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Tricrystal Experiments for Testing Pairing Symmetry in Cuprate Superconductors†

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Based on macroscopic quantum coherence effects arising from pair tunneling and flux quantization, a series of tricrystal esperiments have been designed and carried out to probe the microscopic phase of the pair wavefunction in high-T_c cuprate superconductors. By using a high-resolution scanning SQUID microscope, and the half-integer flux quantum effect in various tricrystal geometrical configurations, we have proven that the order parameter in $YBa_2Cu_3O_7$ has nodes and lobes consistent with d-wave but not with the g-wave pairing symmetry.

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It has been almost ten years since the discovery of high-temperature superconductivity in cuprates [1,2]. The mechanism responsible for HTS remains elusive. An unambiguous determination of the pairing symmetry in this new class of superconductors is crucial in improving this unsettling situation. Although a well-defined test of pairing symmetry does not pin down a specific high-T_c mechanism, it certainly can put a strong constraint on possible theoretical models of the origin of high-temperature superconductivity.

In recent years, there have been numerous experiments [3-5] providing a large amount of data for determining the symmetry of the order parameter in cuprates. Unfortunately, these experiments are quite controversial. The experiments that support d-wave pairing are about equal in number to those in favor of the s-wave symmetry. The cause of this uncertainty stems mainly from the indirect nature of these symmetry tests and/or their incapabability of measuring the phase of the pair wavefunction, i.e. the wavevector(k)-dependent energy gap, $\Delta(k)$. For example, experimental techniques such as high-resolution angle-resolved photo-emission spectroscopy and quasiparticle tunneling measurement can measure the amplitude of the order parameter in the superconducting state (i.e. $|\Delta(k)|$) but not its sign.

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Several recent phase-sensitive pairing symmetry experiments have changed the situation and have yielded strong supporting evidence for d-wave pairing in $YBa_2Cu_3O_{7-\delta}$ (YBCO). Wollman et al. [8] did the first of such phase-sensitive measurements by using the method of Pb-YBCO dc-SQUID interferometry as originally suggested by Sigrist and Rice [9]. However, the results of this experiment were highly controversial [10,11] and were criticized for problems associated with SQUID asymmetry, certain geometrical complications and vortex trapping. Nevertheless, the phase-sensitive experiments [12-17] that followed prove convincingly that the *d-wave* conclusion suggested by Wollman et al. [8] is correct.

In this brief article, we describe the tricrystal experiments which are designed to measure the phase of pair wavefunctions and to test unambiguously the pairing symmetry in copper-oxide superconductors. The details of the tricrystal experiments have been described elsewhere [12,13] and will not be repeated here.

The basic idea of the tricrystal experiments is to obtain the microscopic phase information of a pair wavefunction in cuprate superconductors by making a combined use of two macroscopic quantum coherence measurements, i.e. pair tunneling across a Josephson junction (such as a grain boundary weak-link) and flux quantization in superconducting rings, in particular rings containing so-called π-junction. A π-junction is a Josephson junction with a negative pair tunneling current which leads to a phase shift of π at the junction interface. There have been several theoretical suggestions [9,19-22] as to the cause of the π-junction. Of particular interest is the possibility that a π-junction can be made between two appropriately oriented unconventional superconductors such as heavy-fermion systems [19] and d-wave cuprates [9] in which the energy gap function is supposed to have nodes and lobes.

Based on the consideration of flux quantization [12] and free energy [9,19], it is concluded that the ground state of a superconducting ring with an odd number of π-junctions corresponds to a doubly-degenerate state which is characterized by a spontaneous magnetization of $\pm 1/2\Phi_0$, provided that the condition of $I_cL \gg \Phi_0$ is satisfied, where Φ_0 is the flux quantum ($\Phi_0 = h/2e = 2.07 \times 10^{-7} G$ cm^2), I_c the critical current of the weakest junction in the ring, and L the self-inductance of the ring.

Since the sign of pair tunneling across a grain boundary junction as a function of grain misorientation is well-defined for a given pairing symmetry [3,5], one can design a series of superconducting cuprate rings with three deliberately oriented grains to probe the symmetry of the gap parameter. Using the presence or absence of the half integer flus quantum effect in such tricrystal systems, one can obtain the microscopic phase information of the pair wavefunction (i.e. the sign of the supercurrent I_s) without the need of measuring the magnitude of I_s, which is a complex, unknown function of grain orientation, arising from the effects of disorder at the junction interface [23-26] (i.e. grain boundary) as well as the angular dependence of the pairing interaction.

To test the $d_{x^2-y^2}$ pairing symmetry in cuprate superconductors? tricrystal *(100)* $SrTiO_3$ substrate were designed, using the Sigrist-Rice formula for the angular depence of supercurrent $I_s(\theta_i, \theta_j)$ in the clean limit (perfectly smooth junction interface):

$$I_s(\theta_i, \theta_j) \propto \cos 2\theta_i \cos 2\theta_j \sin \Delta\phi_{ij} \qquad (1)$$

and in the disorder limit (maximum allowable deviation in θ_i and θ_j for the case of a 4-fold rotation symmetry):

$$I_s(\theta_i, \theta_j) \text{ a } \cos 2(\theta_i + \theta_j) \sin \Delta\phi_{ij} \tag{2}$$

where θ_i and θ_j are the angles of the crystallographic axes with respect to the junction interface (Fig. 1) for a grain boundary junction between two superconductors i and j, $\Delta\phi_{ij}$ is the usual Josephson phase angle. The misorientation angles and the angle between the grain boundary planes for the substrate design [12] shown in Fig. l(a) were chosen to ensure that a superconducting cuprate ring, with d-wave pairing symmetry, centered at the tricrystal meeting point, would have one or three K-junctions (the π-ring coniiguration), regardless of the condition of the junction interface [Eqs. (1) and (2)].

On the other hand, the geometrical configuration for the substrate design [13] shown in Fig. l(b), [based on Eqs. (1) and (2)], was chosen to ensure that the product of the signs of the supercurrents of the grain boundary junctions making up the 3-junction ring is always positive (the O-ring geometry). As mentioned earlier, the considerations based on flux quantization and free energy predict that the π-ring should exhibit the half-integer flux quantum effect:

$$\Phi = \pm(n + 1/2)\Phi_0 \tag{3}$$

while the O-ring should show the conventional integer flux quantization:

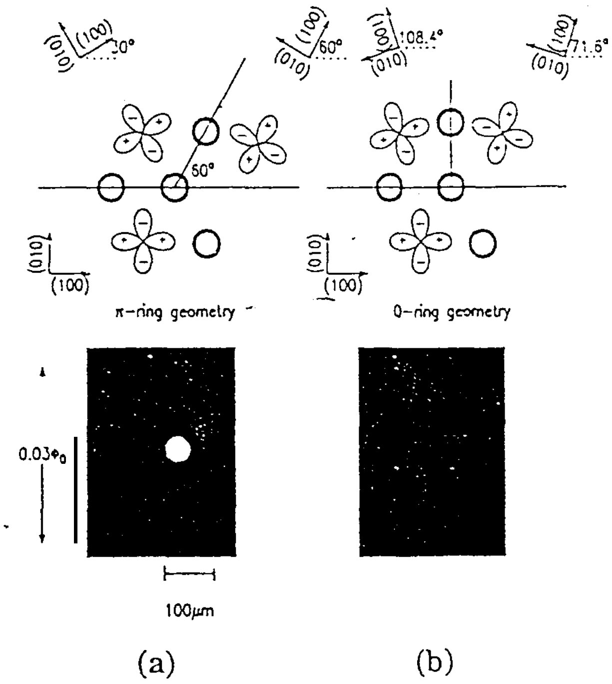

FIG. 1. A schematic of the substrate geometrical configurations (upper section) and the scanning SQUID microscope images of the two tricrystal experiments: (a) r-ring geometry, and (b) O-ring geometry based on d-wave pairing symmetry [Eqs. (1) and (2)].

$$\Phi = \pm n\Phi_0 \tag{4}$$

where n = 0, 1, 2 . . . . . .

Rings (48 μm in inner diameter and *10* μm in width) of $YBa_2Cu_3O_7$ were lithographically patterned from the epitaxial films (1200 Å thick) deposited on the tricrystal substrate as schematically shown in Fig. 1. In addition to the 3-junction ring at the tricrystal intersection point, three O-rings of the same dimensions, two on the grain boundaries and one inside the grain, were also made as controls.

The magnetic flux quantum state of these rings were studied by employing a high-resolution scanning SQUID microscope (SSM). The design and operation of the SSM have beep described elsewhere [27]. As shown in the lower section of Fig. 1, the SSM images of the rings at 4.2 K and nominal zero magnetic field indicate clearly that only the 3-junction x-ring exhibits spontaneous magnetization of half flux quantum. The calibration of the SSM flux measurement is described elsewhere [12,13,18]. The fact that the half-flux quantum effect is observed in the 3-junction s-ring, but not in the others as expected from Eqs. (1) and (2), clearly shows the existence of nodes in the pair wavefunction and represents a strong evidence for d-wave pairing in $YBa_2Cu_3O_7$.

It is worthwhile to mention that, due to the small interaction between the SSM's pick-up loop and the ring [12], our tricrystal experiment is a truly non-invasive measurement of the ground state of the rings. Trapped flux is not a problem because it can be spotted directly by using our SSM if there is any in our sample.

By varying the grain misorientation and the angles between rhe grain boundary planes, we have carried out several tricrystal experiments to elucidate the nature of the half-integer flux quantum effect. The main results of these tricrystal experiments are summarized as follows:

1. The SSM images shown in Figs. 1(a) and 1(b) have ruled out (13) any symmetry-independent mechanisms such as magnetic impurities [21], and electron correlation effect [20] at the grain boundary as the cause of the observed π-junction effect.

2. The absence of the half-integer flux quantum effect in a g-wave only tricrystal experiment with $YBa_2Cu_3O_7$, has ruled out [18] an even parity pair state with a gap varying as ($\cos k_x$ + cos k_y) or cos 48 (i.e. 8 nodes instead of 4 nodes as in the d-wave case).

3. Using the ***d-wave*** tricrystal *geometry* as shown in Fig. 1(a) *we* have demonstrated the half-integer flux quantum effect at the tricrystal meeting point in $YBa_2Cu_3O_7$ tricrystal disks, blanket films, rather than rings to show that the spontaneous magnetization of $1/2\Phi_0$ is a ground-state effect arising from a r-phase-shift due to a node in the gap function and does not depend on the macroscopic sample configurations [28].

4. The half-integer flux quantum effect has been *observed* [29] in high-T, one-layer tetragonal $Tl_2Ba_2CuO_{6+\delta}$ films deposited on a *d-wave* tricrystal (100) Sr Ti O_3 substrate. This result shows that, in addition to the $YBa_2Cu_3O_7$ system, the gap symmetry in this Tl-based cuprate superconductor is consistent with that of a $d_{x^2-y^2}$ pair state.

This observation also suggests that effects arising from the CuO_2 bi-layers, and the Cu-O chains do not play any fundamental role in determining the pairing symmetry in high-T_c cuprate superconductors.

In summary, based on two macroscopic quantum coherence effects, i.e. pair tunneling and flux quantization, *in* tricrystal superconducting systems, a series of tricrystal experiments have been designed and performed to umambiguously test the pairing symmetry in cuprate superconductors. By using a high-resolution scanning SQUID microscope, we have observed the half-integer flux quantum effect in both $YBa_2Cu_2O_7$ and $Tl_2Ba_2CuO_{6+\delta}$ systems, providing strong evidence for a $d_{x^2-y^2}$ pairing symmetry. There are reasons and some indirect evidence to believe that this $d_{x^2-y^2}$ symmetry holds true for all hole-doped cuprate superconductors with optimized T_c. *However* it remains to be demonstated whether s or other types of symmetry exist in non-optimized hole-doped cuprates, electron-doped cuprates, and non-cuprate exotic superconductors such as $Ba_{1-x}K_xBiO_3$ and RNi_2B_2C.

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