Tilt grain-boundary effects in *s*- and *d*-wave superconductors

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We present self-consistent calculations of supercurrent flows in a realistic tilt grain boundary. We obtain the current-phase characteristics in both *s*-wave and *d*-wave superconductors. We do this self-consistently within the framework of the Bogoliubov–de Gennes equations, using a realistic microscopic model of the grain boundary. This yields the *s*- and *d*-wave superconductor order parameters in the vicinity of the boundary and the respective quasiparticle local density of states. [S0163-1829(99)00529-9]

The debate over the superconducting order-parameter in high T_c superconductors has been strongly contested, but has now been settled in favor of a *d*-wave pairing state.^{1,2} The experiments by Tsuei *et al.*³ and Wollman *et al.*⁴ have been most conclusive, especially since they only depend on the phase of the order-parameter and not on the microscopic physics of the energy gap. Photoemission experiments⁵ and the temperature dependence of the penetration depth⁶ also strongly support the *d*-wave picture. However, some controversy still exists concerning possible *s*-*d* mixing in the cuprates. In particular an *s*-wave component has been demonstrated to be induced at interfaces.^{7–9}

In interpreting the Tsuei *et al.* experiments it is essential to understand the superconducting characteristics of grain-boundary (GB) weak links in the cuprates. Understanding the effects of grain boundaries is also of importance for developing possible devices and other applications of high- T_c superconductors. The experiments of Tsuei *et al.*, especially the observations of π -junction behavior, are consistent with the predictions of *d*-wave pairing interpreted using the Sigrist-Rice¹⁰ model for the dependence of the critical current I_c on the grain-boundary angles. On the other hand, the values of I_c measured as a function of grain-boundary angle show an almost exponential dependence on angle,^{11,12} unlike the cosine predicted by the Sigrist-Rice formula for *d*-wave pairing. In trying to explain these findings a number of different models of the interfaces have been studied. Tanaka and co-workers¹³ have looked at the (100) and (110) interfaces and also derived a Josephson current formula for *s*/*I*/*d* and *d*/*I*/*d* grain-boundary structures. Barash *et al.*¹⁴ have considered the temperature dependence of the critical current in *d*-wave junctions. Zhang considered 0°, 45°, and 90° junctions.¹⁵ Zhitomirsky and Walker¹⁶ have also looked at the (110) interface to study the quasiparticle spectra and zero-energy states (ZES). Beltzig *et al.*¹⁷ showed that an induced *s*-wave component existed on the (orthorhombic) (110) boundary giving rise to a splitting in the ZES at a low enough temperature: the latter point they attribute to time-reversal symmetry breaking (TRSB). The review of GB's by

Prester¹⁸ also highlights the possibility of them behaving as though each were an individual Josephson Junction. Gurevich and Pashitskii argued that the near-exponential dependence of I_c on angle was due to the formation of an insulating layer at the grain boundary, associated with the dislocation cores.¹⁹

In this work we address the effects of grain boundaries. We adopt a geometrically realistic model of the tilt grain boundary, as shown in Fig. 1 and solve the Bogoliubov–de Gennes (BdG) equations in real space using the recursion method. We determine how the superconducting order parameter (Δ), the charge density (n), and the quasiparticle local density of states [LDOS, $n(E)$] are affected by our GB. Further, we can apply phase differences in Δ across the boundary and calculate the resulting supercurrent. By calculating the maximum current across the boundary we determine the critical current of the system.

It is important to stress that our method involves three aspects. First, the work has primarily been motivated by the need to establish on firm ground the supercurrent versus order parameter phase relationship. The imposition of a phase difference in the order parameter across the boundary has very importantly necessitated a self-consistent approach so

FIG. 1. The symmetric model tilt grain boundary. By periodicity, we carry out self-consistent calculations on two lines of sites (highlighted) which are then mirrored onto similar sites in the rest of the sample. Also shown is our definition of a *d*-wave 0° phase difference across the boundary (see text).

as to ensure current conservation. A fully self-consistent approach has been shown to give surprisingly different results compared to non-self-consistent calculations.²⁰ Second, we wish to explore the richness of the grain-boundary microstructure and not just flat (100) or twin boundary (110) interfaces. Studies to date have concentrated on these geometries because of their simplicity from which one may always keep their calculations within a k -space framework. Third, in order to facilitate a more complicated GB structure we have had to develop a real-space method, the outline of which can be found in Martin and Annett.²¹ This method is easily extendable to systems more complicated than that shown in Fig. 1, such as anisotropy about the line $x=0$. It should be noted that the only free parameter in our work is the strength of the pairing potential in contrast to the Landau-Ginzburg or one-dimensional models which have a number of free parameters.

For the purposes of this paper, we concentrate on the large-angle grain boundary (53.1°), depicted in Fig. 1. It consists of two square lattices butted together at some angle of misorientation and linked via a *percolation site*. Being periodic in the y direction we only have to undertake calculations for sites on two dissimilar lines of atoms as shown in Fig. 1. For each line of sites we have to go 10 sites deep into the bulk before the order parameter has recovered to its bulk value. For some bonds across the GB the interatomic spacing is less than the bulk spacing. For these bonds we assume that the value for the hopping between sites i and j (t_{ij}) can be calculated by assuming a simple linear form for the hopping integral, i.e.,

$$t_{ij} = -\frac{\sqrt{2}-r_{ij}}{\sqrt{2}-1}, \quad 0 \leq r_{ij} \leq \sqrt{2}, \quad (1)$$

and is zero otherwise. For the geometry of our GB (Fig. 1) every site will have a *connectivity* of 4.

We consider the following two attractive Hubbard models:

$$H = \sum_{\langle i,j \rangle, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.} + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (2)$$

$$H = \sum_{\langle i,j \rangle, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.} + U \sum_{\langle i,j \rangle} n_i n_j \quad (3)$$

with $U < 0$ and $n_i = n_{i\uparrow} + n_{i\downarrow}$. Here U is the usual BCS pairing potential, defined as being a negative constant within a cut-off energy range of $\pm E_c$ either side of the Fermi energy, after which its value is zero. Equation (2) will be referred to as “local,” giving rise to s -wave pairing and Eq. (3) will be termed “nonlocal” giving d -wave pairing. By making the Bogoliubov canonical transformation we diagonalize the Hamiltonian and arrive at the Bogoliubov–de Gennes equations

$$\sum_j \begin{pmatrix} H_{ij} & \Delta_{ij} \\ \Delta_{ij}^* & -H_{ij}^* \end{pmatrix} \begin{pmatrix} u_j^n \\ v_j^n \end{pmatrix} = E_n \begin{pmatrix} u_i^n \\ v_i^n \end{pmatrix}, \quad (4)$$

where $H_{ii} = (-\mu + \frac{1}{2} U n_{ii})$ and $H_{ij} = t_{ij}$ (local), or, $H_{ii} = -\mu$ and $H_{ij} = t_{ij} + \frac{1}{2} U n_{ij}$ (nonlocal). Here μ is the chemical potential, u_i^n and v_i^n are the particle and hole amplitudes on

site i associated with an eigenenergy E_n , and n_{ij} is the appropriate charge density (defined below). To solve these equations we employ the recursion method,²² and together with the methods employed by Martin and Annett,²¹ we obtain a matrix continued fraction for the Green functions. This continued fraction is evaluated exactly to 50 levels after which its elements vary in a predictable manner and therefore can be extrapolated for a further 1500 levels.

We are interested in evaluating the local quasiparticle density of states, the local and nonlocal charge densities ($n_{ii} = \sum_\sigma \langle c_{i\sigma}^\dagger c_{i\sigma} \rangle$ and $n_{ij} = \sum_\sigma \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle$, respectively), and the local and nonlocal order parameters ($\Delta_{ii} = U \langle c_{i\uparrow} c_{i\downarrow} \rangle$ and $\Delta_{ij} = U \langle c_{i\uparrow} c_{j\downarrow} \rangle$, respectively). These quantities may be found from the Green functions, expressions for which have already been given elsewhere.²¹ In the calculations that follow $U = -3.5t$, we have a temperature, T , of $T = 0.01t$, and we introduce a BCS cut-off $E_c = 3.0t$. Iterating the equations for charge densities and order parameters, with the BdG equations, we generate self-consistent solutions. So as not to direct the final SC solution into a local energy minimum, we set the order parameter to zero at the beginning of the calculation on those sites closest in proximity to the boundary. We say self-consistency has been achieved when the Hartree-Fock term and the order parameter change by less than a predefined margin between iterations. For the s -wave case, we can reach 0.5% s.c. typically between 10 or 20 iterations, whereas for the d wave it usually takes over 200 iterations.

By imposing a phase difference φ in the order parameter between the two bulk regions we may now generate current flow across the GB. We initially make the Peierls substitution for t_{ij} , ($t_{ij} \rightarrow t_{ij} e^{-ieA_{ij}/\hbar}$, A_{ij} being the integral of the vector-potential between sites i and j), in Eqs. (2) and (3), and use the definition $I_{ij} = \langle \partial H / \partial A_{ij} \rangle$, to obtain²³

$$I_{ij} = \frac{2t_{ij}e}{\hbar} \text{Re} \left[\frac{1}{\pi} \int_{-\infty}^{+\infty} [G_{ij}(E + i\eta) - G_{ij}(E - i\eta)] \times e^{-ieA_{ij}/\hbar} f(E) dE \right], \quad (5)$$

$f(E)$ being the Fermi-Dirac function. By a suitable choice of gauge we can immediately set $A_{ij} = 0$ everywhere.

When applying phase differences in Δ across a GB it is instructive to note how Δ changes due to the self-consistency, and also observe how the local densities of states and the Hartree-Fock term alter. Figure 2 shows the results for the s -wave case. Figures 2(a) and 2(b) show the evolution of $|\Delta_{ii}|$ across the GB on both the lower (a) and upper (b) lines of SC sites at $\varphi = 0^\circ$ (full line) and also $\varphi = 180^\circ$ (dotted line). The GB obviously has a perturbing effect on the system but note that $|\Delta_{ii}|$ is not depressed on the percolation site ($x=0$) for $\varphi = 0^\circ$. In fact, $|\Delta_{ii}|$ is almost constant as φ is varied; except for $\varphi = 180^\circ$ where $|\Delta_{ii}| = 0$ on the percolation site and is strongly reduced nearby. Note also the small Friedel-like oscillations in $|\Delta_{ii}|$ near the GB. Figure 2(c) shows how the order parameter phase, $\arg(\Delta_{ii})$, varies as a function of the x coordinate through the GB for the $\varphi = 30^\circ$ case. For the 180° case we just have a step function with an arbitrary phase associated with the percolation site since $|\Delta_{ii}| = 0$. For all other phase differences, the phase as a function of x goes as $(\varphi/2)\tanh(x/d)$ where φ is

FIG. 2. (a) The order parameter on the lower line of SC sites at 0° (full line) and 180° (dotted line). The latter goes to zero on the percolation site ($x=0$), (b) same as (a) but for the upper line of SC sites, (c) self-consistently determined evolution of the order-parameter phase on going through the GB for a 30° phase difference, (d) Quasiparticle local density of states at 0° phase difference (full line) and at 180° (dashed line).

the bulk phase difference across the GB and d is a characteristic length scale which we find to be $d=3.5$ for our parameters. This equation holds for both SC lines. Finally, in Fig. 2(d) we show the local density of states on the percolation site at $\varphi=0^\circ$ (full line) and at $\varphi=180^\circ$ (dotted line). At 0° we have the usual BCS-like gap around the Fermi energy. This persists through all our calculated phase differences except at 180° where the gap is suddenly filled in with various resonant states. Although not presented here we note that the Hartree-Fock term $\frac{1}{2}Un_{ii}$ shows the same (enhanced) values on both lines of SC sites at different phase differences.

Now consider the d -wave case. Because each site has four bonds with order parameters Δ_{ij} we can calculate the “net” d -wave contribution at a particular site by considering $\Delta_i^d = \sum_{j=1,4} (-1)^j \Delta_{ij}$. Similarly, the extended- s component is given by $\Delta_i^s = \sum_{j=1,4} \Delta_{ij}$ and will be finite near the boundary because of the broken crystallographic symmetry. A minor difficulty now arises when discussing the d -wave scenario. In the definition of Δ_i^d we must choose a convention for the direction of the positive and negative lobes of the d -wave function. For GB angles close to 45° , such as in Fig. 1, there is an ambiguity in defining the relative orientations of the order parameter lobes either side of the GB. The convention we have chosen is indicated in Fig. 1. In this case the current-phase relationship, $I(\varphi)$, is similar for both s -wave and d -wave cases. For this choice the d -wave order parameter is zero on the percolation site, $x=0$, for zero phase difference, Fig. 3(a), unlike the s -wave case of Fig. 2(a). Using our definition of phase differences we find a maximum d -wave contribution at 180° on the lower line of SC sites (dotted line), which decreases with phase difference, down to 0° (full line) where $|\Delta_{x=0}^d|=0$. The upper line of SC sites [Fig. 3(b)] shows the same qualitative form for Δ_d as for the local s -wave case. At 0° we find maximum extended- s component on the precolation site [full line in Fig. 3(c)], decreasing with increasing phase difference until at 180° we have

FIG. 3. The contributions to the superconducting order-parameter (d -wave) on going through the boundary. The x coordinate is plotted on the horizontal axis. The full line refers to the 0° phase difference, the dashed line refers to 180° : (a) d -wave on lower line, (b) d -wave on the upper line, (c) extended- s on the lower line, (d) extended- s on the upper line.

minimum extended- s contribution (dotted line). Figure 3(d) illustrates how the extended- s component evolves on the upper line of SC sites at either phase difference. Thus we conclude that the extended- s and the d -wave components are in competition such that the extended- s component is maximized at the detriment of the d -wave and vice versa.

Figure 4 shows the calculated currents in both the local s -wave and nonlocal d -wave cases. To calculate the current [using Eq. (5)] we have to consider the flow across all possible routes in just one cell of our sample. In calculating currents it is essential to check current conservation: this is only guaranteed from a self-consistent solution. Here, we find conservation obeyed to within 0.01%. Consider the s wave initially: the variation of current with phase-difference φ is plotted in Fig. 4 (solid line) where the values for phase difference range from 0° to $+180^\circ$. It is immediately clear that the current is not sinusoidal in φ but instead shows a sharp step at 180° . The remainder is roughly that of a saw-tooth albeit with some saturation. The step at $\pm 180^\circ$ can be attributed to resonant states entering the gap.^{24,25} Figure 2(d)

FIG. 4. The supercurrent versus phase difference in the order parameter between the two bulk regions for the s -wave and d -wave cases.

compares the local quasiparticle density of states at $\varphi=0^\circ$ and 180° confirming the presence of resonant midgap states at 180° .

Our calculations for the *d*-wave current are presented in Fig. 4 (dashed line). Again it is approximately a sawtooth: a similar sawtooth has been observed experimentally by Il'ichev *et al.*²⁶ The slope $\partial I/\partial\varphi$ is also positive, and consequently this GB cannot be classified as a π junction: this is consistent with the Sigrist-Rice formula for this geometry. Fogelström and Yip²⁷ note that in certain geometries it is also possible to have a vanishing current at phase differences other than integer multiples of π , and this they attribute to time-reversal symmetry breaking (this has been reported by Il'ichev *et al.*²⁸). Figure 4 shows no such evidence and therefore we conclude that the symmetric grain boundary does not have TRSB.

In conclusion we have developed a real-space method for determining how the order parameter and supercurrents

change with phase difference across a realistic interface in a superconductor. In this paper we have considered a large-angle symmetric tilt grain boundary and considered the local *s*-wave and nonlocal *d*-wave pairing symmetry in the order parameter on an equal footing. We have calculated the LDOS, Hartree-Fock terms, order parameter, and current all self-consistently. By imposing a phase difference φ across the junction we calculated the supercurrent $I(\varphi)$. We found for both the *s* wave and *d* wave that $I(\varphi)$ is nonsinusoidal but exhibits a sawtoothlike behavior which can be attributed to a sudden filling in of the energy gap at $\varphi=180^\circ$. Further, we note no time-reversal symmetry breaking or π -junction behavior in the *d*-wave case.

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