Fractional Vortices as Evidence of Time-Reversal Symmetry Breaking in High-Temperature Superconductors

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We argue that recent experiments by Kirtley *et al.* may show evidence of time-reversal symmetry breaking in $YBa_2Cu_3O_7$ at crystal grain boundaries. We illustrate this through a Ginzburg-Landau model calculation. Further experimental tests are proposed.

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In a recent paper, Kirtley *et al.* [1] reported the observation of magnetic defects at artificially engineered grain boundaries in thin films of the high-temperature superconductor $YBa_2Cu_3O_7$ (YBCO). The grain boundaries were the borders between a triangular YBCO inclusion in a film of YBCO with the crystal axes misoriented with respect to one another in the two domains (inside and outside of the triangle). While the resolution of the magnetic microscope (~ 10 μm which is roughly 10 times the estimated Josephson penetration depth λ_J [2]) used for detection is not sufficient to tell with absolute certainty, the observed magnetic defects appear from their shape and localization to be superconducting vortices carrying small fractions of a flux quantum $\Phi_0 = hc/2e$. These vortices are attached mainly to the corners of the triangle, but occasionally appear along the edges of the triangular inclusion. The purpose of this Letter is to point out that the identification of these defects as fractional vortices, if correct, demonstrates that the materials in question have superconducting order parameters, and thus ground states, that violate time-reversal symmetry $\mathcal{T}$. The experiments cannot tell whether the $\mathcal{T}$ violation was a bulk or interface (grain boundary) effect. Our argument is simply that the flux carried by a vortex measures the *phase defect* of the order parameter along a closed path encircling the vortex, and can therefore be fractional only if the order parameter changes by a phase $\Delta\phi$ *not* a multiple of 2π along this path. The recent Josephson tunneling experiment of Wollman *et al.* [3] and the observation of half-integer flux quanta by Tsuei *et al.* [4] are specific examples of this for which $\Delta\phi$ is an odd multiple of π. Because of specific symmetry properties of the Josephson junctions, their results were interpreted as strong evidence for $d_{x^2-y^2}$-wave pairing symmetry in YBCO, which is a $\mathcal{T}$-conserving superconducting state. On the other hand, the recent experiment of Kirtley *et al.* [1] can be explained only if $\Delta\phi$ is *not* a multiple of π, which requires $\mathcal{T}$ violation.

Let us briefly review the historical context of $\mathcal{T}$ violation in unconventional (both heavy-fermion and high-T_c) superconductivity. It has long been suspected that time-reversal symmetry breaking is responsible for some of the unusual magnetic properties of heavy-fermion superconductors, in particular, $(U,Th)Be_{13}$ and UPt_3 [5,6]. The possible appearance of fractional vortices in these materials has already been suggested [7] and investigated theoretically [8]. The conditions under which a superconductor with a real order parameter in the bulk phase may spontaneously break time-reversal symmetry have also been studied in the context of Ginzburg-Landau theory [9,10]. Surfaces and domain walls were found under certain conditions to favor the formation of a locally $\mathcal{T}$-violating state as a means of lowering the energy cost of an inhomogeneous order parameter [10]. $\mathcal{T}$ violation (specifically, a $d_{x^2-y^2} + i\epsilon d_{xy}$ order parameter) has been predicted in high-T_c superconductivity via the anyon technique applied to the t-J model [11,12]. A superconducting state with $s + id_{x^2-y^2}$ symmetry has also been proposed [13]. However, none of the telltale signs of $\mathcal{T}$ violation has been detected in bulk measurements [14]. This does not preclude the existence of a complex order parameter at surfaces and grain boundaries since bulk measurements are not sensitive to the existence of such a phase. In this Letter we wish to show, at least on a phenomenological level, that such states are indeed possible.

To illustrate our idea we first analyze the properties of superconducting states near an interface by means of a Ginzburg-Landau (GL) theory. A $\mathcal{T}$-violating superconducting state requires the existence of at least two complex order parameter components, η_1 and η_2. We consider here the example of two order parameters belonging to pairing states of different symmetry, $d_{x^2-y^2}$ and d_{xy} [$\psi_1(\mathbf{k}) = k_x^2 - k_y^2$ and $\psi_2(\mathbf{k}) = k_x k_y$], which are nondegenerate under the tetragonal (D_{4h}) as well as orthorhombic (D_{2h}) crystal field symmetry; i.e., the tran-

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sition temperatures of the two order parameters are different. The crystal symmetry of YBCO is D_{2h} in the superconducting phase. From this we can derive a GL free energy functional of η_1 and η_2 with the requirement that it be a scalar under all symmetries of the system (for a review, see Ref. [5]) $F = F_1 + F_2 + F_{12}$ with

$$F_i = \int d^3x[\alpha_i(T)|\eta_i|^2 + \beta_i|\eta_i|^4 + K_i|\mathbf{D}\eta_i|^2], \quad (1)$$

$$F_{12} = \int d^3x[\gamma|\eta_1|^2|\eta_2|^2 + \delta(\eta_1^{*2}\eta_2^2 + \eta_1^2\eta_2^{*2})], \quad (2)$$

where $\alpha_i(T) \propto T - T_{ci}$ (T_{ci}, the bare bulk transition temperature of the order parameter η_i) and β_i, K_i, γ, and δ are real phenomenological parameters which contain all of the relevant physical information of microscopic origin. The gradient terms are given in the gauge invariant form $\mathbf{D} = \nabla - i2\pi\mathbf{A}/\Phi_0$ with $\mathbf{A}$ the vector potential ($\mathbf{B} = \nabla \times \mathbf{A}$) and Φ_0 the flux quantum $hc/2e$. We note that this is *not* the most general Ginzburg-Landau free energy allowed by symmetry. For simplicity we neglect terms which are irrelevant for our discussion and, in particular, use an isotropic gradient term. We shall assume, as suggested from various experimental observations [3,4,15], that in the bulk only the single component $\eta_1 = u_1 e^{i\phi_1}$ exists, while $\eta_2 = u_2 e^{i\phi_2}$ vanishes for all temperatures. Thus, we require that

$$u_1 = \tilde{u}(T) = \sqrt{-\alpha_1/2\beta_1}, \qquad u_2 = 0, \quad (3)$$

which is satisfied for all temperatures below T_{c1} under the conditions

$$[\gamma + 2\delta\cos(2\theta)]\tilde{u}^2 + \alpha_2 > 0, \quad T_{c_1} > T_{c_2}, \quad (4)$$

where $\tilde{u}$ is the asymptotic value of u_1 in the bulk region and $\theta = \phi_1 - \phi_2$ denotes the relative phase between the two order parameter components. For $\delta > 0$, the state with $\theta = \pm\pi/2$ [$\psi(\mathbf{k}) = u\psi_1(\mathbf{k}) \pm iv\psi_2(\mathbf{k})$ or $d_{x^2-y^2} \pm i\epsilon d_{xy}$] is closest to the instability although under condition Eq. (4) not stable for any temperature. The choice $\delta > 0$ can be justified by the fact that a state of the form $d_{x^2-y^2} \pm id_{xy}$ ($\theta = \pm\pi/2$) has a nodeless quasiparticle excitation gap and would gain more condensation energy than a state like $d_{x^2-y^2} \pm d_{xy}$ ($\theta = 0, \pi$) which has zero nodes in the gap.

Let us now use this GL formulation in order to examine the possibility of local $\mathcal{T}$ violation at the interface. For simplicity we consider here the case of a planar interface between a superconducting half space ($\mathbf{n} \cdot \mathbf{x} > 0$) and the vacuum ($\mathbf{n} \cdot \mathbf{x} < 0$) ($\mathbf{n}$, the normal vector of the interface). The effect of the interface is described by boundary conditions at the interface ($x = 0$) which can be formulated in the standard way by

$$\mathbf{n} \cdot \mathbf{D}\eta_i = \eta_i/b_i, \qquad i = 1,2, \quad (5)$$

at $\mathbf{n} \cdot \mathbf{x} = 0$. Here b_i is the so-called extrapolation length depending on the properties and orientation of the interface (see [5,16]). (Note that non-s-wave order parameters are often suppressed in the vicinity of an interface due to scattering effects [5].) We may first treat $u_1(\mathbf{x})$ as though u_2 were zero, considering the GL differential equation obtained by the variation of F with respect to η_1 (we neglect the vector potential for this discussion). For the given geometry u_1 depends only on one spatial dimension which is parallel to the normal vector $\mathbf{n}$ and is homogeneous perpendicular to $\mathbf{n}$. We choose $\mathbf{n}$ to be parallel to the x direction which leads to the following variational equation in the half space $0 < x < \infty$ with the interface located at $x = 0$,

$$K_1\frac{\partial^2 u_1}{\partial x^2} = \alpha_1 u_1 + 2\beta_1 u_1^3. \quad (6)$$

Using the boundary condition, Eq. (3), at $x = 0$ and $u_1(x \to \infty) = \tilde{u}$ we obtain

$$u_1(x) = \tilde{u}\tanh\left(\frac{x + x_0}{\xi}\right) \qquad \text{for } 0 < x < \infty, \quad (7)$$

with $\xi = \sqrt{-2K_1/\alpha_1}$ and $x_0 = (\xi/2)\sinh^{-1}(4b_1/\xi) > 0$. Next, we ask whether this interface state could be unstable against the admixture of a small component u_2. This question can be answered by analyzing the linearized GL equation of u_2 for fixed $u_1(x)$:

$$K_2\frac{\partial^2 u_2}{\partial x^2} = \alpha_2 u_2 + [\gamma + 2\delta\cos(2\theta)]u_1^2(x)u_2. \quad (8)$$

It is easy to see that this equation has the form of a Schrödinger equation for the wave function u_2 of a particle in a potential well for $\gamma + 2\delta\cos(2\theta) > 0$ (including the boundary condition for u_2). The "lowest energy eigenstate," which is a bound state, defines the critical temperature T^* below which the interface state, Eq. (6), is unstable. The corresponding wave function $u_2(x)$ is nodeless for $0 < x < \infty$ and decays exponentially towards the bulk region ($x \to \infty$). For $\delta > 0$, as assumed above, the relative phase θ is $\pm\pi/2$ so that this state breaks time-reversal symmetry and is twofold degenerate. It is not possible to obtain an analytic solution of Eq. (8), in general. However, we can argue that the bound state energy E_0 has to be larger than the bottom of the potential well, $E_0 > -(\gamma - 2\delta)\tilde{u}^2/\cosh^2(x_0/\xi)$. From the definition of T^*, $E_0 = -\alpha_2(T^*) - (\gamma - 2\delta)\tilde{u}^2(T^*)$, we conclude that

$$0 > -(\gamma - 2\delta)\tilde{u}^2(T^*)\tanh^2(x_0/\xi) > \alpha_2(T^*). \quad (9)$$

This leads to the necessary condition that the transition temperature T_{c2} has to be larger than zero to obtain a finite T^* ($<T_{c2}$). Because the bare transition temperatures of both η_1 and η_2 are finite, there is a competition between the two order parameter components which is won by η_1 in the bulk. However, at the interface, where η_1 is suppressed, the other component η_2 can appear.

Our analysis demonstrates that under certain conditions the interface of an unconventional superconductor can generate a locally $\mathcal{T}$-violating state (see also [10,17]). Furthermore, T^* ($<T_{c1}, T_{c2}$) is the temperature where a continuous transition occurs from a $\mathcal{T}$-conserving ($T > T^*$) to a $\mathcal{T}$-violating state ($T < T^*$). This result applies not only to the situation discussed here (superconductor-vacuum interface), but also to interfaces between two superconductors. We do not wish to consider here a possible microscopic basis for our GL model. Rather we are interested in some consequences of a $\mathcal{T}$-violating superconducting phase.

Let us now study the phenomena which occur at a Josephson junction (an interface between two superconductors A and B) if $\mathcal{T}$ violation is present. The following discussion does not depend on whether the $\mathcal{T}$ violation is a bulk or, as discussed above, an interface (junction) phenomenon. Because we have two complex order parameters at the interface, the Josephson phase-current relation consists of four terms

$$J = \sum_{i,j=1,2} J_{ij} \sin(\phi_{iB} - \phi_{jA}), \qquad (10)$$

where J_{ij} are real constants whose sign and magnitude depend on the grain orientation and order parameter magnitude at the interface: $J_{ij} \propto |\eta_{iB}||\eta_{jA}|\chi_i(\mathbf{n}_B)\chi_j(\mathbf{n}_B)$, $\mathbf{n}_{A,B}$ is the junction normal vector on either side and, typically, $\chi_1(\mathbf{n}) = n_x^2 - n_y^2$ and $\chi_2(\mathbf{n}) = n_x n_y$. We assume that the current through the interface vanishes, because, due to screening effects (on a length scale λ_J), such currents can only flow near the boundary of the interface or near a vortex. Furthermore, we assume that the couplings J_{ij} are sufficiently weak so that the relative phase between η_1 and η_2 is not affected, i.e., $\phi_{1A} - \phi_{2A} = \phi_{1B} - \phi_{2B} = \pm\pi/2$ in the $\mathcal{T}$-violating state. This simplification is not important for any of our later conclusions, and a more complete discussion will be given elsewhere.

The latter assumption allows us to minimize the junction energy, $E = -(\Phi_0/2\pi c)\sum_{i,j} J_{ij}\cos(\phi_{iB} - \phi_{jA})$, by choosing the phases such that $J = 0$. We obtain

$$\Delta\phi_a = \phi_{iB} - \phi_{iA} = \pm\tan^{-1}\left(\frac{J_{12} - J_{21}}{J_{11} + J_{22}}\right) \qquad (11)$$

for a junction a with all $J_{ij} > 0$, and

$$\Delta\phi_b = \phi_{iB} - \phi_{iA} = \pi \pm \tan^{-1}\left(\frac{J_{12} - J_{21}}{J_{11} + J_{22}}\right) \qquad (12)$$

for a junction b with $J_{11}, J_{12} > 0$ and $J_{21}, J_{22} < 0$.

We consider now the situation where these two types of junctions, a and b, intersect, forming a grain boundary corner. Such a corner is accompanied with phase winding or a vortex since generally $\Delta\phi_a \neq \Delta\phi_b$. For the calculation of the magnetic flux of this vortex we notice that the supercurrent is given by the expression [derived from Eq. (1) by variation with respect to $\mathbf{A}$]

$$\frac{2\Phi_0}{c}\mathbf{j} = \sum_{i=1,2} K_i u_i^2 \left(\nabla\varphi - \frac{2\pi}{\Phi_0}\mathbf{A} + \nabla\phi_i\right), \qquad (13)$$

with $\eta_j = u_j e^{i(\phi_j + \varphi)}$, $j = 1,2$, and φ a phase of the order parameter continuous even at the grain boundary and $0 \leq \phi_j \leq 2\pi$. We choose a path C encircling the corner at a distance far enough so that $\mathbf{j} = 0$ along C. We denote the segments of C in superconductors A and B by C_A and C_B, respectively. Using $\phi_1 = \phi_2 \pm \pi/2$ the circular integral of Eq. (12) on C leads to the flux

$$\frac{\Phi}{\Phi_0} = n + \left(\int_{C'} d\mathbf{s} + \int_{C''} d\mathbf{s}\right)\cdot\nabla\phi_1 = n + \frac{\Delta\phi_a - \Delta\phi_b}{2\pi}, \qquad (14)$$

where n is the integer winding number of φ. Obviously, the flux at the corner can have any fraction of Φ_0 and is determined only by the properties of the junctions. On the other hand, it is easy to see from our discussion that in case of a $\mathcal{T}$-conserving superconducting state the only fractional vortex is one with half a flux quantum Φ_0 [$\Phi = \Phi_0(n + 1/2)$] [2,18]. (The existence of a fractional phase winding was also proposed in connection with a SQUID involving $\mathcal{T}$-violating superconductors [19].) The field distribution of such vortices would extend along the junction on a length scale of λ_J, while penetrating the bulk only by the London penetration depth $\lambda \ll \lambda_J$.

The twofold degeneracy of the $\mathcal{T}$-violating interface state implies the existence of domains and domain walls. There is a phase winding and flux associated with the intersection of a domain wall and a crystal grain boundary, because the phase jump $\Delta\phi$ at the junction is different on the right- and left-hand sides of a domain wall. Following the above scheme, a domain wall on junction a contains a flux $\Phi/\Phi_0 = n + \Delta\phi_a/\pi$. These vortices are similar to the fractional domain wall vortices analyzed in Ref. [8]. They are not connected with corners, but can essentially be located anywhere on a grain boundary. Hence, we may conclude that our model can account for fractional vortices at the corners and along the edges of the triangular inclusions as observed by Kirtley *et al.* [1].

We add here several remarks. The central point of this work is that *any* superconducting state with fractional vortices containing other than $(n + 1/2)\Phi_0$ flux quanta violates time-reversal symmetry. Fractional vortices are not specific to the $d_{x^2-y^2} + id_{xy}$ state, although in the interest of simplicity we restricted ourselves to this order parameter in our model calculations. Any $\mathcal{T}$-violating combination of at least two nondegenerate order parameter components will lead to the same result. Furthermore, the crystal symmetry of the system (tetragonal or orthorhombic) is only important for the selection of the possible symmetries of the order parameter components, but does not affect the qualitative properties of the Josephson junctions described here. It should be noted also that on the basis of the experiment by Kirtley *et al.* alone, the specific form of $\mathcal{T}$ violation cannot be deduced. Our conclusion that time-reversal symmetry breaking has been seen can only be wrong if the assumption of existence of the fractional vortices is wrong. There are several experiments which would add considerably to our understanding of this matter. One such experiment would be to look for the critical temperature T^* at which $\mathcal{T}$ violation occurs. According to our discussion there would have to be second phase transition below the onset of superconductivity, although this could very likely be a grain boundary phenomenon only. Above this temperature T^* there can be no fractional vortices apart from the ones with $\Phi = \pm\Phi_0/2$. It would also be interesting to look for fractional vortices in different materials such as $HgBa_2Ca_2Cu_3O_8$ or $Bi_2Sr_2CaCu_2O_8$, perhaps utilizing different geometries which might better isolate the grain boundary corners. The existence of a complex order parameter at the interface may also shed new light on the interpretation of Josephson junction experiments such as those of Chaudhari and Lin [20] and Sun *et al.* [21], beyond the analysis given recently by Millis [2].

In this Letter we have shown that (1) the existence of vortices enclosing a fraction of a flux quantum requires the breaking of time-reversal symmetry, and (2) that the converse is also true. We argue that this has been observed at grain boundaries in $YBa_2Cu_3O_7$. Further experiments are needed to deduce the nature and extent of $\mathcal{T}$ violation in high-temperature superconductors.

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