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Symmetry of the Phase of the Order Parameter in YBa$_2$Cu$_3$O$_{7-\delta}$

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Abstract. — We first describe the basic idea behind phase-sensitive measurements to determine the symmetry of the order parameter in YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO). We then review recent experimental work. While there are still some apparent disagreements, a majority consensus appears to have emerged that the order parameter in YBCO is consistent with a d$_{x^2-y^2}$ symmetry, perhaps with an added s-wave component. To further illustrate the nature of these experiments, we discuss our investigation of the angular dependence of the phase of the order parameter. Using a 4.2 K scanning SQUID microscope, we examined thin-film YBCO-Ag-PbIn SQUIDs and measured the phase of the order parameter in twinned YBCO for 13 different tunneling angles in the a – b plane. We find that the pairing symmetry of the order parameter is time-reversal invariant and consistent with a d$_{x^2-y^2}$ symmetry, provided the junction surface is not damaged and the tunneling angle is well-controlled. From a detailed analysis of the data, we conclude that there is less than 2% of any component which breaks time-reversal symmetry. This rules out states such as d$_{x^2-y^2}$ is or d$_{x^2-y^2} + id_{xy}$.

1. Introduction

What is the physical mechanism which produces the high superconducting transition temperature ($T_c$) in YBa$_2$Cu$_3$O$_7$ (YBCO) and other cuprates [1]? At present, this is perhaps the most important question in superconductivity. In recent years, experimentalists have tried to find the answer to this question by making detailed observations of the behavior of the Cooper pairs. This has yielded much new information about the mechanism. For example, compared to pairs in low-$T_c$ superconductors such as Nb or Pb, the pairs in high $T_c$ superconductors can be easily broken at temperatures $T$ which are much less than $T_c$. The presence of such low energy excitations is revealed by Nuclear Magnetic Resonance experiments (NMR) [2–4], microwave penetration depth measurements [5,6], and Angle-resolved photoemission studies [7]. These results cannot be readily explained by conventional phonon-mediated pairing (pure s-wave

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pairing), such as used in the BCS model [8]. As a result, novel theories based on anisotropic s-wave pairing [9,10] or \( d_{x^2-y^2} \) (d-wave) pairing [11-13] have been developed.

The superconducting state predicted by the new theories has many features in common with the superconducting state of low-\( T_c \) superconductors. For example, in both cases electrons are paired and the motion of each pair is described by a macroscopic quantum mechanical wave function or order parameter. In general, the wave function is a complex number with both amplitude and phase. In the BCS model, the interaction is a short range attraction which arises from the exchange of phonons. The short range attraction leads to spherically symmetric s-wave pairing; the amplitude and phase of the wave function are independent of direction (see Fig. 1a). By contrast, in anisotropic s-wave and d-wave theories the magnitude and phase of the pair wave function depend on direction in momentum space (see Figs. 1b and c). In particular, in \( d_{x^2-y^2} \) theories, there is a difference of \( \pi \) between the phase of pairs moving along the \( k_x \) direction and that of pairs moving along the \( k_y \) direction. The result is an order parameter with four lobes of alternating signs (see Fig. 1c): this is just the well-known \( d_{x^2-y^2} \) state of atomic physics.

Recently, there have been several phase-sensitive experiments which have sought to determine whether the high-\( T_c \) superconductor YBCO has an order parameter with an s symmetry, a \( d_{x^2-y^2} \) symmetry, or some other symmetry. While the details of these experiments differ greatly, all of them use Josephson junctions or Superconducting QUantum Interference Devices (SQUIDs) to gain information about the phase.

Fig. 1. — Schematic representation of order parameter for (a) pure s-wave, (b) anisotropic s-wave, and (c) \( d_{x^2-y^2} \) wave pairing. (d) Schematic diagram of a sample SQUID.
2. Basic Idea of Phase Sensitive Experiments

At first sight, it may not be obvious how the phase of the order parameter can be measured. However, more than 30 years ago Josephson [14] showed that if a tunnel junction is used to connect one superconductor to another, a phase difference \( \delta \) between the superconductors leads to the flow of a supercurrent \( I \) between the two superconductors. This result is summarized in the well-known dc Josephson relation:

\[
I = I_0 \sin(\delta),
\]

where \( I_0 \) is the critical current of the junction. Since current flow is easily measured, we can conclude that differences in the phase of the order parameter are directly measurable.

One subtlety which is not apparent from equation (1) is that the main contribution to the tunneling current is from pairs which are incident normal to the junction face. This geometrical dependence is hidden in the parameter \( I_0 \), which includes factors for the probability of transmission through the tunnel barrier. Thus the tunneling current \( I \) carries information about the order parameter along the direction normal to the tunnel junction face. A number of recent experiments on YBCO-Pb junctions have made direct use of this effect to infer information about the order parameter in specific directions.

Many of the experiments on the symmetry of the order parameter use a dc SQUIDs rather than an individual junction. A dc SQUID consists of two junctions connected in parallel to form a closed superconducting loop [15]. The phase-sensitive experiments follow a general approach first suggested by Geshkenbein et al. [16] to study the symmetry of the order parameter in heavy-fermion superconductors. Later, Sigrist and Rice [17] proposed a detailed geometry in which the two junctions are oriented so as to sample the order parameter in different directions (see Fig. 1d). One part of the SQUID loop is made from the conventional s-wave superconductor Pb and the other part from YBCO. In this figure, the upper junction has a face oriented so that its normal vector points along the \( a \)-axis, while the lower junction has a face oriented with its normal vector at an angle \( \theta \) with respect to the \( a \)-axis. Pb is a conventional s-wave superconductor, so that we can take the phase of the order parameter as just \( \phi_p_1 \) in the Pb at the upper junction and \( \phi_p_2 \) at the lower junction, independent of tunneling direction. Similarly, in the YBCO, we can write the phase in the upper junction as \( \phi_1 \) in the direction normal to the junction interface. Similarly, we can write the phase in the lower junction as \( \phi_2 \) in the direction normal to the junction interface. The phase difference across the first junction is thus \( \delta_1 = \phi_1 - \phi_p_1 \), and across the second junction \( \delta_2 = \phi_2 - \phi_p_2 \).

If a pair travels once around the SQUID loop it will develop a total phase change of:

\[
\delta = \delta_1 - \delta_2 + \delta_d(\theta) + 2\pi \Phi / \Phi_0,
\]

where \( \delta_d(\theta) \) is the intrinsic difference in phase in the YBCO between the two tunneling directions which differ by angle \( \theta \), \( \Phi = BA + LJ \) is the total magnetic flux in the SQUID loop, \( \Phi_0 = h/(2e) \) is the flux quantum, \( B \) is the applied field, \( A \) is the pick-up area, \( L \) is the loop inductance, and \( J \) is the screening current. The first two terms are just the phase drops across the two junctions, the third term takes into account how the phase of the order parameter depends on direction in YBCO, and the last term is due to the Aharonov-Bohm effect for a particle of charge \( 2e \). For the wave function to be single-valued, we require that the total phase shift \( \delta = 2n\pi \), where \( n \) is an integer. Thus we can write the flux-phase relation:

\[
2n\pi = \delta_1 - \delta_2 + \delta_d(\theta) + 2\pi \Phi / \Phi_0
\]

It is interesting to note that the intrinsic phase shift \( \delta_d \) enters into equation (2b) in exactly the same way as an extra applied flux of strength \( \Phi_0 \delta_d / 2\pi \). Thus, a phase difference of \( \delta_d = \pi \)
is effectively equal to an added flux of $\Phi_0/2$. This means that it is essential to know the true or absolute magnetic flux $\Phi$ in the SQUID in order to determine $\delta_d$ experimentally.

If YBCO is s-wave symmetric (see Fig. 1a or b), then $\delta_d = 0$ and one gets the well-known flux-phase relation for a SQUID,

$$2n\pi = \delta_1 - \delta_2 + 2\pi \Phi/\Phi_0. \quad (2c)$$

When there is no applied magnetic field $B$, we can use the dc Josephson relation to write the total flux in the SQUID as:

$$\Phi = LJ = LI_0 \sin(\delta_1) = -LI_0 \sin(\delta_2) \quad (3)$$

It is easy to see that one solution to these two relations is $\delta_1 = \delta_2 = 0$ which gives $J = 0$ and $\Phi = 0$. This is the minimum energy state of the system and it has no current flowing around the loop at $B = 0$.

On the other hand, if YBCO has a $d_{x^2-y^2}$ symmetry, and one junction connects to a positive lobe in the YBCO and the other connects to a negative lobe, then $\delta_d = \pi$. Solving equations (2b, 3) in this case reveals that the phase shift tends to cause a screening current $J$ to flow around the SQUID, just as would occur if a flux of $\Phi_0/2$ were applied. If the critical current of each junction is much larger than $\Phi_0/(2L)$, then this results in a spontaneous current of $\pm \Phi_0/(2L)$ which produces a flux of $\pm \Phi_0/2$ in the SQUID loop. Essentially, the spontaneous current tries to cancel the effective flux of $\Phi_0/2$.

The above basic ideas can be made precise by solving the equations of motion for the SQUID. Appendix A provides an overview of such an analysis. In particular, such an analysis is required to understand the behavior of the SQUID if the junction critical current is not large compared to $\Phi_0/(2L)$. to understand the effects of a complex order parameter (which would break time-reversal symmetry), and to understand the effects of a bias current or non-symmetric SQUID parameters.

From these considerations, we can see that in principle it should be a simple matter to determine whether the phase of the order parameter in YBCO depends on direction. One builds a SQUID with junctions oriented in suitable directions and tests for the presence or absence of a current flowing around the SQUID when there is no magnetic field applied to the SQUID.

### 3. Recent SQUID and Junction Experiments

The pioneering measurements on the symmetry of the order parameter in YBCO were made by Wollman et al. [18]. In these experiments, SQUIDs were formed from junctions made by depositing a thin film of Au and then Pb film onto specific faces of single crystals of YBCO (see Fig. 2a). In some of these SQUIDs, one junction was on the $a$-axis face of the YBCO crystal and the other was on the $b$-axis face. These “corner” or “$a-b$” SQUIDs are sensitive to the difference in phase $\delta_d$ between pairs traveling in the $a$ and $b$ directions. For comparison, they also made “edge” or “$a-a$” SQUIDs with both junctions on the same $a$-axis face of the YBCO.

To determine $\delta_d$, Wollman et al. biased a given SQUID with a constant current and then measured the voltage across the SQUID as a function of the applied magnetic field. In a SQUID, the voltage oscillates periodically in the applied field, with a period of $\Phi_0$. The minimum voltages occur at values of the flux where the phase differences across the junctions, $\delta_1$ and $\delta_2$, differ by an integral multiple of $2\pi$. The fluxes at which the minima occur are thus related to $\delta_d$, the phase difference between the $a$ and $b$-axis directions.
Unfortunately, the relationship between the voltage minima and the flux is not as simple as discussed in the previous section because the device is biased into the finite voltage state; i.e., the measurements are taken with a current $I$ flowing through the SQUID loop. This current can introduce additional magnetic flux into the loop. This happens if one side of the SQUID loop has a different inductance than the other (inductance asymmetry) or if the junctions have different critical currents (critical current asymmetry). To correct for this, Wollman et al. recorded voltage minima for different bias currents and then linearly extrapolated the results to $I = 0$. In zero magnetic field, they reported that the extrapolated minimum of the voltage always occurred at a flux of about $\Phi_0/2$ in the $a-b$ SQUIDs and 0 for the $a-a$ SQUIDs. This corresponds to a phase difference $\delta_d = \pi$ between the $a$ and $b$-axis directions and thus is consistent with $d_{x^2-y^2}$ pairing. Their results have been supported by several later experiments using Josephson junctions [19–21] and YBCO-Nb SQUIDs [22].

By way of contrast, we next consider the Josephson junction experiments of Sun et al. [23]. In these experiments, tunnel junctions were made by first depositing a thin film of Ag (thickness of about 1 mm) onto the $c$-axis face of a crystal of YBCO. A film of Pb was then deposited on top of the Ag to complete the $c$-axis junction (see Fig. 2b). For pure $d_{x^2-y^2}$ symmetry, the wave function has a node in the $c$-direction, and thus one expects no critical current. In addition, even if tunneling arises from pairs which tunnel within a small solid angle about the $c$-axis, the four lobes of the $d_{x^2-y^2}$ wave function would contribute equally, and with opposite sign, so as to yield no net current in zero applied field. In fact, Sun et al. found a maximum critical current in zero applied field and well-behaved modulation of the critical current with applied magnetic field. This result suggests that the junctions have a uniform critical current density, and that the pairing symmetry is $s$-wave or, at the very least, is not pure $d_{x^2-y^2}$.
Taken at face value, the experiments of Wollman et al. and Sun et al. yield apparently contradictory results. This open up several possibilities, which we now examine. First, because YBCO is orthorhombic and not tetragonal, in fact, one would not expect a pure \( d_{x^2-y^2} \) symmetry [24]. Rather, one expects the order parameter to be distorted so that one lobe is larger than the other, while maintaining a \( \pi \)-shift between the \( a \) and \( b \)-axis direction. In principle this could explain observed tunneling in \( c \)-axis junctions because then the positive and negative lobes would not cancel exactly. However, some of the samples which were measured were twinned. The presence of an equal number of twinned regions (in which the YBCO \( a \)-axis switched direction with the \( b \)-axis) would lead to zero average current, even in the presence of an orthorhombic distortion. This null current result in twinned crystals would also hold if the distortion was caused by a combination of an \( s \) and \( d_{x^2-y^2} \) symmetry.

A second possibility has been suggested by Tanaka [25]; even with pure \( d_{x^2-y^2} \) symmetry, one would expect to see a second order tunneling current out of the \( c \)-axis. In this case, the tunneling would follow a \( \sin(2\phi) \) current-phase relation rather than the usual \( \sin(\phi) \) dependence given by equation (1). This dependence would produce measurable effects when the junction is exposed to microwave fields. In particular, Shapiro steps would appear in the current-voltage characteristics at voltages of \((n/2)f\Phi_0\) instead of \(nf\Phi_0\), where \( n \) is an integer and \( f \) is the microwave frequency. This possibility has been tested in a recent experiment by Kleiner et al. [26] using YBCO-Pb junctions. They find that all the steps are separated by \( nf\Phi_0 \), which is consistent with first order tunneling.

Another possibility is that, in the experiment of Sun et al., the tunneling is not happening in the \( c \)-direction, but along the \( a \) or \( b \) axes where a step or other defect occurs in the crystal face. To produce a well-behaved modulation of the critical current with applied field, the steps would have to be closely spaced. We note that Sun et al. has reported using an AFM to examine the flatness of the films and finds little evidence for such steps. In addition, the presence of steps would tend to introduce “corner junctions”. If YBCO has a \( d_{x^2-y^2} \) symmetry, such corner junctions would produce a distinctive flux modulation pattern with a minimum critical current at zero applied flux. We note that just such distinctive patterns have been observed by Iguchi and Wen [19] in Pb-YBCO \( c \)-axis junctions and by Wollman et al. in \( a-b \) corner junctions [21].

From the above observations, it is clear that the results of Sun et al. are consistent with \( s \)-wave pairing and \( s \)-wave pairing mixed with a small \( d_{x^2-y^2} \) component. But, a pure \( d_{x^2-y^2} \)-pairing symmetry is completely inconsistent with their results. For a mixed symmetry of \( s \) and \( d_{x^2-y^2} \), the consistency depends on whether YBCO is twinned or untwinned. When the YBCO is untwinned, \( d_{x^2-y^2} \)-pairing mixed with a small \( s \)-wave component would produce a finite junction critical current in zero applied field. However, for twinned YBCO, the situation is less clear and it appears that averaging over many twins would give zero critical current if the \( d_{x^2-y^2} \)-pairing component was sufficiently large. Since some of their YBCO samples were heavily twinned, their results could be explained by either \( s \)-wave pairing or \( s \)-wave pairing mixed with a small \( d_{x^2-y^2} \) component.

This might suggest that something is wrong in the SQUID and junction experiments [18–22]. In principle, there are several effects which could lead to an erroneous conclusion, including: (i) trapped vortices in the superconductor which linked half of a flux quantum into the \( a-b \) SQUID loops but not the \( a-a \) SQUID loops, (ii) systematic errors in determining the magnetic field or in determining the relative field at two different SQUIDs, (iii) problems with applying a linear extrapolation technique to a non-linear device such as SQUID, and (iv) the presence of trapped flux in the Josephson junctions.

The possibility that the original experiments might be in error lead to a second round of experimental work using different techniques. To avoid possible problems, it is necessary to check for and eliminate any trapped flux in the samples, measure the magnetic field accurately,
and quantify all essential parameters without relying on extrapolation. At present the best technique for accomplishing this appears to be to use a scanning SQUID microscope [27–29]. SQUID microscopes presently have a spatial resolution in the 5–50 µm range and can typically sense magnetic flux which is of order 2 × 10⁻⁶Φ₀ with a 1 second average. They can easily detect single flux quanta pinned in a superconductor and can be used to determine the precise level of magnetic field present.

Along these lines, Tsuei et al. [30] used a 4.2 K scanning SQUID microscope to examine superconducting YBCO rings which were deposited on a tri-crystal substrate. One ring had three grain boundary junctions while two other rings had two grain boundary junctions (see Fig. 2c). The orientation of the grain boundaries was chosen so that, if YBCO is a dₓ²−ᵧ² superconductor, then there would be an intrinsic phase shift of π across each grain boundary junction. This would lead to a net phase shift δₐ = π for a pair which went around the three-junction ring. In zero applied magnetic field, such a π-shift would produce a flux of ±Φ₀/2, provided the junctions had large enough critical currents. In contrast, the rings with two junctions should show δₐ = 0 shift and hence no screening current. In near-zero magnetic field, magnetic images taken using the scanning SQUID microscope revealed a flux of Φ₀/2 in the three-junction ring and zero flux in the rings with two junctions. This strongly suggested a dₓ²−ᵧ² pairing symmetry in YBCO.

The experiment of Tsuei et al. eliminates the possible shortcomings noted above in earlier SQUID and junction work and greatly strengthens the case for a dₓ²−ᵧ² pairing symmetry in YBCO. However, a few minor points can be raised. First, Tsuei et al. noted that their results could be explained if there was magnetic π-scattering in each of the junctions - three junctions would yield an overall phase change which was an odd multiple of π. This possibility has since been ruled out by scanning SQUID results on YBCO-Pb devices with two junctions [31] and by scanning SQUID tests on three junction SQUIDs where the angles are chosen so that δₐ = 0 [32]. Second, many Tunneling Electron Microscopy (TEM) studies [33–35] reveal large facets (10-100 nm) with various orientations along the grain boundaries, regardless of grain boundary angles and substrates. Such non-uniform interfaces cause large spatial variations in the critical current density because the YBCO can be strongly coupled along the facets. More importantly, the phase along the junction could vary from 0 to π, depending on the orientations of the facets. Although Tsuei et al. [30] took into account various types of small-scale disorders such as interface roughness, impurities, strain, oxygen deficiency, etc., they did not consider the effect of possible irregular phase distributions along the grain boundaries in the presence of large facets.

However, we noted that facets occurring along the grain boundaries probably don't affect Tsuei et al.’s experimental results as long as the grain boundary angle is not too close to 45°. This is because TEM studies [35] seem to show that junctions tend to have a small fraction of large angle facets: the fractional area of π-facets is less than 20%. In addition, it should be pointed out that such faceting effects could not cause an s-wave superconductor to produce a d-wave signature, rather it would just tend to obscure details of the underlying symmetry. Finally, it should be noted that the barrier in YBCO-YBCO grain boundary junctions is fundamentally not well-understood and that the coupling between the superconductors is not necessarily weak. Taken together with the occurrence of faceting, this complicates any further analysis of the details of the pairing symmetry.

We note that, with the exception of experiments on tri-crystals [20, 30, 32], most of the symmetry measurements have been done using junctions between YBCO and Pb. To perform a thorough test of the pairing symmetry in such a system, Mathai et al. [31] used a scanning SQUID microscope to examine thin film YBCO-Pb SQUIDs. In these SQUIDs, the c-axis oriented YBCO film was etched using Ar ion-milling to expose a-axis and b-axis edges. Since

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4. Testing the Angular Dependence of the Order Parameter

We can conclude that the scanning SQUID experiments have yet to find any errors in the original reports, and strongly support a $d_{x^2-y^2}$ symmetry. Given that significant experimental discrepancies remain, it is interesting to consider what other tests could be applied to further establish the nature of the pairing symmetry in YBCO. One strategy is to look more closely at the details of the order parameter so as to put more restrictions on the presence of additional components. In the remainder of this paper, we present results from one such test, in which we sought to determine the phase of the order parameter as a function of the tunneling direction.

To build our YBCO-Ag-PbIn SQUIDs, we first use an X-ray diffraction $\Phi$-scan to determine the orientation of the crystal axes of a (100) LaAlO$_3$ substrate. We next use in-situ pulsed laser deposition to deposit a 150 nm thick film of YBCO and then a 300 nm film of SrTiO$_3$. The YBCO film grows with the $c$-axis normal to the plane of the substrate and is heavily twinned. The locations of the YBCO edge junctions are defined using photolithography. Where a junction is to be formed, the edges of the YBCO film are exposed by first etching through the SrTiO$_3$ using a 10% HF solution and then using an Ar ion-mill to etch away the exposed YBCO layer. During the milling, the ions are incident at a fixed angle of $\chi = 45^\circ$ from the $c$-axis and $\phi = 45^\circ$ from the $a$-axis. As discussed below, this means that some of the SQUIDs have a junction which faces toward the incident Ar ion stream.

After removing the photoresist, we clean the edges of the YBCO film using Ar ion-milling and then thermally evaporate 120 nm of Ag. The sample is then removed from the chamber and annealed at 450 °C in 760 Torr of O$_2$. We then clean the Ag surface using Ar ion-milling and deposit a 300 nm Pb (In 5 at. wt. %) film. The Ag and Pb layers are patterned using photolithography and Ar ion-milling to form the junction counter-electrodes and complete the SQUID loops. In our SQUIDs, the junctions are formed in such a way that one junction faces the $a$-axis and the other faces at angle $\theta$ with respect to the $a$-axis (see Fig. 1d). All the sample SQUIDs have a square washer shape with a 50 $\mu$m long inner hole side length and 250 $\mu$m long outer side length.

Using the above procedure, we fabricated 20 SQUIDs with different angles. Measurements showed that 13 of the SQUIDs had critical current which was sufficiently large that we could measure the phase of the order parameter. We note that most of the remaining devices with small critical current had one junction which faced toward the milling direction, whereas in
the other devices, both junctions faced away from the incident Ar ions during the milling step. Thus we concluded that to a large extent the differences in critical currents reflected the effectiveness of the milling on the junctions, with the best SQUIDs having junctions which faced away from the milling direction. We note that junctions which faced away from the incident Ar ions have a low angle milling on the surface which produces a smooth surface (see Fig. 5).

After fabrication, the chip is mounted onto the sample stage of a 4.2 K scanning SQUID microscope. The microscope has a vacuum can and uses a variable-temperature sample stage which allows us to heat the sample above the Tc of YBCO. Magnetic shielding is provided by means of a 4.2 K Pb shielding can and two cylindrical, concentric, room-temperature, mumetal shields. The sensor SQUID is a small Nb-PbIn SQUID (see Fig. 3a) which is operated in an ac flux-locked feedback loop by means of 100 kHz room-temperature electronics [36]. To operate the sensor SQUID, we apply a dc bias current of about 150 μA. In ordinary operation, the feedback circuit supplies a dc feedback flux and a 100 kHz ± Φ0/4 modulation flux to a feedback coil which is deposited on the sensor SQUID (see Fig. 3a). We use a 2.5 cm diameter field coil to apply a uniform magnetic field to the sample SQUIDs and the sensor SQUID. For a time-reversal test, we have also installed switches which allow us to reverse the lines supplying the feedback current.

To begin a measurement, we first identify the position of each sample SQUID. To do this, we position the sensor SQUID about 100 μm above the sample chip and apply a uniform low frequency magnetic field with the field coil. We then scan the sample while recording the strength of the low frequency field as a function of position. The field is screened by superconducting regions so that a scanning SQUID image of the sample shows the location of the superconducting lines and sample SQUIDs. We then use the microscope to take an image

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**Fig. 3.** — (a) Schematic of the Nb-PbIn sensor SQUID showing bias current I_b and feedback current I_f. (d) Illustration of J vs. B taken with positive bias/feedback current. (e) Illustration of J vs. B taken with negative bias/feedback current.
of the static field in the sample, with no current in the field coil. If there is residual field trapped in the magnetic shielding, the static field image will again show variations in the field when the SQUID scans over superconducting parts of the sample. From the contrast in the resulting image, we can accurately gauge the strength of the residual field in the apparatus [37]. Typically this is about 50 to 100 nT. We then use the field coil to cancel out this residual field. The static field image also allows us to check for trapped vortices in the sample. If any are found, we heat the sample above $T_c$, cool down, and then re-image repeating the procedure until no trapped flux is detected.

Once the sample is cleared of vortices, we position the sensor at the center of a sample SQUID and record the feedback output as we slowly sweep the magnetic field applied to the sample. With the sensor SQUID in a flux-locked feedback loop [37], the feedback output voltage is proportional to the magnetic field at the location of the sensor SQUID; i.e. it is a sum of the applied field and the field produced by the screening currents flowing in the sample SQUID. After subtracting off a linear term to account for the direct coupling of the applied field into the sensor, the resulting data corresponds to a measurement of the screening current, $J^+$, versus field $B$ (see Fig. 4a). Here the $+$ superscript just means that the bias and feedback currents of the sensor SQUID flow in the “positive” direction as shown in Figure 3b.

To perform a time-reversal symmetry test, we check whether the screening current reverses from $J$ to $-J$ upon when the magnetic field is reversed. To do this properly, we must reverse all the currents, including those in the sensor SQUID, since these currents also produce magnetic field. Figures 3b and c show the geometry and currents involved.

Figures 4a and b show screening current vs. magnetic field curves for the 120° and -45° SQUIDs, respectively. The lines in these figures are the data $J^+(B)$ data (with positive bias and feedback currents) while the squares represent data $-J^-(-B)$ data (with reversed bias and feedback arrangement). As the plot shows, $J^+(B)$ is very similar to $-J^-(-B)$, and thus we can see that the data shows good time-reversal symmetry. Examination of the other devices on the chip shows the same behavior, i.e. at first sight the time-reversal symmetry is quite good, and is independent of the junction angle.

We note that a good time-reversal symmetry implies that $\delta_d$ is very close to either 0 or $\pi$. In particular, a time-reversal breaking term would produce $\delta_d$ not equal to an integral multiple of $\pi$.

To provide quantitative information about how close $\delta_d$ is to zero or $\pi$ requires additional analysis. To do this, we first compute:

$$\chi^2 = \sum \frac{[J^+(B - B_0) - J_0 + J^-(-B + B_0)]^2}{[\sigma_+^2 - \sigma_-^2]}$$

(4)

where the sum is taken over all $N$ data points, $\sigma_+$ (or $\sigma_-$) is the estimated random error in the screening currents for the positive (or negative) data set, $B_0$ is the residual magnetic field in the apparatus, and $J_0$ takes into account any fixed offsets in the zero of the feedback output. We then minimize $\chi^2$ with respect to $B_0$ and $J_0$.

In general, there are about $N \approx 4000$ data points and we find that $\chi^2$ is close to $N$, but not sufficiently close to $N$ to be a statistically good fit. The reason why can be seen by examining Figures 4a and b. For example, some screening lines on the positive data set are clearly longer than those on the negative data. This implies that the screening currents did not exactly reverse from $J$ to $-J$, and that there is a small time-reversal breaking term in the data.
Fig. 4. — (a) Screening current vs. applied field for $\theta = 120^\circ$ SQUID. The inset shows screening currents near $B = 0$. (b) Screening current vs. applied current for $\theta = -45^\circ$ SQUID. The inset shows screening currents near $B = 0$. 
Table I. — *Measured time breaking component* $\delta_x$ *in units of* $\pi$ *for 13 different tunneling directions.*

<table>
<thead>
<tr>
<th>Angle</th>
<th>$\delta_x/\pi$</th>
<th>Angle</th>
<th>$\delta_x/\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.001</td>
<td>160</td>
<td>$-0.040$</td>
</tr>
<tr>
<td>40</td>
<td>0.005</td>
<td>$-10$</td>
<td>$-0.010$</td>
</tr>
<tr>
<td>60</td>
<td>0.010</td>
<td>$-45$</td>
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<tr>
<td>100</td>
<td>0.056</td>
<td>$-50$</td>
<td>0.025</td>
</tr>
<tr>
<td>120</td>
<td>$-0.005$</td>
<td>$-140$</td>
<td>$-0.053$</td>
</tr>
<tr>
<td>130</td>
<td>$-0.030$</td>
<td>$-150$</td>
<td>0.012</td>
</tr>
<tr>
<td>135</td>
<td>0.011</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The magnitude of the time breaking term can be estimated by introducing the parameter $\delta_x$ and calculating the new sum

$$
\chi^2 = \sum \left[ \frac{J^+(B - B_0) - J_0 + J^-(B + B_0) + \frac{J^- \Phi_0 \partial I_e \delta_x}{I_e A \pi \partial B}}{\sigma_A^2 + \sigma^2} \right]^2
$$

(5)

where $A$ is the pickup area of the SQUID, $I_e$ is a function of $B$ which defines the envelope of the $J^-$ *versus* $B$ data, and $\delta_x$ is the amount by which the phase differs from an integral multiple of $\pi$. We note that the envelope function $I_e$ is simply due to the single junction diffraction effect and is essential for determine the absolute level of flux in the SQUID (see Appendix A). The last term in the numerator takes into account effects produced by the presence of a small time-reversal breaking term. It can be shown that a small time-reversal breaking effectively creates a difference in the applied flux coupled into the SQUID loop for the forward and reverse biased measurements. As a result, critical currents for the forward and reverse measurements are not equal and thereby some screening currents near the envelops does not reverse from $J$ to $-J$.

Table I lists values of $\delta_x$ found by minimizing the equation (5) with respect to $J_0$, $B_0$, and $\delta_x$. We note that $\delta_x/\pi$ typically varies over the range of $\pm2\%$ and that this variation appears to be random. We believe that this residual level of time breaking in the data is due to slow drifts in the background field in our apparatus. The presence of such terms would produce the same effect as a small time-reversal breaking term, $\delta_x$. From these results, we can conclude that $\delta_d$ is within about $2\%$ of 0 or $\pi$ for any given device.

The procedure described above also allows us to accurately determine the residual field in the apparatus. With the residual magnetic field known, in principle, we need only examine the screening plot to determine the level of circulating current $J$ when $\Phi = 0$. However, in practice, the sensor SQUID produces a local perturbing fields which has little effect in determining zero field, but which can introduce a significant amount of flux into the sample SQUID. Thus the total flux, $\Phi_n$, in the sample SQUID may not be zero at $B = 0$. It is essential to accurately measure any perturbing flux from the sensor or else the conclusions will be misleading.

To proceed, we determine the mutual inductance between the sample SQUID and feedback line, and the mutual inductance between the sample SQUID and bias line. Essentially, this is done by making small changes in the feedback current or the bias current and noting how much the $J(B)$ characteristics shift along the $B$ axis. The exact procedure is somewhat complicated,
but it allows us to measure the perturbing flux from the sensor SQUID at any relative position between the sample and sensor SQUIDs. Typically, we arrange the position of the SQUID so that the perturbing flux is small compared to a flux quantum. However, for accurate measurements, it is essential to determine the perturbing flux to much better than a flux quantum.

Using the above procedure, we find the point on the $J(B)$ curve which corresponds to a total applied flux of zero. For all the SQUIDs in this chip, we find that there is no spontaneous screening current in any of our sample SQUIDs at zero flux. As discussed in Appendix A, if $\delta_d = \pi$ this behavior is expected for a SQUID which has one junction with a critical current much less than about $\Phi_0/(2L)$. This means that for SQUIDs with a small critical current, the screening current is zero for both $s$ and $d$-wave symmetries, and one cannot simply test for the presence or absence of half-integral flux quantization to determine the symmetry.

Although the circulating current is zero when one junction has a small critical current, there is one remarkable difference between the $\delta_d = 0$ and $\delta_d = \pi$ cases. If the intrinsic phase shift $\delta_d = 0$, $J$ is induced so as to oppose any small applied field (see Appendix A, Fig. 6a). On the other hand, for $\delta_d = \pi$, a small applied magnetic field induces screening current which generates flux which adds to the original flux (see Appendix A, Fig. 6b).

We note that this behavior is essentially the Wohlleben effect [38]. The main signature of the Wohlleben effect is a paramagnetic susceptibility at low applied fields. Such behavior has been observed in granular high-$T_c$ superconductors such as Bi$_2$Sr$_2$CaCu$_2$O$_8$. It is interesting to note that initial observations of the Wohlleben effect produced some of the first evidence for $d$-wave pairing in high-$T_c$ superconductors. However, it should be pointed out that, in principle, such paramagnetic effects could be also seen in an $s$-wave superconductor [39] if trapped flux provided an additional flux of $\Phi_0/2$ (see Appendix A, Fig. 6a).

The inset to Figure 4a shows a detail of the screening currents in the $120^\circ$ SQUID near $\Phi = 0$. The screening current changes rapidly as the magnetic field increases and, more importantly, the induced field adds to the applied field: this is exactly as expected for a $\pi$-shift. For comparison, the inset to Figure 4b shows results for the $-45^\circ$ SQUID. The direction of the screening current is so as to oppose the applied field, as expected for a $0$-shift.

We have repeatedly and independently applied this technique to 13 different SQUIDs on the chip. As shown in Figure 5, we find that there is a $\pi$-shift for $40^\circ$, $60^\circ$, $100^\circ$, $120^\circ$, $130^\circ$, $135^\circ$, $160^\circ$ and $-150^\circ$. For $30^\circ$, $-10^\circ$, $-45^\circ$, $-50^\circ$ and $-140^\circ$, we find that there is a $0$-shift with respect to the $a$-axis direction. In addition, we have included results from Mathai et al. [31] at $0^\circ$ and $-90^\circ$.

Needless to say, if YBCO were $s$-wave, one would not expect a $\pi$-shift, no matter what the junction angle. However, we note that for a $d_{x^2-y^2}$ symmetry, one would not expect a $\pi$-shift for $40^\circ$, $160^\circ$ or $-150^\circ$. Similarly, one would not expect a $0$-shift for $-50^\circ$. We believe that this behavior, while not ideal, is easily understood as a result of our fabrication procedure. As noted above, we employ an ion mill which etches the junction faces from a particular direction. In Figure 5, the SQUIDs from $-45^\circ$ to $135^\circ$ (the unshaded portion of Fig. 5) have both junctions facing away from the milling direction. On the other hand, SQUIDs from $135^\circ$ to $-45^\circ$ have one junction which faced the milling direction (the shaded portion of Fig. 5). One expects the tunneling to depend on the quality of the junctions and high angle ion bombardment is well known to cause surface damage. One consequence is that SQUIDs at $170^\circ$, $-170^\circ$, $-135^\circ$, $-130^\circ$, $-120^\circ$, $-110^\circ$, and $-60^\circ$ had critical currents which were too small to allow us to measure $\delta_d$. In addition, SQUIDs at $160^\circ$ and $-150^\circ$ are not expect to produce reliable results. In view of this, we now believe that the SQUIDs in the shaded area of Figure 5 simply do not have well-fabricated junctions and should be discarded from further analysis. We also
Fig. 4 - $\delta_d$ vs. tunneling angle. Empty squares represent tunneling angles for which there was a very small current and as a result the time-reversal test was not performed. Squares labeled with $\pi$ are for SQUIDs with $\pi$ phase shift while those labeled with 0 had no phase shift. The * shows data taken from reference [30].

We note that the anomalous behavior at $40^\circ$ and $-50^\circ$ could well be due to imperfect alignment of the substrate or local deviations of the junction face from a straight line.

In view of our results, we now discuss the possibility of mixed pairing symmetries such as $d_{x^2-y^2} + s$. We note that for a pure $d_{x^2-y^2}$ symmetry, the phase shift is zero for an angle $<45^\circ$ and $\pi$ for an angle $>45^\circ$. The presence of an additional s-wave component would cause the phase to change at an angle other than $45^\circ$. As discussed above, there are uncertainties in determining the true tunneling angles from the photolithographically patterned angles, and this makes it difficult to determine the transition angle accurately. More importantly, our films are heavily twinned and thus a junction at an angle with respect to the $a$-axis will have the phase averaged over the different twin orientations. We note that the reproducibility of the results of Tsuei et al. and Mathai et al. imply that the order parameter must be locked in a positive way across twin boundaries, so that there is a single phase of the order parameter in the direction determined by the substrate $a$ or $b$ axis, as opposed to the local twin’s $a$ or $b$ axis. In other words, a junction that spans many twinned regions would show no preference of $a$ over $b$, and one expects a change in phase at $45^\circ$, even if there is a small s-wave component. Thus it is not possible to draw conclusions about the presence of a real small s-wave component in the present experiment.

5. Conclusions

In conclusion, we can summarize the status of recent work by noting that all of the SQUID measurements reported so far are consistent with a $d_{x^2-y^2}$ symmetry of the order parameter in YBCO. The SQUIDs were made by different researchers, using different types of junctions (YBCO-YBCO, YBCO-Ag-Pb, or YBCO-Au-Pb), on different types of YBCO (twinned and untwinned single crystals, and twinned thin films), and measured using different experimental methods. Similarly, there are several experiments on junctions in the $a-b$ plane and the $c$-axis
which are consistent with a $d_{x^2-y^2}$ symmetry. However, the experiment of Sun et al. on c-axis Josephson junctions are consistent with s-wave pairing and, even after some consideration, it is not evident that these experiments are consistent with a $d_{x^2-y^2}$ symmetry.

To completely resolve the issue, experimental work is needed to more precisely determine the form of the order parameter. In particular, experiments which determine the angular dependence of the order parameter on untwinned YBCO-Pb SQUIDs would be very revealing. In a preliminary experiment on twinned films, we found time-reversal symmetric behavior for 13 different tunneling directions. This rules out pairing symmetries which contain a real component plus an imaginary component such as $d_{x^2-y^2} + id_{xy}$ or $d_{x^2-y^2} + is$. In addition, our phase shift vs. angle measurements support a $d_{x^2-y^2}$ symmetric pairing in YBCO, although twinning and difficulties in controlling the tunneling direction preclude a more detailed analysis. In particular, our results do not rule out a real superposition of s and d, such as $d_{x^2-y^2} + s$.

Acknowledgments

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Appendix

Theory of Phase Shifts in dc SQUIDs

In this Appendix, we briefly review the theory of the dc SQUID in so far as it concerns the effects of the intrinsic phase shift in YBCO-Pb SQUIDs. We will assume that in zero magnetic field the two junctions in the SQUID have critical currents $I_{01} = (1 - \alpha)I_0$ and $I_{02} = (1 + \alpha)I_0$, respectively. Here $I_0$ is the average critical current in zero applied field and $-1 < \alpha < 1$ quantifies the different magnitude of the critical current in the two junctions. We also assume that in an applied magnetic field the junctions themselves can intercept flux $\Phi_1$ and $\Phi_2$, leading to junction critical currents which depend on the field. For the purposes of this analysis we assume a simple single junction diffraction pattern. For example, for non-zero applied field, the critical current of junction 1 is:

$$I_{01} = (1 - \alpha)I_0 \sin(\pi \Phi_1/\Phi_0)/(\pi \Phi_1/\Phi_0).$$  \hspace{1cm} (6)

With these definitions, the equations of motion for the SQUID become [40]:

$$I_0 \frac{\partial \delta_1}{\partial t} = -(1 - \alpha)I_0 \frac{\sin(\pi \Phi_1/\Phi_0)}{\pi \Phi_1/\Phi_0} \sin(\delta_1) + \frac{I}{2} - J$$ \hspace{1cm} (7)

$$I_0 \frac{\partial \delta_2}{\partial t} = -(1 + \alpha)I_0 \frac{\sin(\pi \Phi_2/\Phi_0)}{\pi \Phi_2/\Phi_0} \sin(\delta_2) + \frac{I}{2} + J$$ \hspace{1cm} (8)

$$J = I_0 \left( \frac{\delta_1 - \delta_2 + \delta_4 - 2\pi \Phi_a/\Phi_0}{\pi \beta} \right)$$  \hspace{1cm} (9)

where $\delta_1$ and $\delta_2$ are the phase differences across junction 1 and 2, respectively, $t$ represents time in units of $\Phi_0/(2\pi R I_0)$. $I$ is the SQUID bias current, $\beta = 2 LI_0/\Phi_0$, $L$ is the inductance of the SQUID loop, $J$ is the circulating current in the SQUID loop, and $\Phi_a$ is the magnetic flux applied to the SQUID.
Fig. 6. — (a) Simulated $J$ vs. $\Phi$ of s-wave SQUID for $\delta_d = 0$. The dynamic inductance is positive at $\Phi = 0$: $1/L = -\partial J/\partial \Phi > 0$. (b) Simulated $J$ vs. $\Phi$ of d-wave SQUID for $\delta_d = \pi$. The inductance is negative at $\Phi = 0$: $1/L = -\partial J/\partial \Phi < 0$.

The parameter $\delta_d$ describes the intrinsic phase difference between the two tunneling directions. For example, if both junctions are oriented along the $a$-axis face of YBCO, there is no phase shift and $\delta_d = 0$. On the other hand, if one junctions is normal to the $a$-axis face while the other is normal to the $b$-axis, the phase shift depends on the pairing symmetry of the order parameter in YBCO; $\delta_d$ is 0 for s-wave pairing and $\pi$ for $d_{x^2-y^2}$ pairing. Since one of two junctions in our SQUIDs is always normal to the $a$-axis direction, by measuring $\delta_d$, we can determine the relative phase shift between the $a$-axis and the tunneling directions.

We note that $\delta_d$ only enters into equation (9), and that it simply adds to the applied flux $\Phi_a$ in the sample. Further consideration of this fact shows that all the effects produced by an intrinsic phase shift $\delta_d = \pi$ are equivalent to applying an effective flux of $\Phi_0/2$ to the SQUID loop.

Equations (7-9) are easy to solve in the zero voltage state, for which $\partial \delta_1/\partial t = \partial \delta_2/\partial t = 0$. For a SQUID in which both junctions have large critical currents ($\beta = 2LI_0/\Phi_0 > 1$), the screening current is approximately proportional to $-\Phi/L$ near zero magnetic fields [30]. As a result, for $\delta_d = \pi$, there is a spontaneous screening current of $-\Phi_0/(2L)$ to oppose the effective flux of $\Phi_0/2$, while there is no screening current for $\delta_d = 0$ [30,31].
It is also worth noting that for a SQUID with very small critical currents or large difference in the critical current between the junctions, it is impossible to maintain a screening current of \( \Phi_0/2L \). In this case, the only possible value of screening current is zero and both s and d-wave pairings will produce no self-screening current at \( B = 0 \).

Figures 6a and b show screening current \( J \) versus applied flux \( \Phi \) for SQUIDs with \( \delta_d = 0 \) (s-wave) and \( \delta_d = \pi \). For these plots, we chose the parameter \( \beta = 1 \) and \( \alpha = 0.9 \). We note that the two plots are quite similar, except that the \( J - \Phi \) curves for \( \delta_d = \pi \) are shifted by \( \Phi_0/2 \) with respect to those for \( \delta_d = 0 \), as expected. Because the junction critical currents depend on the applied magnetic flux, the screening current is a maximum near \( \Phi = 0 \) and decreases as the magnitude of the applied flux increases. This results in an overall envelope \( I_c(\Phi) \) which defines the critical current at any applied field.

For a time-reversal breaking order parameter in YBCO, \( \delta_d \) has an intermediate value between 0 and \( \pi \), depending on the magnitude of an imaginary component [37]. The larger the imaginary component, the more \( \delta_d \) deviates from 0 or \( \pi \).

References


