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Evidence for a non-*s*-wave superconducting order parameter in $YBa_2Cu_3O_{6.6}$ with $T_c = 60$ K

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Several recent phase-sensitive-tunneling experiments have indicated that $YBa_2Cu_3O_{6.9}$ is not an *s*-wave superconductor. In this work we report an analogous experiment on a related cuprate superconductor, $YBa_2Cu_3O_{6.6}$, with $T_c = 60$ K. The critical current vs applied field of a Pb-$YBa_2Cu_3O_{6.6}$ single crystal corner Josephson junction is measured and compared with the theory. As a control experiment, measurements are made on a Pb-$YBa_2Cu_3O_{6.6}$ edge junction. The results are consistent with a *d*-wave order parameter for $YBa_2Cu_3O_{6.6}$. It is thus unlikely that the results of previous similar experiments on almost fully oxygenated $YBa_2Cu_3O_{6.6}$ may simply be explained by the presence of the Cu-O chains.

A great deal of attention has recently been focused on determining the symmetry of the superconducting order parameter of cuprate superconductors. This interest has stimulated some recent phase sensitive tunneling experiments and their results indicate that the order parameter for $YBa_2Cu_3O_{6.9}$ (YBCO) may have *d*-wave symmetry.[1–7] A *d*-wave order parameter was originally suggested as a possible explanation for the complex superconducting phase diagrams of some heavy-electron superconductors.[8] More recent work on the *t*-*J* and Hubbard models, which are often considered appropriate for the high-T_c cuprates, generally require a *d*-wave order parameter in their superconducting ground state.[9] Later theoretical work showed that many experimental results are compatible with a *d*-wave order parameter.[10] Other, more exotic order parameters, such as $d+id$ or $s+id$, must also be considered.

In order to determine the symmetry of the superconducting order parameter several tunneling experiments capable of measuring the phase of the Josephson supercurrents in single junction or multiple junctions have been performed. The idea for such experiments, aimed to investigate heavy-electron superconductors, was first suggested by Geshkenbein and Larkin.[11] This suggestion was adapted to the typical features of cuprate superconductors with the proposal of Sigrist and Rice,[12] that Josephson supercurrents from an *s*-wave superconductor into a $d_{x^2-y^2}$-wave superconductor will have a current-phase relation given by

$$I = I_0 (n_x^2 - n_y^2) \sin \Delta\phi. \tag{1}$$

Here, n_x and n_y are the x and y components of the unit normal vector of the junction interface. The phase difference between the superconducting condensates on either side of the junction is expressed as $\Delta\phi$. For the case of the cuprate superconductors, this normal vector is chosen to lie in the CuO_2 ab plane with $x=a$ and $y=b$. If the superconducting order parameter has $d_{x^2-y^2}$-wave symmetry then from Eq. (1) it is clear that Josephson tunneling into the $\mathbf{x}$ direction will be out of phase by π with the tunneling into the $\mathbf{y}$ direction. The first tunneling results that were reported for $YBa_2Cu_3O_{6.9}$ (Ref. 1) were consistent with Eq. (1), implying that this material might be a *d*-wave superconductor. More complex order parameter symmetries such as $d+id$ or $s+id$ could not be ruled out, but the results of Ref. 1 were not consistent with a simple *s*-wave order parameter. This first indication got support from other work[2–4] and more recently from the results of Refs. 5–7. All of those results are in favor of a non-*s*-wave order parameter, of which pure *d*-wave symmetry is the simplest possibility. We also note additional work in Refs. 13 and 14, which indicated *s*-wave superconductivity in cuprate materials, however.

All of the above mentioned phase-sensitive measurements have been performed on $YBa_2C_3O_{6.9}$, and it is clearly a necessity to perform similar tests on other cuprate superconductors. In this work we describe phase sensitive measurements of Josephson tunneling into the ab plane of single crystals of $YBa_2Cu_3O_{6.6}$. This type of measurement on this material is of primary interest for two reasons. First, the effect of varying charge-carrier doping on the symmetry of the superconducting order parameter is unknown and has not been addressed theoretically. Second, the argument that the presence of copper-oxygen chains might influence the results of the current-phase experiments and only mimic the *d*-wave symmetry[17] may be tested in this way. It is well established that oxygen deficiency in compounds of the YBCO series results in interrupted Cu-O chains. Our experimental results imply that the order parameter for $YBa_2Cu_3O_{6.6}$ is not of the *s*-wave variety.

The single crystals used in this study were grown by the low-cooling method.[18] A diagram of the experimental arrangement is given in the inset to Fig. 1. A similar method to that used in Refs. 1 and 6 was used to fabricate the Josephson junctions for this experiment. A thin film of Ag of 1000 Å was evaporated on the edges and corners of the single crystals and annealed to produce low resistance contacts of about $R_n = 0.01$ Ω. A second thin film of 6000 Å Pb was evaporated on top to produce the Josephson junctions. For the edge junction the thin films were evaporated on the a or b face of the crystal, while for the corner junctions the films covered both faces at the corner. At 4.2 K these junctions had critical currents on the order of 30 μA, and since the size of the junctions were on the order of 100×50 μm^2 this leads to a current density on the order of 5 A/m^2. From these parameters the Josephson penetration depth λ_J can be calculated to be on the order of 1000 μm. Since the size of our junctions is much less, this would imply that these junctions are not in

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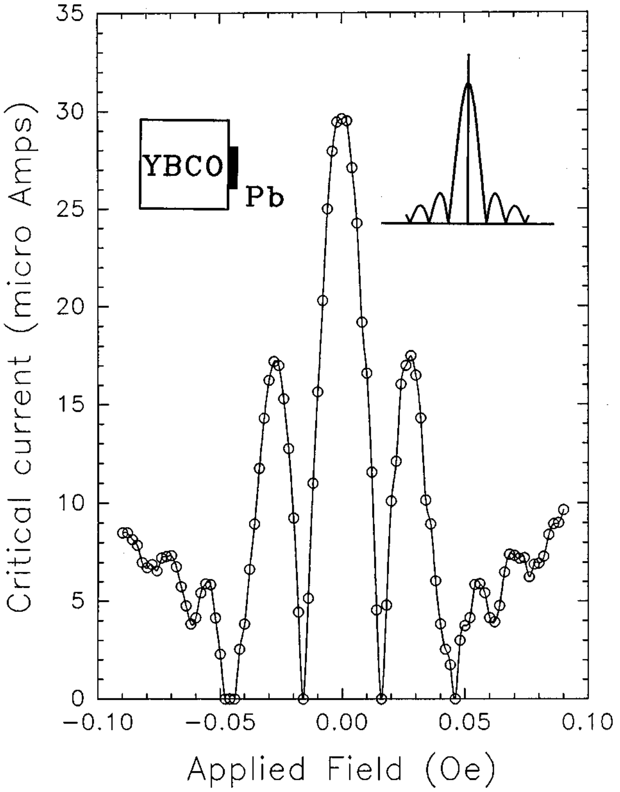

FIG. 1. Critical current vs applied field for an edge Josephson junction between $YBa_2Cu_3O_{6.6}$ and Pb at $T=4.2$ K. Solid lines connect the data given by the open circles. The left inset shows the experimental arrangement and the right inset is the ideal behavior of such a junction given by Eq. (2). This result serves as a control experiment since its behavior is independent of the (s- or d-wave) symmetry of the order parameter of $YBa_2Cu_3O_{6.6}$.

the long junction limit. Previous authors[5,19] have shown that for junction sizes greater than λ_J vortices may nucleate in the junction and make order parameter symmetry measurements impossible.

The current and voltage leads were attached directly to the YBCO crystal and the thin films with silver epoxy and paint, respectively. The crystal was embedded in stycast 1266 epoxy for support. The edge junction critical current vs applied field pattern in Fig. 1 indicates that the period for a complete oscillation is of the order of 0.04 G. Due to the geometry of the samples they have a demagnetizing factor of approximately ten when the applied field is parallel to the c axis, which implies that the field at the junction is actually 0.4 G. From this field, the cross sectional area of the junction can be estimated to be approximately $\Phi_0/B \sim 5\times10^{-7}$ cm^2. Since the width of the junction is approximately 100 μm this area indicates that the sum of the penetration depths of the superconductors plus the thickness of the silver film is 5000 Å which is approximately correct.

The directionality of injection of the Cooper pairs or quasiparticles is important to obtain phase information of the order parameter, so the quality conditions of the junctions were carefully controlled. Only crystals with smooth faces on a submicron scale, verified by scanning electron microscopy, were used. A rectangular shape in the ab plane is required to ensure that corner junction tunneling occurs at an angle of 90°. The T_c of the crystals was measured resistively to be 60 K.

Any magnetic fields present in the junction area will affect the critical currents measured and therefore several precautions were taken to reduce the ambient fields. The experiments were performed in an rf shielded room and the leads were filtered for frequencies above 10 kHz. A three-axis Helmholtz coil was used to cancel the earth's field to within several mOe. A μ-metal cylinder and two concentric Pb superconducting cylinders with caps surrounded the apparatus to provide additional shielding. Subsequent examination of the sample space with a flux-gate magnetometer showed that the resulting background field was less than 1 mOe at room temperature. Care was also taken to keep magnetized objects away from the glass cryostat. The critical-current values were read directly from the IV curves of the junctions, as monitored by an oscilloscope.

If one considers single junction Josephson tunneling between two s-wave superconductors, the equation for the relation between the critical current and the applied field is

$$I_c = I_m \left| \frac{\sin(\pi\phi/\phi_0)}{\pi\phi/\phi_0} \right|. \tag{2}$$

Here I_m is the maximum critical current, ϕ is the flux through the junction, and ϕ_0 is the flux quantum. Figure 1 shows an example of the critical current versus field for an edge $YBa_2Cu_3O_{6.6}$-Pb junction (open circles). The data does not show a perfect Fraunhofer diffraction pattern predicted by Eq. (2) (right inset Fig. 1). Instead, the peak heights decay at a slower rate. This implies that the tunneling current is not uniform across the junction area. At higher fields the critical current appears to increase, but this is due to an increased measurement error. The I-V characteristics are less well structured and an exact value for the critical current is more difficult to evaluate. Thus these values for the critical current should be considered as upper bounds. Nevertheless, and more importantly, the critical current is a maximum for zero applied field. This result should hold for the geometry shown in the left inset to Fig. 1, whether the symmetry of the order parameter of the $YBa_2Cu_3O_{6.6}$ is d wave or s wave. This experiment therefore serves as a control.

We now consider the case of a corner junction (left inset to Fig. 2) where the order parameter symmetry of the $YBa_2Cu_3O_{6.6}$ will become apparent. If one side of the junction provides tunneling into the a direction of the $YBa_2Cu_3O_{6.6}$ crystal and the other tunnels into the b direction of the CuO plane, then according to Eq. (1) the supercurrents will be out of phase by π. This configuration is equivalent to the previous superconducting quantum interference device (SQUID) arrangements,[1,2,7] but the area of this SQUID is very small, i.e., the size of the junction. For this case the same calculation as for Eq. (2) can be done, and from Ref. 6 one obtains

$$I_c = I_0 = A \left| \frac{\sin^2(\pi\phi/2\phi_0)}{(\pi\phi/2\phi_0)} \right|. \tag{3}$$

An essential feature of this equation is that the critical current is *always* a minimum at zero applied field. A plot showing the general shape of $I_c(\phi)$ according to Eq. (3) is given

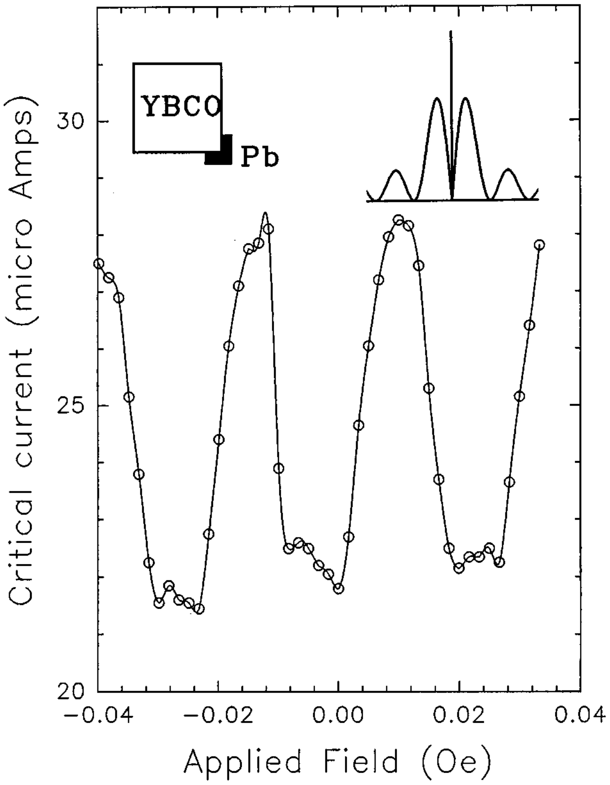

FIG. 2. Critical current vs applied field for a corner Josephson junction between $YBa_2Cu_3O_{6.6}$ and Pb as depicted in the left inset. The right inset shows the ideal behavior [Eq. (3)] of this junction if the $YBa_2Cu_3O_{6.6}$ has a d-wave order parameter. As indicated by the data (open circles), the critical current has a minimum at zero applied field which is evidence that $YBa_2Cu_3O_{6.6}$ is a d-wave superconductor.

in Fig. 2 (right inset). The main panel shows the data which was taken for this geometry. As before, the nonuniform current density across the junction causes a deviation from ideal behavior, nevertheless the most significant feature of Eq. (3) is reproduced, namely, a minimum of the critical current at zero applied field. If instead the $YBa_2Cu_3O_{6.6}$ were an s-wave superconductor one would expect a similar result as that obtained in Fig. 1.

The effect of trapped flux on the situation can be modelled by adding an extra constant flux as described in Ref. 6. This results in an asymmetrical and aperiodic critical current with field, and thus is readily recognizable by experiment. All the patterns presented here are seen to be fairly symmetrical about zero applied field, and so it can be concluded that the effects of trapped flux are not significant. In Fig. 3, a field of approximately 10 G was applied to an edge junction and removed, which certainly trapped some vortices near the junction. The result shows a critical current versus field pattern that is nonperiodic with applied field, and results in amplitudes of apparently unpredictable magnitude. It is clear that the presence of trapped flux produces an unmistakable signature. The results for corner junctions were reproduced successfully on another crystal. Several other unsuccessful attempts were made to create Josephson junctions on other crystals; the main difficulty encountered was obtaining a thin enough barrier to enable Josephson tunneling.

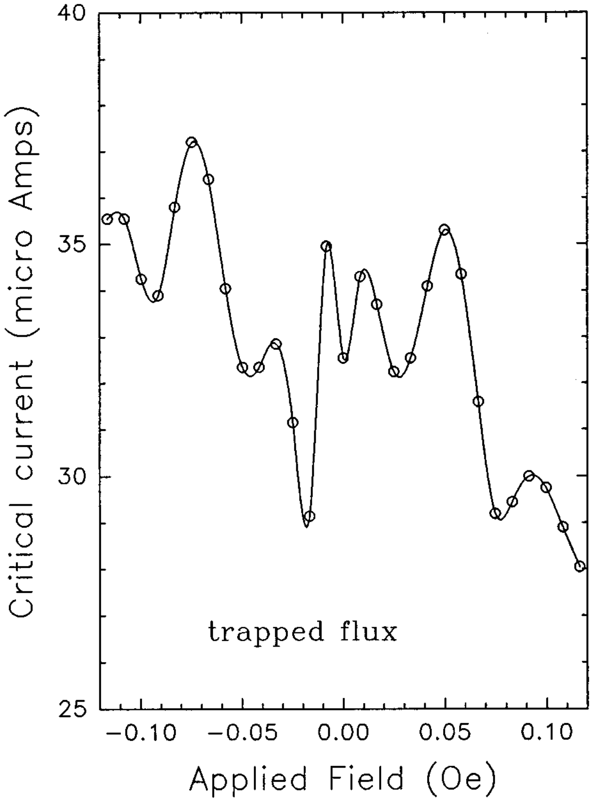

FIG. 3. Critical current vs applied field for an edge Josephson junction between $YBa_2Cu_3O_{6.6}$ and Pb. Flux has been intentionally trapped in the junction and an asymmetry and aperiodicity is apparent.

A complication of previous phase-sensitive tunneling experiments is due to asymmetry of the two sides of the "corner" junctions. Because of the unequal currents in the two sides of the SQUID's, a phase shift due to the resulting circulating current occurred. The procedure most often used was to extrapolate the phase to zero bias current in order to measure the true phase shift due to the symmetry of the order parameter. This phase shift due to the asymmetry of the bias current is proportional to $\delta\Phi/\Phi_0 = L(J_1 - J_2)/\Phi_0$, where L is the inductance of the SQUID loop and $J_1 - J_2$ is the circulating current. Since the inductance of the loop was proportional to the radius a, which could be on the order of 1 mm, the SQUID inductance was of order 10^9 H. This was sufficient to give a significant phase shift with only a small circulating current. For these thin film measurements the radius of the loop is nonexistent and so the inductance and thus phase shift is estimated to be three orders of magnitude smaller. Therefore the effect of an unbalance between the two sides of these thin film junctions will not cause a measurable phase shift in the critical current patterns. As described in Ref. 6 any junction asymmetry here will simply create a pattern intermediate to the expected s- and d-wave results. Any significant junction asymmetry has the effect of raising the minimum in the critical current at zero bias. Complete asymmetry will simply produce the solution shown in Fig. 1 for the edge junction.

The symmetrical critical-current pattern for positive and negative fields in Figs. 1 and 2 indicates that trapped flux is not significant here. The only reasonable conclusion for the observed minimum in critical current at zero applied field is that there must be a phase difference close to π that occurs between the currents injected on either side of the corner junction arrangement. A d-wave type superconducting order parameter for $YBa_2Cu_3O_{6.6}$ is consistent with these observations according to Eq. (1). Other more exotic possibilities, such as mixtures of s and d type symmetries of the superconducting order parameter is also consistent with the data, provided that the d component dominates. An s-wave order parameter in the cuprate cannot provide the necessary phase shift, unless some other explanation can be found to explain the π phase difference between tunneling in the a and b directions. Several authors have reported anomalies in tunneling characteristics of the cuprate superconductors which are often explained by pair weakening by localized states in the junction,[15] or pair breaking by spin flip scattering.[16] Spin flip and localized state scattering may be capable of producing significant phase shifts at the junction interfaces. These effects may be occurring in our junctions, but would not affect the interpretation of our results because these mechanisms are expected to be independent of the direction of the injected supercurrent. Therefore, no difference would be expected for the critical current vs field patterns for the edge and corner junctions, which is in contradiction to our data. For this reason, we believe that these tunneling barrier effects are not responsible for the observed π phase shifts.

Subsequent to the recent phase-sensitive tunneling experiments on $YBa_2Cu_3O_{6.9}$, it was suggested that the CuO chains in $YBa_2Cu_3O_{6.9}$ are the cause for the phase shifts[17] by speculating that the order parameter for the chains (along the a axis) has an opposite sign to that for the planes. Since our experiment shows that the π phase shift persists for $YBa_2Cu_3O_{6.6}$ in the absence of 40% of the oxygen in the CuO chains, this poses a difficulty for this explanation. While the exact nature of the oxygen vacancies in our crystals is unknown, our result suggests that the CuO chains seem not to be responsible for the observed π phase shift in $YBa_2Cu_3O_{6.9}$.

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