Experimental Test for Subdominant Superconducting Phases with Complex Order Parameters in Cuprate Grain Boundary Junctions

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We propose and implement a direct experimental test for subdominant superconducting phases with broken time-reversal symmetry in d-wave superconductors. The critical current of 45°-asymmetric grain boundary junctions is shown to be extremely sensitive to the predicted onset of a complex order parameter at (110) surfaces and near magnetic impurities. Measurements in pure Ni-doped $YBa_2Cu_3O_{7-x}$ junctions indicate that the symmetry at the surface is consistent with pure d-wave at all temperatures, putting limits on the magnitude and chiral domain structure of any subdominant symmetry component.

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It has recently been recognized that the order parameters of unconventional superconductors may be unstable in the presence of perturbations as a result of their strong magnitude and phase anisotropy. In the high temperature cuprate superconductors, the $d_{x^2-y^2}$ state dominant in the bulk [1,2] is readily suppressed at surfaces, at interfaces with other materials, in vortex cores, and in the vicinity of impurities. The fragility of the d-wave state is a result of the phase change of π between orthogonal directions. At a (110) surface, all specular reflection trajectories undergo a phase change of π, forming via Andreev reflection bound surface states with zero energy [3]. These states are observed as a zero bias conductance peak in tunneling spectroscopy experiments [4–6] and as a modification of the low temperature penetration depth [7,8]. The occupation of these states suppresses the d-wave order parameter, and it has been suggested that a secondary pairing interaction or subdominant component of the primary pairing interaction could induce a complex mixture phase at the surface [9,10]. The observation of a zero-magnetic field splitting of the zero bias conductance peak in the a-b plane quasiparticle tunneling [9,11] may be evidence for broken time-reversal symmetry, consistent with a complex superconducting order parameter at the surface. A similar effect may occur due to scattering from magnetic impurities in the cuprates [12], and some experiments have observed an abrupt drop in the thermal conductivity of Ni-doped $Bi_2Sr_2CaCu_2O_{8+d}$ crystals [13] that may be interpreted as the opening of an energy gap in all directions, again consistent with the onset of a complex order parameter.

In this Letter, we present an experiment designed to test specifically for the formation of a complex order parameter along the (110) surface of $YBa_2Cu_3O_{7-x}$ (YBCO) films by measuring the variation of the critical current of grain boundary junctions with temperature and magnetic field. Calculations demonstrate that the onset of a complex superconducting order parameter has a dramatic effect on the magnitude and magnetic field diffraction patterns of the supercurrent in this geometry. Measurements of the critical current in 45°-asymmetric grain boundary junctions of YBCO over a wide temperature range are consistent with pure $d_{x^2-y^2}$ symmetry, showing no evidence for complex secondary phases. Similar results are obtained for Ni-doped films in which a bulk transition to a complex state has been suggested.

Josephson tunneling is ideal for searching for subdominant superconducting phases because it provides a directional probe of the order parameter within a coherence length or so of the surface. The most direct way to test for the presence of a complex order parameter is to perform a corner SQUID or corner junction interferometry experiment with planar faces orthogonal to the (100) and (110) directions [1]. In this configuration, a complex order parameter has a phase shift between 0 and π, yielding a characteristic modulation pattern. However, since smooth (110) faces are not attainable in cuprate crystals, we instead make use of the extensively studied bicrystal thin film grain boundary Josephson junction. The critical current of such junctions is a strong function of the misorientation angle [14] due to the anisotropy of the d-wave order parameter, structural mismatch at the interface, and band-bending effects [15]. Another important feature of grain boundary junctions is faceting of the barrier plane caused during film growth by the competing grain orientations along the interface. For most grain boundary orientations, the faceting has little effect and the junction critical current varies with magnetic field according to the usual Fraunhofer diffraction pattern. However, for 45°-asymmetric junctions, in which the lobe of the bulk d-wave order parameter in one electrode and the node in the other are oriented normal to the interface, the critical current modulates with applied magnetic field in a complicated manner that reflects the detailed faceting along the grain boundary and the symmetry of the order parameter at the junction interface [16].

To illustrate this, we calculate the critical current of the grain boundary junction as a function of applied magnetic field for different order parameter symmetries. To model the grain boundary junction, we assume a random distribution of facet widths and angles. This distribution is unique to each junction, depending strongly on the angle and uniformity of the substrate grain boundary interface and the growth kinetics of the deposited cuprate film. From atomic

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force microscopy images, it is estimated that typical facet widths range from 5–100 nm, with a wide range of angles. There has been considerable theoretical work on the critical current of uniform grain boundary junctions, taking into account various factors that may affect the Josephson tunneling, such as the order parameter symmetry, interface roughness, the Andreev bound states, surface currents, and the transmissivity of the barrier [17,18]. However, there is no accepted model for the critical current in grain boundary junctions, and many of the treatments predict features (such as nonmonotonic variation of the critical current with temperature) that are not observed experimentally. Thus, we adopt the simple picture that the Josephson tunneling in each facet is directional, with critical current density proportional to the product of the magnitudes of the order parameters in the direction normal to the interface in the two electrodes and to the sine of the relative phase between them. The phase includes the local difference between the quantum mechanical phases in the electrodes resulting from the unconventional symmetry, as well as that produced by the magnetic flux threading the barrier. This model captures the essential element that these quantities depend on the local orientation of the grain boundary interface relative to the *a*-*b* axes of the films in the electrodes. We consider only the effect of the applied magnetic field, neglecting any fields produced by the tunneling currents. This "short junction" limit is valid since the width of our junctions (5–20 μm) is small compared to the Josephson penetration depth $\lambda_J = (\Phi_0/2\pi\mu_0\tau J_c)^{1/2}$, typically 25–50 μm for our devices.

Shown in Fig. 1 is the meander profile for a 10-μm-wide junction with 25 facets randomly angled from $+45°$ to $-45°$ from the nominal grain boundary interface. We calculate the critical current for this junction as a function of the magnetic flux threading the barrier for four pairing symmetries: s, $d_{x^2-y^2}$, and the complex mixture states $d_{x^2-y^2} + id_{xy}$ and $d_{x^2-y^2} + is$. For s-wave, the magnitude and phase of the order parameter is uniform, giving a Fraunhofer diffraction pattern. For pure d-wave, the faceting causes a variation of the magnitude and relative sign of the order parameter, resulting in a suppression of the critical current and a complicated modulation with applied field that persists out to high magnetic fields. The field modulation patterns have several characteristic features. First, the maximum critical current always occurs at a finite magnetic field for which the various facets of the junction are brought into phase. Second, despite its complex structure, the modulation pattern is perfectly symmetric with respect to magnetic field polarity in the short junction limit; self-field effects can introduce a small polarity asymmetry due to inhomogeneous current flow across the junction. Finally, there is a fundamental field modulation period set by the junction width and the magnetic barrier thickness of the junction and so is the same for all facet distributions, whereas the critical current at low fields may exhibit either a peak or a dip, depending on the faceting distribution.

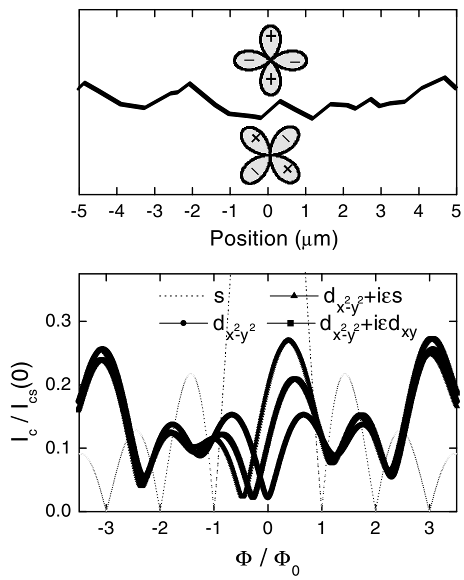

FIG. 1. (a) Faceting for the 45°-asymmetric grain boundary interface. (b) Calculated critical current modulation for this junction for s, $d_{x^2-y^2}$, $d_{x^2-y^2} + i\epsilon d_{xy}$, and $d_{x^2-y^2} + i\epsilon s$ symmetries, assuming $\epsilon = 0.20$.

For a complex order parameter, $d + id'$ or $d + is$, the modulation pattern is significantly altered. The zero-field critical current is dramatically enhanced, which is expected since the presence of the secondary pairing component removes the node in the order parameter facing the interface in one of the electrodes, allowing a substantial tunneling contribution. More strikingly, the polarity symmetry is broken, resulting in an asymmetry in the critical current modulation pattern that is most pronounced for small magnetic fields. This asymmetry is a direct manifestation of the broken time-reversal symmetry characteristic of a complex superconducting order parameter. For different facet distributions, the detailed shape of the diffraction pattern changes, but the key qualitative features remain the same.

These phenomena provide a sensitive test for the existence of a complex order parameter in the superconducting electrodes of a grain boundary junction. In Fig. 2(a), we demonstrate the effect of an s-wave secondary out-of-phase order parameter component by showing critical current diffraction patterns for several values of ϵ, the relative size of the subdominant s component in a $d_{x^2-y^2} + is$ superconductor. To quantify the sensitivity, Figures 2(b) and 2(c) show the enhancement of the zero-field critical current $I_c(0)$ and the onset of the fractional polarity asymmetry $\alpha(H) = \{[I_c(+H) - I_c(-H)]/[I_c(+H) + I_c(-H)]\}$, averaged over values of applied flux from $-10\Phi_0$ to $+10\Phi_0$, as a function of ϵ for $d + is$ and $d + id'$ symmetries. If a secondary order parameter component onsets at a specific phase transition temperature well below T_c, as has been predicted, we would expect ϵ to onset and grow as the temperature is decreased, causing an abrupt change in the critical current.

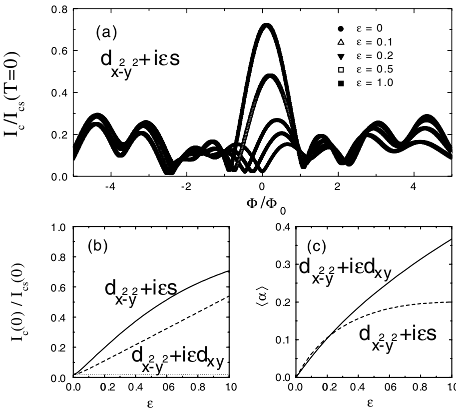

FIG. 2. (a) Calculated critical current modulation of the junction in Fig. 1 for $d_{x^2-y^2} + i\epsilon s$ symmetry and a range of subdominant components $0 \leq \epsilon \leq 1$. (b) Calculated enhancement of $I_c(0)$ vs ϵ for $d_{x^2-y^2} + i\epsilon d_{xy}$ and $d_{x^2-y^2} + i\epsilon s$ symmetries. (c) Calculated onset of critical current asymmetry $\alpha(H) = \{[I_c(+H) - I_c(-H)]/[I_c(+H) + I_c(-H)]\}$ vs ϵ for $d_{x^2-y^2} + i\epsilon d_{xy}$ and $d_{x^2-y^2} + i\epsilon s$ symmetries.

We have made measurements of the magnetic field variation of the critical current of a large number of 45°-asymmetric grain boundary junctions over a wide range of temperatures from T_c down to 0.3 K. $YBa_2Cu_3O_{7-x}$ thin films of thickness 100 nm were grown on 45°-asymmetric bicrystal substrates by pulsed laser deposition (growth temperature 830 °C, oxygen pressure 0.5 Torr, power 450 mJ), yielding a T_c of 85–92 K, with a transition width of 1–2 K, as determined from two-coil magnetic screening measurements. We also made films with Ni doping (3%–5%), which had a slightly lower T_c (~80 K) and a broader transition (~5 K). The films were patterned into strips of width 5–20 μm using Ar-ion milling, producing grain boundary junctions with typical areas of 10^{-8} cm^2. The Ni-doped films were measured in a dilution refrigerator down to 100 mK.

To measure the critical current, we used a feedback technique in which the bias current is automatically controlled to maintain a small voltage level across the junction, typically 10 μV, as the magnetic field or temperature is varied. The critical currents increase monotonically as the temperature is lowered below T_c, exhibiting a nearly linear dependence over much of the temperature range, as shown in the inset in Fig. 3. The zero field critical current is typically 1–10 μA, corresponding to an average current density of 100–1000 A/cm^2. The modulation of the critical current at $T = 4$ K for this junction, plotted in Fig. 3, has the complex structure expected for a junction with pure d-wave symmetry in which the order parameter changes sign. The critical current is maximum at about 12 G, rather than at zero-magnetic field, and is nearly symmetric with respect to polarity. The measured average asymmetry parameter $\langle\alpha\rangle$ at the peak currents is no more than 3% for this junction, typical of all junctions we have measured.

Figure 4 shows the critical current vs field at a series of different temperatures for (a) a pure YBCO and (b) a 5%-Ni-doped junction. In both cases, the magnitude of the critical current increases with decreasing temperature, but the modulation pattern retains the same shape, reproducing each detailed feature and, in particular, remains symmetric with respect to field polarity over the entire temperature range.

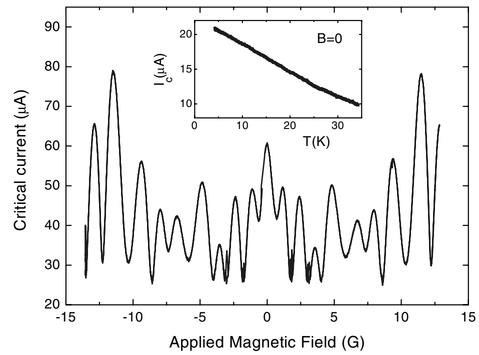

FIG. 3. Measured critical current modulation at $T = 4$ K for a 45°-asymmetric YBCO grain boundary interface. The inset shows the measured $I_c(0)$ vs temperature.

In all junctions studied to date, both pure and Ni doped, the polarity asymmetry of junctions cooled in zero field is typically a few percent and is never larger than 5%. This level of asymmetry is consistent with that expected from experimental uncertainty, self-field effects, and/or trapped magnetic flux in the vicinity of the junction. More significantly, we have never observed any abrupt increases in either the zero-field critical current or the polarity asymmetry, which have been predicted to occur at a phase transition to a state with a complex order parameter as the junctions are cooled. Based on a comparison of our simulations and measurements, we would place an upper

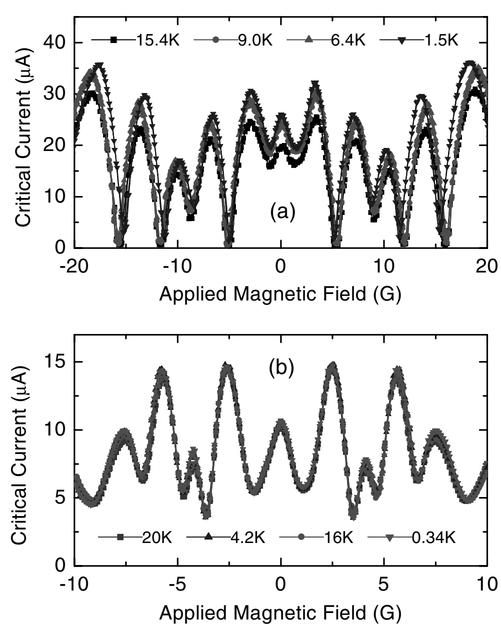

FIG. 4. Measured critical current modulation at a series of temperatures for (a) a pure YBCO junction and (b) a 5%-Ni-doped YBCO junction.

bound on the fractional magnitude of an out-of-phase s or d_{xy} component added to the $d_{x^2-y^2}$ order parameter at about 1%. We note that we also do not find evidence for the onset of a real (in-phase) subdominant order parameter component, which would exhibit an increased zero-field critical current but no polarity asymmetry.

These results raise the question of why we do not observe the onset of a substantial complex order parameter, as has been predicted by theoretical treatments. One scenario is that the complex order parameter region induced at the interface forms domains of alternating chirality, e.g., $d + is$ or $d - is$. Such domaining is not energetically favorable due to the domain wall energy (of order the Josephson coupling energy), but could nucleate as metastable states when a secondary phase onsets. We have simulated the effect of chirality domaining by putting a random spatial distribution of domains on each electrode of the junction. Because of the alternating sign of the secondary order parameter component, the net increase in the critical current in the complex phase is substantially reduced. However, the domaining effectively increases the density of facets on which the order parameter phase modulates, increasing both the magnetic field range and the magnitude of the polarity asymmetry. Thus, domain formation should actually enhance rather than obscure the effects of a complex order parameter at the interface.

A second scenario is that no complex superconducting phases are formed in our samples. One reason could be that the relatively high transmission coefficient of grain boundary junctions does not allow sufficient Andreev reflection to produce the zero energy bound states that are responsible for the suppression of the d-wave order parameter at the surface. However, it should be noted that the transmission coefficient of the 45°-asymmetric grain boundary junctions considered here is not particularly large, with current densities of only 100–1000 A/cm^2. This is supported by measurements of the conductance vs voltage in such junctions which show a pronounced zero bias conductance peak [19], similar to that observed in planar tunnel junctions on thin films and crystals with in-plane orientations. We also note that it has been predicted that proximity coupling between the electrodes may induce complex phases even in high transmission junctions [20]. A second option is that the d-wave order parameter is suppressed, but that the conditions near the interface (density of states, pairing interaction, etc.) are not conducive to the formation of a secondary out-of-phase superconducting component so that the $d_{x^2-y^2}$ state remains stable at all temperatures. In either case, the results suggest that the apparent time-reversal symmetry breaking observed in tunneling spectroscopy and low temperature transport measurements may arise from some microscopic mechanism, rather than from nucleation of a macroscopic superconducting region with complex order parameter symmetry. Primary candidates include magnetic surface states, antiferromagnetic bond currents, and barrier defects.

In conclusion, we have proposed and implemented a new experimental test for the onset of complex order parameter symmetry at surfaces and near impurities in unconventional superconductors. Measurements in YBCO and Ni-doped YBCO junctions are consistent with pure $d_{x^2-y^2}$ symmetry, with less than 1% mixture of a subdominant superconducting phase.

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