Experimental Proof of a Time-Reversal-Invariant Order Parameter with a π shift in $YBa_2Cu_3O_{7-\delta}$

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To determine the symmetry of the order parameter in superconducting $YBa_2Cu_3O_{7-\delta}$ (YBCO), we use a scanning SQUID microscope at 4.2 K to perform independent experiments on six YBCO-Ag-Pb SQUIDs. We find completely unambiguous evidence for a time-reversal-invariant order parameter with a phase shift of π between the **a** and **b** directions of YBCO. Our results are inconsistent with purely s-wave symmetric pairing and are strongly suggestive of $d_{x^2-y^2}$ symmetric pairing in YBCO.

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At present, there is enormous controversy concerning the symmetry of the order parameter in the high transition temperature (T_c) superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO) [1]. The work we report here greatly extends the pioneering experiment of Wollman *et al.* [2], who first reported results on YBCO-Pb SQUIDs. Their conclusion of $d_{x^2-y^2}$ symmetric pairing has been supported by some recent work on Josephson junctions and SQUIDs [3–5], but not by other work [6,7]. In our own work, we have found that common effects produced by trapped vortices, magnetic field gradients, measuring currents, or asymmetries in the SQUIDs can mimic those produced by d-wave superconductivity. In light of this, the disagreements in prior work are neither surprising nor reassuring. In this Letter, we describe experiments which use a scanning SQUID microscope and a time-reversal-invariance test to provide consistent unambiguous evidence that YBCO has a time-reversal-invariant order parameter with a π shift between the crystal **a** and **b** directions.

To understand how a SQUID can be used to find the pairing symmetry of a superconductor, consider Fig. 1(a), which shows a schematic of our type a-b SQUID. One half of the SQUID is made from the s-wave superconductor Pb and the other half from YBCO [2]. The two Josephson junctions allow tunneling of pairs between the superconductors, with one junction oriented normal to the YBCO **a** axis and the other normal to the **b** axis. If no magnetic field B is present and YBCO has a $d_{x^2-y^2}$ symmetry, then pairs tunneling through the **a**-axis junction have a phase shift of π with respect to pairs tunneling through the **b**-axis junction. Thus, a pair which travels once around the SQUID loop acquires an *intrinsic* phase shift of π. Such a π shift produces a current J circulating around the loop. If $\beta = 2LI_0/\Phi_0 \gg 1$, then a π shift generates $LJ \approx \Phi_0/2$ of flux in the loop, where $\Phi_0 = h/2e$ is the flux quantum, L is the SQUID loop inductance, and I_0 is the average critical current of the junctions at $B = 0$. No such intrinsic phase shift, circulating current, or half quantized flux would be produced at $B = 0$ if YBCO had s-wave symmetry or if the SQUID had a type a-a geometry, i.e., both junctions oriented normal to the **a** axis [see Fig. 1(b)].

In principle, the above ideas can be used to determine the pairing symmetry. However, in practice, great care is required because such a circulating current can arise from any small magnetic field. Such fields can be created by the measuring apparatus, by vortices in the superconducting films, or by bias current flowing in the SQUID.

The above qualitative discussion can be made mathematically precise. The equations of motion for a SQUID

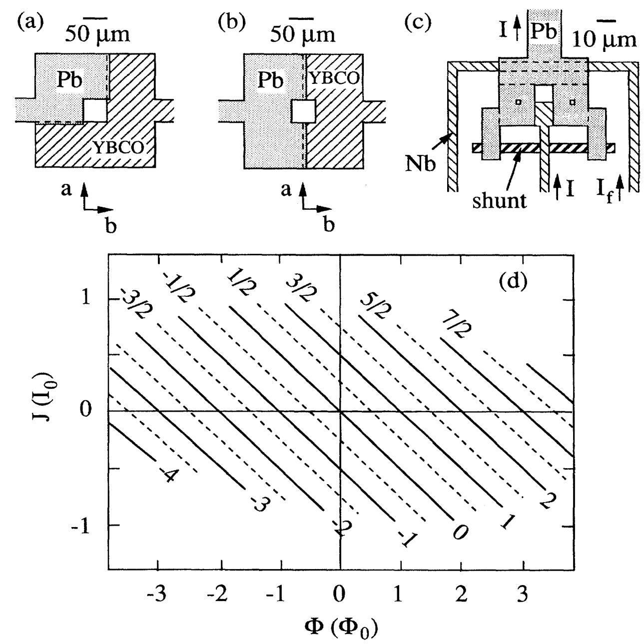

FIG. 1. (a) Schematic of type a-b sample SQUID, dashed lines show location of YBCO-Ag-PbIn edge junctions, (b) type a-a SQUID, (c) Nb-PbIn sensor SQUID showing bias current I and feedback current I_f. (d) Solid lines show schematic $J(\Phi)$ for SQUID with $\delta_d = 0$. Segment labels indicate total number of flux quanta in the SQUID loop. Dashed lines show schematic $J(\Phi)$ for SQUID with $\delta_d = \pi$.

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are [8]

$$I_0\dot{\delta}_1 = -I_1 \sin(\delta_1) + I_b/2 - J\,, \quad (1)$$

$$I_0\dot{\delta}_2 = -I_2 \sin(\delta_2) + I_b/2 + J\,, \quad (2)$$

$$J = I_0(\delta_1 - \delta_2 + \delta_d - 2\pi\Phi/\Phi_0)/(\pi\beta)\,, \quad (3)$$

where δ_1 and δ_2 are the phase differences in the superconducting order parameter across the junctions, the dot represents a derivative with respect to $2\pi R I_0 t/\Phi_0$, R is junction resistance, t is time, Φ is the flux applied to the SQUID loop, I_b is the SQUID bias current, $I_1 = (1 - \alpha)I_0 f(\Phi_1)$ and $I_2 = (1 + \alpha)I_0 f(\Phi_2)$ are the critical currents of the junctions, α is the critical current asymmetry factor, Φ_1 and Φ_2 are the magnetic flux linked into the junctions, and for junctions with uniform critical current density, $f(\phi) = \sin(\pi\phi/\Phi_0)/(\pi\phi/\Phi_0)$ [9]. The factor δ_d fully describes the effect of pairing symmetry [10]; for the *a-b* geometry, $\delta_d = 0$ for *s*-wave YBCO and π for $d_{x^2-y^2}$ YBCO, while for the *a-a* geometry $\delta_d = 0$.

Given Φ and setting $I_b = 0$, solving Eqs. (1)–(3) shows that a SQUID with $\beta \gg 1$ has several metastable states available to it. Plotting J vs Φ yields a series of nearly straight parallel line segments [solid lines in Fig. 1(d) for $\delta_d = 0$ and dashed lines for $\delta_d = \pi$]. Each segment has a slope of about $1/L$ and is displaced from its neighbor by Φ_0 along the flux axis. The segment lengths are determined by the field dependent I_1 and I_2, so that the overall plot has an envelope. On any segment, the total flux in the SQUID loop ($LJ + \Phi$) is at a nearly constant quantized level $n\Phi_0$. If $\delta_d = 0$, then $n = (0, \pm 1, \pm 2, \ldots)$, whereas if $\delta_d = \pi$, then $n = (\pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \ldots)$. As a result, plots of J vs Φ are very similar for $\delta_d = 0$ or π; they differ only by a $\Phi_0/2$ flux shift.

We note that only in special cases are Eqs. (1)–(3) time-reversal symmetric, by which we mean that if J is a solution for given I_b and applied fluxes, then $-J$ is a solution if I_b and all fluxes are reversed. This symmetry holds for $\delta_d = 0$ or π, the *s*- or *d*-wave cases, but not for any intermediate values. Intermediate values of δ_d correspond to time-reversal breaking states, such as formed by a complex superposition $s + id$. Thus the time-reversal properties of Eqs. (1)–(3) are directly related to the time-reversal properties of the order parameter.

While both the $\delta_d = 0$ or π cases are time-reversal symmetric, the difference between them can be clearly revealed under a time-reversal transformation. For $\delta_d = 0$ there is a state which has no flux quanta ($n = 0$) in the SQUID loop and carries no circulating current when $B = 0$. Under time reversal, this $n = 0$ "central state" maps onto itself; i.e., it time reverses to a state with $n = 0$ [11]. All other states map onto distinct time-reversed states; e.g., a state with $n = 1$ flux quanta time reverses to a state with $n = -1$. As discussed below, we can exploit the unique properties of the $n = 0$ state to identify it experimentally. By contrast, for $\delta_d = \pi$ *there is no* $n = 0$ *state so that every state time reverses onto a distinct state.* We can thus use the presence or absence of the $n = 0$ state to provide a completely unambiguous determination of the pairing symmetry. Time-reversal invariance also provides a powerful test for trapped flux [12]; since trapped flux does not reverse with applied field, it causes an apparent breaking of time-reversal symmetry [13].

To build the YBCO-Ag-Pb sample SQUIDs, we use x-ray diffraction to orient a (100) $LaAlO_3$ substrate and then use pulsed laser deposition to grow a bilayer of 150 nm of YBCO ($T_c \approx 88$ K) followed by 300 nm of $SrTiO_3$. The YBCO edge junction electrodes are defined using photolithography, a 10% HF solution to etch the $SrTiO_3$ layer, and Ar ion milling to pattern the YBCO layer. We then evaporate 120 nm of Ag, anneal at 450 °C in 760 Torr of O_2, clean the Ag surface using the ion mill, and deposit a 300 nm Pb (In 5 at. wt %) film. The Ag and Pb layers are patterned using photolithography and ion milling. Three *a-a* and three *a-b* SQUIDs are made simultaneously on the substrate (see Table I).

We use a 4.2 K scanning SQUID microscope [14–16] to measure our sample SQUIDs. The microscope operates at 4.2 K in a vacuum can with a variable temperature stage for heating the sample above the T_c of YBCO. The scanning SQUID or "sensor" is a small Nb-PbIn SQUID [see Fig. 1(c)].

To begin a measurement, we first use the SQUID microscope to determine the static magnetic field [14] and then use a field coil to null the field to better than $\Phi_0/10$ in the sample SQUIDs. We next take magnetic images of the sample and, if trapped flux is found, thermally cycle the sample until all the flux is gone. This typically takes two or three thermal cyclings. The sensor SQUID is then placed over the center of a sample SQUID (with $I_b = 0$) and the flux produced by its circulating current J is recorded as a function of applied magnetic field. We ramp the field back and forth with varying amplitude to access all the metastable states [dots in Fig. 2(a)]. To obtain data for a time-reversal comparison, we decrease the applied field to zero and note which metastable state the SQUID is left in [square in Fig. 2(a)]. We next open

TABLE I. Sample SQUID parameters. γ is the ratio of effective SQUID loop area (1.25×10^{-8} m^2) to junction area. R is junction resistance. Last column shows δ_d/π with experimental uncertainty.

SQUID	I_0 (μA)	R (mΩ)	β	γ	δ_d/π
*a–a*1	100	410	8	14	-0.01 ± 0.04
*a–a*2	90	840	7	11	0.08 ± 0.10
*a–a*3	100[a]	200[a]	8[a]	15	0.10 ± 0.04
*a–b*1	270	500	21	13	1.02 ± 0.08
*a–b*2	130	280	10	11	1.13 ± 0.12
*a–b*3	100[a]	240[a]	8[a]	12	0.91 ± 0.07

[a]Measured without magnetic shielding.

the feedback loop, reverse the feedback lines and current bias, and restart the feedback. We then take a new set of $J(\Phi)$ data [lines in Fig. 2(a)], noting which metastable state the sample SQUID was in when we restarted the feedback [large circle in Fig. 2(a)]. For convenience, we call the first data set "positive" and the second set "negative."

For a good time-reversal comparison, it is essential to reverse all currents to the sensor SQUID because it applies a significant perturbing field to the sample. Although the perturbation is small in the *a-a* SQUIDs and we have reduced it by using a relatively large separation between the sensor and the sample (100–200 μm), the effect is significant in the *a-b* SQUIDs due to their different geometry. This is evident in Fig. 2(a) for SQUID *a-b*1 in that the positive data set does not map onto *itself* after reflecting about the J and B axes [11]. By contrast, when *all* the fields are reversed, including those produced by the sensor, we find consistent and excellent time-reversal symmetry; i.e., the positive data set and time-reversed negative data set are virtually identical (see Fig. 2). Analysis shows that time-reversal invariance holds equally well for the *a-a* and *a-b* SQUIDs (see Table I), implying that the order parameter in YBCO has *no* significant time-breaking term.

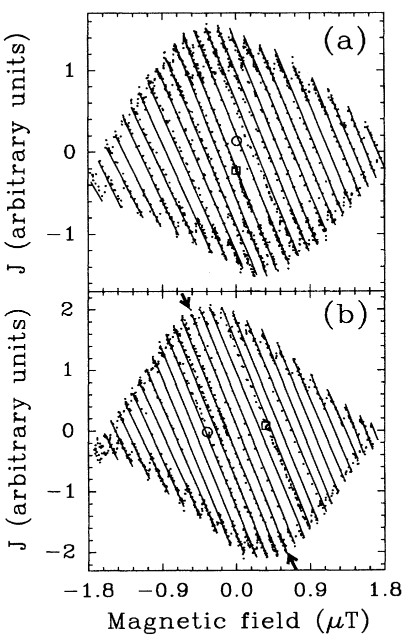

FIG. 2. (a) Dots are measured J vs magnetic field for SQUID *a-b*1 with positive sensor bias. Open square shows ending SQUID state n for positive data. Lines represent data with negative sensor bias (for time-reversal comparison, these data have been reversed about J and B axes). Open circle shows beginning state for negative data set, i.e., state $-n$ taking into account the time-reversal transformation. Note circle lies adjacent to segment n, i.e., on $n + 1$, so that $n + 1 = -n$. Hence circle is on $n = +\frac{1}{2}$, square on $-\frac{1}{2}$, and no state maps to itself. (b) Corresponding data for SQUID *a-a*1. The ending SQUID state n for positive bias (open square) and the time-reversed starting state $-n$ for the negative data set (open circle) obey $n - 6 = -n$. Hence the square and circle are on $n = \pm 3$ and half way between is segment which time reverses to itself, the $n = 0$ state, indicated by arrows.

Given time-reversal invariance, we now find the pairing symmetry. We know which metastable line segment the SQUID ends on for each positive $J(\Phi)$ measurement and which one it begins on for the succeeding negative measurement. If the SQUID does not jump to another state when the feedback is switched, then the ending positive state and beginning negative state will have the same number n of flux quanta in the SQUID loop. With this correspondence known, we now compare a positive data set to a time-reversed negative data set. Under time reversal, the beginning negative state n will get mapped to state $-n$ on the positive data set. As discussed above, if there is a state with n flux quanta in it which gets time-reversal mapped to a state with *the same n,* then $n = 0$ and $\delta_d = 0$.

Experimentally, we find that if a segment is not too small and we are away from its ends, it is easy to maintain the sample SQUID in the same state when we switch the sensor SQUID leads [17]. Independent data sets were taken on each of the six sample SQUIDs, and the field reversal procedure was repeated four times for each data set to check reproducibility. We obtain completely repeatable mappings, independent of which segment the SQUID is left on. In the *a-a* SQUIDs, there is always a central state which maps to itself under time reversal, as expected [e.g., see Fig. 2(b)]. In the *a-b* SQUIDs, we never find a central state [e.g., see Fig. 2(a)]. The results, summarized in Table I, consistently indicate a π shift in YBCO. Since our YBCO films are heavily twinned, this consistency implies that the phase of the order parameter is locked across the twin boundaries. We find δ_d by fitting the envelope of the positive data to that of the time-reversed negative data and then measuring the deviations of the SQUID states from a perfect overlap. Analysis of results on the three *a-b* SQUIDs yields $\delta_d = (0.98 \pm 0.05)\pi$. Given our sample geometry, such a π shift is consistent with $d_{x^2-y^2}$ symmetric pairing in YBCO and is completely inconsistent with purely *s*-wave symmetric pairing.

Further confirmation of a π shift comes from a magnetic images of the sample SQUIDs. Figure 3(a) shows an image of SQUID *a-a*1 in its central state, with positive bias in the sensor SQUID and $B \approx 0$. The image is nearly dipolar with a diagonal zero-field line. Detailed simulations using a sensor-sample separation of 120 μm show the pattern is due to perturbing flux from the feedback and bias currents in the sensor SQUID [see Fig. 3(b)]. Upon reversing the SQUID leads, the image changes (not shown). Averaging the positive and negative images removes the effect of the perturbing flux and reveals any trapped flux or circulating current. We calibrate any circulating current by measuring the height (or depth) of a line scan through the center of the image. We then compare this with the signal measured for a circulating current change of $1\Phi_0$ from screening data over the center of the SQUID. As shown in Fig. 3(c), we see no trapped flux and little circulating current (producing less than $-0.15\Phi_0$ flux). Figures 3(d)–3(f) show corresponding images for SQUID a-$b1$ in state $n = \frac{1}{2}$ at $B \approx 0$. The average image, Fig. 3(f), does not show any trapped flux but clearly reveals a circulating current producing about $-0.6\Phi_0$ of flux, direct evidence that the SQUID is in state $n \approx -\frac{1}{2}$.

In view of our results, some remarks are in order concerning prior experiments. In most experiments, no arrangements existed for guaranteeing the absence of trapped flux in the SQUIDs [2,4,5]. Similarly, some prior experiments [2,5] have used an invalid linear extrapolation from the finite voltage state to deduce the symmetry [18]. Also, where sufficient prior data have been published [2–4], we note that it shows apparent time-reversal breaking [11], indicating the presence of trapped flux or other perturbing fields. Drawing conclusions from such data is inherently suspect [12], since effects which destroy time-reversal invariance can also mimic d-wave superconductivity. We also note the Tsuei *et al.* [3] have suggested that the observation of half-quantized flux in their single tricrystal ring sample could be due to magnetic π scattering in each of the ring's three junctions. Because all our devices have just two junctions, such π scattering cannot be an explanation. Finally, we note that prior SQUID work involved comparing results on different types of SQUIDs [2,3,5]. However, different types necessarily have different geometries and parameters, so that comparisons can go astray. By contrast, our experiment gives direct evidence of a π shift in each a-b SQUID, with each a-a SQUID providing an independent test for systematic errors.

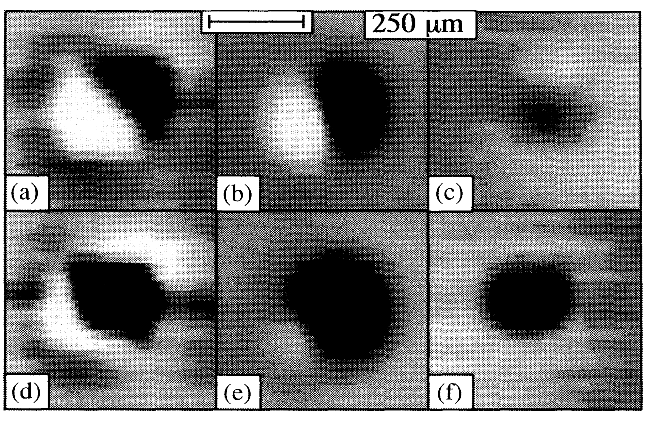

FIG. 3. Images of SQUID a-$a1$ in state $n = 0$ at $B \approx 0$ (a) with positive sensor bias, (b) simulated positive image, and (c) average of positive and negative images showing no trapped flux and little circulating current. Images of SQUID a-$b1$ in state $n = -\frac{1}{2}$ at $B \approx 0$ (d) with positive sensor bias, (e) simulated positive image, and (f) average of positive and negative images showing no trapped flux but the presence of circulating current producing about $-0.6\Phi_0$ of flux. Magnetic field range is 40 nT from black to white.

In conclusion we have found consistent unambiguous proof of a time-reversal-invariant order parameter with a π shift in YBCO. This suggests that the ultimate cause for the high T_c of YBCO is a novel pairing mechanism [19].

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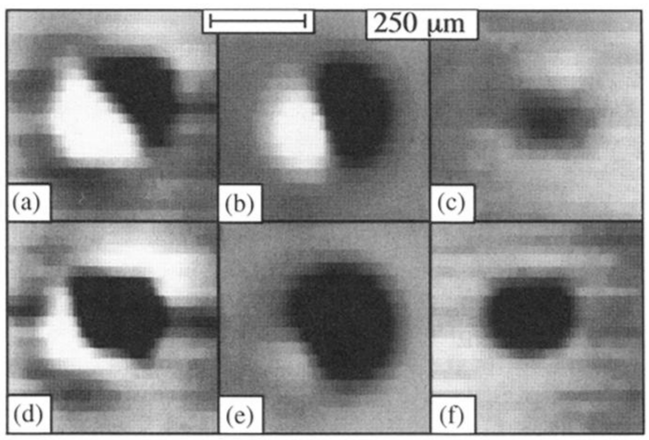

FIG. 3. Images of SQUID a-$a1$ in state $n = 0$ at $B \approx 0$ (a) with positive sensor bias, (b) simulated positive image, and (c) average of positive and negative images showing no trapped flux and little circulating current. Images of SQUID a-$b1$ in state $n = -\frac{1}{2}$ at $B \approx 0$ (d) with positive sensor bias, (e) simulated positive image, and (f) average of positive and negative images showing no trapped flux but the presence of circulating current producing about $-0.6\Phi_0$ of flux. Magnetic field range is 40 nT from black to white.