Boundary Effects and the Order Parameter Symmetry of High-Tc Superconductors

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Apparently conflicting phase-sensitive measurements of the order parameter symmetry in the high-Tc cuprate superconductors may be explained by regions near surfaces in which the order parameter symmetry is different than in the bulk. These surface states can lead to interesting and testable effects.

Phase-sensitive measurements on the high temperature superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ have yielded two potentially conflicting sets of results for the symmetry of the superconducting order parameter \[ \rho. \] Measurements involving currents flowing in the CuO$_{2}$ planes, such as the corner-junction SQUID experiments \[ \gamma, \delta \], the corner-junction flux modulation experiments \[ \epsilon, \zeta \], and the tricrystal ring experiments \[ \eta \] indicate an order parameter with primarily $d_{x^2-y^2}$ symmetry under rotations in the plane ($\Delta(k) \sim \cos k_x - \cos k_y$). The presence, however, of Josephson tunneling perpendicular to the CuO$_{2}$ planes between heavily-twinned YBCO and a conventional $s$-wave superconductor \[ \alpha \] suggests an order parameter with a significant $s$-wave component \[ \beta \].

A bulk order parameter of mixed $s$ and $d_{x^2-y^2}$ symmetry could explain both sets of experiments. An order parameter with this mixed symmetry, for a material which is otherwise macroscopically symmetric under 90° rotations (heavily twinned YBCO), requires either a first order transition or two separate bulk phase transitions. So far, there has been no convincing evidence for either of these. In this paper, then, we assume that the order parameter in the bulk superconductor transforms as one irreducible representation of the rotation group $D_{4h}$, either $s$ or $d_{x^2-y^2}$.

Using a Ginzburg-Landau model in which both $s$ and $d_{x^2-y^2}$ order parameter symmetries are allowed, but only one is favored in the bulk, we find that there are two possibilities consistent with both the CuO$_{2}$ plane and $c$-axis tunneling experiments.

The first possibility is that the order parameter is $s$-wave in the bulk and a $d$-wave component is mixed in at faces normal to the CuO$_{2}$ planes (Fig. 1a). This does not require any special choice of parameters; there is an instability to mixing near these faces. The symmetry being tested is rotation in the CuO$_{2}$ plane and placing an edge in that plane breaks the symmetry explicitly. This always causes mixing. The amount of mixing depends on the energetics: if the $d$-wave component is strongly disfavored (as might be expected in a conventional superconductor), the mixing is small. If there is a close competition, the mixing may be large. In addition, we find that for this case the mixing can explain the CuO$_{2}$ plane experiments only if the order parameter breaks time reversal invariance at the surface: it must have the form $s + id$ there.

The second possibility is that the order parameter is $d$-wave in the bulk and a surface state forms which mixes in an $s$ component on the face perpendicular to $c$-axis (Fig. 1b). This occurs only under certain conditions. The two components must inhibit each other, in the sense that the presence of one makes the other energetically less favorable. In addition, the effect of the $c$-axis boundary must be such that the magnitude of the $d$-wave component decreases significantly from its bulk value near the edge. In that case, the $s$-wave component is less suppressed near the surface and a localized region of mixed symmetry can develop \[ \theta \].

The presence of the surface state normal to the $c$-axis is sensitive to the boundary conditions. This may explain the difficulty in achieving $c$-axis junctions, as well as the variability among samples of angle-resolved photoemission spectroscopy studies of the gap magnitude \[ \xi \]. The photoemission studies see the topmost CuO$_{2}$ layer. Variations in surface properties affect the boundary conditions, which in turn affect whether the order parameter has the form $d+s$, $d+is$ or pure $d$ at the surface, each of which has a different momentum dependence.

The $c$-axis surface state may also lead to “$\pi$-junction” behavior. In a SQUID loop between YBCO and a conventional superconductor, with junctions normal to the $c$-axis, the configuration with opposite relative phases on the two junctions will lead to a net phase difference of $\pi$ in the absence of an applied magnetic field.

For both possibilities discussed above, the starting point is the Ginzburg-Landau free energy \[ \chi \]

\[
F = F_s + F_d + F_{sd} + \frac{1}{8\pi} \int d^3r \, B^2 , \quad (1)
\]

\[
F_s = \int d^3r \left[ \kappa \psi_i |\mathbf{D}\psi_i|^2 + a_i(T) |\psi_i|^2 + b_i |\psi_i|^4 \right]
\]

\[
F_{sd} = \int d^3r \left[ \lambda_1 |\psi_s|^2 |\psi_d|^2 + \lambda_2 (\psi_i^* \psi_d^2 + \psi_i^2 \psi_d^2) + (\gamma^s \psi_d^2 (D_x^2 - D_y^2) \psi_s + c.c.) \right].
\]
The CuO$_2$ planes are in the x-y directions, the magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$, the gauge invariant gradient operator $\mathbf{D} = \nabla - 2i\mathbf{A}/c$, and the index $i$ runs over $s$ and $d$. We now consider the two cases separately.

**Bulk s case:** We consider a homogeneous system in the absence of a magnetic field, for which the gradient terms in $F$ vanish in the bulk. A purely s-wave solution to Eq. (1) exists when $a_s < 0$ and $a_d + |a_s| \lambda_1 - 2\lambda_2 > 0$. If $a_d < 0$ and $a_s + |a_d| \lambda_1 - 2\lambda_2 > 0$, then a purely d-wave solution also exists. As long as $a_s^2/b_s > a_d^2/b_d$, the s-solution has lower energy than the d-solution and is the stable global minimum of the free energy.

Ordinarily, near a boundary, a stability criterion follows from considering the change in energy due to adding a small $\psi_d$ to the bulk $\psi_s$ solution:

$$\delta F = \psi_s^* \left[ -\kappa_d \partial_x^2 + a_d + \lambda |\psi_s|^2 \right] \psi_d + O(\psi_d^4) ,$$

where

$$\lambda \equiv \lambda_1 + 2\lambda_2 \cos 2\theta_{sd} ,$$

$\theta_{sd}$ is the relative phase between the s and d order parameters, $\psi_s(x)$ is the unperturbed solution, and we consider a boundary along the x direction. If the operator in brackets has an eigenstate with negative eigenvalue, the energy will be lowered by forming a surface state. If there are no negative eigenvalues, the system is stable against the formation of a surface state.

This stability criterion assumes that the gradient terms mixing the the s and d components in $F_{sd}$ can be neglected. For a boundary which is in the a-b plane, this will not necessarily be true. Near a boundary, the s-wave component may decrease, in which case the gradient terms in $F_{sd}$ contribute. These add a term linear in $\psi_d$ to Eq. (1). The effect of a linear term is that the energy can always be lowered by turning on a small $\psi_d \neq 0$, that is, there is an instability to mixing.

This instability occurs only for boundaries in the a-b plane because boundaries in this plane explicitly break the rotational symmetry being tested: they allow a term such as $\psi_s^*(D_x^2 - D_y^2) \psi_d$ to contribute to the free energy. For a boundary along the $c$-axis, there is no equivalent linear-order mixing through gradients.

The form of the magnitudes $\mathbf{S}(\mathbf{r}) \equiv |\psi_s(\mathbf{r})|$ and $\mathbf{D}(\mathbf{r}) \equiv |\psi_d(\mathbf{r})|$ near the boundary will depend in detail on the Ginzburg-Landau parameters and the boundary conditions. The relative phase $\theta_{sd}$ between $\psi_s$ and $\psi_d$ is easier to understand. There are only two terms in the free energy given in Eq. (1) which depend on this phase:

$$\lambda_2 S^2 D^2 \cos 2\theta_{sd} + \gamma D (\partial_x^2 - \partial_y^2) S \cos \theta_{sd} ,$$

where we have assumed there are no spontaneous phase gradients (currents) at the edge. The second term is minimized for a relative phase difference between the s and d components of 0 or $\pi$ depending on the sign of $\gamma$. However, for a given system, this term will prefer opposite phases on the faces normal to the $\hat{x}$ and $\hat{y}$ directions: $s + d$ on one face and $s - d$ on the other. Such a configuration is not consistent with the corner junction experiments because there will be no net phase shift in a loop formed between two adjacent faces.

The first term in Eq. (1), however, favors $\theta_{sd} = \pm \pi/2$ when the coefficient $\lambda_2$ is positive, and $\theta_{sd} = 0$ or $\pi$ when $\lambda_2$ is negative. If $\theta_{sd} = \pm \pi/2$ at the minimum then the second term does not contribute and there is no preference from this surface energy for either sign. The corner energy is minimized for a uniform phase around the material, and the result is $s + id$ at every face or $s - id$ at every face. This solution, which occurs when $\theta_{sd}$ is such that $\lambda_2 < 0$ and the first term dominates the second term at the minimum, has the potential to be consistent with the corner junction experiments.

Both the single corner junction and tricrystal ring experiments, however, place strong limits on the amount of $s$ which is present at the surface. In order for the bulk s scenario to explain these results, the parameters must be fine tuned so that the amount of residual s-wave order parameter near the surface is small. This makes the picture somewhat unlikely, although not yet ruled out.

**Bulk d$_{x^2-y^2}$ case:** In this case, we assume that the corner junction experiments are detecting the intrinsic, bulk order parameter symmetry and that surface states with mixed symmetry form at the faces perpendicular to the c-axis.

The energy cost of adding a small $\psi_s$ solution to a bulk $\psi_d$ solution is

$$\delta F = \psi_s^* \left[ -\kappa_s \partial_z^2 + a_s + \lambda |\psi_d|^2 \right] \psi_s + O(|\psi_s|^4) ,$$

where $\kappa$ is defined in Eq. (1) and we now consider a boundary along the $\hat{z}$-direction. When the operator in brackets develops a bound state with a negative energy satisfying the appropriate boundary conditions, a surface state will form.

The boundary conditions determine the presence of the surface state in the following way. If $\psi_d$ near the surface decreases very little from its bulk value, then the $\psi_s$ component will be as suppressed as it is in the bulk and a surface state is unlikely to form. Conversely, if $\psi_d$ does decrease significantly, a surface state may be induced. More explicitly, the boundary condition at an interface can be written in general $\eta(z) = \psi(0)/L$, where $L$ measures the extent to which the order parameter is suppressed at the interface. At a superconductor-insulator boundary $L \rightarrow \infty$, so $\psi(0)$ is close to the bulk value, whereas at a superconductor-metal boundary $L \rightarrow 0$, so that $\psi(0)$ nearly vanishes. Therefore boundaries which are more superconductor-metal like enhance
the likelihood of a surface state forming.

The symmetry of the surface state will depend on the sign of the $\lambda_2$ defined in Eq. (2); the state will have the form $s \pm id$ for positive $\lambda_2$ and $s \pm d$ for negative $\lambda_2$ \[13\]. For a given system (fixed $\lambda_2$), the plus and minus states are degenerate, and this can lead to the effects illustrated in Figs. 2 and 3. The Josephson energy for the SQUID loops shown in Fig. 2 can be written

$$E_J(\Phi) = E_{Ja} \cos \phi_a + \eta E_{Jb} \cos \phi_b ,$$

(6)

where $E_{Ja}$ are the Josephson coupling energies for the top and bottom junctions $(i = a, b)$, $\phi_i$ are the phase differences across these junctions, and $\eta$ is $\pm 1$. The phase differences satisfy

$$\phi_a - \phi_b = 2\pi \frac{\Phi}{\Phi_0} ,$$

(7)

where $\Phi$ is the net flux enclosed in the loop and $\Phi_0 =hc/2e$ is the flux quantum \[18\]. The configuration in which the top and bottom junctions have misaligned $s$ components ($\eta = -1$) adds an additional phase shift of $\pi$ because the conventional superconductor couples only to the $s$ component of the order parameter (assuming a tunnel junction in which higher order tunneling matrix elements can be neglected). The result, for symmetric junctions, is shown in Fig. 4. Minimizing the Josephson energy yields a net phase shift of $\Phi_0/2$ between the flux dependence of the $\eta = +1$ and $\eta = -1$ configurations.

This phase shift leads to several interesting behaviors. In the high-inductance limit, the $\eta = -1$ configuration in Fig. 4 will cause spontaneous currents generating half-integral flux quanta, as in the tricrystal ring configurations. The half-integral periodicity of $E_J(\Phi)$ is also reflected in a half-integral periodicity in the flux dependence of the critical current, which will be seen if the system can probe both configurations in achieving the maximum supercurrent. We also note that an asymmetric junction, for which $E_1 \neq E_2$, causes the resulting $E_J(\Phi)$ to oscillate between $-|E_1 - E_2|$ and $-|E_1 + E_2|$, instead of 0 and $-2E_1$ as in Fig. 4, but the periodicity with $\Phi_0/2$ remains the same.

There are several other interesting consequences of a mixed symmetry surface state. First, for the state normal to the $c$-axis, there should be a surface phase transition, at a temperature $T_{s,c}$ below the bulk $T_c$, where the $s$-wave component of the order parameter disappears. This would most likely occur at too high a temperature to be seen in the Josephson tunneling into a conventional superconductor, but might be seen in photoemission. There is some preliminary evidence from photoemission studies on Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ that at a temperature $\approx .8$ to $9.9T_c$ there is an increase in anisotropy of the gap magnitude, as would occur if a surface $s$-wave contribution to the order parameter were disappearing \[19\]. Second, the relative phase angle between the two components, $\theta_{sd}$, is a dynamical variable and its oscillations, which occur as long as there is a charging energy (a capacitance in the Josephson equations), are a new collective mode of the order parameter. This mode is charged, since $|\psi_s| \neq |\psi_d|$, and will therefore be pushed up near the plasma frequency, but is distinct from the usual plasma mode. The mode will disappear at the temperature $T_{s,c}$ of the surface phase transition.

This work was stimulated by many interesting discussions with S. Kivelson and V. Emery. I would also like to thank D. Rokhsar for valuable discussions and J. Clarke, J.-W. Gan, and D.-H. Lee for helpful comments. This work was supported by a Miller Research Fellowship from the Miller Institute for Basic Research in Science.

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FIG. 1. Two possibilities consistent with both sets of phase sensitive experiments: (a) A surface state of mixed $s$ and $d$ symmetry forms normal to the CuO$_2$ planes in a bulk $s$-wave superconductor; (b) A surface state of mixed symmetry forms parallel to the CuO$_2$ planes in a bulk $d$-wave superconductor.

FIG. 2. Two possible configurations of a $d$-wave superconductor, with surface states of mixed symmetry, in a SQUID loop with a conventional superconductor.

FIG. 3. Josephson energy of the two configurations in Fig. 2. The $\eta = +1$ configuration behaves as an ordinary SQUID, but the flux dependence for the $\eta = -1$ configuration is shifted by $\Phi_0/2$. The result is that the ground state energy of the system (solid line) is periodic with period $\Phi_0/2$ rather than $\Phi_0$. 