IMPORTANCE OF HYBRID PAIRS IN TWO BAND AND HIGH T_c SUPERCONDUCTORS

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We consider a system of two hybridized bands (a and c states) in the presence of electron-phonon interaction.We analyze a current debate in the literature concerning the importance of hybrid (a-c) superconducting pairs in the system. We explain the origin of the discrepancies for the case where the energy difference between the bonding and anti-bonding bands at the Fermi energy is larger than the Debye energy. Using a Hartree-Fock tight-binding model for a high T_c superconductor, derived from band structure calculations, we show that more than a third of the superconducting pairs in the system are of hybrid (d-p) character.

Several theoretical works dealt with superconductivity in two-band systems (see for example refs. 1-6). Most of the models were used to describe properties of heavy fermion superconductors. Some of them consider the electron-phonon interaction as the mechanism responsible for superconductivity [3-6]. The studies of refs. 4 and 6 conclude that superconducting pairs built with one electron of each band (hybrid pairs) play a secondary role and that always one of the two types of intraband pairs dominates. On the other band, the author of ref.5 claims that when the hybridization is large, the presence of hybrid pairs is important. Here, we show that the latter is in fact the case and we define how large the hybridization should be. The conclusions of ref.4 concerning hybrid pairs are invalid because of an unfortunate mistake in a sign of the relevant coupling constant (G_{123} of ref.4 should always be attractive).

It seems that the authors of ref.6 ascribe the discrepancy with the results of ref.5 to the fact that they considered all the effective electron-electron interactions which appear after performing the canonical transformation [5], while in ref.5 only some terms were retained. We argue in this paper, that the main difference between both works, which reflects directly on the number of hybrid pairs, is the hypothesis concerning the hybridization.

After a general discussion, we consider the specific case of a simple tight-binding model based on band structure calculations [7] and already used to explain the instabilities and critical temperature of $La_{2-x}M_xCuO_4$ [8]. This allows us to replace the hypothesis usually made concerning the hybridization and band structures [5,6] for more realistic ones.

The starting Hamiltonian of the system can be written in the form [5]:

$$H = H_{el} + H_{ph} + H_{el-ph} \tag{1}$$

where

$$H_{el} = \sum_{k\sigma} \varepsilon^a_k a^+_{k\sigma} a_{k\sigma} + \sum_{k\sigma} \varepsilon^c_k c^+_{k\sigma} c_{k\sigma} + \sum_{k\sigma} (V_k a^+_{k\sigma} c_{k\sigma} + h.c.) \tag{2}$$

$$H_{ph} = \sum_{qr} \hbar\, \omega_{rq}\, b^+_{rq} b_{rq} \tag{3}$$

$$H_{el-ph} = \sum_{ee'} \sum_{kqr\sigma} g^{kq}_{ee'} (b_{rq} + b^+_{r-q})\, e^+_{k+q\sigma}\, e'_{q\sigma} \tag{4}$$

Here e, e' are used to denote one of the bands (a or c). $e^+_{k\sigma}$ creates an electron with energy ε^e_k, wave vector $\vec{k}$ and spin σ in the e band.

The angular momentum degeneracy is neglected. b^+_{rq} creates a phonon in the r mode, with wave vector $\vec{q}$ and energy ω_{rq}. H_{el} represents the purely electronic part of the Hamiltonian.

The last term in Eq.(2) is the hybridization. Eq.(3) describes the purely phononic part and Eq.(4) the electron-phonon interaction.

Arguments justifying the application of model (1)-(4) or similar ones to heavy fermion systems can be found in refs.9 and 2.

For the high Tc system $La_{2-x}M_xCuO_4$, a model of the same form was developed [8] on the basis of the two dimensional tight-binding model proposed by Mattheis [7] to reproduce the essential features of his band structure calculations near the Fermi energy. In this model one of the bands (we choose the "a" one) represents Bloch states built with Cu 3d orbitals of x^2-y^2 symmetry. The other band is a linear combination of the 2p orbitals of O(2) atoms, which are directed along the Cu-O(2) nearest neighbour distance:

$$c^+_{k\sigma} = \frac{p^+_{xk}\sin(k_x a/2) - p^+_{yk}\sin(k_y a/2)}{(\sin^2(k_x a/2) + \sin^2(k_y a/2))^{1/2}} \qquad (5)$$

Here a is the lattice parameter and $p^+_{x_i k}$ are Bloch states of the $2p_{x_i}$ orbitals of the O(2) atoms which have their nearest-neighbour Cu atoms in the x_i direction.

The parameters of the model take the explicit form [8]:

$$\varepsilon^a_k = \varepsilon_{Cu} \quad , \quad \varepsilon^c_k = \varepsilon_O \qquad (6)$$

$$V_k = iV_o\,(\sin^2(k_x a/2) + \sin^2(k_y a/2))^{1/2} \qquad (7)$$

$$g^{kq}_{ac} = -\beta V_o \left(\frac{\hbar}{2N\,\omega_{rq}[\sin^2(k_x a/2)+\sin^2(k_y a/2)]}\right)^{1/2} \times$$

$$\times \Big\{\frac{1}{2\sqrt{M_{Cu}}}\,\vec{e}^{(r)}_{Cu}(\vec{q})\cdot[\vec{1}_x\sin(k_x a)+\vec{1}_y\sin(k_y a)] -$$

$$-\frac{1}{\sqrt{M_O}}\,[\vec{e}^{(r)}_{o_x}(\vec{q})\cdot\vec{1}_x\,\sin(k_x a/2)\cos((k_x+q_x)a/2) +$$

$$+\vec{e}^{(r)}_{o_y}(\vec{q})\cdot\vec{1}_y\,\sin(k_y a/2)\cos((k_y+a_y)a/2]\Big\} \qquad (8)$$

$$g^{kq}_{aa} = g^{kq}_{cc} = 0 \qquad (9)$$

and as it should be because of the hermiticity of the Hamiltonian:

$$g_{ca}^{k,q} = \overline{g_{ac}^{k+q,\ -q}} \tag{10}$$

where the bar over the second member indicates complex conjugation. $\vec{e}_y^{(r)}(\vec{q})$ denotes the polarization vector for atom Y of the unit cell for the corresponding vibration mode. From band structure calculations [7,10] one has:

$$V_o = -\sqrt{3}(pd\sigma) = 3.2\ \text{eV}\ ,\ \varepsilon_{Cu} - \varepsilon_O \cong 3.5\ \text{eV},$$

$$\beta = (pd\sigma)^{-1}\ d(pd\sigma)/dr \cong -\ 1.6\ \text{Å}^{-1} \tag{11}$$

It is important to note that for systems with inversion symmetry, the invariance of the Hamiltonian under inversion imposes restrictions on the parameters of the model. The electron and phonon operators under inversion change in the following way:

$$Ie_k^+ = P_e\ e_{-k}^+ \tag{12}$$

where $P_e^2 = 1$. If the e states are Bloch functions constructed with atomic orbitals, P_e is the parity of the atomic orbitals[11]. For the phonons $P_b = -1$. As a consequence one should have:

$$\varepsilon_{-k}^e = \varepsilon_k^e,\ V_{-k} = P_a P_c V_k,\ g_{e\ e'}^{-k,-q} = -P_e P_{e'} g_{e\ e'}^{k,q}, \tag{13}$$

Almost no attention has been paid to these symmetry requirements [1-6] although some physical properties depend critically on the signs appearing in eqs.(13), especially for f-d systems [9,11,12] where $P_f P_d = -1$. For the high Tc model we are considering, although the p states are odd, the linear combination of Eq.(5) and the d states transform like (12) with $P_c = P_d = 1$. This happens because the two band model was derived from a multiband one in which the d orbitals mix with more than one degenerate p band [8].

In the usual treatments of model (1)-(4) the phonons are eliminated through a canonical transformation [5-6]. This leaves the Hamiltonian described by Eq.(2) plus effective electron-electron interactions. The normal properties of the system are described by Eq.(2) alone. Diagonalization of H_{el} gives a bonding and an antibonding band:

$$\begin{aligned} \beta_{k\sigma}^+ &= -w_k a_{k\sigma}^+ + u_k\ e^{-i\psi k}\ c_{k\sigma}^+ \\ \alpha_{k\sigma}^+ &= u_k\ e^{i\psi k}\ a_{k\sigma}^+ + w_k\ C_{k\sigma}^+ \end{aligned} \tag{14}$$

with

$$E_k^{\alpha(\beta)} = \frac{\varepsilon_k^a + \varepsilon_k^c}{2} (\pm)\, r_k, \quad r_k = \left[\left(\frac{\varepsilon_k^a - \varepsilon_k^c}{2}\right)^2 + |V_k|^2 \right]^{1/2}$$

$$u_k = \left[\frac{1}{2} + \frac{\varepsilon_k^a - \varepsilon_k^c}{4r}\right]^{1/2}, \quad w_k = (1-u_k^2)^{1/2}, e^{i\psi k} = \left|\frac{V_k}{V_k}\right| \tag{15}$$

The effective electron-electron interaction acts only in a region of width $2\omega_D$ around the Fermi energy, where ω_D is the Debye energy. In the following we assume that for each $\vec{k}$ at least one of the states α or β is outside the range of the interaction:

$$|E_k^\alpha - \varepsilon_F| > \omega_D \quad \text{or} \quad |E_k^\beta - \varepsilon_F| > \omega_D \tag{16}$$

where ε_F is the Fermi energy. As a consequence, using (13) one sees that superconducting pairs of the form $\alpha^+_{-k\sigma}, \beta^+_{k\sigma}$, do not appear and that for each $\vec{k}$ at most one of the pairs $\alpha^+_{k\sigma}\alpha^+_{-k\sigma'}$, $\beta^+_{k\sigma}\ \beta^+_{-k\sigma'}$ can exist. Here we assume as usual zero total momentum of the pair. The hypothesis (16) is the most usual case to be expected and is certainly valid in the model for $La_{2-x}M_xCuO_4$ where the Fermi level is near E_Q^α, $\vec{Q} = (\pi/a, \pi/a)$[8]. As can be seen replacing (6),(7) and (11) in (15), only antiboding states with given $\vec{k}$ cross the Fermi energy and the bonding states for the same $\vec{k}$ (or $-\vec{k}$) lie several eV below the Fermi energy. Nevertheless, hypothesis (16) is not valid for heavy fermion systems if the Fermi level is "pinned" near a dispersionless f band and $|V_k|\ \ \omega_D$ for $\vec{k}$ at the crossing of the f and d bands.

Since in terms of bonding and antibonding bands, Eq.(16) implies that only one type of pairs exists for each $\vec{k}$, the relative importance of aa, cc and ac pairs for each $\vec{k}$ is given directly by the coefficients u_k, w_k of Eq.(15), independently of the particular form of $g^{kq}_{ee'}$. Defining the relative proportion of hybrid pairs by (we supress the spin indices since the result does not depend on singlet or triplet pairing):

$$R_h^k = \frac{|\langle a_k^+\ c_{-k}^+\rangle|^2 + |\langle a_{-k}^+\ c_k^+\rangle|^2}{|\langle a_k^+ a_{-k}^+\rangle|^2 + |\langle c_k^+ c_{-k}^+\rangle|^2 + |\langle a_k^+ c_{-k}^+\rangle|^2 + |\langle a_{-k}^+ c_k^+\rangle|^2} \tag{17}$$

we obtain using Eqs.(13)-(15):

$$R_h^k = \frac{|V_k|^2}{2|V_k|^2 + (\varepsilon_k^q - \varepsilon_k^c)^2/2} \tag{18}$$

The corresponding result for aa and cc pairs is $R^k_{aa} = u_k^4 (w_k^4)$ and $R^k_{cc} = w_k^4 (u_k^4)$, if condensation of αα (ßß) pairs takes place. The R^k values coincide with the corresponding Eqs.-(17) of ref.5. We see that the relative importance of hybrid pairs is determined by the ratio between the hybridization and half the difference of the dispersion relations, for the values of $\vec{k}$ for which one of the hybridized bands crosses the Fermi energy. For $2|V_k| \gg |\varepsilon^a_k - \varepsilon^c_k|$ (as in the tight-binding model proposed by Mattheis for $La_{2-x}M_xCuO_4$ [7]) $R^k_{aa} = R^k_{cc} = 1/4$, $R^k_h = 1/2$. If instead $V_k = 0$,

$R^k_h = 0$ (as long as hypothesis (16) is valid).

In both refs.5 and 6 the hypothesis of homothetic bands ($\varepsilon^c_k = C\varepsilon^a_k$) is made, while the hypothesis concerning the hybridization is different: a) $V_k = V$ in ref.5; b) $V_k = V\varepsilon^a_k$ in ref.6. As a consequence of b) u_k and w_k are independent of $\vec{k}$ and this allows the authors of ref.6 to include all the electron-electron interactions coming from the canonical transformation and to simplify the otherwise involved self-consistency equations with the only additional hypothesis of constant $g^{kq}_{ee'}$. However, to ask that in one and the same surface in the reciprocal space, the two conditions $\varepsilon^a_k = \varepsilon^c_k$ and $V_k = 0$ are simultaneously satisfied restricts considerably the validity of the model. As a direct consequence of the assumption made in ref.6, Eq.(17) gives $R^k_h = V/[2V + (1-C)^2/2] \cong 0.02$ for the parameters chosen there. The fact that the number of hybrid pairs is much larger than 2% in their work is probably due to the breaking of hypothesis (16) in their model(αß pairing becomes important). Nevertheless Eq.(16) is valid for large enough hybridization ($|V_k| > \omega_D$) and in this regime, the claim that increasing the hybridization gap decreases the role of f-d pairing [6] is not valid any more, as can be seen from the V_k dependence of $E_k(\beta)$ and R^k_h (Eqs.(15) and (18)).

Assumption a) of constant hybridization is in fact satisfied for $\vec{k}$ at the Fermi energy in the model for $La_{2-x}M_xCuO_4$. Then, in the one-dimensional numerical analysis of ref.5, the different R^k depend on the position of the Fermi energy with respect to the crossing point of the two bands (see Fig.1 of ref.5) and do not reduce to featureless constants when Eq.(16) is valid. Note that for systems with one f and one d orbital per unit cell, both hypothesis a)and b) do not satisfy the symmetry requirements (13) with

$P_fP_d = -1$. Nevertheless we can still conclude that hybrid pairs are important if $2|V_k| > |\varepsilon_k^a - \varepsilon_k^c|$ (or in terms of the hybridized bands $2\sqrt{2}|V_k| > E_k^\alpha - E_k^\beta$)over most of the Fermi surface.

Finally, we can easily determine the numbers R^k giving the intensity of different types of pairs for the model for $La_{2-x}M_xCuO_4$ that we consider here, using Eqs.(6), (7) and (15). These numbers do not depend on $\vec{k}$ in this case. The Fermi surface is determined from [8]:

$$\cos(k_x a) + \cos(k_y a) = f(x) \qquad (18)$$

with $f(0) = 0$. Using the parameters given by (11) one gets $R_{dd} = .55$, $R_h = .38$, $R_{pp} = .07$. The variation with x is very small. Changing $\varepsilon_{Cu} - \varepsilon_0$ to 2.26 eV or lower values, R_h becomes larger than R_{dd}.

In conclusion we have shown that for large enough hybridization the relative importance of hybrid pairs is large, in agreement with ref.[5]. In particular they begin to dominate when at the Fermi surface the hybridization is larger than both the Debye energy and the difference of unperturbed band energies. Conclusions in the opposite sense are due to a mistake in the relevant interactions [4] or to very special assumptions concerning the hybridization [6]. We have illustrated the result for the specific case of a model proposed for high Tc superconductors [8] with realistic parameters obtained from band structure calculations.

In this particular case, the superconductivity can be studied within a one band model (antibonding α states only) with effective $\alpha\alpha$ interactions [5,8]. In the general case, even if hypothesis (16) is satisfied, one should consider the interaction between $\alpha\alpha$ and $\beta\beta$ pairs condensating in different regions of the Fermi surface [13].

An interesting problem that remains still to be attacked is that which arises when Eq. (16) is no more valid, as may be the case for some heavy fermion systems, taking into account all the effective electron-electron interactions coming from the canonical transformation [5], and using realistic assumptions for the parameters satisfying the symmetry requirements (13). A step in that direction is made in ref.12.

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