Proximity-induced time-reversal symmetry breaking at Josephson junctions between unconventional superconductors

Kazuhiro Kubok and Manfred Sigrist
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

We argue that a locally time-reversal symmetry breaking state can occur at Josephson junctions between unconventional superconductors. Order parameters induced by the proximity effect can combine with the bulk order parameter to form such a state. This property is specifically due to the intrinsic phase structure of the pairing wave function in unconventional superconductors. Experimental consequences of this effect in high-temperature superconductors are examined.

A growing number of experiments demonstrates that the superconducting state in some of the high-temperature superconductors (HTSC) possesses an unconventional order parameter which changes sign under a 90°-rotation in the copper-oxide plane [1]. For a tetragonal system this state is commonly referred to as a d-wave state, where the Cooper pairing occurs in a channel belonging to an irreducible representation of the point group $D_{4h}$, which is different from the trivial representations, i.e., “s-wave”. Many of these experiments use the Josephson effect, which allows a direct probe of the phase properties of a superconducting order parameter. While the Josephson effect in conventional (s-wave) superconductors is described only by the phase difference between the order parameters on both sides of an interface, the situation is more complicated if the pair wave function of two connected superconductors has an intrinsic phase structure like in the d-wave state. The sign change of the d-wave state (generic pair wave function: $\psi(k) = \cos k_x - \cos k_y$) between the x- and y-direction corresponds to a phase difference of $\pi$. Due to this intrinsic phase structure, the relative orientation of the pair wave function of two connected superconductors and the geometry of the connecting interface are important to determine the phase relation between the order parameters on both sides [2,3]. For d-wave superconductors two types of Josephson junctions can occur, one where the interface energy is minimized by a phase difference $\varphi = 0$ (standard 0-junction) and the other with $\varphi = \pi$ (π-junction) [4]. In multiply connected superconducting systems the latter type can lead to frustration effects and twists of the order parameter phase [5]. Resulting phenomena like the occurrence of spontaneous supercurrents and the modification of standard interference patterns (SQUID) have been exploited in experiments to determine the symmetry of the order parameter [5].

In this letter we add a new feature to the properties of interfaces between unconventional superconductors. We examine the effect of the reflection of Cooper pairs at the interface and the mutual proximity of the two superconductors, both of which can introduce Cooper pair amplitudes in channels of symmetries different from that of the bulk pairing state. These additional pairing components can exist only in the immediate vicinity of the interface and decay exponentially towards the bulk. However, their presence has important consequences for the interface properties because they modify the Josephson effect via their influence on the current-phase relation. The admixed order parameters originating from reflection and proximity usually prefer a relative phase of 0 or $\pi$ with the bulk order parameters on both sides of the interface, resulting in states conserving time-reversal symmetry. We will show here that under certain conditions the relative phase can change leading to a state which breaks time-reversal symmetry at the interface. It was shown by Sigrist, Bailey and Laughlin [6] that this kind of interface state may explain a recent experiment done by Kirtley et al. where fractional vortices have been observed at boundaries between differently oriented films of the HTSC YBa$_2$Cu$_3$O$_7$−δ (YBCO) [7].

We discuss this problem using the Ginzburg-Landau (GL) theory of a d-wave order parameter in a tetragonal system ($D_{4h}$) and consider only one admixed order parameter (s-wave) which does not occur in the bulk. This choice is motivated by the experimental results introduced above [3] and the recent finding that the critical behavior at the onset of superconductivity suggests a single component bulk order parameter in HTSC [8]. The general GL free energy expansion for these two components, $\eta_d$ (d-wave) and $\eta_s$ (s-wave), in two dimensions is given by

$$F = \int d^2x \left\{ \sum_{j=d,s} (a_j(T)|\eta_j|^2 + \beta_j|\eta_j|^4 + K_j|\mathbf{D}\eta_j|^2 \right\}$$

$$+ \frac{1}{2} \gamma_2 (\eta_d^2)^2 + \frac{1}{2} \gamma_2 (\eta_s^2)^2$$

$$+ 2\tilde{K} \{(D_x\eta_d^*)^*(D_x\eta_s) - (D_y\eta_d^*)^*(D_y\eta_s) \} + c.c. \right\} + \frac{1}{8\pi} (\nabla \times \mathbf{A})^2$$

(1)

with $a_j(T) = \alpha_j (T - T_c^j)$ and $\alpha_j$, $\beta_j$, $K_j$, $\gamma_1$, $\gamma_2$ and $\tilde{K}$ are real coefficients ($j = d, s$). The gauge invariant gradient is given by $\mathbf{D} = \nabla - i(2\pi/\Phi_0)\mathbf{A}$ with $\mathbf{A}$ as the vector.
potential and $\Phi_0 = \hbar c/2e$ is the standard flux quantum. We consider the properties of an infinite planar interface with the geometry shown in Fig.1 where the crystal main ($x$-) axis of the side A is pointing perpendicular to the interface, while the orientation of the side B is described by the angle $\theta$ between the interface normal vector and the crystal main ($x$-) axis ($-\pi/2 \leq \theta \leq \pi/2$). In this arrangement the effects of interest occur only on side B. Thus, we will neglect the detailed description of side A and represent it simply by a complex (bulk) order parameter $\eta_s$. It can have d-wave symmetry, but s-wave symmetry would not change any of our conclusions qualitatively. The properties of the interface are described by additional interface terms in the GL free energy

$$ F_{IF} = \int dS[g_s(\theta)|\eta_s|^2 + \tilde{g}(\theta)(\eta_s^* \eta_s + \eta_s \eta_s^*)] + t_1(\theta)(\eta_s^* \eta_d + \eta_s \eta_d^*) + t_2(\theta)(\eta_s^* \eta_s + \eta_s \eta_s^*)]. \quad (2) $$

The first two terms describe the reflection properties of the interface (IF) for the side B, i.e.: $\eta_d \rightarrow \eta_d$ in the first and $\eta_d \leftrightarrow \eta_s$ in the second term (we neglect the $\eta_s \rightarrow \eta_s$ contribution). The latter two terms represent the lowest order coupling between the two sides, A and B. By symmetry argument we find that $\tilde{g}(\theta + \pi/2) = -\tilde{g}(\theta)$ and $t_1(\theta + \pi/2) = -t_1(\theta)$. Thus, we choose $\tilde{g} = g_0 \cos(2\theta)$ and $t_1 = t_0 \cos(2\theta)$ with $g_0,t_0 < 0$ as a generic angle dependence. We neglect any $\theta$-dependence in $t_2$ because none is required by symmetry ($t_2 < 0$). The signs of $g_0$, $t_0$ and $t_2$ are chosen by convention defining the specific gauge of the order parameter phases. The coefficient $g_d$ is in general positive and describes the suppression of the d-wave order parameter at the interface (see (3)). The variational minimization scheme for the GL free energy includes these interface terms into the boundary conditions.

This GL theory contains two competing tendencies for the relative phase, $\varphi_s - \varphi_d$, of the order parameters $\eta_j = |\eta_j| \exp(i\varphi_j)$, $j = s, d$. The last three terms in $F_{IF}$ (Eq.2)) are minimized by $\varphi_s - \varphi_d = 0$ for $|\theta| < \pi/4$ and $\varphi_s - \varphi_d = \pi$ for $\pi/4 < |\theta| < \pi/2$. In either case, the state at the interface is invariant under time-reversal operation. On the other hand, if we assume that $\gamma_2 > 0$, the coupling term $\eta_s^2 \eta_s^2 + \eta_s^2 \eta_s^2$ in Eq.(1) favors energetically $\varphi_s - \varphi_d = \pm \pi/2$, a state which breaks time-reversal symmetry (s+id-wave state). (The assumption of positive $\gamma_2$ is natural, since it would lead to a fully gapped state which is energetically more favorable as weak-coupling studies of various microscopic models show.) In the following we study the competition between the tendency to keep or to break time-reversal symmetry near the interface and some physical consequences.

Although our choice of geometry allows to reduce the problem to one spatial dimension ($\tilde{x} = x \cos \theta + y \sin \theta$ on side B), these GL equations can only be solved numerically in general. Fortunately, it is possible to understand the essential properties of the competing effects at the interface qualitatively by using a simple variational ansatz for the order parameter. We assume that as in HTSC the transition temperature $T_{cd}$ of the d-wave order parameter is finite, while that of the s-wave is very small or zero, $T_{cs} \ll T_{cd}$ such that in the bulk only $\eta_s$ is finite for $0 < T < T_{cd}$ (and $\eta_d$ on the side A). In our variational treatment $\eta_d$ shall be real and independent of position on the side B, and $\eta_d$ on the side A shall have a fixed modulus $\tilde{\eta}$ and a phase $\chi$. $\eta_s = \tilde{\eta} \exp(i\chi)$ ($\eta_d(T), \tilde{\eta}(T)$ are identical to their bulk values). Hence, this ansatz neglects the direct effect of the interface on the modulus of the d-wave order parameter. The s-wave component $\eta_s$ is complex and decays exponentially towards the bulk on the side B, $\eta_s(x) = \tilde{\eta}_0 e^{-x/\xi}$ and $\tilde{\eta} = \tilde{\eta}_1 + i\tilde{\eta}_2$. The part of the free energy (per unit interface area) depending on the variational degrees of freedom, $\xi, \tilde{\eta}$ and $\chi$, is obtained straightforwardly

$$ F_{var}(\xi \tilde{\eta}, \chi) = K_+ \tilde{\eta}_1^2 + K_- \tilde{\eta}_2^2 + 2\{\tilde{g}(\theta)\tilde{\eta}_1\tilde{\eta}_1 + t_1(\theta)\tilde{\eta}_d \cos \chi \}
+ t_2(\theta)\tilde{\eta}_d \cos \chi + \tilde{\eta}_d \sin \chi \} \quad (3) $$

with $K_+ = K_s + a_\pm \xi^2$ and $a_\pm = a_s + (\gamma_1 + \gamma_2)\tilde{\eta}_d^2$. To be consistent with our assumption that $\eta_s = 0$ in the bulk we require $a_\pm > 0$. Further, we choose $a_- < a_+ (\gamma_2 > 0)$. By minimizing $F_{var}$ we find that $\xi$ is always finite with $K_s/a_+ \leq \xi^2 \leq K_s/a_-$. Some simple algebra leads to the following equation for $\chi$,

$$ \sin \chi [\cos \chi + \{(t_1 K_+ + 2\xi\tilde{\eta}_2)K_- \}
4\tilde{\eta}_d^2 \gamma_2 \gamma_2 \eta_d] = 0. \quad (4) $$

One set of solutions of this equation is $\chi = 0$ and $\pi$ ($\sin \chi = 0$) which leads to $\tilde{\eta}_1 \neq 0$ and $\tilde{\eta}_2' = 0$ such that the relative phase between $\eta_s$ and $\eta_d$ is 0 or $\pi$. Energetically $\chi = 0$ ($\tilde{\eta}_1 > 0$) is favored for $|\theta| < \pi/4$ (0-junction) and $\chi = \pi$ ($\tilde{\eta}_1 < 0$) for $|\theta| > \pi/4$ (π-junction). However, also the term in [...] can vanish giving an alternative solution of Eq.(4) with $\chi$ different from the above two limiting values. Both $\tilde{\eta}_1$ and $\tilde{\eta}_2$ are finite in this case. This state is two-fold degenerate because the application of the time-reversal operation ($\eta \rightarrow \eta^*$) corresponding to $\chi \rightarrow -\chi$ and $\tilde{\eta}_1 \rightarrow \tilde{\eta}_1^*$ leads to a different state with the same free energy. Consequently, this solution violates time-reversal symmetry $T$. It is easy to see that the energy is indeed minimized by this state if $\gamma_2$ is positive. From Eq.(4) it is obvious that the $T$-violating state can only occur if the modulus of the second term in [...] is smaller than 1. This condition can be satisfied by an appropriate choice of the angle $\theta$, because this term is proportional to $\cos(2\theta)$ via $t_1$ and $\tilde{g}$, which can be arbitrarily small for $\theta$ close to $\pm \pi/4$. 

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From the above consideration the condition for the instability of the time-reversal invariant state is obtained as

$$\cos(2\theta) = \pm \left| \frac{t_2^2 \gamma_2 \eta(T^*) \eta_d(T^*)}{(a_x + \gamma_1 \eta_d)^2 \sqrt{K s_0 a_x - t_2 g_0}} \right|, \quad (5)$$

where $T^* (\sim T_{cd})$ denotes the critical temperature of the second order transition to the $T$-violating state for a given angle $\theta$. The denominator on the right hand side of this equation is only weakly dependent on $T^*$ close to $T_{cd}$ so that $T^*$ is large for $\theta$ near $\pm \pi/4$, and is $T_{cd}$ at $\theta = \pm \pi/4$. We show a schematic phase diagram, $T$ versus $\theta$, corresponding to Eq.(5) (Fig.2). The $T$-violating phase appears in a certain range of $\theta$ around $\pi/4$ and the region of this phase becomes wider with decreasing temperature. The specific shape of the phase boundary line depends on properties of the system, in particular, of the interface.

Let us now investigate important consequences of the existence of a $T$-violating interface state, which result from the properties of its Josephson current-phase relation,

$$I = I_c g(\varphi) = I_d g(\varphi + 2\pi) \quad (6)$$

where $\varphi$ is the phase difference between the order parameters $\eta_0$ and $\eta_d$ and $g(\varphi)$ is a 2$\pi$-periodic function of $\varphi$ ($|g(\varphi)| \leq 1$). The specific form of $g$ is not important here and will be discussed elsewhere. The interface state with minimal energy corresponds to $I = 0$ and its twofold degeneracy implies that two functions, $g_+$ and $g_-$, exist with $g_+(\chi) = 0$ and $g_-(\chi) = 0$, each belonging to one of the two states. There are two possible situations: I) $g_+(\varphi) \neq g_-(\varphi)$ describing both different (meta)stable states as a function of $\varphi$, and II) $g_+(\varphi) = g_-(\varphi)$ where the two $T$-violating states can be adiabatically connected with each other by changing $\varphi$ from $+\chi$ to $-\chi$. The spatial variation of $\varphi$ along the interface (with coordinate denoted as $x'$) is described by a generalized Ferrel-Prange equation which is identical to a Sine-Gordon equation for standard Josephson junctions ($g(\varphi) = \sin \varphi$),

$$\frac{\partial^2 \varphi}{\partial x'^2} = \lambda_J^{-2} g(\varphi), \quad (7)$$

with $\lambda_J = (\Phi_0 c/8\pi^2 d I_c)^{1/2}$ as the characteristic length scale ($d$: the effective magnetic width of the interface). As in conventional interfaces the spatial variation of $\varphi$ yields a finite local magnetic flux $\phi(x') = (\Phi_0/2\pi) \partial \varphi(x')/\partial x'$. The integrated magnetic flux between two points, $x'_a$ and $x'_b$, on the interface is given by $\Phi = (\varphi(x'_b) - \varphi(x'_a)) \Phi_0/2\pi$.

As a consequence, a spatial variation of the interface properties can lead to the occurrence of magnetic field distributions. In particular, at the border between two different homogeneous interface segments, (a) and (b), characterized by their specific values of $\varphi_0$ (denoted as $\varphi_0^{(a)}$ and $\varphi_0^{(b)}$, respectively), we find a continuous change of $\varphi$ from $\varphi_0^{(a)}$ to $\varphi_0^{(b)}$ on a length scale $\lambda_J$. On distances much larger than $\lambda_J$ from the border of the segments $\varphi$ is $\varphi_0^{(j)}$ in segment (j). The flux associated with the variation of $\varphi$ is located in the vicinity of the border and is $\Phi = (\varphi_0^{(b)} - \varphi_0^{(a)}) \Phi_0/2\pi$. Obviously $\Phi$ is not an integer (half-integer) multiple of $\Phi_0$, but can have an arbitrary value. It cannot be determined by simple topological arguments, but depends on the specific properties of the interface. Because the phase twist at the border between segment (a) and (b) corresponds to a winding of the phase $\varphi_d$ by a fractional multiple of $2\pi$, this flux line may be considered as a fractional vortex. Similarly fractional vortices can occur on a homogeneous interface due to the twofold degeneracy of the $T$-violating interface state. Two types of domains with $\varphi_0 = +\chi$ and $-\chi$, respectively, are possible. If present on the same interface, they are separated by domain “walls”. There we find a kink of the width $\lambda_J$ in $\varphi$ connecting the two values of $\varphi_0$ and yielding a flux $\Phi = \pm \chi \Phi_0/\pi$ (see also 11).

We now propose an experiment to test our picture. Let us consider a thin film consisting of two parts with orientations of their crystalline axes different by 45°. The boundary shall be circularly curved (see Fig.3). The point P would correspond to an interface with angle $\theta = \pi/4$ and $\theta$ changes continuously as we turn away from P. Hence, along the interface we scan through a certain range of angles $\theta$. If time-reversal symmetry were conserved everywhere, we would see a vortex with $\Phi = \Phi_0/2$ at P, because P separates two interface segments where one has $\varphi_0 = 0$ and the other = $\pi$ 11. The field distribution of the vortex becomes more localized if we cool the system because the penetration depth $\lambda_J$ along the interface shrinks with lowering temperature. On the other hand, if our scenario is correct we expect that the phase $\varphi_0$ varies continuously from 0 to $\pi$ near P within a certain range of $\theta$. This range extends with lowering temperature (see Fig.2), such that the resulting field distribution becomes more extended further as the system is cooled, while the total flux always equals to $\Phi_0/2$. The observation of the field distribution by a (magnetic) microscope should allow to prove or disprove our scenario based on these qualitative properties.

In summary, we pointed out that important properties of an interface between d-wave or other unconventional superconductors result from the intrinsic phase structure of the pairing wave function $\psi(k)$ which cannot be found in conventional (s-wave) superconductors. While some interface coupling effects favor a $T$-invariant state, in the bulk rather a $T$-violating state is preferred. In the competition between these two tendencies it is important that the interface coupling effects can be arbitrarily small by choosing the interface geometry appropriately, i.e., the crystalline orientation of the two connected superconductors. Thus, proximity-induced order parameter compo-
nents can combine with the bulk order parameter to form a $T$-violating interface state. We emphasize that such conditions cannot be satisfied in conventional (s-wave) superconductors, in general. Therefore the proximity-induced time-reversal breaking interface state is a consequence of unconventional superconductivity. For the sake of simplicity we restricted ourselves to the case of a system with tetragonal crystal field symmetry. We note here, however, that a slight orthorhombic distortion of the lattice (as it is present in real materials) does not change our conclusions qualitatively. It leads to some minor modifications which are beyond the scope of this letter and will be discussed elsewhere in detail.

We are grateful to P.A. Lee, T.M. Rice, K. Ueda, A. Furusaki, Y.B. Kim, D.K.K. Lee, C. Bruder and D. Scalapino for helpful and stimulating discussions. We acknowledge financial supports by Swiss Nationalfonds (M.S.) and by Ministry of Education, Science and Culture of Japan (K.K.). M.S. would like to thank the Institute for Solid State Physics of the University of Tokyo and the University of Tsukuba for their hospitality during the time when this work has been finished.

![FIG. 1. Interface between d-wave superconductor A and B. The shading on either side indicates the direction of the crystalline x-axis (the z-axis points out of the plane).](image1)

![FIG. 2. Schematic phase diagram in terms of temperature and crystal orientation of side B. The shaded region denotes the $T$-violating phase separating the 0- and the $\pi$-junction phases. Within the shaded region $\chi$ changes continuously.](image2)

![FIG. 3. Schematic arrangement of superconducting films for a test-experiment. The direction of shading indicates the crystalline orientation. The region A may be a d- or an s-wave superconductor, while B must have d-wave symmetry. The point P corresponds to the angle $\theta = \pi/4$ and $\tilde{\theta} = \pi/4 - \theta$.](image3)

* Permanent address: Department of Physics, Kobe University, Kobe 657, Japan.

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