Energy Gap Structure in Bilayer Oxide Superconductors

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We consider a model for bilayer superconductors where an interlayer pairing amplitude $\Delta_\perp$ co-exists with intralayer pairing $\Delta_{ii}$ of $d_{x^2-y^2}$ symmetry. This model is motivated by a recent photoemission experiment reporting the splitting of the nodes of the energy gap. In addition to offering a natural explanation of this observation, the model has a number of new experimental consequences. We find that the new state is accompanied by a spontaneous breaking of the tetragonal symmetry. We also find that the out-of-phase oscillation of $\Delta_{ii}$ and $\Delta_\parallel$ gives rise to a new Raman active mode. The phase of $\Delta_\parallel$ may also become imaginary, leading to a state which breaks time reversal symmetry, which may have important implications for tunnelling experiments.

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In the past two years, there has been mounting evidence for nodes in the gap in oxide superconductors [1,2]. Recently, a new class of experiments which are phase sensitive have provided strong evidence for a sign change of the order parameter as a function of angle [3,4], consistent with $d$ symmetry. At the same time, there are several experiments which appear to be inconsistent with the simple $d_{x^2-y^2}$ state. For example, Sun et al [3], have made tunnel junctions between $YBa_2Cu_3O_7-\delta$ ($YBCO$) and Pb and obtained Josephson current along the $c$-axis. Secondly, a recent report of fractional vortices tied to grain boundary interfaces [4] has been interpreted as requiring a time reversal symmetry breaking state near the interface [5]. Finally, Ding et al [6] measured the energy gap as a function of angle using angular resolved photoemission in $Bi_2Sr_2CaCu_2O_8$ ($Bi-2212$) and claim that the energy gap does not vanish along $(\pi, \pi)$ as expected for the $d_{x^2-y^2}$ state. Instead, the node is split into two, lying approximately $10^\circ$ from the $45^\circ$ line. Another group [7] also reported a finite energy gap in the $(\pi, \pi)$ direction and studied its temperature dependence. Taken together, these experiments suggest that the energy gap structure may be more complicated than $d_{x^2-y^2}$. In this paper we show that a modification of the $d_{x^2-y^2}$ state due to interlayer pairing provides a scenario whereby the experiments mentioned above can be explained. Our picture also leads to a number of predictions which can be tested experimentally.

Band structure calculations have yielded a surprisingly large interlayer hopping term between the bilayers, given by $t_{\perp}(\vec{k})c_{\alpha\sigma}(\vec{k})c_{\beta\sigma}(\vec{k})$ where 1 and 2 refer to the layers. Chakravarty et al [10] have proposed the parametrization

$\tilde{t}_{\perp}(\vec{k}) = \frac{1}{4} t_{\perp}^0 (\cos k_x a - \cos k_y a)^2$ with $t_{\perp}^0 \approx 0.24$ eV.

Andersen et al [11] recently showed that the unusual $\vec{k}$ dependence originates from hopping via the Cu 4s orbitals, and that it leads to an interlayer exchange energy of order $J_{\perp} \approx 20$ meV, consistent with the lower bound of 8 meV given by neutron scattering [12]. It has been proposed [13,14] that the relatively large exchange term, when enhanced by intralayer antiferromagnetic correlations, is responsible for the spin gap phase found in bilayer systems [15]. Furthermore, Ubbens and Lee [13] have argued that in the superconducting phase, a pairing amplitude $\Delta_{ij} = \langle c_{ij\uparrow}(\vec{r})c_{ij\downarrow}(\vec{r}) \rangle$ appears in addition to the intraplane order parameter $\Delta_{ii\parallel}(\vec{n}) = \langle c_{ii\parallel\uparrow}(\vec{r})c_{ii\parallel\downarrow}(\vec{r}+\vec{n}) \rangle$, $i = 1, 2$ which is of $d$ symmetry. This leads to a quasi-particle dispersion relation $\tilde{E}_{\pm}(\vec{k}) = (\xi_k^2 + |\Delta_{ii\parallel}|^2)^{1/2}$ where $\xi_k = k_x - i \mu_\perp \Delta_{ii\parallel}(\vec{k})$ and $\Delta_{ii\parallel}$ are proportional to $\Delta_{11} = \Delta_{22}$ and $\Delta_{12}$ respectively. Since the nodes of this state are given by the zeros of $|\Delta_{ii\parallel}|$, if $\Delta_{ii\parallel}$ has $d_{x^2-y^2}$ symmetry, the nodes are shifted from the 45° direction and split into two nodes [13]. This provides a natural explanation of the observation by Ding et al [6].

Encouraged by the experiment, we decided to re-examine the interlayer pairing model. Ubbens and Lee [13] included $J_{\perp}$ but not the $t_{\perp}$ term in their consideration. In this paper we add both the $t_{\perp}$ and $J_{\perp}$ terms to the standard $t - J$ model. Whereas Ubbens and Lee attempted to justify the appearance of $\Delta_{12}$ microscopically, in this paper we take a more phenomenological approach and assume the co-existence of $\Delta_{ii\parallel}$ and $\Delta_{ii\perp}$. This is motivated by experiment: as far as we know, the present scenario is the only one which is consistent with both the node splitting [6] and the sign change of the order parameter as $\vec{k}$ varies from $0$ to $\pi/2$, as required by the corner SQUID experiment [6]. The purpose of this work is to explore the consequences of the assumed interlayer pairing amplitude, so that further experiments can confirm or falsify this picture.

We begin by treating the bilayer $t - J$ model (including $t_{\perp}$ and $J_{\perp}$) using the slave boson mean field method, which is equivalent to the Gutzwiller approximation. The tight binding band $\epsilon(\vec{k}) = -2t_{\parallel}(\cos k_x a + \cos k_y a)$ is split into bonding and anti-bonding bands $g_{\pm} = (c_{\pm} \pm c_{\mp})/\sqrt{2}$ with dispersion $\epsilon_{\pm}(\vec{k}) = \epsilon(\vec{k}) \pm t_{\perp}(\vec{k})$, where $t_{\perp}$ is of order $J$ and $t_{\perp}(\vec{k}) \simeq X_0 t_{\perp}(\vec{k})$ where $X_0$ is of order $x$, the doping concentration. Thus, in the mean field theory the effective interlayer hopping is reduced by $x$, simply because in the strongly correlated metals, the electron, on average, must find a vacancy to hop.
The resulting Fermi surface is shown in Fig 1 for \( x = 0.15 \). As emphasized by Anderson [16], in the normal state, coherent hopping is really not possible between the layers. We expect the bonding-antibonding splitting to be smeared out, but a region of low lying excitations may exist in the \( \vec{k} \) space between the two Fermi surfaces. Fig. 1 bears a striking resemblance to the photoemission data of Dessau et al [17].

In the superconducting state, coherent hopping between the planes indeed occurs, and we should take the band splitting seriously. With the basis sets \( \{ c_{1,\vec{k}↑}, c_{1,-\vec{g}↓}, c_{2,\vec{k}↑}, c_{2,-\vec{g}↓} \} \), the mean field Hamiltonian takes the form

\[
\begin{bmatrix}
\epsilon(\vec{k}) - \mu & \Delta_{||}(\vec{k}) & i \Delta_{\perp}(\vec{k}) \\
-\Delta_{||}^* & -\epsilon(\vec{k}) + \mu & -i \Delta_{\perp}(\vec{k}) \\
i \Delta_{\perp}^* & -i \Delta_{||}(\vec{k}) & -\epsilon(\vec{k}) + \mu
\end{bmatrix}
\]

It is easily seen that the bonding anti-bonding bands \( g_{\pm} \) block diagonalize this matrix, so that the \( g_{\pm} \) bands are separately paired by \( \Delta_{\pm}(\vec{k}) = \Delta_{||}(\vec{k}) \pm \Delta_{\perp} \), resulting in the quasi-particle spectrum

\[
E_{\pm}(\vec{k}) = (\xi_{\pm}(\vec{k})^2 + |\Delta_{||}(\vec{k}) \pm \Delta_{\perp}|^2)^{1/2}
\]

where \( \xi_{\pm}(\vec{k}) = \epsilon_{\pm}(\vec{k}) - \mu \). We can choose \( \Delta_{||} \) to be real and positive. If \( \Delta_{\perp} \) is also real and positive, the nodes are split as before, but the split nodes are associated with the \( \pm \) bands separately, as indicated in Fig. 1. It is clear from Fig. 1 that for real \( \Delta_{\perp} \), the onset of interlayer pairing implies a spontaneous breaking of the tetragonal symmetry of the model. This is a consequence of the inclusion of \( t_{\perp} \). The two degenerate states of the broken symmetry correspond to \( \Delta_{\perp} \) being positive or negative. We shall refer to these degenerate states as \( d \pm s \). Due to the vanishing of \( t_{\perp}(\vec{k}) \) along \((\pi, \pi)\), this asymmetry is difficult to resolve near the nodes. However, in a given domain, the \( g_{\pm} \) band has a different gap along \( MY \) than \( MY \) and the resulting asymmetry in the electronic state is expected to couple linearly to the orthorhombic strain \( \epsilon = (a-b)/(a+b) \).

There is one additional complication to this discussion, in that we should consider the possibility that \( \Delta_{\perp} \) is purely imaginary. We shall refer to this state as \( d + is \), which has a minimum gap of \( |\Delta_{\perp}| \). Indeed, a mean field calculation shows that this state is lower in energy than \( d + s \). The Ginzburg-Landau free energy is given by \( F = F_0 + F_e \), where for simplicity we have fixed \( \Delta_{11} = \Delta_{22} = |\Delta_{||}| \).

\[
F_0 = a_{||}|\Delta_{||}|^2 + b_{||}|\Delta_{||}|^4 + a_{\perp}|\Delta_{\perp}|^2 + b_{\perp}|\Delta_{\perp}|^4 + d_{\perp}|\Delta_{\perp}^2| |\Delta_{||}|^2 + d_{\parallel}(\Delta_{||}^2\Delta_{\perp}^2 + c.c.)
\]

\[
F_e = \alpha \epsilon (\Delta_{||}^2 + c.c.)
\]

where \( F_e \) describes the linear coupling to the strain discussed earlier. [14] In mean field theory, we found that \( d_1 = 4d_2 > 0 \). If we write \( \Delta_{\perp} = |\Delta_{\perp}| e^{i\phi} \), the \( d_2 \) term is proportional to \( \cos 2\phi \) with a positive coefficient, and is minimized by \( \phi = \frac{\pi}{2} \). The \( F_e \) term, on the other hand, is proportional to \( \cos \phi \), so that \( \phi = 0 \) or \( \pi \) (the \( d \pm s \) state) is stabilized in systems with pre-existing orthorhombic distortions such as \( YBCO \). In tetragonal systems, we add an elastic energy term \( F_E = \frac{1}{2}\kappa^2 \epsilon^2 \) to \( F \) and minimize with respect to \( \epsilon \). This produces a term \( -2(\alpha^2/\kappa^2)|\Delta_{||}|^2|\Delta_{\perp}|^2 \cos^2 \phi \) which opposes the \( d_2 \) term. The \( d + s \) state is stabilized provided \( \alpha^2/\kappa^2 > 2d_2 \). The observation of split nodes in the nominally tetragonal \( Bi-2122 \) presumably means that this condition is satisfied and \( d + s \) is stabilized. Thus we predict that, for bilayer systems with tetragonal symmetry, a superconducting state with split nodes is accompanied by a spontaneous breaking of the tetragonal symmetry. The \( Bi-2122 \) compound is not truly tetragonal due to the superlattice modulation in the \((\pi, \pi)\) direction, but the \( a \) and \( b \) lattice constants are predicted to become unequal at low temperature. The best test of the prediction is probably in tetragonal materials such as the bilayer mercury compounds. Even in \( YBCO \), we expect an additional distortion below \( T_c \). There is evidence for this in the literature [18]. The coupling to lattice distortions also lead us to expect anomalies in the transverse ultrasonic spectrum below \( T_c \) [13].

As mentioned earlier, the \( d + s \) state explains the photoemission data of ref. 8. Indeed, the lower branch min \((\Delta_{++}, \Delta_{--})\) shown in the insert of Fig. 1 can be fitted to the experimental data with \( \Delta_{||}(\vec{k} = 0) \approx 30 \text{ meV} \) and \( \Delta_{\perp} \approx 5 \text{ to } 9 \text{ meV} \) [20]. In ref. 8, only data associated with the \( g_- \) band (dashed line in Fig. 1) was shown. The question arises as to what happened to the upper branch of the insert in Fig. 1. Two possibilities need to be examined: the photoemission may be from a single domain of \( d + s \) state or from multiple domains of \( d + s \) and \( d - s \). In the first case we expect a single peak with different gaps \((\Delta_{||}(\vec{k} = 0) \pm \Delta_{\perp})\) at the \( M - Y \) and \( M - M \) crossings. In the second case the peak should be a superposition of two peaks with a splitting of \( 2\Delta_{\perp} \). The data is consistent with a splitting of \( 10 \text{ meV} \) or less [20] which may require a slight angular dependence of \( \Delta_{\perp}(\vec{k}) \) so that it is smaller along \( \Gamma - M \) than along \( \Gamma - Y \). At present, data is not available which covers both \( \Gamma - M \) and \( \Gamma - Y \) quadrants in the same sample, so that these two possibilities cannot be distinguished.

The existence of several order parameters should lead to new collective modes, which are amplitude and phase modes associated with \( \Delta_{ij} = |\Delta_{ij}| e^{i\phi_{ij}} \), \( i, j = 1, 2 \). The amplitude modes are expected to be high in frequency and damped and we shall focus on the phase modes only. There are three modes corresponding to the three phase degrees of freedom.
(1) The in-phase oscillation of $\Delta_{11}, \Delta_{22}, \Delta_{12}$ is the Bogoliubov-Anderson mode which is coupled to total charge density and pushed up to the plasma frequency.

(2) The out-of-phase mode $\phi_{11} - \phi_{22}$. Recently this mode was discussed in the context of the interlayer tunnelling model of Chakravarty et al [1]. However, as pointed out by Wu and Griffin, the existence of this mode is a general feature of two layers coupled by Josephson tunnelling and was described by Leggett [2], who noted that the usual phase-number commutation relation $[\phi_{ii}, N_i] = 2i$ implies a coupling of $\phi_{11} - \phi_{22}$ to $N_1 - N_2$, i.e., to charge transfer between the planes. The mode frequency $\omega_J$ can be computed by combining the Josephson relations $\phi = 2eV$ and $\dot{\phi}_{12} = E_J \sin \phi$ with $eV = \gamma n_{12}$, where $\gamma = C^{-1} + d\mu/dn$. $n_{12}$ is the interlayer density oscillation, $C$ is the capacitance per area, and $E_J \approx \tilde{t}_\alpha^2 N^2(0)|\Delta|^2$ is the Josephson energy per area between the planes. We find $\omega_J = (2E_J\gamma)^{1/2}$ which just is the Josephson plasma frequency. If we ignore the capacitance term and approximate $\gamma = d\mu/dn$ by $N(0)^{-1} \approx J a^2$, we find that $\omega_J \approx x_{\Delta \perp}(\Delta / J)^{1/2}$ which is quite stable, so that this mode is probably strongly damped.

(3) Finally, the mode which is of greatest interest to us is the out-of-phase oscillation between $\phi_{12}$ and $\phi_{11} = \phi_{22}$. Since the free energy given by Eq. (3) depends weakly on this phase difference, we expect this mode to be low-lying in frequency. Furthermore, this phase mode leads to a rearrangement of the quasi-particle spectrum in the plane, since a change in $\phi_{12}$ from 0 to $\pi$ interpolates between the $d+s$ and $d+is$ states. This should couple to charge oscillation within each plane, but with the total charge conserved within each layer. Thus, we expect this mode to be Raman active. To confirm this qualitative picture, we have carried out a collective mode calculation in a model where we introduce phenomenological attractive coupling constants to stabilize $\Delta_{\|}$ and $\Delta_{\perp}$. We treat this model in mean field theory and carry out an expansion around the mean field in a standard way [3]. For simplicity we have set $\epsilon = 0$. We find that the globally stable states correspond to either $\Delta_{\|}$ or $\Delta_{\perp} = 0$, while the $d+is$ state lies slightly higher in energy but is locally stable. The global energy balance depends on details of the interaction and the presence of $\epsilon$. For example, a sufficiently large $\epsilon$ will stabilize the $d+s$ state because of the linear coupling in Eq. (4). Since our goal in the part of the analysis is to understand the collective mode rather than the microscopic origin of the energy gaps, we proceed to expand about the locally stable $d+is$ state.

We find that the Josephson mode $\phi_{11} - \phi_{22}$ decouples as expected. Setting $\phi_{11} = \phi_{22}$, we find that $\phi_{11}, \phi_{12}$ and $\rho_2$ are coupled, where $\rho_2$ is the $l = 2$ component of the density fluctuation in the plane. The $3 \times 3$ matrix can be diagonalized. Details of this calculation will be given elsewhere, but the main result is an estimate of the out-of-phase mode frequency, which turns out to be of order $|\Delta_{\perp}|$. For $|\Delta_{\perp}| \ll |\Delta_{\|}|$, its damping should be small. Furthermore, its coupling to $\rho_2$ implies that it is Raman active in the $B_{1g}$ symmetry [2]. The detection of this mode will be a strong confirmation of the existence of $\Delta_{\perp}$.

Next we examine what effects the more complicated order parameter structure have for tunnelling experiments. In ref. 4, tunnelling is between oxide superconductors across a grain boundary. A reasonable tunnelling Hamiltonian may be of the form $H_t = t_0 \sum_{i=1,2} c_{iL}^\dagger c_{iR} + c.c.$ which will lead to a Josephson coupling of the form

$$H_J = T_J(\Delta_{+L}^1 \Delta_{+R} + \Delta_{-L}^1 \Delta_{-R} + c.c.)$$ (5)

The two terms in Eq. 5 will generate two Josephson currents with different dependences on the grain boundary orientation [3]. However, at present the half integer flux experiment in specially designed rings is done on twinned samples, so that the $d \pm s$ domains are difficult to distinguish from the pure $d_{2-2}^{-}$ state.

In the experiment which measures the critical current of a SQUID loop [3], the tunnel junctions are between the oxide superconductor and a conventional superconductor, and the tunnelling current is in the $a-b$ plane. In this case, it may be more reasonable to assume a tunnelling Hamiltonian of the form $H'_t = t_0 \sum_{i=1,2} c_{iL}^\dagger c_{iR} + c.c.$ where $c_{iR}$ destroys an electron in the conventional superconductor. In this case, only the symmetric order parameter $\Delta_{+}$ forms the Josephson coupling. Thus, in principle, if a single domain sample can be made with variable junction orientations, the shift of the node shown by the solid line in the insert of Fig. 1 can be detected.

Since the current is observed along the $c$ axis between $YB_{CO}$ and a conventional superconductor. The $d+s$ state by itself cannot explain why the critical current is relatively insensitive to whether the $YB_{CO}$ is untwinned or highly twinned. This is because the coupling to the lattice strain $\epsilon$ (shown in Eq. (4)) will lock the $d+s$ state to one set of twins and the $d-s$ states to the other. Since the $d$ order parameter is insensitive to twinning (otherwise the phase sensitive experiment of references 3 and 4 will not work in twinned samples), the Josephson current will have opposite signs on the two sets of twins and tend to cancel. One possible way out of this dilemma is to postulate the existence of regions where the $d+is$ becomes stabilized. This is plausible due to the small energy differences expected and can happen near the twin boundaries. With this assumption a net Josephson current may be obtained. We defer a detailed discussion of this possibility to a later publication [4].

The trapped fluxes on grain boundaries between $YB_{CO}$ films with different orientations are measured and interpreted as being due to the appearance of fractional
charged vortices [1]. Such vortices require the existence of a time-reversal symmetry breaking state near the interface [2]. Recently, Kuboki and Sigrist [2] offered an explanation of this state as being due to an admixture with a proximity induced $s$ component of the order parameter. In our picture, the possible existence of the complex $d + i s$ state near an interface suggests an alternative origin of the time-reversal symmetry breaking state. The two alternatives can be distinguished by searching for similar effects in single layer materials.

Finally, we address the issue of the possibility of a second phase transition below $T_c$. Usually, a Landau theory of the form given by Eq. (3) with two order parameters implies two phase transitions, because the coefficients $a_\perp$ and $a_\parallel$ change signs at different temperatures. In the underdoped case, the transition is complicated by strong fluctuation effects, so that, in some sense, the spin gap transition may be considered the first transition, and the superconducting $T_c$ the second transition. This raises the interesting possibility that the situation may be reversed in optimally doped or overdoped cases, which would imply that the transition at $T_c$ is to a pure $d_{x^2-y^2}$ order parameter, followed at some lower temperature by the onset of interlayer pairing ($\Delta_\perp \neq 0$). Recently, a second transition at 30K is reported in $T_2$ measurements in fully oxygenated samples of $YBCO$ [24]. Obviously, it will be interesting to look for lattice distortions near this temperature. Another interesting possibility is to study the fate of the fractional vortices at temperatures above 30K.

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Figure 1. Mean field calculation of the Fermi surface including hopping between bilayers for hole doping $x = 0.15$. The parameters $t/J = 3, t^{(0)}_1/J = 2.4$ and $J_+/J = 0.2$ are used. The solid and dashed lines are the Fermi surfaces for the bonding ($g_+$) and antibonding ($g_-$) bands. Solid and dashed arrows indicate the approximate location of the nodes associated with $\Delta^+$ and $\Delta^-$ in the $d + s$ state. The inset shows a schematic picture of the angular dependence ($\theta = 0$ is along the $\Gamma - M$ axis) of the gap functions $|\Delta^+|$ (solid) and $|\Delta^-|$ (dashed) for the $d + s$ state ($\Delta^+$ real and positive). Note that $\Delta^\pm$ are associated with the solid and dashed Fermi surfaces respectively. For the $d - s$ state, $|\Delta^+|$ is given by the dashed line.