Experimental test for subdominant superconducting phases with complex order parameters in cuprate grain boundary junctions

W. K. Neils and D. J. Van Harlingen

Department of Physics, University of Illinois at Urbana-Champaign, 1110 W. Green St., Urbana, Illinois 61801

(Received November 19, 2018)

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 are shown to be extremely sensitive to the predicted onset of a complex order parameter at (110)-surfaces and near magnetic impurities. Measurements in YBCO and Ni-doped YBCO 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.

PACS numbers: 74.20.Rp, 74.50.+r

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 is readily suppressed at surfaces, at interfaces with other materials, in vortex cores, and in the vicinity of impurities. This suppression may allow the emergence of localized regions with different symmetries, possibly including phases with complex order parameters that break time-reversal symmetry. These states are of scientific interest, offering unique opportunities for studying novel phases in superconductor systems, and may also be important for understanding the microscopic pairing mechanism and for the implementation of high temperature superconducting materials in electronic devices.

The fragility of the d-wave state is a result of the phase change of $\pi$ between orthogonal directions. At a (110)-surface, all specular reflection trajectories undergo a phase change of $\pi$, forming via Andreev reflection bound surface states with zero energy. These states are observed as a zero bias conductance peak in tunneling spectroscopy experiments and as a modification of the low temperature penetration depth. 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. The observation of a zero-magnetic field splitting of the zero bias conductance peak in a-b plane quasiparticle tunneling, 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, and some experiments have observed an abrupt drop in the thermal conductivity of Ni-doped BSCCO crystals 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 YBCO films by measuring the variation of the critical current of grain boundary junctions with temperature and magnetic field. We present calculations demonstrating 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.

The most straightforward way to test for the presence of a complex order parameter is to perform a corner SQUID or corner junction experiment with planar faces orthogonal to the (100) and (110)-directions. In this configuration, a complex order parameter has a phase shift between 0 and $\pi$, 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 $\theta$, falling off exponentially to a minimum value at $\theta = 45°$ that is roughly three orders of magnitude smaller than the thin film critical current density. This variation is largely due to the due to the anisotropy of the d-wave order parameter, with additional contributions from the structural mismatch at the interface and band-bending effects. 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 [11].

To demonstrate 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 AFM images, it is estimated that typical facet widths range from $5 - 100\,\text{nm}$, with a wide range of angles. We assume that the local critical current density is proportional to the product of the magnitudes of the order parameters in the two electrodes and the relative phase across the junction, which 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. Because of faceting, these quantities depend on the local orientation of the grain boundary interface, which selects the tunneling direction, 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 ($5 - 20\,\mu\text{m}$) is small compared to the Josephson penetration depth $\lambda_J = (\Phi_0/2\pi\mu_0\tau J_e)^{1/2}$, typically $25 - 50\,\mu\text{m}$ for our devices.

Shown in Figure 1 is the meander profile for a $10\,\mu\text{m}$-wide junction with 25 facets randomly-angled from $+45^\circ$ to $-45^\circ$ 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 the Fraunhofer diffraction modulation pattern familiar from single slit optical interference and typically observed for Josephson junctions in conventional BCS superconductors. For d-wave symmetry, the variation of facet angles causes a corresponding variation of the magnitude and, more importantly, the sign of the order parameter across the junction, resulting in a substantial suppression of the critical current and a complicated modulation with applied field that persists out to high magnetic fields. There are several characteristic features of the field modulation pattern for d-wave symmetry. 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 always symmetric with respect to magnetic field polarity in the short junction limit; including self-field effects can introduce a small polarity asymmetry due to the inhomogeneous current flow across the junction. Finally, the fundamental field modulation period observed is set by the overall width and magnetic barrier of the junction and so is the same for all random facet distributions, whereas the critical current at low fields may exhibit either a peak or a dip, depending on the faceting.

![Faceting for the 45°-asymmetric grain boundary interface](image)

FIG. 1. (a) Faceting for the 45°-asymmetric grain boundary interface. (b) Calculated critical current modulation for this junction for $s$, $d_{x^2-y^2}$, $d_{x^2-y^2} + id_{xy}$ and $d_{x^2-y^2} + is$ 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 Figure 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 $\epsilon$, the relative size of the subdominant $s$ component in a $d_{x^2−y^2} + is$ superconductor. To quantify the sensitivity, Figure 2(b,c) shows the enhancement of the zero-field critical current $I_c(0)$ and the onsets 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 $\epsilon$ for $d + is$ and $d + id'$ symmetries. If a secondary order parameter component is varied, the critical currents increase monotonically as the temperature is decreased. Figure 2(d) shows the critical current vs. temperature predicted for the modeled junction, using a simple model in which $I_c(T) \sim \Delta(T)$, which we assume to have a BCS temperature dependence. This sharp increase in critical current, and the simultaneous onset of polarity asymmetry, would be a definitive signature of the nucleation of a complex order parameter.

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 0.3K. YBa$_2$Cu$_3$O$_{7-\delta}$ thin films of thickness 100nm were grown on 45°-asymmetric bicrystal substrates by pulsed laser deposition (growth temperature 830°C, oxygen pressure 0.5Torrs, power 450mJ), yielding a $T_c$ of 85-92K, with a transition width of 1-2K, as determined from two-coil magnetic screening measurements. We also made films with Ni doping ($3\%-5\%$), which had a slightly lower $T_c$ (80K) and a broader transition (5K). The films were patterned into strips of width 5–20µm 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 100mK.

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 10µV, 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 of Figure 3. The zero field critical current is typically 1–10µA, corresponding to an average current density of 100–1000A/cm$^2$. The modulation of the critical current at $T=4K$ for this junction, plotted in Figure 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 12G, 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 3%-Ni-doped junction. In both cases, the magnitude of the critical current increases with decreasing tempera-
ture, 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.

![Graph A](image1.png)

**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.

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 10%. 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 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.

It is important to consider possible reasons why we might 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 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 along the interface on the (110)-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 enhance rather than obscure the formation of a complex order parameter at the interface.

A second scenario is that no complex superconducting phases are formed. 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\(^\circ\)-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 [17] 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 [18]. A second option is that the d-wave order parameter is suppressed, but that the conditions near the interface (density of states, pairing interaction, ...) 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, low temperature transport, and local magnetic field measurements may arise from some microscopic mechanism, rather than 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 surface and near impurities in unconventional superconductors. The critical current magnitude and magnetic field modulation of 45\(^\circ\)-asymmetric grain boundary junctions are shown to be extremely sensitive to the onset of an out-of-phase secondary order parameter, characterized by a dramatic enhancement in the zero field current and an asymmetry with respect to magnetic field polarity. 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.

We wish to thank Joe Hilliard, Chris Michael, and Tony Banks for vital technical assistance. This work is supported by the National Science Foundation grant NSF-DMR99-72087 and by the Department of Energy grant DEFG02-96ER45439. We acknowledge extensive use of the Microfabrication Laboratory and the DOE Center for Microanalysis of Materials in the Frederick Seitz Materials Research Laboratory.

[1] D. A. Wollman et al., Phys. Rev. Lett. 71, 2134 (1993); D. J. Van Harlingen, Rev. Mod. Phys. 67, 515 (1995).
[2] C. C Tsuei et al., Phys. Rev. Lett. 73, 593 (1994).
[3] C. R. Hu, Phys. Rev. Lett. 72, 1526 (1994).
[4] J. Geerk et al., Z. Phys. 73, 329 (1988).
[5] J. Lesueur et al., Physica C 191, 325 (1992).
[6] M. Covington et al., Phys. Rev. Lett. 79, 277 (1997).
[7] H. Walter et al., Phys. Rev. Lett. 80, 3598 (1998).
[8] A. Carrington et al., [cond-mat/0011183].
[9] M. Matsumoto and H. Shiba, J. Phys. Soc. Japan 64, 1703 (1995).
[10] L. J. Buchholtz et al., J. Low Temp. Phys. 101, 1079 (1995).
[11] R. Krupke and G. Deutscher, Phys. Rev. Lett. 83, 4634 (1999).
[12] A.V. Balatsky, Phys. Rev. Lett. 80, 1972 (1998).
[13] R. Movshovich et al., Phys. Rev. Lett. 80, 1968 (1998).
[14] D. Dimos et al., Phys. Rev. Lett. 61, 219 (1988).
[15] H. Hilgenkamp and J. Mannhart, Appl. Phys. Lett. 73, 265 (1998).
[16] H. Hilgenkamp, J. Mannhart, and B. Mayer, Phys. Rev.B 53, 14586 (1996).
[17] L. Alff et al., Phys. Rev. B 55, 14757 (1997).
[18] M. Fogelstrom and S.-K. Yip, Phys. Rev. B 57, R14060 (1998).