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Time-reversal symmetry-breaking states near grain boundaries between *d*-wave superconductors

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In this paper we study the order parameter and density of states near a grain boundary between two $d_{x^2-y^2}$ superconductors. We examine broken time-reversal symmetry near the interface. In particular we show that, under suitable circumstances, time-reversal symmetry must be broken even when the order parameter is purely $d_{x^2-y^2}$ everywhere in space. [S0163-1829(98)53022-6]

The $d_{x^2-y^2}$ order parameter, appropriate to the hole-doped oxide superconductors, preserves time-reversal symmetry (TRS) in the bulk. At surfaces and interfaces it is now known that time-reversal symmetry may be broken. NIS tunneling experiments by Covington *et al.*[1] indicate a time-reversal symmetry breaking (TRSB) state locally at surfaces.[2] Fractional fluxes at corners of interfaces in inclusion experiments by Kirtley *et al.*[3] strongly indicate that TRS may also be broken at grain boundaries.[4–7] In this paper we discuss the origin of the TRSB state and contrast TRSB at low and high transmission interfaces.

At a surface or interface with low transmission, TRSB can occur in the presence of subdominant pairing interaction in channels other than the dominant $d_{x^2-y^2}$. In this case order parameters corresponding to those channels can appear near the interface.[8,9] For example, if a subdominant pairing interaction is present in the s-wave channel, then, under suitable conditions, the order parameter near the interface can have a $d \pm is$ symmetry. The order parameter thus breaks TRS locally. A prerequisite for the TRSB state is substantial pair breaking at the interface, i.e., the misorientation of the surface normal to crystal a axis should be close to $\pi/4(\mathrm{mod}\ \pi/2)$.

The above is in contrast to the case where there is a reasonably high transmission probability of electrons across the interface. In this case the subdominant pairing interaction is not necessary for TRSB at the interface.[5,10,11] TRSB occurs even when the order parameter is purely $d_{x^2-y^2}$ everywhere near the interface. The origin of this TRSB state is a proximity effect and it arises because the minimum energy state for the interface corresponds to a state with a finite phase difference, $\Delta\chi = \chi_R - \chi_L$, across the junction. Here χ_L and χ_R are the phases of the order parameter on either side far away from the interface. $\Delta\chi$ is other than an integral multiple of π for the TRSB state. In this case states with minimum total interface free energy occur in pairs related by time reversal: if $\Delta\chi$ corresponds to a state with minimum energy, there is also a nonequivalent but degenerate state with $\Delta\chi = -\Delta\chi$. An interface at its minimum energy configuration will have TRS spontaneously broken. In contrast to the one discussed in the preceding paragraph, this is the more likely route to TRSB when the transmission probability across the interface is moderate to high and when the misorientation between the two superconductors is close to $\pi/4(\mathrm{mod}\ \pi/2)$.[11,12]

As is well known, Josephson effects occur in the presence of an interface with finite transmission. At a general phase difference between the two superconductors, a dissipationless current, J_x, can flow through the interface. If the order parameter itself does not break TRS, then the current across the interface is always zero for $\Delta\chi$ being an integral multiple of π. However, under appropriate conditions there can be additional values of $\Delta\chi$ where the net current across the interface vanishes. Previously one of us[5] has explained how this can occur for a pinhole junction by considering the sum of contributions to the current from different parts of the Fermi surface. These new states with zero net current occur as a combined result of nonsinusoidal current-phase relationships and sign changes of the order parameter. The $J_x = 0$ states correspond to states where the junction energy is at a relative extrema as a function of the phase difference $\Delta\chi$. In particular, it can be shown that the new $J_x = 0$ states, if they exist, correspond to energy minima.[5]

In this paper we study a planar interface with uniform transmission. In general a current flows through the interface. The corresponding states possess finite flow energy densities even far away from the interface. Here we focus on the set of states with $J_x = 0$ for which this contribution is absent. In these states the gradient of the phase of the d-wave order parameter vanishes as $x \to \pm\infty$. We shall show that many of the statements concerning the new energy minimum states mentioned above for the pinhole[5] are still correct for the planar interface, provided appropriate minor modifications are made. If the order parameter is purely $d_{x^2-y^2}$, it is easy to verify that states which correspond to $J_x = 0$ with $\Delta\chi = 0$ or π with χ piecewise constant are always possible. At not too small transmission across the interface, there may be other states with different $\Delta\chi$ which also correspond to $J_x = 0$ and under appropriate conditions states with $\Delta\chi \neq 0$ or π will correspond to the minimum energy. We shall compare the free energies, order parameters, and densities of states (DOS) of these $J_x = 0$ states. Apart from its intrinsic interest, we shall see that the DOS provides an alternative view of the mechanisms for TRSB. A signature of a TRSB state is that the zero energy bound states at $\varepsilon = 0$ are shifted away from the midgap and that spontaneous currents along the interface are nucleated.[8,9]

The occurrence of zero energy bound states (ZEBS) for nontransmitting surfaces has already been extensively investigated (Ref. 2 and references therein). For order parameters real up to a gauge transformation, ZEBS are present for the quasiparticle paths along which a sign change of the order parameter occurs. ZEBS are also common for interfaces with finite transmission if TRS is preserved ($\Delta\chi=0$ or π). One can show rigorously[13] that ZEBS are present irrespective of the value of the transmission coefficient whenever there are quasiparticle paths such that a quasiparticle experiences a sign change of the order parameter if it is either transmitted or reflected. For interfaces between superconductors with large misorientation and in states which preserve TRS, ZEBS occur over a large part of the Fermi surface. The existence of these low energy bound states corresponds to severe pair breaking near the interface. These ZEBS can be pushed to finite energies by allowing a finite phase difference between the two superconductors. Correspondingly we shall show that the magnitude of the order parameter for the TRSB state (denoted simply by $\Delta\chi\neq 0$ below) is larger than the corresponding states with $\Delta\chi=0$ or π. The formation of ZEBS and the suppression of the order parameter near the interface suggest that the $\Delta\chi=0$ or π states are energetically unfavorable compared with the TRSB state.[14] This is verified by a calculation of the free energy.

For definiteness, we model the interface as an ideal, smooth barrier with a δ function potential. In this case, the interface can be parametrized by $\mathcal{D}_0$, the coefficient of transmission for normal incidence. The transmission coefficient $\mathcal{D}(\phi)$ for momenta $\hat{\mathbf{p}}_f$ at an angle ϕ with respect to the interface normal is given by

$$\mathcal{D}(\phi)=\frac{\mathcal{D}_0\cos^2\phi}{1-\mathcal{D}_0\sin^2\phi}. \tag{1}$$

The order parameter $\hat{\Delta}(x)$ is calculated self-consistently using boundary conditions at the interface parametrized by $\mathcal{D}(\phi)$ (see Refs. 11 and 12 for details). We start with an initial ansatz of the order parameter $\hat{\Delta}(x)$, which in general possesses a phase difference far away from the interface. At each iteration step the current across the interface is also calculated. Then a gauge transformation depending on the calculated current is performed on the order parameter to relax $\hat{\Delta}$ towards the state with $J_x=0$. Note that once self-consistency is achieved, particle conservation will be respected (see, e.g., Ref. 15). J_x is then x independent and thus $J_x=0$ at all x. After obtaining the self-consistent order parameter we evaluate the free energy[16] and the DOS. All DOS below are obtained at energies $\varepsilon+i\gamma$, with $\gamma=0.05T_c$ simulating a broadening of energy levels that would occur naturally in nonideal systems.

We first confine ourselves to pure $d_{x^2-y^2}$ order parameter. We write

$$\Delta(\hat{\mathbf{p}}_f,x)=\eta_d(x)\sqrt{2}\,\cos[2(\phi-\alpha)], \tag{2}$$

which defines the complex order parameter $\eta_d(x)$ with $\alpha=\alpha_L$ or α_R for the left and right sides of the interface, respectively. Here α_L and α_R denote the orientations of the crystals on the two sides of the interface. They specify the angle between the $\hat{a}$ axis and hence the positive lobe of the order parameter with respect to the normal to the interface.

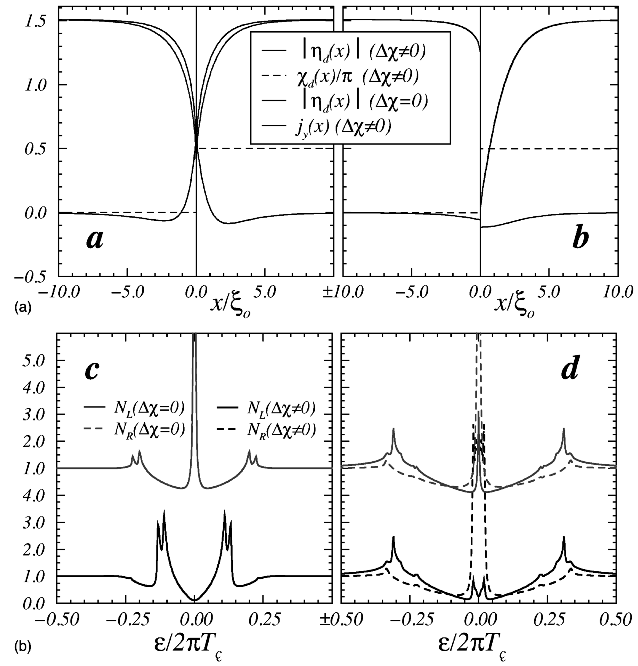

FIG. 1. The magnitude $|\eta_d|$ and the phase χ_d of the order parameter η_d for $\alpha_L=0$ and $\alpha_R=\pi/4$ at $T=0.2T_c$ for the states corresponding to $\Delta\chi=0$ and to the energy minimum with TRSB $\Delta\chi\neq0$. The states with $\Delta\chi\neq0$ have a transverse current density j_y along the boundary. In the lower panels (c) and (d) are the corresponding DOS on the two sides of the interface. $\mathcal{D}_0$ is 1.0 in (a) and (c) and 0.3 in (b) and (d). The units are k_BT_c for $|\eta_d|$ and $2ev_fN_f|\eta(\infty)|$ for current densities in all graphs. $\xi_0\equiv\hbar v_f/2\pi T_c$.

We find that TRSB is most significant at low temperatures and when the misorientation $\theta=\alpha_R-\alpha_L$ is close to $\pi/4(\mathrm{mod}\ \pi/2)$.

As a representative example we consider $\alpha_L=0$ and $\alpha_R=\pi/4$ at a relatively low temperature, $T=0.2T_c$. The order parameters are as shown in Fig. 1 for both the states with $\Delta\chi=0$ and the ones corresponding to energy minima with $\Delta\chi\neq0$. As can be seen from an examination of Fig. 1 the phase difference $\Delta\chi$ of the minimum energy state is $\pi/2$. This state is degenerate with its time-reversed partner $-\pi/2$. The states with $\Delta\chi=0$ are also degenerate with the corresponding ones with $\Delta\chi=\pi$ with the same DOS. As claimed the order parameter of the $\Delta\chi\neq0$ state has a larger amplitude than the one with zero phase difference for a given transparency. This difference decreases as $\mathcal{D}_0$ decreases. At $\mathcal{D}_0=0.3$ the difference in magnitudes is almost undetectable. The corresponding DOS are shown in Fig. 1 for the two different set of states. The states with $\Delta\chi=0$ have large DOS near $\varepsilon=0$. For the state with $\Delta\chi\neq0$ these ZEBS are pushed to finite energies, away from $\varepsilon=0$. These shifts (splits) are largest for $\mathcal{D}_0=1$ and decrease for small $\mathcal{D}_0$. As $\mathcal{D}_0\rightarrow0$ the DOS becomes independent of $\Delta\chi$. We also calculated the junction energies for the different states. These are listed in Table I, which shows explicitly that the $\Delta\chi=\pi/2$ states have lower energies. That the TRS state cannot be the minimum energy state and that the energy minimum state is at $\Delta\chi=\pi/2(\mathrm{mod}\ \pi)$ may actually be expected from an argument based on symmetry and continuity.[5,17] It is notable that in the small transmission limit, $\mathcal{D}_0=0.3$, $\Delta\chi=0$ and $\Delta\chi=\pi/2$ have almost the same free energy. As seen in Fig. 1, the DOS for the

TABLE I. Free energy per unit surface area calculated as $\Delta\mathcal{F}=\mathcal{F}_{junc}-\mathcal{F}_{bulk}$ for the junctions shown. The unit of $\Delta\mathcal{F}$ is $N_f(\hbar v_f)(2\pi T_c)$. N_f is the normal state DOS.

(α_L,α_R)	State	$\Delta\mathcal{F}$ $\mathcal{D}_0=1.0$	$\Delta\mathcal{F}$ $\mathcal{D}_0=0.7$	$\Delta\mathcal{F}$ $\mathcal{D}_0=0.3$
$\left(0,\frac{\pi}{4}\right)$	$\Delta\chi=0$	0.127	0.125	0.116
	$\Delta\chi\neq0$	0.109	0.119	0.115
$\left(-\frac{\pi}{12},\frac{\pi}{6}\right)$	$\Delta\chi=0$	0.133	0.132	0.130
	$\Delta\chi=\pi$	0.120	0.119	0.123
	$\Delta\chi\neq0$	0.108	0.117	0.123

two states are also similar except for some small differences near $\varepsilon=0$. At this small $\mathcal{D}_0$ the phase difference $\Delta\chi\neq0$ is inefficient in pushing the states that were originally at $\varepsilon=0$ to finite energies.

The DOS recovers to its bulk value as one moves away from the interface as shown in Fig. 2. At $x\approx10\xi_0$ the bulk d-wave DOS is well recovered showing only exponential tails of the structure at the interface.

The value of $\Delta\chi$ where the interface energy is a minimum depends on the orientations of the crystals, the transmission coefficient, and temperature. An example is as shown in Fig. 3 (cf. Refs. 11,12). The comparison between the free energies for the orientation $(\alpha_L,\alpha_R)=(-\pi/12,\pi/6)$ is also shown in Table I.

Recent experiments[1] indicate that the oxide superconductors probably also have an attractive s-wave channel with a strength such that the bare T_c for the s wave is about 10% of that of the dominant d wave.[2] While in the bulk the order parameter is purely d wave, near the interface both d- and s-wave components can coexist. In this case the order parameter is

$$\Delta(\hat{\mathbf{p}}_f,x)=\eta_d(x)\sqrt{2}\,\cos[2(\phi-\alpha)]+\eta_s(x). \qquad (3)$$

In Fig. 4 we have plotted the order parameters η_d,η_s of the minimum energy states for $(\alpha_L,\alpha_R)=(0,\pi/4)$ and for

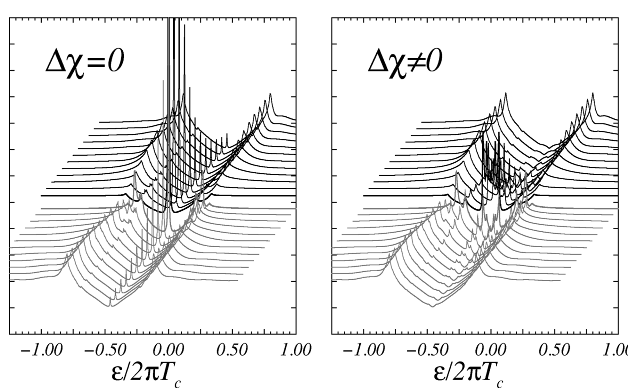

FIG. 2. The spatial dependence of the DOS for an interface with $\mathcal{D}_0=0.7$. The orientation is ($\alpha_L=0$, $\alpha_R=\pi/4$). The lower (upper) set of DOS are for the left- (right-) hand side of the interface. The DOS are sampled at a spacing of $1\xi_0$. The thick lines indicate the DOS at the interface location.

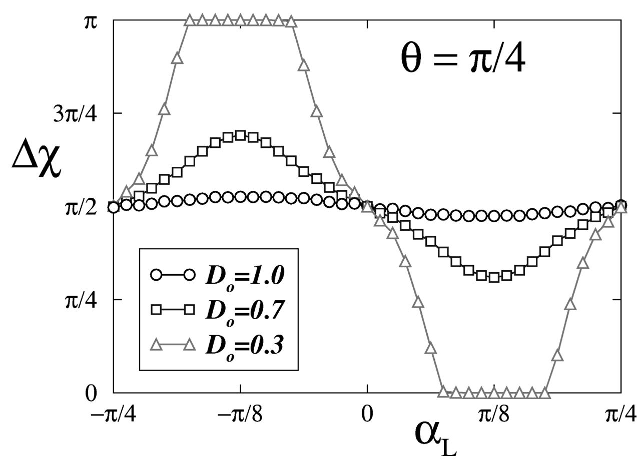

FIG. 3. The phase difference $\Delta\chi$ that minimizes the interface free energy as a function of α_L. The misorientation angle θ is kept fixed at $\pi/4$. The temperature is $0.2T_c$.

different transparencies. For all $\mathcal{D}_0$ the phase difference between the d-wave order parameters on the two sides of the interface is $\pi/2$ as in the case without the s-wave component of the order parameter. In our gauge where the d-wave order parameter is real for $x\rightarrow-\infty$, the s-wave component η_s is real for all x, being positive for $x>0$ and negative for $x<0$.[18] The order parameter for $x>0$ is in the TRSB combination $s+id$. For the large transmission $\mathcal{D}_0=1$ both the order parameter η_d and the DOS are qualitatively equal to the pure $d_{x^2-y^2}$ state shown in Figs. 1(a) and 1(c). It is clear that the s-wave channel does not play an important role. It is rather the tails of the off-diagonal parts of the Green's function of either side of the interface that are leaking into the

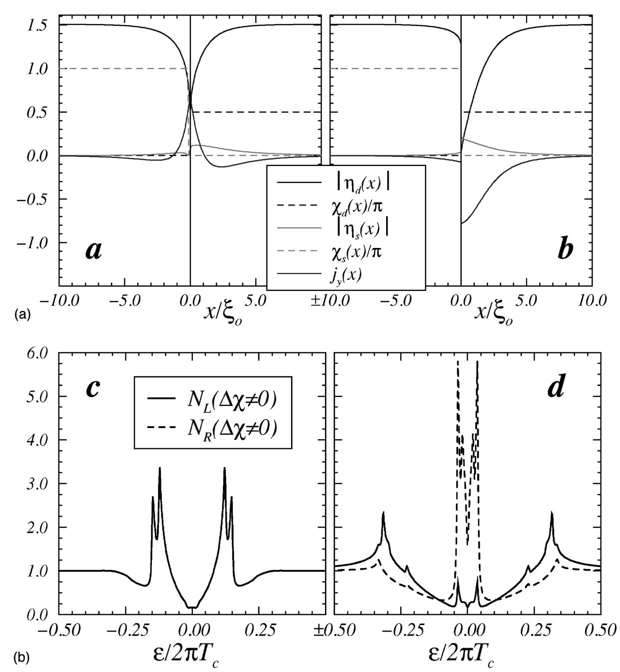

FIG. 4. The order parameters η_d and η_s and the transverse current j_y for $\alpha_L=0$ and $\alpha_R=\pi/4$. $T=0.2T_c$ and the subdominant $T_{c2}=0.1T_c$. The transparency, $\mathcal{D}_0$, of the boundary is 1.0 and 0.3 in panels (a) and (b). The corresponding DOS at the interfaces are in the lower panels (c) and (d).

opposite side that give the dominant TRSB. Hence, for large transmission the main mechanism for TRSB is the proximity effect even with a subdominant channel of moderate strength present. As $\mathcal{D}_0$ is reduced the side with $\alpha=\pi/4$ shows increasing pair breaking due to reflection of quasiparticles by the interface and the TRSB gets more localized to this right-hand side. This is also seen in the transverse current density, $j_y(x)$, which is much larger on this side. In the small $\mathcal{D}_0$ limit the proximity effect is gradually shut off and the presence of the subdominant channel is largely responsible for the TRSB state.

The DOS shown in Figs. 1 and 4 display considerable structure. These results are very different from those where the suppression of the order parameter near the interface is ignored (not shown). In particular, additional bound states are present at finite energies. These bound states are the result of Andreev-scattering processes due to amplitude changes, in addition to sign changes in the order parameter.

In conclusion, we have investigated time-reversal symmetry breaking at interfaces, in particular those with high transmission. We have shown how this TRSB can be understood from the density of states and the free energy of the interface. However, whether the TRSB is driven by the proximity effect or by a subdominant pairing channel will depend on the transmission properties of the interface. Direct observation of the DOS and conductance peak splitting via tunneling into the grain boundary by scanning tunneling microscopy or NIS experiments analogous to Ref. 1 should be possible. TRSB via the proximity effect is important if the relative misorientation of the two crystals is close to $\pm\pi/4$ and the transmission of the interface is moderate to high. In this case the entry into a TRSB state will not depend strongly on spatial variations of the interface orientation such as meandering as demonstrated in Fig. 3.

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