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## Author Manuscript

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# Inelastic Neutron Scattering of Lanthanoid Complexes and Single-Molecule Magnets

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**Abstract:** Single-molecule magnets (SMMs) are discrete metal complexes that retain their magnetization below a certain temperature, with possible applications in quantum information processing, molecular spintronics and high-density data storage. Complexes of lanthanoid(III) ions have proven highly successful in the field, with some exhibiting magnetic hysteresis at liquid nitrogen temperatures. Inelastic neutron scattering (INS), widely used for the study of the crystal-field splitting engendered by the coordination environment of metal centers, can afford a wealth of information when applied to the study of these molecular nanomagnets, as the SMM properties arise from the electronic structure of the lanthanoid(III) ions. Although relatively underutilized to date, INS can be employed alongside crystal-field analysis, and/or ab initio calculations, to understand how subtle structural changes impact SMM behaviour. In this Microreview we discuss the application of INS to the study of lanthanoid complexes, to elucidate both crystal field splitting and exchange coupling in coupled metal-radical and metal-metal SMMs.

## 1. Introduction

The magnetic properties of the trivalent lanthanoid (Ln) ions are of fundamental interest and practical importance, in both extended solids and discrete complexes. The presently burgeoning field of lanthanoid single-molecule magnets (SMMs) was spurred by the 2003 discovery that bis-phthalocyanine (PcH<sub>2</sub>) lanthanoid complexes, [LnPc<sub>2</sub>]<sup>−</sup> can exhibit the same slow relaxation of magnetization and magnetic hysteresis as SMMs based on 3d metals.<sup>[1][2]</sup> Since then, Ln-SMMs have begun to dominate the field. Recently, blocking temperatures of Ln-SMMs have increased

markedly, with several dysprosium cyclopentadienyl metallocenes exhibiting magnetic hysteresis in the range 60–80 K, and energy barriers to magnetisation reversal up to  $1500 \text{ cm}^{-1}$ .<sup>[3–6]</sup>

For Ln-SMMs, the magnetic behaviour stems from the large unquenched orbital angular momentum of the metal ion. For the Ln(III) ions the electronic configuration can be described using a Russell-Saunders coupling scheme, resulting in  $^{2S+1}L_J$  levels. The crystal field (CF) acting on the lanthanoid(III) ion splits the spin-orbit coupled  $J$  levels into linear combinations of  $M_J$  microstates. The order and composition of these microstates can be tuned by modification of the ligand environment.<sup>[7]</sup> Unlike 3d-SMMs, Ln-SMMs commonly relax via a combination of pathways, including thermally activated Orbach, Raman and direct processes,<sup>[8]</sup> as well as through quantum-tunnelling of the magnetization (QTM).<sup>[9]</sup> To understand the dynamic magnetic behaviour, it is essential to elucidate the CF contribution to the electronic structure of the lanthanoid(III) ions. A variety of experimental techniques can be used to investigate the electronic structure of Ln-SMMs including dc and ac magnetometry,<sup>[10,11]</sup> torque magnetometry,<sup>[12]</sup> as well as electron paramagnetic resonance (EPR),<sup>[13]</sup> far infrared (FIR)<sup>[14–16]</sup> and optical spectroscopies.<sup>[17]</sup> Experimental data are often interpreted by fitting the data to CF models obtained from symmetry analysis of the structure from single crystal X-ray crystallography.

A relatively underutilized, but powerful, technique for investigating CF excitations of lanthanoid(III) SMMs is inelastic neutron scattering (INS), where resonances are measured following energy transfer to or from a scattered neutron. Inelastic neutron scattering can also be used to probe exchange coupling by measuring the corresponding magnetic excitations.<sup>[18,19]</sup> An essential approach to elucidating electronic structure is to employ multiple experimental techniques, in combination with appropriate computational methods. This can be particularly important in the case of lower symmetry lanthanoid(III) coordination geometries, or in systems complicated by exchange coupling, as there are almost always too many CF and exchange parameters to be fit with the limited data available in an INS or magnetic study alone.

The use of INS to elucidate the electronic structure in 3d-SMMs and related complexes was reviewed by Güdel et al. in 2003 and Amoretti et al. in 2008, with a focus on determination of zero-field splitting and exchange coupling.<sup>[20,21]</sup> Historically, INS was first applied to CF splitting in extended lanthanoid systems, starting with the work by Brockhouse in the early 1960s,<sup>[22]</sup> but the past few years have seen a number of studies of discrete molecular complexes. In 2016, Waldmann et al. surveyed aspects related to determination of exchange coupling in lanthanoid systems by INS.<sup>[23]</sup> More recently, the use of neutron scattering techniques for the study of coordination complexes was reviewed by Xue et al.<sup>[24]</sup> The scope of the present Microreview is to survey more

broadly the employment of INS to elucidate the electronic structure of molecular lanthanoid complexes and Ln-SMMs.

## 2. Inelastic Neutron Scattering

Neutrons have several unique features which make neutron scattering techniques well-suited to condensed matter spectroscopy. Neutrons are highly penetrating and sensitive to the nuclei of the atoms in a compound, due to their lack of electrical charge. Despite the zero charge, neutrons have a spin angular moment of  $s = 1/2$  and thus have a magnetic moment. This intrinsic magnetic moment allows them to interact with the unpaired electrons in a system, and therefore they are ideal for investigating the magnetic properties of materials. The kinetic energy ( $E$ ) of a neutron is given by:

$$E = \frac{h^2}{2m\lambda^2} = \frac{\hbar^2 k^2}{2m} \quad (1)$$

where  $m$  is the mass of a neutron,  $\lambda$  its wavelength, and  $k$  the wavenumber. The energy range of many processes in condensed matter such as magnons, phonons and crystal field excitations is comparable to the energy of a neutron in a typical source.<sup>[25]</sup>

When a neutron interacts with matter, one of three things can happen. The neutron can be absorbed by the nucleus, it can be scattered by the nucleus, or it can be scattered by the interaction between the neutron magnetic moment and the magnetic field generated by unpaired electrons in the sample. This ability to interact with the unpaired electrons of a given ion or extended solid allows neutron scattering to be used as a spectroscopic probe for magnetic transitions. When a neutron scatters, the momentum transfer to the sample,  $\mathbf{Q}$ , is given by:

$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f \quad (2)$$

where  $\mathbf{k}_i$  is the incident neutron wave-vector, and  $\mathbf{k}_f$  the final neutron wave-vector. The energy transfer is then given by:

$$\hbar\omega = E_i - E_f = \frac{\hbar^2}{2m}(k_i^2 - k_f^2) \quad (3)$$

where  $\omega$  is the angular frequency, and  $E_i$  and  $E_f$  the initial and final energy respectively. For cases where  $\mathbf{k}_i = \mathbf{k}_f$ , there is elastic scattering from the sample. For inelastic scattering processes, this equality no longer holds, and there is a corresponding loss or gain in the energy of the neutron. In

this case the energy of an excitation, be it vibrational or magnetic, can be directly measured. Typically, neutron wavelengths between 1 and 10 Å are used to probe excitations of interest, corresponding to an energy transfer up to around 650 cm<sup>-1</sup> (8 cm<sup>-1</sup> ≈ 1 meV ≈ 11.6 K).

Unlike in X-ray scattering, neutrons scatter with seemingly randomly absorption coefficients and scattering cross-sections across the periodic table, which is of great use in neutron diffraction, where elements near each other in the periodic table can be easily distinguished. Every isotope also has a specific coherent and incoherent scattering cross-section, where scattering either depends on the direction of **Q** or is uniform in all directions, respectively. Naturally abundant hydrogen, for example, has a large incoherent neutron scattering cross-section of 80.27 barn due to the difference in scattering lengths of the two possible nucleus–neutron interactions.<sup>[25]</sup> In comparison, deuterium has a much smaller incoherent scattering of 2.05 barn.<sup>[26]</sup> The majority of SMM complexes contain hydrogenous organic ligands, which means this is a considerable disadvantage for INS studies.

The information typically obtained from a neutron scattering experiment is the scattering function  $S(\mathbf{Q}, \omega)$  as the Fourier transform in both space and time of the time-dependent pair correlation function.<sup>[27]</sup> The scattering function contains all the information from a neutron scattering experiment. The **Q** dependence of  $S(\mathbf{Q}, \omega)$  tells us about structure, i.e. where atoms or electron density is; the  $\omega$  dependence gives information about dynamics. Transitions observed in the scattering function obey detailed balance:

$$S(-\mathbf{Q}, -\omega) = S(\mathbf{Q}, \omega) e^{-\hbar\omega/k_B T} \quad (4)$$

meaning that transitions observed on the neutron energy loss side of the spectrum (sample energy gain) will also be observed on the neutron energy gain side (sample energy loss).

## 2.1. Instrumentation

There are two main types of INS instruments used for measuring CF excitations (Figure 1). The first neutron spectrometers were triple-axis (also known as three-axis) spectrometers, as designed by Brockhouse in 1961.<sup>[28]</sup> A typical triple-axis setup involves selection of an incident neutron with **k<sub>i</sub>** determined by a crystal monochromator (the first axis), which interacts with a sample (the second rotation axis) and the scattered neutron with **k<sub>f</sub>** is selected on a crystal analyzer (the third axis). In this way the final neutron energy can be measured at different orientations of a sample. The second instrument, a time-of-flight (TOF) spectrometer, involves measuring the neutron energy (via its velocity) by measuring the time taken for the neutrons to travel a given distance. This technique requires either a pulsed neutron beam, such as from a pulsed spallation neutron source, or a chopper

used on a continuous neutron source like a nuclear reactor. Typically, direct geometry TOF spectrometers are used, where the final energy  $E_f$  is measured, with a constant initial energy  $E_i$ . Indirect geometry spectrometers instead involve sample irradiation with a white neutron beam, with the incident energy measured by time-of-flight, and the final neutron energy monitored. Triple-axis spectrometers have advantages when measuring single crystal data, as  $\mathbf{Q}$  is measured point by point in  $(\mathbf{Q}, \omega)$  space. While triple-axis and TOF spectrometers can give unique information into the scattering from single crystal samples, triple-axis spectrometers can give very detailed and high  $Q$  resolution information, while modern TOF spectrometers survey large regions of four-dimensional space due to large multi detectors, with scattering is recorded simultaneously over many scattering angles.<sup>[29]</sup> It is worth noting that the majority of inelastic experiments on SMMs are undertaken on powder samples. In addition, there are other techniques using backscattering and spin echo spectrometers, which can give micro and nano eV resolution respectively. Crystal field excitations are generally in the cold ( $E < 80 \text{ cm}^{-1}$ ) to thermal ( $80 < E < 650 \text{ cm}^{-1}$ ) neutron energy range, and as such most spectrometers used in their study are either cold or thermal spectrometers. Key features of the INS instruments that have been employed in the studies presented in this review are presented in [Table 1](#).

Neutron beams for INS are typically monochromated in two different ways — either Bragg reflection from a single crystal can be used to select only neutrons of a certain wavelength in a manner similar to the crystal monochromators used for X-ray spectroscopy, or the beam is chopped using multiple choppers, as the transit time between choppers is governed by their energy.

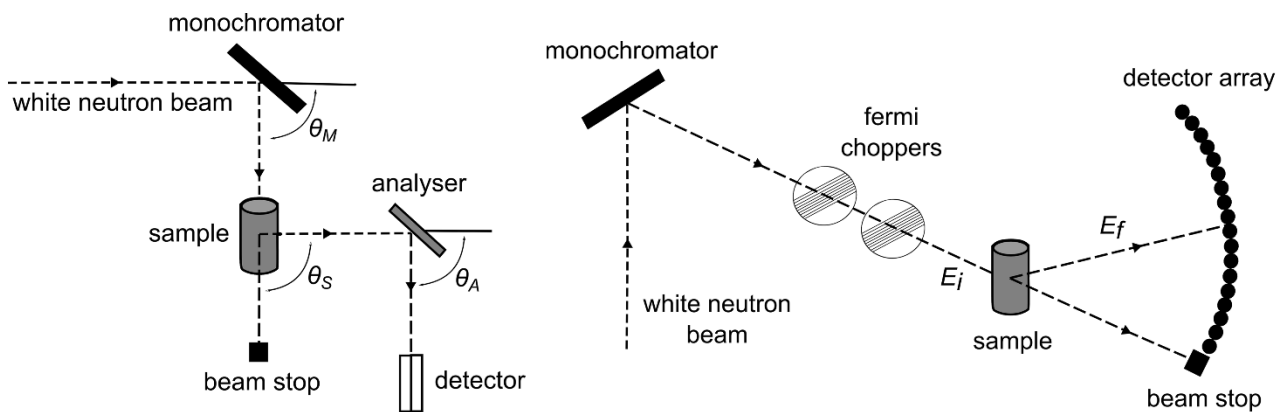


**Figure 1.** Schematic diagram illustrating the general principle of triple-axis (left) and TOF (right) INS spectrometers. In a triple axis spectrometer, three angles  $\theta_M$ ,  $\theta_S$  and  $\theta_A$  can all be varied to measure different points in  $S(\mathbf{Q}, \omega)$  space. In a direct geometry TOF spectrometer,  $E_i$  is selected and  $E_f$  is measured by measuring the time between sample and detector.

**Table 1.** Selected INS Instruments employed for the studies in this Minireview. All spectrometers mentioned here are TOF instruments.

| Instrument               | Facility <sup>[a]</sup>                           | Key Features                                                                                    |
|--------------------------|---------------------------------------------------|-------------------------------------------------------------------------------------------------|
| PELICAN <sup>[30]</sup>  | ACNS, ANSTO, Australia                            | XYZ polarisation analysis                                                                       |
| MARI <sup>[31]</sup>     | ISIS, Rutherford Appleton Laboratory, UK          | Very high energy transfer (up to 8,100 cm <sup>-1</sup> ).                                      |
| LET <sup>[32]</sup>      | ISIS, Rutherford Appleton Laboratory, UK          | Very large detectors (4 m high). Very low background. Repetition rate spectroscopy.             |
| IN4C <sup>[33]</sup>     | ILL, France                                       | Thermal neutrons (up to ~800 cm <sup>-1</sup> ). Being upgraded to have polarisation analysis.  |
| IN5 <sup>[34]</sup>      | ILL, France                                       | Very large detectors — ideal for high resolution.                                               |
| TOFTOF <sup>[35]</sup>   | MLZ, Germany                                      | High resolution and good signal to noise                                                        |
| AMATERAS <sup>[36]</sup> | Material and Life Science Facility, J-PARC, Japan | Very high resolution (micro eV) at large energy transfers. Allows repetition rate spectroscopy. |
| FOCUS <sup>[37]</sup>    | SINQ Spallation Source, PSI, Switzerland          | Can be operated in time-focusing mode.                                                          |

<sup>[a]</sup>ACNS: Australian Centre for Neutron Scattering; ANSTO: Australian Nuclear Science and Technology Organisation; ILL: Institut Laue-Langevin; MLZ: Maier Leibnitz Zentrum; J-PARC: Japan Proton Accelerator Research Complex; PSI: Paul Scherrer Institut.

## 2.2. Practical considerations of Inelastic Neutron Scattering

The energy scale of INS measurements is typically in the same range as the magnetically-relevant energy levels of paramagnetic molecular systems. The technique has been of great use in elucidating the zero-field splitting in transition metal SMMs, for example in the pioneering Mn<sub>12</sub> acetate SMM [Mn<sub>12</sub>O<sub>12</sub>(OAc)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>],<sup>[38–40]</sup> as well as in many other SMMs based on 3d metals.<sup>[41,42,51,52,43–50]</sup>

Many lanthanoid systems can be readily studied with neutron scattering techniques. Historically, the focus of neutron studies has been on compounds of Ce, Pr, Nd, Tb, Ho and Yb (and diamagnetic Y); both as many important magnetic materials incorporate these metals and because these metals all have relatively low neutron absorption cross-sections.<sup>[19,22,53–59]</sup> Complexes

incorporating Dy, despite dominating the field of Ln-SMMs, are rarely studied using INS.<sup>[10][60]</sup> This is due to the large neutron absorption cross-section of  $^{164}\text{Dy}$  (2840 barn for 2,200  $\text{ms}^{-1}$  neutrons) giving a large absorption cross-section for naturally abundant Dy (see Table 2).<sup>[26]</sup> It is rarely possible to study compounds containing Gd, and only when isotopically enriched, — the incredibly high neutron absorption cross-section of naturally abundant Gd is such that it is often used as a material for neutron shielding.<sup>[26,61]</sup>

**Table 2.** Neutron coherent scattering ( $\sigma_c$ ), incoherent scattering ( $\sigma_i$ ) and absorption ( $\sigma_a$ ) cross-sections for naturally abundant selected rare-earth (RE) metals and 2,200 ms<sup>-1</sup> neutrons and electronic ground terms for the trivalent ions.<sup>[7,26]</sup>

|                                          | Y                           | La                          | Ce                            | Pr                          | Nd                            | Pm                          | Sm                            | Eu                          | Gd                            | Tb                          | Dy                             | Ho                          | Er                             | Tm                          | Yb                            | Lu                          |
|------------------------------------------|-----------------------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|--------------------------------|-----------------------------|--------------------------------|-----------------------------|-------------------------------|-----------------------------|
| Cross-section                            |                             |                             |                               |                             |                               |                             |                               |                             |                               |                             |                                |                             |                                |                             |                               |                             |
| $\sigma_c$ / barn                        | 7.55                        | 8.53                        | 2.94                          | 2.64                        | 7.43                          | 20.0                        | 0.422                         | 6.57                        | 29.3                          | 6.84                        | 35.9                           | 8.06                        | 7.63                           | 6.28                        | 19.4                          | 6.53                        |
| $\sigma_i$ / barn                        | 0.15                        | 1.13                        | 0.001                         | 0.015                       | 9.2                           | 1.3                         | 39                            | 2.5                         | 151                           | 0.004                       | 54.4                           | 0.36                        | 1.1                            | 0.1                         | 4                             | 0.7                         |
| $\sigma_a$ / barn                        | 1.28                        | 8.97                        | 0.63                          | 11.5                        | 50.5                          | 168                         | 5,922                         | 4,530                       | 49,700                        | 23.4                        | 994                            | 64.7                        | 159                            | 100                         | 34.8                          | 74                          |
| electronic<br>ground term<br>for RE(III) | <sup>1</sup> S <sub>0</sub> | <sup>1</sup> S <sub>0</sub> | <sup>2</sup> F <sub>5/2</sub> | <sup>3</sup> H <sub>4</sub> | <sup>4</sup> I <sub>9/2</sub> | <sup>5</sup> I <sub>4</sub> | <sup>6</sup> H <sub>5/2</sub> | <sup>7</sup> F <sub>0</sub> | <sup>8</sup> S <sub>7/2</sub> | <sup>7</sup> F <sub>6</sub> | <sup>6</sup> H <sub>15/2</sub> | <sup>5</sup> I <sub>8</sub> | <sup>4</sup> I <sub>15/2</sub> | <sup>3</sup> H <sub>6</sub> | <sup>2</sup> F <sub>7/2</sub> | <sup>1</sup> S <sub>0</sub> |

3

For a lanthanoid(III) ion, the magnetic scattering cross-section for unpolarized neutrons by the CF split states is given by:

$$\frac{d^2\sigma}{d\Omega d\omega} = N(\gamma r_0)^2 \frac{k_f}{k_i} F^2(\mathbf{Q}) e^{-2W(\mathbf{Q})} \sum_{\alpha,n,m} p_n \left[ 1 - \left( \frac{Q_\alpha}{Q} \right)^2 \right] |\langle \Gamma_m | \hat{J}^\alpha | \Gamma_n \rangle|^2 \delta(\hbar\omega + E_n - E_m) \quad (5)$$

Here  $N$  is the number of magnetic ions,  $\gamma$  is the gyromagnetic ratio,  $r_0$  is the classical radius of an electron,  $e^{-2W(\mathbf{Q})}$  is the Debye-Waller factor,  $\alpha$  is  $x, y$  or  $z$ ,  $p_n$  is the Boltzmann population of level  $\Gamma_n$ ,  $Q_\alpha$  is the respective magnetic interaction operator and  $\hat{J}^\alpha$  is the respective angular momentum operator.<sup>[62]</sup> This expression can be derived using perturbation theory, from Fermi's Golden Rule, as neutrons interact weakly with the matter of interest, and contains all necessary information to identify and characterise a given transition

For CF transitions, the peak energies in an INS spectrum depend on the energy splitting between levels, provided the transition selection rule of  $\Delta M_J = 0, \pm 1$  is fulfilled. In many lanthanoid SMMs, the wavefunctions are comprised of mixed microstates due to low symmetry, which affects the intensities of the peaks observed in the INS spectra. Peak intensities are also influenced by the magnetic form factor  $F(\mathbf{Q})$  (Equation 5) which can be estimated for small momentum transfers by using an analytical dipole approximation of the lowest-order spherical harmonics.<sup>[63]</sup> For single ions,  $F^2(\mathbf{Q})$  typically falls off with increasing  $\mathbf{Q}$ , and thus allows identification of magnetic transitions from other contributions such as phonons.

Elucidation of the phonon spectra of Ln-SMMs is often more important than for transition metal complexes. The CF splitting of Ln-SMMs tends to be larger than the zero-field splitting of  $3d$  SMMs, and so Ln-SMMs tend to have higher energy barriers and hysteresis temperatures than SMMs based on  $3d$  metals. This complicates INS studies, however, as the CF transitions of interest often lie in the same energy range as the phonon spectrum. As mentioned earlier, the intensity of CF transitions will fall off as a function of  $\mathbf{Q}$  due to the magnetic form factor, while the intensity of a phonon will increase with  $\mathbf{Q}^2$ . In many cases it is possible to identify CF transitions from phonon transitions by looking at this  $\mathbf{Q}$ -dependence, although if there is a phonon at a similar energy, or the  $\mathbf{Q}$ -dependence is not clear, one can use other methods. The trivalent rare-earth ions have similar ionic radii thus it is often possible to synthesize isomorphous diamagnetic analogues with a similar phonon spectrum. This allows the phononic background to be measured with a good degree of accuracy, thus a common strategy is to measure the diamagnetic Y, La or Lu analogue.<sup>[15,16,23,60,64–67]</sup> The paramagnetic spectrum of interest can then be presented following subtraction of the diamagnetic “phonon” spectrum. The phonon spectrum of a sample can also be simulated either from DFT calculations or from analytical methods.<sup>[27]</sup>

In non-deuterated samples, or samples with phonons in the same energy range as magnetic transitions, transitions on the neutron gain side and hot transitions on the neutron loss side can be hard to observe. Both types of transitions require thermal population of excited states so are often weak at intermediate temperatures; however, thermal broadening at higher temperatures can make it hard to distinguish peaks from the background.

Complementary information can often be obtained using neutrons of varying wavelength. Longer wavelength neutrons will have a narrower overall energy transfer range but will also have a higher resolution. Shorter wavelength neutrons will give a much larger energy range, allowing observation of higher energy transitions on the neutron loss side of the INS spectrum. There is, however, a corresponding loss in the instrumental resolution, so often different neutron energies are used to provide complementary information

As neutrons interact so weakly with matter, typical sample masses of a gram or larger are often needed for powder INS measurements. This is a disadvantage of INS compared to other spectroscopic techniques, although modern spectrometers deal better with smaller sample sizes. Powder samples are generally contained in an aluminium sample holder, usually an annular or flat plate geometry. Where multiple scattering is an issue (for example in samples with a high percentage of hydrogen resulting in a large incoherent scattering cross section), very thin sample cans are used to mitigate this issue. For single crystal measurements, large crystals of mass > 500 mg are usually required. As this can be very synthetically challenging, several slightly smaller crystals can be indexed, and aligned to make an effective “single” crystal for measurement.<sup>[40]</sup>

A significant advantage to the neutrons weak interaction with matter is that neutron spectroscopy allows for the use of sample environments covering a huge range of temperatures such as cryostats and furnaces, high pressure such as pressure cells, and magnetic fields up to several tesla using large magnets. Typical INS measurements on SMMs are undertaken at low temperatures down to 1.5 K, with variable temperature measurements allowing elucidation of the nature of transitions, while measurements down to dilution temperatures (~ 50 mK) can also be readily undertaken. The use of hydrostatic pressure cells has been used for 3d-SMMs to contract the coordination environment, changing the energy level splitting and exchange coupling strength to tune magnetic relaxation, which can be observed in the energy of INS transitions.<sup>[39,42,45,68]</sup> Measurements in applied magnetic fields have also been used in INS of SMMs and other inorganic solids, where the evolution of transitions in a field gives additional information about the identity of CF transitions and exchange coupling.<sup>[40,51,52,69–71]</sup>

### 2.3. Inelastic Neutron Scattering of Lanthanoid Ions in Extended Solids

Inelastic neutron scattering, and neutron spectroscopy in general, has historically been used in studying the CF splitting and behaviour of lanthanoid(III) ions in both metallic and extended solids, and has proven invaluable in understanding the origin of their fundamental properties.<sup>[72]</sup> Several notable families of compounds where the CF splitting of the lanthanoid(III) ion has been determined include  $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , the rare earth pyrochlore oxides, and "dimeric"  $\text{Cs}_3\text{Ln}_2\text{X}_9$  ( $\text{X} = \text{Cl}, \text{Br}$ ). The compounds of formula  $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$  are defect perovskite structures consisting of  $\text{Ba(II)}$  ions sandwiched between  $\text{CuO}_4$  ribbons and  $\text{CuO}_2$  planes, with the lanthanoid ions found between  $\text{CuO}_2$  planes. The Y analogue, also known as YBCO, was the first compound found to exhibit superconductivity above liquid  $\text{N}_2$  temperatures.<sup>[55]</sup> Many of the compounds with paramagnetic lanthanoids substituted for the Y(III) ions still display superconductivity. Extensive INS studies have been invaluable in understanding the CF splitting and other magnetic transitions and thus mechanisms of these unconventional superconductors.<sup>[56,59,73,74]</sup> Inelastic neutron scattering has also been crucial in understanding the behaviour of magnetic pyrochlore oxides of formula  $\text{A}_2\text{B}_2\text{O}_7$  where A is usually a trivalent lanthanoid ion and B either a *d*- or *p*-block element.<sup>[75]</sup> These materials are geometrically spin frustrated in cases where A is paramagnetic, and present spin-ice, spin-liquid and other magnetic phenomena. Inelastic neutron scattering studies have been used in these materials to determine the CF splitting of the lanthanoid(III) ions, as well as in investigation of the dynamics of these materials at different temperatures.<sup>[76–85]</sup> The CF splitting and exchange coupling in the lanthanoid dimeric  $\text{Ln}_2\text{X}_9^{3-}$  units of  $\text{Cs}_3\text{Ln}_2\text{X}_9$  has also been extensively studied for  $\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{and Yb}$ , with typical modulated **Q** intensity of the transitions indicative of exchange coupling observed.<sup>[19,57]</sup> The weak exchange coupling in these systems can be elucidated from fitting of scattering data to appropriate Hamiltonians.<sup>[86]</sup>

### 3. Investigation of Crystal Field Splitting in Ln complexes and Ln-SMMs

Understanding structural effects on the CF splitting of lanthanoid complexes is of great importance for the development of high performance Ln-SMMs. Several spectroscopic techniques have been used to probe the splitting of the ground *J* multiplet in Ln-SMMs.<sup>[87–93]</sup> Luminescence spectroscopy is not always feasible due to non-radiative relaxation processes and ligand absorption. Far-infrared spectroscopy can also be used to probe CF splitting and has the practical advantage of not requiring a neutron facility. However, deconvolution of magnetic peaks from phononic peaks is not as simple, as FIR gives no information about the **Q**-dependence of a transition, so magnetic field-dependent measurements are often essential. Both FIR and luminescence spectroscopy can have lower resolution when compared to the resolution on some INS instruments such as AMATERAS at the Material and Life Science Facility at the Japan Proton Accelerator Research Complex (J-PARC).

Fast spin-lattice relaxation due to large spin-orbit coupling, as well as complicated hyperfine interactions, renders EPR spectroscopy of the lanthanoids relatively difficult. These techniques all offer the advantage that samples do not need to be large or deuterated, neutron absorption is not an issue, meaning complexes with Gd or Dy can be readily measured, and access to a nuclear reactor or spallation source is not required. However, for many complexes with CF transitions in the energy range accessible by INS, the technique offers a direct probe of the splitting of the ground  $J$  multiplet and so has been used to precisely determine the CF levels, as can be seen in several examples that follow. Elucidation of this energy level splitting is also of importance in understanding the mechanisms of slow relaxation. Orbach relaxation through an excited state (often the lowest energy excited state) can be ruled out if there is not a microstate near the  $U_{eff}$  energy found from fitting of magnetic data.<sup>[94]</sup> The relative intensities of transitions can also give an idea of the amounts of mixing and lower symmetry components of the crystal field, which are a contributing factor to QTM in many compounds.<sup>[11]</sup>

The family of archetypal Ln-SMMs,  $[\text{LnPc}_2]^-$  (**1-Ln**, Figure 2), were studied by INS on the MARI beamline at the ISIS Neutron and Muon Source at the Rutherford Appleton Laboratory, UK.<sup>[15]</sup> The **1-Tb** analogues, which have the highest  $U_{eff}$  of the family of  $230\text{ cm}^{-1}$ ,<sup>[1]</sup> were not measured as the lowest energy transition is expected to be too high in energy to be observed within the energy range of the instrument. Instead, the tetrabutylammonium SMM analogues **1-Dy** and **1-Ho** were measured. Despite the high absorption cross section of natural abundance Dy and the lack of deuteration, there was a clear CF transition at  $37\text{ cm}^{-1}$  present at 5 K for **1-Dy** (Figure 3), which was also apparent in the FIR spectrum. This matches well with the fitted relaxation barrier height from powder susceptibility measurements of  $34\text{ cm}^{-1}$ , indicating that the Dy-SMM relaxes through the first excited doublet via an Orbach relaxation mechanism. The group modelled the INS data using complete active space self-consistent field (CASSCF)<sup>[95]</sup> ab initio calculations; however, there is disagreement in the literature from various ab initio studies about the nature of the lowest energy microstates. The lowest energy INS transition; however, appears to be either a cold transition (i.e. a transition from the ground microstate) from a mostly pure  $M_J = |\pm 13/2\rangle$  to  $M_J = |\pm 11/2\rangle$  or from  $M_J = |\pm 11/2\rangle$  to  $M_J = |\pm 13/2\rangle$ . For the Ho analogue, there are two observed CF transitions in the INS spectrum, which are also observed in the FIR spectrum. The experimental data could be described well assuming either a  $|\pm 6\rangle$  or a  $|\pm 5\rangle$  ground microstate, so CASSCF calculations were again employed, which found that all microstates in the ground multiplet are mixed. The study reinforces the need for combined computational, magnetochemical and spectroscopic methods in determining the nature of SMM behaviour, as fitting of the magnetic data alone often does not allow for good reproduction of spectroscopic data.

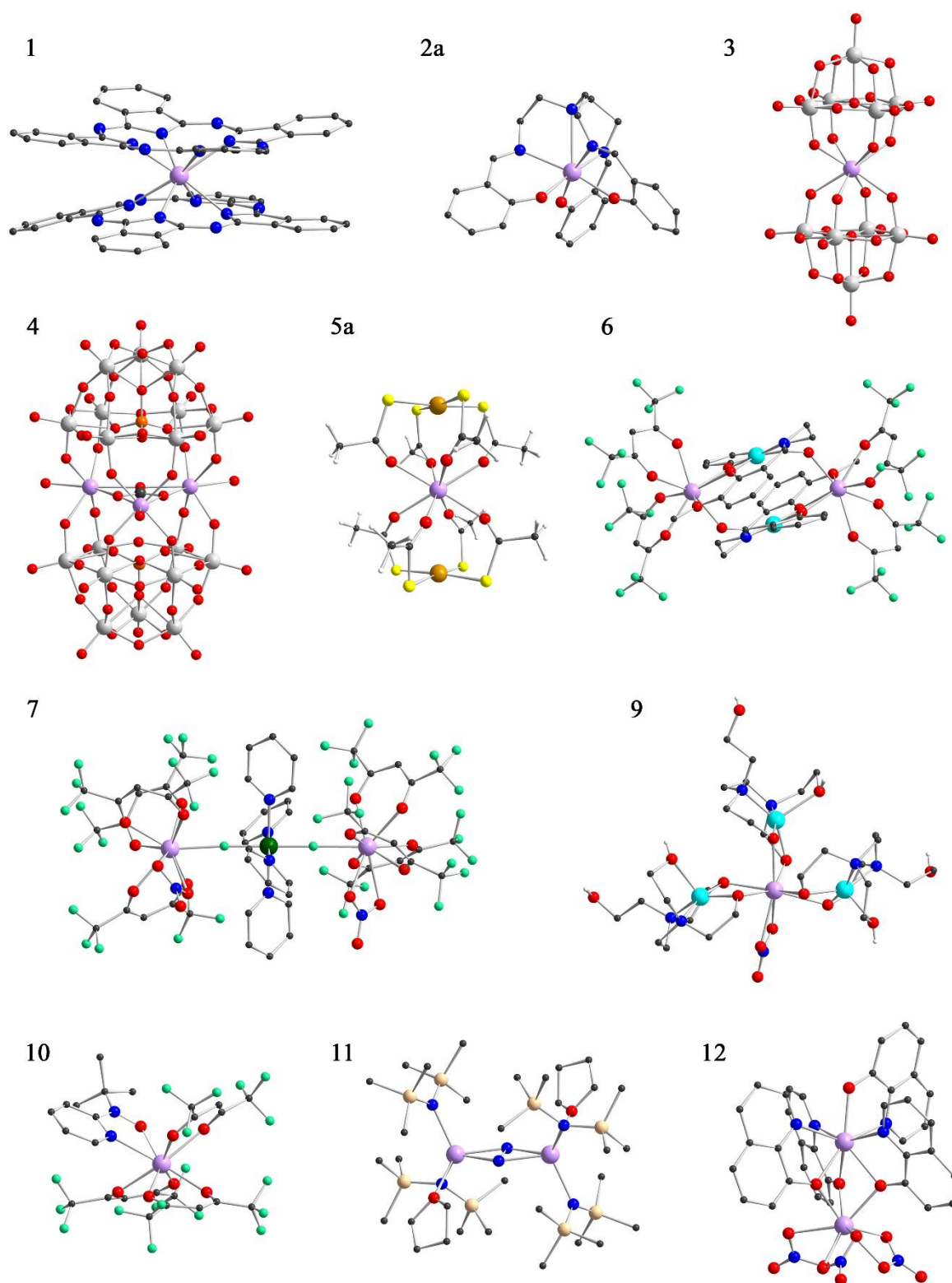


**Figure 2.** Molecular structures of selected complexes discussed in this review. Colour code = C (dark grey), N (blue), O (red), F (pale green), Si (cream), P (orange), S (yellow), Cr (dark green), Cu (cyan), Ln (purple), W (light grey), Pt (gold). Selected hydrogen atoms, solvent and counterions omitted for clarity.

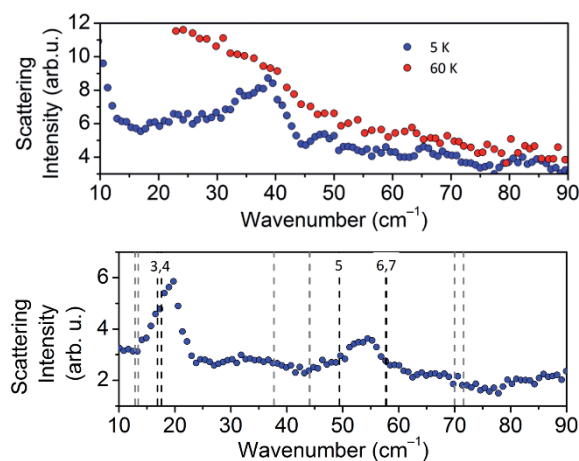


**Figure 3.** INS spectra of **1-Dy** (above) at temperatures as indicated at an incident energy of 130  $\text{cm}^{-1}$  and **1-Ho** (below) at 5 K at an incident energy of 101  $\text{cm}^{-1}$ , grey (black) lines indicate the energy levels as calculated by ab initio methods before (after) applying a scaling factor of 1.31. Spectra collected on MARI at ISIS. Adapted from Ref. [15] with permission from the Royal Society of Chemistry.

The ability of small changes in the lanthanoid coordination sphere to significantly affect the magnetic behaviour of 4f molecular magnets is also evident from a family of [Er(trensall)] (**2-Er**,  $\text{H}_3\text{trensall} = 2,2',2''\text{-tris(salicylideneimino)triethylamine}$ ) complexes.<sup>[64]</sup> The unsubstituted trensal analogue (**2a-Er**) has a crystallographic 3-fold symmetry axis through the ligand and Er(III) ion (**Figure 2**). The slight structural change associated with derivatisation of the ligand to yield either a 3-I-5-Me-trensall (**2b-Er**) or a 5-Cl-trensall complex (**2c-Er**), affords either 3-fold symmetry or no axial symmetry at the Er(III) ion, respectively. Both the **2a-Er** and **2c-Er** analogues are SMMs in small applied fields, with the ac susceptibility data of the unsubstituted analogue fit to a combination of QTM and Raman relaxation processes. Inelastic neutron scattering on the IN4 and IN5 TOF spectrometers at Institut Laue-Langevin (ILL), France, rule out an Orbach relaxation mechanism, as the magnetic transition to the lowest energy excited state at 53  $\text{cm}^{-1}$  doesn't fit the obtained  $U_{\text{eff}}$  barrier of 20  $\text{cm}^{-1}$  for **2a-Er**. There are 3 observed INS transitions, identified by comparison with a diamagnetic **2a-Y** analogue, and scaling of a high temperature spectrum of **2a-Er** by a Bose factor to estimate the phonon spectrum (**Figure 4**). The position of the transitions agrees very well with those reported from previously reported absorption and luminescence spectra of the same complex.<sup>[96]</sup> Crystal field parameters obtained from fitting the unsubstituted complex using  $C_3$  symmetry agree well with those found by CASSCF ab initio calculations; however there is worse agreement of the three magnetic features in the INS spectrum of **2b-Er**, suggesting a structural difference between the temperature at which the crystal structure was obtained (122 K)

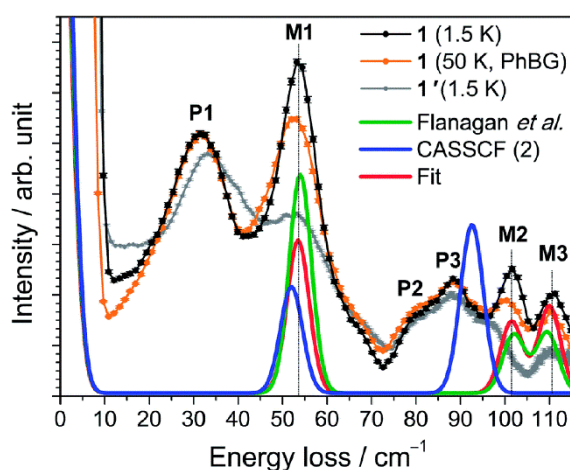


**Figure 4.** Measured and calculated INS spectra of **2a-Er** (black) and **2a-Y** (grey) at 1.5 K and  $\lambda = 2.2$  Å, phonon background as calculated from the 50 K spectrum (orange), simulated spectrum using literature CF values (green),<sup>[96]</sup> CASSCF calculated spectrum (blue) and simulated spectrum from fitting of the INS data (red). Spectra collected on IN4 and IN5 at ILL. Adapted from Ref. [64] – Published by the Royal Society of Chemistry.

Some of us and collaborators have studied the CF splitting in lanthanoid polyoxometalate complexes extensively using INS. The high oxophilicity of lanthanoid(III) ions renders lacunary polyoxometalates ideal multidentate ligands for Ln-SMMs.<sup>[97–104]</sup> An added advantage is the steric bulk of many polyoxometalates, helping to minimise undesirable intermolecular interactions. We have employed INS to investigate two families of polyoxometalate-based Ln-SMMs.<sup>[65–67]</sup> The first molecule studied was the SMM-analogue Na<sub>9</sub>[Tb(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>] (**3-Tb**) which was investigated on the PELICAN TOF beamline at the Australian Centre for Neutron Scattering (ACNS), Australia.<sup>[65]</sup> The central lanthanoid(III) is sandwiched between two tetradentate lacunary polyoxotungstates (**Figure 2**). An advantage of polyoxometalates over organic ligands for INS is the lack of hydrogen atoms requiring deuteration. Nevertheless, the samples of **3-Ln** investigated by INS were recrystallized from D<sub>2</sub>O, the co-crystallized water in these compounds being the only source of

hydrogen. Interestingly, INS of these samples indicate twice as many CF transitions as initially expected for the molecule based on literature semi-empirical electrostatic calculations.<sup>[105]</sup> Scrutiny of the INS sample revealed two distinct polymorphic phases, which could not be distinguished using magnetometric measurements alone. The coordination environment of the Tb center in both polymorphs is distorted square antiprismatic, although slight differences are evident, with one polymorph more distorted from ideal  $D_{4d}$  point symmetry. These slight structural differences confer a subtly different CF splitting of the ground  $^6H_{15/2}$  state of the Tb(III) ions. Theoretical INS spectra were calculated from the transition probabilities and CF energies from CASSCF/RASSI (RASSI = restricted active space state interaction)<sup>[106]</sup> ab initio calculations, confirming the presence of two different sets of spectra from the two polymorphs.

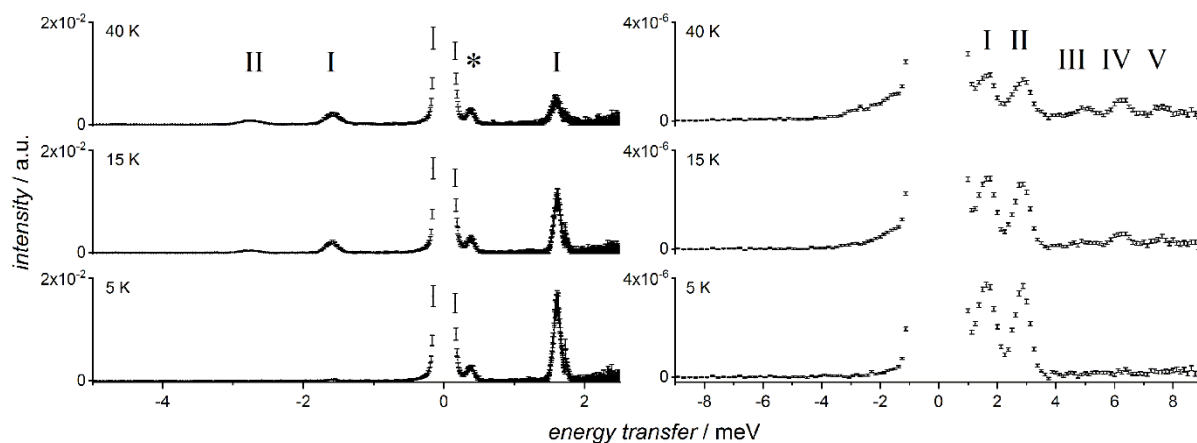


**Figure 5.** INS spectra of a pure phase of **3-Tb** at various temperatures with  $\lambda = 4.74 \text{ \AA}$  (left) and  $\lambda = 2.37 \text{ \AA}$  (right) collected on PELICAN at ANSTO. Magnetic transitions are labelled with Roman numerals; a spurious peak is indicated with an asterix. Adapted with permission from ref.<sup>[66]</sup> Copyright 2017 American Chemical Society.

A pure sample of one polymorph of **3-Tb** was later investigated (Figure 5), together with pure polymorphs of the Nd, Ho and Er analogues on PELICAN, providing a systematic study of the family of SMMs.<sup>[66]</sup> All analogues exhibit CF transitions within the energy range measured, with well-defined transitions observed. This family were some of the first lanthanoid polyoxometalate SMMs discovered, and there has been a lot of interest in their electronic properties, including extensive EPR spectroscopic studies.<sup>[104][103]</sup> The **3-Ho** analogue is of particular interest, as it functions as a spin qubit, due to atomic clock transitions of the Ho(III) ion.<sup>[107]</sup> The well resolved INS data obtained at various temperatures and wavelengths provided an accurate description of the lowest lying energy levels of the Ln(III) ions, allowing a better description of the magnetic

properties. These experimental data also provided an important experimental benchmark for ab initio calculations on these large computationally expensive systems. The ab initio determined wave functions corresponding to the CF levels were employed to assign the INS transitions allowed by selection rules and were in good agreement with the observed positions and relative intensities of the INS peaks.

Two deuterated members of the family of trinuclear  $\text{Na}_{11}[\{\text{Ln}(\text{OH}_2)\}_3\text{CO}_3(\text{PW}_9\text{O}_{34})_2]$  complexes (**4-Ln**, Ln = Ho and Er) were studied using the same combined computational and INS approach as **3-Ln**.<sup>[67]</sup> Three crystallographically distinct lanthanoid(III) ions are bridged by an  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ -carbonate, with a capping trilacunary polyoxotungstate above and below the plane of the lanthanoid centers (Figure 2). Each lanthanoid center has an additional 7<sup>th</sup> coordination site filled by an aqua ligand. By comparison with the deuterated **4-Y**, as well as analysis of temperature and Q-dependence, two peaks of magnetic origin were observed for **4-Ho** at 4 and 24  $\text{cm}^{-1}$  (0.5 and 3 meV, Figure 6). Both peaks are well resolved, albeit much broader than instrumental resolution. Broadening from either vibrational dampening of excitations or energy dissipation, or unresolved splitting due to three slightly different Ho(III) ion coordination environments would be expected to give a Lorentzian line shape. The peak broadening in this system is Gaussian, much like that in  $\text{Tb}_2\text{TiO}_7$ , a frustrated pyrochlore oxide spin liquid.<sup>[75]</sup> This is assumed to be due to a random field experienced by each Ho(III) ion caused by the surrounding fluctuating magnetic moments. The temperature dependence of both peaks indicates they are both cold transitions. Ab initio CASSCF calculations of **4-Ho** match the magnetic data well, although were performed considering all three Ho(III) ions in the molecule to be identical, despite slight differences in their coordination environments, as the complete Hamiltonian is too complicated to calculate ab initio. These calculations are consistent with two INS-active transitions from the ground microstate, although decomposition of the wave functions is difficult as all the states are mixed. Broadening of the INS transitions is also expected due to the three different Ho(III) centres, but as there seem to be several effects causing broadening, it is difficult to resolve this. Inelastic neutron scattering of **4-Er** showed three transitions on the neutron gain side, in the lower resolution 4.74 Å configuration, while in the 2.37 Å configuration the corresponding transitions on the neutron loss side are apparent. Calculations performed for the three Er sites find the ground microstate term is a dominant mixture of  $|\pm 15/2\rangle$  and  $|\pm 11/2\rangle$  states for each ion. The ground state *g*-tensor of each Er(III) ion is almost purely axial, with each principal magnetic axis almost coplanar with the ring formed by the three ions. Unlike in a toroidal orientation of the axes, each axis is directed radially, because of competing antiferromagnetic superexchange interactions through the carbonate bridge and dipolar

interactions. The calculated energy levels are in reasonable agreement with the measured transitions from INS, despite the INS spectra fit again considering all three Ln(III) ions as equivalent.

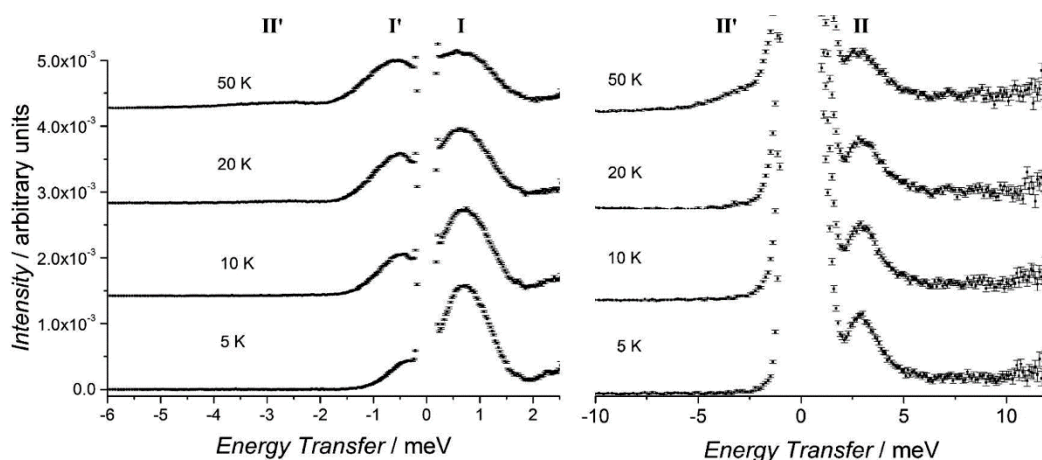
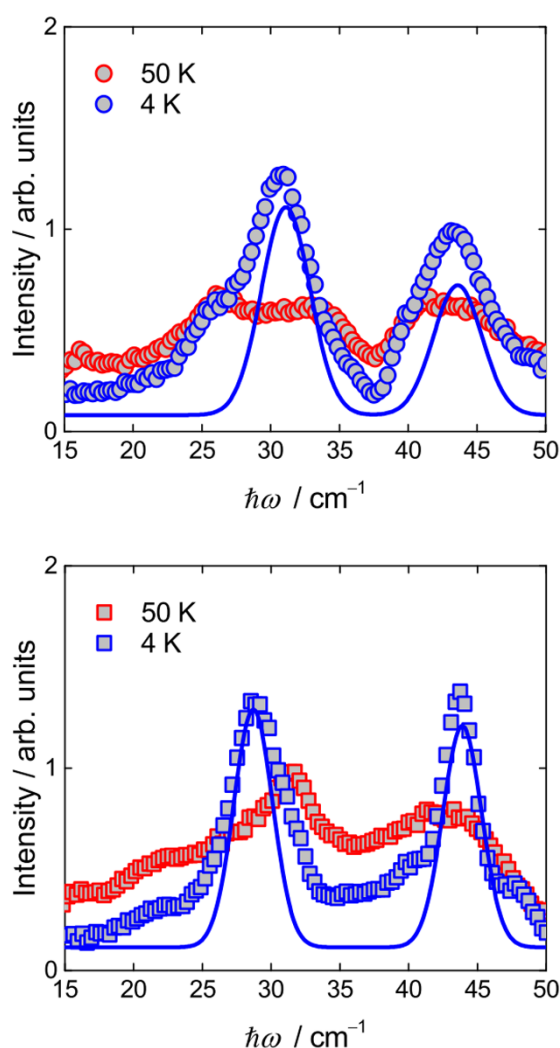


**Figure 6.** INS spectra of **4-Ho** at various temperatures with  $\lambda = 4.74 \text{ \AA}$  (left) and  $\lambda = 2.37 \text{ \AA}$  (right) collected on PELICAN at ANSTO. Magnetic transitions are labelled with Roman numerals. Reprinted with permission from ref.<sup>[67]</sup> Copyright 2016 American Chemical Society.

Elucidating the factors influencing QTM is important for the design of better Ln-SMMs and information in this regard was obtained following INS studies of the metalloligated Dy complexes  $[\text{Dy}\{\text{Pt}(\text{SAC})_4\}_2]^{4-}$  (**5-Dy**,  $\text{SAC}^- = \text{thioacetate}$ ; **Figure 2**). The two salts investigated exhibit different local coordination environments at the Dy(III) center.<sup>[60,108]</sup> The first,  $(\text{NEt}_4)[\text{Dy}\{\text{Pt}(\text{SAC})_4\}_2]$  (**5a-Dy**) has a twist angle of  $24.11^\circ$  between the two squares formed by the metalloligand coordinating O atoms, compared to the  $(\text{PPh}_4)[\text{Dy}\{\text{Pt}(\text{SAC})_4\}_2]$  (**5b-Dy**) compound, which has a  $44.52^\circ$  angle. This near  $45^\circ$  twist angle in **5b-Dy** gives the Dy complex a near  $D_{4d}$  symmetry compared to the lower  $C_4$  symmetry in **5a-Dy**. This is reflected in the magnitude of the tunnel-splitting observed in the two compounds, with the higher symmetry complex exhibiting an almost 3-fold reduction. Here, INS experiments on the direct geometry multi-chopper cold neutron time-of-flight spectrometer TOFTOF at Maier Leibnitz Zentrum (MLZ), Germany and the direct geometry high-flux thermal neutron time-of-flight spectrometer IN4C at ILL were undertaken to identify CF excitations in the two samples, with the phonon spectra obtained from measuring the isomorphous Y analogues.<sup>[60]</sup> For both Dy compounds, there are two observed cold transitions in the INS spectra, from a majority  $|\pm 11/2\rangle$  ground doublet to the first and second excited microstates of majority  $|\pm 9/2\rangle$  and  $|\pm 13/2\rangle$  character. For **5a-Dy**, there is an excitation at  $31.1 \text{ cm}^{-1}$  corresponding to a transition to the predominantly  $|\pm 9/2\rangle$  first excited microstate, with a second transition to the higher  $|\pm 13/2\rangle$  at  $43.6$

1  $\text{cm}^{-1}$ . For **5b-Dy**, the change in geometry and symmetry leads to an inversion in the microstate  
 2 identities, with a first transition at  $28.7 \text{ cm}^{-1}$  to an almost pure  $|\pm 13/2\rangle$  state and a second to the  
 3  $|\pm 9/2\rangle$  state at  $43.9 \text{ cm}^{-1}$ . From fitting of luminescence data, INS, and powder magnetization, CF  
 4 parameters for the two systems as well as the energy level splitting can be simulated. Of note is a  
 5 much higher fourth order extradiagonal CF parameter in **5a-Dy**, which corresponds to a lower  
 6 purity of the ground  $|\pm 11/2\rangle$  doublet. The difference in purity of the microstates is reflected in the  
 7 relative intensities of the two transitions in the two compounds (**Figure 7**), due to a higher degree of  
 8 QTM in **5a-Dy**. Here INS has proved an invaluable tool in investigating subtle changes in  
 9 coordination geometry in Ln-SMMs.



11  
 12 **Figure 7.** Variable temperature INS spectra of salts of **5a-Dy** (above) and **5b-Dy** (below) with  $\lambda =$   
 13  $3.0 \text{ \AA}$  collected on TOFTOF at MLZ. The blue lines are simulated spectra using CF parameters  
 14 obtained from fitting multiple sets of spectroscopic and magnetometric data. Adapted from Ref  
 15 [60].

The Tb, Ho and Er analogues of **5b-Ln** have also been studied by cantilever torque magnetometry (CTM) and INS on TOFTOF at MLZ and FOCUS at SINQ.<sup>[109]</sup> Cantilever torque magnetometry at 2 K suggests that the Ho analogue exhibits easy-axis magnetic anisotropy, while Tb and Er exhibit easy-plane magnetic anisotropy, through analysis of the sign of the magnetic torque. Interestingly, both Ho and Er exhibit a switch in the sign of the magnetic torque with increasing temperature, indicating a change in magnetic anisotropy from easy-axis to easy-plane and vice versa, at 18 K and 45 K respectively. For all complexes, the CF parameters obtained from fitting INS and CTM were used to simulate high field EPR, and refined if need be. Inelastic neutron scattering of **5b-Tb** reveals one cold transition at  $14\text{ cm}^{-1}$  and one hot transition at  $37\text{ cm}^{-1}$ . The fitting of these data together with the torque magnetometry, confirms the nature of the of the lowest lying microstates as being low  $M_J = |0\rangle$ ,  $|\pm 1\rangle$  and  $|+2\rangle+|-2\rangle$  for the ground microstate and next highest states respectively. The INS data of **5b-Ho** is slightly more complex, showing both two cold transitions from a ground  $|+4\rangle+|-4\rangle$  microstate, while three hot transitions become apparent at higher temperature. The **5b-Er** complex shows only one INS transition, from a  $M_J = |\pm 1/2\rangle$  to a  $M_J = |\pm 3/2\rangle$  microstate. The switch in magnetic anisotropy in **5b-Er** from easy-plane becomes apparent at 50 K as the easy-axis doublets of  $|\pm 13/2\rangle$  and  $|\pm 15/2\rangle$  become thermally occupied. This is the first observation by torque magnetometry of a switch in magnetic anisotropy upon variation of temperature or field, due to a purely single-ion process, which was interpreted with the aid of CF fitting of INS data.

#### 4. Probing Exchange Interactions in Ln-SMMs with INS

Attempts to improve the  $U_{\text{eff}}$  and hysteresis temperature of Ln-SMMs has included coupling Ln centers with one or more other spin carriers, such as a radical ligand, a transition metal ion or an additional lanthanoid ion, to increase the overall magnetic moment of the complex, much like in transition metal coordination cluster SMMs.<sup>[9,10,110–112]</sup> Coupling with a radical ligand has also been proposed as a method of shifting QTM from zero-field to remove the zero-field QTM that is frequently observed in Dy-SMMs and detrimental to memory applications.<sup>[111]</sup> Magnetic susceptibility measurements fall short in elucidating the magnetic nature and electronic structure of such complexes, as lanthanoid CF excitations and exchange splitting are often in the same energy range, so alternative spectroscopic means are required, such as INS, as excitations based on exchange interactions are allowed by the selection rules. Neutron scattering has a distinct advantage over FIR and EPR spectroscopies in this case as exchange coupling can be directly measured in the

absence of an applied magnetic field, simplifying analysis significantly. Neutron spectroscopy also yields the **Q**-dependence of exchange transitions, which gives spatial information.<sup>[19,113]</sup> As mentioned previously, exchange-coupled rare-earth(III) ions have been well studied in extended solids, and the same techniques can be applied to discrete molecular complexes.

#### 4.1. 3d-4f systems

The first mixed 3d-4f SMM discovered in 2003 was the tetranuclear Tb<sub>2</sub>Cu<sub>2</sub> square complex [Cu(1-(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxy-benzylideneamino)-ethane)Tb(hfac)<sub>3</sub>]<sub>2</sub> (**6-Tb**), in which each crystallographically equivalent Tb(III) ion is exchange-coupled through oxo-bridges to two adjacent Cu(II) complex units.<sup>[114]</sup> The strong anisotropy of the Tb(III) ions and the large overall magnetic moment gives rise to an energy barrier to reversal of magnetization, assuming a purely Orbach relaxation mechanism, of around 15 cm<sup>-1</sup>. A large 6 g sample of approximately 50% deuteration was measured on IN5 at ILL, as the exchange coupling between adjacent Tb(III) and Cu(II) ions was overestimated by fitting of the magnetic susceptibility data alone and investigation of the Tb CF splitting by optical spectroscopy was not possible due to overlap of the Cu(II) and Tb(III) absorption bands.<sup>[115]</sup> The INS spectra of **6-Tb** (Figure 8) feature both a cold transition at 19 cm<sup>-1</sup> and a hot transition at 12.5 cm<sup>-1</sup>, with corresponding peaks on the neutron energy loss side at higher temperatures. Using an exchange-charge model where the CF splitting of the Tb(III) ion is described by 4 parameters instead of 27 CF parameters, the magnetic susceptibility data and INS were simultaneously fit to give a good reproduction of both sets of data, and two Tb...Cu ferromagnetic exchange interactions of  $J_{ex} = 2.83$  and  $0.64$  cm<sup>-1</sup> ( $\mathcal{H}_{ex} = -J_{ex(1)}(\hat{J}_1 \cdot \hat{S}_2 + \hat{J}_2 \cdot \hat{S}_1) - J_{ex(2)}(\hat{J}_1 \cdot \hat{S}_1 + \hat{J}_2 \cdot \hat{S}_2).$ )

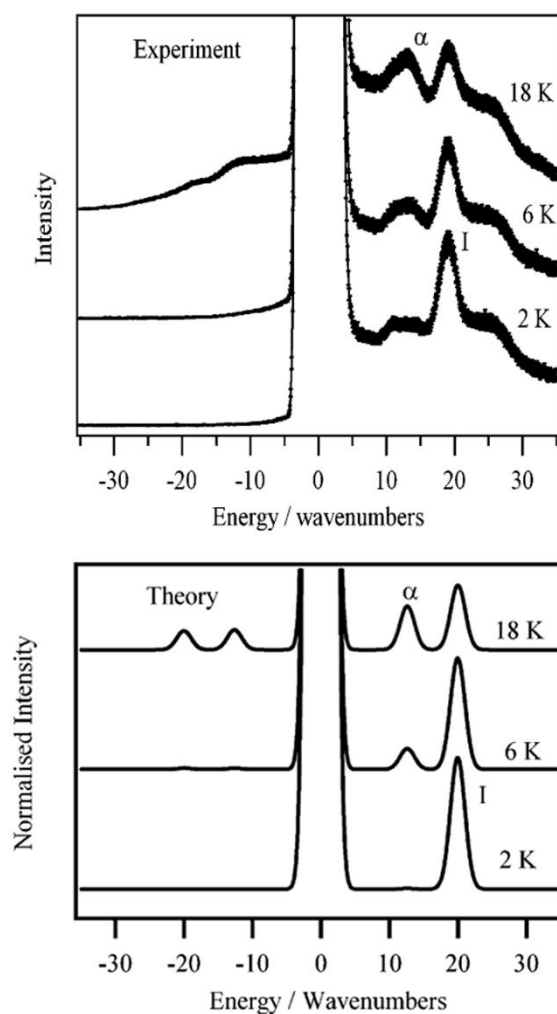


**Figure 8.** INS spectra of **6-Tb** at indicated temperatures and  $\lambda = 3.4 \text{ \AA}$  (left) and simulated spectra using calculated exchange-charge model parameters (right) collected on IN5 at ILL. Adapted with permission from ref.<sup>[77]</sup> Copyright 2009 American Chemical Society.

The fluoride-bridged trinuclear complex  $[\text{Dy}(\text{hfac})_3(\text{H}_2\text{O})-\text{CrF}_2(\text{py})_4-\text{Dy}(\text{hfac})_3(\text{NO}_3)]$  (**7-Dy**) exhibits a field-induced ferrimagnetic to ferromagnetic configuration of the magnetic moments in X-ray magnetic circular dichroism (XMCD).<sup>[116]</sup> It was studied by INS on the direct-geometry TOF spectrometer IN5 at the ILL to elucidate the nature of the lowest energy microstates. In the lower resolution  $4.8 \text{ \AA}$  neutron wavelength configuration, there is a single transition observed (peak I) at  $3.4 \text{ cm}^{-1}$  (Figure 9) which agrees well with an energy barrier to reversal of magnetization of  $3.0 \text{ cm}^{-1}$  as determined from muon-spin relaxation measurements. Using an excited-state Hamiltonian, operating on the restricted space of the ground and first-excited Kramers doublets of each of the magnetic ions of **7-Dy**, this was found to be a transition from an overall or total  $M_J = M_{\text{tot}} = |\pm 25/2\rangle$  to a  $|\pm 27/2\rangle$  state. In the higher resolution  $6.5 \text{ \AA}$  spectra, fine structure in transition I is apparent. Although the simulations based on the Hamiltonian used reproduce the other experimental

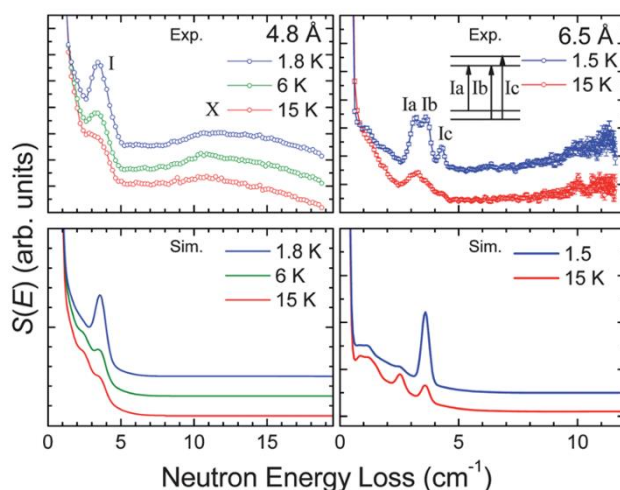


**Figure 9.** INS spectra of **7-Dy** collected at indicated temperatures and wavelengths collected on IN5 at ILL (top) and simulated spectra with best-fit parameters (bottom). Adapted with permission from ref.<sup>[116]</sup> – Published by the Royal Society of Chemistry.

Another heterodinuclear Tb-Cu complex investigated by INS is the SMM [TbCu(o-vanillate)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>], (**8-Tb**) studied on the TOF spectrometer AMATERAS at J-PARC.<sup>[117]</sup> Using a repetition rate multiplication technique (RRM),  $Q$ - $\omega$  maps with several  $E_i$  could be obtained simultaneously. The INS spectrum shows two excitations, at 14 and 98 cm<sup>-1</sup> (1.7 and 12.3 meV). The ac susceptibility measurements indicate that the dinuclear complex is a SMM with a  $U_{eff}$  of 12 cm<sup>-1</sup>, corresponding to relaxation through the first excited state.<sup>[118]</sup> The phase modulation of the  $Q$ -dependence of  $S(Q, \omega)$  for the lower energy transition (labelled (i) in **Figure 10**), indicates the states involved are a result of exchange coupling between the Tb(III) and Cu(II) ions. In the higher resolution configuration, there are also hyperfine interactions apparent in the 14 cm<sup>-1</sup> (1.7 meV) transition. Hyperfine interactions for the Tb and Cu nuclear spins would be expected to split each state into 16, although only the major splitting is resolved. Both the  $Q$ -dependence and hyperfine splitting match well with an  $S(Q, \omega)$  calculated from an appropriate choice of a Hamiltonian with a ligand field component (using three CF parameters), an exchange component, and a hyperfine component.

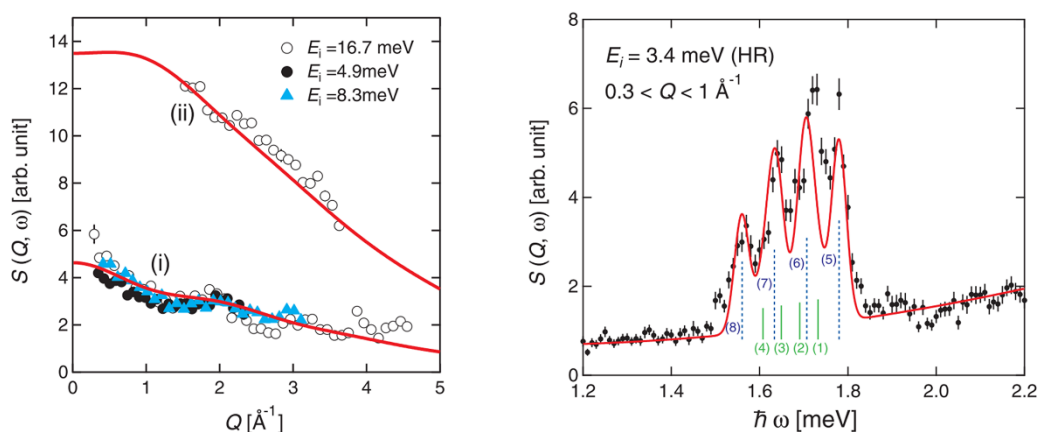


**Figure 10.** INS data for **8-Tb**, left:  $Q$  dependence of  $S(Q, \omega)$  of excitations (i) and (ii) at  $T = 3.5$  K at selected incident energies. Right: Energy dependence of  $S(Q, \omega)$  measured in the high-resolution condition. Spectra collected on AMATERAS at J-PARC. Adapted with permission from ref.<sup>[117]</sup> Copyright 2013 by the American Physical Society.

The same group studied **8-Tb** by quasi-elastic neutron scattering (QENS), where broadening of the elastic line is observed due to relaxational processes with no net energy gain or loss.<sup>[118]</sup> Using several spectrometers including TOFTOF and AMATERAS, they determined a second relaxation process, from fitting the QENS data, obtaining a thermally-activated QTM mechanism through microstates at  $121 \text{ cm}^{-1}$ .

Bidentate  $\text{CuH}_2\text{edte}$  metalloligands ( $\text{H}_2\text{edte} = N,N,N',N'$ -tetrakis(2-hydroxyethyl)ethylenediamine) were used with  $\text{Ln} = \text{Tb}, \text{Dy}$  to synthesise tetranuclear compounds of formula  $[\text{LnCu}_3(\text{H}_2\text{edte})_3(\text{NO}_3)]^{2+}$  (**9-Ln**).<sup>[119]</sup> The **9-Tb** compound is a SMM with a modest  $U_{\text{eff}}$  of  $12 \text{ cm}^{-1}$ , while **9-Dy** is a field-induced SMM. Due to coupling with the  $\text{Cu(II)}$  ions, **9-Dy** has an integer  $M_{\text{tot}}$  and thus shows strong zero-field QTM. To probe the ground  $J$  multiplet splitting and exchange coupling, INS measurements on nitrate salts of both analogues were performed on the TOF spectrometer FOCUS at the spallation source SINQ at the Paul Scherrer Institut, Switzerland. In the INS spectrum of both analogues there are two clear cold magnetic transitions, of which the higher energy peak appears to be comprised of two overlapping peaks (Figure 11). The INS spectra were modelled using an effective Hamiltonian considering six anisotropic  $\text{Ln-Cu}$  exchange parameters, and assuming the CF splitting would be out of the energy range measured. The best fit for **9-Tb** corresponds to a  $M_{\text{tot}} |\pm 15/2\rangle$  ground state of ferromagnetically aligned spins, with all three excitations to three  $|\pm 13/2\rangle$  states, each corresponding to a  $\text{Cu}$  spin flip. Similarly, for the **9-Dy** the three transitions could all be fit as

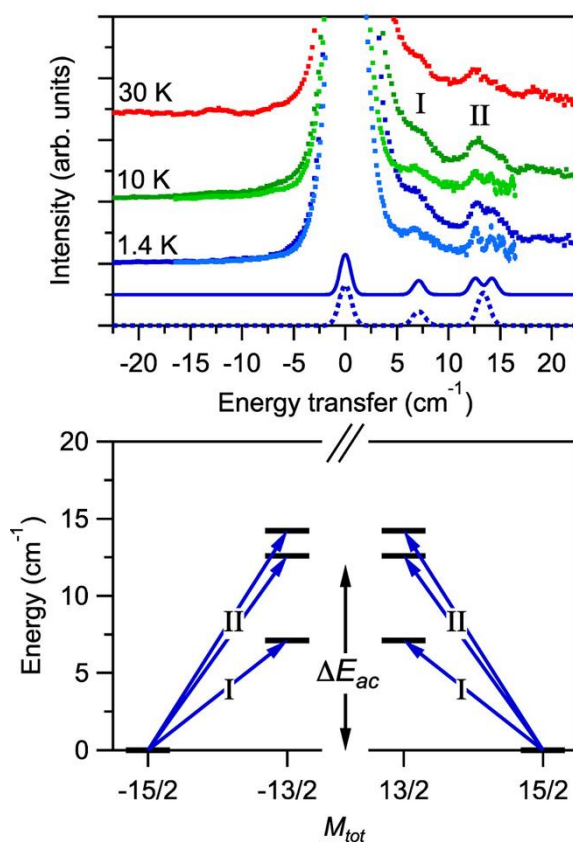


**Figure 11.** Variable temperature INS spectra of **9-Tb** with  $\lambda = 4.3 \text{ \AA}$  (dark blue, dark green, red) and with  $\lambda = 5.5 \text{ \AA}$  (light blue, light green) collected on FOCUS at SINQ with spectra calculated using two sets of exchange parameters (solid blue and dashed blue lines) (above) and energy level diagram based on effective exchange interactions, with blue arrows denoting INS transitions (below). Adapted from ref.<sup>[119]</sup> Copyright 2014 American Chemical Society.

## 4.2. 2p-4f systems

Due to the limited radial extension of the 4f orbitals, another approach to increasing the overall magnetic moment in lanthanoid complexes is to incorporate radially diffuse 2p orbitals of radical ligands. An example of this 2p-4f coupling is found in the compound  $[\text{Tb}(\text{hfac})_3(2\text{pyNO})]$  (**10-Tb**, 2pyNO = *t*-butyl 2-pyridyl nitroxide; **Figure 2**).<sup>[120]</sup> The compound crystallises with two independent molecules in each unit cell, with two separate characteristic  $U_{\text{eff}}$  values. Interestingly,

the difference between the two molecules is the torsion angle between the radical 2pyNO ligand and the Tb(III) center, with molecule 1 exhibiting a Tb–O–N–C torsion angle of 15.8(7)° compared to molecule 2 with a 3.8(7)° angle. A 75% deuterated polycrystalline sample was studied on the direct geometry AMATERAS time-of-flight spectrometer at J-PARC. In the lower resolution (66.0 cm<sup>-1</sup> incident neutron energy) configuration, two magnetic excitations are observed, one at 30 (3.7 meV) and one at 39 cm<sup>-1</sup> (4.9 meV). With the higher resolution (62.5 cm<sup>-1</sup>) configuration, the first peak is resolved as two transitions separated by 2.7 cm<sup>-1</sup> (0.34 meV), labelled as Ia and Ib (Figure 12). These are of unequal intensity at 3.8 K but are equivalent in intensity at 30 K. The temperature dependence of the peak intensity is consistent with Ib being a transition from the ground state, while Ia originates from a transition from a first excited microstate. Along with observations from high field high frequency EPR measurements, all the transitions observed are assigned as originating from exchange interactions of the ground  $M_J = |\pm 6\rangle$  pseudodoublet of the two Tb(III) ions with the  $S = 1/2$  organic ligand. Both transitions Ia and Ib are assigned as transitions involving one molecule of **10-Tb**, where the higher torsion angle has changed the symmetry of the exchange, while transition II originates from the second molecule.

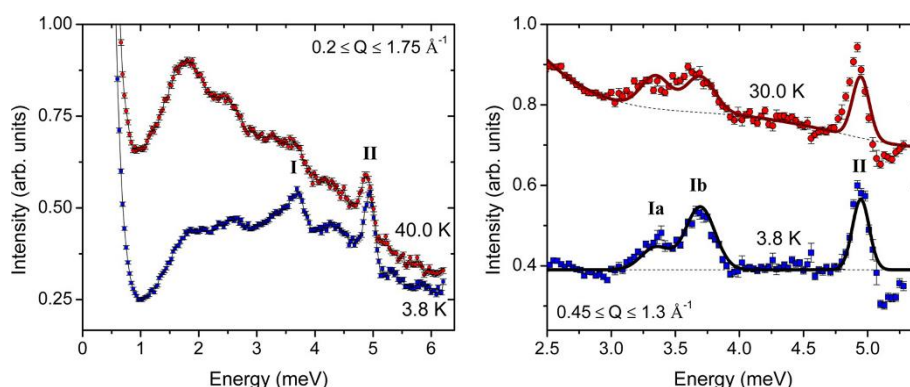
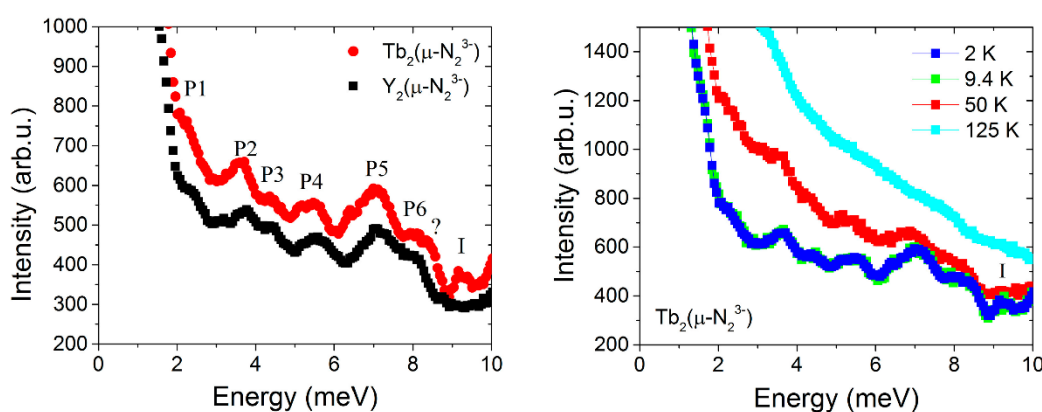


**Figure 12.** INS spectra of **10-Tb** at varying temperature and  $E_i = 66.0 \text{ cm}^{-1}$  (left) and  $E_i = 62.5 \text{ cm}^{-1}$  (right) collected on AMATERAS at J-PARC. Solid lines are simulated spectra. Adapted with permission from ref.<sup>[120]</sup> Copyright 2015 American Chemical Society.

The reduced  $\text{N}_2^{3-}$  radical-bridged Tb-SMM  $[\text{K}(\text{18-crown-6})(\text{THF})_2][\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Tb}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$  (**11-Tb<sup>red</sup>**) exhibits one of the highest blocking temperatures of a polynuclear SMM of 14 K.<sup>[121]</sup> The INS of **11-Tb<sup>red</sup>**, **11-Y<sup>red</sup>**, and the “parent” compound **11-Tb**, with a diamagnetic bridging ligand, were studied on the time-of-flight spectrometer LET at ISIS.<sup>[23]</sup> The spectrum of the parent compound shows one strong cold magnetic transition at 6 cm<sup>-1</sup> (0.75 meV), with a less intense transition at 40 cm<sup>-1</sup> (5 meV), Figure

13). The INS spectrum of **11-Tb<sup>red</sup>** shows several features, of which only one is assigned as a magnetic transition at 74 cm<sup>-1</sup> (9.2 meV), by comparison with the spectrum of **11-Y<sup>red</sup>**. To model the INS of the parent compound, a simplified Ising dimer model was employed, on the basis of weak ferromagnetic coupling in the magnetic susceptibility. Using a reduced Hamiltonian, the higher energy transition is assigned to a CF excitation from a ground  $|\pm 6\rangle$  state to a first excited  $|\pm 5\rangle$  state, while the lower energy 6 cm<sup>-1</sup> transition to a spin-flip transition of one of the sites. This corresponds to a  $J_{ex} = -0.17$  cm<sup>-1</sup> ( $\mathcal{H}_{ex} = -J_{ex}(\hat{J}_1 \cdot \hat{J}_2)$ ) between the two Tb(III) ions, the first direct determination of a Ln...Ln exchange interaction by INS. The single transition in the **11-Tb<sup>red</sup>** spectrum could, however, not be satisfactorily modelled using the same point charge model and exchange interactions as the parent compound. At higher temperatures of 100 and 125 K, there is also significant broadening of the elastic line, suggesting quasi-elastic neutron scattering, possibly due to rotation of the trimethylsilyl group.



14  
15 **Figure 13.** INS spectra of **11-Tb<sup>red</sup>** at  $E_i = 94.4$  cm<sup>-1</sup> at 2 K with comparison to the **11-Y<sup>red</sup>**  
16 analogue (left) and with varying temperature (right) measured at LET at ISIS. Adapted from ref.<sup>[23]</sup>

### 4.3. A 4f-4f system

19 Another example of Ln...Ln exchange is the symmetric complex [Dy<sub>2</sub>(hq)<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub>]·MeOH (**12-Dy**  
20 hqH = 8-hydroxyquinoline) (Figure 2), a dinuclear SMM which, due to non-co-linearity of the two  
21 Dy anisotropy axes, shows strong QTM because of the resultant transverse magnetic interactions.  
22 The **12-Er** and **12-Yb** analogues were chosen as a model for a combined spectroscopic and  
23 theoretical approach.<sup>[16]</sup> Each molecule contains two lanthanoid(III) ions, one located in the “hq”  
24 ligand pocket, and one in the “NO<sub>3</sub>” pocket. In the INS spectra (Figure 14), transitions  
25 corresponding to both pockets are apparent. INS spectra collected on LET, IRIS and MARI at ISIS  
26 and FIR were used to validate the CASSCF calculations, in order to obtain the g-matrix orientations

of the ions. Using  $g$ -tensors obtained from EPR of selectively site doped **12-Ln@Y** and **12-Ln@Lu** analogues, the local electronic structure was then determined. Combining the fitting of the pure **12-Ln** EPR spectra yielded information on the coupling in the system. For the **12-Er** analogue, dipolar coupling is the dominant exchange coupling pathway with a contribution from a superexchange pathway, while for **12-Yb**, superexchange through the Ln–O–Ln bridge dominates. Clearly for these more complex polynuclear SMMs a combined experimental approach is required when using only powder INS measurements, as there are too many parameters to allow unambiguous characterisation for the number of transitions typically observed in an INS experiment.

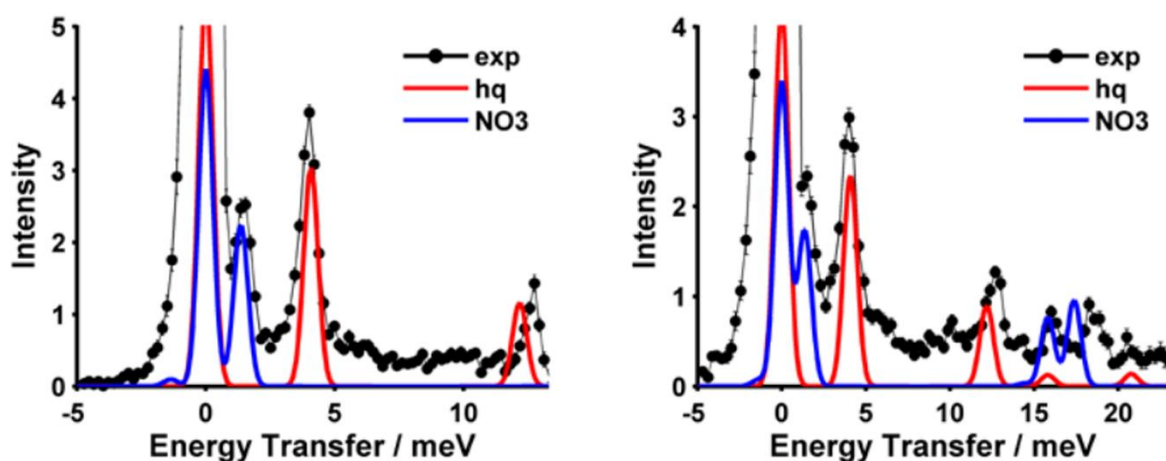


**Figure 14.** INS spectrum of **12-Er** at  $E_i = 120 \text{ cm}^{-1}$  (left) and  $200 \text{ cm}^{-1}$  (right) at 5 K with **12-Lu** diamagnetic background subtracted measured on MARI at ISIS. The red (blue) line is the INS spectrum simulated from ab initio calculated CF parameters for the “hq” (“NO<sub>3</sub>”) pocket. Adapted from Ref.<sup>[16]</sup>. Copyright 2018 American Chemical Society.

## 5. Conclusions and Future Outlook

Inelastic neutron scattering is an invaluable technique for elucidating the CF splitting in mononuclear lanthanoid complexes in conjunction with other experimental techniques, or with ab initio and crystal field analysis. Spectroscopic techniques are well-suited for determining the effect of slight geometry changes in molecular nanomagnets, which is essential to understanding the electronic structure of such complexes and ultimately for designing high-performance SMMs. Theoretical modelling is important for electronic structure elucidation, but the development of satisfactory modelling methods relies on high quality data for benchmarking, and INS is proving

indispensable for this purpose. The incorporation of additional paramagnetic centers, to both reduce QTM and increase the overall magnetic moment in Ln-SMMs, introduces further parameters to consider, which cannot be determined from fitting magnetic data alone. Along with techniques such as FIR and EPR spectroscopies, INS is an invaluable tool. Despite the inherent barriers to performing INS experiments, ranging from the relative scarcity of neutron sources to the requirement for large samples and the difficulties associated with hydrogenous and adsorbing samples, this is still a thriving field. Neutron scattering also has several advantages in the ability to probe  $\mathbf{Q}$ , which yields spatial information about an excitation, and the ease of complex sample environments. Many of the measurements that have been made are only possible due to the new generation of spectrometers which have been built in recent decades with greater detector coverage, high flux and low measuring background, as well as advances in the resolution of instruments.

Other important information can be obtained from INS experiments and this has been highlighted by the work that has been done in the more developed field of 3d transition metal single molecule magnets. This includes experiments undertaken on single-crystals, with added 3D information about transitions of interest, which for SMMs allows determination of directionality as well as dynamical correlations between magnetic ions.<sup>[122]</sup> This is exemplified in single-crystal measurements of Mn<sub>12</sub> and of a Cr<sub>8</sub> ring.<sup>[123,124]</sup> In a related Cr<sub>7</sub>Co ring, a similar 4D experiment was used to elucidate the directionality of the exchange, which for complexes involving anisotropic metal ions can often not be well-described by an isotropic exchange model.<sup>[125]</sup> Other advances in the field involve “time-resolved” INS of a single crystal of the Mn<sub>12</sub> complex, in which using the application of a magnetic field, the Kramers doublets are split, and the population of various energy states as a function of time can be monitored, providing a means of investigating the relaxation times.<sup>[40]</sup> Studies such as these could allow elucidation of relaxation effects in SMMs, although the applicability of this to lanthanoid systems is yet to be demonstrated. Polarised neutrons are also available on some beamlines and can be used to unambiguously distinguish between phonon transitions and magnetic transitions, which in systems with a dominant phonon spectrum could provide easier identification of what magnetic transitions are present. The major technical developments with instrumentation that will likely drive new discoveries is a new wave of time-of-flight instruments either dedicated to measuring with polarised neutrons or with them as an additional experimental option. This includes HYSPEC at the SNS,<sup>[126]</sup> LET at ISIS,<sup>[127]</sup> PELICAN at ANSTO,<sup>[30]</sup> POLANO at J-PARC<sup>[128]</sup> and TOPAS at FRM II.<sup>[129]</sup> Polarised neutron techniques allow magnetic, coherent and incoherent scattering to be separated experimentally; such capabilities have been successfully implemented on triple-axis spectrometers and to some extent on the time-of-flight diffuse scattering spectrometer D7 at ILL. It is anticipated that the new generation will allow

larger regions of reciprocal space to be mapped with polarised neutrons, to allow the easy identification of magnetic modes, but will also provide experimental evidence for any mixing of magnetic and phonon modes. Finally, the European Spallation source will enter service in the next decade. The long pulse width and high intensity of this source are an exciting prospect for new instrumentation and potentially revolutionary experiments.

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**Keywords:** inelastic neutron scattering • lanthanoids • single-molecule magnets • crystal field splitting • exchange coupling

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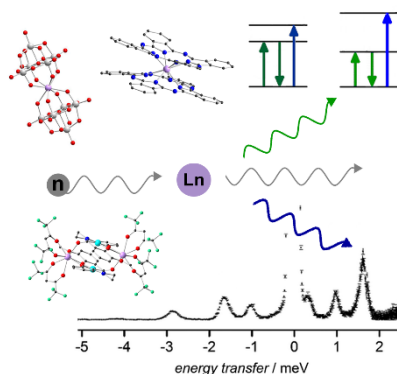
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## 1 Table of Contents Entry

2 Lanthanoid(III) complexes constitute state-of-the-art single-molecule-magnets (SMMs), exhibiting  
3 slow magnetic relaxation and magnetization quantum tunnelling, which arise from the electronic  
4 structure of the lanthanoid(III) ion. Inelastic neutron scattering is a powerful but underutilized  
5 technique for elucidating the electronic structure that affords SMM behaviour.



1 **Biographical Sketches**

2 ***Maja Dunstan***



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Maja Dunstan obtained her BSc and MSc in Chemistry at the University of Melbourne. She has been a research student under the supervision of Colette Boskovic since 2015, with a focus on synthesis and characterization of molecular nanomagnets with redox-active ligands. Currently, she is undertaking a PhD investigating the magnetic properties of lanthanoid complexes with inelastic neutron scattering.

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12 ***Richard Mole***



Richard Mole received his PhD in inorganic chemistry from the University of Cambridge in 2007. This was followed by postdoctoral work at the Maier Leibnitz Zentrum, Munich, where he worked on the thermal triple-axis spectrometer PUMA. Richard moved to the Australian Nuclear Science and

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23 ***Colette Boskovic***



Colette Boskovic obtained her BSc(Hons) and PhD degrees from the University of Melbourne, undertaking research under the supervision of Tony Wedd. After post-doctoral stints with George Christou at Indiana University and Hans Güdel at the University of Berne, she returned to the University of Melbourne in 2004, where she is now Associate Professor. Her research interests lie in the fields of molecular magnetism, polyoxometalate chemistry, lanthanoid chemistry, redox-active ligands

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and switchable molecular materials.