongest peak in the spectrum. Robustness of

Table 1

The signal-to-noise ratio of each peak increases with filtering from A (raw data with background normalisation and rotation) to B (Hough transform with background normalisation and rotation) to C (cluster method with background normalisation and rotation) to D (B and C combined).

Peak #	Peak signal to noise			
	Set A	Set B	Set C	Set D
1	1.287	3.330	10.083	10.651
2	2.357	4.891	16.965	17.686
3	8.154	16.922	57.946	60.391
4	1.451	3.374	12.360	13.025
5	3.813	7.779	26.118	27.367
6	2.464	4.144	13.250	13.996
7	2.191	4.884	16.767	17.584
8	1.693	3.357	10.526	11.040

The noise level is given by the fitted constant background coefficient.

Table 2

The full width half maximum and the dependence on filtering method.

Peak #	FWHM (column channels)			
	Set A	Set B	Set C	Set D
1	8(1)	5.6(2)	6.4(2)	6.4(2)
2	6.1(6)	5.6(1)	5.9(3)	5.8(2)
3	6.3(6)	5.83(5)	6.0(3)	5.96(5)
4	6.0(7)	6.3(2)	7.0(2)	7.0(2)
5	5.7(7)	6.00(7)	6.0(3)	5.8(2)
6	8.6(8)	7.4(4)	7.9(1)	7.7(2)
7	6.6(7)	6.3(3)	6.2(3)	6.2(1)
8	5.2(6)	5.8(1)	6.7(3)	6.8(1)

The FWHM is most stable with linear correlation filtering (set B).

Table 3

The centroid of the strongest peak, relative to Set A position, appears to remain stable within about one σ .

3rd peak centroid (column channels)			
Set A	Set B	Set C	Set D
0.00(8)	0.10(7)	0.10(7)	0.10(7)

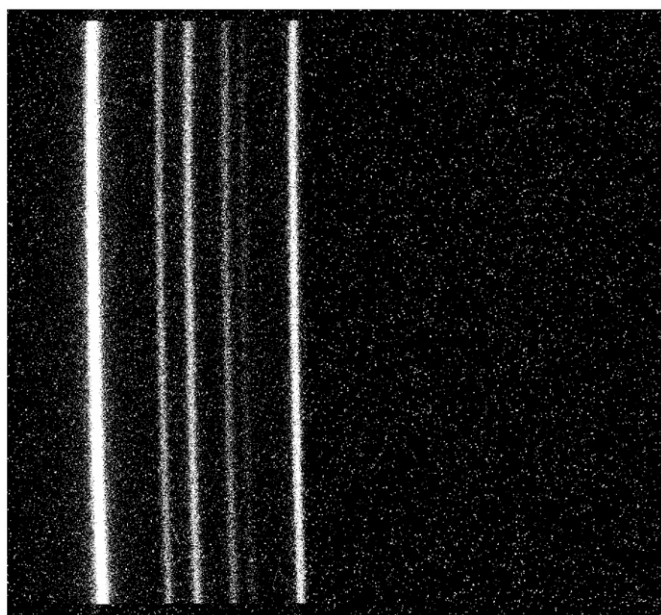


Fig. 4. The sum of the results of applying the linear correlation filter method to each He-like Ti data image.

Table 4

This table shows the peak position and intensity of each peak across all filtering methods relative to the strongest peak (the third peak).

Peak #	Relative peak position (column channels)				Relative intensity			
	Set A	Set B	Set C	Set D	Set A	Set B	Set C	Set D
1	−151.7(5)	−152.6(3)	−153.0(2)	−152.9(2)	0.20(2)	0.20(2)	0.19(1)	0.19(1)
2	−23.1(2)	−23.2(2)	−23.1(2)	−23.0(2)	0.28(2)	0.28(2)	0.29(1)	0.29(2)
4	30.2(3)	30.1(2)	30.5(2)	30.4(2)	0.17(2)	0.21(2)	0.25(1)	0.25(1)
5	68.8(1)	69.2(2)	69.4(1)	69.4(1)	0.41(2)	0.47(2)	0.46(2)	0.46(2)
6	121.9(3)	121.6(2)	121.8(2)	121.8(2)	0.41(3)	0.30(2)	0.30(2)	0.30(2)
7	197.4(2)	197.1(2)	197.1(2)	197.1(2)	0.28(2)	0.31(2)	0.30(2)	0.31(1)
8	306.1(2)	306.0(2)	306.0(2)	306.0(2)	0.17(1)	0.20(1)	0.20(1)	0.21(1)

The dimensionless relative intensity is the integrated area of a peak relative to that of the strongest peak. The relative peak position measures the consistency within errors of the relative centroid locations and hence of the calibration. The second strongest (peak 5) shifts by circa $2\text{--}3\sigma$ in position, doubling with Cluster Filtering. Peaks 4, 5 and 6 in particular show strong dependencies with filtering.

this simple rotation optimisation was tested by shifts in angular rotation from the final result by 0.25° .

5. Results

Four sets of results from the Rydberg series of H-like Ti data were generated for comparison: no cosmic-ray filtering (set A); Linear Correlation filtering (set B); Cluster filtering (set C); combined Linear Correlation and Cluster filtering (set D). Each set of results was created through event identification, spectrum creation (through a rotation and column sum of all the event images), and spectrum fitting (the fit function was a sum of 8 Voigt functions with a common gaussian width and a constant background for the noise).

Table 1 shows the signal-to-noise ratio for each peak in each filter method. The noise estimate was given by the constant background level from the fit. This measures the strength of the filter. The combination filter was stronger than either sub-filter. Hence the sub-filters filter out different components of the cosmic ray noise and of the X-ray signal (as was expected). Table 1 demonstrates that all methods yielded dramatic improvement in separating real (X-ray) signal from noise or correlated components, by factors up to 7–9.

Table 2 illustrates the dependence of the peak full width half maximum on filtering method. The fitted centroid and width of the strongest peak (peak 3) is stable under all methods of filtering (Table 3), supporting the idea that for strong lines each of these approaches has a valid construction. The raw rotated image (set A) may be broadened by artificial (poor) definitions of the background and hence FWHM, by the noise or cosmic rays themselves, and by poor definitions of the lines due to statistics, which might yield a larger width. However, filtered data should be stable in FWHM if all processing has avoided distortion, and conversely should always be larger if the processing has involved distortion and loss of definition of peaks. Results suggest that the weakest components (1, 4 and 8) increase their apparent FWHM from set B to C to D. This suggests that weak peaks are distorted and that Set B minimises this effect.

Table 4 gives the relative peak position and relative intensity as measures of peak distortion. Relative integrated intensities are normalised to the strongest peak in this table. The distortions of intensity generally increase with the strength of the filter, in support of the observations relating to the FWHM. The second strongest peak (5) shifts by circa $2\text{--}3\sigma$ (B) in relative intensity,

with the shift doubling with the energy cluster filtering (C). Peaks 4, 5 and 6 in particular show strong dependencies with filtering, both with integrated relative intensities and with centroid location. Of course, both of these measures are the primary outputs for calibration of scientific results using a CCD detector.

6. Conclusion

The stability and robustness of filtering cosmic-ray noise from low intensity X-ray data from CCD cameras is an important problem. Three filtering methods have been compared. The FWHM of the spectral line is most stable (most narrow) with the Hough transform (B). Cluster methods (C) may increase noise and widths on weak lines. The cluster method is a strong filter compared to the linear correlation filter but can distort centroids and relative intensities. The linear correlation method appears to distort less. The strongest filtering is achieved by combining both filters in which case the distortions are typically enhanced further. All methods appear moderately robust under test conditions on real data. The tentative conclusion is that the minimum filter (B) is the preferred for weak signals, as it appears to avoid distortions. However, more work is clearly needed both to optimise and investigate these and further alternate models in the presence of important but weak signals, for CCD investigations or indeed for any pixel-based imaging.

References

- [1] L.T. Hudson, J.D. Gillaspay, J.M. Pomeroy, C.I. Szabo, J.N. Tan, B. Radics, E. Takacs, C.T. Chantler, J.A. Kimpton, M.N. Kinnane, L.F. Smale, *Nuclear Instruments and Methods in Physics Research A* 580 (2007) 33.
- [2] D. Groom, *Experimental Astronomy* 14 (1) (2002) 45.
- [3] M. Donahue, C.A. Scharf, J. Mack, Y.P. Lee, M. Postman, P. Rosati, M. Dickinson, G.M. Voit, J.T. Stocke, *The Astrophysical Journal* 569 (2002) 689.
- [4] C.T. Chantler, *Radiation Physics and Chemistry* 71 (2004) 611.
- [5] C.T. Chantler, J.M. Laming, D.D. Dietrich, W.A. Hallett, R. McDonald, J.D. Silver, *Physical Review A (Atomic, Molecular, and Optical Physics)* 76 (4) (2007) 042116.
- [6] C.T. Chantler, J.M. Laming, J.D. Silver, D.D. Dietrich, P.H. Mokler, E.C. Finch, S.D. Rosner, *Physical Review A (Atomic, Molecular, and Optical Physics)* 80 (2) (2009) 022508.
- [7] C.T. Chantler, D. Paterson, L.T. Hudson, F.G. Serpa, J.D. Gillaspay, E. Takacs, *Physical Review A* 62 (4) (2000) 042501.
- [8] A. Henins, *Review of Scientific Instruments* 58 (1987) 1173.
- [9] S. Brennan, P.L. Cowan, R.D. Deslattes, A. Henins, D.W. Lindle, B.A. Karlin, *Review of Scientific Instruments* 60 (1989) 2243.
- [10] R.O. Duda, P.E. Hart, *Commun. ACM* 15 (1) (1972) 11.

Characterization of the $K\beta$ spectral profile for vanadiumL. F. Smale, C. T. Chantler,^{*} and M. N. Kinnane*School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia*

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(Received 23 December 2012; published 26 February 2013)

Characteristic radiation is used extensively in most high-accuracy x-ray experiments as a standard for calibration, both in laboratory physics and in astrophysics. $K\alpha$ and $K\beta$ radiations have complex asymmetric structure in their spectral profiles, especially for transition metals. Instrumental broadening in x-ray experiments shifts peak energies by small but significant amounts, especially for critical investigations. The spectral profiles must include an account of instrumental broadening so as to be able to transfer the calibration between experiments. We present a transferable characterization of the vanadium $K\beta$ spectral profile, using high-accuracy laboratory experiments. The peak energy of vanadium $K\beta_1$ is then found to be 5426.962 ± 0.015 eV. This result decreases the uncertainty by a factor of 4.7 compared with Bearden and Burr [*Rev. Mod. Phys.* **39**, 125 (1967)]. Characterization of the profile also permits an accurate and transferable standard and methodology. In the Supplemental Material we present the full profile with uncertainties for use in further analysis using the methodology presented.

DOI: [10.1103/PhysRevA.87.022512](https://doi.org/10.1103/PhysRevA.87.022512)

PACS number(s): 32.30.Rj, 32.70.-n, 78.70.-g

I. INTRODUCTION

Fluorescent characteristic radiation results from atomic transitions where an electron decay fills a vacancy. The excitation process that creates the vacancy may also excite other electrons leaving other vacancies, yielding a fluorescent decay energy dependent upon the process involved. Thus characteristic radiation is produced by dominant transitions and an array of satellites.

A number of excitation processes produce characteristic radiation, including electron bombardment, x-ray absorption, and inelastic x-ray scattering. These processes all involve an energetic incoming particle exciting the atom. When the incoming particle has an energy just above threshold, the excited states and the shape of the characteristic energy profile sensitively depend upon the energy of the incoming particle [1–3]. However, it has been found that for electron bombardment, when the energy of the electron is at least 2.5 to 3 times the threshold energy of the dominant transition, the excited state and thus the profile shape of the characteristic radiation stabilize and indeed appear to be approximated well by the latest predictions from relativistic quantum mechanics, following the sudden approximation for the excitation process [4]. This condition makes it possible to characterize the profile of $K\beta$ radiation in a way that is robust to incoming electron energy variation.

Authors have argued for standard x-ray sources using a fixed anode tube, for rotating anode sources, for exotic synchrotron x-ray excitation, and for electron-beam ion-trap excitations in order to produce a clean or well-defined spectral profile which can be used as a calibration standard. In this work we use an exotic location but a simple fixed source excitation following

the standard technique of many past researchers. The question is, what is the stable profile which is thereby obtained, and how can it be robustly used, fitted, and modeled in secondary and perhaps critical experiments?

The far-from-threshold spectral profile of the characteristic radiation of an element [5] requires advanced relativistic quantum theory for its elucidation. Characteristic radiation has been used for decades in most high-accuracy x-ray experiments as a standard for calibration. Improving the understanding of the spectral profile of characteristic $K\alpha$ and $K\beta$ radiation under these circumstances will improve measurements in the x-ray regime and will provide reliable data from which insights into theory may flow.

Experimentally, spectral profiles for characteristic radiation have been described by semiempirical fitting of 5 or 7 component peaks for the $K\alpha$ spectra [6,7]. Theoretical models of the characteristic radiation profile shape are dominated by diagram lines, representing x-ray emission from atomic transitions with electron decay, from the ground state plus a core vacancy and an excited electron to the ground state with the core vacancy filled and a higher n vacancy. Additional components, theoretically and empirically, are contributed by satellite lines caused by shake-up and shake-off effects. This set of transitions is complex, especially for elements with open subshells such as the transition metals. Progress in such theory has been slow until recently [8,9]. The empirical modeling through fitting functions tends to conceal part of the theoretical complexity by using the sum of a small number of Lorentzian, Gaussian, Voigt, or instrumental functions. Nevertheless, important physical insight is often claimed for these empirical components, which is also worthy of investigation.

A concerted effort to experimentally characterize the experimental energies of characteristic radiation was undertaken and compiled by Bearden and Burr in 1967 [10]. This has been complemented by theoretical computations by Desclaux [11]

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TABLE I. Characteristic radiation peak data. The V $K\alpha$ data are from Chantler *et al.* [18]; the rest of the data are from Deslattes *et al.* [12]. The peak energies of the $K\beta$ radiation have an uncertainty larger than those for $K\alpha$ energies by an order of magnitude.

Spectral profile peak	Reference peak energy (eV)	Peak energy uncertainty (ppm)
Titanium $K\alpha_1$	4510.899	2.08
Titanium $K\alpha_2$	4504.920	2.09
Vanadium $K\alpha_1$	4952.131	1.21
Vanadium $K\alpha_2$	4944.651	2.22
Chromium $K\alpha_1$	5414.804	1.31
Chromium $K\alpha_2$	5405.538	1.31
Manganese $K\alpha_1$	5898.801	1.42
Manganese $K\alpha_2$	5887.685	1.43
Vanadium $K\beta_1$	5427.32	13.0

and Deslattes *et al.* [12] based on the relativistic approaches of Grant [13]. Recently, much experimental work has sought good empirical models of the spectral profiles of the radiation [14–16]. Deslattes *et al.* [12] compiled this experimental work in tables of energies of the observed maxima of characteristic spectra. As shown in Table I, uncertainties in peak energies reported for $K\alpha$ for Z from 22 to 26 are of the order of 1 to 2 parts per million (ppm). However, the peak energy of the vanadium $K\beta$ profile [10] has an uncertainty an order of magnitude larger at 13 ppm.

The data collection methods used in this body of research generally used a double-flat-crystal spectrometer with the Bond method [6,7,17] or a curved-crystal spectrometer [14]. Raw spectra are often deconvolved with a measured or fitted instrumental broadening. Either way, each spectrum is fitted empirically. The peak of each empirical fit has normally been used as the measure of each peak energy.

It is not immediately clear how to use these characterizations as standards in experiments with a different instrumental broadening. Chantler *et al.* [18] addressed this concern by providing a consistent set of empirical fit functions for a range of elements with allowances for typical functional instrumental broadening. In particular, a prescription of the influence and effect of specific broadening on the robustness of the measures of transition energy can thereby be investigated and improved.

A large volume of research has targeted $K\beta/K\alpha$ x-ray intensity ratios [19]. Perhaps 40 papers on this are found in *Physical Review*, with hundreds appearing in other journals [20–22]. Most such publications rely upon low-resolution solid-state detectors measuring the gross intensity of the lines, which can neither resolve the detailed shape of the $K\beta$ spectra nor provide high-accuracy energies. Of course, by being particularly low resolution, the value returned from energy calibration will be an effective weighted mean of the profile intensity and a very different energy compared with the medium-resolution peak energy.

Profiles of chemical energy shifts of the V $K\beta$ spectrum of compounds of vanadium compared with that of pure vanadium have also been conducted using more sensitive instruments [23,24]. Those works are focused on changes in peak separation, perhaps with uniform instrumental broadening, and thus do not attempt to report the detailed line shape on an absolute

energy scale. An interesting recent paper on this area [25] discusses the components of $K\beta$ transitions and satellites but not for vanadium, and indeed, there are no absolute energies reported in that paper.

Thus the only report of which we are aware of a measurement of the characteristic V $K\beta$ line on a claimed well-defined energy scale is by Bearden and Burr [10]. That paper reports the peak energy but requires recalibration by Deslattes *et al.* [12]. After recalibration it is provided as 5427.320(71) eV. No information is provided about how instrumental broadening was dealt with. Noting that V $K\beta$ is an asymmetric line, it is likely that this literature value is significantly affected by shifts caused by instrumental broadening. A theoretical calculation of the energy of the peak of V $K\beta$ is 5430.00(94) eV [12]. The 3.4 standard error discrepancy between theory and experiment is unlikely to be explained by statistical fluctuation and points to a problem in either theory or experiment.

This paper presents a measurement of the vanadium $K\beta$ spectral profile produced by electron bombardment far above the threshold energy and a transferable characterization of the profile leading to a measurement of the energy of vanadium $K\beta_1$. The inclusion of broadening effects in the fitting method enables the results to be transferable to a large range of experimental conditions. Specifically, the characterization can be used in a straightforward manner in experiments where the level of instrumental broadening is difficult to determine.

II. EXPERIMENTAL SETUP

The source of the characteristic radiation was a set of transition-metal foils ($Z = 22$ to 26), each of which was placed in a 20-keV electron beam produced by an electron gun. This source produced $K\alpha$ and $K\beta$ radiations with incident energies far above threshold for each of the metal foils. The radiation source was used for calibration lines as well as for the V $K\beta$ profile itself.

Data collection involved using a Johann geometry curved-crystal spectrometer with position-sensitive x-ray detection. Figure 1 shows a diagram of the setup in terms of the

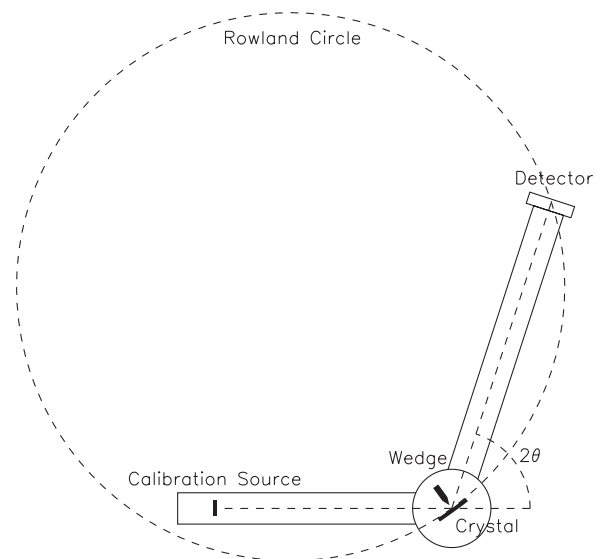


FIG. 1. Schematic diagram of the experimental setup.

three major experimental variables involved: the chosen transition-metal target that emits the characteristic radiation (the calibration source), the angle of the arm that the detector sits on (2θ), and an adjustable “Seemann wedge” to adjust bandpass, instrumental broadening, and the contribution of complex systematics. The angle θ was measured by a gravity-referenced clinometer mounted on the crystal housing. A fixed anode x-ray source at the Oxford energy beam and ion trap (EBIT) [26] was employed.

III. DATA COLLECTION

Seven calibration series were conducted. Each series used a different wedge position and different integration times, so that the diffraction theoretical modeling must make accurate independent predictions of each geometry of each position. Each series was a series of different offset positions of the detector, hence allowing the consistency of the functional with different diffraction angles and geometry to be investigated. The data were collected in pseudoevent mode, so each x-ray event was independently recorded. Within each calibration series, $K\alpha$ and $K\beta$ spectral profiles from $Z = 22$ to 26 were collected. Each spectral profile type was collected at three to five arm angles to sample profiles at different positions on the detector in order to investigate the dispersion function and the detector response function. The remarkable consistency of the results demonstrates the robustness of the code and calibration methodology discussed below. The remaining variance is thus an explicit characterization of all such systematic deficiencies.

IV. $K\alpha$ CALIBRATION PROFILE MODELING

Each $K\alpha$ profile was fitted with functions provided by [18]. Each function of energy or detector position is a sum of six Voigt profiles, with a common Gaussian width to model the instrumental broadening. They map x-ray intensity to x-ray energy. Five fitting parameters were used in the fits of each detector profile: (i) an energy offset, (ii) an energy scale (in eV/mm) to map from detector position to energy, (iii) an intensity scale, (iv) a constant intensity background, and (v) a common Gaussian broadening width representing the additional instrumental broadening of the spectrometer system.

These highly accurate $K\alpha$ characterizations allow the assignment of peak energies to the peak detector positions for each spectrum at each clinometer voltage. Figure 2 illustrates how one such fit leads to two calibration points. The residuals show a small structure which is well centered on the main component peaks and contains noise within one standard deviation.

V. VANADIUM $K\beta$ PROFILE MODELING

As well as the standard reference calibration profiles, V $K\beta$ profiles were also collected and characterized on intensity and detector position axes. To define a characteristic line shape function, each of the spectra were fit with a sum of three Voigt functions with a common Gaussian width σ and a constant intensity background B . The i th Voigt function used in the

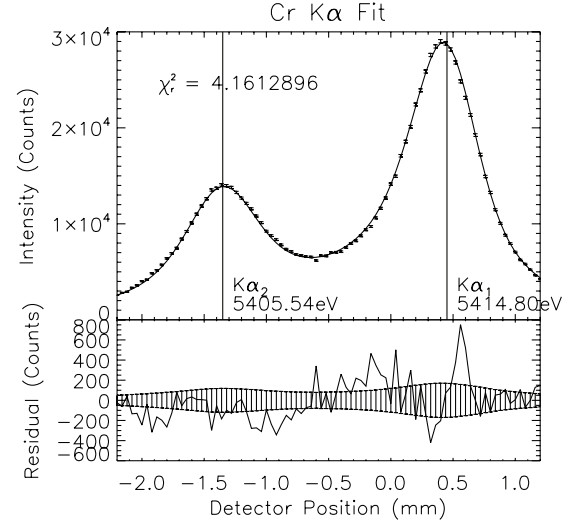


FIG. 2. Typical fit of Cr $K\alpha$ spectrum, yielding two calibration points (Cr $K\alpha_1$ and Cr $K\alpha_2$, constraining the spectrometer dispersion (calibration) function. The fit has a χ^2_r of 4.2. The $K\alpha_1$ peak has an energy of 5414.8045(71) eV and a detector position of 0.4510(12) mm. The $K\alpha_2$ peak has an energy of 5405.5384(71) eV and a detector position of $-1.3507(21)$ mm. The crystal clinometer voltage was $-1.705582(11)$ V.

characterization is defined to be

$$V(x; A_i, C_i, W_i, \sigma_i) = A_i \int_{-\infty}^{\infty} \frac{e^{-x'^2/(2\sigma_i^2)}}{\sigma_i \sqrt{2\pi}} \frac{W_i/2}{\pi[(x - C_i - x')^2 + (W_i/2)^2]} dx', \quad (1)$$

where A_i is the integrated area of the Lorentzian profile, C_i is the centroid of the profile, W_i is the Lorentzian full width at half maximum (FWHM), and σ_i is the Gaussian broadening standard deviation. The Gaussian broadening FWHM is $2\sqrt{2 \ln 2} \sigma_i \approx 2.35 \sigma_i$. Thus the spectra containing a V $K\beta$ spectral profile was modeled with

$$P(E; B, \sigma, A_1, C_1, W_1, A_2, C_2, W_2, A_3, C_3, W_3) = B + \sum_{i=1}^3 V(E; A_i, C_i, W_i, \sigma). \quad (2)$$

All the samples of the V $K\beta$ profile were independently measured and fitted with this method. The relative intensities, positions, and widths of the Voigt functions of the fits were consistent with one another. That is, the determined parametrization from one representative profile was found to be within the uncertainty of other profiles and their independent parametrizations. Further, each representative determination was able to be used as a calibration functional for the other profiles. Hence minimum uncertainty results are reported. The characteristic parameters of these fits are shown in Table II, with positions converted to energies. Figure 3 shows a typical fit for one of the vanadium $K\beta$ spectra.

All V $K\beta$ profiles were then refit under the constraints of these optimized parameters. Each refit had free parameters characterizing the overall intensity, position, detector position to energy-scale conversion, instrumental broadening, and the

TABLE II. The full characterization of the V $K\beta$ spectral profile on an absolute energy scale. The parameters are used in Eq. (2). Amplitudes A_i , centroids C_i , and widths W_i of individual components were obtained from a fit on the intensity versus detector position axis. The detector position axis was transformed to an absolute energy scale via the calibration procedure. The Gaussian width σ was 0.804(25) eV. The background was 749(24) counts.

Proportion of area $\frac{A_i}{\sum_{i=1}^4 A_i}$	Integrated area A_i (counts)	Centroid C_i (eV)	Width W_i (eV)
0.258(21)	160280(12941)	5418.20(35)	18.86(83)
0.236(18)	146750(11207)	5424.50(11)	5.48(21)
0.507(14)	315345(8472)	5426.998(13)	2.498(69)

background of the spectral profile in the specific geometry of the measurement. As each refit had a slightly different instrumental broadening due to geometry changes, the transferable reference position of the peak of each profile was the position of the maximum of the fit function with the Gaussian width set to zero. All refits were reliable and consistent with the original fits as discussed above. Therefore, this characterization allows for a consistent transferable standard in this measurement, in the calibration of the dispersion function, and for any subsequent independent measurement. It enabled a consistent measurement of peak position on any V $K\beta$ profile for any local instrumental broadening.

VI. DISPERSION FUNCTION AND ENERGY CALIBRATION

A dispersion function is required to map a clinometer voltage and a spectral profile measured on a detector position axis (such as in Fig. 3) to a spectral profile measured on an absolute energy axis. The dispersion function consists of a theoretical model of the experimental setup provided by the dynamical diffraction code MOSPLATE [27,28], a clinometer

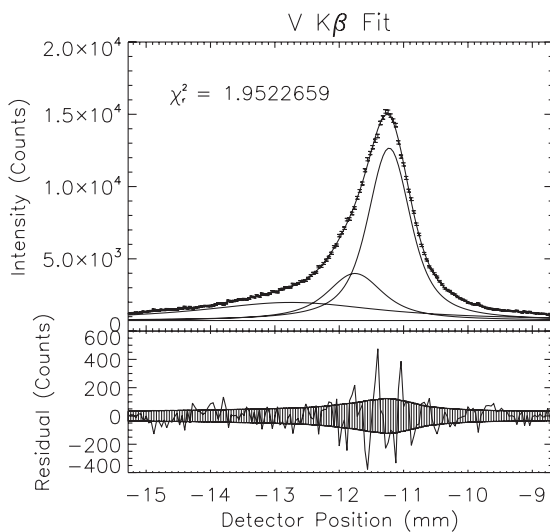


FIG. 3. Typical fit of a V $K\beta$ spectrum. The crystal clinometer voltage was $-1.781742(11)$ V, and the detector position was $-11.234(1)$ mm. The $K\beta_1$ peak has an energy of $5427.104(61)$ eV.

calibration function, and a detector dispersion calibration function.

MOSPLATE calculates the diffraction profile at the detector (and thus peak position) of a particular energy of an x ray at a particular angle θ . These calculations of peak position sample the MOSPLATE model function for the diffraction profile peak position D as a function of peak energy E (the energy of the x ray) and crystal angle θ :

$$D = D_{\text{mos}}(E, \theta). \quad (3)$$

This model also implicitly defines functions that calculate E and θ from the remaining variables:

$$E = E_{\text{mos}}(D, \theta), \quad (4)$$

$$\theta = \theta_{\text{mos}}(D, E). \quad (5)$$

The clinometer calibration function $I(V; P_I)$ maps the clinometer voltage V to the dispersion crystal angle θ :

$$\theta = -I(V; P_I), \quad (6)$$

where $I(V; P_I)$ is defined to be

$$I(V; P_I) = \text{asin}\left(\frac{V - P_{I,2}}{P_{I,0}}\right) - P_{I,1} + \sum_{i=0}^n P_{I,(i+3)}(V - P_{I,2})^i \quad (7)$$

and P_I is the vector of fitting parameters.

The second calibration function, the detector dispersion calibration function $D(x; P_D)$, maps the recorded detector position x in output units to the theoretical detector position D in millimeters. The map from x to D was defined by

$$D(x; P_D) = \sum_{i=0}^1 P_{D,i} x^i, \quad (8)$$

where P_D is the vector of fitting parameters.

Using this dispersion function, an energy can be assigned to a detector position x for any clinometer voltage V through

$$E(x, V; P_D, P_I) = E_{\text{mos}}(D(x; P_D), -I(V; P_I)). \quad (9)$$

Equations (7) and (8) define the calibration of an experimental configuration (i.e., a calibration series). The calibration process was reduced to simultaneously finding the P_I and P_D fitting parameters that best fit the $K\alpha$ data and produced an internally consistent measurement of the V $K\beta$ peak energy for each calibration series. This process makes optimum use of the statistical information for the determination of the profile and dispersion function.

VII. DISPERSION AND DETECTOR

The process to find the fitting parameters P_I and P_D for the calibration entails four major steps: clinometer precalibration, clinometer calibration first estimate, calibration fitting, and detector scale correction. First, the clinometer precalibration made a preliminary characterization of the angle of incline to voltage function $V_{\text{pre}}(I)$ of the clinometers:

$$V_{\text{pre}}(I) = P_{V,0} \sin(I - P_{V,1}) - P_{V,2} + \sum_{i=0}^8 P_{V,(i+3)} V^i. \quad (10)$$

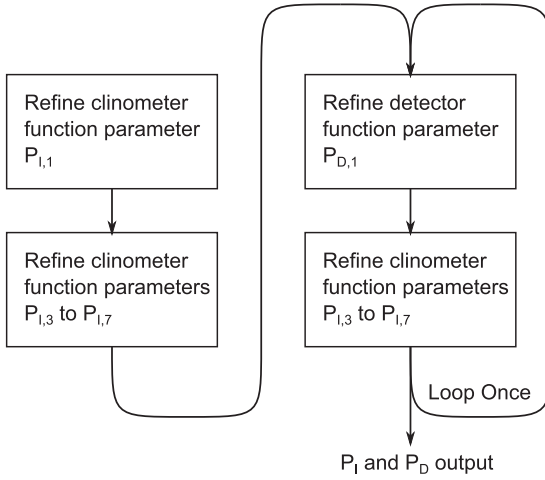


FIG. 4. Schematic of the calibration fitting stages. Each stage is a round of refitting.

Second, an estimate of the clinometer calibration function involved generating data with the $V_{\text{pre}}(I)$ function, inverting the data, then fitting the inverted data with $I(V; P_I)$ [Eq. (7)], where n (the order of the polynomial involved) was set to 3. This function includes parameters for the clinometer response and also for typical mechanical response functions. The fitted P_I parameters then provided a reasonable estimate as to how the clinometers have functioned in the setup.

Finally, calibration fitting was a six-stage process that started with estimates of P_I and P_D (Fig. 4). Each stage made a refinement of either P_I or P_D through one round of refitting.

The six-stage calibration fitting used the interlinked K_α peak energy, peak position, and clinometer voltage calibration data. These data were processed in one of two ways prior to fitting to generate the dispersion function. Either I_{data} or D_{data} was calculated. I_{data} is a set of calculated data that corresponds to the expected clinometer angle for each peak based on the energy and detector position.

$$I_{\text{data}} = -\theta_{\text{mos}}(D(x, P_D), E). \quad (11)$$

It has uncertainty ΔI_{data} :

$$\Delta I_{\text{data}}^2 = \left(\frac{\partial \theta_{\text{mos}}}{\partial E} \Delta E \right)^2 + \left(\frac{\partial \theta_{\text{mos}}}{\partial D} \right)^2 \times \left[\sum_{ij} \frac{\partial D}{\partial P_{D,i}} \frac{\partial D}{\partial P_{D,j}} C_{D,ij} + \left(\frac{\partial D}{\partial x} \Delta x \right)^2 \right]. \quad (12)$$

D_{data} is a set of calculated data that corresponds to the expected theoretical detector position for each peak based on the energy and crystal angle.

$$D_{\text{data}} = D_{\text{mos}}(E, -I(V; P_I)). \quad (13)$$

It has uncertainty ΔD_{data} :

$$\Delta D_{\text{data}}^2 = \left(\frac{\partial D_{\text{mos}}}{\partial E} \Delta E \right)^2 + \left(\frac{\partial D_{\text{mos}}}{\partial \theta} \right)^2 \times \left[\sum_{ij} \frac{\partial I}{\partial P_{I,i}} \frac{\partial I}{\partial P_{I,j}} C_{I,ij} + \left(\frac{\partial I}{\partial V} \Delta V \right)^2 \right]. \quad (14)$$

The six stages of fitting were designed to find a set of fitting parameters P_I and P_D that are self-consistent. Each fit used one of two sets of axes: axis set 1, which was I_{data} vs V , and axis set 2, which was D_{data} vs x . The first fit was of axis set 1 (calculated using the estimated P_D parameters) with $I(V; P_I)$ only allowing the refinement of $P_{I,1}$. This found an overall offset to $I(V; P_I)$. The second fit was again of axis set 1 with $I(V; P_I)$ using the P_I from fit 1 as an estimate, this time only allowing the refinement of $P_{I,3}$ through $P_{I,7}$. This fitted the fine details of $I(V; P_I)$. The third fit was of axis set 2 (calculated using the refined P_I parameters from the second fit) with $D(x; P_D)$. The fourth fit was of axis set 1 (calculated using the refined P_D parameters from the third fit) with $I(V; P_I)$ only allowing the refinement of $P_{I,3}$ through $P_{I,7}$ (as in the second fit). Fits five and six are a repeat of the third and fourth fits using the output of fit four as the input of fit five. This method generates the P_I and P_D parameters along with associated covariance error matrices C_I (from the sixth fit) and C_D (from the fifth fit). These six stages of this third step are diagramed in Fig. 4.

Finally, a detector scale refinement investigated the value of $P_{D,1}$ (the detector scale) by grid search to minimize the uncertainty and variance of the weighted mean of the peak energy of all $V K\beta$ spectra. A low uncertainty (variance) in the weighted mean represents greater consistency between independent spectra. For each $P_{D,1}$ value in the grid search there was a three-step process: (1) a fit of axis set 1 to refine the clinometer calibration function in the context of that detector scale, (2) modeling of the $V K\beta$ peak position and clinometer voltage data for all of the calibration series using Eq. (9) to generate a set of $V K\beta$ peak energies and uncertainties for the calibration series, and (3) computing the weighted mean and corresponding uncertainty from the variance of the set of energies. The final calibration was then represented by the refined fitting parameters, which reflect the experimental minimization of systematic variance around $V K\beta$.

VIII. ENERGY UNCERTAINTIES

The uncertainty in the energy of a peak position ΔE is made up of four sources of uncertainty: (i) the statistical precision of the determination of the peak of the spectral fit (Δx_{fit}), (ii) the uncertainty due to the detector dispersion fit, (iii) the noise in clinometer voltage ΔV , and (iv) the clinometer calibration function fitting uncertainties. The following equation for ΔE is a sum of the four terms representing these uncertainty components:

$$\Delta E^2 = \left(\frac{\partial E}{\partial x} \Delta x_{\text{fit}} \right)^2 + \sum_{ij} \frac{\partial E}{\partial P_{D,i}} \frac{\partial E}{\partial P_{D,j}} C_{D,ij} + \left(\frac{\partial E}{\partial V} \Delta V \right)^2 + \sum_{ij} \frac{\partial E}{\partial P_{I,i}} \frac{\partial E}{\partial P_{I,j}} C_{I,ij}. \quad (15)$$

$C_{D,ij}$ is the i, j th element of the covariance error matrix from the detector dispersion function fit, while $C_{I,ij}$ is the i, j th element of the covariance error matrix from the clinometer calibration function fit. Table III shows average values of these various contributions to ΔE for a single $V K\beta$ spectrum.

TABLE III. Error budget for the peak energy of the three spectral profiles of V $K\beta$ that go into the final energy determination. Since the three determined energies are consistent, the final energy measurement has a smaller uncertainty. The value of $\sqrt{\chi_r^2}$ for the clinometer calibration fit was 8.3, while its value for the detector dispersion function fit was 18.6.

Uncertainty source	Average contribution to energy uncertainty for an individual V $K\beta$ spectrum (ppm)
V $K\beta$ spectrum fit $\frac{\partial E}{\partial x} \Delta x_{\text{fit}}$	0.98
Detector dispersion function fit $\sqrt{\sum_{ij} \frac{\partial E}{\partial P_{D,i}} \frac{\partial E}{\partial P_{D,j}} C_{D,ij}}$	0.021
Clinometer noise $\frac{\partial E}{\partial V} \Delta V$	1.3
Clinometer calibration fit $\sqrt{\sum_{ij} \frac{\partial E}{\partial P_{I,i}} \frac{\partial E}{\partial P_{I,j}} C_{I,ij}}$	0.12
Total uncertainty	1.6

IX. $K\beta$ PEAK ENERGY

Fits of the V $K\beta$ spectra provide relatively independent measurements of the peak energy of V $K\beta$. These peak energies are shown in Fig. 5. There is a systematic functional in the dispersion of measured energies with the crystal angle. These data are pooled with their weighted mean, reflecting the total uncertainty including the remnant systematic error.

Combining these data using a weighted mean results in a measurement of the V $K\beta$ profile peak energy of 5426.962(15) eV (2.7 ppm uncertainty). This measurement is inconsistent with the theoretical value of 5430.00(94) eV [12]. The 3.038-eV discrepancy is just over 3.2 standard deviations and is reflective of the theoretical inaccuracy and imprecision.

The uncertainty of this measurement is a factor of 4.7 improvement over the experimental literature value of 5427.320(71) eV (13 ppm uncertainty) [10]. The 0.358 eV

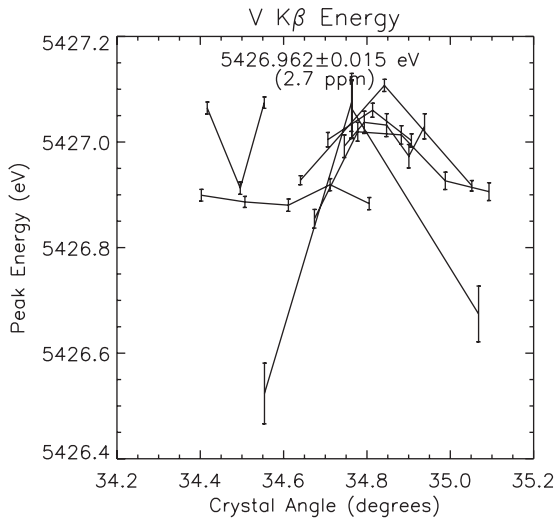


FIG. 5. The peak energies of the fits of individual V $K\beta$ energy spectra. Each of the seven series represents a subset of the data corresponding to a different configuration of the spectrometer. Hence each series must be modeled with a different prediction of the dynamical diffraction code suited to the geometry. Within each subset consecutive points correspond to a methodical stepping of arm position (θ) so that each profile falls on a different part of the detector area. The variance observed is a sign of limitations and systematics of the whole procedure. Therefore the pooled variance correctly represents the robustness of the final determination of profile and energy.

discrepancy is just over 5.0 standard deviations of the previous work. This discrepancy is therefore unlikely to be the result of a statistical fluctuation but is likely evidence of error in one of the two experimental values, possibly due to the inconsistency of instrumental broadening in the prior work or a discrepancy in the characterization of the shape (and thus the peak energy) of the spectrum. Since an account of instrumental broadening is not provided for in the prior work, the discrepancy may be attributable to instrumental broadening therein.

X. USE OF THE CHARACTERIZATION OF VANADIUM $K\beta$

We have presented a transferable characterization of V $K\beta$ in terms of a sum of Voigt functions with a common instrumental (Gaussian) broadening (Table II). For an arbitrary experiment, the instrumental broadening should be refitted to the relevant profile, while the relevant contributions and widths of each component should remain the same. Fitting of an overall amplitude, the energy scale, and the background to the experimental data should be all that is required to maintain the accuracy of the transfer.

Specifically, we measure the V $K\beta$ profile and fit it with

$$P_{\text{fit}}(X; B, \sigma, A, X_1, X_2) = P\left(X; B, \sigma, A, X_1, W_1 \frac{X_2 - X_1}{C_2 - C_1}, AA_2/A_1, X_2, W_2 \frac{X_2 - X_1}{C_2 - C_1}, AA_3/A_1, (C_3 - C_1) \frac{X_2 - X_1}{C_2 - C_1} + X_1, W_3 \frac{X_2 - X_1}{C_2 - C_1}\right), \quad (16)$$

where the A_i , C_i , and W_i come from Table II and the X_i parameters are the positions of the first two Voigt peaks, A is the area of the first peak, σ is the Gaussian width of all the Voigt peaks, and B is the background height. This characterization of V $K\beta$ can be usefully transferred to other experiments to generate calibration points for high-accuracy x-ray experiments. The absolute value of the determined peak free from instrumental broadening should then correspond to our result with the given uncertainty. In the Supplemental Material [29] we present the full profile with uncertainties for use in further analysis using the methodology presented.

XI. CONCLUSION

The spectral profile of V $K\beta$ was measured and characterized in a transferable way. The characterization involved

modeling the profile with four Lorentzian peaks convolved with an overall Gaussian. The Gaussian is recommended as a reasonable approximation for modeling additional instrumental broadening. The individual widths, positions, and relative intensities for each Lorentzian component are described and tabulated. The V $K\beta$ peak energy was found to be 5426.962(15) eV. This is an improvement in uncertainty by a factor of 4.7 over prior work. Further, the full profile is deposited for general use or to directly compare to a calibration

profile without the parametric modeling. We recommend that the component modeling is reliable and much more accurate than previous approaches and is a recommended standard methodology for future x-ray calibration.

ACKNOWLEDGMENT

We would like to acknowledge Alexis Illig for her care and assistance in proofreading.

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- [1] S. Galambosi, H. Sutinen, A. Mattila, K. Hämäläinen, R. Sharon, C. C. Kao, and M. Deutsch, *Phys. Rev. A* **67**, 022510 (2003).
 - [2] M. Fritsch, C. C. Kao, K. Hämäläinen, O. Gang, E. Förster, and M. Deutsch, *Phys. Rev. A* **57**, 1686 (1998).
 - [3] M. Deutsch, O. Gang, K. Hämäläinen, and C. C. Kao, *Phys. Rev. Lett.* **76**, 2424 (1996).
 - [4] C. T. Chantler, J. A. Lowe, and I. P. Grant, *J. Phys. B* **46**, 015002 (2012).
 - [5] C. T. Chantler, J. A. Lowe, and I. P. Grant, *Phys. Rev. A* **82**, 052505 (2010).
 - [6] M. Deutsch, G. Hölzer, J. Härtwig, J. Wolf, M. Fritsch, and E. Förster, *Phys. Rev. A* **51**, 283 (1995).
 - [7] G. Hölzer, M. Fritsch, M. Deutsch, J. Härtwig, and E. Förster, *Phys. Rev. A* **56**, 4554 (1997).
 - [8] C. T. Chantler, A. C. L. Hayward, and I. P. Grant, *Phys. Rev. Lett.* **103**, 123002 (2009).
 - [9] J. A. Lowe, C. T. Chantler, and I. P. Grant, *Phys. Lett. A* **374**, 4756 (2010).
 - [10] J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.* **39**, 125 (1967).
 - [11] J. P. Desclaux, *At. Data Nucl. Data Tables* **12**, 312 (1973).
 - [12] R. D. Deslattes, E. G. Kessler, P. Indelicato, L. de Billy, E. Lindroth, and J. Anton, *Rev. Mod. Phys.* **75**, 35 (2003).
 - [13] I. P. Grant, *Adv. Phys.* **19**, 747 (1970).
 - [14] D. F. Anagnostopoulos, R. Sharon, D. Gotta, and M. Deutsch, *Phys. Rev. A* **60**, 2018 (1999).
 - [15] D. F. Anagnostopoulos, D. Gotta, P. Indelicato, and L. M. Simons, *Phys. Rev. Lett.* **91**, 240801 (2003).
 - [16] J. Schweppe, R. D. Deslattes, T. Mooney, and C. J. Powell, *J. Electron Spectrosc. Relat. Phenom.* **67**, 463 (1994).
 - [17] W. L. Bond, *Acta Crystallogr.* **13**, 814 (1960).
 - [18] C. T. Chantler, M. N. Kinnane, C.-H. Su, and J. A. Kimpton, *Phys. Rev. A* **73**, 012508 (2006).
 - [19] S. Raj, H. C. Padhi, P. Palit, D. K. Basa, M. Polasik, and F. Pawłowski, *Phys. Rev. B* **65**, 193105 (2002).
 - [20] O. Sogut, E. Bykkasap, and H. Erdogan, *Radiat. Phys. Chem.* **64**, 343 (2002).
 - [21] S. Raj, H. C. Padhi, D. K. Basa, M. Polasik, and F. Pawowski, *Nucl. Instrum. Methods Phys. Res., Sect. B* **152**, 417 (1999).
 - [22] H. C. Padhi, C. R. Bhuinya, and B. B. Dhal, *J. Phys. B* **26**, 4465 (1993).
 - [23] S. Fazinic, M. Jaksic, L. Mandic, and J. Dobrinic, *Phys. Rev. A* **74**, 062501 (2006).
 - [24] L. Mandić, S. Fazinić, and M. Jakšić, *Phys. Rev. A* **80**, 042519 (2009).
 - [25] S. P. Limandri, A. C. Carreras, R. D. Bonetto, and J. C. Trincavelli, *Phys. Rev. A* **81**, 012504 (2010).
 - [26] J. D. Silver, A. J. Varney, H. S. Margolis, P. E. G. Baird, I. P. Grant, P. D. Groves, W. A. Hallett, A. T. Handford, P. J. Hirst, A. R. Holmes *et al.*, *Rev. Sci. Instrum.* **65**, 1072 (1994).
 - [27] C. T. Chantler, *J. Appl. Crystallogr.* **25**, 674 (1992).
 - [28] C. T. Chantler, *J. Appl. Crystallogr.* **25**, 694 (1992).
 - [29] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevA.87.022512> for further analysis.

Characterization of the titanium $K\beta$ spectral profile

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Received 26 December 2012, in final form 24 May 2013

Published 13 June 2013

Online at stacks.iop.org/JPhysB/46/145601

Abstract

Transition metals have $K\alpha$ and $K\beta$ characteristic radiation possessing complex asymmetric spectral profiles. Instrumental broadening normally encountered in x-ray experiments shifts features of profiles used for calibration, such as peak energy, by many times the quoted accuracies. We measure and characterize the titanium $K\beta$ spectral profile. The peak energy of the titanium $K\beta$ spectral profile is found to be 4931.966 ± 0.022 eV prior to instrumental broadening. This 4.5 ppm result decreases the uncertainty over the past literature by a factor of 2.6 and is 2.4 standard deviations from the previous standard. The spectrum is analysed and the resolution-free lineshape is extracted and listed for use in other experiments. We also incorporate improvement in analysis applied to earlier results for V $K\beta$.

 Online supplementary data available from stacks.iop.org/JPhysB/46/145601/mmedia

1. Introduction

High accuracy, absolute x-ray energy calibration is of great importance to making progress in x-ray science, including a better basis to test and develop QED and inner-shell process theory. Characteristic radiation (principally $K\alpha$ and $K\beta$ radiation) is often used as a calibration standard as the profiles are robust, stable and cheap to produce. The structure is properly modelled through the relativistic quantum theory of the atom, which has recently undergone significant development, especially for copper $K\alpha$ [1]. Characterizations of the profiles permits new tests and understanding of atomic theory.

Excitation processes produce characteristic radiation including electron bombardment, x-ray absorption and inelastic x-ray scattering. These processes all involve an energetic incoming particle exciting the atom, and can be subject to sensitive chemical shifts and solid state effects. When the incoming particle has an energy just above threshold, the excited states and the shape of the characteristic energy profile sensitively depend upon the energy of the incoming particle [2, 3]. For electron bombardment, when the energy of the electron is at least 2.5 to 3 times the threshold energy of

the dominant transition, the excited state and profile shape of the characteristic radiation stabilize. This condition makes it possible to characterize the profile of $K\beta$ radiation in a way that is robust to incoming electron energy variation. Standard x-ray sources include fixed anodes, rotating anodes, synchrotron excitation and others. We use a simple fixed source excitation following the standard technique of many past researchers. The question is, what is the stable profile which is thereby obtained, and how can it be robustly used, fitted and modelled in secondary and perhaps critical experiments?

A concerted effort to experimentally summarize experimental energies of characteristic radiation was undertaken and compiled by Bearden and Burr in 1967 [4]. This has been complemented by theoretical computations by Desclaux [5] as well as experimental measurement and compilation by Deslattes *et al* [6]. That review work summarized the peak energies of measured transitions without regard for the shifts and change of shape of the spectra due to experimental and instrumental broadening. Thus it is particularly difficult to compare advances in theory to results from high accuracy experiments. RMBPT has shown success with the inclusion of correlations to high-order and of the Auger shift. Quantum mechanics predict a shift and

Table 1. Characteristic radiation peak energy data from Chantler *et al* [19] and Deslattes *et al* [6]. The peak energy of the $K\beta$ radiation has a larger uncertainty than for $K\alpha$ radiation by an order of magnitude.

Spectral profile peak	Reference peak energy (eV)	Peak energy uncertainty (ppm)
Titanium $K\alpha_1$	4510.899 [6]	2.08
Titanium $K\alpha_2$	4504.920 [6]	2.09
Vanadium $K\alpha_1$	4952.131 [19]	1.21
Vanadium $K\alpha_2$	4944.651 [19]	2.22
Chromium $K\alpha_1$	5414.804 [6]	1.31
Chromium $K\alpha_2$	5405.538 [6]	1.31
Manganese $K\alpha_1$	5898.801 [6]	1.42
Manganese $K\alpha_2$	5887.685 [6]	1.43
Titanium $K\beta_1$	4931.83 [6]	12.0
Vanadium $K\beta_1$	5427.32 [6]	13.0

a broadening when a state is degenerate with a continuum [7, 8]. Significant advances in theory have been based on the relativistic approaches of Grant [9].

Experimental spectral profiles for the characteristic radiation of transition metals are represented by semi-empirical fitting of multiple components—using typically five or seven peaks for $K\alpha$ spectra [10, 11]. Theoretical modelling of characteristic radiation profile shape is dominated by diagram line computations, which represent x-ray emission energies of electron decay from the ground state with a core-hole and an excited electron, to the ground state with the core-hole filled and a higher n hole. Additional components, theoretically and empirically, are contributed by satellite lines caused by shake-up and shake-off effects. This set of transitions is complex, especially for elements with open subshells such as the transition metals. Progress in the details of such theory has accelerated recently [12–15]. Empirical modelling using fitting functions for a sum of a small number of Lorentzian, Gaussian, Voigt or instrumental functions tends to conceal the theoretical complexity of the many CSF transitions.

Efforts to find good empirical models of spectral radiation have continued from the work of Deutsch *et al* and Hölzer *et al* of the 1990s [16, 10, 17, 11, 18]. Deslattes *et al* [6] includes a summary of these efforts, which is summarized with [19] in table 1 with experimental energies and uncertainties for $K\alpha$ characteristic peaks for $Z = 22$ –26. The uncertainties for the $K\alpha$ energies in this range are on the order of 1 to 2 parts per million (ppm). However, the quoted uncertainty of the titanium $K\beta$ peak energy [4] (table 1) is an order of magnitude larger at 12 ppm, limiting accuracy and calibration in this region of energy. In part, this is driven both by the weakness of $K\beta$ compared to $K\alpha$, and the difficulty of calibration with suitable flux at low energies. In particular, although a nearby $K\alpha$ spectrum can be used to calibrate some experiments, the $K\beta$ adds a more critical and more difficult calibration affected by instrumental broadening but which is however less easily affected by vignetting. It therefore represents both a challenge and an opportunity for sharper and much more constrained calibration of accurate energies. We propose here and elsewhere to use a maximal calibration series including both $K\alpha$ and $K\beta$ characteristic lines. Other

methods are possible. However, until now, the accuracy of the determination of $K\beta$ transitions generally precluded their utility for such purposes. This is the subject of the current paper.

Data collection methods generally use a single flat crystal spectrometer employing the Bond method [10, 11], or a curved crystal spectrometer [16]. In the experimental work arising from Germany [10, 11], raw spectra were deconvolved with a measured or fitted instrumental broadening, and each deconvolved spectrum was fit empirically with Lorentzians. The peak location of each empirical fit was taken to be the measure of each peak energy.

It is not immediately clear how to use these characterizations as standards for experiments with any different instrumental broadening. Chantler *et al* [19] addressed this concern by providing a consistent set of empirical Voigt fit functions for a range of elements ($21 \leq Z \leq 25$) including an approach to allow for instrumental broadening effects.

There has been some interest in the shape of the Ti $K\beta$ profile over the years [20–24]. Much of this has been relating to efforts in calibration, as discussed above; but also because the characteristic signature provides valuable information about atomic structure, molecular and solid state effects including valence, ionization state, and Fermi levels in addition to electron correlations, excitation dynamics and relaxation processes. Interest has been raised in the identification of radiative Auger energies, KM_1 quadrupole decay, $K\beta^{III}$ and $K\beta^{IV}$ double ionization processes and other processes sometimes labelled $K\beta'$ and $K\beta_5$. Additionally, x-ray astronomy has observed numerous K spectra of transition metals arising from plasmas of different types, and characterization of the profile can yield clues as to the nature of the plasma. This work has all been relative to the peak reported by Bearden and Burr [4], regarded as problematic in that the resolution and broadening shift was not calibrated.

A theoretical calculation of the peak energy for the diagram line of Ti $K\beta$ is 4930.86(85) eV [6], consistent with the experimental result reported. However, the relatively high uncertainty in the Ti $K\beta$ peak energy compared to those of $K\alpha$ makes Ti $K\beta$ a good candidate for improved characterization.

This paper presents the characterization of the titanium $K\beta$ profile leading to a measurement of the energy of titanium $K\beta$ peak energy after removal of instrumental broadening. The inclusion of broadening effects in the fitting method enables the results to be transferable to a large range of experimental conditions. Specifically, the characterization, or indeed the profile itself, can be simply used in experiments where the amount of instrumental broadening is difficult to measure.

2. Method of creation of the titanium $K\beta$ standard profile

2.1. Experimental setup

A curved crystal spectrometer maps energy into position on a linear detector. The energy corresponding to each position along the detector is determined by measuring strong $K\alpha$

spectra, the peak values of which are known to $\simeq 1$ ppm from published measurements. This calibration is then used to place the $K\beta$ spectrum on an energy scale. The measured spectrum is fitted by a sum of four Voigt functions with a common Gaussian width, representing the resolution function. Setting the Gaussian width to zero yields the ‘intrinsic’ resolution-smearing-free lineshape, the peak position of which may be taken as an instrument-independent Ti $K\beta$ energy.

Experimental apparatus included a 20 keV electron bombardment x-ray source and a Johann geometry curved crystal spectrometer with position-sensitive x-ray detection. The apparatus was at the Oxford EBIT [25] as part of the calibration series for a test of QED. Figure 1 shows the arrangement of the calibration source, diffracting crystal, and detector. Significant details included the calibration anode, the Bragg angle of the arm that the detector sits on (2θ) an adjustable ‘Seemann wedge’ and a Germanium (220) crystal. The arm angle was fully adjustable with low hysteresis on the gearing and high reproducibility. The housing for the crystal is mechanically linked to the detector arm such that the crystal surface bisects the angle between the source and detector arm, so the crystal angle (θ) is half the arm angle. The crystal and arm angles are measured by gravity referenced electronic clinometers that output a raw voltage (V) which must be calibrated to clinometer angle I and then to θ . The Seemann wedge controls the band-pass of radiation through the crystal. One source of instrumental broadening is the gap between the wedge and the crystal surface. A multi-wire gas proportional counter with a backgammon configuration was used to detect x-rays, as well as provide good linearity and resolution in the dispersion axis.

For the calibration of the spectrometer, crystal alignment, and detector scale, a series of calibration spectra was collected in successive diffracting positions in order to assess systematics and evaluate the dispersion function. Table 1 provides the list of reference lines and their provenance, together with $K\beta$ references for comparison. Clearly, the $K\beta$ spectra currently provide poor reference lines compared to the $K\alpha$ series or primary lattice spacing calibrations. The increased uncertainty is well-understood to be due to statistical precision and the $K\beta$ intrinsic asymmetry—however, this paper explains how to realize determinations of the $K\beta$ transitions with an accuracy approaching that of the $K\alpha$ transitions.

2.2. Mosplate diffraction theory

The experimental process was modelled by the dynamical diffraction code, Mosplate [26, 27]. Mosplate predicts and models diffraction phenomena with effects on energy determination of 100–500 parts-per-million (ppm), and characterizes these with an accuracy and stability below 1 ppm. Diffraction phenomena of interest include the formal refractive index correction, but also crucial and independent dynamical diffraction depth penetration and geometric lateral shifts due to x-rays penetrating the crystal. Depth penetration of the dynamical wavefield can be a dominant systematic in curved crystal spectrometry but may be an even more significant effect in flat crystal spectrometry. Lateral shifts

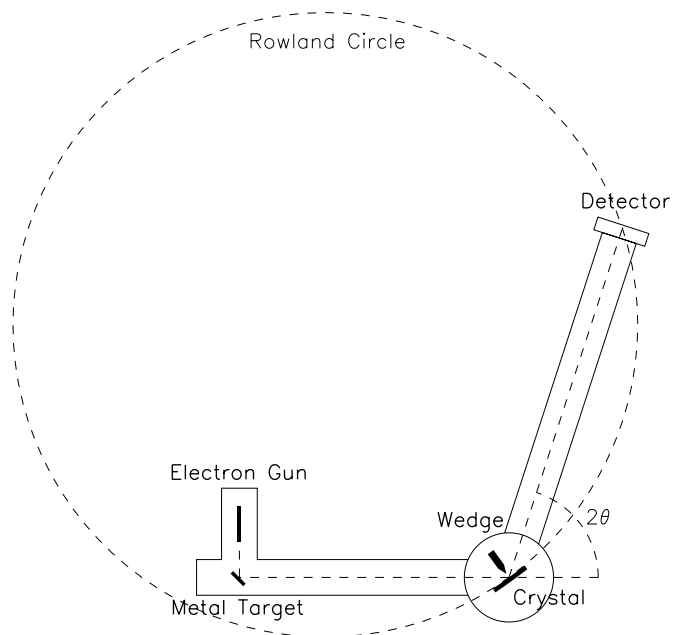


Figure 1. Schematic diagram of experimental setup.

can dominate in curved crystal spectrometry and are often a similar order of magnitude. Corrections for asymmetry and polarization are typically responsible for another 30 ppm. The refractive index shift, of order 100–200 ppm, is easily computed to high accuracy given knowledge of the (crystal) structure. However, the total or effective diffraction correction of 100–300 ppm, must be determined accurately to 1% or better. Figure 2 presents the effective refractive index based on the source location, size, crystal position and curvature, and detector location. The functional with respect to calibration lines is clear and stable, and more importantly the three curves presented reflect different detector–source positions (different Bragg angles to the axis of the crystal) which are set and characterized in the analysis. The associated uncertainty is of order 1.5 ppm, very similar to the uncertainty of the knowledge of the characteristic radiation energies. Figure 3 presents the similar effective shifts of the computed lines but including the changes of profile shape etc for one setting. The scale of the differential shifts and noise strongly support the final accuracy estimate of this uncertainty of 1.5 ppm.

For each x-ray energy E and crystal angle θ , Mosplate calculates the x-ray intensity spectrum we expect to see on the detector. The incident wavefield is computed by ray tracing performed from a point grid at the source to a point grid on the cylindrically curved crystal. The wavefield is then propagated through the crystal to find the diffracted wavefield at the exit surface of the crystal. The diffracted fields are then used as a source to ray trace to the final diffracted image on the detector. Once an appropriate range of single energy spectra is calculated at different crystal angles, a theoretical peak position, D , for each spectrum is computed.

These calculations of theoretical peak position sample the Mosplate model function for the peak position D and profile as a function of peak energy E and crystal angle θ :

$$D = D_{\text{mos}}(E, \theta). \quad (1)$$

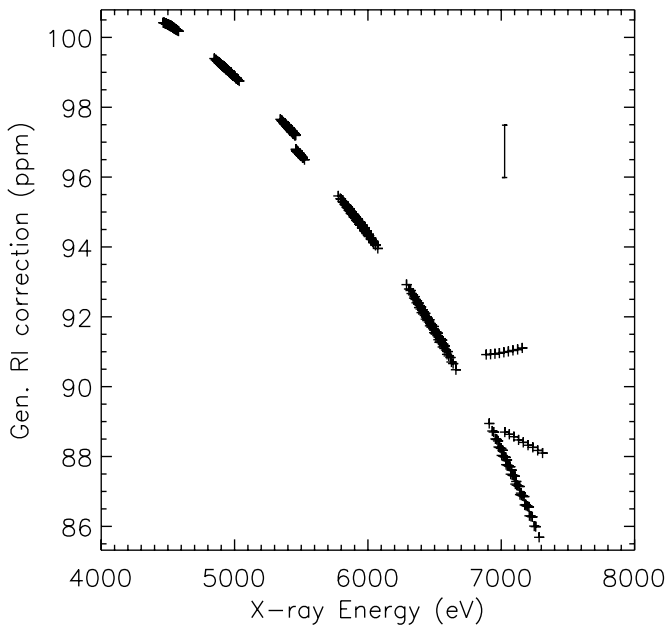


Figure 2. This figure shows the effective refractive index correction given the specific geometry of the source, crystal and detector system. Note particularly (i) that the functional and convergence are well below the 1.5 ppm estimate (ii) the dispersion of the curves at higher energies is not uncertainty but predictive of the change in geometry depending upon the source-crystal axis angle. In other words, the variation is due to Mosplate correctly predicting the functional with position. Illustrated on the side is the estimated uncertainty of the characterization including input uncertainties, computed with an approximately 1.5 ppm uncertainty error bar. This estimate would be substantively different with a flat crystal geometry.

This model also implicitly defines functions that calculate E and θ from the remaining variables:

$$E = E_{\text{mos}}(D, \theta) \quad (2)$$

$$\theta = \theta_{\text{mos}}(D, E). \quad (3)$$

These functions are interpolated between the sampling frequency of E and θ for which the results of $D_{\text{mos}}(E, \theta)$ are computed to high accuracy. Interpolation uncertainty is negligible by design.

2.3. Data collection

Seven calibration series were conducted with a variety of wedge positions, offset positions of the detector, and integration times to interrogate systematics and confirm the accuracy of the theory. Data was collected in pseudo-event mode, so each x-ray is recorded as a separate pulse, rather than in an integrating detector. In each calibration series, $K\alpha$ and $K\beta$ spectral profiles from $Z = 22$ – 26 were collected. Each spectral profile type was collected at three to five detector arm angles, in order to investigate the dispersion function and the detector response function.

2.4. $K\alpha$ profile modelling

The $K\alpha$ profiles were fitted as functions of energy provided by [19]. Each of these functions are a sum of six Voigt profiles,

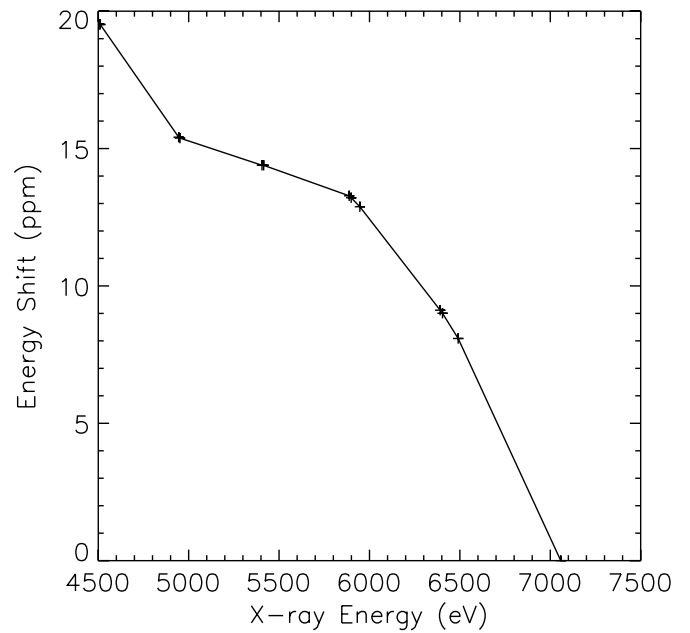


Figure 3. The energy shift from Bragg's law predicted by Mosplate, including peak and profile shifts as used in the computation, with an estimated uncertainty of 1.5 ppm.

with a common Gaussian width to model the instrumental broadening, which map x-ray energy to x-ray intensity. The energy offsets, Lorentzian widths, and relative amplitudes of the Voigt profiles are set by [19]. Each of the $K\alpha$ experimental profiles were measured on a detector position axis rather than directly on an energy axis, so the profiles were fit by refining five fitting parameters: (i) a scale and (ii) an offset to map the detector position to energy, (iii) an intensity scale to model the overall intensity of the profile, (iv) a constant intensity background, and (v) a common Gaussian broadening width.

These highly accurate $K\alpha$ characterizations provide a suite of peak energies correlated with the peak detector positions of each profile at each clinometer voltage. Figure 4 shows how one such fit leads to two calibration points.

2.5. Titanium $K\beta$ profile fitting

Ti $K\beta$ profiles were also collected and characterized on intensity and detector position axes. To define a characteristic lineshape function, each of the spectra were fitted using a sum of four Voigt functions with a common Gaussian width σ and a constant intensity background, B . Past literature has often used Lorentzians or Gaussians, which are generally inadequate. Profile decomposition can be made in principle with arbitrary functions. However, it is preferred that each component, even if semi-empirical in nature, should have a broadening representative of a real diagram line. The number of components is partially limited, or fixed, by the information content. It is obvious that at least three are required to produce the asymmetry. If three Voigts are attempted, there is a strong residual signature which is proof of the requirement for a fourth component. Equally, it is seen from table 2 that the area involved in the fourth peak is minor and that remaining residuals from figure 3 almost fully lie within the one standard

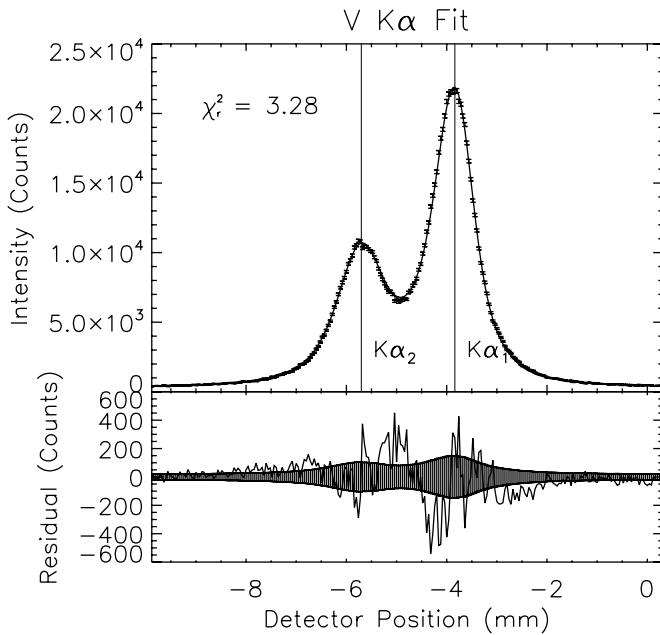


Figure 4. Typical fit of V K α spectrum using only five scaling parameters, yielding two calibration points (V K α_1 and V K α_2 which constrain the spectrometer dispersion function). The fit has a χ^2_r of 3.28. The K α_1 peak has an energy 4952.131(6) eV and detector position $-3.8157(14)$ mm. The K α_2 peak has an energy 4944.651(11) eV and detector position $-5.6973(26)$ mm. The crystal clinometer voltage was $-1.074\,9865(99)$ V.

Table 2. Characterization of the Ti K β spectral profile. The profile is fully characterized on an absolute energy scale through a sum of component Lorentzians convolved with a Gaussian instrumental broadening. Integrated areas A_i , centroids C_i and FWHMs W_i of individual components were obtained from a fit of intensity against detector position. The detector position axis was transformed to an absolute energy scale via the calibration procedure. The Gaussian width $\sigma = 1.244(41)$ eV. The background was $B = 831(26)$ counts. The second and third components are dominant, contributing more than three quarters of the intensity of the spectrum while the fourth component is very weak. The third and fourth component widths are dominated by the Gaussian instrumental width. The first component is very broad relative to the entire K β spectrum.

Relative area $\frac{A_i}{\sum_{i=1}^4 A_i}$	Integrated area A_i (counts)	Centroid C_i (eV)	FWHM W_i (eV)
0.199(24)	120 700(14 700)	4925.37(50)	16.3(10)
0.455(23)	276 000(13 700)	4930.096(75)	4.25(19)
0.326(22)	197 700(13 200)	4931.967(16)	0.42(22)
0.0192(54)	11 660(3250)	4935.59(16)	0.47(44)

error band. Hence there is no evidence for a fifth peak in the data itself.

The i th Voigt function used in the characterization is defined to be:

$$V(x; A_i, C_i, W_i, \sigma_i) = A_i \int_{-\infty}^{\infty} \left(\frac{e^{-x'^2/(2\sigma_i^2)}}{\sigma_i \sqrt{2\pi}} \right) \times \frac{W_i/2}{\pi[(x - C_i - x')^2 + (W_i/2)^2]} dx' \quad (4)$$

where A_i is the integrated area of the Lorentzian profile, C_i is the centroid of the profile, W_i is the Lorentzian full width

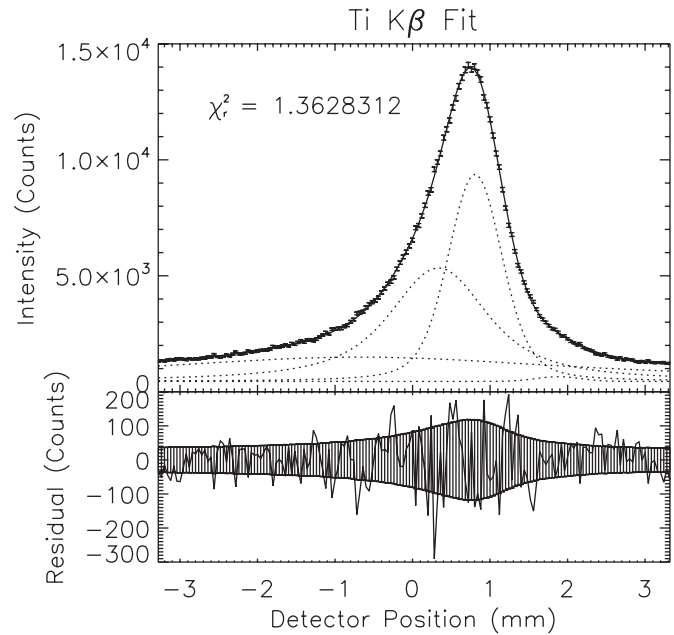


Figure 5. Typical fit of a Ti K β spectrum. The crystal clinometer voltage was $-1.012\,9597(74)$ V and the peak detector position was $0.8089(14)$ mm. Fitting parameters are provided in table 2.

half maximum (FWHM) and σ_i is the Gaussian broadening standard deviation. The Gaussian broadening FWHM is $2\sqrt{2 \ln 2} \sigma_i \approx 2.35\sigma_i$. Thus the spectra containing a Ti K β spectral profile were modelled with:

$$P(x; b, \sigma, A_1, C_1, W_1, A_2, C_2, W_2, A_3, C_3, W_3, A_4, C_4, W_4) = B + \sum_{i=1}^4 V(x; A_i, C_i, W_i, \sigma_i = \sigma). \quad (5)$$

A large collection of independent measurements of Ti K β profiles were fitted with this method. The relative intensities, positions and widths of the Voigt functions were consistent in all fits (to better than one standard error of the scaled fitting parameters), so the minimum uncertainty results are reported. The characteristic parameters of these fits are shown in table 2 with the position axis converted to energy. Figure 5 shows a typical fit for one of the Ti K β spectra.

These optimum parameters were then used to constrain refits of all the Ti K β profiles. Each refit had free parameters characterizing the overall intensity, position, detector position to energy scale conversion, instrumental broadening and background of the spectral profile in the specific geometry of the measurement. As each refit had a slightly different instrumental broadening due to geometry changes, the transferable reference position of the peak of each profile was the position of the maximum of the fit function with the Gaussian width set to zero. All refits were reliable and consistent with the original fits (to within one standard error of scaled parameter values); but the characterization allows for a consistent transferable standard both in this measurement, the calibration of the dispersion function, and for any subsequent measurement by other authors. This enabled a consistent measurement of peak position on any Ti K β profile for any local instrumental broadening.

2.6. Dispersion function for energy calibration

Two calibration functions are required to map the dispersion function and detector profile to an absolute energy axis. The clinometer calibration function $\theta = -I(V; P_I)$ maps the clinometer voltage V to the clinometer angle I and the dispersion crystal angle θ which reflects the theoretical Mosplate model crystal angle. $I(V; P_I)$ is defined to be:

$$I(V; P_I) = a \sin\left(\frac{V - P_{I,2}}{P_{I,0}}\right) - P_{I,1} + \sum_{i=0}^n P_{I,(i+3)} (V - P_{I,2})^i \quad (6)$$

where P_I is the vector of fitting parameters.

A second calibration function, the detector dispersion calibration function $D_2(x; P_D)$, maps the recorded detector position x in output units to the theoretical detector position D in mm. The map from x to D was defined by:

$$D_2(x; P_D) = \sum_{i=0}^1 P_{D,i} x^i \quad (7)$$

where P_D is the vector of fitting parameters.

Using this calibration, an energy can be assigned for any detector position x and any clinometer voltage V :

$$E(x, V; P_D, P_I) = E_{\text{mos}}(D_2(x; P_D), -I(V; P_I)). \quad (8)$$

Equations (6) and (7) define the calibration of an experimental configuration (i.e. a calibration series). The calibration process was reduced to simultaneously finding the P_I and P_D fitting parameters that best fit the $K\alpha$ data and produced an internally consistent measurement of the Ti $K\beta$ peak energy for each calibration series. This optimized the statistical information for the determination of the profile and dispersion function. We use the evidence of the data to define a minimum-variance solution for parametrization of the dispersion function. In one sense this is a variant of a least-squares hypothesis, used widely in all statistical fitting but here we use it directly to assess the variance of the final measured energies.

2.7. Determination of energy uncertainty

Following equation (8), the uncertainty in the energy assigned to a detector position measurement, ΔE , was due to four primary sources of uncertainty: (i) detector position (Δx), (ii) detector dispersion fit $C_{D,ij}$, (iii) noise in clinometer voltage (ΔV), and (iv) clinometer calibration function fitting $C_{I,ij}$.

$$\Delta E^2 = \left(\frac{\partial E}{\partial x} \Delta x\right)^2 + \sum_{ij} \frac{\partial E}{\partial P_{D,i}} \frac{\partial E}{\partial P_{D,j}} C_{D,ij} + \left(\frac{\partial E}{\partial V} \Delta V\right)^2 + \sum_{ij} \frac{\partial E}{\partial P_{I,i}} \frac{\partial E}{\partial P_{I,j}} C_{I,ij} \quad (9)$$

where $C_{D,ij}$ is the i, j th element of the covariance error matrix from the detector dispersion function fit. Likewise, $C_{I,ij}$ is the i, j th element of the covariance error matrix from the clinometer calibration function fit.

The clinometry calibration function covariance includes all uncertainties from clinometer nonlinearity, peak and energy uncertainty of $K\alpha$ transitions and fitting, diffraction

Table 3. Error budget for the peak energy of all the spectral profiles of Ti $K\beta$ that go into the final energy determination. Since the resultant determined energies show evidence of additional variance, the final energy determination has a larger uncertainty than this ideal 1.6 ppm for an individual spectrum.

Uncertainty source	Average contribution to energy uncertainty for an individual Ti $K\beta$ spectrum (ppm)
Ti $K\beta$ spectrum fit ($\frac{\partial E}{\partial x} \Delta x_{\text{fit}}$)	0.98
Detector dispersion function fit ($\sqrt{\sum_{ij} \frac{\partial E}{\partial P_{D,i}} \frac{\partial E}{\partial P_{D,j}} C_{D,ij}}$)	0.021
Clinometer noise ($\frac{\partial E}{\partial V} \Delta V$)	1.3
Clinometer calibration fit ($\sqrt{\sum_{ij} \frac{\partial E}{\partial P_{I,i}} \frac{\partial E}{\partial P_{I,j}} C_{I,ij}}$)	0.14
Total uncertainty	1.6

theory uncertainty and variance and other contributions. $K\alpha$ peak position uncertainties are as detailed in table 1, and the uncertainties of the refractive index correction, dynamical diffraction modelling, geometric uncertainty and computational instability are approximately 1.5 ppm. These are included as input uncertainties of the $C_{I,ij}$ coefficients. Any temperature uncertainty cancels in the modelling (for this calibration methodology) because it produces an overall shift and not a relative shift of the spectra. The impact of uncertainty of the source position upon the diffraction computations is almost negligible. Further, the correlated uncertainty of more complex diffraction estimates cancels to first order. We detail the fitting procedure in the [appendix](#). Table 3 shows the average magnitudes of these various contributions to ΔE outlined in section 2.7 for a single Ti $K\beta$ spectrum.

3. Definition of titanium $K\beta$ standard

3.1. $K\beta$ peak energy

Fits of the Ti $K\beta$ spectra provide independent measures of the peak energy of Ti $K\beta$, shown in figure 6. There is a systematic functional in the dispersion of measured energies with crystal angle. These data are pooled with their weighted mean reflecting the total uncertainty including the remanent systematic error.

The resulting measurement of the Ti $K\beta$ profile peak energy is 4931.966(22) eV. This 4.5 ppm uncertainty is reduced from the larger uncertainty for individual fits given in table 3. Combining consistent samples in a weighted mean reduces uncertainty. We also computed the result after removing the two or three most significant outliers at the bottom of the graph, and the result changed insignificantly within sigma. The accuracy arises from the distribution of the results which are indeed clustered correctly about the centre of the detector. While the systematic could be asymmetric, we assume that it is symmetric and that our sampling measures this distribution. The previous theoretical reference value is 4930.86(85) eV [6]. The 1.106 eV or 1.3 standard deviation discrepancy from this is reflective of the claimed imprecision of the theoretical literature value.

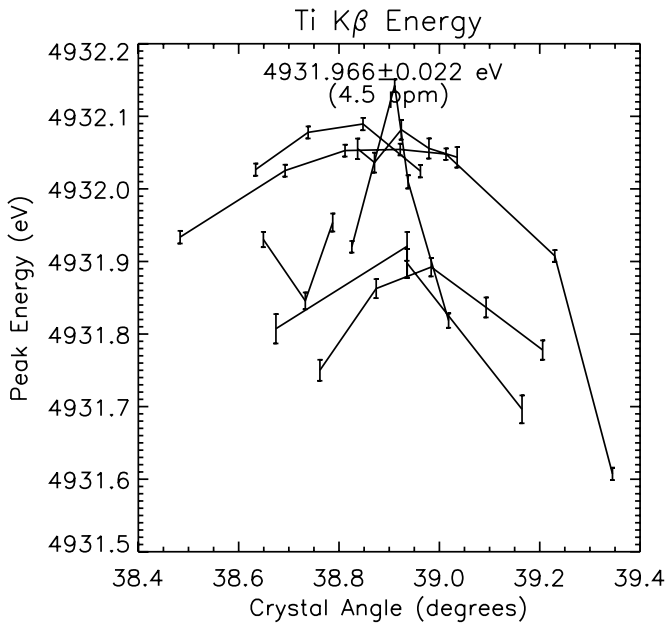


Figure 6. The peak energies of the fits of individual measured Ti K β spectra. Each of the seven lines represents an independently measured set of results from the full calibration series, derived by methodical stepping of the spectrometer arm length so that the profile stepped across the detector area. The variance is larger than the point precision, indicating sources of systematics. The characterization function drifts off towards the edges of the detector, where vignetting or other loss of efficiency may affect the calibration. Further, some of the linked series have offsets, whether from minor hysteresis or e.g. temperature variations. The overall consistency and hence robustness of the independent measurements yields a final pooled uncertainty of 4.5 ppm.

The new measurement represents a factor of 2.6 improvement in the uncertainty compared with the prior experimental value of 4931.827(59) eV, which had a 12 ppm uncertainty [4]. The discrepancy is 0.139 eV or about 2.4 standard deviations. Since an account of instrumental broadening is not given in the earlier experimental measurement, the 0.139 eV discrepancy is likely attributable to instrumental broadening. The relationship between peak energy and instrumental broadening is shown in figure 7. The asymmetry of the peak means that the greater the broadening, the more the peak energy is shifted to lower values. Hence any instrumental broadening will shift the peak energy significantly. We therefore present the instrumental-independent location and parameterization, so that it can be used with a general experimental methodology in situations with higher or lower resolution, in order to maintain an accurate calibration and energy transfer.

4. Use of the characterization of titanium K β

This paper offers a transferable characterization of Ti K β in terms of a sum of Voigt functions with a common instrumental (Gaussian) broadening, presented in table 2. This characterization functions as a standard reference for use in arbitrary experimental environments, where the instrumental broadening will be different. The instrumental broadening

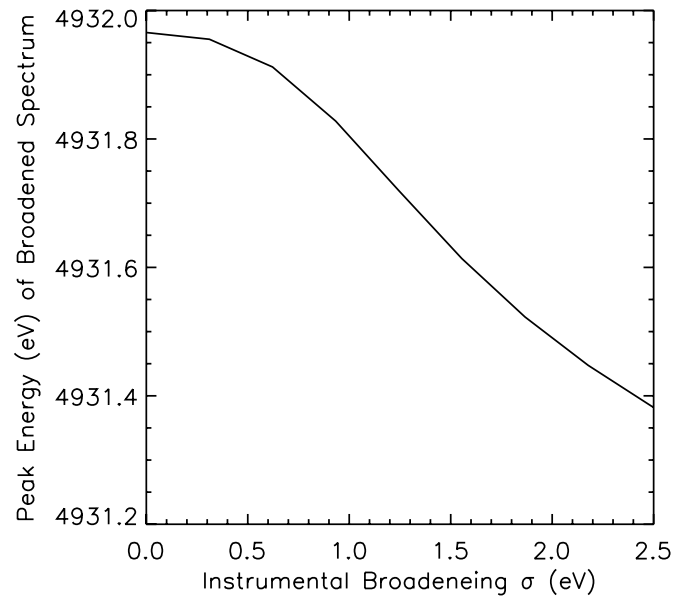


Figure 7. The peak energy of the fitted model function of the Ti K β spectra as a function of the instrumental broadening. The measured broadening of the spectrum of 1.24(4) eV and the asymmetry of the peak leads to a shift of peak position of 0.25 eV or 50 ppm.

should be fitted to the relevant profile, while the percentage contributions and eV widths of each component should remain unchanged. Fitting of an overall amplitude coefficient, the energy scale, and background to the experimental data should be all that is required to maintain the accuracy of the transfer. The simplest improvement over the previous literature is that a user may measure the Ti K β profile, remove the instrumental broadening, locate the peak position and then use the above determination to calibrate the spectrum.

A more accurate and transferable methodology would be to measure a Ti K β line as part of the calibration and then fit it with:

$$P_{\text{fit}}(X; B, \sigma, A, X_1, X_2) = P\left(X; B, \sigma, A, X_1, W_1 \frac{X_2 - X_1}{C_2 - C_1}, \frac{AA_2}{A_1}, \right. \\ \left. X_2, W_2 \frac{X_2 - X_1}{C_2 - C_1}, \frac{AA_3}{A_1}, (C_3 - C_1) \frac{X_2 - X_1}{C_2 - C_1} + X_1, W_3 \frac{X_2 - X_1}{C_2 - C_1}, \right. \\ \left. \frac{AA_4}{A_1}, (C_4 - C_1) \frac{X_2 - X_1}{C_2 - C_1} + X_1, W_4 \frac{X_2 - X_1}{C_2 - C_1} \right) \quad (10)$$

where the A_i s, C_i s and W_i s come from table 2, the X_i parameters are the positions of the first 2 Voigt peaks, A is the area of the first peak, σ is the Gaussian width of all the Voigt profile components and B is the background height. This characterization of Ti K β can be directly transferred to other experiments to generate calibration points for high accuracy x-ray experiments.

An alternative methodology would be to use the directly measured and calibrated profile attached to this paper as supplementary material (ti_deposition.txt)(available from stacks.iop.org/JPhysB/46/145601/mmedia), though with correction for any broadening from the instrumental function. Use this directly, fitting only the amplitude, detector scale and background to yield an accurate and transferable standard.

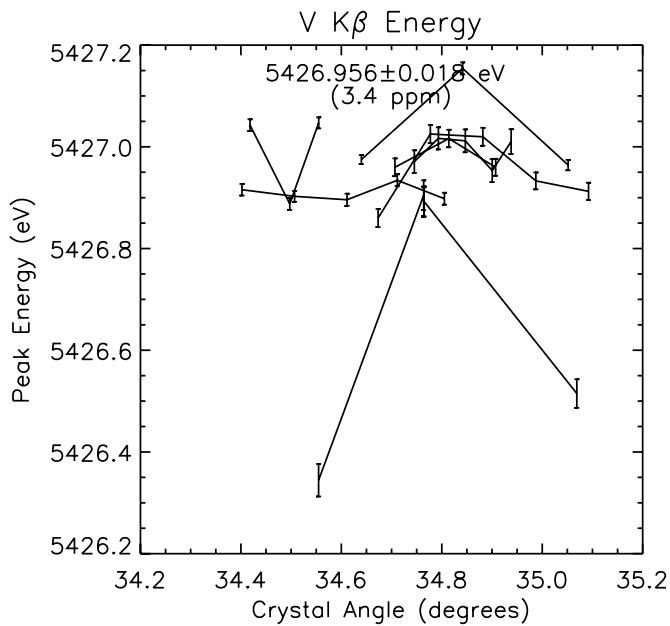


Figure 8. The peak energies of the fits of individual measured V K β spectra. Each of the seven lines represents an independently measured set of results from the full calibration series, derived by methodical stepping of the spectrometer arm length so that the profile stepped across the detector area. The variance is larger than the point precision, indicating sources of systematics. The characterization function drifts off towards the edges of the detector, where vignetting or other loss of efficiency may affect the calibration. Further, some of the linked series have offsets, whether from minor hysteresis or e.g. temperature variations. The overall consistency and hence robustness of the independent measurements yields a final pooled uncertainty of 0.0184 eV or 3.4 ppm.

Table 4. The full characterization of the V K β spectral profile on an absolute energy scale. The parameters in this table are used in equation (5). Amplitudes A_i , centroids C_i and widths W_i of individual components were obtained from a fit on the intensity versus detector position axis. The detector position axis was transformed to an absolute energy scale via the calibration procedure. The Gaussian width σ was 0.805(25) eV. The background was 749(24) counts.

Proportion of area $\frac{A_i}{\sum_{i=1}^4 A_i}$	Integrated area A_i (counts)	Centroid C_i (eV)	Width W_i (eV)
0.258(21)	160 000(13 000)	5418.19(35)	18.86(83)
0.236(18)	147 000(11 000)	5424.50(11)	5.48(21)
0.507(14)	315 300(8500)	5426.992(13)	2.499(69)

5. Redefinition of vanadium K β standard

A definition of a vanadium K β standard was reported by the present authors in [28]. The calibration in that paper relied on fits of narrower (less robust) ranges of the K α spectra in section 2.4 and neglected propagating the uncertainty from the diffraction theory of Mosplate added to the calibration fitting. This previous result yielded a definition of the vanadium K β profile peak energy of 5426.962(15) eV. Applying the modified methods in this paper results in a characterization of the V K β profile presented in table 4. The peak energy was found to be 5426.956(18) eV as shown in figure 8. This represents a shift of 0.006 eV (0.4 of a standard error). The small shift shows

that the two results are consistent with each other as expected, and that the earlier characterization was in fact robust within stated uncertainty.

6. Conclusion

The spectral profile of Ti K β was measured and characterized in a transferable methodology. The characterization involved modelling the profile with four Lorentzian peaks convolved with an overall Gaussian. The Gaussian is recommended to model additional (instrumental) broadening, so long as significant profile vignetting is not involved—that is, so long as the profiles are complete K β profiles and not truncated by the source size or slit width. In fact, this method reveals the significance of any such vignetting by returning a high χ_r^2 value for the fits, and by being strongly dependent on crystal or diffracting angle with a clear asymmetry of the fit. The individual widths for each Lorentzian component are described and tabulated. The Ti K β peak energy was found to be 4931.966(22) eV. This is an improvement in uncertainty by a factor of 2.6 over the previous best reported result. It must be remembered that the previous tabulated value had not resolved the issue of instrumental broadening as a significant source of peak shift. We have deposited the full profile for use by advanced researchers or for direct comparison with a calibration profile without the parametric modelling. We recommend that the component modelling is reliable and much more accurate than previous approaches and is a recommended standard methodology for future x-ray calibration. The V K β profile characterization was also updated with a new methodology and found to be consistent within uncertainty of the prior analysis.

Appendix. Dispersion function and detector position

Fitting parameters P_I and P_D for each calibration were determined following four major steps: clinometer pre-calibration; clinometer calibration first estimate; calibration fitting; and detector scale correction. Preliminary clinometer pre-calibration entailed an experimental characterization of the angle of incline to voltage function ($V_{\text{pre}}(I)$) of the clinometers in isolation:

$$V_{\text{pre}}(I) = P_{V,0} \sin(I - P_{V,1}) - P_{V,2} + \sum_{i=0}^8 P_{V,(i+3)} V^i. \quad (\text{A.1})$$

Second, an estimate of the clinometer calibration function was constructed by generating data with the $V_{\text{pre}}(I)$ function, inverting the data, and then fitting this data with $I(V; P_I)$ (equation (6)) where a third order polynomial was found to be adequate.

Third, calibration fitting was a six stage process beginning with estimation of P_I and P_D (figure A1). Each stage made a refinement of either P_I or P_D through one round of refitting. At the end of this step, the fitted P_I parameters reflected the measured clinometer functionals. The six stage calibration fitting used the interlinked K α reference peak energy, detector peak position and clinometer voltage calibration data to robustly determine the dispersion function, with a set of K α

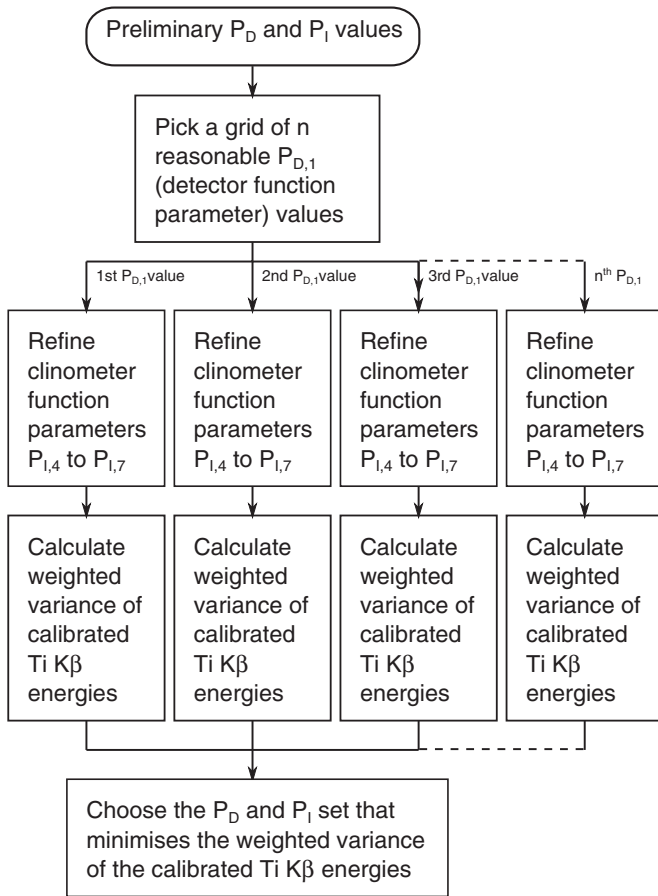


Figure A1. Refitting process schematic.

measurements defining the robustness and consistency of the determination. Prior to each fitting, this data was processed to produce one of two axis sets, I_{data} or D_{data} .

Axis set 1 fitted I_{data} versus V where I_{data} is the set of calculated data providing the expected clinometer angle for each peak based on the energy and detector position.

$$I_{\text{data}} = -\theta_{\text{mos}}(D_2(x, P_D), E). \quad (\text{A.2})$$

It has uncertainty ΔI_{data} :

$$\Delta I_{\text{data}}^2 = \left(\frac{\partial \theta_{\text{mos}}}{\partial E} \Delta E \right)^2 + \left(\frac{\partial \theta_{\text{mos}}}{\partial D} \right)^2 \left(\sum_{ij} \frac{\partial D}{\partial P_{D,i}} \frac{\partial D}{\partial P_{D,j}} C_{D,ij} + \left(\frac{\partial D}{\partial x} \Delta x \right)^2 \right). \quad (\text{A.3})$$

Axis set 2 fitted D_{data} versus x where D_{data} is the set of calculated data providing the expected theoretical detector position for each peak based on the energy and crystal angle.

$$D_{\text{data}} = D_{\text{mos}}(E, -I(V; P_I)). \quad (\text{A.4})$$

It has uncertainty ΔD_{data} :

$$\Delta D_{\text{data}}^2 = \left(\frac{\partial D_{\text{mos}}}{\partial E} \Delta E \right)^2 + \left(\frac{\partial D_{\text{mos}}}{\partial \theta} \right)^2 \left(\sum_{ij} \frac{\partial I}{\partial P_{I,i}} \frac{\partial I}{\partial P_{I,j}} C_{I,ij} + \left(\frac{\partial I}{\partial V} \Delta V \right)^2 \right) \quad (\text{A.5})$$

The first fit of axis set 1 was calculated using the estimated P_D parameters with $I(V; P_I)$ and only allows the refinement of $P_{I,1}$. The second step was a refit of axis set 1 with $I(V; P_I)$ using the P_I from fit 1 as a estimate, this time only allowing the refinement of $P_{I,4}$ through $P_{I,7}$, fitting the fine details and secondary functional parameters of $I(V; P_I)$. The third fit was of axis set 2, calculated using the refined P_I parameters from the second fit, using $D(x; P_D)$. Fourthly, results from this third step were then used to refit axis set 1 and $I(V; P_I)$ allowing the refinement of $P_{I,4}$ through $P_{I,7}$, as in the second fit. Fits five and six are a repeat of the third and fourth fits using the output of fit four as the input of fit five. This method generates the P_I and P_D parameters along with associated covariance error matrices C_I from the sixth fit and C_D from the fifth fit.

Finally, a detector scale refinement investigated the value of $P_{D,1}$ (the detector scale) by grid search to minimize the uncertainty and variance of the weighted mean of the peak energy of all Ti K β spectra. A low uncertainty (variance) in the weighted mean represents greater consistency between independent spectra. For each $P_{D,1}$ value in the grid search there was a three step process: (1) a fit of axis set 1 to refine the clinometer calibration function in the context of that detector scale; (2) modelling of the Ti K β peak position and a clinometer voltage data for all of the calibration series using equation (8) to generate a set of Ti K β peak energies and uncertainties for the calibration series; (3) computing the weighted mean and corresponding uncertainty from the variance of the set of energies. The final calibration was then represented by the refined fitting parameters which reflect the experimental minimization of systematic variance around Ti K β . For clarity, we provide a schematic summarizing the refinement process (figure A1).

References

- [1] Chantler C T, Lowe J A and Grant I P 2010 Multiconfiguration Dirac-Fock calculations in open-shell atoms: convergence methods and satellite spectra of the copper K α photoemission spectrum *Phys. Rev. A* **82** 052505
- [2] Fritsch M, Kao C C, Hämäläinen K, Gang O, Förster E and Deutsch M 1998 Evolution of the Cu K $\alpha_{3,4}$ satellites from threshold to saturation *Phys. Rev. A* **57** 1686
- [3] Deutsch M, Gang O, Hämäläinen K and Kao C C 1996 Onset and near threshold evolution of the Cu K α x-ray satellites *Phys. Rev. Lett.* **76** 2424–7
- [4] Bearden J A and Burr A F 1967 Reevaluation of x-ray atomic energy levels *Rev. Mod. Phys.* **39** 125–42
- [5] Desclaux J P 1973 *At. Data Nucl. Data Tables* **12** 312
- [6] Deslattes R D, Kessler E G, Indelicato P, de Billy L, Lindroth E and Anton J 2003 X-ray transition energies: new approach to a comprehensive evaluation *Rev. Mod. Phys.* **75** 35–99
- [7] Indelicato P, Boucard S and Lindroth E 1998 Relativistic and many-body effects in K, L, and M shell ionization energy for elements with and the determination of the 1s lamb shift for heavy elements *Eur. Phys. J. D* **3** 29–41
- [8] Mooney T, Lindroth E, Indelicato P, Kessler E G Jr and Deslattes R D 1992 Precision measurements of K and L transitions in xenon: experiment and theory for the K, L, and M levels *Phys. Rev. A* **45** 1531
- [9] Grant I P 1970 *Adv. Phys.* **19** 747

- [10] Deutsch M, Hölzer G, Härtwig J, Wolf J, Fritsch M and Förster E 1995 $K\alpha$ and $K\beta$ x-ray emission spectra of copper *Phys. Rev. A* **51** 283–96
- [11] Hölzer G, Fritsch M, Deutsch M, Härtwig J and Förster E 1997 $K\alpha_{1,2}$ and $K\beta_{1,3}$ x-ray emission lines of the 3d transition metals *Phys. Rev. A* **56** 4554–68
- [12] Chantler C T, Hayward A C L and Grant I P 2009 Theoretical determination of characteristic x-ray lines and the copper $K\alpha$ spectrum *Phys. Rev. Lett.* **103** 123002
- [13] Lowe J A, Chantler C T and Grant I P 2010 A new approach to relativistic multi-configuration quantum mechanics in titanium *Phys. Lett. A* **374** 4756–60
- [14] Chantler C T, Lowe J A and Grant I P 2010 Multiconfiguration Dirac–Fock calculations in open shell atoms: convergence methods and satellite spectra of copper $K\alpha$ photoemission spectrum *Phys. Rev. A* **82** 052505
- [15] Lowe J A, Chantler C T and Grant I P 2011 *Ab initio* determination of satellite intensities in transition-metal photoemission spectroscopy using a multiconfiguration framework *Phys. Rev. A* **83** 060501
- [16] Anagnostopoulos D F, Sharon R, Gotta D and Deutsch M 1999 $K\alpha$ and $K\beta$ x-ray emission spectra of metallic scandium *Phys. Rev. A* **60** 2018–33
- [17] Anagnostopoulos D F, Gotta D, Indelicato P and Simons L M 2003 Low-energy x-ray standards from hydrogenlike pionic atoms *Phys. Rev. Lett.* **91** 240801
- [18] Schweppe J, Deslattes R D, Mooney T and Powell C J 1994 Accurate measurement of Mg and Al $K\alpha_{1,2}$ x-ray energy profiles *J. Electron. Spectrosc. Relat. Phenom.* **67** 463–78
- [19] Chantler C T, Kinnane M N, Su C-H and Kimpton J A 2006 Characterization of $K\alpha$ spectral profiles for vanadium, component redetermination for scandium, titanium, chromium, and manganese, and development of satellite structure for $Z = 21$ to $Z = 25$ *Phys. Rev. A* **73** 012508
- [20] Limandri S P, Carreras A C, Bonetto R D and Trincavelli J C 2010 $K\beta$ satellite and forbidden transitions in elements with $12 \leq Z \leq 30$ induced by electron impact *Phys. Rev. A* **81** 012504
- [21] Koster A S and Mendel H 1970 X-ray $K\beta$ emission spectra and energy levels of compounds of 3D-transition metals—I: oxides *J. Phys. Chem. Solids* **31** 2511–22
- [22] Uršič M, Kavčič M and Budnar M 2003 Second order radiative contributions in the $K\beta_{1,3}$ x-ray spectra of 3d transition metals and their dependence on the chemical state of the element *Nucl. Instrum. Methods Phys. Res. B* **211** 7–14
- [23] Morita S and Fujita J 1985 $K\beta$ x-ray transition energies of M-shell-ionized ions of Ti through Ni in a plasma *Phys. Rev. A* **31** 3299
- [24] Mandić L, Fazinić S and Jakšić M 2009 Chemical effects on the $K\beta$ and $K\beta_{2,5}$ x-ray lines of titanium and its compounds *Phys. Rev. A* **80** 042519
- [25] Silver J D *et al* 1994 The Oxford electron-beam ion trap: a device for spectroscopy of highly charged ions *Rev. Sci. Instrum.* **65** 1072–4
- [26] Chantler C T 1992 X-ray diffraction of bent crystals in Bragg geometry: I. Perfect-crystal modelling *J. Appl. Crystallogr.* **25** 674–93
- [27] Chantler C T 1992 X-ray diffraction of bent crystals in Bragg geometry: II. Non-ideally imperfect crystals, modelling and results *J. Appl. Crystallogr.* **25** 694–713
- [28] Smale L F, Chantler C T, Kinnane M N, Kimpton J A and Crosby D N 2013 Characterization of the $K\beta$ spectral profile for vanadium *Phys. Rev. A* **87** 022512

Methodology for the characterisation of characteristic spectral profiles, applied to chromium $K\beta$

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The investigation of tests of quantum electrodynamics in the X-ray regime down to 2–20 parts per million (ppm) amplifies the need for improved characterisation of asymmetric reference sources and energies in this regime. While several transition metal characteristic energies have been defined, most are not referenced to accurate profiles or robust links to the metre via X-ray optical interferometry. Lower intensity $K\beta$ transitions have relatively poor accuracy – we ask how to determine $K\beta$ transitions to an accuracy approaching those of $K\alpha$ transitions. Instrumental broadening normally encountered in X-ray experiments shifts the features of profiles used for calibration, such as peak energy, by a significant amount many times the quoted accuracies. We present a study of a methodology used recently to determine energies and profiles experimentally down to 4.5 and 2.7 ppm for Ti and V $K\beta$. In this study, we investigate the robustness of the methodology for a difficult data set and demonstrate that the approaches to and characterisation of the chromium $K\beta$ spectral profile are consistent with accurate measurements in the literature down to 24 ppm. The peak energy of the chromium $K\beta$ spectral profile is found to be 5946.68(14) eV prior to instrumental broadening. Characterisation of the spectral profile of the radiation, including the instrumental broadening, allows us to obtain an accurate and notably transferable standard. Significantly, we present a widely applicable methodology for achieving and using this standard. This approach has been used down to an accuracy of 2–5 ppm. Copyright © 2015 John Wiley & Sons, Ltd.

Introduction

High accuracy, absolute energy calibration is crucial to progress in X-ray science. Characteristic radiation – $K\alpha$ and $K\beta$ – produced with electron bombardment, where the incident electron energy is at least 2.5–3 times the threshold energy, is often used as a calibration standard as the profiles are stable and cheap to produce. These spectral profiles are robust under different excitation conditions, as they reflect the atomic and electronic structure of the elements. Characterisations of the profiles permit new tests and understanding of inner-shell processes and fundamental atomic theory, including quantum electrodynamics.^[1,2]

The structure is properly modelled through the relativistic quantum theory of the atom, which has seen recent improvement.^[3] A concerted effort to experimentally summarise experimental energies of characteristic radiation was undertaken and compiled by Bearden *et al.* in 1967.^[4] This has been complemented by theoretical computations by Desclaux^[5] and further experimental and theoretical compilation by Deslattes *et al.*^[6] That review work reports the energy of the dominant transition (diagram lines) without regard for the shifts and change of shape of the spectra due to satellite lines or profile asymmetry. It remains particularly difficult to compare advances in theory to high accuracy experiment. Significant advance in theory since then has been based on the relativistic approach of Grant.^[7]

Experimental spectral profiles for the characteristic radiation of transition metals are represented by semi-empirical fitting of multiple components – using typically five or seven peaks for $K\alpha$ spectra.^[8,9] Recent work has demonstrated that new approaches can yield a more robust standard.^[10–12] Conversely, theoretical modelling of characteristic radiation profile shape is dominated by diagram lines, representing X-ray emission energies detailing

the electron decay from atomic transitions: an excited electron with a core hole decays to the ground state with the core filled and a higher n hole. Additional components, theoretically and empirically, are contributed by satellite lines caused by shake-up and shake-off effects. This set of transitions is complex, especially for elements with open sub-shells such as the transition metals. Progress in the details of such theory has been slow until recently.^[13–16] Empirical modelling using fitting functions for a sum of a small number of Lorentzian, Gaussian, Voigt or instrumental functions fails to reveal the theoretical complexity of the many configuration state function transitions.

Efforts to find good empirical models of spectral radiation have continued from the work of Deutsch *et al.* and Hölzer *et al.* in the 1990s.^[8,9,17–19] Deslattes *et al.*^[6] include a summary of these efforts, summarised in Table 1 with experimental energies and uncertainties for $K\alpha$ characteristic peaks for Z from 22 to 26 and including Chantler *et al.*^[20] The uncertainties for the $K\alpha$ data are on the order of 1 to 2 parts per million (ppm). The uncertainty of the literature value of the chromium $K\beta$ peak energy^[4] (Table 1) is 1.7 ppm.

Data collection methods often use a single flat crystal spectrometer employing the Bond method^[8,9] or a curved crystal spectrometer.^[17] In the experimental work arising from

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Table 1. Characteristic radiation peak energy data from the literature

Spectral profile peak	Reference peak energy (eV)	Peak energy uncertainty (ppm)
Titanium $K\alpha_2$	4504.920	2.09
Titanium $K\alpha_1$	4510.899	2.08
Vanadium $K\alpha_2$	4944.651	2.22
Vanadium $K\alpha_1$	4952.131	1.21
Chromium $K\alpha_2$	5405.538	1.31
Chromium $K\alpha_1$	5414.804	1.31
Manganese $K\alpha_2$	5887.685	1.43
Manganese $K\alpha_1$	5898.801	1.42
Iron $K\alpha_2$	6391.03	1.5
Iron $K\alpha_1$	6404.01	1.5
Chromium $K\beta_1$	5946.82	1.7

The V $K\alpha$ data are from Chantler *et al.*^[20] the Fe $K\alpha$ and Cr $K\beta$ data are from Hölzer *et al.*^[9] and the rest of the data are from Deslattes *et al.*^[6]

Germany,^[8] raw spectra were deconvolved with a measured, fitted or simulated instrumental broadening, and each deconvolved spectrum was fit empirically. The peak location of each empirical fit was taken to be the measure of each peak energy. The deconvolution of spectra limits the understanding of error propagation. It is not immediately clear how to use these characterisations as standards for experiments with different instrumental broadening. Chantler *et al.*^[20] addressed this concern by providing a consistent set of empirical fit functions for a range of elements ($21 \leq Z \leq 25$) including an approach to allow for instrumental broadening effects.

There has been some interest in the shape of the Cr $K\beta$ profile recently.^[21–25] This work has related to the problematic peak reported by Bearden *et al.*^[4] Hölzer *et al.*^[9] reported an experimental line shape and peak energy (listed in Table 1). A theoretical calculation of the peak energy for the diagram line of Cr $K\beta$ is 5947.1(10) eV^[6] in good agreement with older theory and the experimental value but a much larger uncertainty than the experimental result. Given the recent characterisations of Ti $K\beta$ and V $K\beta$,^[10,11] it is valuable to investigate the robustness of this approach in comparison with alternate approaches. This is the subject of this paper.

This paper presents a measurement of chromium $K\beta$ and a characterisation of the profile as well as presenting a study of the robustness of the self-consistent determination of the dispersion function. The inclusion of broadening effects in the fitting method enables the results to be transferable to a larger range of experimental conditions. Specifically, the characterisation, or indeed the profile itself, can be simply used in experiments, where the amount of instrumental broadening is difficult to measure. More important than the energy determination, the profile definition, or the characterisation, is the demonstration of the methodology down to 24 ppm. We present a study of a methodology used recently to determine energies and profiles experimentally down to 4.5 and 2.7 ppm.^[10,11] We study chromium $K\beta$ as representative of the weaker $K\beta$ transitions, but with excellent previous measurement from the literature.^[6] Further, this data set is optimised for Ti $K\beta$ and V $K\beta$ as demonstrated by recent publications, but we here apply the methodology to the extreme edge of the calibration

region. We demonstrate that the approaches to and characterisation of the chromium $K\beta$ spectral profile are consistent with accurate measurements in the literature down to 24 ppm.

Method of investigation of the chromium $K\beta$ standard

To create a chromium $K\beta$ standard, the profile was measured using a wavelength dispersive technique, calibrated by the set of $K\alpha$ lines in Table 1. The calibration was optimised in a number of different ways to check the robustness and methodology. The $K\beta$ profile was fit with a sum of Voigt functions with a common Gaussian width to model instrumental broadening.

Experimental setup

The source of the $K\alpha$ radiation used for calibration and the measured Cr $K\beta$ line consisted of an electron gun firing 20 keV electrons at a collection of metal targets ($Z = 22–26$), each of which was placed in the electron beam separately. Data collection employed a Johann geometry curved crystal spectrometer with position-sensitive X-ray detection at the Oxford EBIT.^[26] Figure 1 shows the arrangement of the X-ray source, diffracting crystal and detector. The electron beam incident on the transition metal target results in the emission of characteristic X-ray radiation. The detector arm is set at a Bragg angle of 2θ , and an adjustable 'Seemann wedge' limits the diffracting region of illumination of the Germanium (220) Bragg crystal. The arm angle is fully adjustable, with low hysteresis on the gearing and high reproducibility. The housing for the crystal is mechanically linked to the detector arm, such that the normal vector to the crystal surface bisects the angle between the source and detector arm. Thus, the crystal angle (θ) is half the detector arm angle. The crystal and detector arm angles are measured by gravity-referenced electronic clinometers, each outputting a raw voltage, V . The V s are calibrated to θ . The Seemann wedge permits adjustment of the band-pass of radiation through the crystal and limits the instrumental broadening.

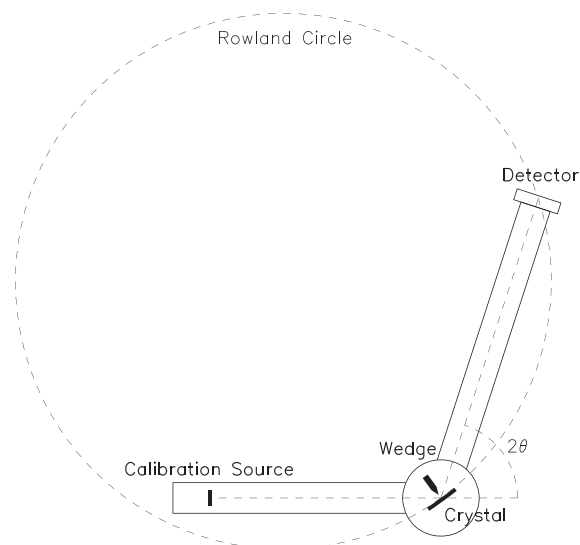


Figure 1. Schematic diagram of experimental setup. The calibration source is the source of the $K\alpha$ radiation used in calibration and the Cr $K\beta$ radiation. Details of the setup can be found in the Section on Experimental Setup.

By varying the wedge position, the crystal curvature perfection and the consistency of prediction from dynamical diffraction theory are investigated. A multi-wire gas-proportional counter with a backgammon configuration was used to detect the characteristic X-rays, providing good linearity and resolution in the dispersion (detector) axis and enabling the collection of position data for each X-ray detection event.

The electron gun was normal to both the path of the X-rays from the target to the crystal and to the path of the X-rays from the crystal to the detector. Transition metal targets were mounted at 45° to both the electron beam and the path from the selected target to the crystal. The radius of the spot size of the electron beam on the selected target was 5(1) mm. The distance from the target to the crystal was 350(3) mm, and the radius of the Roland circle was 1371(10) mm. The distance from the crystal to the active region of the detector was 1500(5) mm. The calibration source was placed in an off-focus position, to increase the accuracy and to reduce the sensitivity of the resulting spectra to the spatial intensity distribution of the source. The aim is to image the wavelength intensity distribution of the source, not its spatial intensity distribution.

The crystals of germanium were manufactured and calibrated by the National Institute of Standards and Technology (prior to curvature) and are near-perfect single crystals. There is, therefore, no mosaic spread and no orientational distribution function to include. Mosplate does indeed include any scale of mosaicity in the code and computation, so this would be easy to include; however, the crystals have none. Thermal (Debye-Waller) parameters are important and are included for the estimated temperature on an isotropic basis, as is normal for symmetric and monatomic solids. The value of σ^2 used is 0.5661(26) Å² for $T = 293\text{K}$, with a linear expansion coefficient of $5.7 \times 10^{-6} \text{K}^{-1}$.^[27]

For the calibration of the spectrometer, crystal alignment and detector scale, a series of calibration spectra was collected in successive diffracting positions in order to assess systematics and evaluate the dispersion function. Table 1 provides the list of reference lines with their energies and provenance, together with the Cr K β reference for comparison.

Diffraction theory

The experimental setup was modelled by the dynamical diffraction code, Mosplate.^[28,29] Mosplate predicts and models diffraction phenomena that have an effect on energy determination up to the order of 100 ppm and characterises these to an accuracy better than 1 ppm. These diffraction phenomena include lateral shifts in position due to X-rays penetrating the crystal to some depth and refractive index corrections. The refractive index shift, of order 100 ppm, must be determined accurately to 1% or better. Lateral shifts in curved crystal spectrometry may be of a similar order of magnitude. Corrections for asymmetry and polarisation are typically responsible for another 30 ppm, while depth penetration of the dynamical wavefield can dominate in curved crystal spectrometry but can be even more significant for flat crystal spectrometry.

For a particular X-ray energy, E , and crystal angle, θ , Mosplate calculates the X-ray intensity spectrum we expect to see on the detector. The incident wavefield is computed by ray tracing performed from a point grid at the source to a point grid on the cylindrically curved crystal. The wavefield is then propagated through the crystal to find the diffracted wavefield at the exit surface of the crystal. The diffracted field distributions in position and angle

at the crystal surface are then used as a source to ray trace to the detector. For each single energy, a range of spectra are calculated at different crystal angles. A peak position, D , is then computed for each of these spectra. These calculations are performed by sampling the Mosplate model function for the peak position, D , and profile as a function of peak energy, E , and crystal angle, θ :

$$D = D_{\text{mos}}(E, \theta) \quad (1)$$

This model also implicitly defines functions that calculate E and θ from the remaining variables:

$$E = E_{\text{mos}}(D, \theta) \quad (2)$$

$$\theta = \theta_{\text{mos}}(D, E) \quad (3)$$

For active use, these functions are interpolated between the sampling frequency of E and θ , for which the $D_{\text{mos}}(E, \theta)$ are computed to high accuracy. Interpolation uncertainty is negligible - well below 1 ppm.

Data collection

Seven calibration series were collected, each with a different wedge position and different integration times, so that the diffraction theoretical modelling must make accurate independent predictions of each geometry at each position. Within each calibration series, K α and K β spectral profiles from $Z = 22$ –26 were collected. Each spectral profile type was collected at three to five arm angles, thereby sampling profiles and angular settings at different positions on the detector. This allowed detailed and independent investigations of the dispersion function and the detector response function. The remarkable consistency of the results demonstrates the robustness of the code and calibration methodology as discussed later; the remaining variance is thus an explicit characterisation of any systematic deficiencies, which could contribute to theoretical or experimental inconsistency or error.

K α profile modelling

For $Z = 22$ –25, K α profiles were fitted as functions of energy as defined by Chantler *et al.*^[20] Each of these functions is a sum of six Voigt profiles with a common Gaussian width to model the instrumental broadening, and maps X-ray energy to X-ray intensity. The energy offsets, Lorentzian widths and relative amplitudes of the Voigt profiles are defined by Chantler *et al.*^[20] For the $Z = 26$ Fe K α profile, the same type of data for a sum of Voigt profiles were given by Hölzer *et al.*^[9] Each of the K α experimental profiles were measured on a detector position axis rather than directly on an energy axis, so the profiles were fit by refining five fitting parameters:

1. a detector scale and
2. a detector offset to map the detector position to energy,
3. an intensity scale to model the overall intensity of the profile,
4. a constant intensity background, and
5. a common Gaussian broadening width.

These highly accurate K α characterisations allow the assignment of peak energies to the detector positions of each profile at each clinometer voltage. Figure 2 shows how one such fit leads to two calibration points for a measured Mn K α spectrum.

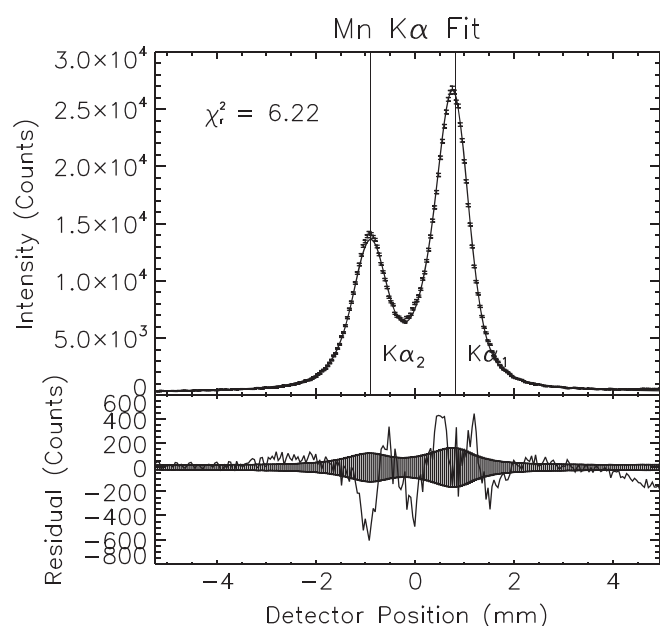


Figure 2. Typical fit of Mn K α spectrum, yielding two calibration points (Mn K α_1 and Mn K α_2), which constrain the spectrometer dispersion function. This particular fit has a χ^2 of 6.2. The K α_1 peak has an energy of 5898.8010(84) eV and detector position of 0.8154(16) mm. The K α_2 peak has an energy of 5887.6859(84) eV and detector position of $-0.8850(25)$ mm. The crystal clinometer voltage was $-2.2499502(79)$ V.

Chromium K β profile fitting

Twenty-seven Cr K β profiles were also collected and characterised on intensity and detector position axes. To define a characteristic line shape function, each of the spectra were fitted using a sum of four Voigt functions with a common Gaussian width, σ , and a constant intensity background, B . The i th Voigt function used in the characterisation is defined to be:

$$V(x; A_i, C_i, W_i, \sigma_i) = A_i \int_{-\infty}^{\infty} \frac{e^{-x'^2/(2\sigma_i^2)}}{\sigma_i \sqrt{2\pi}} \frac{W_i/2}{\pi[(x - C_i - x')^2 + (W_i/2)^2]} dx' \quad (4)$$

where A_i is the integrated area of the Lorentzian profile, C_i is the centroid of the profile, W_i is the Lorentzian full width at half maximum (FWHM) and σ_i is the Gaussian broadening stan-

dard deviation. The Gaussian broadening FWHM is $2\sqrt{2\ln 2}\sigma_i \approx 2.35\sigma_i$. Thus, the spectra containing a Cr K β spectral profile were modelled with

$$P(x; B, \sigma, A_1, C_1, W_1, A_2, C_2, W_2, A_3, C_3, W_3) = B + \sum_{i=1}^3 V(x; A_i, C_i, W_i, \sigma_i = \sigma) \quad (5)$$

All 27 measured Cr K β profiles were separately fitted with this method. The relative intensities, positions and width parameters of the Voigt functions were consistent with one another, so the minimum uncertainty functionals are reported. The fits were done with a sum of four Voigt functions, though one of the Voigt function intensities hit the fitting constraint that enforced a non-negative Voigt function intensity. This means that three Voigt functions were sufficient to represent Cr K β as measured. The characteristic parameters of these fits are shown in Table 2 with the position axis converted to energy. Figure 3 shows a typical fit for one of the Cr K β spectra.

These characteristic parameters were then used to constrain refits of all the Cr K β profiles. Each refit had free parameters characterising the overall intensity, position, detector position to energy scale conversion, instrumental broadening and background of the spectral profile in the specific geometry of the measurement. As each refit had a slightly different instrumental broadening due to geometry changes, the transferable reference position of each profile peak was taken to be the position of the maximum of the fit function with the Gaussian width set to zero. All refits were reliable and consistent with the original fits: the characterisation allows for a consistent transferable standard in this measurement, in the calibration of the dispersion function, and for any subsequent independent measurement by other authors. This enables a consistent measurement of peak position of Cr K β spectra for any particular instrumental broadening, where the spectra are not significantly vignetted by the effects of source size or a slit width. Fitting spectra with this method would reveal the significance of any such vignetting by returning a high χ^2 value for the fits. In the current situation, the method enabled a more consistent use of the literature experimental and theoretical standards.

Optimisation of the dispersion function

The Appendix describes the mathematical formalism for summarising the fitting procedure for the dispersion function used for the data analysis and the core methodology for deriving a series

Table 2. Characterisation of the Cr K β spectral profile

Relative area $\frac{A_i}{\sum_{i=1}^3 A_i}$	Integrated area A_i (counts)	Centroid C_i (eV)	FWHM W_i (eV)
0.333(20)	219011(13177)	5937.00(31)	19.84(60)
0.209(18)	137415(11971)	5943.70(16)	5.74(32)
0.458(15)	300778(9767)	5946.705(24)	2.37(11)

The profile is characterised on an absolute energy scale using a sum of component Lorentzians convolved with a common Gaussian instrumental broadening. Integrated areas (A_i), centroids (C_i) and FWHMs (W_i) of individual components were obtained from a series of fits of intensity against detector position. The detector position axis was then transformed to an absolute energy scale using the calibration procedure. The Gaussian width $\sigma = 1.517(32)$ eV. The background was $B = 629(23)$ counts. The third component dominates the height of the profile, while the first and second components fill out the low energy profile asymmetry.

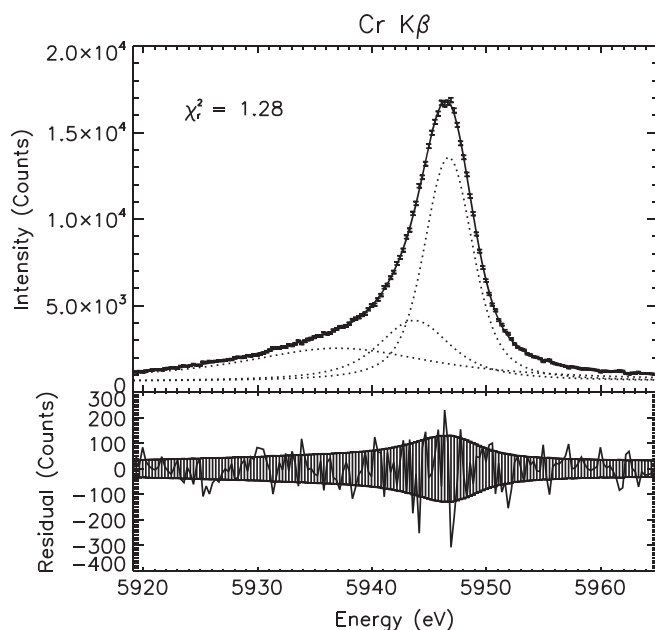


Figure 3. Typical fit of a Cr K β spectrum. The points with error bars are the experimental data, the solid line is the fitted sum of Voigt functions, and the three dotted lines are the three individual Voigt components with the background offset. The corresponding fitting parameters are provided in Table 2.

of fitted energy determinations of chromium K β from the dispersion function. The fitting procedure used in this work is improved from that of previous results^[10,11] by: (1) the inclusion of the Fe K α_1 and Fe K α_2 data in the calibration fitting; and (2) the pooling of all K α data for a given wedge position into the same fit rather than separating them by wedge and collection time. The uncertainties near Cr K β are large due to it being on the edge of the range of arm angles included in the fitting procedure so that the addition of the Fe K α data better constrained the dispersion fits in the Cr K β arm angle range. The pooling of calibration data by wedge position led to a better distribution of good data and therefore less variance in the Cr K β peak energy.

A key question on robustness is whether the optimisation criteria can distort the analysis, variance and result. If robust and consistent, the optimised result should minimise variance and preserve a consistent central energy determination. Hence, we investigated the self-consistency of a series of alternate optimisations, each minimising a different measure of quality of the calibration fitting. These are measures (a) through (e). Each optimisation was a three-step process:

1. for a range of detector scales, there was a fit of I_{data} versus V (defined in the Appendix), which refined the clinometer calibration function in the context of that detector scale;
2. for each detector scale, a calculation of the measure to be minimised was made; and
3. the detector scale and clinometer calibration function that minimised the measure was then selected.

The first and third optimisations have been used in past analyses to determine the energy and profile of Ti K β and V K β . Following these past results, the range of energy of interest in this study is and should be that of Cr K β . We provide the others to prove both that they are consistent and to reveal difficulties of the minimisa-

tion. Figure 4(a)–(e) provides the resulting distributions of Cr K β peak energies for each of the optimisations.

The first optimisation (Fig. 4(a)) minimised measure (a): the χ^2_r value of the Ti K β peak energy measurements (preferred in the work of Chantler *et al.*^[11]). In this optimisation of the set of independent measurements of the Cr K β peak energy, there is a clear slope in the results for each calibration series that represents a possible systematic error in $P_{D,1}$, the detector scale parameter. This is a result of $P_{D,1}$ being optimised only for crystal angles where the Ti K β line was measured. The remainder of optimisations (Fig. 4(b)–(e)) was minimising combinations of the dispersion of Ti K β , V K β , Cr K β and the K α lines.

The second optimisation (Fig. 4(b)) minimised measure (b): the sum of two values – (1) the χ^2_r value of the Ti K β peak energy measurements, and (2) the χ^2_r value of the V K β peak energy measurements.

The third optimisation (Fig. 4(c)) minimised measure (c): the χ^2_r value of the V K β peak energy measurements (preferred in the work of Smale *et al.*^[10]).

The fourth optimisation (Fig. 4(b)) minimised measure (d): the sum of four values – (1) the χ^2_r value of the Ti K β peak energy measurements, (2) the χ^2_r value of the V K β peak energy measurements, (3) the χ^2_r value of the Cr K β peak energy measurements, and (4) the χ^2_r value of the clinometer calibration function fit which is a measure of the spread of the K α data around the literature values.

The last optimisation (Fig. 4(e)) minimised measure (e): the χ^2_r value of the Cr K β peak energy measurements. It is to be expected that the uncertainty in the region of interest is minimised by this approach, and that the result is likely to be optimum using this last method. By definition, the systematic error reflected in the slope of each calibration is minimised. Note that this optimisation only locally minimises this systematic around the Cr K β arm angles, away from this range, the systematic is visible.

What insight is presented in the comparisons of these figures? They demonstrate that all wedge settings are not uniformly well defined, and that while the uncertainty of each point from the statistical fitting is very well defined, of order 2–3 ppm, the systematic uncertainties clearly dominate and are some 10 times this value. Earlier analysis and past results for Ti K β and V K β ^[10,11] used data from Sc K α through Mn K α but neglected Fe K α . The divergence of constraint at Cr K β energies demanded the inclusion of analysis of Fe K α profiles so that the dispersion function was interpolated rather than extrapolated to the region of interest. Nonetheless, the constraint was not uniformly effective because the quantity and quality of the individual peak profiles varied from one wedge setting to another. Hence, the collection of profiles for each wedge setting will not in general be equally well defined. Perhaps more importantly, this study demonstrates that any sensible optimisation system yields a similar agreement and pattern of discrepancy, and a similar final uncertainty. We investigated a more extensive set, but these illustrate the general principle that under normal circumstances this methodology is robust.

The remaining error (scatter) between the calibration runs reflects that Cr K β was at the far edge of the calibrated region of the crystal angle range, so that the variance observed is deliberately maximised in this study. We emphasise that effectively the same dispersion function and optimisation as presented in measure (a) yielded no large systematic in the energy regime of Ti K β and yielded a final consistency at the $\sigma = 4.5$ ppm level or

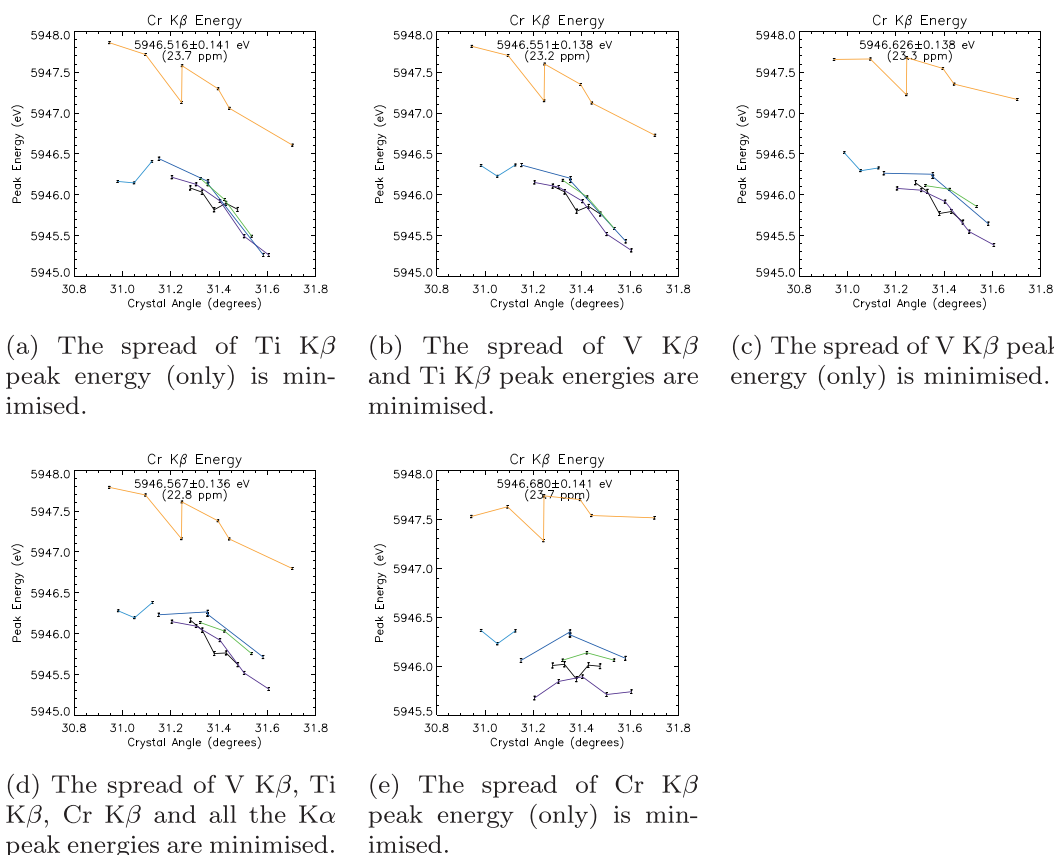


Figure 4. The Cr K β peak energies of individual measured spectra. Each sub-figure is the result of a different χ^2_r measure that has been optimised – measures (a)–(e). Each of the six lines in each sub-figure are results from a single wedge position, derived by methodical stepping the spectrometer arm angle so that the profile is stepped across the detector area. Each point fit is statistically precise to 1–3 parts per million, but the scatter between wedges and positions is less accurate. The slopes from left to right in Fig. 4(a)–(d) are indicative of a correlation between the dispersion function (energy versus diffracting angle) and the detector calibration (energy or angle versus detector position). This systematic results from the correlation of parameters and the fact that this has not been minimised in these plots. Measure (e) (Fig. 4(e)) reduces this systematic in the energy region of Cr K β and is sufficient to yield an accurate determination of the detector scale and minimisation of slope systematics, with a smaller variance and dispersion. While it also yields a higher accuracy, it remains consistent with the earlier optimisations and methods.

± 0.022 eV,^[11] while that presented in measure (c) yielded no large systematic in the energy regime of V K β and yielded a final consistency at the $\sigma = 2.7$ ppm level or ± 0.015 eV.^[11] Indeed, in the latter measurement and characterisation, the individual point uncertainties were 1.6 ppm. The point is that we expect and observe divergences due to limited accuracy of subsets with different wedge settings near the edge of the interpolation region.

Figure 5 presents the weighted mean values of the peak energy for each optimisation (measures (a)–(e)) in comparison to the peak energy reported by Hölzer *et al.*^[9] The energies reported here are all consistent with each other and are all within 1.5 sigma of Hölzer *et al.*^[9] Optimising the calibrations to minimise the across detector systematic error for the Cr K β profile peak energy leads to a value for the energy to be within one σ of the previous measurement. This shows an ability of this calibration method to be tuned to different energies within the same data set through the minimisation of the systematic error at those energies. Table 3 shows the averages of these various contributions to energy uncertainty for a single Cr K β spectrum as outlined in Section on Determination of Energy Uncertainty.

Definition of chromium K β standard

K β peak energy

All five calibrations based on minimising measures (a)–(e) are consistent. It is reasonable to report any of these results. By definition, the calibration that worked best is based on measure (e), the calibration that minimises the χ^2_r value of the Cr K β peak energy measurements (Fig. 4(e)). This dispersion function calibration is used in the remainder of the paper.

The weighted mean results in a measurement of the Cr K β profile peak energy of 5946.68(14) eV. This 24 ppm uncertainty is larger than that for an individual fit given in Table 3 and is a result of the remaining systematic error between wedge positions and positions across angle and the detector. Comparing this value to the prior theoretical literature value of 5947.1(10) eV,^[6] the 0.42 eV discrepancy is just over 0.42 standard deviations and is a reflection of the theoretical imprecision. Further, this is an improved result compared with that of the current theory.^[6]

Conversely, the prior experimental literature value of 5946.823(11) eV (1.7 ppm uncertainty)^[4,9] is a more accurate determination of the peak energy for that specific experimental configuration. The discrepancy is 0.143 eV or about 1.01 standard deviations so is in excellent agreement even in this difficult

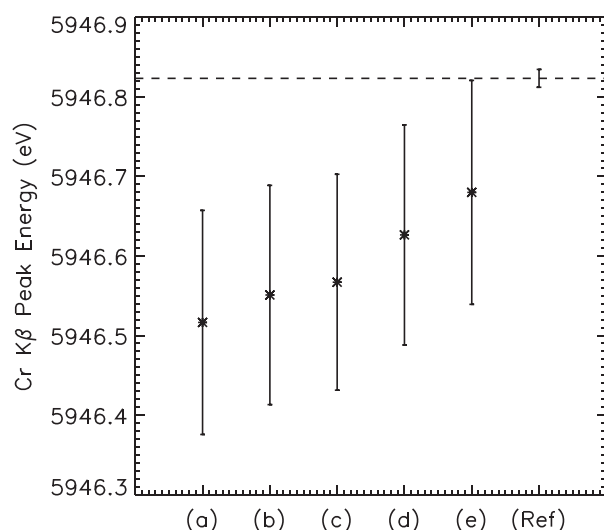


Figure 5. The mean peak energies of the fits of individually measured Cr $K\beta$ spectra for each optimisation method compared to the literature value. Note that all of these, despite different ansatz, yield results consistent with one another to within one standard error. Further, the optimised method focussing on the region of interest gives the highest accuracy and lies within one standard error of the best literature value for the peak energy.^[9]

Table 3. Typical uncertainty budget for the peak energy of each of the spectral profiles of Cr $K\beta$ in the final plots and which contribute to the energy determination

Uncertainty source	Average contribution to energy uncertainty for an individual Cr $K\beta$ spectrum (ppm)
Cr $K\beta$ spectrum fit ($\frac{\partial E}{\partial x} \Delta x_{fit}$)	1.0
Detector dispersion function fit ($\sqrt{\sum_{ij} \frac{\partial E}{\partial p_{Dij}} \frac{\partial E}{\partial p_{Dj}} C_{D,ij}}$)	0.21
Clinometer noise ($\frac{\partial E}{\partial V} \Delta V$)	1.3
Clinometer calibration fit ($\sqrt{\sum_{ij} \frac{\partial E}{\partial p_{ij}} \frac{\partial E}{\partial p_{ij}} C_{i,ij}}$)	0.93
Total uncertainty	1.9

The energy measurements show evidence of an unknown variance, likely involved in the experimental and geometrical parametrisation but includes any uncertainty from theory for known and estimated wedge positions. Therefore, the final energy determination has a larger uncertainty than this ideal 1.9 ppm for the individual spectrum, as required and determined by the observed variance. The independent self-consistency shown in this work is invaluable in uncovering sources of systematic uncertainty that might otherwise go unnoticed and remain unanalysed.

arrangement (at the edge of the calibration series). An advantage of the characterisation presented in this work is that the error bars on the characterisation allow for profile and geometry-dependent variation and, more particularly, prove the methodology used here and in prior papers down to a valuable limit. A comparison of the profile fit in Hölzer *et al.*^[9] and this work is presented in Fig. 6.

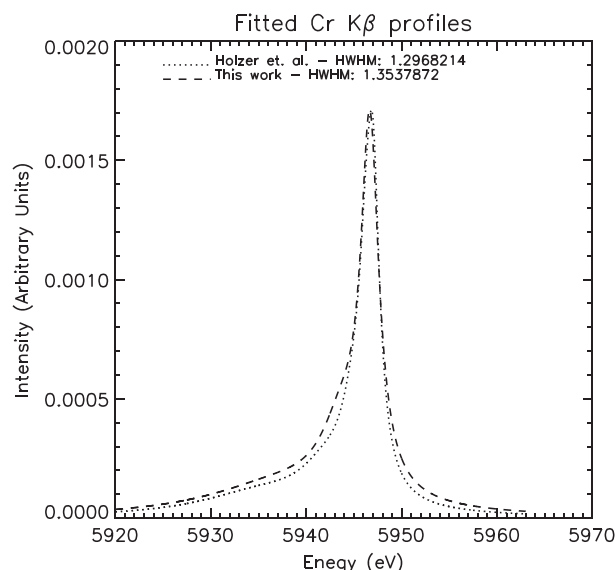


Figure 6. The spectral profile of Cr $K\beta$ measured in this work (dashed line) compared to that reported in Hölzer *et al.*^[9] (dotted line). As presented here, the dashed line is a sum of 3 Lorentzians with parameters given in Table 2. This corresponds to setting the Gaussian width that represents instrumental broadening to 0 eV. The resolution and half width at half maxima (HWHMs) of the two results are in agreement to within 4%. Being a sum of 6 Lorentzians, the characterisation in Hölzer *et al.*^[9] is smoother. This is expected as the 1.4 eV instrumental broadening obtained in the current work smooths out the spectrum so that Hölzer *et al.*^[9] can capture some higher resolution information. It should be noted that Hölzer *et al.*^[9] deconvolved the $K\beta$ spectrum before fitting with an unreported broadening.

Conclusion

The spectral profile of Cr $K\beta$ was measured and characterised in a transferable way. The characterisation involved modelling the profile with four Lorentzian peaks convolved with a common Gaussian. The Gaussian is recommended to model additional (instrumental) broadening, so long as significant profile vignetting is not involved, that is, that the profiles are complete $K\beta$ profiles not truncated by the source size or a slit width. This method will reveal the significance of any such vignetting by returning a high χ^2_r value for the fits and by being strongly dependent on crystal or diffracting angle. The individual widths and component parametrisation are given explicitly for each component. The Cr $K\beta$ peak energy was found to be 5946.68(14) eV. This is a 24 ppm result. The component modelling is reliable and a recommended standard methodology for future X-ray calibration. Most importantly, this study demonstrates that even near the edge of a calibrated region, with strong variance of results from systematics, the computed final uncertainties accurately reflect the uncertainty of the measurement, even when modelled by a range of distinct optimisations.

Acknowledgements

The authors acknowledge the experimental team, including Mark Kinnane, as well as funding from the ARC for this work. We acknowledge the assistance of our collaborators at the Oxford EBIT including David Crosby.

References

- [1] C. T. Chantler, M. N. Kinnane, J. D. Gillaspay, L. T. Hudson, A. T. Payne, L. F. Smale, A. Henins, J. M. Pomeroy, J. N. Tan, J. A. Kimpton, E. Takacs, K. Makonyi, Testing three-body quantum electrodynamics with trapped Ti^{20+} ions: evidence for a Z-dependent divergence between experiment and calculation, *Phys. Rev. Letts.* **2012**, *109*, 153001–1–5.
- [2] A. T. Payne, C. T. Chantler, M. N. Kinnane, J. D. Gillaspay, L. T. Hudson, L. F. Smale, A. Henins, J. A. Kimpton, E. Takacs, Helium-like titanium X-ray spectrum as a probe of QED computation, *J. Phys.* **2014**, *B47*, 185001–1–8.
- [3] C. T. Chantler, J. A. Lowe, I. P. Grant, Multiconfiguration Dirac–Fock calculations in open-shell atoms: convergence methods and satellite spectra of the copper $K\alpha$ photoemission spectrum, *Phys. Rev. A* **2010**, *82*(5), 052505.
- [4] J. A. Bearden, A. F. Burr, Reevaluation of X-ray atomic energy levels, *Rev. Mod. Phys.* **1967**, *39*(1), 125–142.
- [5] J. P. Desclaux, *At. Data Nucl. Data Tables* **1973**, *12*, 312.
- [6] R. D. Deslattes, E. G. Kessler, P. Indelicato, L. de Billy, E. Lindroth, J. Anton, X-ray transition energies: new approach to a comprehensive evaluation, *Rev. Mod. Phys.* **2003**, *75*(1), 35–99.
- [7] I. P. Grant, *Adv. Phys.* **1970**, *19*, 747.
- [8] M. Deutsch, G. Hölzer, J. Härtwig, J. Wolf, M. Fritsch, E. Förster, $K\alpha$ and $K\beta$ X-ray emission spectra of copper, *Phys. Rev. A* **1995**, *51*(1), 283–296.
- [9] G. Hölzer, M. Fritsch, M. Deutsch, J. Härtwig, E. Förster, $K\alpha_{1,2}$ and $K\beta_{1,3}$ X-ray emission lines of the 3d transition metals, *Phys. Rev. A* **1997**, *56*(6), 4554–4568.
- [10] L. F. Smale, C. T. Chantler, J. A. Kimpton, D. N. Crosby, M. N. Kinnane, Characterization of K beta spectral profile for vanadium, *Phys. Rev.* **2013**, *A87*: 022512–1–7.
- [11] C. T. Chantler, L. F. Smale, J. A. Kimpton, D. N. Crosby, M. N. Kinnane, A. J. Illig, Characterization of titanium K beta spectral profile, *J. Phys.* **2013**, *B46*: 145601–1–10.
- [12] A. J. Illig, C. T. Chantler, A. T. Payne, Voigt profile characterisation of copper K alpha, *J. Phys.* **2013**, *B46*: 235001–1–11.
- [13] C. T. Chantler, A. C. L. Hayward, I. P. Grant, Theoretical determination of characteristic X-ray lines and the copper $K\alpha$ spectrum, *Phys. Rev. Lett.* **2009**, *103*(12), 123002.
- [14] J. A. Lowe, C. T. Chantler, I. P. Grant, A new approach to relativistic multi-configuration quantum mechanics in titanium, *Phys. Lett. A* **2010**, *374*(47), 4756–4760.
- [15] C. T. Chantler, J. A. Lowe, I. P. Grant, Multiconfiguration Dirac–Fock calculations in open-shell atoms: convergence methods and satellite spectra of the copper $K\alpha$ photoemission spectrum, *Phys. Rev. A* **2010**, *82*(5), 052505.
- [16] J. A. Lowe, C. T. Chantler, I. P. Grant, *Phys. Rev. A* **2011**, *83*(6), 060501.
- [17] D. F. Anagnostopoulos, R. Sharon, D. Gotta, D. Moshe, $K\alpha$ and $K\beta$ X-ray emission spectra of metallic scandium, *Phys. Rev. A* **1999**, *60*(3), 2018–2033.
- [18] D. F. Anagnostopoulos, D. Gotta, P. Indelicato, L. M. Simons, Low-energy X-ray standards from hydrogenlike pionic atoms, *Phys. Rev. Lett.* **2003**, *91*(24), 240801.
- [19] J. Schweppe, R. D. Deslattes, T. Mooney, C. J. Powell, Accurate measurement of Mg and Al $K[\alpha]_{1,2}$ X-ray energy profiles, *J. Electron. Spectrosc. Relat. Phenom.* **1994**, *67*(3), 463–478.
- [20] C. T. Chantler, M. N. Kinnane, C. H. Su, J. A. Kimpton, Characterization of $K\alpha$ spectral profiles for vanadium, component redetermination for scandium, titanium, chromium, and manganese, and development of satellite structure for $z = 21$ to $z = 25$, *Phys. Rev. A* **2006**, *73*(1), 012508.
- [21] S. P. Limandri, A. C. Carreras, R. D. Bonetto, J. C. Trincavelli, $K\beta$ satellite and forbidden transitions in elements with $12 \leq z \leq 30$ induced by electron impact, *Phys. Rev. A* **2010**, *81*, 012504.
- [22] A. S. Koster, H. Mendel, X-ray k emission spectra and energy levels of compounds of 3D-transition metals–I: oxides, *J. Phys. Chem. Solids* **1970**, *31*(11), 2511–2522.
- [23] M. Uršič, M. Kavčič, M. Budnar, Second order radiative contributions in the $K\beta_1$, 3 X-ray spectra of 3D transition metals and their dependence on the chemical state of the element, *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, *211*(1), 7–14.
- [24] S. Morita, J. Fujita, $K\beta$ X-ray transition energies of M-shell-ionized ions of Ti through Ni in a plasma, *Phys. Rev. A* **1985**, *31*(5), 3299.
- [25] L. Mandić, S. Fazinić, M. Jakšić, Chemical effects on the $K\beta^*_{\{ \}} \}$ and $K\beta_{\{ \{ 2, 5 \}}}$ X-ray lines of titanium and its compounds, *Phys. Rev. A* **2009**, *80*(4), 042519.
- [26] J. D. Silver, A. J. Varney, H. S. Margolis, P. E. G. Baird, I. P. Grant, P. D. Groves, W. A. Hallett, A. T. Handford, P. J. Hirst, A. R. Holmes, D. J. H. Howie, R. A. Hunt, K. A. Nobbs, M. Roberts, W. Studholme, J. S. Wark, M. T. Williams, M. A. Levine, D. D. Dietrich, W. G. Graham, I. D. Williams, R. O’Neil, S. J. Rose, The Oxford electron-beam ion trap: a device for spectroscopy of highly charged ions, *Rev. Sci. Instrum.* **1994**, *65*(4), 1072–1074.
- [27] M. Deutsch, M. Hart, E. Cummings, *Phys. Rev. B* **1990**, *42*, 1248.
- [28] C. T. Chantler, X-ray diffraction of bent crystals in Bragg geometry. I. Perfect-crystal modelling, *J. Appl. Crystallogr.* **1992**, *25*(6), 674–693.
- [29] C. T. Chantler, X-ray diffraction of bent crystals in Bragg geometry. II. Non-ideally imperfect crystals, modelling and results, *J. Appl. Crystallogr.* **1992**, *25*(6), 694–713.

APPENDIX

We here discuss the calibration of the energy axis. This is the definition form of the dispersion function through calibration functions, the method of propagating error bars through the calibration functions to find uncertainty in energy and a method finding dispersion function through calibration function fitting.

Dispersion function

Two calibration functions are required to map the dispersion function and detector profile to an absolute energy axis. The clinometer calibration function $I(V; P_i)$ maps the clinometer voltage V to the clinometer angle I , while the supplementary relation $\theta = -I$ maps the clinometer angle to the dispersion crystal angle θ which reflects the theoretical Mosplate model crystal angle, thus:

$$\theta = -I(V; P_i) \quad (\text{A.1})$$

$I(V; P_i)$ is defined to be:

$$I(V; P_i) = \arcsin \left(\frac{V - P_{i,2}}{P_{i,0}} \right) - P_{i,1} + \sum_{i=0}^n P_{i,(i+3)} (V - P_{i,2})^i \quad (\text{A.2})$$

where P_i is the vector of fitting parameters.

A second calibration function, the detector dispersion calibration function $D_2(x; P_D)$, maps the recorded detector position x in output units to the theoretical detector position D in mm. The map from x to D was defined by:

$$D_2(x; P_D) = \sum_{i=0}^1 P_{D,i} x^i \quad (\text{A.3})$$

where P_D is the vector of fitting parameters.

Using this calibration, an energy can be assigned for any detector position x and any clinometer voltage V :

$$E(x, V; P_D, P_i) = E_{\text{mos}}(D_2(x; P_D), -I(V; P_i)) \quad (\text{A.4})$$

Eqns A.2 and A.3 define the calibration of an experimental configuration (i.e. wedge position). The calibration process was reduced to simultaneously finding the P_i and P_D fitting parameters that best fit the $K\alpha$ data possibly combined with a minimisation of the variance of another interesting line’s measured peak energy at the same time (in this experiment: Ti $K\beta$, V $K\beta$ or Cr $K\beta$). This optimised the statistical information for the determination of the $K\beta$ profile peak energy and the dispersion function.

Determination of energy uncertainty

Following Eqn A.4, the uncertainty in the energy assigned to a detector position measurement, ΔE , was due to four sources of uncertainty:

1. the determination of the detector position (Δx),
2. the detector dispersion fit $C_{D,ij}$,
3. the noise in clinometer voltage (ΔV), and
4. the clinometer calibration function fitting $C_{I,ij}$.

$$\Delta E^2 = \left(\frac{\partial E}{\partial x} \Delta x \right)^2 + \sum_{ij} \frac{\partial E}{\partial P_{D,i}} \frac{\partial E}{\partial P_{D,j}} C_{D,ij} + \left(\frac{\partial E}{\partial V} \Delta V \right)^2 + \sum_{ij} \frac{\partial E}{\partial P_{I,i}} \frac{\partial E}{\partial P_{I,j}} C_{I,ij} \quad (\text{A.5})$$

where $C_{D,ij}$ is the i, j th element of the covariance error matrix from the detector dispersion function fit while $C_{I,ij}$ is the i, j th element of the covariance error matrix from the clinometer calibration function fit.

The clinometer calibration function covariance includes all uncertainties from clinometer nonlinearity, peak and energy uncertainty of $K\alpha$ transitions and fitting, diffraction theory uncertainty and variance and other contributions. While the $K\alpha$ peak position uncertainties are as detailed in Table 1, the uncertainties of the refractive index correction and temperature variation are approximately 1 ppm. Indeed, any temperature uncertainty primarily cancels in the modelling. The impact of uncertainty of the source position upon the diffraction computations is almost negligible. Further, the correlated uncertainty of more complex diffraction estimates cancels to first order.

Calibration function fitting

The specific process which was undertaken to find the fitting parameters P_I and P_D for each calibration followed four major steps: the clinometer pre-calibration; the clinometer calibration first estimate; the calibration fitting; and the detector scale correction. First, preliminary clinometer pre-calibration entailed an experimental characterisation of the angle of incline to voltage function ($V_{pre}(I)$) of the clinometers in isolation:

$$V_{pre}(I) = P_{V,0} \sin(I - P_{V,1}) - P_{V,2} + \sum_{i=0}^8 P_{V,(i+4)} V^i \quad (\text{A.6})$$

Second, an estimate of the clinometer calibration function was constructed by generating data with the $V_{pre}(I)$ function, inverting

the data and then fitting these data with $I(V; P_I)$ (Eqn A.2) where the order of the polynomial was set to $n = 3$.

Third, calibration fitting was a four stage process beginning with estimation of P_I and P_D . Each stage made a refinement of either P_I or P_D through one round of fitting.

The first was to fit the $I(V; P_I)$ function to I_{data} versus V where I_{data} is a set of calculated data predicting the expected clinometer angle for each peak based on the energy and detector position:

$$I_{data} = -\theta_{mos}(D(x, P_D), E) \quad (\text{A.7})$$

It has uncertainty ΔI_{data} :

$$\Delta I_{data}^2 = \left(\frac{\partial \theta_{mos}}{\partial E} \Delta E \right)^2 + \left(\frac{\partial \theta_{mos}}{\partial D} \right)^2 \left(\sum_{ij} \frac{\partial D}{\partial P_{D,i}} \frac{\partial D}{\partial P_{D,j}} C_{D,ij} + \left(\frac{\partial D}{\partial x} \Delta x \right)^2 \right) \quad (\text{A.8})$$

This first fit allowed only allows the refinement of $P_{I,1}$ (the overall offset to $I(V; P_I)$).

The second stage was a refit of I_{data} versus V with $I(V; P_I)$ using the P_I from fit 1 as a estimate, this time only allowing the refinement of $P_{I,4}$ through $P_{I,7}$, fitting the fine details and secondary functional parameters of $I(V; P_I)$.

The third stage was to fit $D(x; P_D)$ to D_{data} versus x , where D_{data} is a set of calculated data that provides the expected theoretical detector position for each peak based on the energy and crystal angle:

$$D_{data} = D_{mos}(E, -I(V; P_I)) \quad (\text{A.9})$$

It has uncertainty ΔD_{data} :

$$\Delta D_{data}^2 = \left(\frac{\partial D_{mos}}{\partial E} \Delta E \right)^2 + \left(\frac{\partial D_{mos}}{\partial \theta} \right)^2 \left(\sum_{ij} \frac{\partial I}{\partial P_{I,i}} \frac{\partial I}{\partial P_{I,j}} C_{I,ij} + \left(\frac{\partial I}{\partial V} \Delta V \right)^2 \right) \quad (\text{A.10})$$

Both P_D parameters were free in this fit.

Lastly, results from the third stage were then used to refit I_{data} versus V using $I(V; P_I)$, allowing the refinement of $P_{I,4}$ through $P_{I,7}$, as in the second fit. This method generates the P_I and P_D parameters along with associated covariance error matrices C_I from the fourth fit and C_D from the third fit.

At the end of this four stage step, the fitted P_I parameters characterised how the clinometers functioned in the setup through fitting the interlinked $K\alpha$ peak energy, peak position and clinometer voltage calibration data.

C

Additional Publications

The following publications are indirect results of the work presented in this thesis. The present author had a contribution to each. They are reprinted in full in this appendix.

- CT Chantler, NA Rae, MT Islam, SP Best, J Yeo, LF Smale, J Hester, N Mohammadi, and F Wang. Stereochemical analysis of ferrocene and the uncertainty of fluorescence XAFS data. *Journal of Synchrotron Radiation*, 19(2):145–158, 2012
- CT Chantler, MN Kinnane, JD Gillaspay, LT Hudson, AT Payne, LF Smale, A Henins, JM Pomeroy, JN Tan, JA Kimpton, E Takacs, and K Makonyi. Testing Three-body Quantum Electrodynamics with Trapped Ti^{20+} Ions: Evidence for a Z-Dependent Divergence between Experiment and Calculation. *Physical Review Letters*, 109:153001–1–5, 2012
- CT Chantler, MN Kinnane, JD Gillaspay, LT Hudson, AT Payne, LF Smale, A Henins, JM Pomeroy, JA Kimpton, E Takacs, and K Makonyi. Testing Three-body Quantum Electrodynamics with Trapped Ti^{20+} Ions: Evidence for a Z-Dependent Divergence between Experiment and Calculation, Reply. *Physical Review Letters*, 110:159302, 2013
- CT Chantler, AT Payne, JD Gillaspay, LT Hudson, LF Smale, A Henins, JA Kimpton, and E Takacs. X-ray measurements in helium-like atoms increased discrepancy between experiment and theoretical QED. *New Journal of Physics*, 16(12):123037, 2014
- AT Payne, CT Chantler, MN Kinnane, JD Gillaspay, LT Hudson, LF Smale, A Henins, JA Kimpton, and E Takacs. Helium-like titanium x-ray spectrum as a probe of QED computation. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 47(18):185001, 2014

- LT Hudson, JD Gillaspay, JM Pomeroy, CI Szabo, JN Tan, B Radics, E Takacs, CT Chantler, JA Kimpton, MN Kinnane, and LF Smale. Detection of faint X-ray spectral features using wavelength, energy, and spatial discrimination techniques. *Nuclear Instruments and Methods in Physics Research A*, 580: 33–36, 2007
- JA Kimpton, MN Kinnane, LF Smale, CT Chantler, LT Hudson, A Henins, CI Szabo, JD Gillaspay, JN Tan, JM Pomeroy, et al. Data acquisition system development for the detection of X-ray photons in multi-wire gas proportional counters. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 580(1):246–249, 2007
- AT Payne, JA Kimpton, LF Smale, and CT Chantler. Optimisation of the spatial linearity in backgammon-type multi-wire gas proportional counters-The relevance of charge cloud distribution. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 619(1):190–197, 2010

Stereochemical analysis of ferrocene and the uncertainty of fluorescence XAFS data

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Methods for the quantification of statistically valid measures of the uncertainties associated with X-ray absorption fine structure (XAFS) data obtained from dilute solutions using fluorescence measurements are developed. Experimental data obtained from 10 mM solutions of the organometallic compound ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, are analysed within this framework and, following correction for various electronic and geometrical factors, give robust estimates of the standard errors of the individual measurements. The reliability of the refinement statistics of standard current XAFS structure approaches that do not include propagation of experimental uncertainties to assess subtle structural distortions is assessed in terms of refinements obtained for the staggered and eclipsed conformations of the C_5H_5 rings of ferrocene. Standard approaches (*XFIT*, *IFEFFIT*) give refinement statistics that appear to show strong, but opposite, preferences for the different conformations. Incorporation of experimental uncertainties into an *IFEFFIT*-like analysis yield refinement statistics for the staggered and eclipsed forms of ferrocene which show a far more realistic preference for the eclipsed form which accurately reflects the reliability of the analysis. Moreover, the more strongly founded estimates of the refined parameter uncertainties allow more direct comparison with those obtained by other techniques. These XAFS-based estimates of the bond distances have accuracies comparable with those obtained using single-crystal diffraction techniques and are superior in terms of their use in comparisons of experimental and computed structures.

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Printed in Singapore – all rights reserved**Keywords:** fluorescence; X-ray absorption fine structure; ferrocene; standard error.

1. Introduction

The subtle inter-relationship between the electronic and molecular structure of transition metals and the impact on reactivity underpin their proliferation as the catalysts for biological and industrial processes. For homogeneous catalysis in solution it is vitally important to have available methods that determine, reliably, the structural details needed to understand details of the reaction path. This, to some, is the *raison d'être* of spectroscopy. Notwithstanding the possibilities presented by optical, EPR (electron paramagnetic resonance) and NMR (nuclear magnetic resonance) spectroscopy for particular systems, X-ray absorption fine structure (XAFS) provides the best general approach for structural characterization at the molecular level for metal species in low concentration. While there is an extensive literature demonstrating the application of XAFS to the identification of the coordinating atoms and extraction of geometrical information from analysis employing multiple scattering formalisms, any assessment of the derived geometry is limited by difficulties in

assessing the reliability of the individual experimental observations.

The difficulty in assessing the statistical reliability of the XAFS data is greatly accentuated in cases where fluorescence detection is employed, *i.e.* for the study of samples in dilute solutions. This paper is concerned with quantification of the accuracy and precision of fluorescence XAFS measurements. Ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$ (di-cyclopentadienyl iron), discovered in 1951 (Kealy & Pauson, 1951; Miller *et al.*, 1952), is a prototype of sandwich molecular complexes which epitomizes the different bonding interactions possible between metals and organic molecules and is central to the award of the Nobel prize to Fischer and Wilkinson in 1973 (Fischer & Wilkinson, 1993). The molecule has well defined redox chemistry and is a popular reference material for electrochemical studies conducted in non-aqueous solvents and is an ideal test case for *in situ* electrochemical cells for XAFS and X-ray absorption near-edge structure (XANES) studies.

An interesting aspect of the structural chemistry of ferrocene is the orientation of the two cyclopentadienyl rings. The

initial interpretation of the crystallography suggested a 'staggered' conformation giving a molecule with D_{5d} symmetry, but this was subsequently revised with the 'eclipsed' (D_{5h}) form believed to be more stable by perhaps 4 kJ mol^{-1} (Haaland & Nilsson, 1968; Haaland, 1979). When compared with axial distortions of Jahn–Teller distorted octahedral complexes or square-planar tetrahedral isomerism of four-coordinate complexes, differences in the relative orientations of the cyclopentadiene rings of ferrocene present a serious test of the ability of XAFS methods to reveal subtle differences in the molecular structure. Moreover, since the main differences in structure will be manifested by multiple-scattering interactions, the problem also allows assessment of experimental and theoretical approaches to analysis at the interface of the XANES and XAFS regions.

For absorption spectroscopy, the X-ray extended range technique (XERT) can provide defined accuracies and uncertainties in XAFS experiments (e.g. Tran *et al.*, 2003c), and investigate experimental systematics including harmonic contamination (de Jonge *et al.*, 2004b; Tran *et al.*, 2004). This allows absolute intensity measurements of X-ray attenuation, including measurements in the XAFS region (e.g. de Jonge *et al.*, 2005, 2007; Glover *et al.*, 2008; Islam *et al.*, 2010; Rae *et al.*, 2010a), and can measure X-ray absorption with an accuracy below 0.05%. It should be possible to obtain reliable data on chemical bonding, thermal effects and anharmonicity, as well as to establish the absolute fluorescent radiation yield. However, the analysis even of accurate absorption data is hampered by difficulties in the propagation of experimental uncertainty, which is exacerbated in the case of fluorescence spectra from dilute samples. Past analyses of XAFS data from ferrocene have found no difference between possible models (Vedrinskii *et al.*, 1991; Ruiz-Lopez *et al.*, 1988; Schnitzler *et al.*, 2006).

Standard methods used by the XAFS community to define coordination environments of an absorbing atom can, for example, distinguish coordination number, changes in absorber–scatter distance or square-planar–tetrahedral isomerism. However, the absence of a statistically rigorous method of assessing the reliability of the individual measurements, particularly in the case of fluorescence experiments, not only has the potential to give misleading results but also limits the possibility of assessing whether the experimental data are of a quality to support even the asking of such questions. We focus on the processing of X-ray absorption spectra (XAS) obtained from frozen solutions of ferrocene data collected at the Australian National Beamline Facility (ANBF) in Tsukuba, KEK, Japan, using a conventional fluorescence geometry. In particular we set out the corrections needed to bring the independent observations from a multi-element detector onto the same absolute intensity scale. This permits a more detailed statistical analysis of the spectra than has previously been reported.

Most XAFS data are represented by a single reduced plot such as Fig. 1. This shows clearly the sharp edge jump after K -shell ionization of the central iron atom, together with the interference wave of the resulting photoelectron reflecting

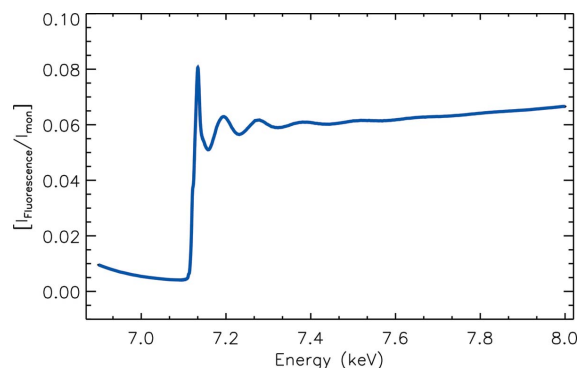


Figure 1

The standard average output using *AVERAGE* for a 10 mM solution of ferrocene.

from surrounding electron density of the coordinated ligands. The fluorescence signal arises from the relaxed iron $K\alpha\ 2p-1s$ transition lying in energy somewhat below the continuum, and was measured in a 36-channel segmented germanium detector, configured to report the counts in the energy region-of-interest (ROI) corresponding to the iron fluorescence $K\alpha$ region.

Standard analysis in the Australian XAFS research community uses the package *AVERAGE* (Ellis & Freeman, 1995a) to reduce the dataset to this plot. Standard analysis may then use *IFEFFIT* (Newville, 2001) or alternatively *XFIT* (Ellis & Freeman, 1995b) and *FEFF* (Version 6.1) (Rehr *et al.*, 1991) for example to further reduce this to a χ versus k plot, scaled or otherwise, which is then fitted with the usual array of XAFS parameters. In the case of the high-symmetry molecule ferrocene the XAFS may be modelled using five independent variables [E_0 , S_0^2 , $C(x)$, $C(y)$ and $\sigma^2(C)$] if the scattering from hydrogen is neglected and seven otherwise (if the cyclopentadiene ring is planar).

Inspection of Fig. 1 immediately reveals that the data are subject to systematic errors, especially noting the gradual increase of absorption coefficient with energy above the edge and the peculiar signature below the edge with the qualitative form of an extended quadratic. These distortions of data do not prevent XAFS analysis, as baseline subtraction allows extraction of χ , but these and other effects conspire to obstruct determination of statistically robust estimates of the uncertainty of individual measurements. This, we argue, prevents the use of XAFS methods for the examination of more subtle structural questions such as the staggered or eclipsed structures of ferrocene, or perhaps the percentage of each if there is some thermal disorder. The conformation of the cyclopentadienyl rings may be examined by comparison of the refinement statistics using model structures of the two conformers, or models in which the Fe–C interactions are not equivalent. Assessment of the significance of any discrepancy between the refinement statistics relies on the reliability of primary experimental observations, this most sensibly being statistically based. Clearly it is critical to be able to assess both the accuracy and precision of the data in order to establish whether the question posed is able to be answered with any sort of reliability.

In this paper, we (i) develop a methodology for determining robust standard errors from such typical datasets; (ii) discuss the fluorescence theory for data reduction; (iii) develop techniques for error propagation in least-squares fitting and (iv) illustrate their potential applied to a subtle and long-standing problem of ferrocene.

2. Conformers of ferrocene

The high-symmetry conformations of ferrocene are illustrated in Fig. 2. The iron atom, Fe^{2+} , is centrally located between two parallel cyclopentadienyl rings where the rings are either eclipsed D_{5h} when viewed down the symmetry axis or have a staggered D_{5d} conformation (*i.e.* where one ring is rotated relative to the other by an angle of $2\pi/5$ to yield an inversion centre).¹

Early determinations of ferrocene assumed that the D_{5d} conformation was the stable form, based in part upon symmetry properties, and it was not until well after the determination of the X-ray structure of ruthenocene, $\text{Ru}(\text{C}_5\text{H}_5)_2$, for which the D_{5h} structure appeared to be the refined structure (Hardgrove & Templeton, 1959; Seiler & Dunitz, 1980), that the question of the stability of ferrocene conformation was raised (Seiler & Dunitz, 1979*a,b*). However, for the Fe case, the X-ray structure appeared complicated by disorder (dynamic or static), and the situation remains unclear, even in recent reviews (Yamaguchi *et al.*, 2007). In particular, the early assumption of an ideal staggered conformation was questioned and a necessary disorder of either staggered or eclipsed, or partially staggered, molecules in crystalline form has been developed. The crystallographically refined conformation appears to depend upon crystallization temperature and monoclinic, triclinic or orthorhombic phase. The energy and property differences between the D_{5d} and the D_{5h} conformers of ferrocene appear small (Coriani *et al.*, 2006), which makes it possible that the two conformers may be thermally interchangeable, *i.e.* there is a small rotational energy barrier.

In relation to characterization of molecular structure, X-ray and neutron diffraction reveal accurate mean lattice positions of electron or nuclear density, and hence differences between these mean positions may be obtained for well defined crystals. XAFS has a strong potential advantage over these techniques in that it directly samples the dynamic and static intramolecular disorder and hence the molecular and electronic structure of the complex including the bond lengths. Exploitation of this advantage requires high-quality accurate data.

Important questions that must be addressed with any experimental investigation are ‘How accurate is this experimental dataset?’ and, perhaps with greater concern, ‘How precise is this dataset?’ If the dataset is highly accurate, then it can be used for any purpose, including testing of theory,

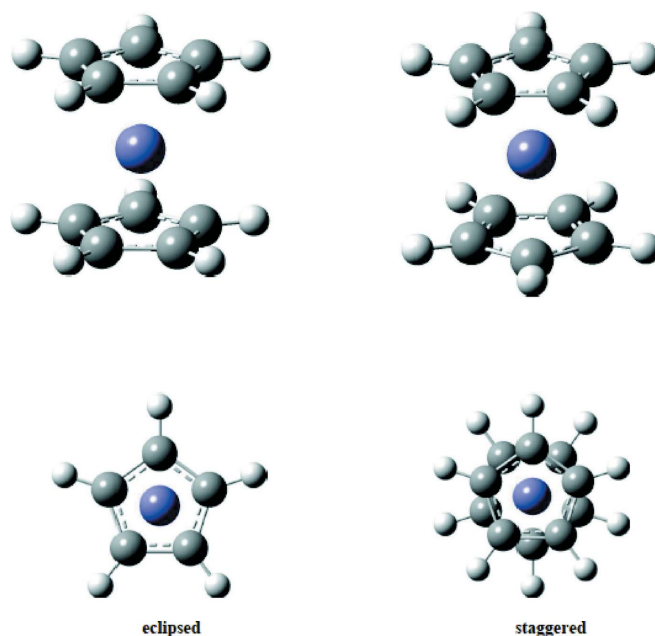


Figure 2

A model of the ferrocene molecule with staggered (D_{5d}) and eclipsed (D_{5h}) symmetries.

investigation of edge-jump ratios, derivation of form factors, and of course investigations of XANES and XAFS. If it is highly precise but of uncertain accuracy, then the first three applications may be invalidated but the dataset may, after normalization, be excellent for XANES or XAFS investigations. A critical question of this investigation is whether accurate XAFS datasets can reliably resolve conformational ambiguity.

3. Brief experimental

In order to avoid microcrystallization at the low temperatures of 10–20 K in the cold cell (cryostage), solutions of 10 mM ferrocene were prepared using a mixed solvent of (50%) CH_3CN acetonitrile and (50%) $\text{C}_3\text{H}_7\text{CN}$ butyronitrile. The standard XAFS configuration at ANBF was followed, involving a monitor upstream (ion chamber, 10 cm, 70% He, 30% nitrogen-filled) and the 36-element Ge planar detector (EURISYS EPIX 36-64-7-ER). The detector contains 36 channels with an order of 6×6 channels forming a square area of (50 mm $\times$ 50 mm) with each pixel capturing an area of 8 mm $\times$ 8 mm. The output file runs from channels 0 to 34 (the last pixel is dead), with 0 being the top downstream end and incrementing horizontally. The approximate gap between the active area of each channels is 0.4 mm. So, the separation of pixel centres at the detector surface is 8.4 mm. Three scans of the XAFS region were made to provide more reliable data, so each point in energy has 35×3 repetitions (one per active detector channel, one per scan).

Raw signals from the detector channels are fed to digital signal processing (DSP) modules [DXP4C-2X modules from XIA (Warburton *et al.*, 1999)] which calculate the total incoming count rate (ICR) for all energies, the energy binned

¹ An interactive version of Fig. 2 is available as supplementary data for this paper (Reference: WA5021). Services for accessing these data are described at the back of the journal.

count rate (OCR) and the total counts in the energy region of interest.

The angle of the sample in fluorescence (the solution cell) is very close to 45° to the incident beam. The central position of the detector is aligned to be approximately 45° to the solution cell or approximately 90° to the incident beam. In the vertical direction this is well aligned to within 1 mm; in the horizontal direction it is probably accurate to within 5 mm.

4. Intrinsic precision of the dataset

Fig. 3 plots all the scans of the dataset, given by $I_{\text{dnp}}/I_{\text{mon}}$ where I_{dnp} is the raw count received within the region of interest of a single channel of the detector, while I_{mon} is the raw count of the monitor, the upstream ion chamber. This normalization does not correct for air path, scattering, harmonic or other parameters investigated by XERT; this is a typical conventional dataset. It also does not correct for detector channel offsets or scale errors; both monitor and detector channels typically measure a non-zero count per second as electronic noise. However, this is the standard data which is used for fluorescence studies at ANBF and elsewhere. Channel 35 is dead, and channel 34 (the purple line at the bottom) has virtually zero sensitivity, and is excluded from further data analysis. A second major point is that the different channels have extraordinarily different values for $I_{\text{dnp}}/I_{\text{mon}}$. Indeed, we have plotted this to suggest a systematic effect, discussed below.

Fig. 3 looks somewhat confusing, so it may be sensible to compress the dataset from 105 scans (3 scans per channel $\times$ 35 channels) into 34 lines, each of which is an average of the corresponding three scans for that channel. Additionally there is a very well known effect of dead-time in the fluorescence detector, caused by the processing time of the channel from the raw data into the region of interest. The dead-time is conveniently determined for the scattering detector because we have one signal (a fast processing signal) prior to

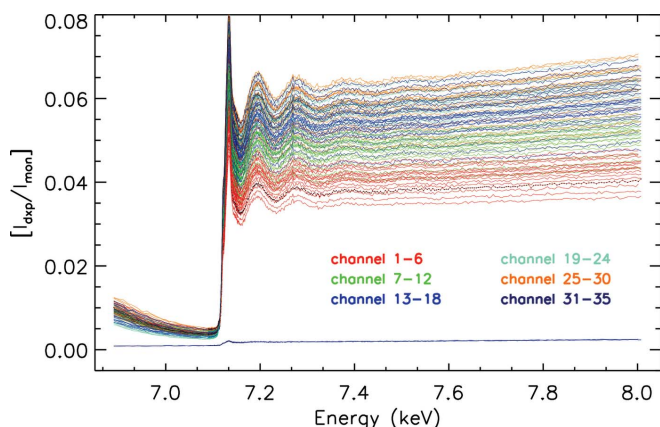


Figure 3
Plot of the full dataset for the raw detector signal within the fluorescence region-of-interest divided by the monitor signal. There are 36 segmented detector channels arranged in a square, and the dataset collected three consecutive scans of the energy range presented. Colour coding is based on vertical columns of detector elements.

measuring the energy (using electronic signal processing and then an analogue-to-digital conversion into energy bins) I_{ICR} , and a similar count of all photons tagged after this energy conversion I_{OCR} . Hence the number of pulses lost owing to dead-time is given by the difference between these two numbers, and the dead-time-corrected spectra are generated by $I_{\text{dnp}}/I_{\text{mon}} \times (I_{\text{ICR}}/I_{\text{OCR}})$.

Correction of the results obtained for each detector channel by implementing the dead-time correction and taking the average of the three independent scans gives an improvement in the signal-to-noise ratio, as expected, but with only a small improvement of the variance of the signal for the different detector components (Fig. 4). This set of observations may be used to compute the averaged χ versus k spectrum with standard errors giving the explicit absolute (and relative) uncertainty of each point (Fig. 5). However, the relative error thereby obtained is large owing to a systematic variation in the signal intensity which is correlated with the identity of the detector element (Fig. 4). This is a major result, although perhaps not too complex; we have a standard error of our official average result.

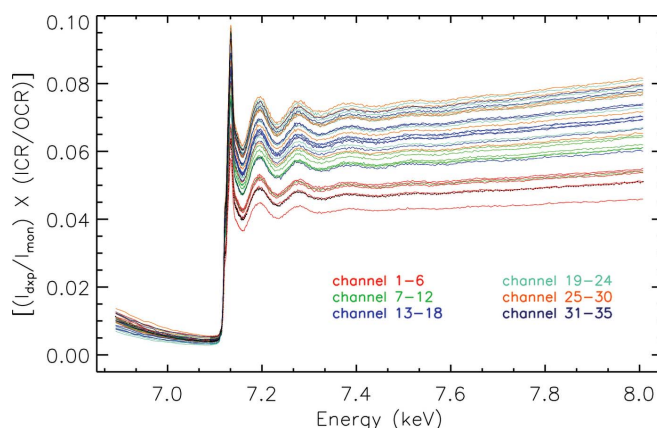


Figure 4
The full usable dataset for the raw detector signal within the fluorescence region-of-interest divided by the monitor signal, normalized by the detector dead-time correction. Each trace represents the unweighted average of the corrected ratios of the three independent scans.

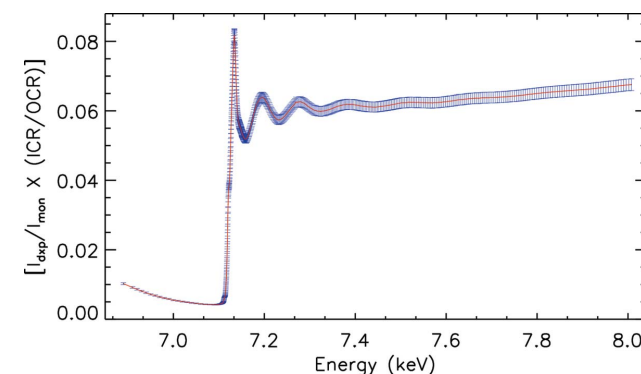


Figure 5
The average signal of the 34 usable detector channels, corrected for detector dead-time, with a standard error representing the precision of determination of the individual data points.

5. Alternative analytic approaches to multi-pixel data

If we investigate further a single scan, with three repeated scans thereof, we can construct a line (just as in Fig. 4) but with a standard error formed from the consistency of the three scans for that channel. If there were electronic drift, a limitation of normalization by the monitor, some scale or amplifier drift with time, or any other functional dependence with time, then we will observe variation between the scans, and the resulting standard error will represent our ability to determine the average for that particular channel. Hence this uncertainty map will provide a measure of our information content for that particular channel. This is provided by way of example, for channel 1, in Fig. 6. The points are relatively noisy, but the standard error is provided by the consistency of the scans, so really is quite noisy. In absolute terms, this standard error is poor below the edge, though with large oscillations, and relatively well defined at higher energies above the edge. The greatest dispersion is in the near-edge region, in part owing to energy drifts and counting statistics. In part, this is a deliberate experimental optimization of the data collection routine; the code counts longer for regions higher in k and hence above the edge, leading to better statistical determination. This variance is not due to dark count correction nor air path correction, but may have causes in alignment, beam motion on sample and ROI settings.

We could therefore process the reduced dead-time-corrected average given by Fig. 5 with its corresponding standard error (a perfectly self-consistent approach); or one could process an individual fluorescence detector channel with its uncertainty as illustrated by Fig. 6. While the latter would be self-consistent, it may be consistent or inconsistent with any other fluorescence detector channel.

If it is supposed that the systematic variation is due to differences in sensitivity of the individual channels owing to pixel thickness, detector pathlength or other scaling or offset parameters, then this may be addressed by normalization of the signal in a self-consistent manner. The amplifier settings have been calibrated with a flat field, and ROIs have been set, so these uncertainties should be small. For the purposes of this argument, Fig. 7 provides the set of all scans and channels

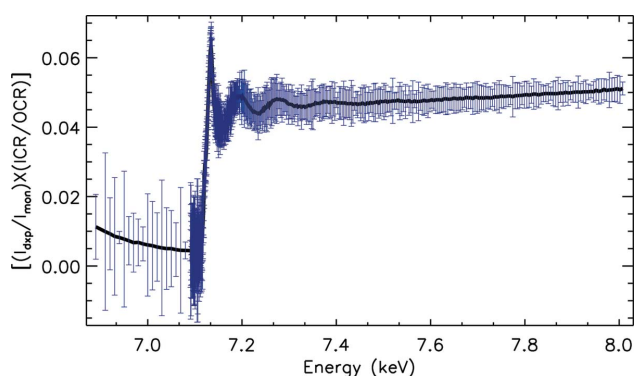


Figure 6
The average and standard error of the dead-time-corrected fluorescence signal normalized to the monitor reading, from three independent scans (detector channel 1).

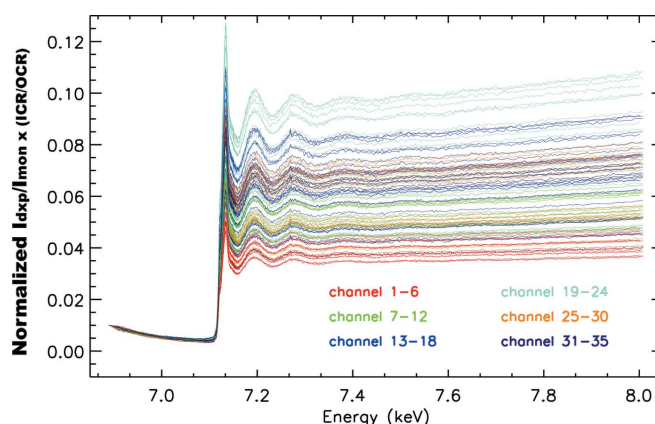


Figure 7
The full usable dataset for the raw detector signal divided by the monitor signal, normalized by the detector dead-time correction, and each scan is normalized to the first pixel average.

normalized to the first pixel of the XAFS scan. This scaling lowers the variance in the pre-edge region but accentuates the variance at and above the edge. Significantly, the dependence of the variance in signal with the position of the detector channel evident in the earlier plots (Figs. 3 and 4) is retained and amplified with this normalization of the data. Therefore the increase in variation is not due to random noise associated with the first data point. Hence, the specific approach of Fig. 7 dramatically increases the standard errors and is *not* justified by the data.

6. Theoretical interpretation of segmented fluorescence data

An alternate explanation of the systematic variation in the signal from the different detector elements may be related to the geometry-dependent efficiency of fluorescence detection. This requires an understanding of the nature of the fluorescence process, and perhaps initially to revisit the absorption process. Absorption is conventionally given by the Beer–Lambert equation,

$$I = I_0 \exp[-(\mu/\rho)(\rho t)], \quad (1)$$

where I_0 is the incident X-ray beam intensity, (μ/ρ) is the X-ray mass absorption coefficient of the material for the energy of the X-ray beam, and t is the thickness of the foil. The beauty of this is that the negative values of the natural logarithms of the measured ratios of I/I_0 ,

$$-\ln(I/I_0) = [(\mu/\rho)(\rho t)] = \mu t, \quad (2)$$

plotted against t [or (ρt)], fall on a straight line with slope μ [or (μ/ρ)]. Hence the mass absorption coefficient, the photoelectric coefficients, the scattering components and the form factors of the material can be directly evaluated from the logarithm of the normalized ratio. Of course, this requires careful correction for detector efficiencies and air path (Tran *et al.*, 2003b), scattering (Tran *et al.*, 2004), harmonics (Tran *et al.*, 2003a), detector linearity (Barnea *et al.*, 2011), energy calibration (Rae *et al.*, 2010b), thickness calibration (Tran *et*

al., 2004), bandwidth (de Jonge *et al.*, 2004a) *etc.*, but yields a highly accurate measurement of the coefficients with the correct scaling and relative amplitudes for processing using, for example, *XERT* for XAFS analysis (Chantler, 2009, 2010).

However, for fluorescence, to first order we have

$$I_{f_0} = f I_0 \{1 - \exp[-(\mu/\rho)(\rho t_p)]\}, \quad (3)$$

where I_{f_0} is the total number of fluorescence photons produced, t_p is the pathlength through the sample, f is the fluorescence yield for the probability of producing a fluorescent photon (in normal geometries specifically a $K\alpha$ photon if the experiment is around the K -shell, or a characteristic L -shell photon if the experiment is around the L -shell *etc.*) after the process of photoabsorption and photoionization [we should label (μ/ρ) with the subscript 'pe' for the photoelectric effect only, and an asterisk indicating that only the component absorbed in the active centre producing a fluorescent photon is relevant, *i.e.* as $(\mu/\rho)_{pe}^*$]. Again, to first order, these fluorescent photons are emitted isotropically. Some simple analysis suggests an improved functional as

$$I_f = \frac{f I_0 \Omega (\mu/\rho)_{pe}^* / 4\pi \cos \theta_{inc}}{[(\mu/\rho)/\cos \theta_{inc}] + [(\mu_f/\rho)/(\cos \theta_{out})]} \times \left\{ A - \exp \left[-\frac{(\mu/\rho)(\rho t)}{\cos \theta_{inc}} - \frac{(\mu_f/\rho)(\rho t)}{\cos \theta_{out}} \right] \right\}, \quad (4)$$

where t is the depth of penetration into the material, Ω is the solid angle subtended by the detector channel, θ_{inc} is the angle of incidence of the incident X-rays (relative to the normal), θ_{out} is the angle of emission of the fluorescent X-rays (relative to the normal), (μ_f/ρ) is the mass attenuation coefficient of the material for the fluorescent photon energy, and the integration constant A may be (loosely) estimated as $A = 1$ (the limit as $t \rightarrow 0$ μ m). Some similar derivations have been presented elsewhere (Bunker, 2010; Troger *et al.*, 1992).

Given a realistic geometry, the number of fluorescent X-rays detected (in the relevant region of interest) should include losses due to air path (air), detector windows (w) *etc.* and detector quantum efficiencies overall (ϵ) as

$$\frac{I_{f_{detected}}}{I_{0_{monitored}}} = \frac{I_f}{I_0} \left[\frac{\epsilon_{det}(E)}{\epsilon_{mon}(E)} \right] \exp \left[-\frac{(\mu_f/\rho)_{air}(\rho t_{air})}{\cos \theta_{air}} - \frac{(\mu_f/\rho)_w(\rho t_w)}{\cos \theta_w} \right]. \quad (5)$$

$t_{air}/\cos \theta_{air}$ is the pathlength from the sample (surface) to the front face of the detector (window) and $t_w/\cos \theta_w$ is the pathlength through, for example, a detector window of thickness t_w . Here we have emphasized the energy dependence of the relative efficiencies of the detectors, as this is quite important. We note that these formulae do not fully incorporate such higher-order effects as bandpass, divergence, polarization and nano-roughness (Glover *et al.*, 2009), but are nonetheless very useful. These latter, finer, effects will be addressed in a subsequent publication.

For normal fluorescence XAFS geometries, the multi-element detector is placed at 90° to the incident beam, with the fluorescent sample, solid or solution, placed at an angle of

45° to the incident beam. A particular detector channel will correspond to an emission angle θ_{out} which varies depending upon how close the sample stage is to the detector and its orientation *etc.* Similarly, the air path for the fluorescent X-ray to the detector, and the angle for the window attenuation, may then be given by

$$\theta_{wh} \simeq \theta_{airh} \simeq \theta_{outh} - 45^\circ. \quad (6)$$

Some simple observations ensue:

(i) While the equation is a little complex, several of the components are fixed by the geometry. If they are known, then the information content can be recovered effectively.

(ii) Whereas, after correction for systematics, the absorption geometry can yield a straightforward and beautiful relation from the logarithm of the normalized intensity ratio, for a range of physical and theoretical interpretations, this is not the case for the fluorescence equation.

(iii) If L is the distance from the sample surface to the detector, then we may approximate $\Omega \simeq D/L^2$ where D is the area of the individual detector element.

(iv) θ_{out} varies across the detector and especially between detector channels, so if the detector channel centres are separated by a distance C (known to good accuracy) and some central detector point is indeed at 45° to the sample surface, then the angle of emission in the plane of incidence is $\theta_{outh} = 45^\circ + \tan^{-1}(nC/L)$ where n is the number of channel elements from the central point. In general, owing to misalignment, we should generalize this to $\theta_{outh} = \theta_0 + \tan^{-1}(nC/L)$. Note, extremely importantly, that, because of the sample self-absorption, different detector channels with different pathlengths will have very strongly different self-absorption correction factors. In principle, the data can be analysed to correct for self-absorption. Channels on the downstream side of the detector have approximately a single angle, and hence a single self-absorption correction; and, for example, those on the other side (upstream) have a much smaller self-absorption correction. While this self-absorption correction is strongly energy-dependent especially owing to $(\mu/\rho)(E)$, it is monotonic.

(v) Hence the pattern of the data expected from different channels is 'exactly' as given in Figs. 3 and 4; and these can be fitted and corrected for self-absorption to provide a more robust dataset with greater information content.

(vi) In many fluorescent geometries, square channel arrays are deliberately quite close to the sample stage to improve scattered fluorescent signals. Then the solid angle to a particular detector channel is important and we must use $\cos \theta_{out} = \cos \theta_{outh} \cos \theta_{outv}$ where v is the vertical angle, which is zero in the plane of incidence. Then $\cos \theta_{outv} = \tan^{-1}(mC/L)$ where m is the number of channel elements from the plane of incidence in the vertical axis.

(vii) In summary, the main parameters are θ_0 and L , allowing potential reduction of the whole equation to a consistent dataset with maximal information content.

(viii) As has been expressed elsewhere (Newville, 2004; Bunker, 2010), there are two particularly useful limits for fluorescence measurements. In the *thin sample limit* where

$(\mu/\rho)\rho t \ll 1$, the $1 - \exp(X)$ term expands by Taylor series expansion, cancelling the denominator (and the self-absorption correction) so that

$$\frac{I_{f,\text{detected}}}{I_{0,\text{monitored}}} = \frac{f t \Omega(\mu/\rho)_{\text{pe}}^* \varepsilon_{\text{det}}(E)}{4\pi \cos \theta_{\text{inc}} \varepsilon_{\text{mon}}(E)} \times \exp \left[-\frac{(\mu_f/\rho)_{\text{air}}(\rho t_{\text{air}}) + (\mu_f/\rho)_{\text{w}}(\rho t_{\text{w}})}{\cos(\theta_{\text{out h}} - 45^\circ) \cos(\theta_{\text{out v}})} \right], \quad (7)$$

and to first order the observed intensity ratios are proportional to the photoelectric coefficient and the XAFS structure may be cleanly extracted. This *thin sample limit* is invalid whenever a dispersion between detector elements is observed, i.e. almost always.

(ix) The second convenient limit is the *thick dilute sample limit* where $(\mu/\rho)\rho t \gg 1$ but $(\mu/\rho)_{\text{pe}} \ll (\mu/\rho)$, the exponential goes to zero yielding

$$\frac{I_{f,\text{detected}}}{I_{0,\text{monitored}}} = \frac{f \Omega(\mu/\rho)_{\text{pe}}^* / 4\pi \cos \theta_{\text{inc}}}{[(\mu/\rho) / \cos \theta_{\text{inc}}] + [(\mu_f/\rho) / \cos \theta_{\text{out}}]} \frac{\varepsilon_{\text{det}}(E)}{\varepsilon_{\text{mon}}(E)} \times \exp \left[-\frac{(\mu_f/\rho)_{\text{air}}(\rho t_{\text{air}}) + (\mu_f/\rho)_{\text{w}}(\rho t_{\text{w}})}{\cos(\theta_{\text{out h}} - 45^\circ) \cos(\theta_{\text{out v}})} \right]. \quad (8)$$

If and only if the energy dependence of the denominator is small (dominated by scattering coefficients or background absorption), then the angular self-absorption can be modelled and the corrected intensity ratio provides the photoelectric absorption coefficients for theoretical modelling using XAFS analysis. However, for most samples, the thin limit is not obeyed (the self-absorption function which we see in Figs. 3 and 4 would be suppressed). Similarly, for most of the X-ray regime $(\mu/\rho)_{\text{pe}}$ is dominant and is not dominated by the scattering coefficients. For a typical metallic XAFS investigation, the concentration must be very low for $(\mu/\rho)_{\text{pe}}$ of the active fluorescent centre in the sample to be dominated by background absorption $(\mu/\rho)_{\text{pe}}$. Then, of course, the signal and statistical precision are also very low.

The absorption coefficient for our current investigation of ferrocene at 10 mM is provided in Fig. 8. While the iron photoelectric absorption coefficient is a small fraction of the solvent photoabsorption, it is still 6% of the total above the

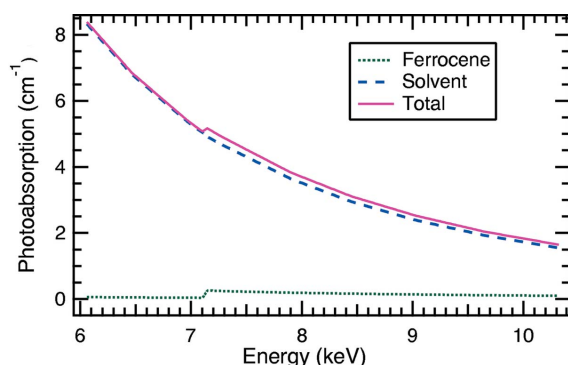


Figure 8
Photoelectric absorption coefficient of the 10 mM iron centre of ferrocene as a component of the total photoabsorption of the solution. Equation (4) will provide more accurate amplitudes for XAFS analysis than equation (8).

edge. Hence, as is often stated, this sort of concentration is a compromise between observing a strong fluorescence signal and introducing large distortions owing to self-absorption. Perhaps of equal concern, especially in this experiment, is that the cell is 2 mm deep. Using the total attenuation in the solution cell indicates that we are far from the ‘thick’ limit. Hence this identifies systematic errors and distortions of the XAFS spectrum, which will affect strong peaks in the oscillations more than minima.

Hence, while both extreme limits are used in conventional analysis of fluorescence XAFS, in this case and many others the limiting forms are unrealistic or infeasible, and one should use the full analytic form we have presented. Therefore, in what follows, we use our original equations (4) and (5).

A single horizontal strip of detector pixel outputs is given in Fig. 9, showing the variance observed earlier. The fits of this single strip of channels in the horizontal plane are given in Fig. 10. This is the result from five channels (1, 7, 13, 19, 25). The dispersion is dramatically reduced, thereby proving the accuracy of the model. By also including the vertical angle, we can fit all 34 channels with just two parameters: θ_0 is approximately half a channel width and $L \simeq 50$ mm, and yielding Fig. 11 as the resulting final average of the corrected scans, with much reduced standard error. This analysis has dramatically increased the information content with which to use XAFS analysis to investigate the staggered *versus* eclipsed structures of ferrocene, for example. There is some residual dispersion (of course); part of this will remain intrinsic, and

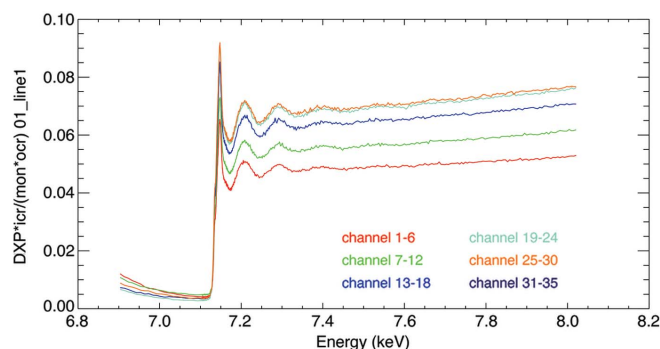


Figure 9
Spectra obtained from a single horizontal line of detector channels.

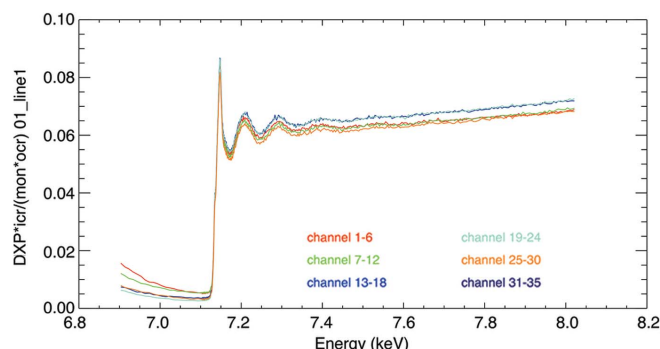


Figure 10
A fitted set of the spectra correcting for self-absorption for a single strip of horizontally arranged detector channels shown in Fig. 9.

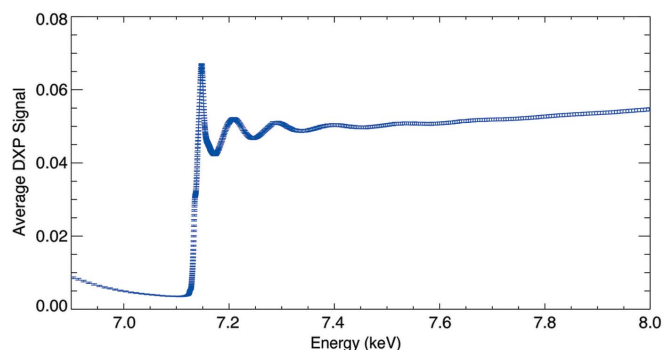


Figure 11

The average signal for the self-absorption fitted spectra with uncertainty. The standard error of the detector channels of the fitted plot is dramatically reduced, and information content of the data is enhanced to possibly define a discriminant for the puzzle of the staggered or eclipsed conformations of ferrocene.

part may be due to normalization error, pixel response function, dark count correction, efficiency corrections, roughness or non-uniformity. Either way, this final set of standard errors represents explicitly the information content of each measurement.

The job of processing I_0/I for XAFS analysis is a little complex. For absorption measurements, analysis will naturally take the logarithm, while for fluorescence data, under some limits, analysis would extract the information from the ratio directly. Then, a background function, perhaps ideally an atomic or free-atom function, is subtracted and the spectrum above the cut-off energy E_0 is transformed into χ versus k plots. Conversely, other theoretical approaches will plot directly against theory in (μ/ρ) versus E space, still with a fitting parameter for a starting edge position E_0 . Rather than getting embroiled in these details, the standard route for extracting χ from the XAFS spectra will be adopted.

However, the background subtraction algorithm used is the standard *IFEFFIT* spline approach rather than an atomic baseline subtraction; the approach used can certainly distort the XAFS oscillations and features, especially at the far ranges of the dataset. In this case there is distortion at high k ($14.5 < k < 15.0 \text{ \AA}^{-1}$, i.e. at the end of the dataset) but the conclusions are robust whether this range is included or excluded from the modelling. Additionally, it is well known that error in the offset energy dramatically distorts χ at low- k (Glover & Chantler, 2007), and is addressed below; but this is separate from the distortion introduced by poor background subtraction, though they can both have a great effect at low k . It is simplest to comment that the low- k background subtraction errors in this analysis are effectively removed by the low- k cut-off to the fitting range, and that low- k errors in structural details are not addressed by the raising or lowering of the heights of particular oscillations.

7. XAFS analytical procedures

The theoretical difference signatures between D_{5d} and D_{5h} conformations, illustrated in Fig. 12, are moderately large up

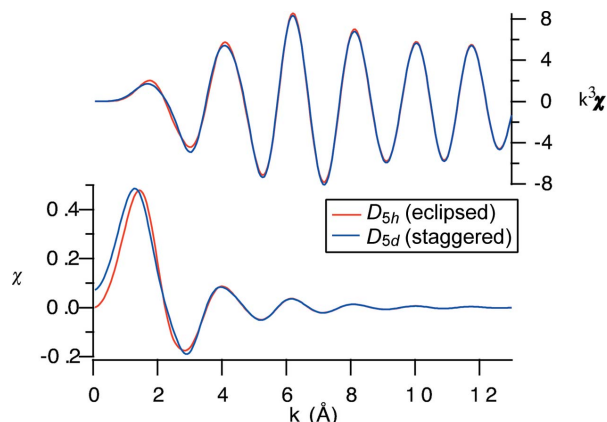


Figure 12

$k^3\chi$ versus k plots for ferrocene in staggered (blue) and eclipsed (red) conformations (theory, *FEFF*) (right-handed axis, top plots); and plots of χ versus k showing differences up to 10% in χ (lower plots, left-hand axes). These differences are very difficult to measure in standard XAFS analysis.

to a k of about $4 \text{ \AA}^{-1}$ but remain observable up to a k of 8 or $12 \text{ \AA}^{-1}$ (with a magnitude of 0.01 and rapidly decreasing). These differences are very difficult to measure in standard XAFS analysis because uncertainties are not propagated and correlation amongst fitting parameters are often large. It is also well known that *FEFF* (especially early versions, and other muffin-tin theoretical approaches) has great difficulty in experimental modelling at low k , which is one of the key reasons for standard analysis to use both a window function (i.e. to fit over a restricted k -range) and a k^2 or k^3 weighting. Some recent theoretical developments are improving the modelling of low- k , including *FEFF* and *FDM* approaches, but for consistency these are not the subject of the current discussion, and instead current versions for *XFIT* and standard versions for *IFEFFIT* are compared on a common footing.

We have investigated three approaches to modelling the experimental χ versus k spectrum: (i) *XFIT* using the corrected averaged plot but no propagation of uncertainty; that is, having uniform error bars throughout k , or uniform error bars for data weighted by k^2 or k^3 ; (ii) *IFEFFIT* using the corrected averaged plot but no propagation of uncertainty; (iii) an *IFEFFIT*-like approach developed by our group (Smale *et al.*, 2006; Glover *et al.*, 2010) but incorporating, propagating and fitting the derived error bars as explicit in Fig. 11.

The *IFEFFIT*-like approach follows a traditional least-squares fitting procedure of $\chi(k)$, but with uncertainties in $\chi(k)$ at each k -point provided by the propagation of experimental uncertainty derived from the experimental variance and in principle from any systematic uncertainties, point-by-point. Hence any fitting of $\chi(k)$ versus k , or $k^2\chi(k)$ versus k , or $k^3\chi(k)$ versus k , for example, will return uncertainties in fitted parameters given by the least-squares method but with accurate amplitudes based upon the standard errors of the source data.

At least in the standard implementation of *XFIT*, the fit appears to follow an R -factor minimization rather than a least-

squares technique or a χ^2 minimization. *IFEFFIT* follows a conventional unweighted χ^2 minimization. The *IFEFFIT*-like routine follows an explicitly weighted χ^2 minimization. It is also known that χ^2 values output by *IFEFFIT* (or *XFIT*) are not reliable measures of goodness-of-fit. Hence, general advice is to consider the relative χ_r^2 of disparate models and to determine the best fit from the smallest value. We can use this approach in all three methods.

8. XAFS results: the conformation of ferrocene

We now focus on the question of the stereochemistry of ferrocene molecules. Clearly, the results depend upon k -range. We have investigated $0 < k < 15$, $1 < k < 15$, $2 < k < 15$, $3.2 < k < 15$, $3.6 < k < 14.5$, and other ranges (k is implicitly and always given in units of $\text{\AA}^{-1}$ as standard throughout the rest of this paper). In a range of detailed investigations we have completed a first fit, recomputed *FEFF* paths with the new spacing, completed a second fit, recomputed the *FEFF* paths with the new atom sites, and fitted for the translation of the cyclopentadienyl ring above the iron atom along the fivefold axis. The relative χ^2 values obtained remained robust in these later cycles of refinement. That is, they generally improved by small amounts or were stable to within uncertainty. We emphasize that each comparison between fitting packages was made using exactly the same k -range, k -weighting, model and constraints.

FEFF involves computation of independent photoelectron wave paths up to some maximum pathlength $r_{\max}$. We investigated the modelling for $r_{\max} = 4, 5, 6 \text{ \AA}$. In general, consistent (robust) conclusions were obtained for the choice of conformation within these series; but χ_r^2 was clearly improved with $r_{\max} = 5 \text{ \AA}$ compared with $r_{\max} = 4 \text{ \AA}$. We view this as an endorsement at this level of the *FEFF* code, and an endorsement of the significance of outer paths in the molecular system, even though the individual amplitudes are fairly weak. Hence further discussion will correspond to the $r_{\max} = 5 \text{ \AA}$ option only.

XFIT analysis returned claimed χ_r^2 values typically around 4.3, 0.078, 0.005 and 0.0003. Despite the unphysical χ_r^2 values, all modelling (different k ranges and other variations) suggested that the ‘eclipsed’ conformation represented the better fit. Surprisingly, the relative χ_r^2 values were typically a factor of 2.5 or 8 lower for the eclipsed model than for the staggered model, despite the theoretical *FEFF* differences being really quite small and the number of degrees of freedom being identical. Irrespective of the cause of this, we must be aware that the lack of error bar propagation will question this conclusion.

IFEFFIT analysis returned claimed χ_r^2 values typically around 530, 105, 45, heavily dependent upon the choice of k -weighting, as expected. Generally, the conventional implementation without propagation of errors for the individual measurements, with variable windowed k -range, suggested that the staggered conformation represented the correct structure. Equally surprisingly, the significance of the result appeared generally highly conclusive, with the staggered

conformation yielding a χ_r^2 a factor of three or two better than that for the eclipsed conformation. However, there were exceptions, including using k^0 -weighting or the $0 < k < 15$ range. Most analysts would conclude that this is normal and expected, and that neither k^0 -weighting nor using $0 < k < 15$ yields a robust or reliable result for *FEFF*. Analysis of XAFS normally assumes a weighting of k^2 or k^3 and a lower window cut-off of approximately $k = 3$ precisely because the user is investigating the higher oscillation periodicity and because the theoretical formalism is designed for this range, and not for the low- k range. The evidence of our analysis supports the conventional need for a window or k -range when modelling XAFS, and a lower cut-off of order $k = 3$ (and in the case of *IFEFFIT* and *XFIT* that k^2 or k^3 weighting should be used), since we observe that the fitting parameters tend to become unreliable; the residuals remain large, especially in the high- k range, S_0^2 tends to drop to 0.7, for example, and occasionally σ^2 , the thermal parameter, becomes negative. With this caveat, then the conclusion from *IFEFFIT* on this moderately accurate dataset would be conclusively in favour of the staggered conformation.

The key point here is that different fitting methods can yield dramatically different conclusions under these circumstances, especially when the experimental uncertainty is not propagated, and when an individual χ_r^2 output cannot be directly investigated but can only be compared in a relative manner.

Our new *IFEFFIT*-like analysis propagates the experimental uncertainties, though as mentioned above can explicitly distort them to mimic the k^n weighting approaches. In general, these k^2 and k^3 weighting options emphasize the high- k oscillations of XAFS at the expense of the natural error bars and the first one or two oscillations. Once again, a robust conclusion was obtained. χ_r^2 values only have proper meaning for the k^0 -weighting option, *i.e.* where the uncertainties are explicitly propagated without distortion. In this case we find naturally that χ_r^2 is smaller when a smaller k -range is fitted, and values vary typically from $\chi_r^2 = 4$ ($0 < k < 15$, $r_{\max} = 4$) to $\chi_r^2 = 1.7$ ($0 < k < 15$, $r_{\max} = 5$) or $\chi_r^2 = 2.1$ ($1 < k < 15$, $r_{\max} = 4$) to $\chi_r^2 = 1.02$ ($1 < k < 15$, $r_{\max} = 5$), or χ_r^2 values of 0.4 (for $2 < k < 15$, $r_{\max} = 5$). A dramatic success of our approach to report is that we have achieved χ_r^2 values of order unity.

However, these k ranges are not particularly robust nor reliable. The pattern of XAFS oscillations is poorly followed and the discrepancies at low k must force us to question the reliability of the fit and the *FEFF* theory to cover this range. In some cases, S_0^2 dropped to below 0.7, and σ^2 became negative. Hence, while the formalism fitted the model, it could hardly be claimed that the parameters retained their original meaning. *IFEFFIT* and similar programs permit constraints and restraints. It is generally reasonable to require $0.85 < S_0^2 < 1.1$ and $\sigma^2 > 0$. When this is not observed in a free fit, it can simply mean that the parameters are not independent but are correlated, and hence ill-defined as specific physical values.

Inspection of the residuals, or the experiment and fitted profiles themselves, shows that the theoretical (fitted) location of the first peak at $k \simeq 1.5$ is far from the experimental value of $k \simeq 1.8$; similarly, a pronounced asymmetry on the low- k side

of the second extrema (trough) at $k \simeq 3$ is quite poorly modelled in all fits. This is a strong justification for focusing on the k -range where the model function appears to match the experimental data and yield a reliable result. Additionally, the experimental range for $14.5 < k < 15.0$, the last part of the experimental data, appears distorted, quite possibly by the (standard) background-subtraction algorithm. Hence, the range of reliable data where by-eye agreement between experiment and fitted theory is obtained suggests a useful maximal fitting range of $3.6 < k < 14.5$ for this dataset. Explicit uncertainties computed above $k = 14.5$ also argue for this upper limit.

None of these uncertainty-propagating *IFEFFIT*-like analyses produce factors of two or eight in relative χ_r^2 between the fits of the different conformations. This is another strong endorsement of the procedure. In general, the preferred model has an absolute χ_r^2 (on this basis) reduced by approximately 10–15% compared with the less optimized model. This fit does not attempt to model $0 < k < 3.6$, but the qualitative structure in this region is clearly not modelled by the fit or theory. In observing the basic theoretical differences illustrated by Fig. 12, the differences in relative χ^2 seem much more reasonable, or even remarkable given the small signatures of difference and the relatively constrained k -range. Such a discrepancy is in principle sufficient to draw a conclusion, though such a conclusion would be fraught if uncertainties were not propagated, as we have just discussed.

Narrower k ranges yielded $\chi_r^2 = 0.09$ (for $3.6 < k < 14.5$, $r_{\max} = 5$). This suggests that our derived experimental uncertainties are modest overestimates by an average factor of perhaps three. While the determination of individual point uncertainty in this approach was independent, there was clearly some correlated uncertainty (between channels and points in k) which would lead to overestimated input standard errors, and hence one might expect χ_r^2 values somewhat less than unity when the theoretical model is valid. This is indeed what is observed. Future work will seek to improve the determination of fluorescence and other experimental uncertainty to yield an optimum dataset for analysis.

The final results are plotted in Figs 13–17. Table 1 presents the parameters fitted and their uncertainties for the optimized model discussed. Both χ versus k and $k^2\chi$ are presented to permit comparison with typical standard fits, and to allow the central region of XAFS oscillations to be inspected more clearly.

For $3.6 < k < 14.5$, $r_{\max} = 5$, the eclipsed conformation provides an improved fit by 11% compared with the staggered model, with no constraints or restraints. The deviation above $k = 14.5$ (not fitted in this or any model) is most likely due to the standard background subtraction being inadequate near the maximum of the dataset. When the weighting is distorted by k^2 or k^3 weighting, the same result is obtained, with typically 3% discrepancy. Interestingly, the same conclusion regarding conformation is obtained for the $2 < k < 14.5$, $r_{\max} = 5$, range, although a constraint of S_0^2 is needed to prevent the physical parameter from becoming less meaningful. The

Table 1
Fitted parameters for the minimum χ_r^2 models for each conformer.

	Conformation	
	Eclipsed	Staggered
Fitted parameters		
χ_r^2	0.089	0.099
ΔE_0 offset (eV)	-1.72 ± 0.94	-2.21 ± 1.04
$1 + \alpha$ scaling of lattice	1.0036 ± 0.0037	1.0021 ± 0.0041
σ^2 thermal parameter	0.0049 ± 0.0013	0.0048 ± 0.0014
S_0^2 amplitude reduction	1.069 ± 0.086	1.063 ± 0.093
Fixed values (Å)		
Fe(x, y, z)	0, 0, 0	0, 0, 0
C1(x, y, z)	1.6555, 1.2007, 0.0000	1.6555, 1.2007, 0.0000
C2(x, y, z)	−1.6555, 1.2007, 0.0000	−1.6555, −1.2007, 0.0000
C3(x, y, z)	1.6555, −0.9714, 0.7058	−1.6555, 0.9714, 0.7058
C4(x, y, z)	−1.6555, −0.9714, 0.7058	1.6555, −0.9714, 0.7058
C5(x, y, z)	1.6555, −0.9714, −0.7058	−1.6555, 0.9714, −0.7058
C6(x, y, z)	−1.6555, −0.9714, −0.7058	1.6555, −0.9714, −0.7058
C7(x, y, z)	1.6555, 0.3710, 1.1420	1.6555, 0.3710, 1.1420
C8(x, y, z)	−1.6555, 0.3710, 1.1420	−1.6555, −0.3710, 1.1420
C9(x, y, z)	1.6555, 0.3710, −1.1420	1.6555, 0.3710, −1.1420
C10(x, y, z)	−1.6555, 0.3710, −1.1420	−1.6555, −0.3710, −1.1420
Derived parameters including α scale uncertainty (Å)		
Fe—C ₅ †	1.6555 (1.0036 $\pm$ 0.0037)	1.6555 (1.0021 $\pm$ 0.0041)
Fe—C1	2.045 (1.0036 $\pm$ 0.0037)	2.045 (1.0021 $\pm$ 0.0041)
C—C	1.4116 (1.0036 $\pm$ 0.0037)	1.4116 (1.0021 $\pm$ 0.0041)
Fe—C ₅	1.6615 $\pm$ 0.0061	1.6590 $\pm$ 0.0069
Fe—C1	2.0524 $\pm$ 0.0076	2.0493 $\pm$ 0.0084
C—C	1.4167 $\pm$ 0.0052	1.4146 $\pm$ 0.0058

† C₅ is the centroid of the C₅ ring.

preference of conformation does not depend upon this constraint, but the meaning of the parameters does.

The figures emphasize the difficulty of drawing conclusions on XAFS interpretation by eye, or by any χ^2 measure which does not represent the information content of the dataset, *i.e.* the experimental uncertainties. The standard plots are represented by Figs 14 and 16 but these do not show the significance of the reduction in χ_r^2 owing to the improved fitting of the

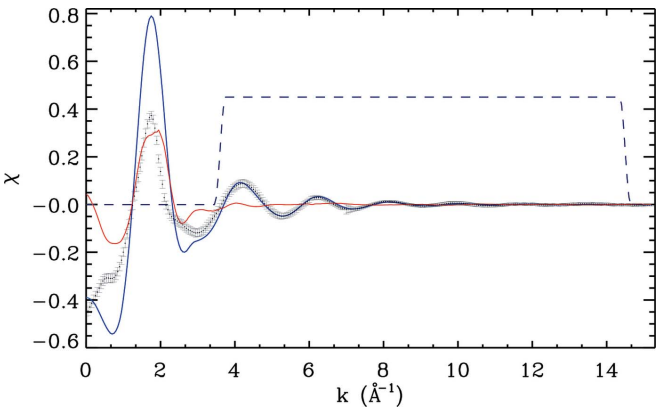


Figure 13
Fitted χ versus k plots for ferrocene in staggered conformation are shown. Blue line: theory, *FEFF*. The window function for $3.6 < k < 14.5$ is shown by the dashed line. Diamonds: experiment with propagated uncertainty as standard error (error bars). Red line: residual light. Discrepancies in the medium and high k region are not visible.

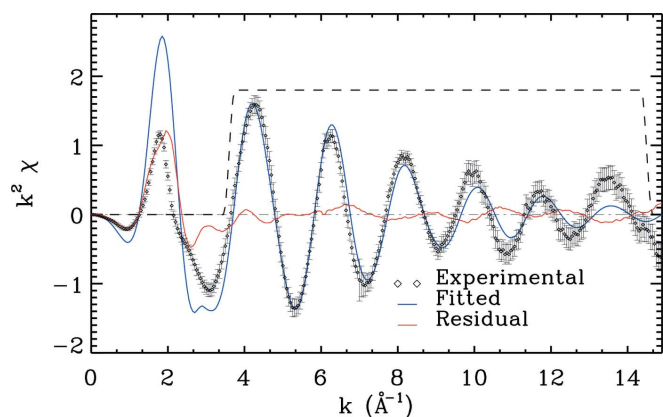


Figure 14
Fitted $k^2\chi$ versus k plots for ferrocene in staggered conformation. Legend as per Fig. 13. The uncertainties at higher k define the information content of the dataset. While the periodicity and general fit is very good, amplitude and attenuation discrepancies are visible.

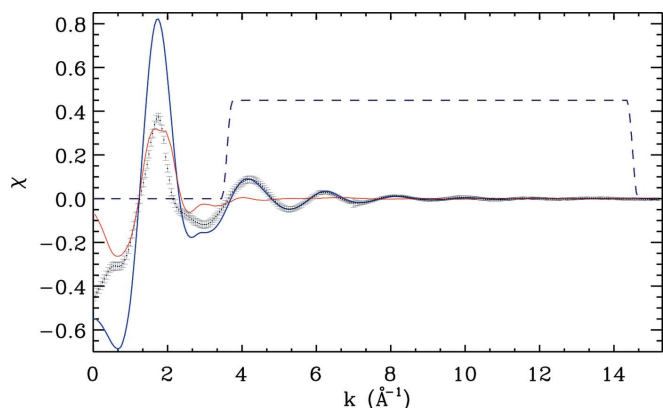


Figure 15
Fitted χ versus k plots for ferrocene in eclipsed conformation are shown. Blue line: theory, *FEFF*. The window function for $3.6 < k < 14.5$ is shown by the dashed line. Diamonds: experiment with propagated uncertainty as standard error (error bars). Red line: residual light. By eye, improvements of 11% in χ_r^2 are not visible.

features at $k \simeq 4.3$ and $k \simeq 5.3$. The differences are subtle, but become visible in the residual Fig. 17. The disorder observed at room temperature for crystalline ferrocene is interestingly not apparent in these plots; that is, the information content does not appear blurred beyond a plausible thermal parameter. The residuals display strong deviation at low k , which is the cause for the standard low- k cut-off, and which we would argue is due to the theory presented needing improvement in the future. Within the range of k fitted in any of the schemes, there is a common pattern of residual or ‘mis-fit’ apparent in Fig. 17. The shared oscillation of both conformers with k seems significantly larger than the difference between them (11%). It would be helpful to better understand the remaining residual. Since the residual has an oscillatory component, it would be interesting to test whether this might be due to multiple scattering, or a longer distance, perhaps to the solvent ion. Fourier transforms of the fits are not presented here for two reasons: one is the difficulty of interpreting, by eye, fits without error propagation (notoriously difficult for Fourier transforms, as known from crystallography) and the dangers of

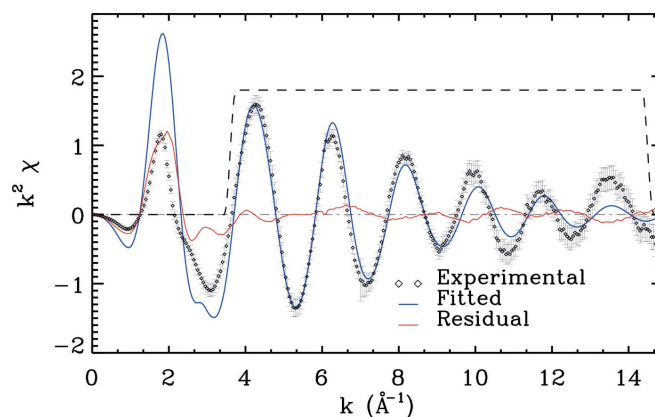


Figure 16
Fitted $k^2\chi$ versus k plots for ferrocene in eclipsed conformation. Legend as per Fig. 15. Here the uncertainties at higher k give the information content of the dataset. While the periodicity and general fit is very good, amplitude and attenuation discrepancies remain visible.

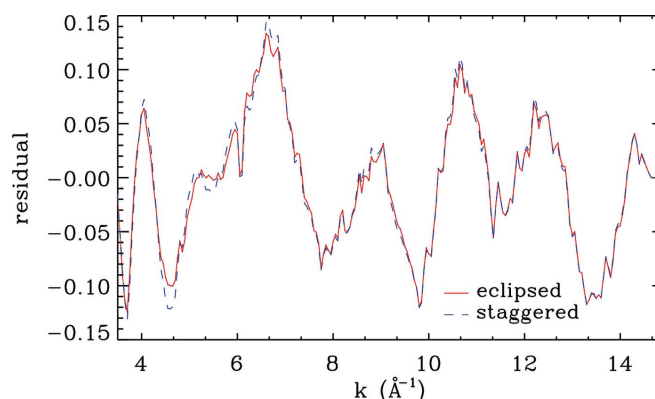


Figure 17
Residual plots for the eclipsed (red line) versus staggered (dashed line) conformations. The dominant signature, as theoretically expected, lies in the lower k range, and repeatedly suggests the eclipsed conformation as a better representation of the data compared with the staggered conformation. This is in agreement with the broad brushstroke of crystallographic determinations.

inconsistent transforms especially due to E_0 or k offsets of the origin; and secondly because the *raison d'être* of this manuscript has been the introduction of error propagation in the analysis of fluorescence spectra using the conventional approaches of *XFIT* and *IFEFFIT*. However, we can confirm that Fourier transform analysis, combined with judicious filtering, can demonstrate that much of the structure of the residual between experiment and either modelling appears in unphysical low- R space far from any bonding region.

In principle, Table 1 permits conclusions to be drawn about bond distances, thermal parameters, amplitude reduction coefficients and energy offsets, as summarized in Table 2. We note that we have made modest investigation of additional parameter modelling (*e.g.* by adding a lateral expansion of the C_5 -rings) and that this yielded no significant reduction of χ_r^2 . The simplest statement of the final analysis is that the structure is converged and that remaining variation in α (scale of molecular structure) and S_0^2 (scale of backscattering/oscillation amplitude) are consistent with no change within uncertainty;

Table 2

Comparison of experimental bond lengths (Å) and theoretical predictions.

Bond	XAFS eclipsed <i>T</i> 10 K	e-scattering†	Neutron‡ 173 K	X-ray diffraction§ 98 K	XRD¶ 101 K	XRD†† 173 K	MP2‡‡	CCSD/T‡‡	This study§§ Theory
Lattice	–			Orthorhombic	Triclinic	Monoclinic			
Fe–C1	2.0524 ± 0.0076	2.064 ± 0.003	± 0.003–0.005	2.056, 2.059 ± 0.005	2.046, 2.052 ± 0.007	2.033–	1.910	2.056	2.065
Range		–	[2.005–2.050]	[2.051–2.062]	[2.041–2.052]	[2.017–2.048]			
C–C	1.4167 ± 0.0052	1.440 ± 0.002	± 0.005–0.009	1.429, 1.431 ± 0.006	1.426, 1.433 ± 0.007	1.395–	1.441	1.433	1.428
Range		–	[1.349–1.468]	[1.421–1.437]	[1.423–1.429]	[1.346–1.441]			
Fe–C ₅	1.6615 ± 0.0061	1.660 ± 0.003	–	1.658 ± 0.006	1.646 ± 0.007	1.651–	1.464	1.655	1.670

† Haaland & Nilsson (1968). ‡ Takusagawa & Koetzle (1979). § Seiler & Dunitz (1982). ¶ Seiler & Dunitz (1979b). †† Seiler & Dunitz (1979a). ‡‡ Coriani *et al.* (2006). §§ B3LYP/m6-31G model.

that there is a reasonable thermal parameter reflecting actual ellipsoids or structural disorder; and that the δE_0 offset is weakly determined; however, these will be explored in a later investigation.

At this point, although intriguing, the fitting uncertainties speak for themselves. While the fitting uncertainties are quite competitive with techniques of electron scattering, neutron diffraction and X-ray crystallography, we must remind ourselves that each is asking a different question of a different sample. The relative consistency in this sense is then remarkable.

Past analyses of XAFS data from ferrocene (Vedrinskii *et al.*, 1991; Shuvayev *et al.*, 1985) noted the importance of the spherical wave approach and the muffin-tin potentials (both used in this analysis) but showed no sensitivity to conformation. They claimed that discrepancies in the residuals were due to multiple-scattering processes discussed by Ruiz-Lopez *et al.* (1988), but noted significant discrepancy from analytical models of two other groups (Teo & Lee, 1979; McKale *et al.*, 1988). Perhaps the most detailed analysis of the XAFS of ferrocene was completed in 1988 (Ruiz-Lopez *et al.*, 1988), with an extensive discussion of the development of theoretical calculations and XAFS data extending to $k = 16.5 \text{ \AA}^{-1}$ compared with our $k = 15.5 \text{ \AA}^{-1}$ and an earlier $k = 12 \text{ \AA}^{-1}$ (Cramer *et al.*, 1976). They noted that no useful comparison could be made with the earlier dataset owing to this range over k -space. Perhaps a more poignant reason is that the early work (Cramer *et al.*, 1976) used analytic methods appropriate for the time but which would, even in 1988, have been regarded as superceded. We note that their Fig. 5 displays significant oscillations in the Fourier transform which appear more as artefacts than as bonding orbitals.

The 1988 study (Ruiz-Lopez *et al.*, 1988) concluded that double and triple scattering paths were explicitly necessary and observed in the structure; however, they did not observe any differences between the conformations which would for example have been revealed by double scattering paths, as has been done in this study. Further, full XANES analysis on the conformers was found to yield a null result; that is, there was no distinction between conformers. This conclusion may be attributed to the short range of XANES investigated, but it lies in conflict with our theoretical results for the XAFS structure. One of the difficulties of comparison of this analysis lies in their predominant use of the Fourier transform (R -

space) presentation and fitting, with filtering or otherwise, which of course can be quite sensitive to the origin for the transform. Additionally, a recent paper (Schnitzler *et al.*, 2006) discusses ferrocene XAFS and presents near-edge XANES, and a Fourier transform thereof, but without further analysis nor discussion.

The bond lengths Fe–C and C–C, as well as the distance between Fe and the centre of cyclopentadienyl (C_5H_5) rings, Fe–C₅ in the eclipsed ferrocene (D_{5h}) listed in Table 2, agree well between the experiments and available theory. For example, our experimental Fe–C bond length is given by $2.0524 \pm 0.0076 \text{ \AA}$ ($T = 10 \text{ K}$), which is in an excellent agreement with $2.064 \pm 0.003 \text{ \AA}$ of Haaland & Nilsson (1968) using electron scattering techniques, 2.056 or $2.059 \pm 0.005 \text{ \AA}$ ($T = 98 \text{ K}$) in an orthorhombic symmetry (Seiler & Dunitz, 1982) and 2.046 or $2.052 \pm 0.007 \text{ \AA}$ ($T = 101 \text{ K}$) in a triclinic symmetry (Seiler & Dunitz, 1979b), together with other earlier X-ray determinations such as the presumed monoclinic determination at $2.033 \text{ \AA}$ ($T = 173 \text{ K}$) (Seiler & Dunitz, 1979a). The three results from the same research group suggest that the Fe–C bond slightly decreases as the temperature increases.

We have computed potentials and bond lengths within the density functional theory (DFT) based B3LYP/m6-31G(d) formalism (Mitin *et al.*, 2003). Given that the measured Fe–C bond length varies from $2.005 \text{ \AA}$ to $2.064 \text{ \AA}$, the present theoretical value of $2.065 \text{ \AA}$ using the DFT-based B3LYP/m6-31G(d) is well within the experimental range and uncertainties. In addition, this Fe–C bond length is significantly longer than the Fe–C length of diatomic iron carbide $FeC(X^3\Delta)$ at $1.581 \text{ \AA}$ calculated by recent multi-reference variational *ab initio* models (Tzeli & Mavridis, 2010). The measured C–C bond length of ferrocene is in the range 1.395 – $1.440 \text{ \AA}$ as given in Table 2. The present measurement gives this bond length as $1.4167 \text{ \AA}$, which is supported by our DFT-based theory of $1.428 \text{ \AA}$. The weighted mean C–C bond length for cyclopentane is given by $1.483 \pm 0.009 \text{ \AA}$ (Song *et al.*, 2004). The results for the C–C bond length of ferrocene indicate that the cyclopentane rings in ferrocene exhibit character between C–C and C=C bonding, leaning more towards the C=C side than cyclopentane. Finally, the distance between Fe and the centre of the pentagonal carbon ring is given by $1.6615 \text{ \AA}$ from the present measurement, which agrees well with $1.670 \text{ \AA}$ from our theoretical calculations. Of the three available

quantum mechanical models, that is, MP2, CCSD(T) and DFT-B3LYP, the present DFT model can provide excellent results with respect to accuracy and computational costs.

Neutron diffraction and X-ray crystallographic determinations are of a crystal lattice, with different determined space groups in different phases at different temperatures; however, the input standard deviations show that the technique of fluorescence XAFS can be competitive even for biometallic systems, if and only if the intrinsic experimental uncertainties are propagated. Additionally, the method of XAFS deliberately measures dynamic (and static) bond lengths, rather than differences of mean lattice parameters. The implications of this investigation particularly include an understanding of the strength of π bonding (multi-centre bonding) in organometallics; and key implications about crystallographic past determinations and space groups. There are numerous other implications of a biochemical nature, but we will address these in further investigations.

Can this conclusion regarding conformation be dominated by systematic uncertainties or random noise in the dataset of individual point errors, or incomplete convergence or the inadequacy of the full model used? Yes, of course. We have shown that a very small signature which is really quite important can be investigated and a tentative conclusion can be made on the basis of critical error analysis, self-absorption correction, uncertainty propagation, and a meticulous investigation of standard XAFS fitting. The conclusion has withstood this analysis, and yet the future must be much brighter still.

Theory has much to say on the crystallographic determinations and on the ferrocene solution modelling. According to accurate quantum mechanical calculations (Coriani *et al.*, 2006) as well as the present theoretical calculation using DFT models (Xu *et al.*, 2003), the staggered conformation appears not to be the energetically most stable form. However, this molecular (DFT) simulation may or may not include crystal packing energies and the requirements of particular space groups. Of course, if a crystal is formed in, for example, orthorhombic symmetry, there will be requirements which may constrain the lattice to be, for example, perfectly staggered or eclipsed. However, in solution there may be significant potential contributed by the surrounding solvent molecules which are certainly not modelled in the current XAFS investigation, and are certainly not present in the crystallographic analyses. In other words, the current best evidence for the conformation of ferrocene in solution is provided by the data of this paper.

The energy difference between the staggered and eclipsed structures is very small, approximately 2 kJ mol^{-1} based on the present DFT-based B3LYP/m6-31G calculations, or $\sim 4 \text{ kJ mol}^{-1}$ (Haaland & Nilsson, 1968; Haaland, 1979). This energy is strongly dependent on the model employed and ranges from 0.42 kJ mol^{-1} using HF to 4.8 kJ mol^{-1} using CCSD(T) (Coriani *et al.*, 2006). The present DFT-based models give 3.2 kJ mol^{-1} using the PBE0/6-31++G(d,p) model and 2.4 kJ mol^{-1} using the B3LYP/m6-31G(d) model. Despite quite different ΔE values between the ferrocene conformers

obtained from various quantum mechanical models, the eclipsed (D_{5h}) conformer is consistently found to be energetically more stable than the staggered (D_{5d}) conformer. At room temperature (300 K), if the energy difference between D_{5d} and D_{5h} is given by an experimental value of 3.8 kJ mol^{-1} , the ratio of D_{5d} and D_{5h} may be approximately 1:5. If this energy difference is 0.42 kJ mol^{-1} as obtained using the HF model, the ratio will become almost 1:1. In either case the thermal ellipsoids would be quite dominant. These questions cannot be explored with the current dataset in isolation. However, this is a ripe area for future research.

9. Conclusions

Fluorescence data and absorption data can be collected to provide independent uncertainty estimates for the whole range of XAFS. This approach will automatically produce weights which can and should be used in XAFS or XANES analysis. The theoretical model of the fluorescence signal will not normally follow the ideal limits. Accurate and valuable data can be obtained from XAFS investigations on concentrated, crystalline or dilute systems, including for standards such as, in this case, ferrocene, and explicitly including disordered systems. Subtle questions which previously could not be contemplated using XAFS or fluorescence detection can certainly be investigated, especially including subtle conformation alternatives in dilute non-crystalline systems. Reflecting upon the divergence of apparent conclusion from different methods without error propagation and hence without a statistically valid χ_r^2 test of significance or information content, there is an urgent need to propagate experimental errors and determine accurate fitted χ_r^2 to confirm the significance of observations. Noting the subtle distinction between the conformers of ferrocene, we are looking towards incisive theoretical analysis of XANES data, as this may be insightful. Ideally the two should complement one another.

Further work will investigate alternative and advanced theoretical approaches to this type of problem, especially including agreement over a more extended range of k . Further work will also investigate more optimized fluorescence data collection, and improved datasets. However, this work has observed the signature of conformation changes in dilute disordered ferrocene solution, in the central XAFS region, and has observed that for this particular system the eclipsed D_{5h} conformation is indicated by the data and the theory modelled. Parameters have been derived with uncertainties which are competitive, and with parameters which are loosely consistent with low-temperature crystallographic determinations of pure ferrocene phases. Latest theory in particular supports the bond lengths, more so than earlier theory or experimental data.

This work was supported by the Australian Synchrotron Research Program which is funded by the Commonwealth of Australia under the Major National Research Facilities Program and by a number of grants of the Australia Research Council. We are grateful for the assistance of Dr Mun-Hon

Cheah at the Australian National Beamline Facility, at beamline 20B of the Photon Factory in Tsukuba, Japan. NM and FW acknowledge Victoria Partnership for Advanced Computing for their supercomputing support.

References

- Barnea, Z., Chantler, C. T., Glover, J. L., Grigg, M. W., Islam, M. T., de Jonge, M. D., Rae, N. A. & Tran, C. Q. (2011). *J. Appl. Cryst.* **44**, 281–286.
- Bunker, G. (2010). *Introduction to XAFS: A Practical Guide to X-ray Absorption Fine Structure Spectroscopy*, pp. 92–95. Cambridge University Press.
- Chantler, C. T. (2009). *Eur. Phys. J. ST*, **169**, 147–153.
- Chantler, C. T. (2010). *Radiat. Phys. Chem.* **79**, 117–123.
- Coriani, S., Haaland, A., Helgaker, T. & Jorgensen, P. (2006). *Chem. Phys. Chem.* **7**, 245–249.
- Cramer, S. P., Eccles, T. K., Kutzler, F., Hodgson, K. O. & Donaich, S. (1976). *J. Am. Chem. Soc.* **98**, 8059–8069.
- Ellis, P. J. & Freeman, H. C. (1995a). *XFIT*, <http://www.esrf.eu/computing/scientific/exafs/xfit.html>.
- Ellis, P. J. & Freeman, H. C. (1995b). *J. Synchrotron Rad.* **2**, 190–195.
- Fischer, E. & Wilkinson, G. (1993). In *Nobel Lectures, Chemistry 1971–1980*, edited by S. Forsen. Singapore: World Scientific.
- Glover, J. L. & Chantler, C. T. (2007). *Meas. Sci. Tech.* **18**, 2916–2920.
- Glover, J. L., Chantler, C. T., Barnea, Z., Rae, N. A. & Tran, C. Q. (2010). *J. Phys. B*, **43**, 085001.
- Glover, J. L., Chantler, C. T., Barnea, Z., Rae, N. A., Tran, C. Q., Creagh, D. C., Paterson, D. & Dhal, B. B. (2008). *Phys. Rev. A*, **78**, 052902.
- Glover, J. L., Chantler, C. T. & de Jonge, M. D. (2009). *Phys. Lett. A*, **373**, 1177–1180.
- Haaland, A. (1979). *Acc. Chem. Res.* **12**, 415–422.
- Haaland, A. & Nilsson, J. (1968). *Acta Chem. Scand.* **104**, 2653–2670.
- Hardgrove, G. L. & Templeton, D. H. (1959). *Acta Cryst.* **12**, 28–32.
- Islam, M. T., Rae, N. A., Glover, J. L., Barnea, Z., de Jonge, M. D., Tran, C. Q., Wang, J. & Chantler, C. T. (2010). *Phys. Rev. A*, **81**, 022903.
- Jonge, M. D. de, Barnea, Z. & Chantler, C. T. (2004a). *Phys. Rev. A*, **69**, 022717.
- Jonge, M. D. de, Barnea, Z., Tran, C. Q. & Chantler, C. T. (2004b). *Meas. Sci. Technol.* **15**, 1811–1822.
- Jonge, M. D. de, Tran, C. Q., Chantler, C. T., Barnea, Z., Dhal, B. B., Cookson, D. J., Lee, W.-K. & Mashayekhi, A. (2005). *Phys. Rev. A*, **71**, 032702.
- Jonge, M. D. de, Tran, C. Q., Chantler, C. T., Barnea, Z., Dhal, B. B., Paterson, D., Kanter, E. P., Southworth, S. H., Young, L., Beno, M. A., Linton, J. A. & Jennings, G. (2007). *Phys. Rev. A*, **75**, 032702.
- Kealy, T. & Pauson, P. (1951). *Nature (London)*, **168**, 1039–1040.
- McKale, A. G., Veal, B. W., Paulikas, A. P., Chan, S.-K. & Knapp, G. S. (1988). *J. Am. Chem. Soc.* **110**, 3763–3768.
- Miller, S., Tebbboth, J. & Tremaine, J. F. (1952). *J. Chem. Soc.* pp. 632–635.
- Mitin, A. V., Baker, J. & Pulay, P. (2003). *J. Chem. Phys.* **118**, 7775–7783.
- Newville, M. (2001). *J. Synchrotron Rad.* **8**, 322–324.
- Newville, M. (2004). *Fundamentals of XAFS*, pp. 23–24. Chicago: CARS, University of Chicago.
- Rae, N. A., Chantler, C. T., Barnea, Z., de Jonge, M. D., Tran, C. Q. & Hester, J. R. (2010a). *Phys. Rev. A*, **81**, 022904.
- Rae, N. A., Islam, M. T., Chantler, C. T. & de Jonge, M. D. (2010b). *Nucl. Instrum. Methods Phys. Res. A*, **619**, 147–149.
- Rehr, J., de Leon, J. M., Zabinsky, S. I. & Albers, R. C. (1991). *J. Am. Chem. Soc.* **113**, 5135–5140.
- Ruiz-Lopez, M. F., Loos, M., Goulon, J., Benfatto, M. & Natoli, C. R. (1988). *Chem. Phys.* **121**, 419–437.
- Schnitzler, M. C., Mangrich, A. S., Macedo, W. A. A., Ardisson, J. D. & Zarkin, A. J. G. (2006). *Inorg. Chem.* **45**, 10642–10650.
- Seiler, P. & Dunitz, J. D. (1979a). *Acta Cryst.* **B35**, 2020–2032.
- Seiler, P. & Dunitz, J. D. (1979b). *Acta Cryst.* **B35**, 1068–1074.
- Seiler, P. & Dunitz, J. D. (1980). *Acta Cryst.* **B36**, 2946–2950.
- Seiler, P. & Dunitz, J. D. (1982). *Acta Cryst.* **B38**, 1741–1745.
- Shuvayev, A. T., Helmer, B. Y., Lyubeznova, T. A., Kraizman, V. L., Mirmilshstein, A. S., Kvacheva, L. D., Novikov, Y. N. & Volpin, M. E. (1985). *Izv. Akad. Nauk SSR*, **49**, 1471–1475.
- Smale, L. F., Chantler, C. T., de Jonge, M. D., Barnea, Z. & Tran, C. Q. (2006). *Radiat. Phys. Chem.* **75**, 1559–1563.
- Song, Q. B., Hu, Y. H., Shen, T. H. & Jin, Z. M. (2004). *Acta Cryst.* **E60**, o539–o541.
- Takusagawa, F. & Koetzle, T. F. (1979). *Acta Cryst.* **B35**, 1074–1081.
- Teo, B. K. & Lee, P. A. (1979). *J. Am. Chem. Soc.* **101**, 2815–2832.
- Tran, C. Q., Barnea, Z., de Jonge, M. D., Dhal, B. B., Paterson, D., Cookson, D. & Chantler, C. T. (2003a). *X-ray Spectrom.* **32**, 69–74.
- Tran, C. Q., Chantler, C. T. & Barnea, Z. (2003b). *Phys. Rev. Lett.* **90**, 257401.
- Tran, C. Q., Chantler, C. T., Barnea, Z. & de Jonge, M. D. (2004). *Rev. Sci. Instrum.* **75**, 2943–2949.
- Tran, C. Q., Chantler, C. T., Barnea, Z., Paterson, D. & Cookson, D. J. (2003c). *Phys. Rev. A*, **67**, 42716.
- Tran, C. Q., de Jonge, M. D., Barnea, Z. & Chantler, C. T. (2004). *J. Phys. B*, **37**, 3163–3176.
- Troger, L., Arvanitis, D., Baberschke, K., Michaelis, H., Grimm, U. & Zschech, E. (1992). *Phys. Rev. B*, **46**, 3283–3289.
- Tzeli, D. & Mavridis, A. (2010). *J. Chem. Phys.* **132**, 194312.
- Vedrinskii, R. V., Bugaev, L. A. & Airapetian, V. M. (1991). *J. Phys. B*, **24**, 1967–1975.
- Warburton, W. K., Hubbard, B. & Zhou, C. (1999). *X-ray Instrumentation Associates*, <http://www.xia.com/Papers/Automat.pdf>.
- Xu, Z. F., Xie, Y., Feng, W. L. & Schaefer, H. F. (2003). *J. Phys. Chem. A*, **107**, 2716.
- Yamaguchi, Y., Ding, W., Sanderson, C. T., Borden, M. L., Morgan, M. J. & Kital, C. (2007). *Coord. Chem. Rev.* **251**, 515–524.

Testing Three-Body Quantum Electrodynamics with Trapped Ti^{20+} Ions: Evidence for a Z-dependent Divergence Between Experiment and Calculation

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(Received 11 May 2012; published 10 October 2012)

We report a new test of quantum electrodynamics (QED) for the w ($1s2p^1P_1 \rightarrow 1s^2S_0$) x-ray resonance line transition energy in heliumlike titanium. This measurement is one of few sensitive to two-electron QED contributions. Systematic errors such as Doppler shifts are minimized in our experiment by trapping and stripping Ti atoms in an electron beam ion trap and by applying absolute wavelength standards to calibrate the dispersion function of a curved-crystal spectrometer. We also report a more general systematic discrepancy between QED theory and experiment for the w transition energy in heliumlike ions for $Z > 20$. When all of the data available in the literature for $Z = 16\text{--}92$ are taken into account, the divergence is seen to grow as approximately Z^3 with a statistical significance on the coefficient that rises to the level of 5 standard deviations. Our result for titanium alone, 4749.85(7) eV for the w line, deviates from the most recent *ab initio* prediction by 3 times our experimental uncertainty and by more than 10 times the currently estimated uncertainty in the theoretical prediction.

DOI: [10.1103/PhysRevLett.109.153001](https://doi.org/10.1103/PhysRevLett.109.153001)

PACS numbers: 12.20.Fv, 31.30.jf, 32.30.Rj, 34.50.Fa

Quantum electrodynamics (QED) is a cornerstone of modern theoretical physics. New activity on this topic has been stimulated by the announcement of a 5σ inconsistency between a 15 ppm measurement of an atomic transition frequency in muonic hydrogen [1] and independent measurements of the proton size, linked together by QED calculations. The high sensitivity of such a measurement to QED is derived in part from the large mass of the bound lepton which shrinks the orbital radius. Another way to reduce the orbital radius and study magnified QED effects is to measure transitions in highly charged ions of increasing Z . QED processes scale as various powers of $Z\alpha$ and significantly affect the quantum observable, namely, transition energies. Moreover, in the high- Z range, some of the perturbative expansions fail, so theoretical methods very different from those used for hydrogen are required. Since QED treatments of low- Z and high- Z systems are undertaken with significantly different starting points and mathematical techniques, precise measurements for ions in the mid- Z range will guide the long-pursued development of a unified computational methodology with very accurate predictions for the entire domain $Z < 100$ [2,3].

Advances in QED theory have been sufficient that one can go beyond one-lepton systems (either free or bound) and explore the three-body quantum problem to high precision, including the investigation of heliumlike atomic systems with two electrons bound to a nucleus. Here, the two-electron QED contributions that are entirely absent in one-electron systems can be probed and compared to various theoretical formulations. In this Letter, we report

a measurement of the strongest resonant transition $1s2p^1P_1 \rightarrow 1s^2S_0$ in He-like Ti (Ti^{20+}) and present a divergence that is becoming evident between precision measurements and the most complete theoretical formulations of transition energies for He-like ions in the mid- Z range between S and Kr.

The context of this report is the systematic investigation of medium- Z two-electron systems that is underway by several research groups [4–8]. New results are infrequent, owing to the need to account for all known systematic effects to ever-exacting levels of precision and the scarcity of run time available at the few facilities capable of producing such highly charged ions. Improvements in measurement precision not only help distinguish between theoretical methods which treat few-electron atomic systems but also check the consistency of various experimental approaches that have very different methodologies (using empirical, semi-empirical, relative, or absolute calibration schemes). A very useful outcome would be if measurements that are traceable to the definition of the meter, as the present one, would be found to agree with measurements done relative to transitions in H-like systems (convenient and precise fiducials in many highly charged ion experiments) that themselves have been calculated using two-body QED [4,8,9]. Such a closing of this measurement loop could help establish hydrogenlike lines of highly charged ions as a new class of transfer standards in x-ray spectroscopy [10,11].

The present work was undertaken at the electron beam ion trap (EBIT) facility at the National Institute

of Standards and Technology [12] using wavelength dispersive spectroscopy from the University of Melbourne to obtain precision diffraction profiles of the $w(1s^2(^1S_0) \rightarrow 1s2p(^1P_1))$, $x(1s^2(^1S_0) \rightarrow 1s^2p(^3P_2))$, $y(1s^2(^1S_0) \rightarrow 1s2p(^3P_1))$, and $z(1s2(1S_0) \rightarrow 1s2s(^3S_1))$ transitions in He-like Ti (labels are standard notation). Earlier work [8,13–15] demonstrated that a thorough understanding of diffraction conditions, dispersion relations, and source systematics can allow the determination of transition energies in highly charged ions to a precision limited by statistics [5,16].

For energy-scale calibration, an electron fluorescence x-ray source was used to provide high-intensity, neutral x-ray lines that are tabulated and traceable to the definition of the meter [17,18], thus providing an absolute measurement, rather than one relative to other spectral lines whose positions are calculated. Scandium, titanium, vanadium, chromium, and manganese target foils provided characteristic K transition energies ($10K\alpha 2p \rightarrow 1s$). The crystal spectrometer employed a Ge(220) crystal bent to 218 cm radius of curvature in reflection geometry. The calibration lines produced diffraction angles that spanned the spectrometer angular rotation range, with manganese $K\alpha$ near the high-energy limit or the smallest angle of diffraction (31.7°), and scandium $K\alpha$ at the low-energy limit with the largest angle of diffraction (49.4°); the Ti^{20+} spectrum was centred around 41.1° . Several clinometers mounted on the spectrometer provided detector and source arm positions relative to Earth's local gravitational field yielding diffracting angles accurate to arcseconds. Because inner-shell neutral atomic lines are asymmetric due to underlying atomic processes [19,20], an extensive investigation of $K\alpha$ peak shapes was undertaken to provide a robust fitting procedure [21] to accurately determine peak profile turning points as well as modeling the doublet as the sum of six Voigt functions. Finally, diffraction angles and detector positions were calculated using a curved-crystal dynamical diffraction modeling code [13,14] to determine photon energy as a function of photon diffraction angle and detector position.

Figure 1 shows the fitted heliumlike Ti spectrum accumulated over several days of experimentation and weeks of calibration. The six observed peaks correspond (from left to right) to the titanium heliumlike z , lithiumlike r , lithiumlike q , heliumlike y , heliumlike x , and heliumlike w transitions. Given that the key components defining the analysis system are the detector and spectrometer, the main two elements of uncertainty relate to an experimentally determined detector response function treated in Ref. [22] and references therein and an experimentally determined dispersion function of clinometer reading versus angle.

The fitted function is the sum of six Voigt profiles and a quadratic background, with the instrumental Gaussian contribution to the total width common to all lines. To suppress correlation error, the width of the weak r line is fixed to a

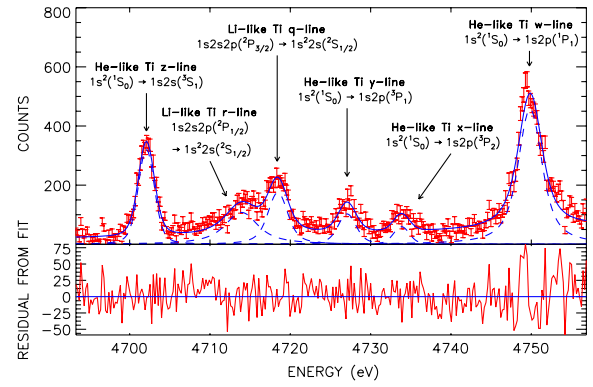


FIG. 1 (color online). Fitted summation of heliumlike titanium data. Dashed peaks represent individual peak profiles. Solid line gives the fit including the background. Residuals from the fit are indicated below. The χ^2_r was 2.9.

physical value, and the quadratic background is centered around the minimum background region of the z transition.

Table I lists the dominant contributions of uncertainty in our measurement of the w line. The two largest contributions (i and ii) are due to the statistical uncertainty in the clinometer readings that enter into the determination of the diffraction angles for both the x-ray calibration lines and the He-like Ti lines. The third largest contribution (iii) is due to the statistical uncertainty in the fit shown in Fig. 1. Detector systematics (iv) include nonlinearities and channels/mm translational scale [23]. Systematic errors in the Ti spectral fit (v) were estimated by an extensive investigation of the effect of changing the assumed form of the fit function, weights, and r -line width in the fit. Statistics relating to the centroid determinations of the calibration lines (vi) and the dynamical diffraction theory [13,14] and functional form of the dispersion relation (vii) are minor.

The w line was thereby determined to be 4749.85 ± 0.07 eV. Under our experimental conditions for a nominal electron beam energy of 10 keV, satellite contamination does not significantly interfere with this spectral line position [5] as confirmed by calculations with the present EBIT conditions using the FAC [24] and NOMAD codes [25].

TABLE I. Sources contributing to the final uncertainty in the energy of the w transition in heliumlike titanium.

Sources		Uncertainty	
		eV	ppm
(i)	Ti angle statistics	0.046	9.7
(ii)	Calibration angle statistics	0.035	7.3
(iii)	Ti x-ray spectra statistics	0.0285	6
(iv)	Detector systematics	0.024	5.1
(v)	Ti fit systematics	0.012	2.6
(vi)	Calibration line spectra statistics	0.0016	0.3
(vii)	Dynamical diffraction corrections	0.00033	0.07
	Total	0.07	15

Our measurement of the w transition energy in Ti^{20+} has an uncertainty smaller than the magnitude of the two-electron QED contributions to the transition energy [26] and therefore offers insight into the current status of agreement between three-body QED theory and experiment. Figure 2(a) compares the present result with earlier measurements of this line in heliumlike Ti. Figure 2(b) puts this result in the broader context of all available measurements for this line in ions with $Z > 15$ in comparison with theoretical predictions.

Drake's [2] pioneering comprehensive calculation of the lowest few energy levels of all heliumlike ions from $Z = 2$ to $Z = 100$ using the unified approach has sufficient accuracy that it has stood as a standard reference for decades. More recently, several groups have built upon previous work with a variety of methods for including additional QED corrections to ever-higher orders. The work of Artemyev *et al.* [26], for example, includes two-electron QED corrections and is one of the most complete treatments to date, so is presented as the reference theory in Fig. 2(b). The theory results of Cheng and Chen [27] and Plante *et al.* [28] are detailed relativistic configuration

interaction and relativistic many-body perturbation theoretical treatments of He-like systems that cover the range of mid- Z and are therefore included for comparison. These three recent works are potential improvements upon Drake's calculation for $Z > 15$.

Figure 2(b) captures the overall state of affairs between experiment and theory for two-electron atomic systems, using the brightest resonance line in He-like highly charged ions as a function of Z . All reported experimental data are presented as averages for each Z , weighted by the published uncertainty estimates. Our new measurement dominates the average shown at $Z = 22$. For the measurement of Bruhns *et al.* [9], we use their claimed absolute uncertainty for direct comparison with our present results and with other claimed absolute measurements. The data are plotted as points relative to the theory of Artemyev *et al.* [26]; theoretical predictions of Refs. [27,28] are also shown as dotted lines beneath and dashed lines above the zero line, respectively. While the theoretical predictions diverge between themselves by less than 10 ppm at $Z = 36$, a much larger and statistically significant deviation exists between the theoretical predictions and the experimental results. This deviation appears to grow systematically with Z . The statistical significance of the deviation does not necessarily grow with Z due to the difficulty of maintaining a similar experimental uncertainty as the total transition energy also grows roughly as Z^2 . The w line has also been reported at even higher Z values in heliumlike Xe [29,30] and U [31], with the former falling below and the latter falling above the Z^3 fit of Fig. 2(b). The reported uncertainties on these high- Z measurements, however, are large enough that they do not distinguish between the fitted curve and the theory. Both are included in the fit of Fig. 2(b).

Fits of the global data set shown to various powers of Z produced χ_r^2 (goodness of fit) that exhibited an optimum at Z^3 with a positive coefficient [given in Fig. 2(b)], demonstrating a deviation from the calculation of Ref. [26] at the 5 standard error level. Our result considered alone deviates from Ref. [26] at the 3 standard error level. Shown is the Z^3 fit along with a shaded region indicating the 68% confidence intervals of the fit. If the fit shown in Fig. 2(b) is restricted to only the eight EBIT measurements, the fit coefficient is virtually unchanged but the χ_r^2 improves from 1.28 to 1.06.

The $1/Z$ expansion [2] to the nominal Z^4 scaling of the Lamb shift gives a Z^3 dependence to first order. While the Z^3 dependence is consistent with the expected scaling of uncalculated screening corrections to the two-loop Lamb shift (e.g., Ref. [32]), the magnitude is unexpectedly large. Z^3 is the best phenomenological description of the divergence given the present accumulated data. The origin of any divergence between experiment and theory could be more complex, involving a variety of QED effects, orders, and Z dependencies. Isotope and nuclear size uncertainties

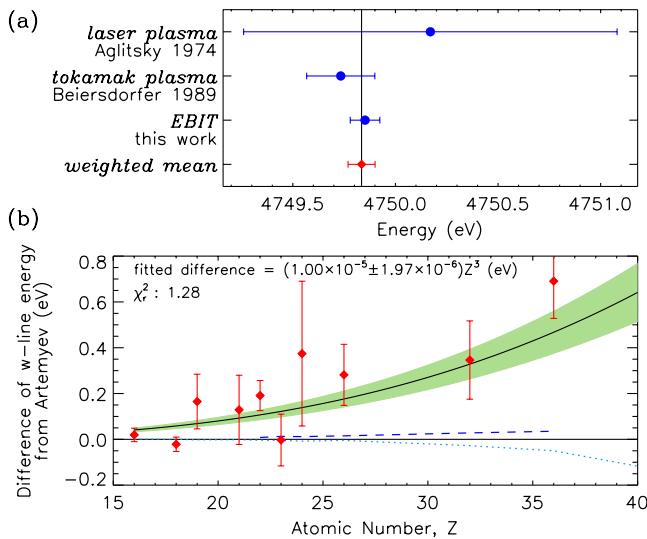


FIG. 2 (color online). (a) Measurements of the w -line transition energy in heliumlike Ti, in temporal order and indicating the nature of the source [41,42]. (b) Experimental results and theoretical predictions for the w -line transition energy in heliumlike systems, plotted as a function of Z after subtracting the theoretical values of Ref. [26]. The weighted mean of multiple measurements for each Z value is shown for clarity. The least-squares fit through the data has a Z^3 dependence relative to Ref. [26]. Included in the plot are EBIT data for $Z = 16$ [4], $Z = 18$ [9], $Z = 22$ (the present work), $Z = 23$ [5], $Z = 32$ [43], $Z = 36$ [6,44] and non-EBIT results for $Z = 16$ [42,45–47], $Z = 18$ [33–36], $Z = 19$ [41,42], $Z = 21$ [41], $Z = 22$ [41,42], $Z = 23$ [41,42,46], $Z = 24$ [41,46], $Z = 26$ [8,41,46,48], $Z = 32$ [10], and $Z = 36$ [7,46,49]. Also shown are the theories of Refs. [27] (positive dashed values) and Ref. [28] (negative dotted values). $\chi_r^2 = 1.28$ or 1.06 considering only EBIT data.

are negligible at $Z = 22$, so we have used ordinary Ti, which can be assumed to be approximately 74% ^{48}Ti .

Our measurement of the strongest resonance line on the heliumlike isoelectronic sequence results in one of the most statistically significant discrepancies from theory for the $1s2p^1P_1 \rightarrow 1s^21S_0$ transition energy. Both the precision of this measurement and its strategic location on the Z axis have enabled a fresh assessment of the overall agreement between experiment and theory along this sequence. By averaging all available experimental data at each value of $Z > 15$, a general trend of divergence from prediction presents itself at the level of 5 standard errors. The evidence for systematically low predicted transition energies suggests that missing terms in three-body QED calculations are much larger than presently anticipated or there is an error in the calculated terms.

In closing, we note directions for future work. Although unaccounted-for systematic errors may tend to cancel when results from different research groups are averaged, a critical evaluation of individual results would provide a necessary complementarity. Work on argon ($Z = 18$), for example, discussed evidence of dominating satellite line contamination under certain experimental conditions [33–36]. While it is believed that the associated uncertainty has been reduced dramatically in recent work on argon [9], detailed independent modeling is important to confirm relative positions and magnitudes of possible satellites that could affect the positions of the w line [37,38]. In addition, new measurements in the unexplored range of $Z = 27\text{--}31$ would enable verification and systematic parametrization of apparent discrepancies with theory, pointing towards better ways of extending QED calculations beyond the two-body problem and into the extreme, high-field regime of highly charged ions. Such work will complement activity in other fields in which high-power lasers are also being used to probe the quantum vacuum, as discussed in Refs. [39,40].

We thank Jonathan Sapirstein, Anton Artemyev, Vladimir Shabaev, Peter Mohr, and Gordon Drake for helpful discussions and Yuri Ralchenko for collisional-radiative modeling. We also acknowledge support from the Australian Research Council.

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- [1] R. Pohl *et al.*, *Nature (London)* **466**, 213 (2010).
- [2] G. W. F. Drake, *Can. J. Phys.* **66**, 586 (1988).
- [3] D. Layzer and J. Bahcall, *Ann. Phys. (Berlin)* **17**, 177 (1962).
- [4] K. Kubicek, H. Bruhns, J. Braun, J. R. C. Lopez-Urrutia, and J. Ullrich, *J. Phys. Conf. Ser.* **163**, 012 007 (2009).
- [5] C. T. Chantler, D. Paterson, L. T. Hudson, F. G. Serpa, J. D. Gillaspy, and E. Takacs, *Phys. Rev. A* **62**, 042 501 (2000).
- [6] K. Widmann, P. Beiersdorfer, V. Decaux, and M. Bitter, *Phys. Rev. A* **53**, 2200 (1996).
- [7] P. Indelicato, J.-P. Briand, M. Tavernier, and D. Liesen, *Z. Phys. D* **2**, 249 (1986).
- [8] C. T. Chantler, J. M. Laming, D. D. Dietrich, W. A. Hallett, R. McDonald, and J. D. Silver, *Phys. Rev. A* **76**, 042 116 (2007).
- [9] H. Bruhns, J. Braun, K. Kubicek, J. R. C. Lopez-Urrutia, and J. Ullrich, *Phys. Rev. Lett.* **99**, 113 001 (2007).
- [10] C. T. Chantler, J. M. Laming, J. D. Silver, D. D. Dietrich, P. H. Mokler, E. C. Finch, and S. D. Rosner, *Phys. Rev. A* **80**, 022 508 (2009).
- [11] D. F. Anagnostopoulos, D. Gotta, P. Indelicato, and L. M. Simons, *Phys. Rev. Lett.* **91**, 240801 (2003).
- [12] J. D. Gillaspy, Y. Aglitskiy, E. W. Bell, C. M. Brown, C. T. Chantler, R. D. Deslattes, U. Feldman, L. T. Hudson, J. M. Laming, E. S. Meyer *et al.*, *Phys. Scr.* **T59**, 392 (1995).
- [13] C. T. Chantler, *J. Appl. Crystallogr.* **25**, 674 (1992).
- [14] C. T. Chantler, *J. Appl. Crystallogr.* **25**, 694 (1992).
- [15] C. T. Chantler, *Appl. Opt.* **32**, 2371 (1993).
- [16] C. T. Chantler, D. Paterson, L. T. Hudson, F. G. Serpa, J. D. Gillaspy, and E. Takacs, *Phys. Scr.* **T80B**, 440 (1999).
- [17] R. D. Deslattes and A. Henins, *Phys. Rev. Lett.* **31**, 972 (1973).
- [18] R. D. Deslattes, E. G. Kessler, P. Indelicato, L. de Billy, E. Lindroth, and J. Anton, *Rev. Mod. Phys.* **75**, 35 (2003).
- [19] C. T. Chantler, A. C. L. Hayward, and I. P. Grant, *Phys. Rev. Lett.* **103**, 123 002 (2009).
- [20] J. A. Lowe, C. T. Chantler, and I. P. Grant, *Phys. Rev. A* **83**, 060 501(R) (2011).
- [21] C. T. Chantler, M. N. Kinnane, C. H. Su, and J. A. Kimpton, *Phys. Rev. A* **73**, 012 508 (2006).
- [22] A. T. Payne, J. A. Kimpton, L. F. Smale, and C. T. Chantler, *Nucl. Instrum. Methods Phys. Res., Sect. A* **619**, 190 (2010).
- [23] A. T. Payne, J. A. Kimpton, M. N. Kinnane, and C. T. Chantler, *Meas. Sci. Technol.* **20**, 025 601 (2009).
- [24] M. F. Gu, in *Proceedings of the 14th APS Topical Conference on Atomic Processes in Plasmas*, edited by James S. Cohen, S. Mazevet, and D. P. Kilcrease, AIP Conf. Proc. No. 730 (AIP, New York, 2004), p. 127.
- [25] Y. V. Ralchenko and Y. Maron, *J. Quant. Spectrosc. Radiat. Transfer* **71**, 609 (2001).
- [26] A. N. Artemyev, V. M. Shabaev, V. A. Yerokhin, G. Plunien, and G. Soff, *Phys. Rev. A* **71**, 062 104 (2005).
- [27] K. T. Cheng and M. H. Chen, *Phys. Rev. A* **61**, 044 503 (2000).
- [28] D. R. Plante, W. R. Johnson, and J. Sapirstein, *Phys. Rev. A* **49**, 3519 (1994).
- [29] D. B. Thorn, M. F. Gu, G. V. Brown, P. Beiersdorfer, F. S. Porter, C. A. Kilbourne, and R. L. Kelley, *Phys. Rev. Lett.* **103**, 163 001 (2009).
- [30] J.-P. Briand, P. Indelicato, A. Simionovici, V. S. Vicente, D. Leisen, and D. D. Dietrich, *Europhys. Lett.* **9**, 225 (1989).
- [31] J.-P. Briand, P. Chevallier, P. Indelicato, K. P. Ziock, and D. D. Dietrich, *Phys. Rev. Lett.* **65**, 2761 (1990).
- [32] I. Lindgren *et al.* (to be published).
- [33] R. D. Deslattes, H. F. Beyer, and F. Folkmann, *J. Phys. B* **17**, L689 (1984).

- [34] J.-P. Briand, J. P. Mosse, P. Indelicato, P. Chevallier, D. D. Girard-Vernhet, A. Chetoui, M. T. Ramos, and J. P. Desclaux, *Phys. Rev. A* **28**, 1413 (1983).
- [35] W. M. Neupert, *Sol. Phys.* **18**, 474 (1971).
- [36] H. D. Dohmann and R. Mann, *Z. Phys. A* **291**, 15 (1979).
- [37] J. D. Gillaspy, C. T. Chantler, D. Patterson, L. T. Hudson, F. G. Serpa, and E. Takacs, *J. Phys. B* **43**, 074021 (2010).
- [38] C. T. Chantler and J. A. Kimpton, *Can. J. Phys.* **87**, 763 (2009).
- [39] J. D. Gillaspy, *JINST* **5**, C10005 (2010).
- [40] M. Marklund, *Nature Photon.* **4**, 72 (2010).
- [41] P. Beiersdorfer, M. Bitter, S. von Goeler, and K. W. Hill, *Phys. Rev. A* **40**, 150 (1989).
- [42] E. V. Aglitsky, V. A. Boiko, S. M. Zakharov, A. Y. Pikuz, and S. A. Faenov, *Sov. J. Quantum Electron.* **4**, 500 (1974).
- [43] S. MacLaren, P. Beiersdorfer, D. A. Vogel, D. Knapp, R. E. Marrs, K. Wong, and R. Zasadzinski, *Phys. Rev. A* **45**, 329 (1992).
- [44] K. Widmann, P. Beiersdorfer, and V. Decaux, *Nucl. Instrum. Methods Phys. Res., Sect. B* **98**, 45 (1995).
- [45] L. Schleinkofer, F. Bell, H.-D. Betz, G. Trollman, and J. Rothermel, *Phys. Scr.* **25**, 917 (1982).
- [46] E. V. Aglitsky, P. S. Antsiferov, S. L. Mandelstam, A. M. Panin, U. I. Safronova, S. A. Ulitin, and L. A. Vainshtein, *Phys. Scr.* **38**, 136 (1988).
- [47] C. L. Cocke, B. Curnutte, and R. Randall, *Phys. Rev. A* **9**, 1823 (1974).
- [48] J.-P. Briand, M. Tavernier, R. Marrus, and J. P. Desclaux, *Phys. Rev. A* **29**, 3143 (1984).
- [49] J.-P. Briand, P. Indelicato, M. Tavernier, O. Gorceix, D. Leisen, H. F. Beyer, B. Liu, A. Warczak, and J. P. Desclaux, *Z. Phys. A* **318**, 1 (1984).

Chantler *et al.* Reply: We find that Epp’s [1] hypothesis—namely, that the current experimental data set is well represented by a small constant or zero offset from the predictions of Artemyev *et al.* [2]—is not supported by standard statistical analysis. We find that adding the new datum recommended by Epp makes the modeled discrepancy that we reported earlier grow with Z even more strongly (rather than more weakly, as Epp suggests). Our primary conclusion [3] of an apparent Z -dependent discrepancy between experiment and theory is unchanged. While Epp suggests that our results extrapolate to problems at very high Z , our present and previous data sets both include data up to and including $Z = 92$, and the reduced chi-squared χ_r^2 values in our original work [3] showed a negligible discrepancy of the fit over this range of Z .

Upon replacing the value for $Z = 18$ from our data set with Epp’s recommended weighted average of 3139.5805(49) eV, we obtain the “expanded” data set. Following the analysis that produced our original Fig. 2 [3], we present in Fig. 1 the χ_r^2 of the monomial function $y = aZ^n$, where y is the discrepancy between experiment and the theoretical calculations of Artemyev *et al.* [2] under the assumption of various orders, n . Epp’s hypothesis ($n = 0$) yields the high $\chi_r^2 = 3.7$; however, the optimum exponent is not $n = 0$ but $n = 5$, suggesting a stronger Z dependence than the original data set. Applying the standard chi-squared statistical hypothesis test to the case $n = 0$, i.e., Epp’s null hypothesis (constant offset hypothesis), we find the probability of observing residuals at least as large as observed to be extremely low: $p = 0.00003$, providing strong evidence that the null hypothesis is false. It is not correct to claim, as Epp suggests, that the data are “fairly fitted” by a constant offset.

The original data set gave similar values of χ_r^2 for $n = 3$ and $n = 4$. If we allow the exponent to take on nonintegral values, we find that the minimum χ_r^2 is an excellent 1.1 for $n = 3.5$. A similar analysis for the expanded data set gives $n = 5.0$, but with χ_r^2 being high: 2.4.

Although the inclusion of the new datum [4] does not change the main conclusions of our earlier paper [3], and the exponent is in reasonable agreement with our previous result, the minimum χ_r^2 more than doubles, suggesting that the expanded data set includes a data point with greatly underestimated uncertainty or that the assumed form of the deviation should be revised.

Epp’s statement that any data set “could be easily fitted more accurately by a full polynomial of third order” is not relevant to our original analysis since we have only presented results in terms of a monomial. The number of fit parameters is the same for our hypothesis and his. The agreement in our original fit remains remarkable.

We take exception to Epp’s implication that our model function is not physically justified and that our “fit does not provide any meaningful insight.” Our physical motivation

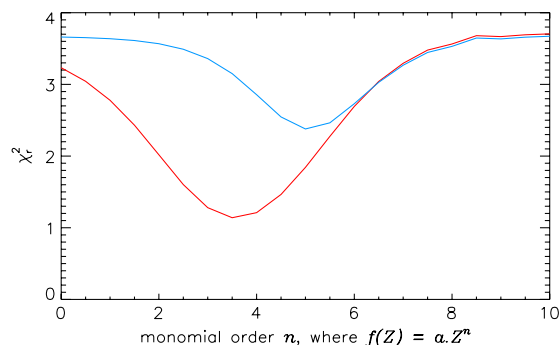


FIG. 1 (color online). Reduced chi square for the original (red, bottom curve) and expanded (blue, top curve) data set as a function of monomial order n , for $N = 12$ values of Z , with one fit parameter.

for assuming a monomial form of the divergence is that this is the underlying *ab initio* analytic form taken by each term in the QED calculation; see e.g., Refs. [5,6]. This provides guidance as to which QED expansion terms might be inadequately computed, although we repeat our caution that “the actual divergence could be the result of a variety of orders and Z dependencies” [3].

As in our original publication, we conclude that at present a Z -dependent divergence between experiment and theory is observed for $Z > 20$. We encourage more work in both theory and experiment that will lead to better characterization, and ultimately better physical understanding, of any disagreement.

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Received 27 February 2013; published 11 April 2013

DOI: [10.1103/PhysRevLett.110.159302](https://doi.org/10.1103/PhysRevLett.110.159302)

PACS numbers: 12.20.Fv, 31.30.jf, 32.30.Rj, 34.50.Fa

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[1] S. W. Epp, preceding Comment, Phys. Rev. Lett. **110**, 159301 (2013).

[2] A. N. Artemyev, V. M. Shabaev, V. A. Yerokhin, G. Plunien, and G. Soff, Phys. Rev. A **71**, 062104 (2005).

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- [3] C. T. Chantler *et al.*, [Phys. Rev. Lett. **109**, 153001 \(2012\)](#).
[4] K. Kubiček, J. Braun, H. Bruhns, J.R. Crespo Lopez-Urrutia, P.H. Mokler, and J. Ullrich, [Rev. Sci. Instrum. **83**, 013102 \(2012\)](#).
[5] G. W. F. Drake, Can. J. Phys. **66**, 586 (1988).
[6] I. Lindgren, S. Salomonson, and J. Holmberg, [arXiv:1212.6482v1](#).

X-ray measurements in helium-like atoms increased discrepancy between experiment and theoretical QED

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Received 10 July 2014, revised 9 October 2014

Accepted for publication 28 October 2014

Published 15 December 2014

New Journal of Physics **16** (2014) 123037

[doi:10.1088/1367-2630/16/12/123037](https://doi.org/10.1088/1367-2630/16/12/123037)

Abstract

A recent 15 parts per million (ppm) experiment on muonic hydrogen ($p^+\mu^-$) found a major discrepancy with quantum electrodynamics (QED) and independent nuclear size determinations. Here we find a significant discrepancy in a different type of exotic atom: a medium- Z nucleus with two electrons. Investigation of the data collected is able to discriminate between available QED formulations and reveals a pattern of discrepancy of almost six standard errors of experimental results from the most recent theoretical predictions, with a functional dependence proportional to Z^n where $n \simeq 4$. In both the muonic and highly charged systems, the sign of the discrepancy is the same, with the measured transition energy higher than predicted. Some consequences are possible or probable, and some are more speculative. This may give insight into effective nuclear radii, the Rydberg, the fine-structure constant, or unexpectedly large QED terms.

Keywords: helium-like quantum systems, relativistic atomic physics, x-ray spectroscopy, QED



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1. Introduction

In this article, we study the pattern of discrepancy between two-electron experiment and theory for x-ray transitions to core holes. Recent work has raised this area as one of the current anomalies in quantum electrodynamics (QED) computation. QED is one of the most important foundations of modern physics. The five-standard-deviation inconsistency between a 15 parts per million (ppm) measurement of a muonic hydrogen transition and theory [1] has led to four years of intensive research by many groups around the world. Leading theorists consider the discrepancy of 0.42 meV to be well outside possible causes within the Standard Model, claimed to have an uncertainty of no more than ± 0.01 meV [2].

This puzzling situation has stimulated much theoretical activity, and it highlights the current difficulty in low- Z atomic spectroscopy that results from complexities of the nucleus. In precision measurements with atomic hydrogen [3], progress is stalled by uncertainties in nuclear form factors and nuclear polarization, both of which render the last few digits of available experimental accuracy underutilized. At high- Z , the strong enhancement of nuclear interactions also limits the degree to which available experimental measurements can be used to test QED [4]. For medium- Z , nuclear uncertainties do not limit the interpretation of atomic spectroscopy. The overall magnitude of the contribution from nuclear size and shape is small, and the uncertainty on the magnitude is smaller still; for the case of titanium, the uncertainty in the nuclear radius, even in early atomic structure calculations, is 0.012 fm [5], which is less than half that of the proton [5] and much less than the 0.42 fm discrepancy from the muonic hydrogen experiment.

Spectroscopy of highly charged ions and muonic atoms probes a relatively unexplored regime of physics, in which the peak of the radial wavefunction of the lepton is reduced by more than an order of magnitude. Effects associated with QED and the nucleus are greatly enhanced, due to the increased overlap of the nucleus with the wavefunction of the orbiting lepton. In the case of muonic hydrogen, the lepton orbital radius is reduced by the mass of the lepton, while in the case of highly charged ions, the lepton orbital radius is decreased by the increased nuclear charge. While hydrogenic (one electron) atomic systems are exotic and are critical challenges for theory and experiments, helium-like (He-like) atomic systems lie at one of the forefronts of QED research [6], because they display qualitatively new effects (including the ‘two-electron Lamb shift’) that are not present at any level in one-electron ions.

Crucial higher-order 1e-QED terms scale as $\alpha^2(Z\alpha)^6$ and $\alpha(Z\alpha)^7$ for hydrogen, while similar 2e-QED terms scale as $\alpha^2(Z\alpha)^6$ and $\alpha^2(Z\alpha)^7$. Hence, an increase in Z results in a dramatic increase in the magnitude of higher-order contributions [7]. If the Z -expansions used for hydrogen remained valid, then a 1 ppm measurement in the middle of the periodic table would be equivalent to testing some higher-order terms in hydrogen to a few parts in 10^{15} [4]. Moreover, in the mid- Z range, some of the perturbative expansions fail, so nonperturbative methods are required. The mid- Z crossover range between neutral atoms and very high- Z , few-electron ions is the focus of this paper. Tests with atoms and muonic hydrogen have focused on the proton radius, while the real cause may lie elsewhere.

Precision measurements of x-ray energies require high resolution and must be undertaken using wavelength dispersive spectroscopy employing Bragg diffraction. Tests of QED in He-like systems often observe the diffraction profile of $w(1s^2(^1S_0) \rightarrow 1s2p(^1P_1))$, and less frequently the $x(1s^2(^1S_0) \rightarrow 1s2p(^3P_2))$, $y(1s^2(^1S_0) \rightarrow 1s2p(^3P_1))$ and $z(1s^2(^1S_0) \rightarrow 1s2s(^3S_1))$ transitions.

2. Inconsistency with the null hypothesis

Taken individually, recently measured He-like transition energies of titanium demonstrate significant deviation from the most recent comprehensive *ab initio* theoretical QED formulation [6], with significances of 2.9 s.e. for the *w*-line [8], 1.4 s.e. for the *z*-line, and 1.3 s.e. and 0.3 s.e. for the *y*- and *x*-lines, respectively [9]. All lie higher than the predictions of theory. The weighted mean of these four deviations from theory (see table 2) is nonzero by 3.2 s.e.

When all the assessed literature claiming absolute measurements for the four lines is taken together and the weighted mean is calculated for each value of $Z > 15$, then compared to the predictions in [6], the χ_r^2 is found to be 3.5 (for no fit parameters), corresponding to a probability of less than $P = 1.2 \times 10^{-5}$ that the data are adequately described by the predictions. This presents a challenging puzzle, as the uncertainty of the predictions is reported to be much smaller than even the most precise experiments, and the results of four independent calculations [6, 10–12] by leading groups agree with each other to within a fraction of the observed deviation from the experiments. Some 18 measurements are added for the *x*, *y*, and *z* transitions, including our recent data. The possibility that the experiments suffer from a common systematic error seems unlikely, given that this set includes 63 results distributed over 28 different experiments from at least 12 different groups, conducted over more than four decades. In addition, the independent measurements at each value of Z are in good agreement with their weighted means.

There are other measurements in the literature at lower values of Z , which are not directly comparable to [6] because that work is only tabulated down to $Z = 12$ and becomes increasingly uncertain as Z is reduced. In fact, the difference in the calculated energy of the ground level with respect to a competing calculation crosses over and changes sign around $Z = 15$.

3. Pattern of discrepancy

Our earlier work analyzed the strongest of the four lines and included data from the literature up through the end of 2011, and suggested a systematic discrepancy from theory with a functional dependence proportional to Z^3 [8]. A later investigation demonstrated that the consideration of non integer exponents led to a minimum at $Z^{3.5}$ [13], as shown in the lower curve in figure 1.

Quadrupling the number of spectral peaks does much more than increase the statistical significance of the deviation. It rules out a range of systematics relating to satellites and line shifts from adjacent peak overlap, for example, which may be unrecognized. The consistent pattern of discrepancy that results when all four lines are included also suggests that the problem lies primarily in the calculation of the ground level (common to all four lines), or that the error in most of the upper levels is of the same magnitude for each value of Z . This makes sense, in that the QED corrections to the ionization energy (as opposed to the total energy) scale in proportion to $1/n^3$ are proportional to the electron density at the nucleus (i.e., the matrix element of the delta function (equation 2, [11])).

Deviations of the experiments from theory for all four lines are plotted as a function of Z (figures 2–5), and are statistically consistent with a single monomial, rising approximately as Z^4 . Theory predicts that the first-order QED corrections (vacuum polarization and self-energy) should scale as approximately Z^4 as well. Specific Feynman diagrams involving virtual photons and electron correlation follow expansions of order Z^4 , $Z^6(1/Z)$, $Z^6(1/Z)^2$, and $Z^4(1/Z)$, for

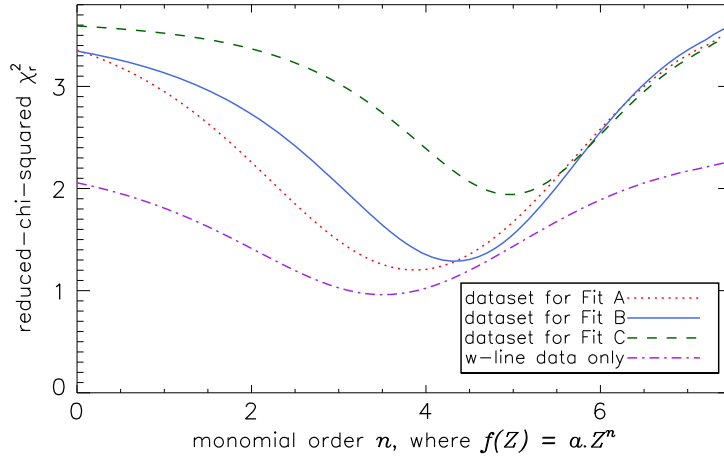


Figure 1. A persistent discrepancy. Plot of χ_r^2 by monomial order for various data sets combining literature values with our experimental results. The dot-dash curve (magenta) includes only measurements of the w -line [13]. The red dotted line is Fit ‘A’, including all absolute w , x , y , and z transition measurements with claimed uncertainties above 10 ppm. The solid blue line represents the χ_r^2 valley including [14]. The green dashed line includes both [14, 15].

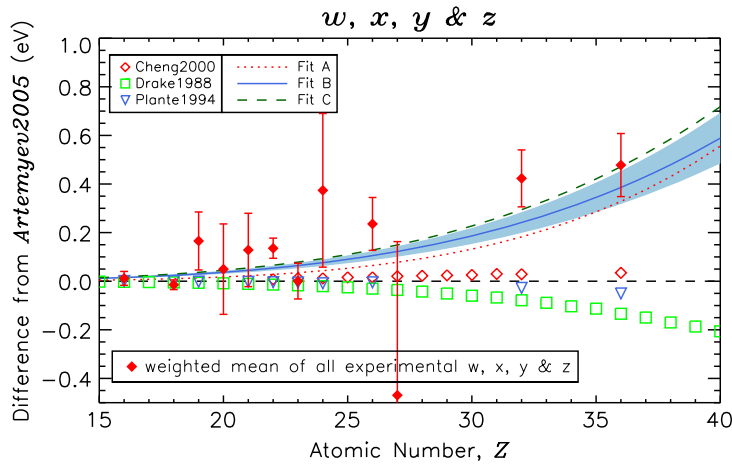


Figure 2. Discrepancy of experimental data from the latest theory for two-electron systems. Difference of weighted mean results for w , x , y , and z transitions. The [red] dotted line is Fit ‘A’ (see text and table 2; Z^4 dependence, $\chi_r^2 = 1.2$). The [blue] solid line is Fit ‘B’ (including [14] and assuming Z^4 dependence, with one s.e. shading - (68%) confidence interval around the fit to demonstrate consistency with the other fits within uncertainty, $\chi_r^2 = 1.3$). The [green] dashed line is Fit ‘C’ including [14, 15], scaling as Z^5 . All are fitted across the range $Z \in [15, 92]$. The error bar shown on each point is the s.e. Experimental results for the w , x , y , and z lines included in Fit ‘A’ are plotted as weighted means for each Z (table 1). Theoretical formulations presented, relative to Artemyev *et al* [6] are Cheng [10], Drake [11], and Plante [12].

example. The current level of accuracy of the experiments does not warrant fitting a polynomial of more than one degree of freedom, so therefore we consider only the coefficient of a monomial of order n , where n is taken to be the constant value that minimizes the χ_r^2 of the deviations of the weighted means at each value of Z from the theoretical predictions. The

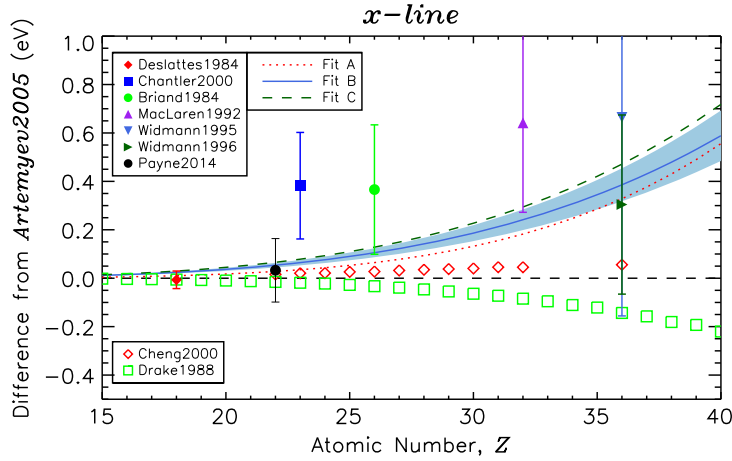


Figure 3. Discrepancy of experimental data from the latest theory for two-electron systems for x ($1s2p^3P_2 \rightarrow 1s^2^1S_0$), plotted across mid- Z ($Z \in [15, 40]$), from Artemyev *et al* [6]. Lines as per figure 2. Experimental results for the x lines included in Fit ‘A’ are plotted for each Z . The result of our recent work is plotted as a black circle. Theoretical formulations presented, relative to Artemyev *et al* [6] are Cheng [10], Drake [11], and Plante [12]. None of these different advanced computations are consistent with the experimental data. Although the result is dominated by the statistical uncertainty for this transition, there is very good agreement with the imputed discrepancy. Experimental results plotted are [9, 16–21].

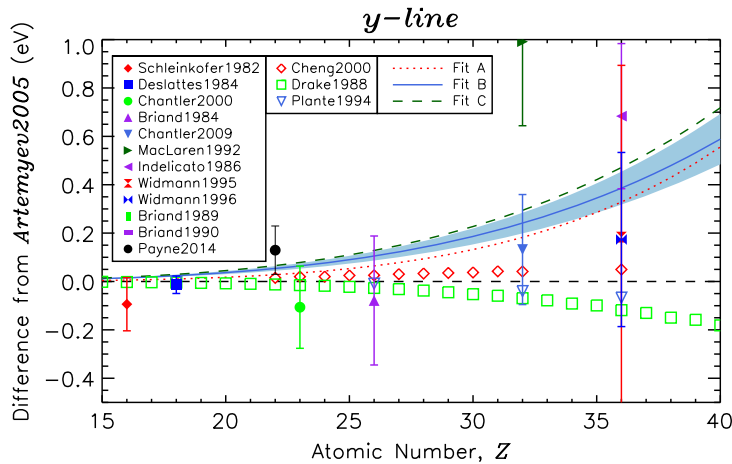


Figure 4. Discrepancy of experimental data from the latest theory for two-electron systems for y ($1s2p^3P_1 \rightarrow 1s^2^1S_0$), as per figure 3. Lines as per figure 2. Experimental results plotted are [9, 16–26].

consideration of a high-order polynomial is self-evidently consistent with Feynman diagram expectation values and correlation orders. The null hypothesis (i.e., a constant offset discrepancy from theory with a zero amplitude) has the same number of fitting coefficients and appears improbable, so we are comparing like with like in the statistical evaluation.

To check the possibility that one or more experimental approaches might have a recurring systematic error, we have performed a variety of robustness tests by systematically deleting all of the data from one or more types of experimental arrangements (those with the most data, with

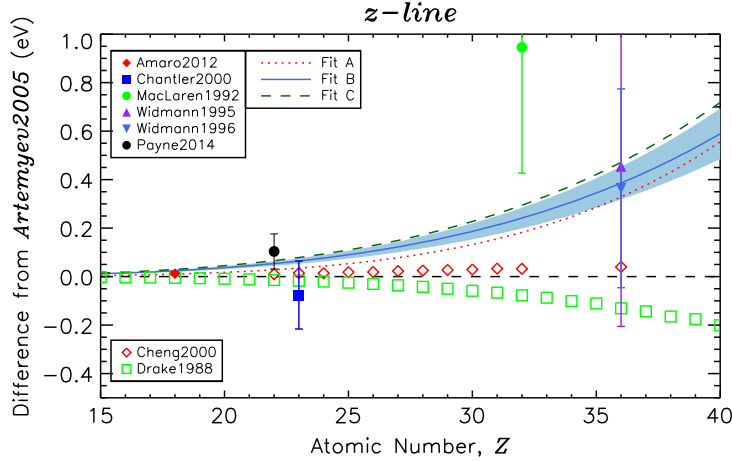


Figure 5. Discrepancy of experimental data from the latest theory for two-electron systems for z ($1s2s^3S_1 \rightarrow 1s^2^1S_0$), as per figure 3. Lines as per figure 2. Experimental results plotted are [9, 14, 17, 19–21].

the smallest error bars, etc) and refit. The data set composed of our results and results prior to 2012 is robust against this test. We also grouped these data by subset of the photon source, and we found robust evidence for a strong Z -dependent deviation from theory. For example, looking at only electron beam ion trap (EBIT) data, since that subset is believed to suffer less from systematic corrections, we find a $Z^{3.2}$ dependence of discrepancy, based on the w -line only, with a $\chi_r^2 = 1.06$. Inclusion of EBIT data from the literature on x , y , and z yields the same optimized dependence of discrepancy ($Z^{3.2}$) and a significance of 4.6 (i.e., a 4.6 standard error discrepancy from theory). Furthermore, the evidence suggests that the measurements in the literature up through 2011 reasonably accurately estimated their errors, and can be treated as statistically independent.

We now consider the effect of two recent measurements in argon [14, 15], which appear to fall into a different category from earlier data. These two measurements claim an uncertainty at the level of nearly one ppm, about an order of magnitude better than the best measurements performed at any other value of Z , and hence bring with them the possibility of significantly skewing the results of a global fit.

The primary conclusion of a Z -dependent discrepancy remains unchanged whether or not these two recent data points are included in the analysis. The statistical consistency of the global deviation fit, however, can be significantly affected. To investigate this, we present the results of three different fits to subsets of the data: Fit ‘A’, including [8, 9, 16–37], Fit ‘B,’ including [14], and Fit ‘C,’ including [14, 15].

We obtain a discrepancy given by Fit ‘A,’ $\Delta E = (2.8 \times 10^{-7} \pm 4.9 \times 10^{-8})Z^4$ eV, $\chi_r^2 = 1.2$. The uncertainty of the fit coefficient represents a 5.74 s.e. deviation from zero. Such a discrepancy would occur in a normal distribution, with a probability of only 5×10^{-9} (5.74 s.e.). This fit represents some 61 spectral lines, and lies within one s.e. of the result based on the w -line only. This fit is presented in figures 2–5, presenting individual data points for the x , y , and z lines, respectively, indicating the common pattern with increasing atomic number. All data are plotted against the theoretical predictions of Artemyev *et al* [6], which has been the benchmark standard for He-like QED theory for a number of years. Three of the most highly

referenced theoretical predictions from 1988 [11], 1994 [12], 2000 [38], and the current standard of 2005 [6] are clustered together, indicating the advance and convergence of scholarship.

Amaro *et al* [14] do not report the w -transition because the state-population mechanisms of the ECRIS source (Electron Cyclotron Resonance Ion Source) rendered it relatively weak. Their reported z -transition is discrepant from theory, with the same sign as our results. Including [14] in the overall fit yields two results with the same goodness-of-fit: (1) $\Delta E = (4.2 \times 10^{-8} \pm 7.4 \times 10^{-9})Z^{4.5}$ eV, $\chi_r^2 = 1.3$, a 5.7 s.e. deviation of the coefficient from zero; and (2) Fit ‘B’ (figures 2–5), with $\Delta E = (2.3 \times 10^{-7} \pm 4.0 \times 10^{-8})Z^4$ eV, $\chi_r^2 = 1.3$, also a 5.7 s.e. deviation from zero. The deep valley of the χ_r^2 surface (figure 1, ‘ w -line’ or Fits ‘A’ or ‘B’) argues strongly for a discrepancy and that a power law with $n \simeq 4$ (to within an uncertainty of about ± 0.5) is the best fit. The χ_r^2 remains consistent with unity, arguing for a self-consistent data set. The consistent patterns of discrepancy can be seen in the plots. The power law dependence is robust and significant in all variations. Fits (1) and (2) (‘B’) lie within 1 s.e. of Fit ‘A’.

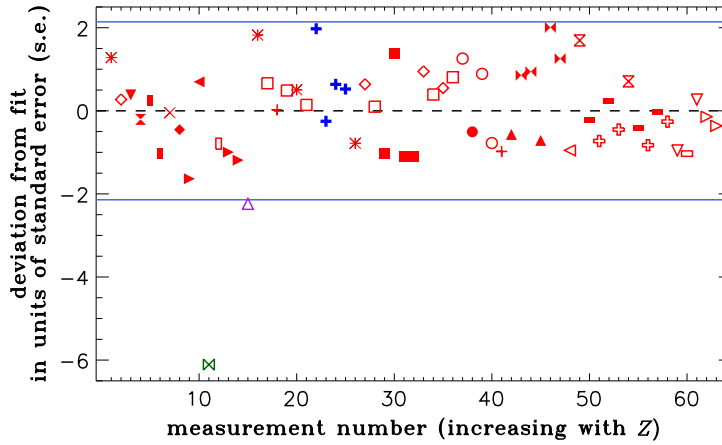
There has been much confusion about the status of experiments at $Z = 18$. Our current Fit ‘A’ predicts a deviation from theory of +0.029(5) eV at $Z = 18$, while [14] found +0.012(9) eV (± 0.0077 eV without inclusion in quadrature of claimed theoretical uncertainty). This [14] is within two s.e. of both our predicted result and the previous theory, despite its low claimed uncertainty of 2.5 ppm (though, of course, in a different experimental regime). This measurement is a high-precision result using a powerful ion source (ECRIS), a new methodology, and discussion of a range of systematics [39]. The paper reports a z -transition, so it could not be discussed in terms of an earlier analysis of the w line consistency, but it can now be discussed in relation to a common trend found in the four lines. The inclusion or exclusion of [14] does not significantly impact the primary or numerical conclusions, nor does it impact the magnitude (number of standard errors) of the discrepancy. Specifically, with or without this data point, the discrepancy is 5.7 s.e. The point also lies within the normal distribution of measured points relative to either Fit ‘A’ or Fit ‘B’.

Including a second recent measurement [15] in the overall fit yields Fit ‘C’, which is also plotted in the figures, $\Delta E = (5.4 \times 10^{-9} \pm 1.1 \times 10^{-9})Z^5$ eV, $\chi_r^2 = 1.9$. This remains a 4.8 s.e. deviation from current theory, within about one s.e. of Fit ‘B’. It [15] does skew the optimal order, but the significance is only marginally weakened and the clear pattern of discrepancy from theory remains manifest under all permutations. This result is still inconsistent with theory, with a probability of only 8×10^{-7} (4.8 s.e. using normal distributions). According to [14], the authors of [15] neglected at least one potentially large 5 ppm shift, especially compared to their claimed uncertainty of 1.5 ppm. Further, this accuracy implies that their published correction for over 60 ppm of line curvature has been corrected to an accuracy of approximately 1 ppm.

Table 1 lists all of the weighted means of the data included in our analysis. Fit ‘A’ included all data cited except [14, 15]; Fit ‘B’ included [14]; and Fit ‘C’ included [14, 15]. For completeness, table 2 lists all 63 experimental results considered herein. From [29], we include only the subset of their data that they designate as arising from ‘direct measurements’ of the satellite correction normalization ratios ($Z < 28$); if we include their higher- Z results in our analysis, it does not significantly change our conclusions, but it does entangle the measurement with complex theoretical modelling untested in this regime. For the measurement of Bruhns

Table 1. Experimental weighted mean values used in this work.

Z	Discrepancy (eV)	σ (eV)
16	0.011 624	0.0285
18 ‘Fit A’	−0.014 71	0.0198
18 ‘Fit B’	0.008 68	0.0072
18 ‘Fit C’	0.002 09	0.0041
19	0.165 49	0.119
20	0.049 57	0.186
21	0.128 42	0.151
22	0.135 63	0.0415
23	0.000 34	0.0736
24	0.373 93	0.316
26	0.235 67	0.1089
27	−0.469 35	0.632
32	0.423 17	0.1171
36	0.477 94	0.1298
54	1.1570	1.080
92	10.8261	29.04

**Figure 6.** Deviation from Fit ‘A’ of the data, published up through [15], in units of the published experimental error bars. The measurement number is given in table 2.

et al [33], we use their claimed absolute uncertainty (rather than their uncertainty relative to calculated values for calibration lines in other ions) for direct comparison with our present results and with other claimed absolute measurements. The consistency of the pattern of discrepancy is remarkable—the discrepancies lie on one side of theory—and this consistency across multiple spectral lines leads to the apparent universality of the fit.

The very recent result [15] stands apart, in part by virtue of its extremely small claimed uncertainty (figure 6). This datum would become consistent with the overall data set if the reported uncertainty were some three to six times the claimed value. Without such an expanded uncertainty, the probability that this point is consistent with the fit of the other points is $P < 10^{-9}$, based upon the 6.1 s.e. discrepancy.

Table 2. Experimental data used in analysis.

Measurement #	Z	Element	Line (eV)	Energy (eV)	σ (eV)	Discrepancy	Reference
1	16	S	w	2461.2735	0.4886	0.6443	[28]
2	16	S	w	2460.6874	0.1465	0.0582	[29]
3	16	S	w	2461.8000	3.0000	1.1708	[30]
4	16	S	w	2460.6410	0.0320	0.0118	[31]
5	16	S	w	2460.6700	0.0900	0.0408	[23]
6	16	S	y	2447.0500	0.1100	-0.0939	[23]
7	18	Ar	w	3139.6000	0.2500	0.0179	[32]
8	18	Ar	w	3139.5830	0.0630	0.0009	[33]
9	18	Ar	w	3139.5517	0.0366	-0.0304	[16]
10	18	Ar	w	3140.1000	0.7000	0.5179	[27]
11	18	Ar	w	3139.5810	0.0050	-0.0011	[15]
12	18	Ar	w	3138.9000	0.9000	-0.6821	[34]
13	18	Ar	x	3126.2830	0.0363	-0.0066	[16]
14	18	Ar	y	3123.5208	0.0362	-0.0136	[16]
15	18	Ar	z	3104.1480	0.0077	-0.0003	[14]
16	19	K	w	3511.4048	0.4972	0.9432	[28]
17	19	K	w	3510.5796	0.1229	0.1180	[35]
18	20	Ca	w	3902.4273	0.1860	0.0496	[29]
19	21	Sc	w	4315.5408	0.1510	0.1284	[35]
20	22	Ti	w	4750.1702	0.9100	0.5261	[28]
21	22	Ti	w	4749.7335	0.1662	0.0894	[35]
22	22	Ti	w	4749.8520	0.0720	0.2079	[8]
23	22	Ti	x	4733.8335	0.1311	0.0327	[9]
24	22	Ti	y	4727.0667	0.1000	0.1294	[9]
25	22	Ti	z	4702.0782	0.0723	0.1036	[9]
26	23	V	w	5204.3904	1.0923	-0.7749	[28]
27	23	V	w	5205.5922	0.5464	0.4269	[29]
28	23	V	w	5205.2644	0.2082	0.0991	[35]
29	23	V	w	5205.1000	0.1400	-0.0653	[17]
30	23	V	x	5189.1200	0.2200	0.3822	[17]
31	23	V	y	5180.2200	0.1700	-0.1064	[17]
32	23	V	z	5153.8200	0.1400	-0.0762	[17]
33	24	Cr	w	5682.6562	0.5209	0.5878	[29]
34	24	Cr	w	5682.3176	0.3978	0.2492	[35]
35	26	Fe	w	6700.7617	0.3621	0.3270	[29]
36	26	Fe	w	6700.7254	0.2010	0.2907	[35]
37	26	Fe	w	6700.9000	0.2680	0.4653	[18]
38	26	Fe	w	6700.4025	0.3172	-0.0322	[36]
39	26	Fe	x	6682.7000	0.2673	0.3661	[18]
40	26	Fe	y	6667.5000	0.2667	-0.0786	[18]
41	27	Co	w	7241.6439	0.6323	-0.4694	[29]
42	32	Ge	w	10 280.3573	0.2715	0.1398	[22]
43	32	Ge	w	10 280.7000	0.2200	0.4825	[19]
44	32	Ge	x	10 259.5155	0.3693	0.6416	[19]
45	32	Ge	y	10 220.9316	0.2275	0.1320	[22]
46	32	Ge	y	10 221.7911	0.3475	0.9915	[19]

Table 2. (Continued.)

Measurement #	Z	Element	Line (eV)	Energy (eV)	σ (eV)	Discrepancy	Reference
47	32	Ge	<i>z</i>	10 181.3324	0.5192	0.9456	[19]
48	36	Kr	<i>w</i>	13 113.8000	1.2000	−0.6705	[55]
49	36	Kr	<i>w</i>	13 115.4500	0.3000	0.9795	[26]
50	36	Kr	<i>w</i>	13 114.7800	0.7100	0.3095	[20]
51	36	Kr	<i>w</i>	13 114.6800	0.3600	0.2095	[21]
52	36	Kr	<i>x</i>	13 091.5300	0.8200	0.6643	[20]
53	36	Kr	<i>x</i>	13 091.1700	0.3700	0.3043	[21]
54	36	Kr	<i>y</i>	13 026.8000	0.3000	0.6835	[26]
55	36	Kr	<i>y</i>	13 026.3000	0.7100	0.1835	[20]
56	36	Kr	<i>y</i>	13 026.2900	0.3600	0.1735	[21]
57	36	Kr	<i>z</i>	12 979.7200	0.6600	0.4544	[20]
58	36	Kr	<i>z</i>	12 979.6300	0.4100	0.3644	[21]
59	54	Xe	<i>w</i>	30 629.1000	3.5000	−0.9512	[24]
60	54	Xe	<i>w</i>	30 631.2000	1.2000	1.1488	[37]
61	54	Xe	<i>y</i>	30 209.6000	3.5000	3.3348	[24]
62	92	U	<i>w</i>	100 626.0000	35.0000	15.1100	[25]
63	92	U	<i>y</i>	96 171.0000	52.0000	1.3700	[25]

The body of experimental literature, arising from many different groups across a range of elements and using quite different experimental excitation and detection methods, is consistent with the approximately Z^4 deviation that we report here. Other authors have considered experimental measurements of QED to deviate from the theories of past work, or have raised questions about specific values of Z [1, 35, 40, 41], but these conjectures have sometimes been reversed in subsequent reports [17, 21], reflecting the scarcity of all- Z data and large uncertainties at the time. Here, both by increasing the accuracy of our own measurement and by performing a meta-analysis of the global data set, we postulate and present statistically strong and systematically consistent evidence for a functional dependence that may relate to specific correlation and Feynman diagrams.

The titanium measurements are the first set of He-like ions in which a highly significant discrepancy has withstood comparison across multiple spectral lines. Previously, investigations typically have either had insufficient signal-to-noise, too narrow a spectral bandpass, or inadequate calibration accuracy needed to show such a pattern of internal consistency. By including extensive data sets from the earlier literature, we minimize the possibility of a specific experimental systematic. By observing and including several lines, we limit the possibility of any asymmetry or line blends from impurities shifting one line in any particular direction.

4. Harmonizing theory and experiment

At present, QED treatment of low- Z and high- Z few-electron systems is undertaken with significantly different starting points and mathematical techniques. This work bridges the two regimes in order to stimulate the development of an improved universal computational methodology. Establishing this is desirable from a fundamental perspective, and crucial for the

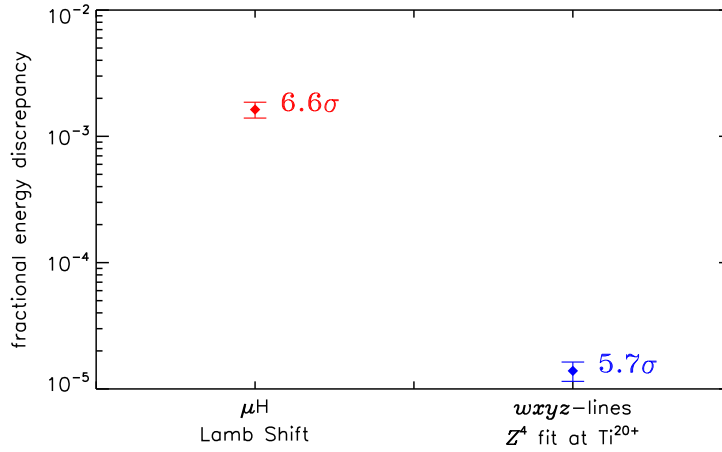


Figure 7. Comparison of the current status of two key discrepancies of QED-sensitive measurements from accepted energy determinations, divided by the magnitude of the energy measured. The scales in different types of experiments are quite different. The error bar shown on each point is the standard error of the measurement. The label gives the ratio of the discrepancy to the uncertainty. The muonic hydrogen Lamb shift energy [48] is compared to the result using the CODATA rms proton charge radius [49]. The He-like $wxyz$ -transition discrepancy is determined as the transition energy difference of our results from the theory of Artemyev [6], as a fraction of that theoretical energy at $Z = 22$.

reliability of a wide range of practical applications. These include new classes of calibration standards based upon hydrogenic and He-like energy levels [14, 42] and the multiplicity of novel laser techniques in high-field and high-energy-density applications [43]. These experimental probes of the quantum vacuum provide the foundations for the determination of current values of the constants of nature, including the Rydberg constant [44] and the fine-structure constant [45]. Finally, this work calls into question the degree to which such atomic physics understanding has converged, and points, like the muonic hydrogen work, to further critical inquiry.

One interpretation of the fact that the same universal fit seems to be consistent for the patterns of discrepancy for w , x , y , and z transitions is that the discrepancy could lie in the computation of the $1s^2$ ground-state energies and Lamb shift. (The QED corrections to the ionization energy scale in proportion to $1/n^3$ is proportional to the electron density at the nucleus (e.g., [11])). The evidence is at least suggestive of a common or similar discrepancy for z ($1s2s\ ^3S_1 \rightarrow 1s^2\ ^1S_0$) and w ($1s2p\ ^1P_1 \rightarrow 1s^2\ ^1S_0$), but there are few measurements of the z transition that meet the accuracy required.

In this case, we could once again have the possibility of a form factor, effective radius, or some such similar interaction, as has been proposed for the muonic hydrogen discrepancy. Indeed, a comparison of the magnitude of the muonic hydrogen discrepancy with the current status for He-like medium- Z systems is intriguing (figure 7). However, extensive theoretical investigation of that anomaly has thus far found no explanation based upon the effective radius, polarization of the nucleus, or shape.

If the $1s$ orbital is responsible, it does not prove an error of one-electron QED, which has been attested in experiments for one-loop terms. It could relate to an interplay between the $1s$ electrons and their correlation energies. The former can be represented by Z^4 terms; the latter by

Z^3 or Z^5 . The various theoretical predictions consider their missing terms to be of different form and power law dependence. What this means is a matter of future work, rather than speculation. We do not impute a failure of two-loop terms, but rather suggest that a cause may lie in two-photon diagrams, or something far more intriguing.

In medium- Z ion transitions, a prior estimate of 0.1 eV was made for the magnitude of missing correlation effects to the QED contributions [6]. This may result in approximately 20 ppm of uncertainty or a miscalculation of atomic transition energies [46]. A recent discussion has highlighted the importance of further investigation of the experimental discrepancies [47]. In the latter development, specific uncalculated terms of order Z^3 are predicted. Theory predicts that the first-order QED corrections (vacuum polarization and self-energy) should scale as approximately Z^4 . Higher-order Feynman diagrams generally include *log* terms or additional powers of $Z\alpha^2$. Correlation terms, especially for two-electron systems, generally involve shielding or coupling, which scales as powers of $(1/Z)$, so the order of the polynomial $n \simeq 4$ is a reasonable hypothesis.

Interestingly (G W F Drake, private communication), the leading term not included correctly by the unified method is of order $\alpha^4 Z^4$, in harmony with the Z^4 scaling that we find for the discrepancy. This can be understood as follows. The second-order relativistic corrections are of leading orders $\alpha^4 Z^6$ and $\alpha^4 Z^5$ (in units of Ry). Both of these are fully accounted for by the unified method. The leading term not accounted for is therefore of order $\alpha^4 Z^4$, which is the next term in the $1/Z$ expansion of the higher-order relativistic corrections. The $\alpha^4 Z^4$ scaling of the uncertainty due to the combined effects of relativity and QED is stated explicitly on p 607 of [11], along with an estimate of the uncertainty from this source.

5. Conclusions and outlook to the future

Over the past several decades, techniques based on the refinement of the understanding of Bragg diffraction, coupled with the development of new methods of producing highly charged ions, have facilitated the measurement of the x-ray spectra of highly charged ions to an accuracy of approximately 10 ppm. Bragg-based measurements at the 1 ppm level raise numerous systematic errors (corrections due to $n \geq 3$ satellites, depth penetration of wavefields, detector registration, and curvature) that have not been adequately addressed in published results to date, and others of less well-defined magnitude in the case of highly charged ions excited by electron collisions (quantum interference shifts) [50, 51].

The quest for high-accuracy absolute spectroscopy in the low- Z ultraviolet-visible regime has advanced technology and provided powerful new tools for research and applications, yielding Nobel Prizes to Hänsch [3] and to Wieman, Cornell, and Ketterle [52]. The work of Hänsch in particular has pushed the uncertainty of the 1S–2S hydrogen transition energy to 4.2 parts in 10^{15} [53]. Core transitions in medium- Z systems cannot be addressed by conventional lasers, so new techniques need to be developed, as discussed here. Efforts in medium- Z systems are limited by available calibration techniques (typically to 15 ppm or so), but with lower fractional accuracy, they can probe similar physics due to the enhancement of contributions [54] (figure 7). A recent paper has provided evidence for a functional discrepancy of measurements of the He-like w line from advanced QED theory [8]. Here we find that this discrepancy also appears in a series of transitions (x , y , z , in addition to w), strengthening the significance of our original finding and allowing the possible origin of the discrepancy in the upper or lower levels

to be investigated. Of course, experimental limitations can be responsible for any discrepancy, but the pattern and independence of the result with data from different sources and groups helps to minimize this possibility. Work from our (and other) groups reported at recent conferences suggests that the trend of discrepancy with theory may be larger (or smaller) than presented here. We encourage more independent research in theory and experiment, and especially recommend blind protocols for analysis.

Our result can be directly related to Z^4 or $Z^6(1/Z)$ expansion terms, for example, or to combinations with multiple terms. In other words, this is suggestive evidence that specific Feynman diagrams involving virtual photons and electron correlation are not fully accounted for. Of course, additional physics with a similar dependence may be present.

References

- [1] Pohl R *et al* 2010 The size of the proton *Nature* **466** 213–7
- [2] Jentschura D 2011 *Ann. Phys., NY* **326** 516
- [3] Udem T, Reichert J, Hänsch T W and Kourogi M 1998 Accuracy of optical frequency comb generators and optical frequency interval divider chains *Opt. Lett.* **23** 1387–9
- [4] Chantler C T and Kimpton J A 2009 Recent developments in x-ray tests of QED *Can. J. Phys.* **87** 769–72
- [5] Johnson W R and Soff G 1985 The Lamb shift in hydrogen-like atoms, $1 \leq Z \leq 100$ *At. Data Nucl. Data Tables* **33** 405–46
- [6] Artemyev A N, Shabaev V M, Yerokhin V A, Plunien G and Soff G 2005 QED calculation of the $n = 1$ and $n = 2$ energy levels in He-like ions *Phys. Rev. A* **71** 062104
- [7] Karshenboim S G and Ivanov V G 2002 Hyperfine structure in hydrogen and helium ion *Phys. Lett.* **B524** 259–64
- [8] Chantler C T *et al* 2012 Testing three-body quantum electrodynamics with trapped Ti^{20+} ions: Evidence for a z-dependent divergence between experiment and calculation *Phys. Rev. Lett.* **109** 153001
- [9] Payne A T, Chantler C T, Kinnane M N, Gillaspay J D, Hudson L T, Smale L F, Henins A, Kimpton J A and Takacs E 2014 Helium-like titanium x-ray spectrum as a probe of QED computation *J. Phys. B: At. Mol. Opt. Phys.* **47** 185001
- [10] Cheng K T and Chen M H 2000 Energy levels of the low-lying states of mid-Z heliumlike ions *Phys. Rev. A* **61** 044503
- [11] Drake G W F 1988 Theoretical energies for the $n = 1$ and 2 states of the helium isoelectronic sequence up to $Z = 100$ *Can. J. Phys.* **66** 586–611
- [12] Plante D R, Johnson W R and Sapirstein J 1994 Relativistic all-order many-body calculations of the $n = 1$ and $n = 2$ states of heliumlike ions *Phys. Rev. A* **49** 3519–30
- [13] Chantler C T *et al* 2013 Testing three-body quantum electrodynamics with trapped Ti^{20+} ions: Evidence for a z-dependent divergence between experiment and calculation, reply *Phys. Rev. Lett.* **110** 159302
- [14] Amaro P, Schlessner S, Guerra M, Le Bigot E-O, Isac J-M, Travers P, Santos J P, Szabo C I, Gumberidze A and Indelicato P 2012 Absolute measurement of the relativistic magnetic dipole transition energy in heliumlike argon *Phys. Rev. Lett.* **109** 043005
- [15] Kubicek K, Braun J, Bruhns H, Crespo Lopez-Urrutia J R and Ullrich J 2012 High-precision laser-assisted absolute determination of x-ray diffraction angles *Rev. Sci. Instrum.* **83** 013102
- [16] Deslattes R D, Beyer H F and Folkmann F 1984 Precision x-ray wavelength measurements in helium-like argon recoil ions *J. Phys. B: At. Mol. Phys.* **17** L689–94
- [17] Chantler C T, Paterson D, Hudson L T, Serpa F G, Gillaspay J D and Takacs E 2000 Absolute measurement of the resonance lines in heliumlike vanadium on an electron-beam ion trap *Phys. Rev. A* **62** 042501
- [18] Briand J P, Tavernier M, Marrus R and Desclaux J P 1984 High-precision spectroscopic study of heliumlike iron *Phys. Rev. A* **29** 3143–9

- [19] MacLaren S, Beiersdorfer P, Vogel D A, Knapp D, Marrs R E, Wong K and Zasadzinski R 1992 Precision measurement of the $K\alpha$ transitions in heliumlike Ge^{30+} *Phys. Rev. A* **45** 329–32
- [20] Widmann K, Beiersdorfer P and Decaux V 1995 Wavelength measurements of the He-like krypton K-shell spectrum *Nucl. Instrum. Methods B* **98** 45–7
- [21] Widmann K, Beiersdorfer P, Decaux V and Bitter M 1996 Measurements of the $K\alpha$ transition energies of heliumlike krypton *Phys. Rev. A* **53** 2200–5
- [22] Chantler C T, Laming J M, Silver J D, Dietrich D D, Mokler P H, Finch E C and Rosner S D 2009 The hydrogenic Lamb shift in germanium, Ge^{31+} and fine structure Lamb shift *Phys. Rev. A* **80** 022508
- [23] Schleinkofer L, Bell F, Betz H-D, Trollman G and Rothermel J 1982 Precision wavelength determination of $2^1P_1 - 1^1S_0$ and $2^3P_1 - 1^1S_0$ transitions in helium-like sulfur ions *Phys. Scr.* **25** 917–23
- [24] Briand J P, Indelicato P, Simionovici A, San Vicente V, Liesen D and Dietrich D 1989 Spectroscopic study of hydrogenlike and heliumlike xenon ions *Europhys. Lett.* **9** 225–30
- [25] Briand J P, Chevallier P, Indelicato P, Zioc K P and Dietrich D D 1990 Observation and measurement of $n = 2 \rightarrow n = 1$ transitions of hydrogenlike and heliumlike uranium *Phys. Rev. Lett.* **65** 2761–4
- [26] Indelicato P, Briand J-P, Tavernier M and Liesen D 1986 Experimental study of relativistic corrections and QED effects in heliumlike krypton ions *Z. Phys. D* **2** 249–50
- [27] Dohmann H D and Mann R 1979 Measurement of the lifetime of the 3P_2 and $^4P_{4/5}$ states in Ar^{16} and Ar^{15} *Z. Phys. A* **291** 15–22
- [28] Aglitskii E V, Boiko V A, Zakharov S M, Pikuz S A and Faenov A Ya 1974 Observation in laser plasmas and identification of dielectron satellites of spectral lines of hydrogen- and helium-like ions of elements in the Na-V range *Sov. J. Quantum Electron.* **4** 500–13
- [29] Aglitsky E V, Antsiferov P S, Mandelstam S L, Panin A M, Safronova U I, Ulitin S A and Vainshtein L A 1988 Comparison of calculated and measured wavelengths of resonance transitions in He-like ions for $Z = 16\text{--}39$ *Phys. Scr.* **38** 136–42
- [30] Cocke C L, Curnutte B and Randall R 1974 X-ray emission from foil-exited sulphur beams *Phys. Rev. A* **9** 1823–7
- [31] Kubicek K, Bruhns H, Braun J, Crespo Lopez-Urrutia J R and Ullrich J 2009 Two-loop QED contributions tests with mid-Z He-like ions *J. Phys.: Conf. Ser.* **163** 012007
- [32] Briand J P, Mossé J P, Indelicato P, Chevallier P, Girard-Vernhet D, Chetoui A, Ramos M T and Desclaux J P 1983 Spectroscopy of hydrogenlike and heliumlike argon *Phys. Rev. A* **28** 1413–7
- [33] Bruhns H, Braun J, Kubicek K, Crespo Lopez-Urrutia J R and Ullrich J 2007 Testing QED screening and two-loop contributions with He-like ions *Phys. Rev. Lett.* **99** 113001
- [34] Neupert M W 1971 Satellite lines in the solar x-ray spectrum *Sol. Phys.* **18** 474–88
- [35] Beiersdorfer P, Bitter M, von Goeler S and Hill K W 1989 Experimental study of the x-ray transitions in the heliumlike isoelectronic sequence *Phys. Rev. A* **40** 150–7
- [36] Chantler C T, Laming J M, Dietrich D D, Hallett W A, McDonald R and Silver J D 2007 Hydrogenic Lamb shift in iron Fe^{25+} and fine-structure Lamb shift *Phys. Rev. A* **76** 042116
- [37] Thorn D B, Gu M F, Brown G V, Beiersdorfer P, Porter F S, Kilbourne C A and Kelley R L 2009 Precision measurement of the K-shell spectrum from highly charged xenon with an array of x-ray calorimeters *Phys. Rev. Lett.* **103** 163001
- [38] Cheng K T, Chen M H, Johnson W R and Sapirstein J 1994 Relativistic configuration-interaction calculations for the ground state and $n = 2$ singlet states of heliumlike ions *Phys. Rev. A* **50** 247–55
- [39] Amaro P *et al* 2014 A vacuum double-crystal spectrometer for reference-free x-ray spectroscopy of highly charged ions *Radiat. Phys. Chem.* **98** 132–49
- [40] Chantler C T 2004 *Radiat. Phys. Chem.* **71** 607–17
- [41] Chantler C T 1992 *PhD Thesis* Oxford University, chapter 2, p216
- [42] Anagnostopoulos D F, Gotta D, Indelicato P and Simons L M 2003 *Phys. Rev. Lett.* **91** 240801
- [43] Wabnitz H *et al* 2002 Multiple ionization of atom clusters by intense soft x-rays from a free-electron laser *Nature* **420** 482

- [44] Weidemuller M 2009 Rydberg atoms: there can be only one *Nat. Phys.* **5** 91–2
- [45] Webb J K, Flambaum V V, Churchill C W, Drinkwater M J and Barrow J D 1999 Search for time variation of the fine structure constant *Phys. Rev. Lett.* **82** 884–7
- [46] Persson H, Salomonson S, Sunnergren P and Lindgren I 1996 Two-electron Lamb-shift calculations on heliumlike ions *Phys. Rev. Lett.* **76** 204–7
- [47] Lindgren I, Salomonson S and Holmberg J 2013 Energy-dependent perturbation theory: possibility for improved tests of quantum-electrodynamics arXiv:1212:6482v1
- [48] Antognini A *et al* 2013 Proton structure from the measurement of 2s-2p transition frequencies of muonic hydrogen *Science* **339** 417–20
- [49] Mohr P J, Taylor B N and Newell D B 2008 CODATA recommended values of the fundamental physical constants: 2006 *Rev. Mod. Phys.* **80** 633–730
- [50] Horbatsch M and Hessels E A 2010 Shifts from a distant neighboring resonance *Phys. Rev. A* **82** 052519
- [51] Sansonetti C J, Simien C E, Gillaspay J D, Tan J N, Brewer S M, Brown R C, Wu S J and Porto J V 2011 Absolute transition frequencies and quantum interference in a frequency comb based measurement of the Li-6, Li-7 D lines *Phys. Rev. Lett.* **107** 259901
- [52] Bennett S C and Wieman C E 1999 Measurement of the 6s–7s transition polarizability in atomic cesium and an improved test of the standard model *Phys. Rev. Lett.* **82** 2484–7
- [53] Parthey C G *et al* 2011 Improved measurement of the hydrogen $1S\sim 2S$ transition frequency *Phys. Rev. Lett.* **107** 203001
- [54] Beiersdorfer P 2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 074032
- [55] Briand J-P, Indelicato P, Tavernier M, Gorceix O, Leisen D, Beyer H F, Liu B, Warczak A and Desclaux J P 1984 Observation of hydrogenlike and heliumlike krypton spectra *Z. Phys. A* **318** 1

Helium-like titanium x-ray spectrum as a probe of QED computation

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Received 19 April 2014, revised 29 June 2014

Accepted for publication 28 July 2014

Published 28 August 2014

Abstract

We discuss the first absolute energy measurements of the intercombination and forbidden transitions (x , y , z) in trapped Ti^{20+} ions to 15 parts per million accuracy. We present new measurements on helium-like titanium, in which the orbital radius is reduced and QED terms are magnified by the increased nuclear charge. The measured transition energies are higher than predicted.

Keywords: helium-like, QED, x-ray spectroscopy, titanium, EBIT

(Some figures may appear in colour only in the online journal)

1. Introduction

Quantum electrodynamics (QED) is one of the most important foundations of modern physics. Recently there have been indications that the theory might be inconsistent with experimental findings. The five standard deviation inconsistency between a 15 ppm (parts per million) measurement of a muonic hydrogen transition and theory [1, 2] has led to four years of intensive research by many groups around the world. A similar inconsistency was raised in the 1998 reevaluation of the fundamental constants of nature [3], wherein the scattering data for the proton size was deemed inadequate within experimental uncertainties. The discrepancy was apparently resolved with improved QED and scattering calculations in the next round of evaluations [4], and a new value of the proton size was recommended based on all data. The large discrepancy in the muonic hydrogen measurement has once again brought into question the proton size, and perhaps QED itself [2]. The discrepancy of 0.42 meV seems well outside possible causes within the Standard Model, which are claimed to have an uncertainty of no more than ± 0.01 meV [5]. Several complementary types of evidence exploring both the nuclear radius and QED spectroscopic discrepancies are summarized in figure 1 including the two-electron system of

helium-like titanium, the subject of the present report. In the case of muonic hydrogen, the lepton orbital radius is reduced by the mass of the lepton, while in the case of highly charged ions the lepton orbital radius is decreased by the increased nuclear charge. While hydrogenic (one-electron) atomic systems represent critical challenges for theory and experiment, helium-like (He-like) atomic systems lie at one of the forefronts of QED research [6] because they display qualitatively new effects (including the ‘two-electron Lamb shift’) which are not present in one-electron ions.

Many QED contributions to atomic energy levels become dramatically larger for high atomic number along an iso-electronic sequence, but lie out of reach of laser techniques. Transitions which lie in the visible region for low- Z systems such as hydrogen become x-ray transitions when the atomic number Z is raised. Alternative theoretical approaches to QED yield different results testable with the precision realized in the present work [12].

This report tests QED by measuring transition wavelengths directly traceable to the length standard. The method is applied to He-like Ti, providing the first absolute measurements of the x , y and z transitions in this ion, and following on from an earlier significant study of the w transition [11]. Tests of QED in helium-like systems often observe the

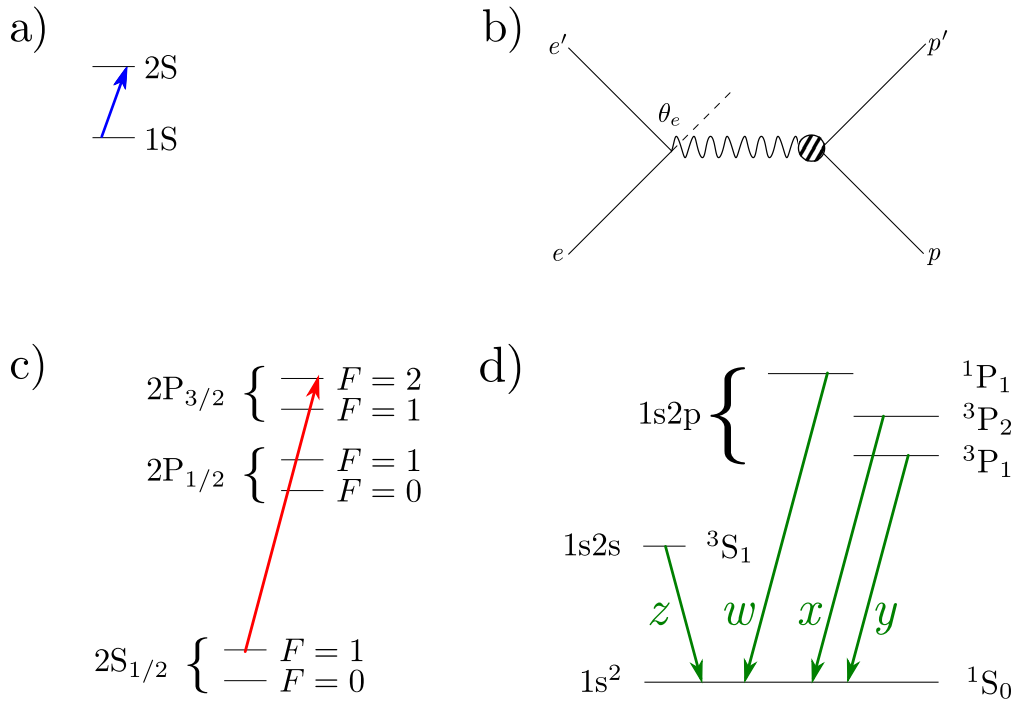


Figure 1. Experimental measurements exploring the discrepancy between QED formulations: (a) the 1S–2S transition frequency in atomic hydrogen [7]; (b) elastic electron–proton scattering [8–10]; (c) the $2S_{1/2}^{F=1} - 2P_{3/2}^{F=2}$ Lamb shift in muonic hydrogen [1]; and (d) the absolute energy of the forbidden (z), resonance (w) and intercombination (x and y) transitions in helium-like ions [11]. Each of these experiments probe QED formulations, and motivate the improvement of theory.

x-ray diffraction profile of the high-intensity spectral lines from the $w(1s^2(^1S_0) \rightarrow 1s2p(^1P_1))$, and less frequently the $x(1s^2(^1S_0) \rightarrow 1s2p(^3P_2))$, $y(1s^2(^1S_0) \rightarrow 1s2p(^3P_1))$ and $z(1s^2(^1S_0) \rightarrow 1s2s(^3S_1))$ transitions.

A key component of the method is the use of an array of ten calibration standards to tie the dispersion function of an x-ray spectrometer to the metre standard with high accuracy. A recent paper has provided evidence for a functional discrepancy of measurements of the helium-like w line from advanced QED theory [11].

Core shell transitions in medium- Z systems cannot be addressed by conventional lasers, so new techniques need to be developed, as discussed here. Efforts in medium- Z systems are limited by available x-ray calibration techniques (typically to 15 ppm or so), but can probe similar physics as the low- Z , UV-visible measurements due to the enhancement of contributions [13]. Here we find that this discrepancy also appears in a series of transitions (x , y , z in addition to w), strengthening the significance of our original finding and allowing the possible origin of the discrepancy in the upper or lower levels to be investigated by possible further theoretical work.

2. Experimental: EBIT

The EBIT [14] at the National Institute of Standards and Technology, Gaithersburg was used to provide highly charged titanium ions. A key advantage of EBITs is the monoenergetic electron beam which can be set to avoid

dielectronic recombination resonances, thereby entirely avoiding the dominant source of satellite line shifts in high precision spectroscopic studies. Another advantage is the absence of Doppler shifts that often limited prior investigations with other sources.

In these experiments the nominal EBIT electron beam energy was set to 10 keV, selected to provide helium-like titanium ions in our case. Trapping and dumping cycle times with total cycle length of 400 ms, and trapping potentials of 200 V–500 V were tuned to maximize the population of helium-like titanium ions and minimize contaminating charge species. A metal vapour vacuum arc [15] was used to produce low charged titanium ions. Nitrogen is introduced to the trap to augment cooling. The trapped ion cloud axial dimension was about 20 mm with a typical electron beam diameter determining the radial extent of the excitation region of 66 μm . Hence the region of x-ray emission is a narrow cylinder in shape, and the detector position can be aligned to give high spectral resolution.

3. Experimental: Bragg diffraction

A Bragg diffraction Johann curved crystal spectrometer is used to collect x-ray spectra (figure 2). This spectrometer has a focusing effect which increases diffracted x-ray flux and minimizes the impact of variations in source location upon measured diffraction angles by over three orders of magnitude compared to flat crystal and von Hamos geometries [16, 17]. The curved crystal produces a circular focal plane (the

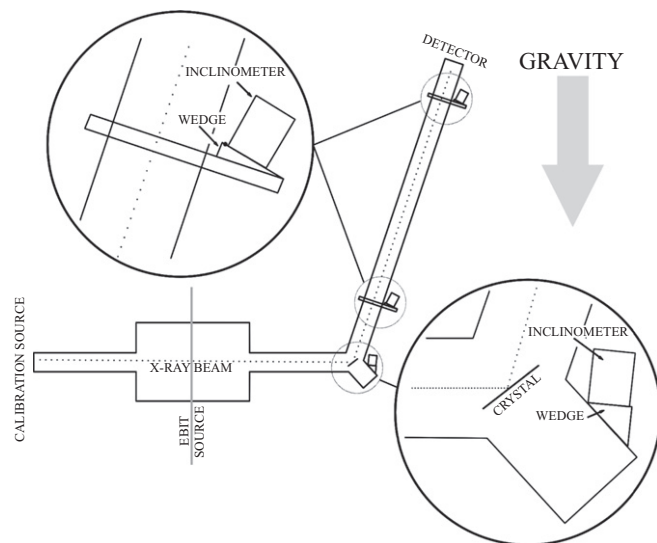


Figure 2. Diagram of the experimental setup showing the location of the gravity referenced inclinometers, the calibration and EBIT sources, and the detector on the Rowland circle. High accuracy x-ray diffraction is used to measure the detailed energy and profile of Bragg diffraction peaks arising from the w , x , y and z transitions of interest in the EBIT.

Rowland circle). Our spectrometer has a mechanical design that keeps the detector at the correct Bragg angle to collect diffracted photons *for all source energies* as the crystal is rotated relative to the source. Spectrometer angles are encoded using gravity-referenced inclinometers, allowing a variety of calibration lines to be used from a wide range of angles. Earlier work [16–19] demonstrated that a thorough understanding of diffraction conditions, dispersion relations and source systematics can allow the determination of transition energies in highly charged ions to a precision limited by statistics [12, 20]. Recent discussions of the history and developments of modelling code and diffraction support these advances [21–23], though the computation of dynamical diffraction penetration of wave fields into the diffracting crystal and the propagation of these profile shifts remains a challenging exercise for packages such as SHADOW, XOP, RAY and others. Together with spectrometer technology improvements, including suppression of spectrometer mechanical systematics, absolute broad energy range calibration and diffraction modelling, this has opened the door for high precision absolute x-ray wavelength measurements by reducing associated experimental uncertainties [24, 25].

Absolute determination of photon energy using Bragg diffraction requires precise determination of lattice parameter and photon diffraction angle. Absolute crystal lattice calibration and comparison of ideally prepared silicon is provided by x-ray optical interferometry (XROI) [26]. A lattice comparator is used to absolutely determine the crystal lattice parameter of silicon, germanium and related materials with the result directly traceable to the metre ($\delta - d$ [27]). For this work a Ge-220 cleaved crystal is used. Diffraction angle determination requires a function to convert measurable spectrometer angles to *absolute* photon diffraction angles.

Reference peaks with energies defined by x-ray reference tables [28] are used as transfer standards from the work of XROI and $\delta - d$ to our curved germanium crystal planes, permitting the transfer of wavelength and angle on an absolute scale. While other work has used one or two such transfer points, a series such as we use here is necessary to identify and constrain systematics and the nonlinear dispersion function to the level required.

The diffracting crystal is a 0.8 mm thick germanium(220) crystal cut to the shape of an equilateral triangle with edge lengths of 25 mm. The crystal is curved by a two-bar crystal bender and mounted so that the crystal pole coincides with the rotation point of the crystal and detector arm. For the collection of the helium-like titanium results presented here the crystal is curved to a radius of 2.18 m which creates a Rowland circle focal plane with a radius of 1.09 m. The distance between the crystal and the EBIT is $663 \text{ mm} \pm 1 \text{ mm}$. The detector arm is a $1365 \text{ mm} \pm 2 \text{ mm}$ long, 65 mm diameter, rigid tube and therefore the crystal to detector distance is fixed for all diffraction angles. In the Johann geometry, different diffraction angles correspond to different distances between the focal plane and diffracting crystal. The radius of curvature of the crystal is selected so that the detector centre intersects the Rowland circle at the angle of diffraction of the helium-like titanium, providing the highest resolution for the transitions being measured. The entire spectrometer is kept in vacuum at a residual pressure of 5×10^{-6} Torr (7×10^{-4} Pa) and isolated from the high vacuum environment of the EBIT by a $125 \mu\text{m}$ thick beryllium window.

The two-bar triangular crystal bender is stable over many years of operation and yields the ideal cylindrical curvature for the relevant crystal planes. The crystal curvature and perfection are measured by topography and interferometry, across the area of the crystal. The uniformity is tested by diffractometry to determine the dispersion function as discussed below, which is the most critical test.

4. Detector

The detector is a multi-wire gas proportional counter constructed and developed at The University of Melbourne [29–31]. A 33 mm diameter circular detector entrance window is covered by $250 \mu\text{m}$ thick beryllium. The interior of the detector is filled with an argon (90%) and methane (10%) gas mixture (P10). X-ray transmission through the entrance window increases from 86% to 90% over the calibration x-ray spectral range of 4–6 keV. The anode wire is maintained at +2150 V dc. A gas pressure of 1.25 atm is used to maximize detector efficiency while maintaining detector window integrity. CCD detectors of nominally higher resolution are often used in other work, but have significant variation of efficiency with energy and flux. Our detectors have demonstrated no significant loss of resolution while having high efficiency and the ability to tune efficiency with gas pressure and type over a suitable energy range.

5. Inclinator

Crystal and detector angles are measured using a series of four independent gravity referenced inclinometers. The angle of an inclinometer is measured by the torque voltage of a pendulum with a *nominal* equation for converting voltage to angle given by $V_{\text{encoded}} = A_2 \times \sin(\theta - A_0) - A_1$, where θ is the angle of the unit to which the inclinometer is attached, A_0 is the intrinsic angular offset of the inclinometer, A_1 is the offset of the encoded voltage and A_2 is the conversion factor between angle and voltage. Each inclinometer used has characteristic parameters which are measured before and after experimental runs to verify temporal stability. The absolute accuracy of each inclinometer reading is ± 0.005 V, at any angle, corresponding to sub-arcsecond accuracies in angle.

6. Calibration source

An electron fluorescence x-ray source is used to provide high-intensity characteristic x-rays. Scandium, titanium, vanadium, chromium and manganese target foils provide characteristic K transition energies (ten transitions of the form $K\alpha: 2p \rightarrow 1s$). The characteristic K transition diffraction angles from Ge-220 planes cover the spectrometer angular rotation range with manganese $K\alpha$ at the high energy limit (smallest angle of diffraction), and scandium $K\alpha$ at the low energy limit (largest angle of diffraction) (figure 2).

Characteristic K peaks of the calibration elements are asymmetric due to underlying atomic processes. An extensive investigation of $K\alpha$ peak shapes was undertaken to provide a robust fitting routine [32] to accurately determine profile peak turning points. $K\alpha$ spectra are fitted using the sum of six Voigt profiles. Centroid locations of $K\alpha_1$ and $K\alpha_2$ peaks, the absolute intensity of the $K\alpha_1$ peak, a common Gaussian width component representative of systematic broadening, and the Lorentzian width of the $K\alpha_1$ peak are left free, while all other parameters were constrained to known standard profile determinations [32]. Figure 3 shows a sample fit of vanadium $K\alpha$ with underlying components. The electron gun spot size at the foil planes was $1.3 \text{ mm} \pm 0.2 \text{ mm}$. Electron beam energy was set to 20 keV for all calibration spectra.

7. Diffraction modelling

Diffraction angles are calculated using curved crystal diffraction modelling code [16, 17] to determine photon energy as a function of photon diffraction angle. Geometric input parameters for determination of the spectrometer dispersion function (crystal lattice parameter, crystal radius of curvature, length of illuminated crystal arc, calibration source to crystal distance, EBIT source to crystal distance, calibration and EBIT source sizes, detector to crystal distance) are taken from measurements of the apparatus prior to and during data collection. The dispersion curve has singularities on the Rowland circle, sensitive to experimental bandpass variations on and off the Rowland circle [16, 17]. Calibration source

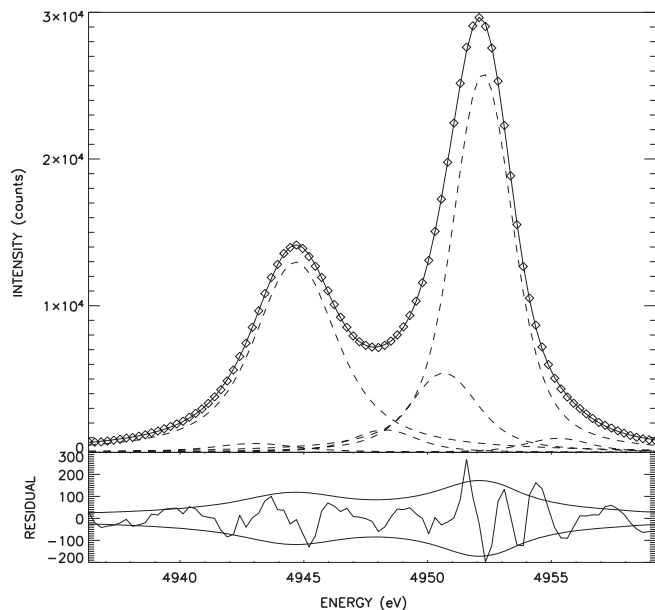


Figure 3. Vanadium $K\alpha$ profile fitted using the high-accuracy methodology provided by [32], fitting the sum of six Voigts with common Gaussian broadening with defined constraints to metrological energies.

wavelength input parameters are taken directly from the work of Deslattes *et al* [28]. Profile peak turning points provide energy fiducials. Inclinometer calibration functions provide four independent measures of the detector arm angle from which a single angle is determined; for example of $41.1199^\circ \pm 0.0006^\circ$ for the w -line. Close agreement between the predicted detector arm angles confirms good self-consistency between the calibration functions of inclinometers and instrumental settings. Final uncertainties in the helium-like titanium transition lines were dominated by uncertainty in fitted peak locations and the inclinometer determined spectrometer angle. Satellite contamination has been argued to be negligible [12].

We emphasize that we perform a calibration of the whole angular range of the spectrometer using multiple reference calibration lines. Both the ion cloud and the calibration sources are well within the Rowland Circle, as required to minimize the influence of source position on spectral response. Unlike flat crystal geometries, where micron translations of source and calibration have direct shift of interpreted positions, the curved crystal geometry is largely insensitive to this. In particular we have modelled such uncertainties as 1.5 mm in source to crystal distance, 20% uncertainty in source size and related possible systematics (see pp 115–300 [33]). In our geometry, these would produce a first-order shift of peak location on the detector of order $(0.1\text{--}0.2) \mu\text{m}$. The collection of similar systematics would lead to an uncertainty of $(0.01\text{--}0.003)$ arc seconds in angle depending upon the configuration used in the experiment (and we used more than one), and these uncertainties correspond to an estimated (negligible) uncertainty of 0.06 ppm. Further, many of these shifts are cancelled in first order by the calibration procedure (see [33]).

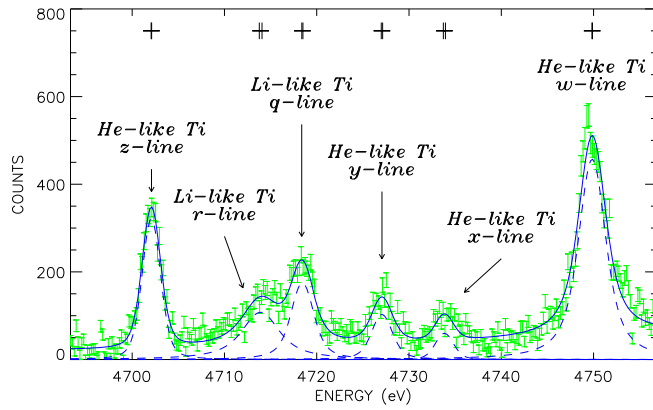


Figure 4. Experimental few-electron titanium spectrum from the EBIT plotted against energy. Raw data (green points with statistical standard error bars) with fitted individual peak profiles (blue dashed) and the full fit including the background (blue line). Centroid locations and uncertainties are shown above each peak as crosses. $\chi_r^2 = 2.9$.

Hence we have uncertainties arising from the reference accuracy of the calibration lines and profiles; from the fits of the data collected from the calibration spectra; from the fits of the data collected from the gravity-referenced inclinometers; and from the overall fit of all of the dispersion function across the range of the spectrometer, and across the range of the detector face. Because the inconsistency of theoretical prediction in the actual geometry is represented as a variance whether due to errors or uncertainties in the calibration reference energy or profile, or in the fits and dispersion function, these uncertainties are included in table 1 in (i–vi) but these are actually dominated by the statistical uncertainty of the individual fits, rather than errors in the calibration reference or dispersion function modelling. In other words, the results are broadly consistent down to the statistical level.

By mapping the whole dispersion function across all angles of the spectrometer we tie down and remove all systematics relating to position offsets, focussing limitations, non-cylindrical curvature, off-axis saddle or spherical curvature, and even anomalous deviations of the calibration suite of characteristic lines tied to the metre. A great advantage of this procedure is that any errors or deviations from these or other sources are reflected in localized or general χ_r^2 and variance of the combined data set. This is as opposed to approaches where a single characteristic line is used, or even two, when anomalous measurement can distort the derived values without an estimate of the systematic error associated with this. This is also as opposed to approaches which use no calibration line but assume a perfect cylindrical unstressed diffracting crystal with zero depth penetration of the quantum mechanical wave field into the crystal (which of course is non-physical).

8. Uncertainties

Figure 4 shows the fitted helium-like Ti spectrum. The six observed peaks correspond to the resonance lines the helium-

like titanium w , lithium-like r , q , and helium-like titanium x , y and z transitions. The w line was analysed in a previous publication [11].

An experimentally determined detector background response function, quantified by calibration of the detector [29–31], is removed prior to the final peak fitting. The fitted function is the sum of six Voigt profiles with a quadratic background, with the instrumental Gaussian broadening common to all lines. Uncertainty is determined by the quadrature sum of contributions deriving from uncertainties in fitted spectral peak locations on the detector, tabulated standard wavelengths, the detector scale factor and inclinometer voltages from Gaussian peak widths.

The final data fit followed Levenberg–Marquardt least-squares analysis using six Voigt peaks, a common Gaussian width and a quadratic background function. Each data point was weighted as, $w_i = (y_i + X)^{-2}$ where y_i is the counting statistic and X represents the background noise observed from the quiescent detector. The r -line width was fixed at 20 channels as indicated by physics (this was a shallow correlated minimum due to the overlap of the q and r weak lithium-like contributions, but the lifetimes of these peaks are known to be similar). Comprehensive grid-searches were additionally performed over the fixed r -line width parameter and the constant background parameter c , to determine the impact of the uncertainty of each on final transition energies.

For an X shot noise of 100 with a one standard error (s.e.) range $X \in [64, 144]$ based on the noise analysis, an r -line width of 20 ± 5 channels and all other fitting parameters free, the final fitted energies and 1 s.e. centroid uncertainties (σ_{centroid}) are listed in table 1. $\sigma_{\text{c-offset}}$ represents the uncertainty in transition energy due to the choice of background function.

Table 1 lists the uncertainty contributions of the final fit, with the calibration function uncertainty in the spectral region dominated by statistics. These uncertainties are summed in quadrature to give a total 1 s.e. uncertainty is 0.0720 eV for the w -line [11] and 0.0723 eV for the z -line. The final uncertainties on the x and y lines are dominated by statistics of the highly charged ion spectra rather than of calibration spectra, yielding uncertainties of 0.1311 eV and 0.1000 eV for the x and y lines respectively.

Taken individually, our measured helium-like transition energies demonstrate significant deviation from the most recent comprehensive *ab initio* theoretical QED formulation [6], with significances of 2.9 s.e. for the w -line, 1.4 s.e. for the z -line, and 1.3 s.e. and 0.3 s.e. for the y - and x -lines respectively. All lie higher than the predictions of theory. The weighted mean of our four deviations from theory (0.138 eV) is non-zero by 3.2 s.e.

The uncertainty in the dispersion calibration function was determined in two different ways, both of which agree very well. First, we estimate the various contributions to the uncertainty in the dispersion function separately (listed in the upper part of table 2). We could add them in quadrature, but this is not strictly correct, as some of the contributions may be mildly correlated and, of course, there could be unanticipated

Table 1. Transition energies with component and final uncertainties. The uncertainty in the absolute energy calibration function is contained within σ_{calib} and is dominated by calibration statistics including that of spectral line determination and clinometer (angle encoding) statistics following Levenberg–Marquardt least squares analysis [11]. The uncertainty in each w , x , y , z centroid (σ_{centroid}) represents the one-standard error (s.e.) centroid uncertainties arising from the fit of the spectral profile from the detector, also dominated by statistics. Additional minor components arise due to detailed investigation of the background function robustness $\sigma_{\text{c-offset}}$ and lithium-like r -line width $\sigma_{\text{r-width}}$. σ_{shot} is the uncertainty arising from the shot noise estimate from the data.

	Ti ²⁰⁺ LINE			
	w	x	y	z
E (eV)	4749.8520	4733.8335	4727.0667	4702.0782
E (eV) [6]	4749.6441	4733.8008	4726.9373	4701.9746
σ_{calib}	0.0650	0.0660	0.0660	0.0670
σ_{centroid}	0.0285	0.1128	0.0748	0.0267
$\sigma_{\text{c-offset}}$	0.0071	0.0096	0.0042	0.0047
$\sigma_{\text{r-width}}$	0.0034	0.0036	0.0010	0.0033
σ_{shot}	0.0089	0.0017	0.0051	0.0006
σ_{Total}	0.0720	0.1311	0.1000	0.0723
σ_{Total}/E (ppm)	15.15	27.69	21.15	15.39

Table 2. Sources contributing to the final uncertainty in E , presented specifically for the w transition. The dominant differences between transition accuracy lie in the statistical uncertainty of the centroid determination, as discussed in the main text. Components below the line are exactly as presented in the main fit. We expand component estimates (i–vi) for contributions to the dominant dispersion calibration function uncertainty, in terms of statistical and systematic components, which were determined directly but are consistent with a summation of components in quadrature. To this one-sigma uncertainty (i–vi) is added in quadrature uncertainties of the centroid fit of the spectrum, an uncertainty from constraining the width of the r component, an estimate of the uncertainty of the determination of the background, and an uncertainty in the estimation of the shot noise, to yield the total uncertainty in E_w .

Sources	Uncertainty	
	(eV)	(ppm)
Statistical—EBIT Data Inclinometry Fit (i)	0.046	9.7
Statistical—Clinometry Calibration (ii)	0.035	7.3
Systematics—Detector Corrections (iii)	0.024	5.1
Systematics—Scale Factor (iv)	0.0026	0.54
Statistical—Detector Calibration Centroids (v)	0.0016	0.3
Systematics—Spectrometer Modelling (vi)	0.00033	0.07
σ_{calib} Dispersion Calibration Function (i–vi)	0.0650	14
σ_{centroid} Statistical—Detector Fit (vii)	0.0285	6
$\sigma_{\text{r-width}}$ Uncertainty- r —Line Width (viii)	0.0034	0.7
$\sigma_{\text{c-offset}}$ Background Uncertainty (c, etc) (ix)	0.0071	1.5
σ_{shot} Uncertainty in Shot noise (x)	0.0090	1.9
Total	0.0720	15.15

sources of additional error. Therefore, we independently estimate the total uncertainty in the dispersion function by recording the ten calibration lines under a variety of angles, and we examine the variance in each of the approximately 30 resulting spectral locations on the detector surface for some ten repeated measurement cycles (of order 300 spectra in total). The latter method gives a slightly (4%) larger uncertainty, which we use in table 2 for σ_{calib} .

In table 2 we present the summary for the w -transition, where we have deliberately expanded the dominant

contribution to detail the component estimates of statistical and systematic contributions to the dispersion (energy) calibration. The two largest contributions (i and ii) are due to the statistical uncertainty in the clinometer readings which enter into the determination of the diffraction angles for both the x-ray calibration lines and the He-like Ti lines. The third largest contribution (vii) is due to the statistical uncertainty in the fit (figure 4). The dominant systematic presented is item (iii), the systematic uncertainty due to detector corrections, includes nonlinearities and channels/mm translational scale [30] which for all lines lies at 5.1 ppm. Further work will doubtless improve this. Systematic errors in the Ti spectral fit (iv, viii, ix, x) were estimated by an extensive investigation of the effect of changing the assumed form of the fit function, weights, and r -line width in the fit. Statistics relating to the centroid determinations of the calibration lines (v) and to the dynamical diffraction theory [16, 17] and functional form of the dispersion relation (vi) are minor.

9. Conclusions and outlook

Our earlier work [11] analyzed only the strongest of the four lines and included data from the literature up through the end of 2011, suggesting a systematic discrepancy from theory with a functional dependence proportional to Z^n . In that previous work [11], only integral coefficients were considered, since most QED terms can be expanded as integral powers of atomic number. The actual minimum occurred for the non-integer optimum of $Z^{3.5}$ [34]. The null hypothesis (that there is no discrepancy from latest theory, or that a constant offset from zero has an offset parameter of 0 eV) disagrees with a normally distributed dataset with a probability of 0.00003 [34]. The new results reported here are in very good agreement with the earlier data set to within uncertainty. This finding eliminates some possible sources of the observed discrepancy at $Z = 22$.

Techniques based on the refinement of the understanding of Bragg diffraction over the past several decades, coupled with the development of new methods of producing highly charged ions, currently enable the measurement of the x-ray spectra of highly charged ions to an accuracy of approximately 10 ppm. Bragg-based measurements at the 1 ppm level raise numerous systematic errors (corrections due to $n \geq 3$ satellites, depth penetration of wavefields, detector registration and curvature) that have not been adequately addressed in published results to date, and others of less well-defined magnitude for the case of highly charged ions excited by electron collisions (quantum interference shifts) [35, 36].

The significance of QED contributions increases with atomic number Z so that investigations at higher energies and atomic numbers are indicated. This can involve other diffracting crystals and crystal planes (e.g. Si 220, Ge 311) and can involve Laue spectrometers; but each of these would be a major undertaking with a multi-year schedule.

These results are the first set of measurements on He-like ions in which a comparison with theory has been undertaken with measurements across multiple spectral lines. All the observed transitions differ significantly, and in the same direction, from the most recent QED calculations. By observing and including several lines we limit the possibility of any asymmetry or line blends from impurities shifting one line in a particular direction.

Acknowledgments

We acknowledge J N Tan, J M Pomeroy and K Makonyi for contributions to general laboratory preparation and for participating in the operation and maintenance of the EBIT or ion injector during this experiment.

References

- [1] Pohl R *et al* 2010 The size of the proton *Nature* **466** 213–7
- [2] Antognini A *et al* 2013 Proton structure from the measurement of 2s-2p transition frequencies of muonic hydrogen *Science* **339** 417–20
- [3] Mohr P J and Taylor B N 2000 CODATA recommended values of the fundamental physical constants: 1998 *Rev. Mod. Phys.* **72** 351–495
- [4] Mohr P J and Taylor B N 2005 CODATA recommended values of the fundamental physical constants: 2002 *Rev. Mod. Phys.* **77** 1–107
- [5] Jentschura U D 2011 *Ann. Phys., NY* **326**
- [6] Artemyev A N, Shabaev V M, Yerokhin V A, Plunien G and Soff G 2005 QED calculation of the $n = 1$ and $n = 2$ energy levels in He-like ions *Phys. Rev. A* **71** 062104
- [7] Parthey C G 2011 Improved measurement of the hydrogen 1S²S transition frequency *Phys. Rev. Lett.* **107** 203001
- [8] Sick I 2003 On the rms-radius of the proton *Phys. Lett. B* **576** 62–67
- [9] Blunden P G and Sick I 2005 Proton radii and two-photon exchange *Phys. Rev. C* **72** 057601
- [10] Bernauer J C *et al* 2010 High-precision determination of the electric and magnetic form factors of the proton *Phys. Rev. Lett.* **105** 242001
- [11] Chantler C T *et al* 2012 Testing three-body quantum electrodynamics with trapped Ti^{20+} ions: evidence for a z-dependent divergence between experiment and calculation *Phys. Rev. Lett.* **109** 153001
- [12] Chantler C T, Paterson D, Hudson L T, Serpa F G, Gillaspay J D and Takacs E 2000 Absolute measurement of the resonance lines in helium like vanadium on an electron-beam ion trap *Phys. Rev. A* **62** 042501
- [13] Beiersdorfer P 2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 074032
- [14] Gillaspay J D *et al* 1995 Overview of the electron-beam ion trap program at NIST *Phys. Scr.* **T59** 392–5
- [15] Brown I and Washburn J 1987 The Mevva ion source for high current metal ion implantation *Nucl. Instrum. Methods Phys. Res.* **21** 201–4
- [16] Chantler C T 1992 X-ray diffraction of bent crystals in Bragg geometry I perfect-crystal modelling *J. Appl. Crystallogr.* **25** 674–93
- [17] Chantler C T 1992 X-ray diffraction of bent crystals in Bragg geometry II non-ideally imperfect crystals, modelling and results *J. Appl. Crystallogr.* **25** 694–713
- [18] Chantler C T 1993 Photographic response to x-ray irradiation I: estimation of the photographic error statistic and development of analytic density–intensity equations *Appl. Opt.* **32** 2371–97
- [19] Chantler C T, Laming J M, Dietrich D D, Hallett W A, McDonald R and Silver J D 2007 Hydrogenic Lamb shift in iron Fe25+ and fine-structure Lamb shift *Phys. Rev. A* **76** 042116
- [20] Chantler C T, Paterson D, Hudson L T, Serpa F G, Gillaspay J D and Takacs E 1999 Precision x-ray spectroscopy at the NIST electron-beam ion trap: resolution of major systematic error *Phys. Scr.* **T80B** 440–2
- [21] Authier A 2013 *X-Ray Standing Wave Technique: Principles and Applications* (Singapore: World Scientific) pp 36–7
- [22] Als-Nielsen J 2008 X-rays and matter—the basic interactions *C. R. Phys.* **9** 479–86
- [23] Uschmann I, Malgrange C and Forster E 1997 Measurement of a bent-crystal rocking curve with oscillations *J. Appl. Crystallogr.* **30** 1150–1
- [24] Paterson D, Chantler C T, Tran C Q, Hudson L T, Serpa F G and Deslattes R D 1997 Absolute calibration of an x-ray spectrometer on the NIST electron-beam ion trap: control, design and systematics *Phys. Scr.* **T73** 400–2
- [25] Gillaspay J D, Chantler C T, Patterson D, Hudson L T, Serpa F G and Takacs E 2010 First measurement of Lyman alpha x-ray lines in hydrogen-like vanadium: results and implications for precision wavelength metrology and tests of QED *J. Phys. B: At. Mol. Opt. Phys.* **43** 074021
- [26] Deslattes R D and Henins A 1973 X-ray to visible wavelength ratios *Phys. Rev. Lett.* **31** 972–5
- [27] Kessler E G Jr, Owens S M, Henins A and Deslattes R D 1999 Silicon lattice comparisons related to the Avogadro project: uniformity of new material and surface preparation effects *IEEE Trans. Instrum. Meas.* **48** 221–4
- [28] Deslattes R D, Kessler E G, Indelicato P, de Billy L, Lindroth E and Anton J 2003 X-ray transition energies: new approach to a comprehensive evaluation *Rev. Mod. Phys.* **75** 35–99
- [29] Kinnane M N, Kimpton J A, de Jonge M D, Makonyi K and Chantler C T 2005 The correction of systematic image deformations inherent to two-dimensional proportional counters *Meas. Sci. Technol.* **16** 2280–6
- [30] Payne A T, Kimpton J A, Kinnane M N and Chantler C T 2009 Simulation and minimization of nonlinear effects in backgammon-type multi-wire gas proportional counters *Meas. Sci. Technol.* **20** 025601
- [31] Payne A T, Kimpton J A, Smale L F and Chantler C T 2010 Optimization of the spatial linearity in backgammon-type multi-wire gas proportional counters: the relevance of charge

- cloud distribution *Nucl. Instrum. Methods Phys. Res. A* **619** 190–7
- [32] Chantler C T, Kinnane M N, Su C H and Kimpton J A 2006 Characterization of K α spectral profiles for vanadium, component redetermination for scandium, titanium, chromium, and manganese, and development of satellite structure for $Z = 21$ to $Z = 25$ *Phys. Rev. A* **73** 012508
- [33] Kinnane M N 2009 Investigations of QED using precision spectroscopy of highly charged titanium ions *PhD Thesis* The University of Melbourne
- [34] Chantler C T *et al* 2013 Testing three-body quantum electrodynamics with trapped Ti^{20+} ions: evidence for a z -dependent divergence between experiment and calculation, reply *Phys. Rev. Lett.* **110** 159302
- [35] Horbatsch M and Hessels E A 2010 Shifts from a distant neighboring resonance *Phys. Rev. A* **82** 052519
- [36] Sansonetti C J, Simien C E, Gillaspay J D, Tan J N, Brewer S M, Brown R C, Wu S J and Porto J V 2011 Absolute transition frequencies and quantum interference in a frequency comb based measurement of the Li-6, Li-7 D lines *Phys. Rev. Lett.* **107** 259901

Detection of faint X-ray spectral features using wavelength, energy, and spatial discrimination techniques

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Available online 22 May 2007

Abstract

We report here our methods and results of measurements of very low-signal X-ray spectra produced by highly charged ions in an electron beam ion trap (EBIT). A megapixel Si charge-coupled device (CCD) camera was used in a direct-detection, single-photon-counting mode to image spectra with a cylindrically bent Ge(220) crystal spectrometer. The resulting wavelength-dispersed spectra were then processed using several intrinsic features of CCD images and image-analysis techniques. We demonstrate the ability to clearly detect very faint spectral features that are on the order of the noise due to cosmic-ray background signatures in our images. These techniques remove extraneous signal due to muon tracks and other sources, and are coupled with the spectrometer wavelength dispersion and atomic-structure calculations of hydrogen-like Ti to identify the energy of a faint line that was not in evidence before applying the methods outlined here.

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PACS: 32.30.Rj; 39.30.+w; 07.05.Kf; 07.85.-m

Keywords: X-ray spectroscopy; Highly charged ions; CCD imaging; Crystal spectroscopy; Cosmic ray removal

1. Introduction

Studies with highly charged ions are motivated by the growing interest in the fundamental mechanisms of radiation interactions with extreme states of matter and their wide array of potential applications. In the course of a program of precision X-ray metrology at the NIST Electron Beam Ion Trap, a wide variety of atomic systems have been studied that exhibit X-ray signal strengths spanning several orders of magnitude. In recent experiments we have used wavelength-dispersive and energy-dispersive X-ray spectroscopy to observe well-resolved intense resonance transitions as well as less-intense features while acquiring the spectra of hydrogen-like and helium-like medium-Z atomic systems.

In this report, we focus on the methods and instruments we have employed for obtaining good signal-to-noise (S/N) X-ray spectra in situations of very low signal strength. This has required the additional step of spatial discrimination by event size, measured in detector pixels of an area detector. As an example, these techniques are then applied to the observation of a faint X-ray line whose energy is obtained by reference to intense, nearby resonance lines of hydrogen-like Ti. More generally, these strategies can find use in other imaging and spectroscopic applications where features of interest are modest compared to the noise level.

2. Experimental method

In the present work, high resolution and favorable S/N are obtained in X-ray spectra by applying a combination of discrimination techniques. In the course of studying hydrogen- and helium-like Ti spectra, titanium is loaded into the NIST EBIT using a newly designed metal vapor

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vacuum arc [1] where it is trapped, highly ionized, and excited by an axially centered electron beam (25.7 kV, 150 mA). X-rays satisfying the diffraction condition of a Ge(220) cylindrically bent [2] crystal spectrometer [3] are dispersed and registered by a 1152 pixel $\times$ 1242 pixel CCD area detector used in direct detection mode. Individual images were integrated for 90 s. This insured the validity of single-photon counting per pixel while keeping the integrated thermal background of the chilled CCD (-40°C) well below registered X-ray signals. Before and after a series of 80 images, a background image was acquired with the EBIT source high-voltage turned off.

A recorded image can be represented by a matrix of numbers wherein each element represents the charge accumulated in a particular pixel during the acquisition, digitized to 16 bits. The pixel intensities have contributions from many sources, many of which are relatively large but unrelated to the physical processes under study. Included in our raw CCD images are contributions due to: (1) X-rays from the EBIT that are diffracted by the crystal spectrometer and registered directly; in general, this could include higher-order diffraction contributions; (2) thermally integrated charge, superimposed with intrinsic fixed-pattern noise as well as patterns due to previous radiation history (damage) of each pixel; (3) electronic readout noise; (4) charge collected in CCD pixels due to energy losses by in-transit cosmic rays; and (5) a smooth, frame-to-frame level drift due to long-term temperature changes of laboratory acquisition electronics.

The following image manipulation and processing techniques can filter out sources (2)–(5) as well as 2nd-order diffracted X-rays, permitting the observation of even very faint, low-count-rate signals of the order of a mHz. A histogram of the pixel values of raw images is dominated by source (2) noise, and is largely removed by subtraction of a “source-off” image matrix from each of a series of images taken while the EBIT was “on” and producing the X-rays of interest. Any global level drift that may have occurred during a long measurement interval is then removed by an offset that aligns the histograms of pixel values of each frame. These histograms of background-subtracted images are dominated by a large number of pixel values that statistically fluctuate around zero, with a small number of pixels with higher values that are due to the X-rays of interest from the source under study as well as unwanted tracks due to energy losses from secondary cosmic rays (penetrating muons [4]). As usual in single-photon detection studies, the condition to achieve high S/N is that the real X-ray photons produce a signature that can be easily separated from the low-level noise. The energy resolution of our CCD is relatively coarse; for example, it is measured to be about 230 eV at Fe $K\alpha$ (6.4 keV). Using the energy-dispersive content of the difference image, a prediscrimination is performed by replacing all pixel values that are well below the signal levels of interest with zero. This leaves mostly zero pixel values in each frame, permitting easy identification and discrimination of “clus-

ters.” A cluster is an event defined as essentially an island of one or more non-zero contiguous pixels surrounded by pixels of zero intensity.

Since the incident signal rate of interest is quite low in the present study, the cosmic-ray background signal is comparable to that from faint lines in the spectra. This background cannot be entirely removed by single-pixel energy-dispersive analysis in those cases where the energy deposited per pixel by the cosmic particle in transit is digitized with values similar to those falling in the energy window of the crystal spectrometer. Hence, we have imported a technique to identify and discriminate against multi-pixel events that we previously developed to analyze X-ray pin-hole image data from an electron cyclotron resonance ion source [5]. The algorithm finds clusters by recursively checking the vertical and horizontal nearest-neighbor pixels and tagging them if there is non-zero signal present. The number of pixels per cluster, and summed values of each pixel of the cluster, are tabulated for possible discrimination against cluster size or total energy. In the image matrix, the summed intensity is placed in the intensity-weighted center of the pixel coordinates, and the remaining pixel values within that cluster are replaced with zero. By additionally applying this spatial-discrimination technique, most tracks due to muons are eliminated while real X-ray events occupying more than one pixel (a few percent of the total) are added to the accounting that would have been excluded in single-pixel discrimination.

After applying these energy- and topological-discrimination techniques for enhancing S/N , the wavelength-dispersed spectrum is analyzed. In general, energy scales are established with calibrated angle-encoding schemes, X-rays of known or calculated wavelengths, modeling of crystal dispersion and source-detector geometry, relative X-ray or angle standards, or some combinations of the above. In the present work, the crystal dispersion and spectrometer geometry are used to identify two bright resonance lines of hydrogen-like Ti. The local energy scale thus established is then used to estimate the energy of a faint (mHz count rate) line that was not evident before applying energy and cluster discrimination.

3. Experimental results

X-ray emissions from highly ionized titanium were studied using a tunable X-ray spectrometer. Coarse tuning is provided by encoding the central screw of the spectrometer sine drive. For the present measurement, the encoder was set to correspond to a nominal X-ray energy of 6.5 keV, motivated in part by observation of unresolved structure in this region using a high-purity Ge detector.

Under the EBIT conditions described in Section 2, a series of 90 s images was acquired, usually in groups of 80, for a total integration time of about 64 h. Difference images were created, any drift reset, and prediscrimination performed by setting to zero all pixels with digitized values < 40 (relative units). From an energy-dispersive calibration

of our CCD, 6.5 keV X-rays are digitized to a value of around 250. This value/event could be distributed into more than one pixel, hence the selection of an asymmetric discrimination interval in the next step.

In the left panel of Fig. 1, we show a 250 pixel $\times$ 400 pixel region of summed CCD frames after replacing each pixel of each frame with either a 1 or 0 depending on whether its digitized value falls into the interval of 170–270. The right side of the figure shows the result of discriminating against the same range of digitization values, but on cluster values rather than individual pixel values. In addition, *all clusters* of size > 3 pixels were also eliminated as probably due to cosmic ray signatures. Fig. 2 compares the spectra derived from these two processed images by column summing the pixel values for the regions shown plus an additional 400

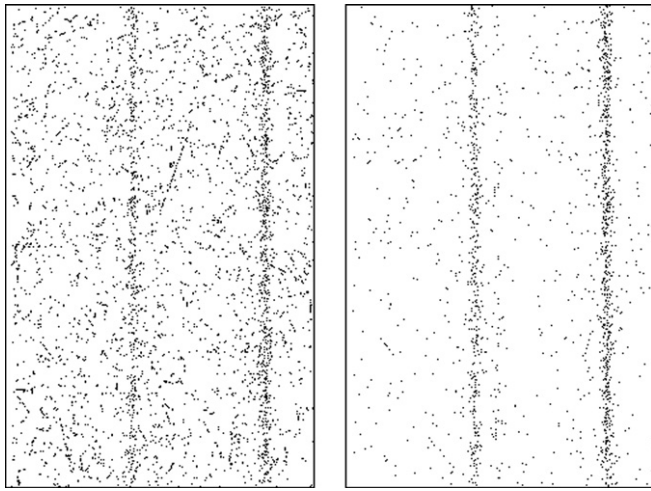


Fig. 1. A 250 pixel $\times$ 400 pixel region of the CCD image, before (left) and after (right) applying the cluster algorithm described herein.

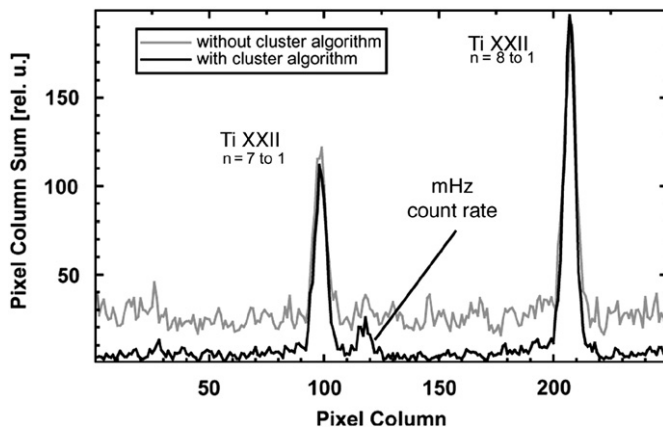


Fig. 2. X-ray spectra due to summing values within each CCD pixel column, before and after accounting for and discriminating against cluster value and size. Note that after application of the spatial-discrimination algorithm, noise is decreased, signal is increased, and the peak labeled “mHz count rate” is now discernible.

contiguous pixel rows for better statistics. Before column summing, the image was rotated 1° since the CCD columns were not exactly perpendicular to the plane of dispersion established by the orientation of crystal planes. Note that 45° muon tracks remain in the right frame; these could be removed by extending the cluster algorithm to also seek along diagonal directions.

4. Discussion

For the present experimental configuration, the source, detector, and crystal geometry were modeled and ray tracing was used to predict the local dispersion. The source-to-crystal distance was 47.2 cm and the crystal-to-detector distance 40.3 cm. The radius of curvature (R_c) of the crystal was determined on the bench using parallel laser beams that focused to $R_c/2$. For this measurement $R_c = 223.5 \text{ cm} \pm 1.3 \text{ cm}$. Ray tracing gives a dispersion of 0.29 eV/pixel ; this number is robust at the level of two significant figures to within dimensional measurement uncertainties. The two bright peaks in the spectrum were fit to Gaussian functions and are separated by 108.6 pixels, or 31.5 eV calculated using the dispersion and nominal pixel size of $22.5 \mu\text{m}$. These peaks are found to be less than 2 eV wide, characteristic of resonant transitions in highly charged ions. Their energy separation compares quite favorably with the 31.6 eV separation of the $n = 8$ to 1 and $n = 7$ to 1 resonance lines of hydrogen-like Ti (using the corresponding spin-orbit-split components) from atomic-structure calculations [6,7]. Using this assignment and the local dispersion thus established, the energy of the faint line is extrapolated to be $6496.5 \text{ keV} \pm 0.4 \text{ eV}$, with the peak centroid dominating this estimate of uncertainty. While it is not the intent of this report to pursue identification of this particular faint line, its energy does correspond to a prominent transition in (Nickel-like) Fe XX, a possible trace contaminant in the ion trap.

5. Conclusion

A variety of techniques are available for observing, calibrating, and identifying features within high-resolution X-ray spectra. We present here a set that finds utility in cases where high resolution, good signal-to-noise, and moderate precision are needed within a low-signal, high-background environment. In particular, the present example required that energy- and wavelength-dispersive spectroscopy be combined with spatial discrimination of clusters to observe and determine the energy of a faint X-ray feature with intensity on the order of the cosmic-ray background in our spectra.

For practical reasons, techniques for very high-precision wavelength determination (not detailed here) are usually reserved for more intense X-ray transitions. Nevertheless, the observation and identification of faint features in X-ray spectra can provide insight into important atomic processes

where asymmetrical branching ratios favor non-radiative decay channels.

References

- [1] G.E. Holland, C.N. Boyer, J.F. Seely, J.N. Tan, J.M. Pomeroy, J.D. Gillaspay, *Rev. Sci. Instrum.* 76 (2005) 073304.
- [2] A. Henins, *Rev. Sci. Instrum.* 58 (1987) 1173.
- [3] S. Brennan, P.L. Cowan, R.D. Deslattes, A. Henins, D. Lindle, B.A. Karlin, *Rev. Sci. Instrum.* 60 (1989) 2243;
- D. Paterson, C.T. Chantler, C.Q. Tran, L.T. Hudson, F.G. Serpa, R.D. Deslattes, *Phys. Scripta T* 73 (1997) 400.
- [4] D. Groom, *Exp. Astronomy* 14 (2002) 45.
- [5] E. Takacs, B. Radics, C.I. Szabo, S. Biri, L.T. Hudson, J. Imrek, B. Juhasz, T. Suta, A. Valek, J. Palinkas, *Nucl. Instr. and Meth. B* 235 (2005) 120.
- [6] M.F. Gu, in *AIP Proceedings* 730 (2004) 127.
- [7] G.W. Erickson, *J. Chem. Ref. Data* 6 (1977) 831.

Data acquisition system development for the detection of X-ray photons in multi-wire gas proportional counters

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Available online 16 May 2007

Abstract

A new data acquisition system coupled to a backgammon-type gas proportional counter capable of single-photon counting over a wide range of count rates has been developed and replaces a CAMAC-based system. The new apparatus possesses improved architecture, interface technology, speed and diagnostic capability. System efficiency and throughput is significantly improved, especially in addressing earlier problems of hardware buffer downloads containing zero or repeat data and inefficient gating control. The new system is a PXI-based data acquisition apparatus including additional electronics, controlled by a graphical programming environment. It allows development of superior diagnostic tools for system optimisation and more stable performance. System efficiency is improved by 10% over a wide range of count rates (0.5 Hz–50 kHz). For the Backgammon Detector type, this represents a significant improvement in performance and applicability over previous systems. Characteristic and few-electron spectra collected on the new acquisition system are illustrated.

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PACS: 07.05.Hd; 07.50.Qx; 07.85.Fv; 07.85.Nc; 32.30.Rj; 34.80.Dp

Keywords: Data acquisition; X-ray detectors; Photon counting; Electronic signal processing; X-ray spectroscopy

1. Introduction

Coupled to the wide variety of sensors and detectors, analogue and digital signal processing and data acquisition has played an essential role in experimental physics. Recent development of digital processing systems where raw signals are directly digitised and processing is software based [1–3] are beginning to show an impact, but current trends complete most of the signal processing prior to digitisation. These data acquisition systems are still crucial and continue to play an important role in experimental physics.

The X-ray Optics group at the University of Melbourne have described a Johann-type curved crystal X-ray spectrometer that was employed for critically testing

Quantum Electrodynamics in highly charged medium-Z systems [4,5]. A backgammon-type multi-wire gas proportional counter (MWPC) was used to detect X-ray photons in two dimensions using a combination of resistive and capacitive charge division. We here detail a new low-cost, high performance data acquisition system overcoming speed and buffer limitations for Backgammon Detector applications.

2. Earlier operation

The system acquires four signals from the detector (for every photon detected) to achieve two-dimensional encoding. The electronics and data acquisition system are designed to cope with a wide range of count rates (<0.5 Hz and >50 kHz) and discriminates against signals originating from low or high-energy photons.

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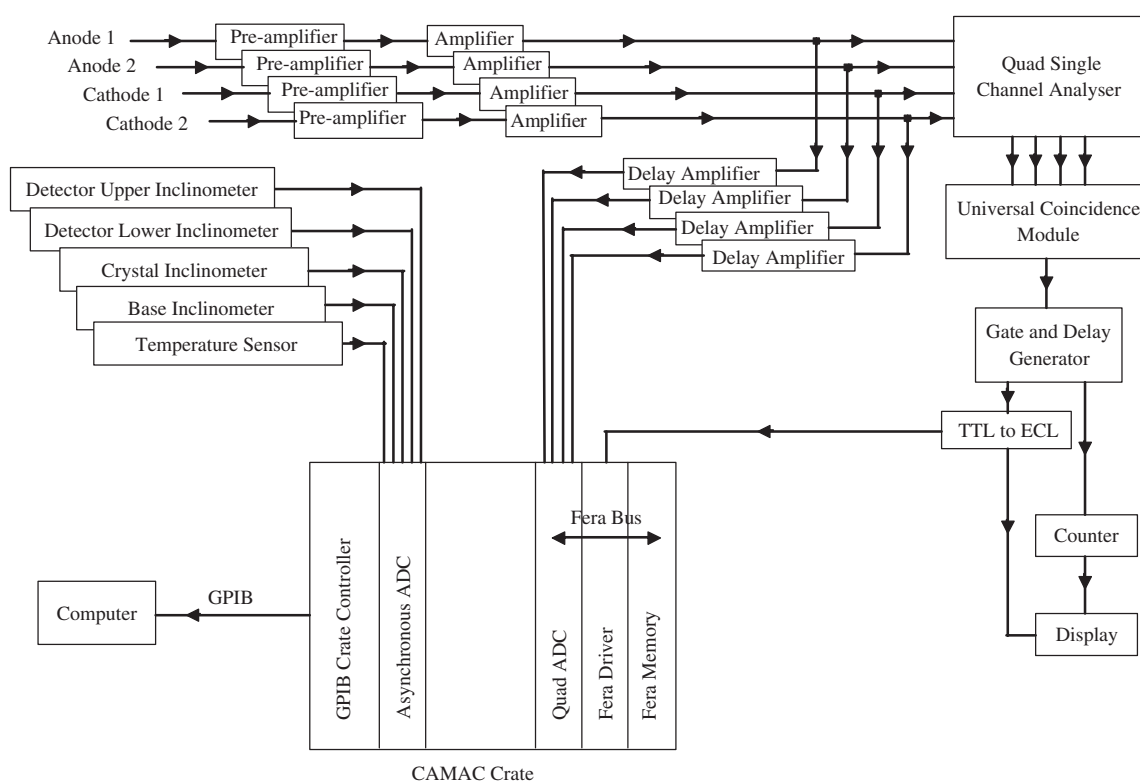


Fig. 1. Schematic of the prior data acquisition system: detector signal processing electronics, inclinometers, Pt resistance temperature sensor and a CAMAC data acquisition chassis controlled by a PC. The control software is K-max version 6.6.1f (Sparrow Inc., USA).

An expanded electronics and data acquisition system acquires inputs from the experimental spectrometer in addition to the detector acquisition system [4]. The additional instrumentation includes four inclinometers (to collect spectrometer theta, 2θ and base angle data) and a Pt resistance temperature sensor. This data acquisition system is shown in Fig. 1. The detector signal acquisition is triggered by the electronics on a coincidence condition and data are simultaneously acquired on four channels. Detector signal processing electronics, data acquisition configuration and operation are described in detail elsewhere [6]. Signals do not require simultaneous sampling, so a fast multiplexer coupled to a scanning A/D converter (16 bits resolution without S/H circuitry) is used (Kinetic Systems model 3516). Each channel acquisition requires $250\mu\text{s}$ (therefore, five channels require 1.25ms) so individual rates are kHz or pooled sampling rates of $100\text{--}500\text{Hz}$. Inclinometer and temperature channels are asynchronously scanned while the hardware buffer is filled with detector data. The system digitises detector and sensor data, stores and processes raw data, and displays detector and spectrometer position information. These functions were programmed using the instrument control and data acquisition software program K-max (Sparrow Inc., version 6.6.1f).

3. Issues for development

The previous system (Fig. 1) performed adequately, however under certain circumstances deficiencies were

apparent. Due to asynchronous digitisation, inclinometer and temperature signal acquisition was dramatically compromised by high detector fluxes. During spectrometer calibration, detector count rates range from 500Hz to 10kHz . Multiple detector data transfers across the CAMAC-PC interface commonly occur each second, resulting in interruption to inclinometer data acquisition.

Coupled with this restriction is the requirement that control commands from the PC be transmitted across the interface, further slowing acquisition time. Thirdly, the data acquisition program accessed a number of external subroutines essential for sorting and processing but in an inefficient manner. These three aspects combined to limit the acquisition of the inclinometer/temperature data in this operational mode to $1\text{--}100\text{Hz}$.

Transfer of data from hardware buffer is commonly facilitated by a single block transfer of the entire buffer contents across the CAMAC-PC interface. This apparently efficient data transfer method is compromised if the buffer is only partially filled during a fill-and-transfer cycle, by significant amounts of zero or old data being transferred along with the newly added data. Algorithms can be run post-acquisition to search for zero or duplicate data, but are a needless complication. Efficient, simple and robust diagnostic tools are essential when analysing signal output for system optimisation and problem solving. The earlier control software restricted the system's 'real-time' diagnostic capability and considerable effort was required to generate diagnostic software routines for signal, digitisa-

tion and data transfer analysis. Hence several limitations affected the prior performance of the detector and inclinometer/temperature acquisition subsystems.

4. New apparatus

The new data acquisition system includes four additional linear gate and stretchers, an extra gate and delay generator and a new data acquisition chassis (Fig. 2). The chassis is a PXI-based system (National Instruments model NI PXI-1031) with two digitisers. The first is a 3 MHz four channel simultaneously sampling 14-bit digitiser (NI PXI-6132) used for detector data acquisition. The second, for inclinometer and temperature data acquisition, is a 1.25 MHz 16 bit 16 channel scanning digitiser (NI PXI-6250). Four linear gate and stretchers (Ortec model 542) sample-and-hold the amplified, shaped and delayed signals. The output from the first gate and delay generator (Ortec model 416A), indicating a coincident event, triggers the input gate for each linear gate and stretcher. The second gate and delay generator (Ortec model 416A) triggers the detector data digitiser. Precise timing of all trigger pulses is required for the system to function optimally.

The PC is remotely connected to the PXI chassis via a high-speed serial MXI-4 interface (National Instruments model NI PXI-PCI833x) that is capable of a sustained data transfer rate of 78 MB/s. In addition to the main function of hardware control, the software program LabVIEW (National Instruments, version 7.1) is used to transfer, store, process and display the data. Test signals generated from the pre-amplifiers were used to optimise the signal processing electronics. Further testing assessed the functionality, performance, stability of the new acquisition system.

5. Results and discussion

Good statistics are vital for highly precise energy assignments. After optimisation of the signal electronics, the initial assessment of the data acquisition system was successful, and a number of details became apparent that were previously undetected due to the limited diagnostic capability in the CAMAC-based system. Robust diagnostic tools are needed to analyse signal output for system optimisation and problem solving. The new control software addresses the system's 'real-time' diagnostic capability and generates diagnostic software routines for signal, digitisation and data transfer analysis. The new system easily interrogates individual channels, sources of noise contributions, buffer errors and impedance mismatch by providing all outputs quickly and independently. Fast sampling rates assess spectrometer mechanical robustness by the inclinometer frequency spectrum. For example, delay and gating optimisation and impedance mismatch issues were all much more readily identified. Zero and repeat data problems previously observed in the CAMAC-based hardware were avoided by removing the hardware buffer.

The acquisition efficiency of the new system was stable at $98 \pm 0.5\%$ tested over the counting rate range 1 Hz–50 kHz. This is a significant improvement over the old system where the data acquisition signal loss was $>10\%$ for detector data only acquisition and was count-rate dependent.

A backgammon-type MWPC coupled to a Johann spectrometer X-ray spectra collected data both at low and moderate fluxes demonstrating the versatility of the system. Fig. 3 illustrates clean two-dimensional V K α characteristic spectra (following Refs. [7,8]). This was recorded at 3.3 kHz. High quality is emphasised in the histogram (Fig. 4). Fig. 5 shows a single helium-like

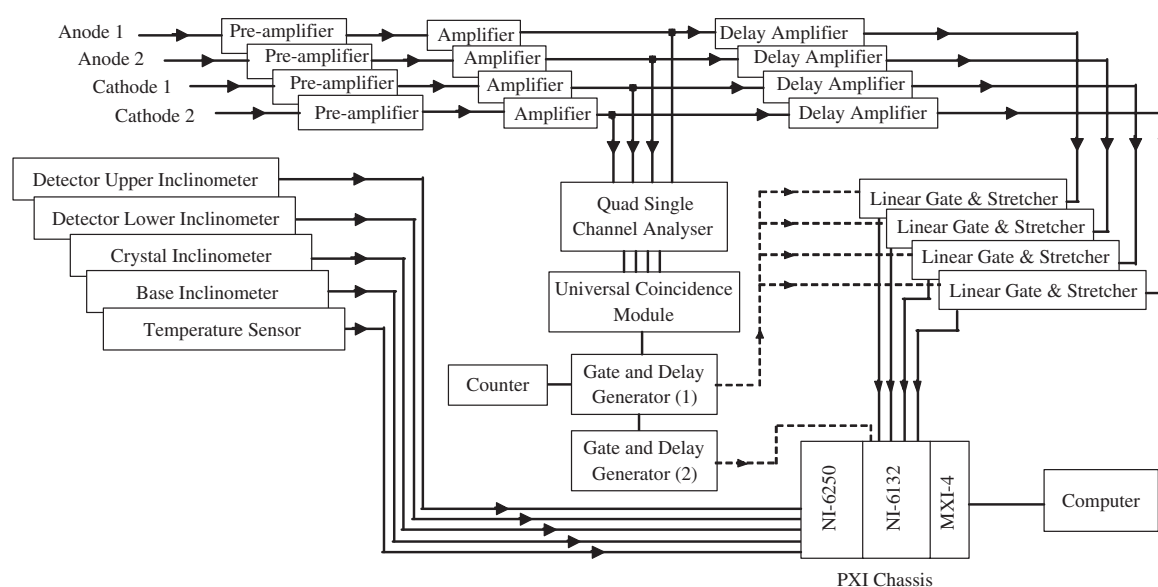


Fig. 2. A schematic of the new data acquisition with the addition of four linear gate and stretchers and a new PXI chassis controlled by the commercial software program LabVIEW. The dotted lines denote the trigger lines.

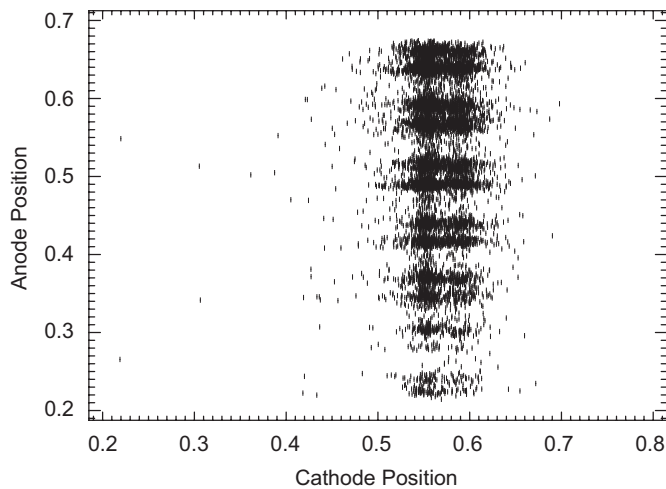


Fig. 3. Detector image of characteristic V K α 1 and V K α 2 doublet monochromated by a Johann curved crystal spectrometer.

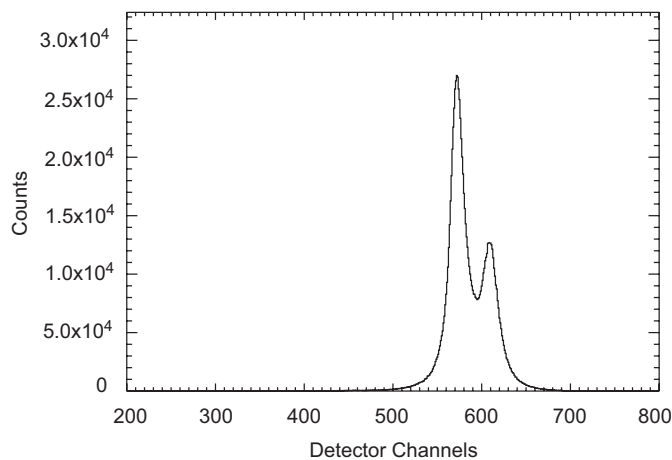


Fig. 4. Histogram of the characteristic V K α output showing well-separated peaks. This spectrum was accumulated at 3.3 kHz in 5 min.

titanium spectrum collected from the Electron-Beam Ion Trap facility at NIST, Gaithersburg, extracted from an experiment covering several days. This spectrum was recorded from a single-data file collected at ~ 0.6 Hz. Background noise levels can dominate. The main peaks are nonetheless clear in the data despite the low signal. This is a useful test illustration of the data acquisition system. Data integrity is often a significant problem with such low count rates especially in a (hardware) buffer-controlled download; this illustration shows an extreme of such a test application, in a quite different regime compared to Fig. 3 and with high resolution (limited by X-ray diffraction

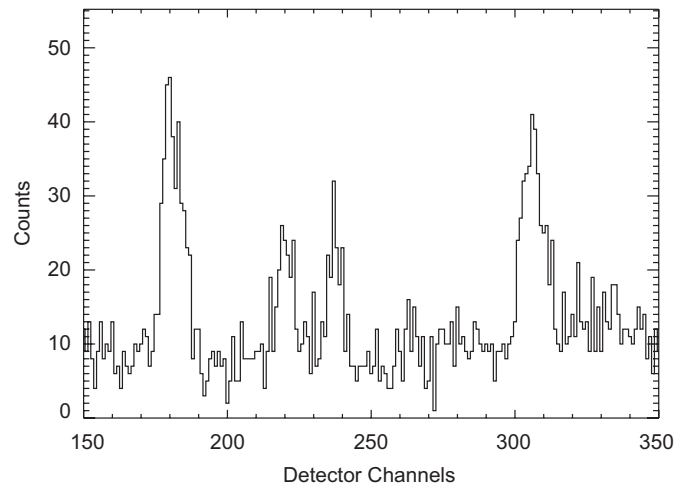


Fig. 5. Histogram of a single He-like titanium spectrum. Data collection time was 2.3 h at approximately 0.6 Hz. The full data set collected data for several days.

instrumental widths) showing a clean low background from all causes including dataway losses and coincidence failures.

The new control system coupled with our signal acquisition electronics is a significant innovation for *backgammon detector* applications generally. In particular, we obtain significantly superior performance compared to an established system; and a dramatic improvement of diagnostic capability and correction time, especially in an on-line experimental situation. We acknowledge the ARC and MNRF in supporting this research. E.T. and B.R. were partially supported by the Hungarian Science Fund (No: OTKA T046454).

References

- [1] A. Laptev, S. Nakamura, H. Harada, Nucl. Instr. and Meth. A 557 (2006) 621.
- [2] F.V. Levchanovski, B. Gebauer, E.I. Litvinenko, A.S. Nikiforov, V.I. Prikhodko, Ch. Schulz, Th. Wilpert, Nucl. Instr. and Meth. A 529 (2004) 413.
- [3] R.J. Scott, R.P. Rassool, M.N. Thompson, D.V. Webb, Nucl. Instr. and Meth. A 539 (2005) 191.
- [4] C.T. Chantler, D. Paterson, L.T. Hudson, F.G. Serpa, J.D. Gillaspay, E. Takacs, Phys. Rev. A 62 (2000) 042501.
- [5] C.T. Chantler, D. Paterson, L.T. Hudson, F.G. Serpa, J.D. Gillaspay, R.D. Deslattes, Phys. Scr. T73 (1997) 87.
- [6] J.A. Kimpton, M.N. Kinnane, C.T. Chantler, Rev. Sci. Instrum. 77 (2006).
- [7] M.N. Kinnane, J.A. Kimpton, M.D. de Jonge, K. Makonyi, C.T. Chantler, 16 (2005) 2280.
- [8] L.F. Smale, et al., Radiat. Phys. Chem. 75 (2006) 1559.



Optimisation of the spatial linearity in backgammon-type multi-wire gas proportional counters—The relevance of charge cloud distribution

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ARTICLE INFO

Available online 21 December 2009

Keywords:

Spatial linearity
MWPC
Detector modelling
X-ray spectroscopy

ABSTRACT

The backgammon-type multi-wire gas proportional counter (MWPC) enables the detection of X-ray photons in two dimensions with a high degree of spatial linearity. An accurate simulation of the detector geometry is developed to further optimise the spatial linearity achievable, by modelling the ideal linear output and through mapping of the experimental residual signature. Three models are presented, each achieving considerable improvements on key linearity measures over previous work, and providing strong evidence for the dependence on charge cloud distribution. Linearity to micron levels across 24 mm are demonstrated for MWPCs.

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1. Introduction

The science of spectroscopy requires precision instrumentation capable of highly linear and spatially resolved response. X-ray spectroscopy additionally requires linearity with respect to energy and intensity, and hence the ability to accurately resolve spectra by energy is paramount.

Since the invention of the multi-wire gas proportional counter (MWPC) by Charpak in 1968 [1], proportional counters have been of fundamental importance not only to the fields of nuclear and elementary particle physics, for which they were developed, but to many other areas such as X-ray spectroscopy, protein crystallography, and medicine [2–5]. The ability of such devices to provide fundamental insight into so many fields of science, eventually led to the award of the 1992 Nobel Prize in Physics to Charpak, ‘for his invention and development of particle detectors, in particular the multiwire proportional chamber’.¹

At the University of Melbourne, high precision tests of Quantum Electrodynamics (QED) have been undertaken using a Johann-type curved crystal spectrometer coupled to an Electron Beam Ion Trap (EBIT) [2,6]. The EBIT produces highly charged ions, uncontaminated by other elements or charge states, and greatly limits thermal and Doppler broadening effects through cooling and confinement. Increased efficiency is achieved by curved crystal focussing, and the use of gravity-referenced inclinometers allows measurement of the diffraction angle to arcsecond

resolution. The backgammon-type MWPC is an integral part of this system with advantages due to its large active detection area, spatial linearity and high efficiency over a range of energies. By contrast, other detector types have good resolution, but the large range of X-ray energies leads to highly variable efficiencies, and restricted detection area. Using this spectrometer system, experimental measurements of atomic transition energies result in fractional uncertainties in energy as low as $(2–4) \times 10^{-5}$ [2].

Recently, multi-wire proportional counters have been reduced in scale and embedded upon a solid matrix to yield multi-strip detectors [7–9] and multilayer printed circuit boards [10]. These latter designs use different physics and different cascade and recombination processes, but fundamentally have the same characteristics in terms of image formation and defect analysis, and hence have very similar functionality regarding sources and characterisation of non-linearities. A general discussion of some key noise limits for these types of detectors has been made, which certainly indicates some key limitations in potential statistical information and hence resolution or linearity [11]. Recent publications have observed very large spatial non-uniformities which can relate to the subject of this investigation [12]. Further new devices are being developed and linearity and resolution are key parameters in their utility, often limited by either charge cloud deposition or non-linearities as discussed [13,14]. However, under ideal circumstances these limitations may be overcome, to reveal intrinsic non-linearities due to limitations of board design which simple charge division approaches do not predict.

A simulation has been developed which accurately describes the internal geometry of the backgammon-type MWPC and has assisted in the identification and minimisation of several sources of non-linear detector output. Fig. 1 illustrates the high degree of

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¹ Presentation speech by Professor Carl Nordling of the Royal Swedish Academy of Sciences, translation from the Swedish text.

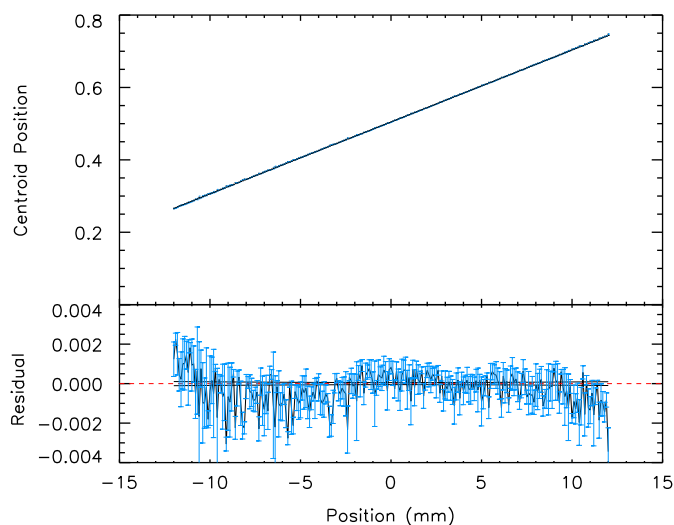


Fig. 1. Fractional centroid position across the detector. Error bars are the standard percentage errors in the determined centroid position. The solid lines are the standard error envelope of the determined linear fit.

spatial linearity obtainable with this detector following these recent developments [15]. Whilst dramatic improvements have been made to linearity measures, unresolved structure still exists within the residual from the linear fit as shown. The work herein further improves the linearity achievable with the backgammon-type MWPC, through an accurate modelling of the detector to show ideal linear output, and through mapping of the experimental residual signature.

2. Detector operation and modelling

2.1. Detector operation

In a MWPC, the source of electrons and ions is the fill gas, which is ionised by an incoming X-ray, and separated by an applied electric field. Through optimisation of parameters such as gas composition, pressure and bias voltage, a counter can be successfully operated in the proportional region whilst maximising spatial resolution.

The detector configuration considered herein is a development on the ‘jeu-de-jacquet’ or backgammon-type X-ray detector [16], and is described in detail elsewhere [15,17]. Two dimensions of position sensitivity are possible with the backgammon-type MWPC, one (coarse) dimension of resolution from the resistive charge distribution of electrons collected along the serpentine anode wire, the other (higher resolution dimension) from the capacitive charge distribution of positive ions collected on the two plates of the backgammon board (Fig. 2). It is this higher resolution dimension which is aligned with the plane of dispersion when the detector is operated as part of the curved crystal spectrometer.

The electronics and data acquisition system (DAQ) employed in the operation of the backgammon-type MWPC are described in full elsewhere [18].

2.2. Detector modelling

An accurate geometrical representation of the MWPC elements was constructed and used as the basis for all simulations. The model accurately reproduces the four output signals (i.e. the two anode signals A and B , and two cathode signals C and D) of the actual detector for an X-ray incident at any cartesian coordinate

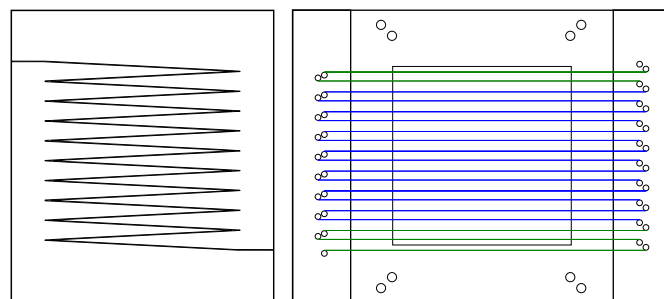


Fig. 2. Shows the backgammon cathode board (left) as divided into two capacitor plates with $100\mu\text{m}$ channel separation. The anode wire configuration (right) is shown configured for previous work with the detector [15].

(x, y) within the proportional chamber, hence mapping $(x, y) \rightarrow (x'(C, D), y'(A, B))$.

Along the anode sensitive dimension, an event within the active region of the detector drifts towards an anode segment, locating the centroid of avalanche formation. As the resistance of the wire is proportional to length, the distance to each end of the anode wire is calculated, and the reciprocals used as the signals A and B to determine the resistive charge division: $y' = A/(A+B)$, where $y' \in [0, 1]$.

In the cathode dimension, the model works by generating a mesh of triangles to represent the geometry of the backgammon board, described as the vertices of polygons. An incident X-ray event is represented by a rectangular distribution of ions surrounding the location of avalanche formation. The radius of this distribution reflects changes in the footprint size. A projection of each charge distribution is made onto the mesh of triangles, and the projected area calculated, proportional to the charge deposited on each side of the backgammon board (defining signals C and D). The position along the cathode axis x' , is then determined by capacitive charge division: $x' = C/(C+D)$, where $x' \in [0, 1]$.

This model has allowed the determination of the cause of a number of non-linear effects observed experimentally in previous MWPC detector designs [19,20]; leading to major improvements to detector configuration and operation [15]. In this current work, the role of the detector simulation is to show ideal linear output, leading to greater understanding of the residual signature, and hence further improve the spatial linearity response of the detector.

2.3. Detector linearity

An important attribute of the backgammon-type MWPC is its spatial linearity over a large area. Prior to testing the spatial linearity, a set of optimised operating conditions (gas composition, pressure and anode bias voltage) was determined. The MWPC was filled with xenon–methane (10% methane in xenon) at 1.91 atm and operated with an anode bias voltage of 2400 V. To test the spatial linearity, a MacScience rotating anode X-ray source was employed to produce a copper spectrum, monochromated to $\text{CuK}\beta$ by a $\text{Si}(111)$ channel-cut crystal. Four hundred $\text{CuK}\beta$ characteristic spectra were collected in $100\mu\text{m}$ steps along the axis of cathode sensitivity across the 40 mm window of the detector. Positioning of the MWPC was achieved by a $0.1\mu\text{m}$ resolution linear stage, with typical on-axis accuracy of $3\mu\text{m}$ and uni-directional repeatability of $0.7\mu\text{m}$.

Each $\text{CuK}\beta$ spectrum was fitted using the sum of two Lorentzian profiles by a Levenberg–Marquardt least squares algorithm, the centroid determined and compared with the detector position on the linear stage. Fig. 1 illustrates the resulting

spatial linearity with residual from a linear fit. Standard errors in the determination of centroid position are shown as error bars, while the standard error envelope of the linear fit is shown in solid lines.

2.4. Linearity modelling

In order to model the ideal spatial linearity of the MWPC, 400 straight line X-ray distributions incident vertically across the entire active region of the detector were simulated. A Levenberg–Marquardt least squares algorithm was employed to perform a linear fit and reproduce the ideal linear output of the detector for a particular charge footprint.

Fig. 3 shows the fractional residuals for a typical circular charge footprint for $\text{CuK}\beta$ radiation. The top graph shows the linear residual for both the experimental data and the model (smooth line). The lower graph shows the experimental residual from the model. Error bars are the standard percentage errors in the determined centroid position. The solid lines are the standard error envelope on the determined model fit.

Residuals (Fig. 3) reveal numerous regions across the detector face that deviate from perfectly linear response. For example, the extreme few millimetres at each side of the active detector region demonstrate a strong trend away (in opposing directions) from a straight line response. The detector model closely emulates the experimental data in these regions, a strong implication of a geometrical cause to the observed departures from linearity.

2.5. Geometrical analysis

An initial analytical study of the circular ion cloud projection onto the backgammon board was performed to gain an understanding of the geometrical and physical cause of the observed residual structure. The projected area of the charge cloud determines the cathode signals, hence the charge collected is expected to contain a functional form similar to that for the area (A) of a chord segment:

$$A(r, \theta) = \frac{r^2}{2} [\theta - \sin \theta] \quad (1)$$

where r is the circle radius and θ the central angle. The centre of avalanche formation and hence centre of each ion cloud projection is necessarily in line with an anode wire segment. A general analytical function for each cathode signal then becomes a sum of positive and negative chord areas for each backgammon segment projected onto, summed over each anode wire.

The derivative with respect to θ of the chord area elements (Eq. (2)) highlights the sensitivity of the geometrical model to the centre of an ion cloud passing over the interface between backgammon segments (due to the $[1 - \cos \theta]$ dependence). For small ion cloud radii, the design of the MWPC is not adversely effected by this sensitivity as each anode wire intersects the boundary of the backgammon segments only at its midpoint. However, as an ion cloud radius becomes appreciably larger than the pitch of the backgammon teeth, the number of chords forming central angles approaching π radians also increases. This cloud radius is of course energy dependant, but is slowly varying.

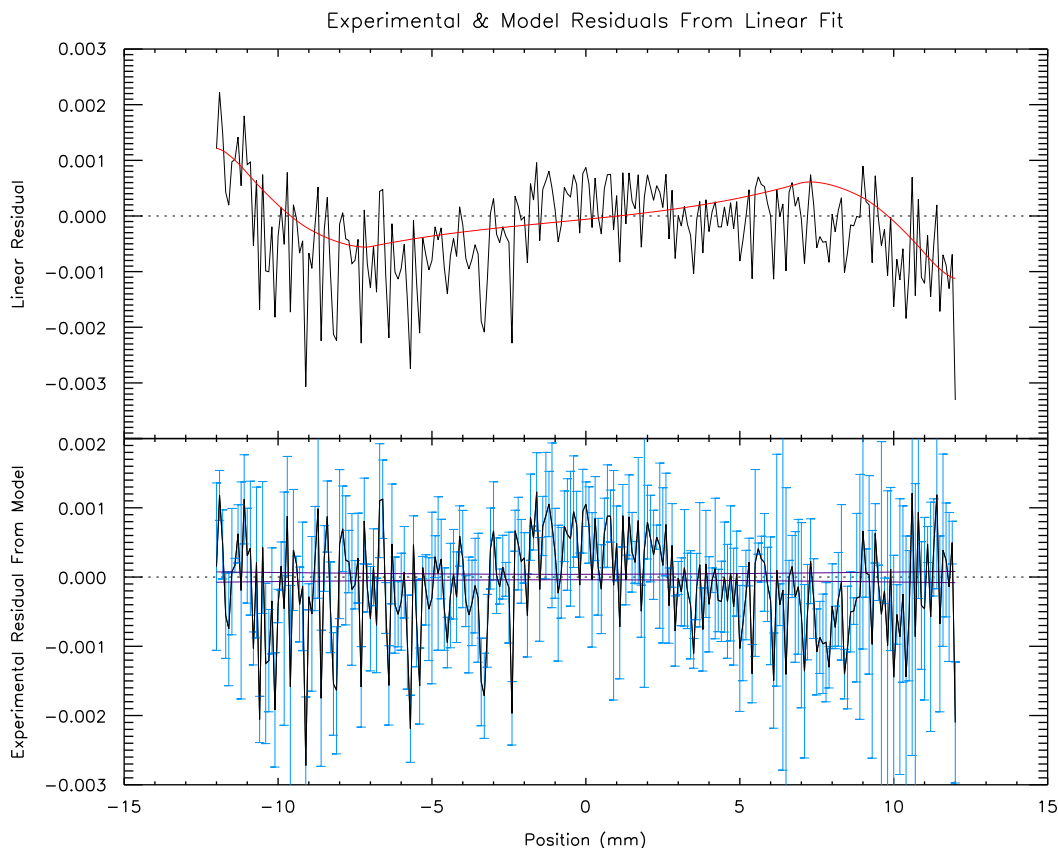


Fig. 3. Shows the fractional residuals for the optimised circular charge footprint with radius of about 8 mm. The top graph shows the linear residual for both the experimental data and the model (smooth line). The lower graph shows the experimental residual from the model. Error bars are the standard percentage errors in the determined centroid position. The solid lines are the standard error envelope on the determined model fit.

The resulting effect to detector response can be the departures from ideal linearity observed both in experiment and simulation

$$\frac{\partial A(r, \theta)}{\partial \theta} = \frac{r^2}{2} [1 - \cos \theta]. \quad (2)$$

3. Analysis of models and measures of linearity

The reduced chi-squared of the experimental data fitted with each detector model is a key indicator of model performance:

$$\chi_r^2 = \sum_{i=1}^{N_y} \frac{w_i (y_i - f_i)^2}{N_y - N_p} \quad (3)$$

where y_i are the experimental values to be fitted, f_i the model values, w_i are the weighting values determined by counting statistics as $1/\sqrt{N}$, N_y the number of values, and N_p the number of fitting function parameters.

Fig. 4 shows the χ_r^2 of the model fit to the experimental data over the parameter space of circular ion cloud radius. The dashed line shows the χ_r^2 for the best linear fit to the experimental data ($\chi_r^2 = 3.08$), therefore any point below this threshold represents an improvement in fit of the data and the minimum χ_r^2 the best set of parameters. These ideal model outputs can then be subtracted from the data to form a residual, which is then fit with a linear function by a Levenberg–Marquardt least squares algorithm, and measures of spatial linearity may then be ascertained.

The fractional uncertainty on the fitted gradient ($\Delta m/m$) and offset ($\Delta c/c$) are useful measures of spatial linearity describing the diagonal elements of the uncertainty in the determined fit parameters. This measure does not discriminate between the models presented but instead yields an indication of potential consistency of results for the interpreted or determined scaling.

For these optimised models, $\Delta m/m = 0.0196\%$ and $\Delta c/c = 0.00547\%$.

The ‘percentage maximum error of the fit’ is a good indication that, subject to noise and statistics, a broad feature or wide separation of peaks (of several pixels or resolution elements) can be resolved or determined to very high accuracy. The standard error of each fit is then,

$$\sigma_f^2 = \sum_{i,j} \text{covar}(p_i, p_j) \chi_r^2 \frac{\partial f}{\partial p_i} \frac{\partial f}{\partial p_j} \quad (4)$$

where $i, j \in [1 \dots N_p]$, p_i and p_j are the fitting parameters, f is the fitting function, and $\text{covar}(p_i, p_j)$ is the covariance matrix of the fitted parameters. The percentage maximum error of the fit then is simply the maximum of σ_f expressed as a percentage of the full detector range including the inactive region (40 mm). With better statistics, or perhaps longer counting times, the random noise component of this is reduced arbitrarily, and the resulting measure looks at the intrinsic significance of non-linearity excursions from a well-defined line.

The ‘average deviation from fit’ is defined as the mean deviation of the detected centroid positions from the linear fit. This is a useful measure of spatial linearity, looking at the typical point-wise excursions over the operational area and estimating the error of a single channel position determination. This measure, however, is affected by limited statistics, but in the absence of statistical limits will provide a strong measure of point-wise departures from linearity.

We define a ‘regional differential non-linearity’ as the mean of the experimental residual from the model after box-car filtering over 11 points (1.1 mm). In this way much of the random experimental noise is suppressed, leaving a good representation of the typical excursion of the detector from the fit. It provides a very useful measure of the scatter present within a local region across the full active detection range.

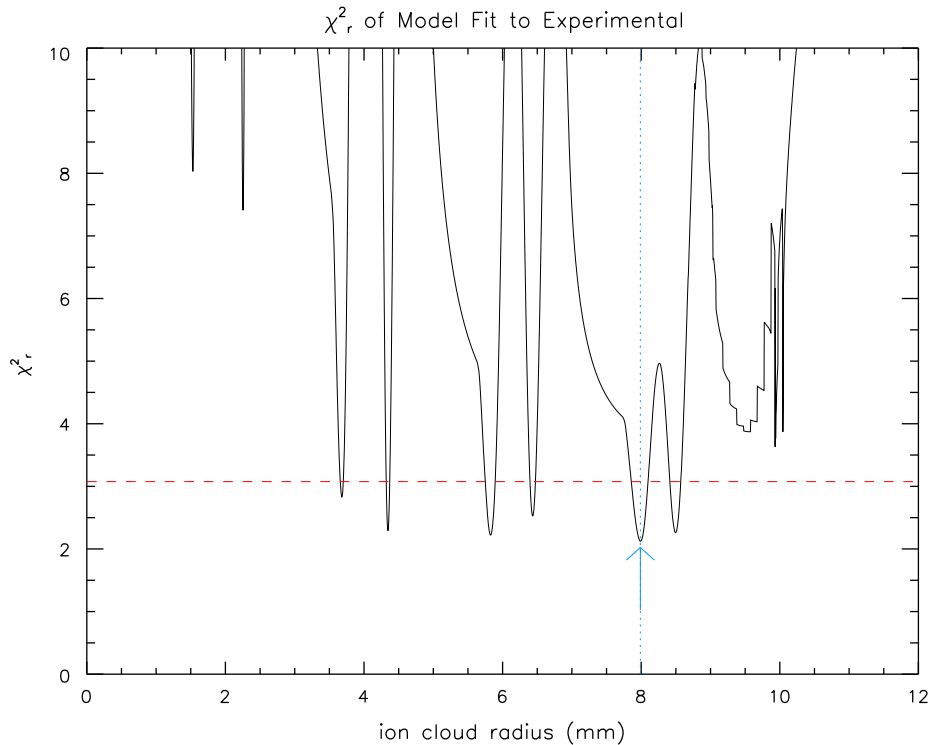


Fig. 4. Shows the χ_r^2 of the circle model fit to the experimental data over the parameter space of ion cloud radius. The arrow highlights the minimum χ_r^2 (2.06) for an ion cloud with an apparent radius of about 8 mm.

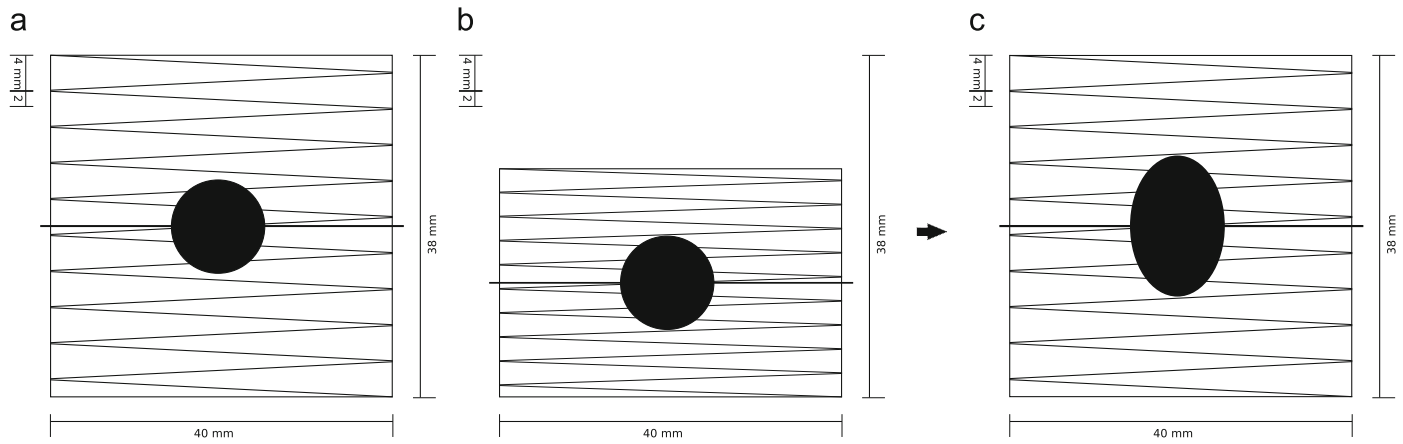


Fig. 5. Shows the means by which an elliptical charge cloud footprint was generated by the scaling of the cathode board dimensions within the model.

The ‘maximum fractional excursion’ is usually due to a few outliers rather than from the full range linearity, but is a good estimate of the worst possible performance. It is calculated as the maximum deviation of a detected position from the fit. Under many circumstances this is a poor estimate, often based on a few points with low statistic, or in a situation where some additional systematic effect caused a defective readout. Often repeating the point a couple of times proves that these points were, for example, 3 or 4 standard deviation random excursions which do not critically affect the detector (linearity) performance.

3.1. Circular model

The first detector model studied was that of a uniform (or top-hat) distribution of charge within a circle, and radii from 0.004 to 20 mm. Fig. 4 shows the χ^2_r of the circular model fit to the experimental data over the parameter space of ion cloud radius. It is clear from this graph that there are six regions over the range of ion cloud radii that the model yields an improvement over the linear fit. The minimum χ^2_r (2.06) is highlighted by an arrow and a dotted line, thus the best circle model was for an ion cloud with an apparent radius of about 8 mm (Fig. 3).

Closer inspection of the fractional residuals for this best circle model (Fig. 3) is important. Within the range of -11 to -2 mm the experimental residual from the model is centred about 0 with only statistical fluctuations remaining. The regions -2 to 3 mm and 3–9 mm of the model yield consistently positive and negative residuals, respectively. The outermost millimetre at each end of the active detection region demonstrates a limitation of the particular model output—here the ideal response is beginning to curve in the opposite direction from the experimental residual.

3.2. Elliptical model

It is expected that to first order a cloud will be circular, but as it sees different fields in orthogonal directions this could easily yield an elliptical shape. Hence the detector model was then extended to simulate a uniform distribution of charge within an ellipse through the introduction of an eccentricity parameter (ϵ). The eccentricity of the charge cloud describes the semi-major radius ($r_{s-major}$ —along the axis of cathode sensitivity) as a percentage of the semi-minor radius ($r_{s-minor}$ —along the anode sensitive dimension), $r_{s-major} = \epsilon r_{s-minor}$.

Definition of an elliptical ion cloud in this way allowed for its simple implementation in the model by a scaling of the backgammon board dimensions as shown in Fig. 5. Fig. 5(a) shows a single circular charge cloud of the desired semi-major

radius. Through scaling the anode sensitive dimension by the eccentricity parameter before projection of the charge cloud (Fig. 5(b)) the resulting charge footprint is equivalent to an ellipse of the desired dimensions (Fig. 5(c)).

The elliptical model was implemented for eccentricities of 10–500% and semi-major radii of 0.004–20 mm, however, many of the resulting simulations were discarded on the basis of being physically unreasonable. Fig. 6 shows the χ^2_r of the remaining ellipse models fit to the experimental data. The red (solid) line shown indicates the χ^2_r for the linear fit, such that any point below this line is an improvement over a straight line fit. As opposed to the six regions of improvement found for the circular model, with the elliptical model it is clear that the addition of the eccentricity parameter has lead to a much broader range of models with a low χ^2_r .

The best ellipse model ($\chi^2_r = 1.94$) was for an ion cloud with an eccentricity of 60%, semi-major radius of about 6.1 mm, and semi-minor radius of about 10.2 mm (Fig. 7). A study of the experimental residual from the model shows a structure similar in features to that of the best circle model, with a few important improvements. The outermost millimetre at each end of the model output now follows the experimental data much more closely, so that the detector ranges between -12 and -2 mm and 9 to 12 mm are dominated only by statistical noise. The regions between -2 and 3 mm and 3 to 9 mm of the model still, however, demonstrate consistently positive and negative residuals.

3.3. Gaussian model

The circular and elliptical models discussed have been based on uniform distributions of charge. The detector simulation was modified to allow for a Gaussian distribution of charge onto the cathode board following each ionisation event. To achieve this, an approximation was made through the weighted sum of a range of circular ion clouds of uniform distribution, centred on the same coordinates, and parameterised by the Gaussian half-width-at-half-maximum (HWHM). The weighting of each circle was determined by the volume of an annulus formed within a solid Gaussian defined by the HWHM. This is an efficient and accurate partitional representation of a true Gaussian, to arbitrary level of approximation.

The number of circular elements used to make up each Gaussian distribution ranged from three to 101. Fig. 8 shows the χ^2_r of an 11-element Gaussian model fit to the experimental data over the parameter space of ion cloud HWHM. The red (dashed) line shown indicates the χ^2_r for the linear fit, such that any point below this line is an improvement over a straight line fit.

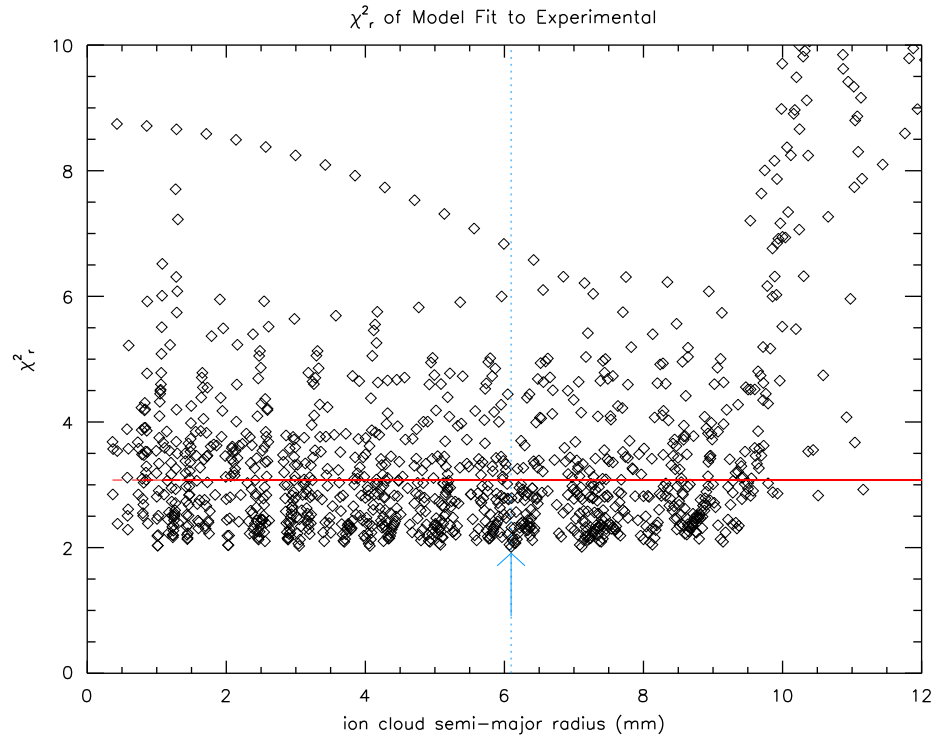


Fig. 6. Shows the χ^2_r of the model fit to the experimental data over the parameter space of ion cloud semi-major radius. Eccentricities of 10–500% are shown. The arrow highlights the minimum χ^2_r (1.94) for an elliptical ion cloud.

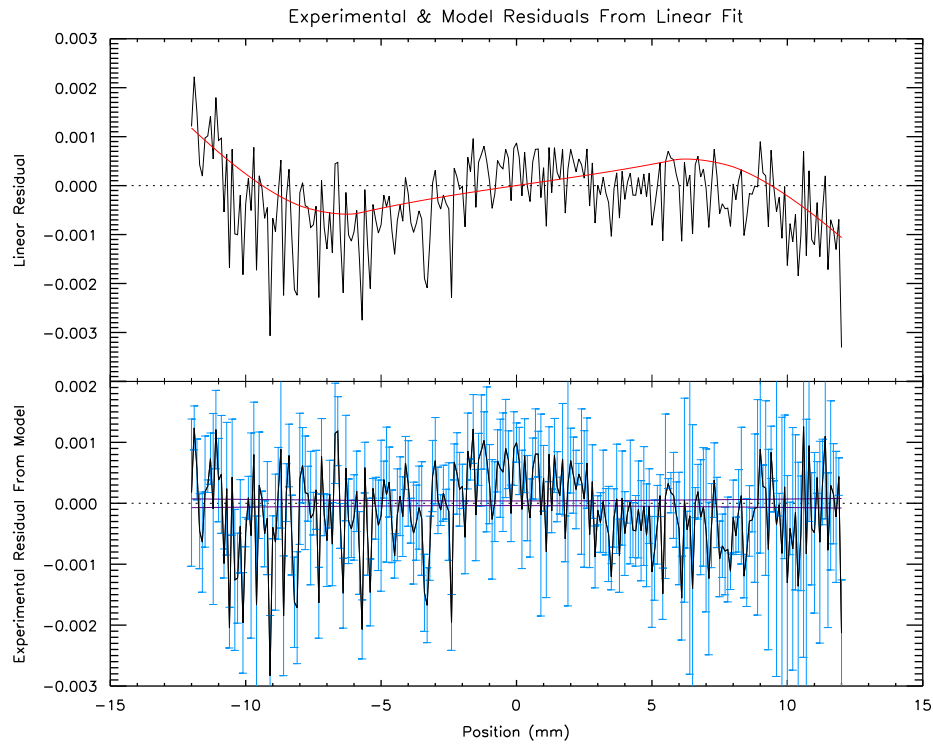


Fig. 7. Shows the fractional residuals for the best elliptical model ($\chi^2_r = 1.94$) with an eccentricity of 60%, semi-major radius of about 6.1 mm, and semi-minor radius of about 10.2 mm. The top graph shows the linear residual for both the experimental data and the model (smooth line). The lower graph shows the experimental residual from the model. Error bars are the standard percentage errors in the determined centroid position. The solid lines are the standard error envelope on the determined model fit.

The range in size over which the elements were chosen was also an important parameter of the model. Distributions within radii of 50–150% HWHM were used for the models shown in Figs. 8 and 9.

The best model constructed for a Gaussian distribution ($\chi^2_r = 1.95$) was for an 11-element Gaussian with approximately 2.6 mm HWHM and elements in the range of [50%,...150%]× HWHM. Fig. 9 shows the fractional residuals for this model.

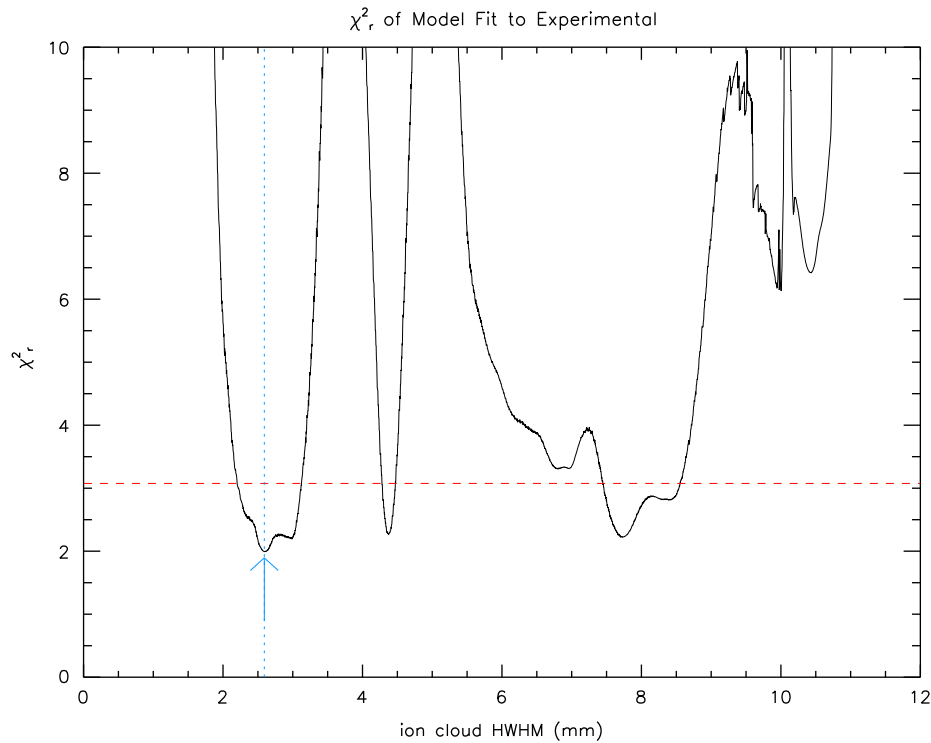


Fig. 8. Shows the χ^2_r of an 11-element Gaussian model fit to the experimental data over the parameter space of ion cloud HWHM. Elements were in the range of $[50\%, \dots, 150\%] \times \text{HWHM}$. The arrow highlights the minimum χ^2_r (1.95) for this model.

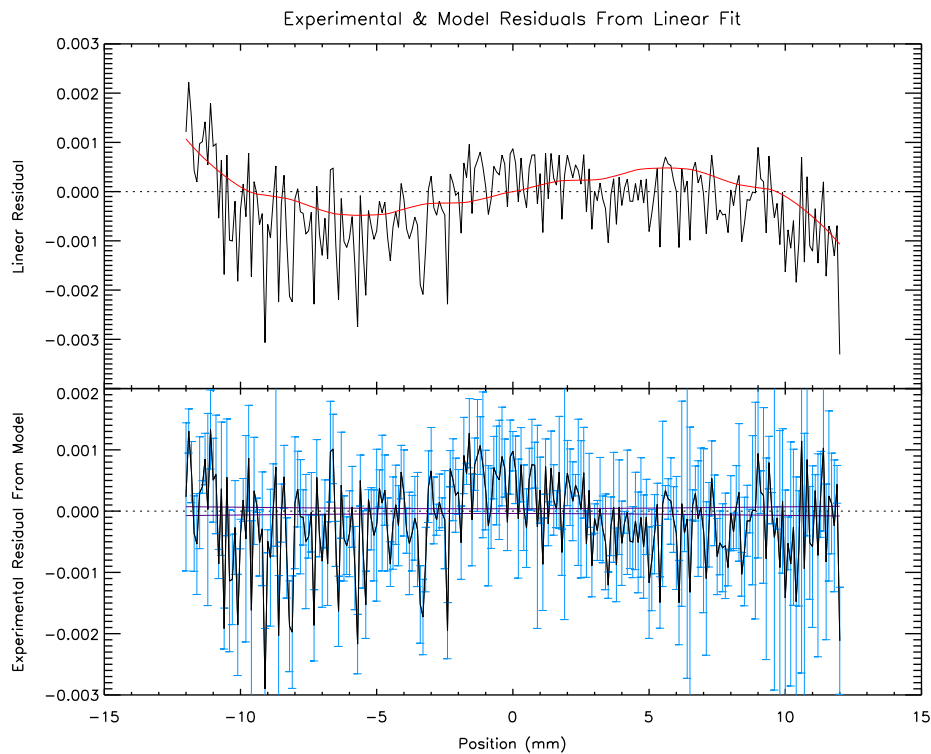


Fig. 9. Shows the fractional residuals for an 11-element Gaussian charge distribution with a HWHM of approximately 2.6 mm. The top graph shows the linear residual for both the experimental data and the model. The lower graph shows the experimental residual from the model (smooth line). Error bars are the standard percentage errors in the determined centroid position. The solid lines are the standard error envelope on the determined model fit.

This optimum has a structure not observed in earlier models. The oscillatory structure is due to the various elements of the distribution causing areas of non-ideal response (Section 2.5). As the number of elements within a distribution was increased, the

Gaussian model output tended to that of the circular model. As such, the residual structure in Fig. 9 was dominated by an artifact of the finite element approximation used to generate the model. While this mapped the experimental data quite

closely, the result was not particularly robust nor physically insightful.

4. Results

For each of the three types of models presented herein (i.e. circular, elliptical and Gaussian model types), an expression for the linearity of the detector was determined, and found to be very close to that of an ideal linear fit, with $x' \in [0, 1]$:

$$x' = (0.0199 \pm 4 \times 10^{-6})x(\text{mm}) + (0.505 \pm 3 \times 10^{-5}). \quad (5)$$

The linearity measures discussed in Section 3 were computed for each of these optimised models. As discussed above, the fitted gradient ($\Delta m/m$) and offset ($\Delta c/c$) are consistent and well-defined showing that the linear functional form is independent of the charge cloud modelling. Results are summarised in Table 1. The Gaussian, circle, and ellipse models show dramatic improvements over the simpler linear model for all (other) linearity measures.

Table 1 shows that the elliptical model best fits the experimental data collected, with a χ_r^2 of only 1.94. This model also exhibits the lowest percentage maximum error of fit at 0.00787% (or 3.2 μm) indicating that features spread across the active region of the detector can be resolved to a high level of accuracy.

Average deviations from fit were calculated to be only 0.0565% and 0.0566% for the Gaussian and ellipse models, respectively. This yields a good indication of the typical error on any single position determination within the detector. As the non-linearity of the translation stage is an order of magnitude better than the experimental results herein, a mechanical cause of the observed non-linearity is safely ignored.

The ellipse model exhibited the best regional differential non-linearity of only 0.0313% an improvement of 35% over the linear model. Likewise, the circle and Gaussian models showed improvements $> 30\%$. While a typical point-wise excursion (from statistical noise or random effects) might deviate by 0.001 in x' , the deviation of a local region is much smoother and much of the structure is well-explained.

Finally, the maximum fractional excursion was minimised for the circle model at 0.272%. Whilst this measure is due to several outliers in the experimental data, which can skew the optimisation of the respective models and the final fit, the demonstrated improvement of 18% indicates that a significant component of the previous deviation was due to an inadequate model (i.e. the need for a representation of the charge cloud).

We note that the spatial range of the detector modelled does affect final optimisation and parametrisation. Modelling the central 20 mm instead of the full active 24 mm detector length yields a very similar slope and offset, and hence fitting uncertainty, but reduces the χ_r^2 by about 10%, and similarly reduces the regional differential non-linearity and maximum

fractional excursion by approximately 10%. Since the improvement is moderately uniform, the results of the full fitting and linearity measures are presented.

5. Conclusion

We have investigated the experimental linear residual of the backgammon-type MWPC, and shown the requirement for a representation of the charge cloud in modelling the ideal linear output of the detector. This paper does not theoretically prove a particular charge cloud shape, nor the ideal uniformity of that particular shape. It remains possible, for example, that key cloud radii might vary across a charge amplification device due to non-uniformities in construction; or that the radius might change with subtle changes in voltage or design; or that particular edge-effects might distort such a cloud shape.

Rather, it demonstrates that there is strong evidence for an approximately circular charge cloud distribution which is approximately uniform in a good typical implementation, and that this does indeed explain key systematic effects in the linearity function. This result thereby improves the potential determination of local structure in backgammon detectors, MWPCs and related charge amplification devices. Further, this paper demonstrates that highly accurate determination of position is possible with this detector type, and other related types, even if the resolution *per se* is not so high as e.g. CCD or other detectors. Of course, this accuracy is attained only with good statistics, and with appropriate modelling of detector response function.

References

- [1] G. Charpak, R. Bouclier, T. Bressani, J. Favier, C. Zupancic, Nuclear Instruments and Methods 62 (1968) 262.
- [2] C.T. Chantler, D. Paterson, L.T. Hudson, F.G. Serpa, J.D. Gillaspay, E. Takács, Physical Review A 62 (042501) (2000) 1.
- [3] K. Assamagan, L. Baker, G. Bayatyan, R. Carlini, S. Danagoulain, T. Eden, K. Egiyan, R. Ent, H. Fenker, L. Gan, A. Gasparian, N. Grigoryan, Z. Greenwood, P. Gueye, O. Hashimoto, K. Johnston, C. Keppel, S. Knyazyan, S. Majewski, A. Margaryan, Y. Margaryan, G. Marikyan, J. Martoff, H. Mkrtchyan, L. Parlakyan, Y. Sato, R. Sawafra, N. Simicevic, V. Tadevosyan, T. Takahashi, L. Tang, G. Vartanyan, W. Vulcan, S. Wells, S. Wood, Nuclear Instruments and Methods in Physics Research A 426 (1999) 405.
- [4] J. Fuzi, Measurement Science and Technology 19 (8) (2008).
- [5] M. Irving, V. Lombardi, G. Piazzesi, M.A. Ferenczi, Nature 357 (1992) 156.
- [6] C.T. Chantler, M.N. Kinnane, C.-H. Su, J.A. Kimpton, Physical Review A 73 (2005) 1.
- [7] E. Gatti, A. Longoni, H. Okuno, P. Semenza, Nuclear Instruments and Methods 163 (1979) 83.
- [8] V. Radeka, R.A. Boie, Nuclear Instruments and Methods 178 (1980) 543.
- [9] F. Piuze, R. Roosen, J. Timmermans, Nuclear Instruments and Methods 196 (1982) 451.
- [10] A.F. Barbosa, Nuclear Instruments and Methods in Physics Research A 371 (1996) 368.
- [11] C. Martin, P. Jelinsky, M. Lampton, R.F. Malina, H.O. Anger, Review of Scientific Instruments 52 (7) (1981) 1067.
- [12] J.F.C.A. Veloso, J.M.F. dos Santos, C.A.N. Conde, R.E. Morgado, X-ray Spectrometry 26 (1997) 237.
- [13] P. Siritiprussamee, K. Fujita, H. Takahashi, H. Niko, K. Nishi, H. Toyokawa, M. Furusaka, T. Ino, S. Kishimoto, H.M. Shimizu, M. Kanazawa, Nuclear Instruments and Methods in Physics Research A 580 (2007) 1119.
- [14] H. Natal da Luz, J.F.C.A. Veloso, N.F.C. Mendes, J.M.F. dos Santos, J.A. Mir, Nuclear Instruments and Methods in Physics Research A 573 (2007) 191.
- [15] A.T. Payne, J.A. Kimpton, M.N. Kinnane, C.T. Chantler, Measurement Science and Technology 20 (2009) 025601.
- [16] R. Allemann, G. Thomas, Nuclear Instruments and Methods 137 (1976) 141.
- [17] J.A. Kimpton, M.N. Kinnane, C.T. Chantler, Review of Scientific Instruments 77 (083102) (2006) 1.
- [18] J.A. Kimpton, M.N. Kinnane, L.F. Smale, C.T. Chantler, L.T. Hudson, A. Henins, C.I. Szabo, J.D. Gillaspay, J.N. Tran, J.M. Pomeroy, E. Takács, B. Radics, Nuclear Instruments and Methods in Physics Research A 580 (2007) 246.
- [19] G.G. Luther, P.L. Cowan, A. Henins, S. Brennan, Nuclear Instruments and Methods in Physics Research A 246 (1986) 537.
- [20] T. Mizogawa, M. Sato, Y. Awaya, Nuclear Instruments and Methods in Physics Research A 366 (1995) 129.

Table 1

Summary of linearity measures by optimised model, fitted across the full active 24 mm detector length; values in bold are the best result for each linearity measure.

Measure	Linear	Gaussian	Circle	Ellipse
χ_r^2	3.075	1.948	2.055	1.938
% Maximum error of fit	0.009916	0.007892	0.008106	0.007871
Maximum error of fit (μm)	3.966	3.157	3.243	3.148
% Regional differential non-linearity	0.0484	0.0332	0.0336	0.0313
% Average deviation from fit	0.0670	0.0565	0.0583	0.0566
% Maximum fractional excursion	0.3307	0.2903	0.2720	0.2831