c-axis Josephson Tunneling in Twinned YBCO Crystals

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Josephson tunneling between YBa$_2$Cu$_3$O$_{7-\delta}$ and Pb with the current flowing along the c-axis of the YBa$_2$Cu$_3$O$_{7-\delta}$ is presumed to come from an s-wave component of the superconductivity in YBa$_2$Cu$_3$O$_{7-\delta}$. Experiments on multi-twin samples are not entirely consistent with this hypothesis. The sign changes of the s-wave order parameter across the $N_T$ twin boundaries should give cancellations, resulting in a small (\(\sqrt{N_T}\)) tunneling current. The actual current is larger than this. We present a theory of this unexpectedly large current based upon a surface effect: disorder-induced supression of the d-wave component at the (001) surface leads to s-wave coherence across the twin boundaries and a non-random tunneling current. We solve the case of an ordered array of d+s and d-s twins, and estimate that the twin size at which s-wave surface coherence occurs is consistent with typical sizes observed in experiments. In this picture, there is a phase difference of $\pi/2$ between different surfaces of the material. We propose a corner junction experiment to test this picture.

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I. INTRODUCTION

Understanding the nature of the order parameter is one of the main challenges in the theory of high-$T_c$ superconductivity. One of the most fundamental issues is the competition between s-wave and d-wave. d-wave is definitely the rule for high-$T_c$ systems, yet there is strong evidence that the electron-doped NdCeCuO material is s-wave. At a microscopic level, this suggests that the mean-field pairing interaction has two eigenvalues which vie for dominance. Understanding this competition would provide insight into the pairing mechanism.

In this regard YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) is of particular interest. In other systems, the square symmetry forces the ordering to be pure d-wave or pure s-wave. The presence of one most likely prevents the emergence of the other because of repulsive terms in the free energy, and the competition has a clear winner. In contrast, YBCO has orthorhombic symmetry. This makes it inevitable that d-wave and s-wave are always mixed. Josephson tunneling experiments with current flowing mainly in the a-b plane have made it clear that the dominant component is d-wave, but a substantial body of work has also demonstrated the existence of Josephson tunneling along the c-axis from YBCO to a Pb electrode, indicative of an s-wave component. It is to be hoped that these latter experiments, if carefully analyzed, can tell us about the strength of the s-wave admixture in the order parameter.

We shall first review the experimental and theoretical situation concerning c-axis tunneling, concluding that there are major theoretical puzzles still to be resolved. Then we shall present a new model of the phenomena which we argue is in agreement with the data as they stand, and how to test the model more thoroughly.

c-axis tunneling from YBCO to Pb was first observed in twinned crystals etched with Br, with an $I_cR_n$ product of as much as 10% of the known gap of about 30 meV. This strongly suggested the presence of an s-wave component of the superconductivity of YBCO, as a pure d-wave current would average to zero over the Fermi surface. However, another possibility was that the current was due to second order tunneling of the d-wave component. This hypothesis predicts the presence of Shapiro steps in the conductivity in units of $hf/4e$, where $f$ is the frequency of the incident radiation. This was ruled out in subsequent microwave experiments. Finally, the question of tunneling through step walls at the surface arises, particularly if it is deeply etched. This would be a process in which the current actually flows in the a–b direction. However, the fabrication of a–b junctions and the observation of tunneling in situ without etching appears to have laid this possibility to rest. The presence of a nonzero s-wave component in YBCO must now be accepted.

Is it reasonable to accept the 10% estimate of s to d which comes from the $I_cR_n$ product at face value? Clearly not, for the following reason. A twinned sample should have a relative population of twins of the two possible orientations given by statistical considerations. The d-wave component must remain coherent through the sample, as is shown by the corner junction experiments. Because the change in orientation reverses the relative sign of s and d we should have roughly equal areas of d+s and d–s superconductivity in the sample, in which case the net current should be zero. More precisely, the net current should be proportional to $I_c\sqrt{N_T}$, where $I_c$ is the critical current of a single twin and $N_T$ is the total number of twins. If we accept this argument, then the actual proportion of s to d would be higher than 10%. This would move the nodes in the...
gap well away from the diagonal in the Brillouin zone. This would be inconsistent with tricrystal experiments. Furthermore, comparison of Josephson currents in single crystals to twinned crystals show similar values and $I_c$ values which range from 0.5 to 1.6 mA for single crystals and from 0.1 to 0.9 mA for twinned samples. These numbers are subject to the objection that one cannot be sure that the tunneling matrix elements are not extremely sensitive to the sample preparation method. Nevertheless, in view of the fact that $R_n$ does not vary wildly from sample to sample, they suggest that a purely statistical analysis of twin populations with a resulting small imbalance of $d + s$ and $d - s$ is not a viable explanation of the data.

The dilemma was deepened by experiments on crystals with much larger twins, large enough so that junctions could be formed which straddled either one or even zero twin boundaries. These showed that the direction of current definitely did change sign across the twin boundary, a fact which can be established unambiguously by investigating the current as a function of field in the plane of the junction. This observation was consistent in all eight samples studied. Also, no such sign changes were observed in the absence of a boundary. These experiments therefore clearly confirm the mechanism of an $s$-wave component controlled by the orthorhombic distortion, without offering any explanation of the large current in heavily twinned samples. One further observation in these experiments may offer a clue, however. The current at zero applied field in single-boundary samples was consistently higher than calculated by looking at the relative sizes of the two twins. We will return to this point below.

Summarizing the experiments, we may say that an $s$-wave component which changes sign across boundaries is clearly present. If it always changes sign, then we cannot explain the data on twinned samples using purely statistical arguments. One possibility is that the twin populations are not equally likely. For example, if the twinning takes place under uniaxial stress, then one orientation would be favored. Experiments which correlate microstructure with Josephson current are needed to rule this out. However, given the size of the Josephson effect in twinned samples, it seems to us that this explanation is somewhat implausible.

The most detailed theory of $c$-axis tunneling proposed to date is that offered by Sigrist et al. Their picture involves no net tunneling from the twins themselves. A time-reversal-breaking state at the twin boundary is predicted which results in a net Josephson current coming from the twin boundaries. This would give a Josephson current which is proportional to the number of boundaries for a fixed surface area. This is not observed, though again one must keep in mind that different samples must be compared to make any such statement, and variations in important microscopic parameters cannot be controlled in such comparisons. In addition, however, the theory predicts a current which has maximum asymmetry (as a function of in-plane angle) when the applied magnetic field is parallel to the boundary. This is an experiment in which the unknown matrix elements are held fixed. This prediction is in conflict with the experimental observations, which are symmetric at parallel orientation.

A quite different proposal was made by Xu et al. These authors postulate a bulk $d + is$ state. In this theory, however, the $s$-component does not change sign across the boundary, which does not agree with the measurements on single-boundary samples in a parallel field.

We present an alternative explanation in which the nonzero tunneling current is the result of a surface effect. YBCO is notorious in photoemission experiments for not showing a gap. This proposal is inspired by the fact that photoemission experiments (with resolutions of order 10 meV or less) have also never succeeded in seeing a gap at the (001) surface in this material (in contrast to Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$). This shows that the magnitude of the gap at this particular surface is much reduced. Furthermore, if this reduction is due to disorder, such as surface scattering, one would expect that the $d$-wave component is relatively much more suppressed than any $s$-wave admixture. A similar suppression could result from an oxygen vacancy concentration gradient. This suppression of the $d$-wave component of the order parameter as we approach the (001) surface of the YBCO in the context of c-axis tunneling is of two central hypotheses of our model and was first suggested by Bahcall. The second crucial ingredient is new: the $d$-wave surface suppression results in a coherent $s$-wave surface layer and hence an enhanced Josephson tunneling current in highly twinned samples without a very large admixture of $s$-wave in the bulk.

\section{II. DOUBLE TWIN MODEL}

Twinned samples are disordered on the $\mu$m scale, the twin boundaries running predominantly along the diagonal of the a-b plane. It is reasonable then to approximate the disordered sample by an array of straight twin boundaries running across the entire sample, which is considered to be semi-infinite. We concern ourselves in this paper with the ordered case in which all twins are of the same width and alternate between $d+s$ and $d-s$. In real samples the twins have varying widths, but we have verified numerically that the basic results are unaffected by neglecting the disorder in the widths. The solution of the ordered model should be periodic with a period of two twins. Therefore, we solve the case of two twins with periodic boundary conditions. The twin boundary occupies the half plane defined by $x = 0$ and $z \leq 0$. The plane $z = 0$ is the (001) surface of the YBCO sample. The model is illustrated schematically in Fig. 1.
We shall write the bulk free energy density in terms of the two order parameters $\Psi_d$ and $\Psi_s$. Spatial variation is allowed only along the x-direction, (normal to the twin boundary), and along the z-direction (normal to the surface). The free energy density is given by:

$$f = \alpha_d(z)|\Psi_d|^2 + \frac{\beta_d}{2} |\Psi_d|^4 + K_{dz}|\partial_z \Psi_d|^2 + K_{dx}|\partial_x \Psi_d|^2 + \alpha_s|\Psi_s|^2 + \frac{\beta_s}{2} |\Psi_s|^4 + K_{sx}|\partial_x \Psi_s|^2 + K_{sz}|\partial_z \Psi_s|^2 + \alpha_{sd}(x)(\Psi_d^* \Psi_s + c.c) + \beta_{sd}|\Psi_s|^2|\Psi_d|^2$$ (1)

Some of the important physical ideas behind our model are displayed by this equation. $\alpha_d$ is a function of position in order to enforce the condition that the d-wave component is suppressed near the surface. Thus $\alpha_d \rightarrow \alpha_{d0} < 0$, a negative constant, as $z \rightarrow -\infty$, deep in the bulk. $\alpha_d$ increases toward 0 as $z \rightarrow 0$ at the surface. $\alpha_{sd}$ is the s-d coupling parameter which is a negative constant deep in the $d + s$ twin and positive constant deep in the $d - s$ twin. $\alpha_{sd}(x) = -\alpha_{sd}(-x)$.

The $\beta_{sd}$ term is the s-d repulsion mentioned in the introduction. We will neglect it in the calculations and have included it here only in order to stress that a large positive $\beta_{sd}$ suppresses all s-d mixing in the absence of the bilinear $\alpha_{sd}$ term. If this term is present, as it is here because of the orthorhombic distortion, then the size of the s admixture is controlled by $\alpha_{sd}/\alpha_d$.

We must also include the free energy of the twin boundaries. Any x axis variation of $\Psi_s$ and $\Psi_d$ will take place within a distance of the order of a coherence length about the twin boundary. Since $\xi_{ab} \approx 20\AA$ is very small compared to the average twin width (0.1 to 10 $\mu$m) we conclude that the detailed structure of the twin boundary is not very important. We will assume a very thin boundary and thus take $\alpha_{sd}$ to be piecewise constant. This is in direct contrast to the Sigrist et al. model in which the current comes from the twin boundaries. In our model the current comes from the twins. We therefore approximate the free energy of the twin boundary by a Josephson-type coupling:

$$f_{TB} = -J_{s}|\Psi_s^+|(|\Psi_s^-| \cos(\phi_s^+ - \phi_s^-) - J_{d}|\Psi_d^+||\Psi_s^-| \cos(\phi_d^+ - \phi_d^-))$$ (2)

where $J_{s}$ and $J_{d}$ are positive. We can also now drop the x axis gradient terms in the bulk free energy. Any x axis variation in the order parameters takes place near the twin boundary and has been included in the boundary energy.

The problem has been reduced to 2 one-dimensional twins which are Josephson coupled. However, only one twin is actually required. As the surface of the YBCO is approached, the magnitude of $\Psi_d$ and $\Psi_s$ should vary in exactly the same way in both the $d + s$ and $d - s$ twins. Only the phases $\phi_s$ and $\phi_d$ are different. But while the phases differ between twins, they are not entirely independent. We set $\phi_d = \phi_s = 0$ in the bulk of the $d + s$ twin, and $\phi_d = 0$, $\phi_s = \pi$ in the bulk of the $d - s$ twin. As the (001) surface is approached, variation in $\phi_d$ and $\phi_s$ should be symmetric about $\pi/2$, while $\phi_d^+$ and $\phi_d^-$ will be symmetric about 0. This allows the boundary energy to be rewritten entirely in terms of the phases in the $d + s$ twin.

$$f_{TB}^d(z) = -J_{d}|\Psi_d(z)|^2 \cos(2\phi_d(z)) + J_{s}|\Psi_s(z)|^2 \cos(2\phi_s(z))$$ (3)

$\phi_s$ and $\phi_d$ in the $d - s$ twin can be deduced immediately, and the problem is now entirely one-dimensional.

### III. Solution

We will solve for the order parameters in the $d + s$ twin. The solution for the $d - s$ twin follows immediately. Our one-dimensional free energy density is:

$$f(z) = w\{\alpha_d(z)|\Psi_d|^2 + \frac{\beta_d}{2} |\Psi_d|^4 + \alpha_s|\Psi_s|^2 + \frac{\beta_s}{2} |\Psi_s|^4 + K_{dz}|\partial_z \Psi_d|^2 + K_{dx}|\partial_x \Psi_d|^2 + K_{sx}|\partial_x \Psi_s|^2 + K_{sz}|\partial_z \Psi_s|^2 + \alpha_{sd}(z)(\Psi_d^* \Psi_s + c.c)\} + -J_{d}|\Psi_d|^2 \cos(2\phi_d) + J_{s}|\Psi_s|^2 \cos(2\phi_s)$$ (4)

where $w$ is the width of a single twin. Performing the usual minimizations, we get:

$$\frac{\delta f}{\delta \Psi_d} = w\{\alpha_d(z)|\Psi_d|^2 + \frac{\beta_d}{2} |\Psi_d|^4 + \alpha_s|\Psi_s|^2 + \frac{\beta_s}{2} |\Psi_s|^4 + K_{dz}|\partial_z \Psi_d|^2 + K_{dx}|\partial_x \Psi_d|^2 + K_{sx}|\partial_x \Psi_s|^2 + K_{sz}|\partial_z \Psi_s|^2 + \alpha_{sd}(z)(\Psi_d^* \Psi_s + c.c)\} + -J_{d}|\Psi_d|^2 \cos(2\phi_d) = 0$$ (5)

and

$$\frac{\delta f}{\delta \phi_d} = w\{\alpha_{sd}|\Psi_s||\Psi_s| \sin(\phi_d - \phi_s) - \frac{1}{2} K_{dz}|\Psi_d|^2 |\partial_z \phi_d|^2 + J_{d}|\Psi_d|^2 \sin(2\phi_d) = 0$$ (6)
The analogous s-wave equations are:

\[
\frac{\delta f}{2\delta |\Psi_s|} = w\{\alpha_s|\Psi_s|^2 + \beta_s|\Psi_s|^3 + \alpha_{sd}|\Psi_d|^2 \cos(\phi_s - \phi_d) \\
+ K_{s\alpha}(\frac{1}{2}\partial_\phi^2|\Psi_s|^2 + |\Psi_s|^2(\partial_\phi^2\phi_s)^2) \\
+ J_s|\Psi_s|^2 \cos(2\phi_s) = 0 \tag{7}
\]

and

\[
\frac{\delta f}{2\delta \phi_s} = w\{-\alpha_{sd}|\Psi_d|^2|\Psi_s|\sin(\phi_s - \phi_d) \\
- \frac{1}{2}K_s|\Psi_s|^2(\partial_\phi^2\phi_s)| - J_s|\Psi_s|^2 \sin(2\phi_s) = 0 \tag{8}
\]

In general, these equations must be solved numerically, but it is instructive to first consider the limit \(K_{dz} = K_{ds} = 0\), which may be obtained analytically. If we consider Eqns. 6 and 8 we see that:

\[
J_s|\Psi_d|^2 \sin(2\phi_d) = J_s|\Psi_s|^2 \sin(2\phi_s) \\
= w\alpha_{sd}|\Psi_s| |\Psi_d| \sin(\phi_s - \phi_d) \tag{9}
\]

where \(\phi_s, \phi_d\) are between 0 and \(\pi/2\). There are only the two obvious solutions: \(\phi_d = \phi_s = 0\) or \(\pi/2\).

The particular solution which minimizes the free energy is dependent upon the relative strengths of the \(s\) and \(d\) intertwin Josephson couplings, \(\alpha_s\) and \(\alpha_{sd}\), i.e. the ratio \(R = J_s|\Psi_s|^2/J_s|\Psi_d|^2\). If \(R > 1\) then \(\phi_s = \phi_d = 0\). If \(R < 1\) \(\phi_s = \phi_d = \pi/2\). This is in the \(d+s\) twin. In the \(d-s\) twin if \(R > 1\) we have \(\phi_d = 0\). If \(R > 0\) then \(\phi_d = -\pi/2\) and \(\phi_s = \pi/2\). The magnitudes are obtained from the coupled set of equations:

\[
|\Psi_s| = -\frac{1}{|\alpha_{sd}|}(\alpha_{d}(z)|\Psi_d|^2 + \beta_d|\Psi_d|^3) \\
|\Psi_d| = -\frac{1}{(\alpha_{sd})}(\alpha_s|\Psi_s|^2 + \beta_s|\Psi_s|^3) \tag{10}
\]

where we have assumed that the intertwin coupling has little effect on the magnitude of the order parameters, that is \(J_s << w\alpha_s\) where \(w\) is the twin width. The exact form of \(|\Psi_s|\) and \(|\Psi_d|\) will depend on the \(\alpha_d(z)\) chosen.

The main effect of finite gradient terms \(K_{s,d}\partial_z\Psi_{s,d}|^2\) in the free energy is to smooth out the variation in the order parameters as the surface is approached. We expect the order parameter magnitudes to be only slightly affected by the introduction of the gradient terms. Variation in \(|\Psi_d|^2\) and \(|\Psi_s|^2\) should depend predominantly on \(\alpha_d(z)\), since \(K_d << |\alpha_d|\) etc. The effect on the phases is more dramatic. For relatively narrow twins, \(\phi_s\) and \(\phi_d\) now undergo a smooth transition from \(\phi_s = \phi_d = 0\) in the bulk of the \(d+s\) twin to \(\phi_s = \phi_d = \pi/2\) at the surface. In the \(d-s\) twin, \(\phi_s\) changes from \(\pi\) to \(\pi/2\) at the surface and \(\phi_d\) from 0 to \(-\pi/2\). The order parameter magnitudes and phases for a model \(\alpha_d(z)\) are shown in Fig. 2.

The degree of smoothing depends upon the strength of the gradient term versus that of the coupling across the twin boundary. The dominant factor in this competition between the gradient and the intertwin coupling energy is the twin width. For very wide twins, the change in surface phase is diminished and may be eliminated altogether.

The maximum c-axis Josephson current is given by:

\[
\frac{J_{max}}{A} = \frac{J_0}{2}\{\sin(\phi_{pb} - \phi_{s}^{d+s}) + \sin(\phi_{pb} - \phi_{s}^{d-s})\} \\
= J_0 \sin(\phi_{s}^{d+s}) \tag{11}
\]

where \(A\) is the junction area and \(\phi_{pb}\) has been chosen to yield the maximum Josephson current. For very
large twins it is not energetically favorable for the phase change to occur. The s-wave phase at the surface alternates between 0 and π across twin boundaries and no net Josephson current flows. As the twins become narrower, a threshold is reached where the s-wave phases start to shift towards π/2 at the surface. The s-wave surface phase alternates between φ_s^{d+s} and φ_s^{d-s} = π − φ_s^{d+s}. Some Josephson coupling is now possible. For very narrow twins φ_s is coherent across the entire surface of the crystal, and the maximum Josephson current flows. The current saturates, and further reduction of twin size has no effect on the current. This is illustrated in Fig. 3.

\[ \Psi_s(x) = sgn(x)\Psi_s^0(1 - e^{-|x|/\xi_s}) \]  

where \( \Psi_s^0 \) is the bulk value. The result for the free energy per unit area of the twin boundary is:

\[ \frac{F_b}{A} = \xi_s\alpha_s|\Psi_s^0|^2 \]  

The c-axis gradient energy is also required and is roughly

\[ \frac{F_g}{A} = K_s|\Psi_s|^2\left(\frac{\pi/2}{s}\right)^2 w \]

where \( w \) is the twin width. Noting that \( K_s/\alpha_s = \xi_c^2 \) and setting \( F_g = F_b \) we obtain:

\[ w = \frac{\xi_{ab} c}{\xi_c s} \]  

For a surface layer with a depth of 100 Å (about 8 unit cells) then we obtain a twin width of approximately 1μm. We emphasize that this is merely an order of magnitude estimate. In addition, it is not clear exactly how deep such a surface layer should be. However, the resulting twin width is not unreasonable. A highly twinned sample of 0.5mm may have as many as 10^3 twins resulting in an average twin width of a few tenths of microns. Thus while we expect no net Josephson current in a lightly twinned sample, our model predicts the net Josephson current observed in more heavily twinned crystals.

**IV. PROPOSED EXPERIMENT**

Our model predicts a nonzero Josephson current resulting from a surface effect. For samples with relatively large twins, we expect a d+s d-s alternation between twins at the surface and no net Josephson current. This explains why experiments on two twin crystals show a sign change in the Josephson coupling to Pb across the twin boundary. In a sample with many smaller twins, however, the coupling between twins wins out and a coherent s-wave surface layer results. We expect this to take place in samples where the average twin width is less than a few micrometers. The s-wave surface layer is π/2 out of phase with the bulk d-wave phase.

We emphasize this fact because the π/2 phase shift is experimentally verifiable. A YBCO-Pb corner junction type experiment with one junction on the (100) surface and the other on the (001) surface of a highly twinned YBCO sample should be able to detect this π/2 phase shift, as was previously suggested by Sigrist et al. We give a schematic diagram of the proposed experimental configuration in Fig. The current maximum as a function of field will be shifted by a quarter of a flux quantum. The Josephson coupling to the Pb at the (100) junction is predominantly due to the YBCO d-wave component since d-wave suppression is not expected at this
surface. Since the c-axis Josephson coupling results from the smaller s-wave component, it is much weaker than the a-axis coupling. The (001) junction should therefore have a much larger area than the (100) junction in order to minimize any DC offset of the interference pattern.

\[ \Phi \]

\[ \text{YBCO} \]

\[ \Phi / \Phi_0 \]

**FIG. 4.** Schematic of proposed YBCO-Pb SQUID experiment. One junction is on the (100) surface of the YBCO, the other on the (001) surface. The $\pi/2$ shift between the bulk d-wave phase and the (001) surface s-wave phase shifts the current maximum by a quarter of a flux quantum.

V. CONCLUSION

The present theory can reconcile the puzzles mentioned at the outset. The surprisingly large value of $I_c R_n$ is ascribed to the partial, coherence of the s-wave component at the surface. The fact this coherence is only partial gives a reasonable account of the overall differences between single crystal and twinned samples. The fact that single-boundary junctions always show a change in sign of the s component is also consistent: in this case the twins are larger. These experiments also show excess current at zero applied magnetic field. This would be consistent with some partial coherence of the s component across the boundary, as the larger (stronger) of the two twins appears to control the weaker one. Hence we believe that the theory can account for all observations. The experiment of the previous section would be a critical test of the theory. Experiments in which the relative twin populations are precisely controlled would serve to rule out the alternative explanation in which the current is due to accidental anisotropy introduced in the growth process.

One important qualitative conclusion about the underlying physics of the bulk can be drawn from this picture: s-wave competes with d-wave in YBCO. If our model is correct, then the naive estimate of 10% admixture of s-wave as a proportion of d-wave remains roughly correct. Expressed in the language of Eq. [1], we have that $|\Psi_s|/|\Psi_d| \sim \alpha_{sd}/(\alpha_s - \alpha_d) \sim 0.1$ at low temperatures. If s-wave were very strongly suppressed by a large positive $\alpha_s$, it would not be so easily induced by the lattice distortion.

The present theory would predict that only those materials with orthorhombic distortion should show c-axis tunneling. Recently, c-axis Josephson tunneling between Ba$_2$Sr$_2$CaCu$_2$O$_{8+x}$ and Pb has been observed in spite of the absence of an orthorhombic distortion in this material. However, due to the fact that $I_c R_n \sim 1\mu eV$, orders of magnitude less than the gap value, we believe that this interesting effect is physically different from that seen in the YBCO experiment.

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