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LETTER TO THE EDITOR

A mean-field approximation to the two-band model for copper oxide superconductors: normal-state properties

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Abstract. The normal-state properties of a high-T_c superconductor are studied using a mean-field approximation. It is found that the excess holes in the oxygen orbitals form unusual metallic bands. The spin of the moving hole is bound as a singlet to the underlying copper spins because of strong exchange interaction. Thus the charge carrier has charge e and spin zero. Binding causes the holes to be heavy, but not as heavy as in a Kondo lattice system. It is also found that the condensation (or binding) temperature, the Fermi temperature and the band gap are distinct (i.e., there is no scaling).

It has been suggested that pairing in high-temperature superconductors (Bednorz and Müller 1986) arises from a purely electronic mechanism. Anderson (1987) has proposed a resonating-valence-bond (RVB) picture based on the large-U one-band Hubbard model for the two-dimensional (2D) copper sublattice with a finite concentration of empty sites. On the other hand, the correct starting point should be a model originally proposed by Emery (1987), which involves both the copper and the oxygen orbitals. Zhang and Rice (1988) have recently constructed a mapping in which the two-band model is reduced to a one-band model. Their main argument is that an excess hole in an oxygen orbital will bind strongly with a copper spin—the binding energy being of the order of J, the oxygen–copper exchange energy. If J is much larger than the copper–copper exchange energy J_{dd}, then the effect is to remove a copper spin, thus creating an 'empty' site on the copper sublattice.

In this Letter, we consider the effect of binding directly in the context of the two-band model. In particular, we study the *normal-state* behaviour of the excess holes when the excess hole concentration is sufficiently large. We consider the model Hamiltonian

$$H = \sum \varepsilon_c c^+_{r\sigma} c_{r\sigma} + \sum \varepsilon_a a^+_{rl\sigma} a_{rl\sigma} + \frac{U}{2} \sum_{r\sigma} n_{r\sigma} n_{r-\sigma} + t \sum (c^+_{r\sigma} f_{r\sigma} + \text{HC}) \tag{1}$$

where $c^+_{r\sigma}$ ($a^+_{rl\sigma}$) creates a hole at the copper (oxygen) site, and $n_{r\sigma} = c^+_{r\sigma} c_{r\sigma}$. The index $l = 1, 2$ denotes the position of the oxygen site relative to a copper site. The operator $f_{r\sigma}$ is the sum of the four a-operators surrounding a copper site:

$$f_{r\sigma} = a_{r1\sigma} - a_{r-\hat{x},1\sigma} + a_{r2\sigma} - a_{r-\hat{y},2\sigma}.$$

In model (1) $\varepsilon_a > \varepsilon_c$, and U is much larger than all the other energy scales, so double occupancy of a copper site is rare. The total hole density is taken to be $n = 1 + \delta$. For

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$\delta = 0$, most of the holes are at the copper sites. Generally, we could add a repulsive U-term for the oxygen sites also. We ignore this term on the assumption that δ is sufficiently small that there are few doubly occupied oxygen sites. The Coulomb repulsion energy V of the copper and oxygen holes is assumed to be smaller than U, and in the simplest approximation serves to renormalise the level positions; we thus assume that ε_c and ε_a are properly renormalised.

We assume that $U \gg \varepsilon_a - \varepsilon_c > t$. Then, for $\delta \geq 0$, there is exactly one hole per copper site, which acts as a pure spin. For $\delta = 0$, the oxygen orbitals can be eliminated perturbatively. This leads to a one-band antiferromagnetic super-exchange model involving the copper spins alone, with the exchange energy $J_{dd} \simeq t^4/(\varepsilon_a - \varepsilon_c)^3$ + higher-order terms. When $\delta > 0$, the excess holes go into the oxygen orbitals. This suppresses the tendency towards antiferromagnetic ordering in the copper sublattice because (i) the oxygen holes move about fairly rapidly between oxygen sites by flipping the copper spins, and (ii) there is a super-exchange interaction between the copper and oxygen holes whose exchange energy ($\simeq t^2/(\varepsilon_a - \varepsilon_c)$ or $t^2/[U - (\varepsilon_a - \varepsilon_c)]$) is much larger than the copper–copper exchange energy, and which directly competes with J_{dd}. For $\delta > 0$, the empty and the doubly occupied states for the copper orbital can be eliminated, which leads to the following approximate Hamiltonian:

$$H = \sum \varepsilon_c c^+_{r\sigma} c_{r\sigma} + \sum \varepsilon_a a^+_{rl\sigma} a_{rl\sigma} - J_1 \sum c^-_{r\sigma} f_{r\sigma} f^+_{r\sigma'} c_{r\sigma'}$$
$$- J_2 \sum f^+_{r\sigma} c_{r\sigma} c^+_{r\sigma'} f_{r\sigma'} + J_{dd} \sum \boldsymbol{S}_r \cdot \boldsymbol{S}_{r'} \qquad (2)$$

where J_{dd} is the copper–copper super-exchange energy and

$$J_1 = t^2/(\varepsilon_a - \varepsilon_c) \qquad J_2 = t^2/[U - (\varepsilon_a - \varepsilon_c)].$$

The Hamiltonian (2) must be supplemented with the constraint that there is exactly one hole per copper site. The J_1 and J_2 terms correspond to processes in which the intermediate state is empty and doubly occupied, respectively. These terms, in addition to exchange interaction, also give rise to effective hopping of the excess holes.

When δ is very small, the antiferromagnetic background will inhibit the motion of the holes, strongly renormalising their masses, and possibly localising them. The problem of a single hole has received considerable attention (Trugman 1988, Shraiman and Siggia 1988, Schmitt-Rink *et al* 1988). For larger δ, the effect of the J_{dd} term is expected to be reduced, and a hole band will be formed. Even without the last term in (2) the properties of such a metal are likely to be vastly different from those of ordinary metals. In this Letter, we study these properties using a simple mean-field theory. As a first approximation, we thus ignore the last term in (2).

The simplest way to handle the constraints (which commute with the Hamiltonian) is to introduce Lagrange multipliers λ_r by adding a term $\sum \lambda_r c^+_{r\sigma} c_{r\sigma}$. In the spirit of the mean-field approximation we replace λ_r by a constant λ— the same value for each site— so the constraints are satisfied only on average.

We note that in the model defined by (2), part of the interaction term can be written as $-J \sum d^+_r d_r$ where $J = J_1 + J_2$ and the singlet objects $d_r = f_r c_{r\uparrow} - f_{r\uparrow} c_r$ behave as approximate bosons, and may condense, binding the oxygen hole to the copper spin.

Although there are two oxygen orbitals for every r, one of these can be decoupled by a simple canonical transformation. This is best done in the momentum space. Let

$$b_{q1\sigma} = \Lambda_q^{-1/2}[(1 - e^{-iq_x}) a_{q1\sigma} + (1 - e^{-iq_y}) a_{q2\sigma}]$$

$$b_{q2\sigma} = \Lambda_q^{-1/2}[-(1 - e^{iq_y})a_{q1\sigma} + (1 - e^{iq_x})a_{q2\sigma}]$$

where

$$\Lambda_q = 4 - \xi_q \qquad \xi_q = 2(\cos q_x + \cos q_y).$$

Then it is easily shown that $f_{q\sigma} = \Lambda_q^{1/2} b_{q1\sigma}$. Since the coupling terms involve only the f-operators, the b_{q2} sector is decoupled and corresponds to a free-hole band of zero band width and energy ε_a.

For the mean-field approximation, let $s_\sigma = \langle c_{r\sigma}^+ f_{r,-\sigma}^+ \rangle = \sigma s$, and $b^2 = \langle f_{r\sigma}^+ f_{r\sigma} \rangle$. Then, making a Hartree–Fock decomposition of the interaction term in (2), we arrive at the mean-field Hamiltonian

$$H_{MF} = E_0 + (\varepsilon_c^* - \mu) \sum c_{q\sigma}^+ c_{q\sigma} + \sum (\varepsilon_b(q) - \mu) b_{q1\sigma}^+ b_{q1\sigma} + (\varepsilon_a - \mu) \sum b_{q2\sigma}^+ b_{q2\sigma}$$
$$- Js \sum \Lambda_q^{1/2} (\sigma c_{q\sigma}^+ b_{-q-\sigma}^+ + \text{HC}) \tag{3}$$

where μ is the chemical potential, $J = J_0 + J_1$, and $E_0 = 2JN(s^2 - b^2)$. The position of the effective copper level is given by

$$\varepsilon_c^* = \varepsilon_c + \lambda + J_2 b^2 - J_1(4 - b^2)$$

where λ is the Lagrange multiplier. Finally

$$\varepsilon_b(q) = \varepsilon_a + J_0 \Lambda_q \qquad J_0 = \tfrac{1}{2}(J_1 - J_2).$$

The band described by $\varepsilon_b(q)$ is generated by the mean-field theory and has a band width $8J_0$. In our model, since $J_0 > 0$ and $0 < \Lambda < 8$, $\varepsilon_b(q) \geqslant \varepsilon_a$. If there is no binding, $s = 0$, and, since there is one hole per copper level, $\varepsilon_c^* = \mu$. At $T = 0$, the upper band described by $\varepsilon_b(q)$ is empty, and all the excess holes go into the b_2 level, so $\mu = \varepsilon_a$. In this case, $b^2 = \langle f_{r\sigma}^+ f_{r\sigma} \rangle = 0$, and the ground-state energy is simply $N(\varepsilon_c + \delta\varepsilon_a - 4J_1)$.

For $s \neq 0$, the last term in (3) describes 'hybridisation' between the b_1 band and the c level. The Hamiltonian is then diagonalised using the canonical transformation:

$$c_{q\sigma} = \cos\theta_q \alpha_{q\sigma} + \sin\theta_q \beta_{-q-\sigma}^+ \qquad b_{q1\sigma} = \cos\theta_q \beta_{q\sigma} - \sin\theta_q \alpha_{-q-\sigma}^+$$

with $\tan 2\theta = 2J\Lambda_q/(\varepsilon_c^* + \varepsilon_b(q) - 2\mu)$. This generates two quasi-hole bands:

$$E_\pm(q) = \tfrac{1}{2}[(\varepsilon_c^* + \varepsilon_b(q) - 2\mu)^2 + 4J^2 s^2 \Lambda_q]^{1/2} \pm \tfrac{1}{2}(\varepsilon_b(q) - \varepsilon_c^*). \tag{4}$$

For $J_1 > J_2$, $E_+(q) > 0$, whereas a portion of $E_-(q)$ is negative (see figure 1). Since energies are measured relative to the chemical potential, this implies the existence of a sharp Fermi surface.

To proceed further, we need to calculate the μ, ε_c^* and the parameter s. For $T = 0$, this means solving the following equations:

$$\tfrac{1}{2}(1 - \delta) = \int_0^{\Lambda_0} d\Lambda\ \rho(\Lambda) \tag{5a}$$

$$\tfrac{1}{2}(1 - \delta) = \int_{\Lambda_0}^{8} d\Lambda\ \rho(\Lambda)(\Lambda + y)/P(\Lambda) \tag{5b}$$

$$J_0/J = \int_{\Lambda_0}^{8} d\Lambda\ \rho(\Lambda)\Lambda/P(\Lambda) \tag{5c}$$

where $P(\Lambda) = [(\Lambda + y)^2 + x^2\Lambda]^{1/2}$, $y = (\varepsilon_c^* + \varepsilon_a - 2\mu)/J_0$, $x = 2Js/J_0$, Λ_0 is the value

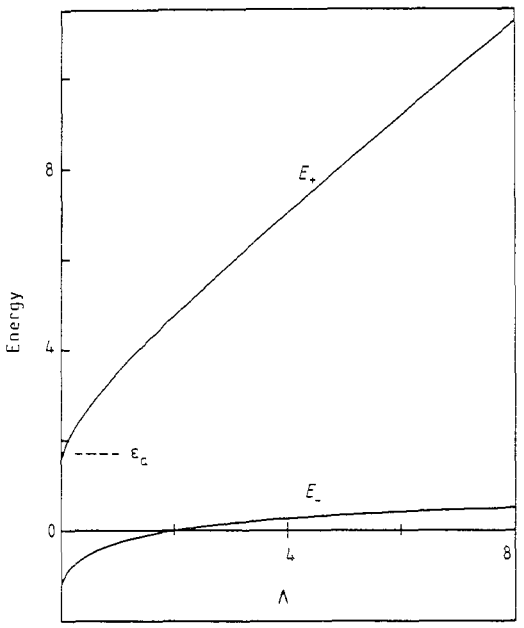

Figure 1. The quasi-hole energy in units of J_0 and as a function of Λ for $z = 0.2$ and $\delta = 0.5$. The position of the oxygen level (i.e. the b_2 band) relative to the Fermi energy is indicated by the broken line.

of Λ at the Fermi surface, i.e. $E_-(\Lambda_0) = 0$, and $\rho(\Lambda)$ is the density of states for Λ. Solving (5), we can determine μ and ε_c^* as functions of $z = J_0/J$ and δ.

Equation (5*c*) determines Λ_0 as a function of δ. Note that $0 < \delta < 1$. If $\delta > 1$, some of the excess holes will go into the b_2 band. Recall that $\Lambda_q = 4 - 2(\cos q_x + \cos q_y)$; since the right-hand side of (5*a*) is positive, $4 \geqslant \Lambda_0 \geqslant 0$, where $\Lambda_0 = 4$ corresponds to $\delta = 0$. Near $\Lambda = 4$ the two-dimensional density of states has a singularity. Thus, close to $\delta = 0$ proper care must be taken in evaluating the integrals in (5).

For finite δ, analytic progress can be made by using a constant density of states. Then we find $\Lambda_0 = 4(1 - \delta) = P(8) - P(\Lambda_0) - \frac{1}{2}x^2 \ln \psi(\Lambda_0)$, and $8z = \Lambda_0 - y \ln \psi(\Lambda_0)$, where

$$\psi(\Lambda_0) = (P(8) + 8 + y + \tfrac{1}{2}x^2)/(P(\Lambda_0) + \Lambda_0 + y + \tfrac{1}{2}x^2).$$

we have determined x and y numerically from these relations for various values of δ and z. Our main results are as follows:

(i) For our choices of parameters $J_1 > J_2$, we have $0 < z < \frac{1}{2}$, where $z = \frac{1}{2}$ corresponds to $U = \infty$ in the original model. We find that there exists a solution for all $0 < z < \frac{1}{2}$ and all $0 < \delta < 1$. The effective copper level position ε_c^* and the chemical potential μ lie below ε_a with $\varepsilon_c^* < \mu$. This means that part of the E_- spectrum is negative. The quasi-hole bands are shown in figure 1. The E_- band is narrow, i.e. quite flat as a function of Λ. This means that the quasi-holes are heavy near the Fermi surface. The bottom of the E_+ band is at $\varepsilon_a - \mu$, and thus coincides with the b_2 level. Since the Fermi surface is at zero, $\varepsilon_a - \mu$ can be considered as a band gap.

(ii) The model exhibits interesting behaviour as z is varied with fixed J and δ. For non-zero s, the condensation or binding energy is given by

$$\Delta E/J = (E_{\text{normal}} - E_{\text{RVB}})/J = 2(s^2 - zb^2).$$

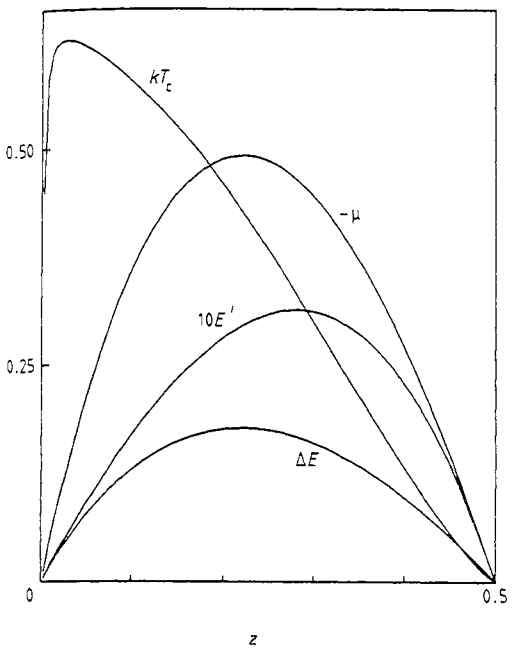

Figure 2. The condensation temperature T_c, the excess energy ΔE, the band gap $\varepsilon_a - \mu$, and ten times the slope of the lower band at the Fermi energy (proportional to T_F) versus $z = J_0/J$. All quantities are in units of J; $\delta = 0.3$ and ε_a is chosen to be zero.

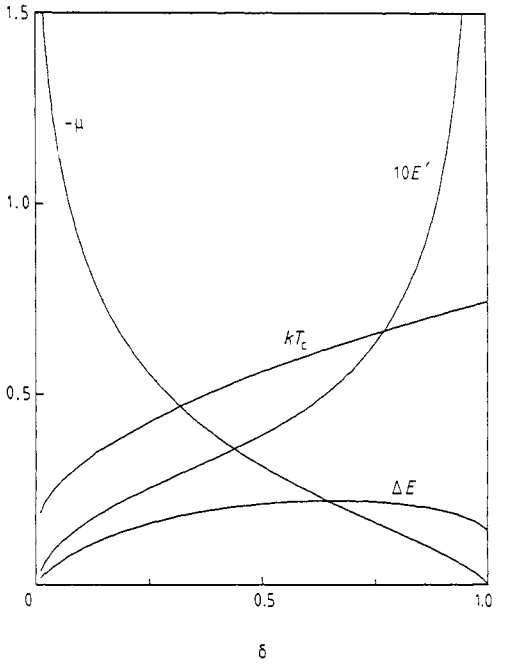

Figure 3. The same quantities as in figure 2 but as functions of δ for $z = 0.2$.

This quantity is positive in the range of parameters studied. However, $\Delta E/J \to 0$ as $z \to 0$ or $z \to \frac{1}{2}$, which means that the condensed state exists for $2(\varepsilon_a - \varepsilon_c) < U < \infty$. It is also interesting that s does not vanish in the limit of $z \to \frac{1}{2}$. However, $\Delta E/J$ vanishes, so the condensed state and the uncondensed state ($s = 0$) become degenerate in this limit (see figure 2). We also point out that $\Delta E/J$ scales roughly with $(\varepsilon_a - \mu)/J$ as a function of z.

(iii) In figure 3, we show various quantities of interest as functions of δ for fixed $z = 0.2$. The chemical potential acquires the largest negative value relative to ε_a at $\delta = 0$. As δ increases, $\varepsilon_a - \mu$ decreases and goes to zero as $\delta \to 1$. For $\delta > 1$ of course we have to consider occupancy of the b_2 band. Both $\Delta E/J$ and s (not shown) vanish at $\delta = 0$, attain maximum values around $\delta \simeq \frac{2}{3}$ and decrease with increasing δ.

We can calculate the condensation temperature T_c by assuming that $s(T_c) = 0$. In this case, $\varepsilon_c^* = \mu$. For finite T, the excess holes will be shared between the b_1 and b_2 bands. Let $\delta = \delta_1 + \delta_2$. Then we obtain, after some algebra,

$$2z = \int d\Lambda \, \frac{\rho(\Lambda)\Lambda}{\Lambda + y} \tanh \frac{J_0(\Lambda + y)}{2kT_c} \tag{6}$$

where

$$y = (kT_c/J_0) \ln(2/\delta_2 - 1)$$

and

$$\exp(-4J_0\delta_1/kT_c) = 1 - \tfrac{1}{2}\delta_2[1 - \exp(-8J_0/kT_c)].$$

For a constant density of states, we have calculated kT_c/J as a function of z and δ. These results are shown in figures 2 and 3. As seen in these figures, kT_c is the same order of magnitude as J. kT_c/J vanishes as $z \to 0$ and $z \to \frac{1}{2}$. For fixed z, kT_c/J increases with increasing δ, first rather rapidly, then more slowly.

The existence of a sharp Fermi surface implies a linear temperature dependence for the low-temperature specific heat. The temperature scale, T_F, associated with the linear term is roughly proportional to the band width of the E_- band. For $T \ll T_F$, we assume that only the E_- band continues to be occupied. Then a Sommerfeld-type expansion can be used to obtain $C/Nk \simeq \pi^2 T/2T_F$, where T_F is approximately given by

$$T_F \simeq 6(\partial E_-/\partial \Lambda)_{\Lambda=\Lambda_0}. \tag{7}$$

Since as a function of Λ the E_- band is rather narrow and flat near the Fermi surface, equation (7) implies a low value for T_F compared with J or T_c. The quantity $10E'(\Lambda_0)/J$ is shown in figures 2 and 3 as functions of z and δ. Clearly, E' is roughly an order of magnitude smaller than kT_c, so T_F is only a fraction of T_c. A small value of T_F reflects a large mass for quasi-particles (in conventional language, a large value for $\gamma \simeq C/T$). Note that this mass renormalisation comes directly from the copper–oxygen interaction, and not from the antiferromagnetic background.

To summarise, we find that in contrast to the case for ordinary metals, the normal state of the copper oxide superconductor is rather unusual. The physical picture is that of the propagation of an oxygen hole whose spin is bound to the copper spins as a singlet. Thus the charge carrier has spin zero and charge e. We find that because of the binding, the hole mass is strongly renormalised. For strong binding, a hole carries a spin in the copper sublattice, giving credence to the Zhang and Rice (1988) picture. The formation of the singlet has also been studied recently for the case of a single copper ion (Eskes and Swatzky 1988).

In many ways, the model is similar to the Kondo lattice. The differences are that the binding to the copper spins is very strong, as seen from the fact that T_c is much larger than T_{Kondo}. Also the number of conduction holes is small, and the holes are not as heavy as in the latter case.

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