Phase diagram of doped oxide superconductors: a slave-boson approach

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A phase diagram for the doped high-temperature superconductors is calculated, using a tight-binding model for the electronic states in the copper oxide planes. The model includes the oxygen $p(x)$ and $p(y)$ orbitals and the copper $3d(x^2-y^2)$ orbitals. The hybridization between the copper $d(x^2-y^2)$ and the oxygen $p(x)$ and $p(y)$ orbitals is considered, with the direct overlap between the p orbitals of neighboring oxygen ions. The Coulomb interaction is treated by the slave-boson mean-field theory. The system shows a phase diagram consisting of a highly correlated metal, for general values of the doping. For hole doping, there also exists a possible high-temperature state with completely localized d electrons. This occurs if the bare charge-transfer energy is sufficiently large. Thus, for the stoichiometric system there are two possible zero-temperature states; a metallic state and a charge-transfer insulator state. The introduction of the p-p hopping matrix element has a significant effect on the phase diagram. The paramagnetic phase of La_2CuO_4 is found to be metallic. The mean-field theory does not include the effects of the antiferromagnetic ordering, that could open an antiferromagnetic Slater gap in the metallic system.

INTRODUCTION

The stoichiometric high-temperature superconductors are insulating and antiferromagnetic,[1] however the origin of the insulating gap remains unknown. Several possibilities have been considered. One possibility is that the insulating gap induced by the antiferromagnetic order.[2] Another is that the gap is the Mott-Hubbard[3,4] band splitting due to the large interaction between the holes on a Cu ion. This latter picture has been modified[5] by including the O p bands which lies between the lower and upper Hubbard bands leading to the charge transfer insulating state. On introducing extra electrons or holes in the Cu-O planes, the Néel temperature is reduced and the antiferromagnetic order disappears.[6] Photoemission experiments show that on doping away from half filling new states appear.[7] The Fermi level is pinned to these states and the intensity associated with this narrow Fermi-level peak keeps growing until the metallic state is reached. For highly doped systems, Fermi-surface measurements[8,9] agree with calculated electronic structures.[10,12] Thus, the states at the Fermi level may be coherent quasiparticle[13-18] states.

At the stoichiometric composition, slave-boson theories[15-18] shows two distinct types of behavior, either metallic or insulating, depending upon the strength of the effective hybridization matrix element compared to the bare charge transfer gap.[15-18] In this Brief Report the phase diagram of the oxide superconductors is examined using a parametrization[11,19-21] of the Cu and O bands.

SLAVE-BOSON MEAN-FIELD THEORY

The relevant low-energy ionic states of Cu are[5] Cu^{2+} and Cu^+, corresponding to the $3d^9$ and $3d^{10}$ configurations. For the stoichiometric system, the Cu ions are in a $3d^9$ and the O ions in a $2p^6$ configuration. The tenfold degeneracy of the $3d$ band is broken by the crystal field splitting into a fully occupied sixfold degenerate t_{2g} band and a partially occupied fourfold degenerate e_g band. The latter is split due to a Jahn-Teller distortion[22] into a fully occupied $d(3z^2-r^2)$ level and a singly occupied $d(x^2-y^2)$ orbital. The crystal field is assumed to lower the energy of the out-of-plane $p(z)$ orbital and leave the $p(x)$ and $p(y)$ orbitals degenerate. Therefore, only the electronic states composed from the copper $d(x^2-y^2)$ orbital and the $p(x)$ and $p(y)$ orbitals of the O ions are considered. The total Hamiltonian is written as

$$H = H_0 + H_I ,\qquad (2.1)$$

where H_0 represents the one-body terms and H_I the interactions between the electrons. The geometry and the wave functions are depicted in Fig. 1. The kinetic energy terms of the Hamiltonian can be written as

$$
\begin{aligned}
H_0 = &\sum_{k,m} E_p(p^\dagger_{x,k,m}p_{x,k,m}+p^\dagger_{y,k,m}p_{y,k,m}) + \sum_{k,m} E_d d^\dagger_{k,m}d_{k,m}\\
&+ \sum_{k,m} [2V\cos(k_x a/2)(p^\dagger_{x,k,m}d_{k,m}+d^\dagger_{k,m}p_{x,k,m}) + 2V\cos(k_y a/2)(p^\dagger_{y,k,m}d_{k,m}+d^\dagger_{k,m}p_{y,k,m})]\\
&- \sum_{k,m} 4t\cos(k_x a/2)\cos(k_y a/2)(p^\dagger_{y,k,m}p_{x,k,m}+p^\dagger_{x,k,m}p_{y,k,m}) ,
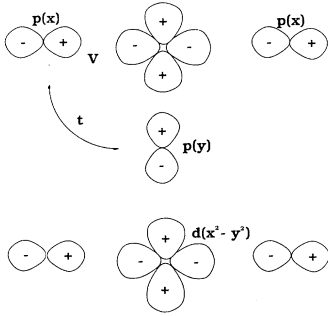\end{aligned}
\qquad (2.2)
$$

FIG. 1. The real-space structure of the two-dimensional copper oxide planes. The form of the copper $3d$ (x^2-y^2) and the oxygen p (x) and p (y) orbitals are shown schematically.

where N_s is the number of unit cells in the lattice, a is the linear dimension of the unit cell, and $d^{\dagger}_{\mathbf{k},m}$, $p^{\dagger}_{y,\mathbf{k},m}$, and $p^{\dagger}_{x,\mathbf{k},m}$, respectively, create an electron with spin m, in the Bloch state labeled by wave vector $\mathbf{k}$ in the bands composed of the d (x^2-y^2), p (y), and p (x) orbitals. The spin index m, takes on N distinct values. The first term represents the binding energy of the degenerate O p (x) and p (y) orbitals, and the second term the binding energy of the Cu $3d$'s. The third and fourth terms are the hybridization of the d with the p (y) and p (x) orbitals on the neighboring O ions. The last term is the direct hopping of electrons between the p (x) and p (y) orbitals on neighboring ions. The slave-boson field is introduced to eliminate H_I which represents the interaction between the holes on the same Cu ion, U_{dd}. The interaction U_{pp}

between holes in the orbitals of the same O ion is smaller and has been shown[19] not to appreciably affect the electronic structure, so we shall neglect this interaction. Also, the interaction U_{pd} between the p electrons and d holes[23] is estimated to be the smallest parameter in the Hamiltonian.

The above Hamiltonian is diagonalized using the standard, infinite U_{dd}, mean-field slave-boson approximation, in which no more than one hole is allowed to be present on a Cu ion. This involves a constraint on a scalar boson amplitude B_0, and results in the d level energy E_d and the hopping matrix element V being self-consistently renormalized to E_d^* and V^*, respectively. The self-consistency equations allow for the trivial solution $B_0=0$, where the constraint implies that the number of electrons in d (x^2-y^2), per site is unity. In this state the d quasiparticle weight is zero, and the d level is dispersionless as it is uncoupled to the p bands because the effective hybridization matrix element V^* is zero.

For electron doping, this trivial solution representing a state with localized d electrons cannot occur. Thus the localized is restricted to the case of hole-doped systems $\delta<0$, and occurs at high temperatures when the bare charge transfer energy E_d-E_p is sufficiently large.

The self-consistency equations always have nontrivial solutions, at zero temperature. Thus, for hole doping, there exists the possibility of a second-order transition between the coherent metallic phase and the incoherent phase as the temperature is increased. The critical temperature T_c above the d states localize is given by the solution of

$$E_d-E_d^*=V^2 2/N_s \sum_{\mathbf{k}} \left\{ \frac{(\cos k_x a/2+\cos k_y a/2)^2[Nf(E_p-4t\cos k_x a/2\cos k_y a/2)-N+1]}{(E_d^*-E_p+4t\cos k_x a/2\cos k_y a/2)} \right.$$
$$\left. + \frac{(\cos k_x a/2-\cos k_y a/2)^2[Nf(E_p+4t\cos k_x a/2\cos k_y a/2)-N+1]}{(E_d^*-E_p-4t\cos k_x a/2\cos k_y a/2)} \right\},$$

$$(2.3)$$

where the renormalized d energy level E_d^* is related to the chemical potential, $\mu(T)$, via $E_d^*=\mu(T)-k_B T\log_e(N-1)$. For hole doping any second-order instability of the low-temperature coherent phase can be inferred from the temperature dependence of the above equation. For a finite value of the hole doping $-|\delta|$ and as the temperature decreases to zero, the chemical potential $\mu(T)$ will decrease and eventually become degenerate with the p bands, first varying according to

$$\mu(T)=E_p+k_B T \ln[4N/-\delta]$$
$$+k_B T \ln\left[\sum_{n=0} \{(2n)!/(n!)^4\}(t/k_B T)^{2n}\right] \quad (2.4)$$

when $k_B T \gg t$, and then would fall in the band at zero temperature. As the chemical potential is pinned to the d level at low temperatures, the d level also becomes degenerate with the p bands. From this, one finds a minimum value for the bare charge transfer energy E_d-E_p above

which the incoherent phase may occur, at temperatures $T>T_c$. For E_d-E_p below this minimum value, the coherent state does not have a second-order transition to the incoherent state.

The sign of t plays an important role in (2.3) such that the critical temperature T_c is drastically smaller for negative t than for positive t. The dependence on the sign of t occurs as the d level hybridizes with the combination, $\cos k_x a/2|px\rangle+\cos k_y a/2|py\rangle$, which for small $\mathbf{k}$ values corresponds to the combination $|px\rangle+|py\rangle$ that diagonalizes the p $(x)-p$ (y) hopping terms, t. Since for positive values of t this is the bonding p orbital, which is energetically far removed from the d level, the hybridization process is relatively inefficient, compared with the negative t case.

At the stoichiometric composition, where $\delta=0-$, the dependence of the effective charge transfer energy $E_d^*-E_p$ on temperature shows that the critical temperature T_c is close to zero. Since the upper band is of

predominantly d character, (2.3) may no longer be satisfied if the bare charge transfer energy $E_d - E_p - 4|t|$ is sufficiently smaller than V^2. That is, by decreasing the relative strength of the bare charge transfer energy, the states at the Fermi energy can delocalize at low temperatures. The phase boundary for this delocalization transition strongly depends upon the sign of t, as inferred from the zero temperature limit. For $k = (E_d^* - E_p)/4|t| > 1$, (2.3) takes the form

$$E_d - E_p = (E_d^* - E_p)$$
$$+ 4V^2/\pi t [\pi/2 - K(k)$$
$$+ (E_d^* - E_p)/4t \{ K(k) - E(k) \}] ,$$
$$(2.5)$$

where $K(k)$ and $E(k)$ are the first and second elliptic integrals,[24] and the summations are divergent for $k < 1$. The left-hand side possesses a minimum, as a function of $(E_d^* - E_p)/4|t|$, which implies that the value of the bare charge transfer energy $E_d - E_p$ is at the boundary between the localized and itinerant phases. This phase boundary line has the asymptotic large $|V/4t|$ form

$$(E_d - E_p)_c = 4|V| - (4t)/2 + t^2/V , \qquad (2.6)$$

whereas for small values of $|V/4t|$, the phase boundary is given by the expression

$$(E_d - E_p)_c = 4|t| + 4V^2/\pi|t|\ln[\pi/2|4t/V|^2] - 2V^2/|t| ;$$
$$t < 0 , \qquad (2.7)$$
$$(E_d - E_p)_c = 4|t| + 2(1 - 2/\pi)V^2/|t|; \quad t > 0 .$$

Using positive t, the $(E_d - E_p)/4t = 1.077$ and $|V|/4t = 0.615$, extracted from tight-binding fits to LDA electronic-structure calculations,[19−21] one finds that for $\delta = 0$ La$_2$CuO$_4$ ought to be in the coherent phase. However, the effect of the term U_{pd} that has been neglected in the analysis will tend to stabilize the incoherent phase.[23] The critical value of the bare charge transfer energy that we find, $(E_d - E_p)_c/4t = 2.1$, is above most values to be found in the literature. This conclusion is similar to the results of Ref. 18. The phase diagram for $\delta = 0$ is shown in Fig. 2.
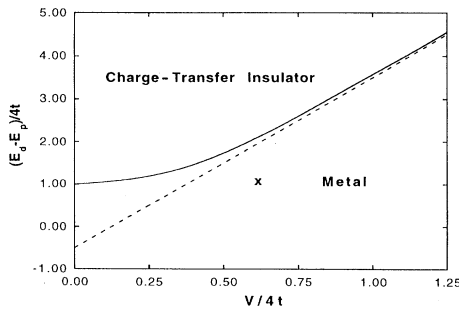
The nature of the phase boundary, can be found by examining the limit $\delta \rightarrow 0+$ of the electron-doped phase, $\delta > 0$. This phase is metallic with the effective hybridization matrix element V^* is greater than $\delta^{1/2}V$. There is always a nontrivial solution of the $T = 0$ self-consistency equations for arbitrary δ and bare charge transfer energies. In the limit $\delta \rightarrow 0+$, and for large $|E_d - E_p|$ the solution has a small value for V^* and the effective charge transfer energy $E_d^* - E_p$ is of the order of $E_d - E_p$. Since for hole doping the effective charge transfer energy, obtained by considering the $T = 0$ limit, is limited to values less than $4|t|(1 + \delta/4N)$ one concludes,[17] that for large bare transfer charge energies there is a discontinuity in E_d^*, hence $\mu(0)$, when going from infinitesimally small positive to negative δ. This discontinuity is indicative that the stoichiometric system is a charge transfer insulator, when the parameters lay in the region above the phase boundary shown in Fig. 2. Thus, one is lead to the speculation that the CuO planes ought to be metallic in stoichiometric La$_2$CuO$_4$, and the observed insulating behavior is due to the existence of three-dimensional antiferromagnetic ordering which opens up a gap at the Fermi surface.[2]

The total quasiparticle density of states is shown in Fig. 3, for $\delta = 0$, where it can be seen that there exist three structures near the Fermi energy, a Van Hove singularity at E_p, a band edge at

$$E = (E_d^* + E_p - 4t)/2 + [\{E_d^* - E_p + 4t)/2\}^2 + 8V^{*2}]^{1/2},$$

and the highest energy Van Hove singularity is found at

$$E = (E_d^* + E_p)/2 + [\{(E_d^* - E_p)/2\}^2 + 4V^{*2}]^{1/2} .$$

Only two of these peaks are below the Fermi energy. This is due to the electronic correlations which varies E_d^*, producing a sheet of nonhybridizing p bands at the Fermi surface in addition to the sheet due to the hybridized d-p bands. The nonhybridizing p states contribute a sheet given by the solution of

$$\mu = 4|t|\cos k_x a /2 \cos k_y a /2 \qquad (2.8)$$

and the hybridized p and d sheets are given by the solution

FIG. 2. The $T = 0$ phase diagram for zero doping, $\delta = 0$, the localized phase occurs for large values of the bare charge transfer gap $(E_d - E_p - 4t)/4t$, and the itinerant phase occurs for the smaller values. The asymptotic variation of the critical boundary is the dashed line. The estimated position of La$_2$CuO$_4$ is marked with an x.
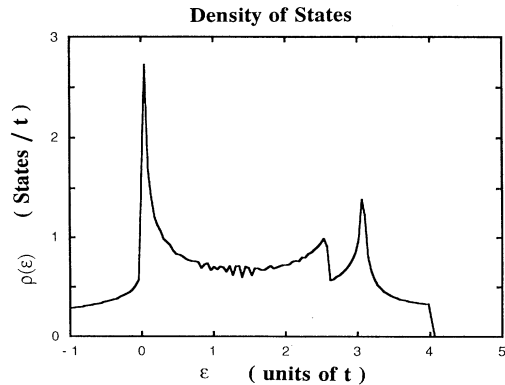

FIG. 3. The energy dependence of the quasiparticle density of states. The units are those of quasiparticles states per unit t, and energy is given in units of t. The zero of energy is defined to be E_p, and the Fermi energy is given by $\mu = 3.05t$.

$$\cos^2 k_x a /2 = (\mu - E_p)[(\mu - E_d^*)(\mu - E_p) - 4V^{*2}\cos^2 k_y a /2](4[V^{*2}(\mu - E_p) + \{t(\mu - E_d^*) - 2V^{*2}\}4t\cos^2 k_y a /2])^{-1} .$$

$$(2.9)$$

These sheets touch at $k_x = k_y = 2\cos^{-1}(\mu /4t)$. The variation of the Fermi energy μ and E_d^* with δ is such that the hybridized d-p portion of the Fermi surface avoids perfect nesting. This happens since, the upper p-d band does not hybridize along the lines $k_x = \pm k_y$, therefore the system may lower its energy by emptying some of the upper band states along other directions and recovering the bonding energy due to the hybridization.

CONCLUSIONS

The phase diagram of the isolated CuO_2 planes of the high-T_c superconductors has been calculated in the mean-field approximation, using the slave-boson technique. The mean-field approximation is expected to be exact for the case of infinite degeneracy or vanishing $1/N$. This approximation has been thoroughly investigated in the context of the single impurity Anderson model, where it is found that an expansion in powers of $1/N$ yields good agreement with the exact Bethe ansatz results.[25] Despite this agreement, doubt has been cast on the reliability of the mean-field approximation[26] in describing systems with a finite value of N. A study of an exactly soluble atomic system[26] has been performed, for which there is a phase transition as a function of N. Although the restrictive conditions imposed on the exactly soluble model do not hold for the Hamiltonian (2.1), some caution should be exercised in judging the reliability of extrapolating results which are exact in the limit $N \to \infty$, to the physical values of N.

In the mean-field approximation the direct p to p hopping has the effect of moving the boundary between the coherent and incoherent phases to larger charge transfer energies. The large magnitude and the sign of the $p - p$ hopping matrix element, relative to the $p - d$ hybridization matrix elements, has a strong effect on the positioning of the phase boundaries. At low temperatures the systems are in the coherent portion of the phase diagram for positive and negative values of the doping. However, inclusion of the nearest-neighbor Coulomb interaction U_{pd} should increase the tendency for the formation of the incoherent state, and the charge transfer insulating state could be stabilized at the stoichiometric composition. The low-temperature insulating behavior in the stoichiometric systems could be attributed to the opening up of an antiferromagnetic Slater gap at the Fermi surface.

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