C-axis Josephson Tunneling Between YBa$_2$Cu$_3$O$_{7-\delta}$ and Pb: Direct Evidence for Mixed Order Parameter Symmetry in a High-T$_c$ Superconductor

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We report a new class of c-axis Josephson tunneling experiments in which a conventional superconductor (Pb) is deposited across a single twin boundary of a YBa$_2$Cu$_3$O$_{7-\delta}$ crystal. We measure the critical current as a function of magnitude and angle of magnetic field applied in the plane of the junction. In all samples, we observe a clear experimental signature of an order parameter phase shift across the twin boundary. These results provide strong evidence for mixed d- and s-wave pairing in YBCO, with a reversal in the sign of the s-wave component across the twin boundary.

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The symmetry of the order parameter in high-temperature superconductors has been a subject of theoretical and experimental debate since their original discovery. Phase-sensitive measurements on YBCO involving currents flowing within the CuO$_2$ planes, such as corner-junction SQUID experiments, corner-junction flux modulation experiments, and tricrystal ring experiments, have indicated an order parameter $\Delta(k)$ with primarily $d_{x^2-y^2}$ symmetry under rotations in the plane $[\Delta(k) \sim \cos k_x a - \cos k_y a]$. The observation, however, of Josephson tunneling perpendicular to the CuO$_2$ planes between heavily twinned YBCO and a conventional s-wave superconductor demonstrated a significant s-wave component. In this Letter, we report results from a new c-axis Josephson tunneling experiment which resolves the apparent conflict between the two groups of experiments and makes a compelling case for mixed order parameter symmetry in YBCO, with a dominant d-wave component and a significant s-wave component.

In the experiment, shown conceptually in Fig. 1(a), a c-axis Josephson tunnel junction straddles a single YBCO twin boundary. Because Pb is an s-wave superconductor, the Pb counterelectrode couples only to the s-wave component of the YBCO order parameter; the net phase difference with any d-wave component integrates to zero. If YBCO were a conventional s-wave superconductor, the critical current $I_c(B)$ would exhibit a Fraunhofer-like dependence on magnetic field strength $B$, applied in the plane of the junction, regardless of the angle of $B$. If, on the other hand, YBCO were predominantly d-wave, any s-wave component to the order parameter would change sign across the twin boundary, yielding a dramatically different angular dependence for $I_c(B)$. For magnetic fields perpendicular to the boundary, $I_c(B)$ would be the same as for a conventional junction, with a maximum at $B = 0$. Magnetic fields parallel to the boundary, however, should produce a local minimum in $I_c$ at $B = 0$, as discussed below; this configuration is analogous to the d-wave corner junction experiment.

The experiments were performed at UC San Diego (UCSD) and UC Berkeley (UCB) on single crystals of YBa$_2$Cu$_3$O$_{7-\delta}$ grown at UCSD and the University of Illinois, respectively. Details of the growth and characterization of sparsely twinned, single crystals of YBa$_2$Cu$_3$O$_{7-\delta}$ with c-axis orientation have been published previously. The large dimensions of the domains, typically 200 x 200 $\mu$m$^2$, allowed us to position Josephson junctions across two twin domains separated by a single twin boundary or even on a single domain. The UCSD junc-

![FIG. 1. (a) Schematic diagram of a Pb/YBCO junction (hatched region) grown across a twin boundary (dashed line). For the YBCO order parameter shown, the s-wave component changes sign across the boundary. (b) Nemarsky microscope photograph of junction B1. The twin boundary runs vertically through the center of the photograph; the Pb strip is the horizontal white region.]
tion fabrication process is described in Refs. [9,13]. Similar techniques were used at UCB except in that an SiO insulating layer, rather than epoxy, was used to define the junction geometry and a Pb$_{0.95}$In$_{0.05}$ rather than Pb source was used to deposit the counter electrode. Figure 1(b) is a photograph of junction B1 taken under a Nomarsky optical microscope; a single YBCO twin boundary is clearly visible. The dimension of the junction perpendicular to the twin boundary is defined by the opening in the SiO layer (L=240 $\mu$m). The dimension of the junction parallel to the twin boundary is determined by the width of the Pb counter electrode (W=180 $\mu$m).

We present results from eight samples, with parameters listed in Table I. To minimize trapped flux, the junctions were cooled slowly from about 125 K to 4.2 K in a dewar surrounded by a $\mu$-metal shield. We measured $I_c(B)$ with the magnetic field $B$ applied in the plane of the junction at a variety of angles relative to the twin boundary. At UCSD, the samples were physically rotated relative to the field. At UCB, two perpendicular pairs of Helmholtz coils were used to rotate the field relative to the sample, providing angular control to $\pm 1^\circ$. All of the junctions displayed low leakage, superconductor-insulator-superconductor tunneling characteristics similar to those seen in previous work [4,13], including a well-defined Pb energy gap (\approx 1.4 meV) and sharp Fiske modes, indicating a high quality tunneling barrier. All of the junctions were in the small junction limit ($L/\lambda_J < 1$, where $\lambda_J$ is the Josephson penetration depth), except for junctions SD3 and B1 where $L/\lambda_J \approx 1.2$ and 1.5, respectively. As shown in Table I, the $I_c^{\max}$, $R_N$ products ($I_c^{\max}$ is the maximum value of $I_c(B)$, $R_N$ is the resistance above the gap) lie between 0.5mV and 1mV, even though the values of $I_c^{\max}$ and $R_N$ vary by more than an order of magnitude. This result suggests that variations in $I_c^{\max}$ and $R_N$ arise from variations in the properties of the tunneling interface and that the properties of the YBCO crystals do not change substantially from sample to sample.

Figures 2 and 3 contain the main result of this paper. Figure 2 shows $I_c(B)$ for junction SD2 with the field parallel to the twin boundary. In addition to a deep local minimum in $I_c(B=0)$, we observe a high degree of symmetry under reversal of both field and current, indicating that the junction is free of significant trapped flux. Figure 3 shows $I_c(B)$ for junction B2a as a function of the angle $\phi$ between the twin boundary and B. For $\phi = -90^\circ$, we observe a conventional, Fraunhofer-like pattern. As we increase $\phi$, two local maxima in critical current develop on either side of the $B=0$ axis, while the value of $I_c(B=0)$ remains constant. These two peaks have a maximum height at $\phi = 0^\circ$, and decrease again as we increase $\phi$ to $+90^\circ$. The behavior shown in Figs. 2 and 3 was observed in all junctions grown across a twin boundary.

The observed, reproducible dependence of the critical current on the angle $\phi$ strongly suggests an interpretation in terms of a sign reversal of the s-wave component of the YBCO order parameter across the twin boundary. We define the geometric asymmetry of the position of the twin boundary within the junction as $\gamma \equiv A_1/A$, where $A_1$ is the area of the smaller twin domain and $A = A_1 + A_2$ is the total area of the junction. For an s-wave component which changes sign across the twin boundary, and for $B$ applied parallel to the boundary, we can write the critical current of a small ($L \ll \lambda_J$), uniform junction as

$$I_c^2(\Phi, \gamma) = (I_0 \Phi_0/\pi \Phi)^2 \left[ 1 + \cos^2 (\pi \Phi/\Phi_0) - \cos (2\gamma \pi \Phi/\Phi_0) - \cos [2(\gamma - 1)\pi \Phi/\Phi_0] \right].$$

Here, $I_0$ is the maximum critical current of the junction with no sign reversal, $\Phi$ is the magnetic flux penetrating the junction, and $\Phi_0 = hc/2e$ is the flux quantum. For $\gamma = 0$ or 1, Eq. (1) yields the conventional result $I_c = I_0 | \sin (\pi \Phi/\Phi_0)/(\pi \Phi/\Phi_0) |$. For $\gamma = 0.5$, we find $I_c = I_0 \sin^2 (\pi \Phi/2\Phi_0)/|\pi \Phi/2\Phi_0|$, which is identical to the result for the $d$-wave corner junction [3,13]. We also calculated $I_c(B)$ as a function of $\phi$; the results for $\gamma = 0.4$ are shown inset in Fig. 3. The predicted behavior is similar to our experimental observations: a continuous variation as a function of $\phi$ from a local minimum at $B = 0$ for fields parallel to the twin boundary to a global maximum at $B = 0$ for fields perpendicular to the twin boundary.

Figure 4 shows $I_c(B)$ for $\phi = 0^\circ$ and $90^\circ$ for junction B2b grown on a single twin domain of the same crystal as in Fig. 3. We observed conventional, Fraunhoffer-like behavior, with a global maximum at $B = 0$, for all values of $\phi$. Because YBCO is orthorhombic, the order parameter is expected to be of the form $d + cs$ within a single domain. The Pb $c$-axis junction couples only to the s-wave component.
component, so that a Fraunhofer-like $I_c(B)$ for all angles $\phi$, as seen in Fig. 4, is expected. The contrast between the data shown in Fig. 4 and the behavior observed in the other seven junctions makes it clear that the minima at $B = 0$ in those junctions are due to the presence of the twin boundary.

In Table I, we summarize $I_c(B)$ for all eight junctions in terms of the ratio $\eta \equiv I_c^0/I_c^{\text{max}}$, where $I_c^0$ is the critical current at zero field and $I_c^{\text{max}}$ is the largest critical current in a field applied parallel to the twin boundary. We also list $\eta_{\phi h}$, the value of $\eta$ computed from Eq. (1) for the measured values of $\gamma$. For a conventional $s$-wave junction, or a twin boundary junction in perpendicular applied fields, $\eta_{\phi h} = 1$. For an ideal, symmetric twin boundary junction ($\gamma = 0.5$) in parallel applied fields, $\eta_{\phi h} = 0$. For the junction B1, with $\gamma = 0.33$, the predicted and measured values of $\eta$ are in good agreement. On the other hand, for the one junction (SD4) for which $\eta$ was measured to be zero, $\gamma$ was 0.42 and $\eta_{\phi h} = 0.22$. For the remaining five junctions with $0.40 \leq \gamma \leq 0.50$, the measured values of $\eta$ are consistently higher than the predicted values. The difference might be due to self-field effects (i.e., the junctions might not be small enough compared to $\lambda$, so that screening can be neglected). However, Kirtley et al. 4 have shown that for $L/\lambda$ as large as 1 the expected $\eta_{\phi h}$ for a symmetric junction ($\gamma = 0.5$) is no more than 0.12; thus self-field effects appear to be too small to explain the discrepancies.

Two possible sources of the discrepancy in $\eta$, which would also explain the observation of non-zero supercurrents in heavily twinned samples [9–13], are: (1) an additional $s$-wave component to the order parameter induced by the presence of the surface [21], and (2) a localized time-reversal breaking $(d + is)$ state at the twin boundary, due to a continuous rotation of the relative phase between $d$ and $s$ [20]. We note that the data in Fig. 3 display some small asymmetry in $B \rightarrow -B$ at intermediate angles. However, the asymmetry vanishes at $\phi = 0^\circ$, to within the limit of our resolution, whereas a time-reversal breaking state at the twin boundary would predict the asymmetry to be a maximum at $\phi = 0^\circ$. We can use the symmetry of the data to place a limit on the degree of time-reversal breaking at a single boundary: we find that the length over which the phase angle rotates must be \( \lesssim 4 \mu m \) [21]. Finally, we note that a non-uniform junction could cause a discrepancy between the predicted and observed values of $\eta$. A spatially varying barrier height would mean that the $\gamma$ inferred from the relative areas of the domains might not reflect the actual asymmetry in critical current magnitudes.

Could the large observed minima in $I_c$ at $B = 0$ arise from trapped vortices in a purely $s$-wave superconductor? A vortex containing flux $\Phi_0$ trapped within the plane of the twin boundary, at an angle $0^\circ \leq \theta < 90^\circ$ relative to

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### FIG. 3. $I_c(B)$ for junction B2a ($\gamma=0.4$) for 10 values of angle $\phi$ relative to the twin boundary. Successive plots are offset vertically by 30 $\mu$A. Center inset: computed values of $I_c/I_0$ vs. $\Phi/\Phi_0$ for a junction with a sign-reversal of the $s$-wave component and $\gamma = 0.4$. Successive plots are offset vertically by 0.3.
consistent with a predominantly unlikely source of the minima. The results are entirely direction, its symmetry with respect to the reversal of ish. The smooth variation of rotated in the plane of the junction, the value of $I_c(0)$ remains constant while the maxima on either side diminish. The smooth variation of $I_c(B)$ with magnetic field direction, its symmetry with respect to the reversal of magnetic field and bias current, and the reproducibility of the results imply that trapped flux is an extremely unlikely explanation of the data.

In conclusion, we find that junctions grown across a single twin boundary of YBCO crystals consistently exhibit a local minimum in $I_c(B)$ at zero magnetic field for fields applied in the plane of the crystal parallel to the twin boundary. As the magnetic field is progressively rotated in the plane of the junction, the value of $I_c(0)$ remains constant while the maxima on either side diminish. The smooth variation of $I_c(B)$ with magnetic field direction, its symmetry with respect to the reversal of magnetic field and bias current, and the reproducibility of the results imply that trapped flux is an extremely unlikely source of the minima. The results are entirely consistent with a predominantly $d_{x^2-y^2}$ pairing symmetry with a sign reversal of the $s$-wave component across the twin boundary.

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TABLE I. Junction length $L$ and width $W$, asymmetry parameter $\gamma$, zero-field critical current $I^c_0$, maximum critical current in a parallel field ($\phi = 0^\circ$) $I^\text{max}_c$, $\eta_{th} \equiv I^0_c/I^\text{max}_c$ calculated from Eq. (1), $\eta$ from experiments, and $I^\text{max}_c R_N$ product for eight $c$-axis YBCO/Pb junctions.

| $L$ (µm) | $W$ (µm) | $\gamma$ | $I^0_c$ (µA) | $I^\text{max}_c$ (µA) | $\eta_{th}$ | $\eta$ | $I^\text{max}_c R_N$ (mV) |
|----------|----------|---------|---------------|-----------------|-----------|------|-----------------|
| SD1      | 250      | 0.45    | 226           | 396             | 0.14      | 0.57 | 1.03            |
| SD2      | 150      | 0.47    | 193           | 815             | 0.08      | 0.24 | 0.90            |
| SD3      | 250      | 0.48    | 300           | 2010            | 0.06      | 0.15 | 1.03            |
| SD4      | 250      | 0.42    | 0             | 28              | 0.22      | 0    | 0.90            |
| B1       | 240      | 0.33    | 780           | 1550            | 0.49      | 0.50 | 0.68            |
| B2a      | 175      | 0.40    | 82            | 158             | 0.28      | 0.52 | 0.51            |
| B2b      | 180      | 0.00    | 300           | 300             | 1.00      | 1.00 | 0.75            |
| B3       | 160      | 0.50    | 10            | 37.6            | 0.0       | 0.27 | 1.00            |

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[21] Using Eq. (29) of Ref. [20], we generated a series of $I_c(B)$ patterns for different values of $\xi/W$. The maximum peak height asymmetry ratio was larger than 1.02, the limit of our resolution for the data in Fig. 2, for $\xi/W \geq 0.017$. 