Orthorhombically Mixed s and $d_{x^2-y^2}$ Wave Superconductivity and Josephson Tunneling

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The effect of orthorhombicity on Josephson tunneling in high $T_c$ superconductors such as YBCO is studied for both single crystals and highly twinned crystals. It is shown that experiments on highly twinned crystals experimentally determine the symmetry of the superconducting twin boundaries (which can be either even or odd with respect to a reflection in the twinning plane). Conversely, Josephson experiments on highly twinned crystals can not experimentally determine whether the superconductivity is predominantly $s$-wave or predominantly $d$-wave. The direct experimental determination of the order-parameter symmetry by Josephson tunneling in YBCO thus comes from the relatively few experiments which have been carried out on untwinned single crystals.
Introduction. Although many of the currently studied high-temperature superconductors are orthorhombic (including YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) and Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, they are often regarded as being approximately tetragonal. Thus, in the current debate concerning the symmetry of the order parameter, the attention has been focussed on attempting to distinguish between order parameters having $s$, $d_{x^2-y^2}$ or possibly other symmetries (see [2] for a recent review). As a result of the orthorhombicity of the high $T_c$ superconductors, however, the $s$ and $d_{x^2-y^2}$ order parameters are coupled [3]. This note discusses some of the consequences of orthorhombicity and of this coupling in the interpretation of Josephson tunneling experiments, and focuses on what can be directly measured experimentally without relying on microscopic theories or models of the superconducting state and the twin boundaries.

Experimental studies of the Josephson effect have been suggested [3] as a method of establishing the order parameter symmetry in the case of unconventional superconductivity. Measurements of the basal-plane Josephson currents in YBCO [7–11] have found these currents to be characteristic of $d$-wave symmetry. On the other hand, a measurement [12] of the $c$-axis Josephson current raised questions about the $d$-wave interpretation.

Below, I study the Josephson currents from an orthorhombic superconductor such as YBCO to an $s$-wave superconductor such as Pb for both single crystal and highly twinned (all twins occurring with equal weight) samples. The superconducting state of YBCO can be shown to be either even or odd with respect to reflection in a twinning plane, and it is demonstrated that Josephson tunneling experiments on highly twinned samples determine this symmetry.

Contrary to current views, however, Josephson experiments on highly twinned samples can not determine whether the superconductivity is predominantly $s$- or $d$-wave. The Josephson current from a single twin contains both $s$- and $d$-wave components (as it must because a single twin is orthorhombic). The averaging over all twins, however, effectively imposes tetragonal symmetry and results in a Josephson current which depends on only a single symmetry component (either $s$- or $d$-wave); which component is selected depends on the superconducting twin-boundary symmetry. Josephson experiments on highly twinned samples will thus measure the magnitude of the selected component, but will give no information on the magnitude of the other component. In order to determine whether the symmetry of the order parameter is predominantly $d$-wave or predominantly $s$-wave, it is essential to measure the relative magnitude of the two components (which can be done on untwinned single crystals, but not on twinned crystals).

In view of the above, the direct experimental determination of the order-parameter symmetry by Josephson tunneling in YBCO thus comes from the relatively few experiments [4] which have been carried out on untwinned single crystals.

Mixed $s$- and $d$-wave superconductivity. The Ginzberg-Landau free energy density describing coupled $s$-wave and $d_{x^2-y^2}$ order parameters ($\psi_s$ and $\psi_d$, respectively) is

$$F = \alpha_s|\psi_s|^2 + \alpha_d|\psi_d|^2$$
$$+ \frac{1}{2}\beta_s|\psi_s|^4 + \frac{1}{2}\beta_d|\psi_d|^4 + \beta_4|\psi_s|^2|\psi_d|^2$$
$$+ (-1)^{\epsilon}\alpha_s(\psi_s^* \psi_d + \psi_s \psi_d^*) + \beta_4(\psi_s^* \psi_d^* + \psi_s \psi_d)$$
$$+ (-1)^{\epsilon}[\beta_1|\psi_d|^2 + \beta_2]|\psi_s|^2](\psi_s^* \psi_d^* + \psi_s^* \psi_d)$$

where $\epsilon = 1, 2$ refers to one of the two possible twin orientations which occurs in the YBCO materials. Except for the factors of $(-1)^{\epsilon}$, which are important below, this free energy has been given in [3]. I assume that the twin boundary between two twins (as in Fig. 1) is a plane of reflection symmetry of the underlying crystal lattice. If the $d$- and $s$-wave order parameters describing superconductivity in twin 1 are $(\psi_d, \psi_s)$, then a reflection in the twinning plane gives a superconducting state of twin 2 described by order parameters $(-\psi_d, \psi_s)$ and having the same free energy as the corresponding state of twin 1; hence the factor $(-1)^{\epsilon}$ which appears at various places in the free energy.

By definition, $d$-wave superconductivity will be modelled by the assumption that $\alpha_s = \alpha_s'(T - T_{d0})$, while $\alpha_d$ is taken to be positive. (Conversely, $s$-wave superconductivity will be modelled by taking $\alpha_s = \alpha_s'(T - T_{cs})$ with $\alpha_d > 0$.) For $d$-wave superconductivity, minimizing $F$ with respect to $\psi_s^*$ in zero external magnetic field gives $\psi_s$ correct to terms linear in $\psi_d$ as

$$\psi_s = (-1)^{\epsilon+1}(\alpha_s/\alpha_d)\psi_d$$

Also $|\psi_d|^2 = \alpha_d'(T_d - T)/\tilde{\beta}_d$; here $\tilde{\beta}_d$ is a constant approximately equal to $\beta_d$ if $\alpha$ is small, and $T_d$ differs from $T_{d0}$ when $\alpha$ is non zero.

Since $\psi_s$ can be found as an expansion in powers of $\psi_d$ (and this is true for both $s$- and $d$-wave superconductivity as these have been defined above), $\psi_s$ can be substituted for in terms of $\psi_d$ only (the coupling to $\psi_s$ nevertheless being implicitly taken into account).

The nature of the superconducting twin boundary between twins 1 and 2 will be determined by the interface free energy per unit area

$$F_{12} = B(\psi_{d1}^* \psi_{d2} + \psi_{d1} \psi_{d2}^*)$$

where, as just explained, $\psi_s$ is implicitly taken into account. If $B < 0$ (or $B > 0$), the free energy is minimized by taking $\psi_{d1} = \psi_{d2}$ (or $\psi_{d1} = -\psi_{d2}$), and the superconducting state will be odd (or even) under reflection in the twin boundary, respectively. Note that if the twin boundary is odd, $\psi_{d1} = \psi_{d2}$, but that because of the factor $(-1)^{\epsilon}$ in the above free energy, $\psi_{d1} = -\psi_{d2}$. Thus,
calling a twin boundary a normal or a \( \pi \) boundary according to whether or not the order parameter changes sign could be ambiguous, and it is better to identify the type of twin boundary by its reflection symmetry.

**Basal-plane Josephson currents.** The twin boundaries in YBCO are normal to the [110] and [\( \overline{1} \)10] directions. A YBCO crystal will consist of some regions where orthorhombic twins are separated by [110] twin boundaries, and other regions where orthorhombic twins are separated by [\( \overline{1} \)10] twin boundaries. For want of a better name, I will use the word “macrodomain” to refer to a region where the twin boundaries all have the same orientation. Thus twinned YBCO can be considered to be made up of [110] macrodomains and [\( \overline{1} \)10] macrodomains. I begin by discussing a [\( \overline{1} \)10] macrodomain, which contains [\( \overline{1} \)10] twin boundaries and two types of twins (twin 1 and twin 2) as shown in Fig.1.

Consider a Josephson junction between twin 1 of YBCO and Pb. The normal \( \mathbf{n} \) (directed from YBCO to Pb) to the plane of the junction is taken to lie in the YBCO a-b plane and to make an angle \( \theta \) with the a-axis of twin 1 (see Fig.1). The Josephson current from twin 1 to Pb is

\[
\theta_1 = ig(\theta_1)(\psi_d^*\psi_{pB} - \psi_d\psi_{pB}^*).
\]

Now write

\[
g(\theta) = d(\theta) + s(\theta)
\]

where

\[
d(\theta) = [g(\theta) - g(\theta + \pi/2)]/2,
\]

\[
s(\theta) = [g(\theta) + g(\theta + \pi/2)]/2.
\]

The constraints of orthorhombic symmetry require

\[
g(\theta) = g(-\theta), \ g(\theta + \pi) = g(\theta),
\]

\[
d(\theta + \pi/2) = -d(\theta), \ s(\theta + \pi/2) = s(\theta).
\]

It is clear from these symmetry properties of \( d(\theta) \) and \( s(\theta) \) (and this will appear in more detail below) that these functions will exhibit characteristic \( d_x^2 - y^2 \)-wave and \( s \)-wave behavior, respectively, in Josephson tunneling experiments; the above separation of \( g(\theta) \) into \( d(\theta) \) and \( s(\theta) \) is thus a fundamental step in the interpretation of the basal plane Josephson tunneling from an orthorhombic superconductor to an \( s \)-wave superconductor in terms of \( d \)- and \( s \)-wave components. The following Fourier series representations of the functions \( g(\theta) \), \( d(\theta) \) and \( s(\theta) \) incorporate the above-mentioned symmetries:

\[
g(\theta) = \Sigma g_n \cos(2n\theta),
\]

\[
d(\theta) = \Sigma d_{2 + 4n} \cos[(2 + 4n)\theta],
\]

\[
s(\theta) = \Sigma s_{4n} \cos(4n\theta).
\]

In all cases the sums are over all integral \( n \) from zero to infinity.

The Josephson current from twin 2 to Pb in the direction \( \theta \) can be obtained from that for twin 1 by reflecting in the twin-twin interface (see Fig. 1). Hence

\[
\theta_2 = -ig\left(\frac{\pi}{2} + \delta - \theta\right)(\psi_{d2}^*\psi_{pB} - \psi_{d2}\psi_{pB}^*).
\]

For the purpose of interpreting corner squid experiments, the current along two orthogonal directions in the basal plane (which will be called the \( x \) and \( y \) directions) will be calculated; the \( x \) and \( y \) directions are chosen to be at angles of \( \theta = \theta_1 + \delta/2 \) and \( \theta = \theta_1 + (\pi + \delta)/2 \) from the \( \mathbf{a}_1 \) direction (see Fig. 1). The angle \( \theta_1 \) (just defined in terms of \( \theta \) by the preceding equations) is used rather than \( \theta \) to define the \( x \) and \( y \) directions because \( \theta_1 = 0 \) is a symmetrical orientation of \( x \) and \( y \) relative to the two twin orientations. Finally, the expressions given below for the Josephson currents will be for currents averaged with equal weights over the two twins in a [\( \overline{1} \)10] macrodomain, and will be given in the form

\[
\theta_{avg,\alpha} = c_{\alpha}(\theta_1)|\psi_d\psi_{pB}| \sin(\phi_d - \phi_{pB})
\]

where \( \alpha \) is \( x \) or \( y \), \( \psi_d = |\psi_d|\exp(i\phi_d) \), and \( \psi_{pB} = |\psi_{pB}|\exp(i\phi_{pB}). \)

For the case of even twin-twin interfaces, \( \psi_{d1} = \psi_{d2} = \psi_d \), and

\[
c_x(\theta_1) = -\left[d(\theta_1^+) - d(\theta_1^-)\right] + s(\theta_1^+) + s(\theta_1^-),
\]

\[
c_y(\theta_1) = -\left[-d(\theta_1^+) - d(\theta_1^-)\right] + s(\theta_1^+) + s(\theta_1^-),
\]

where \( \theta_1^\pm = \theta_1 \pm \delta/2 \). For odd twin-twin interfaces, for which \( \psi_{d1} = \psi_{d2} = \psi_d \),

\[
c_x(\theta_1) = -\left[d(\theta_1^+) + d(\theta_1^-)\right] + s(\theta_1^+) - s(\theta_1^-),
\]

\[
c_y(\theta_1) = -\left[-d(\theta_1^+) + d(\theta_1^-)\right] + s(\theta_1^+) - s(\theta_1^-).
\]

The above discussion (which assumed that the entire crystal was made up of a single [\( \overline{1} \)10] macrodomain) can be extended to the case where both [110] and [\( \overline{1} \)10] macrodomains are present. By assuming that the [110] and [\( \overline{1} \)10] twin boundaries are orthogonal, the expressions for \( c_x \) and \( c_y \) for the [110] macrodomain can be shown to be identical to those for the [\( \overline{1} \)10] macrodomain, except that \( \delta \) is replaced by its negative. Thus, if an average over equally weighted macrodomains is taken, and the phase of \( \psi_d \) is assumed to be the same in both types of macrodomains, the terms in \( c_x \) and \( c_y \) which are odd in \( \delta \) drop out, and results characteristic of perfect tetragonal symmetry are obtained. For even twin boundaries, Josephson currents with \( s \)-wave symmetry are obtained, i.e.

\[
\theta_2 = \theta_{\alpha}(\theta_1) = s(\theta_1 + \delta/2) + s(-\theta_1 + \delta/2)
\]
where an overbar on \( c \) indicates that an average over the two macrodomains has been taken (in addition to the previous average over the two twin types for each macrodomain). For odd twin boundaries, currents with \( d_{x^2−y^2} \)-wave symmetry are obtained, i.e.

\[
\overline{\psi}_x(\theta_1) = -\overline{\psi}_y(\theta_1) = d(\theta_1 + \delta/2) + d(-\theta_1 + \delta/2).
\]

On the other hand, if \( \psi_d \) changes sign going on from the [110] macrodomain to the [1̅10] macrodomain, then even twin boundaries yield \( d_{xy} \)-wave currents with

\[
\overline{\psi}_x(\theta_1) = -\overline{\psi}_y(\theta_1) = d(\theta_1 + \delta/2) - d(-\theta_1 + \delta/2).
\]

where odd twin boundaries yield \( L_z \)-wave (where \( L_z \) is the \( z \)-component of an angular momentum) currents with

\[
\overline{\psi}_x(\theta_1) = \overline{\psi}_y(\theta_1) = s(\theta_1 + \delta/2) - s(-\theta_1 + \delta/2).
\]

Now suppose that the basal-plane Josephson currents in YBCO, when determined on samples in which all twins and macrodomains are present with equal weights, are characteristic of \( d_{x^2−y^2} \)-wave symmetry, as is suggested by experiment [7,10]. From above this implies that the twin boundaries are odd and \( \psi_d \) does not change sign between [110] and [1̅10] macrodomains.

It is to be emphasized that the experiments on heavily twinned samples do not determine experimentally whether the superconductivity in orthorhombic YBCO is predominately \( s \)-wave or predominately \( d_{x^2−y^2} \)-wave. Above, the function \( g(\theta) \) characterizing the basal plane Josephson currents was separated into two components, a \( d \)-wave component \( d(\theta) \) and an \( s \)-wave component \( s(\theta) \). However, as shown above, in the case of odd twin boundaries and \( \psi_d \) not changing sign between macrodomains, the average contribution of the function \( s(\theta) \) to the Josephson currents is zero. Thus, the experiments measure only the \( d \)-wave component \( d(\theta) \), independently of whether \( d(\theta) \) is much greater than or much less than \( s(\theta) \).

Josephson tunneling experiments on untwinned single crystals [7,10] can, of course, classify the superconductivity as being predominately \( s \)- or \( d_{x^2−y^2} \)-wave.

Finally, note that calling the superconductivity predominately \( s \)- or \( d \)-wave according to the relative average magnitudes of \( s(\theta) \) and \( d(\theta) \), while an appropriate definition from the point of view of tunneling experiments, is only one possible definition (and one in which the anisotropy of the tunneling matrix elements will play a role). Another definition which is not necessarily equivalent could be based on the relative magnitudes of the \( s \) and \( d \)-wave contributions to the gap function.

**Josephson currents in the c direction.** Symmetry considerations show that the \( c \)-axis Josephson currents for twins 1 and 2 (e.g. see Fig. 1) have the form

\[
j_{zx} = c_z(-1)^j(\psi_{d1}^*\psi_{p1} - \psi_{d2}^*\psi_{p2}).
\]

For odd twin boundaries, \( \psi_{d1} = \psi_{d2} \), and the Josephson current averages to zero when averaging over an equal weighting of twins 1 and 2. However, in the \( c \)-axis measurements of Josephson tunneling [12], the Josephson current is found not to average to zero. Thus, these experiments would seem to imply that the twin boundaries are even, in contradiction to the result implied by the above interpretation of the basal-plane Josephson current experiments.

**Conclusions.** Josephson tunneling experiments measuring Josephson currents from an orthorhombic superconductor such as YBCO into an \( s \)-wave superconductor such as Pb, and carried out on samples in which all twins and macrodomains have equal weights, experimentally determine the tw-boundary reflection symmetry of the superconducting state. In the case of YBCO, the basal-plane experiments \( \bar{l} \) characteristic of \( d \)-wave symmetry suggest that the superconducting state has odd reflection symmetry with respect to the twinning plane, whereas a \( c \)-axis Josephson experiment [12] suggests that the superconducting state has even twinning-plane symmetry.

A similar analysis carried out for YBCO to YBCO Josephson tunneling shows that here also the experiments on twinned crystals experimentally determine the twin boundary symmetry; the results of [7,8,11] suggest that the twin boundaries have even symmetry, in contrast to the results of [13] which suggest even-symmetry twin boundaries.

The above interpretation assumes that, in twinned crystals, all twins and macrodomains are present with equal weights. If this is not true, the interpretation is not valid. For example, if, in the experiment of Sun et al. [12], twins of type 1 occupied an area of the Josephson junction which was significantly larger than that occupied by twins of type 2, the assumption of odd symmetry twin boundaries would be acceptable since there would then be only a partial cancellation of the Josephson currents, and a nonzero Josephson current would be observed. The results of the \( c \)-axis Josephson experiments and the basal-plane Josephson experiments could then be reconciled. Since this question of the weighting of the different twins and macrodomains is of crucial importance to the interpretation, it would be of interest to try to determine this weighting experimentally, for example by microstructural studies of the Josephson junctions used for both the \( c \)-axis and the basal-plane experiments.

Another important conclusion is that, contrary to currently accepted ideas, Josephson tunneling experiments on orthorhombic YBCO crystals containing all twins and macrodomains with equal weights can not directly experimentally determine whether the superconductivity is predominately \( d \)- or \( s \)-wave (but can, as described above, experimentally determine the nature of the twin boundaries). Our direct experimental knowledge of the order parameter symmetry as determined by Josephson experiments thus comes from experiments performed on untwinned single crystals [14,4].
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Figure Captions

Fig. 1 (a) Shows a $[\overline{1}10]$ twin boundary(DB), the two twins with the directions of their $a$ and $b$ axes, and the interface between YBCO and Pb (ABC) with its normal $n$. (b) Definition of the angles between $a_1$, $a_2$, and $n$. 