Time Reversal Symmetry Breaking States Near Grain Boundaries Between d-wave Superconductors

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(March 24, 2022)

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.

PACS numbers: 74.50.+r, 74.72.-h

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] In this paper we discuss the origin of the TRSB-state and constrain 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. [5] 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 $\frac{\pi}{4}$ (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. [6] TRS 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 $\chi_L$ and $\chi_R$ are the phases of the order parameter on either side far away from the interface. $\Delta \chi$ is other than an integral multiple of $\pi$ 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 non-equivalent 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 last para-
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 ZEBS at \( \varepsilon = 0 \) are shifted away from the midgap and that spontaneous currents along the interface are nucleated. \( \text{(1)} \)

The occurrence of zero energy bound states (ZEBS) for non-transmitting surfaces have already been extensively investigated \( \text{(2)} \) (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 \( \pi \)). One can show rigorously \( \text{(3)} \) 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 both if it is 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 \( \Delta \)) is larger than the corresponding states with \( \Delta \chi = 0 \) or \( \pi \). The formation of ZEBS and the suppression of the order parameter near the interface suggest that the \( \Delta \chi = 0 \) or \( \pi \) states are energetically unfavorable compared with the TRSB state. \( \text{(4)} \) This is verified by a calculation of the free energy.

| (\( \alpha_L, \alpha_R \)) | State | \( D_o = 1.0 \) | \( D_o = 0.7 \) | \( D_o = 0.3 \) |
|-----------------|-------|--------------|--------------|--------------|
| \( (0, \pi/4) \) | \( \Delta \chi = 0 \) | 0.127 | 0.125 | 0.116 |
|                 | \( \Delta \chi \neq 0 \) | 0.109 | 0.119 | 0.115 |
| \( (-\pi/4, \pi/4) \) | \( \Delta \chi = 0 \) | 0.133 | 0.132 | 0.130 |
|                 | \( \Delta \chi = \pi \) | 0.120 | 0.119 | 0.123 |
|                 | \( \Delta \chi \neq 0 \) | 0.108 | 0.117 | 0.123 |

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

\[
D(\phi) = \frac{D_o \cos^2 \phi}{1 - D_o \sin^2 \phi}.
\]

The quasiclassical green’s function \( \tilde{g} \) obeys the usual equation involving \( \hat{\Delta} \) in the bulk, and boundary conditions at the interface parameterized by \( D(\phi) \) (see Refs. \( \text{(11)} \) and \( \text{(12)} \) for details). The numerical procedure is as follows: 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. For the given \( \hat{\Delta}(x) \), we obtain the quasiclassical green’s function \( \tilde{g}(\hat{p}_f, \varepsilon, x) \) along the imaginary axis (here \( \varepsilon = i \varepsilon_n \) where \( \varepsilon_n \)'s are the Matsubara frequencies) via the method described in detail in \( \text{(12)} \). No iteration is needed in this step. The correction to \( \hat{\Delta}(x) \) is determined by the weak-coupling gap equation involving the off-diagonal parts of \( \tilde{g} \). At each iteration 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 \( J_x = 0 \) with the desired sign of \( \hat{g}_{\Delta x \Delta} \). This procedure is repeated until \( \hat{\Delta}(x) \) is consistent with the calculated \( \tilde{g} \) and the condition \( J_x = 0 \). Note that once self-consistency is achieved, particle conservation will be respected (see, e.g., \( \text{(13)} \)). \( J_x \) is then set independently of the order parameter. We find that TRSB is most significant at low temperatures and when the misorientation \( \theta = \alpha_R - \alpha_L \) is close to \( \pi/4 \) (mod \( \pi/2 \)).

With the self consistent order parameter the green’s function \( \tilde{g} \) was evaluated on the real energy axis again via the method in \( \text{(13)} \). From this \( \tilde{g} \) we obtain the density of states. All the DOS below are obtained at energies \( \varepsilon + i \gamma \), with \( \gamma = 0.05 T_c \). This small imaginary part of the energy simulates a broadening of energy levels that would occur naturally in non-ideal systems.

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As representative example we consider \( \alpha_L = 0 \) and \( \alpha_R = \pi/4 \) at a relatively low temperature, \( T = 0.2 T_c \). The order parameters are as shown in Fig.\( \text{1} \) for both the states with \( \Delta \chi = 0 \) and the ones corresponding to energy minima with \( \Delta \chi \neq 0 \). As can be seen from an examination of Fig.\( \text{1} \) 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 \( \Delta \chi \neq 0 \) state has a larger amplitude than the one with zero phase difference for a given transparency. This difference decreases as \( D_o \) decreases. At \( D_o = 0.3 \) the dif-
The DOS recovers to its bulk value as one moves away from the interface. (Fig. 3) At $x \approx 10\xi_o$, 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 (c.f. 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 4.

Recent experiments [i] 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 co-exist. In this case

$$\Delta(p_f, x) = \eta_d(x) \sqrt{2}\cos(2(\phi - \alpha)) + \eta_s(x). \quad (3)$$

In Fig. 4 we have plotted the order parameters $\eta_d, \eta_s$ of the minimum energy states for $(\alpha_L, \alpha_R) = (0, \pi/4)$ and for different transparencies. For all $D_o$ the phase difference between the d-wave order parameters on the two

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FIG. 1. The magnitude $|\eta_d|$ and the phase $\chi_d$ of the order parameter $\eta_d$ 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 $\Delta \chi \neq 0$. The states with $\Delta \chi \neq 0$ 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. $D_o$ is 1.0 in a and c and 0.3 in b and d. The units are $k_B T_c$ for $|\eta_d|$ and $2\pi e\gamma N_f |\eta(\infty)|$ for current densities in all graphs. $\xi_o \equiv \hbar v_f / 2\pi T_c$.

FIG. 2. The spatial dependence of the DOS for an interface with $D_o = 0.7$. 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 $1\xi_o$. 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 $\alpha_L$. The misorientation angle $\theta$ is kept fixed at $\pi/4$. The temperature is $0.2T_c$.
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 $x \to -\infty$, the s-wave component $\eta_s$ is real for all $x$, being positive for $x > 0$ and negative for $x < 0$. The order parameter for $x > 0$ is in the TRSB combination $s+id$. For the large transmission $D_o = 1$ both the order parameter $\eta_d$ and the DOS are qualitatively equal to the pure $d_{x^2-y^2}$ state shown in Figs. 1a and 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 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 $D_o$ 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 $D_o$ 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.

We thank Juhani Kurki-Jarvi and Jim Sauls for discussions and their comments on the manuscript. This research was supported by the the Science and Technology Center for Superconductivity, grant no. NSF 91-20000, the Academy of Finland research grant No. 4385 (SY), and the Åbo Akademi. MF also acknowledges partial support from SFAAF and Magnus Ehrnrooths Stiftelse.

![Graph](image)

FIG. 4. The order parameters $\eta_d$ and $\eta_s$ and the transverse current $j_y$ for $\alpha_L = 0$ and $\alpha_R = \pi/4$. $T = 0.2T_c$ and the sub-dominant $T_{22} = 0.1T_c$. The transparency, $D_o$, 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.

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[1] M. Covington et al., Phys. Rev. Lett. 79, 277 (1997)
[2] M. Fogelström, D. Rainer and J. A. Sauls, Phys. Rev. Lett. 79, 281 (1997); M. Fogelström, M. Palumbo, L. Buchholtz, D. Rainer and J. A. Sauls, preprint
[3] J. Kirtley et al., Phys. Rev. Lett. 76 1336 (1996)
[4] M. Sigrist, D. B. Bailey and R. B. Laughlin, Phys. Rev. Lett. 74 3249 (1995)
[5] S.-K. Yip, Phys. Rev. B 52, 3087 (1995)
[6] M. Sigrist, K. Kuboki, B. Kuklov, D. B. Bailey and R. B. Laughlin, Czech. J. of Physics, 46, 3159 (1996)
[7] D. B. Bailey, M. Sigrist and R. B. Laughlin, Phys. Rev. B 55, 15239 (1997)
[8] L. Buchholtz, M. Palumbo, D. Rainer and J. A. Sauls, J. Low Temp. Phys. 101, 1079 (1995); ibid. 101, 1099 (1995)
[9] M. Matsumoto and H. Shiba, J. Phys. Soc. Japan 64, 1703 (1995); ibid 64 3384 (1995); ibid 64 4847 (1995)
[10] Yu S. Barash, A. V. Galaktionov and A. D. Zaikin Phys. Rev. B 52, 665 (1995)
[11] M. Fogelström, S.-K. Yip and J. Kurki-Jarvi, Physica C, to appear (1998), cond-mat/9709120
[12] S.-K. Yip, J. Low Temp. Phys., 109, 547 (1997)
[13] M. Fogelström and S.-K. Yip, unpublished
[14] Recently, Belzig et al. cond-mat/9801107 have considered TRSB near a twin boundary from a similar point of view.
[15] J. W. Serene and D. Rainer Phys. Rep. 101 221 (1983)
[16] E. V. Thuneberg, J. Kurki-Jarvi and D. Rainer, Phys. Rev. B 29, 3913 (1984)
[17] S.-K. Yip, J. Low Temp. Phys. 91, 203 (1993)
[18] The sign of the order parameter $\eta_s$ can be understood by considering the leakage of the off-diagonal part of the green’s function from one side to the other.