THE ELECTRONIC STRUCTURE OF La_2CuO_4

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ABSTRACT- The electronic structure of the strongly correlated system La_2CuO_4 is calculated, using a realistic 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 3 d (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, as well as the direct overlap between the p orbitals of neighboring Oxygen ions. The Coulomb interaction between the electrons in the d shell of the Copper ions is treated by introducing slave bosons, thereby restricting the allowed Cu ionic configurations in the system to be Cu^{++} and Cu^+. The system may exhibit a phase characterized by the participation of the d electrons in coherent itinerant states. However, there also exists the possibility of another phase characterized by the localization of the d electrons. This second phase occurs when the bare charge transfer energy is sufficiently large. Thus, for the stochiometric system there are two possible zero temperature states; a metallic state and a charge transfer insulator state. The p-p hopping matrix element is large and it is found that its sign, relative to the other hopping matrix elements, has a significant effect on the position of the phase boundary. Inferring values tight-binding integrals from band structure calculations, one concludes that the paramagnetic phase of La_2CuO_4 should be metallic. The electronic structure and Fermi-surface are calculated for this phase. The presence of long ranged anti-ferromagnetic order is expected to open up a Slater gap at the Fermi-energy, yielding the experimentally observed low temperature insulating phase.

INTRODUCTION

The nature of the stochiometric state of the high temperature superconductors is the subject of controversy. It is known that this state is 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 is of the type envisaged by Slater [2] where the gap is induced by the antiferromagnetic long ranged order. Another possibility is that the gap is a manifestation of the Mott-Hubbard [3,4] band
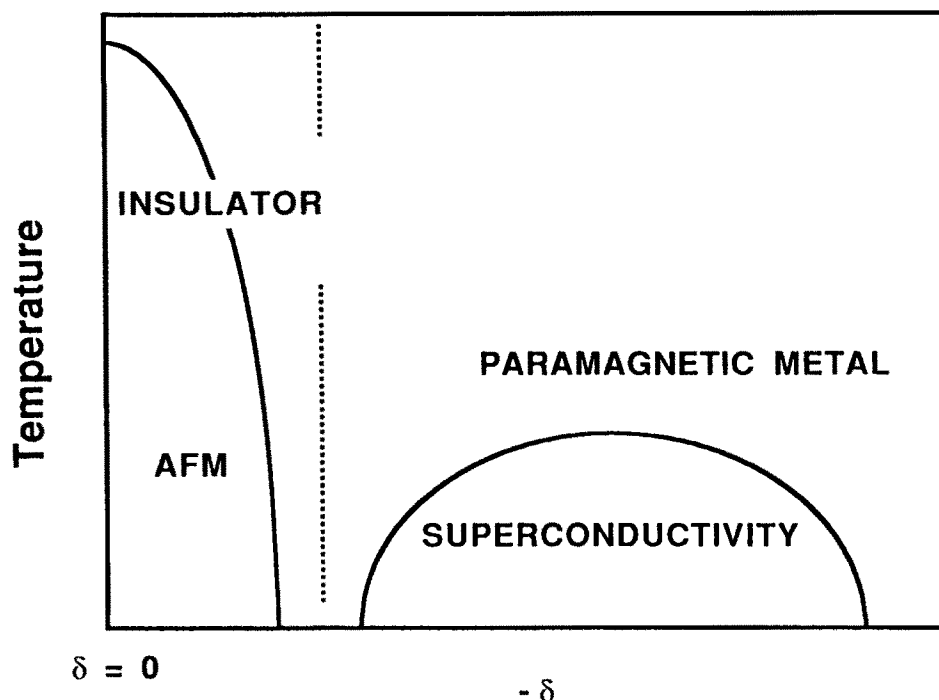

Figure 1.
  The experimentally determined phase diagram of the high temperature superconducting Oxides, as a function of electron and hole doping δ.

splitting due to the high Coulomb energy for introducing more than one hole on a Copper ion. This latter picture has been modified [5] by incorporating the effect of the Oxygen p bands which lies between the lower and upper Hubbard band. For a completely filled p band this leads to the charge transfer insulating state. On doping the systems, by introducing extra electrons or holes in the Copper Oxygen planes, experiments show that the Neel temperature is reduced and eventually the antiferromagnetic order disappears [6]. The experimentally determined phase diagram is shown in figure 1. The system does remain insulating for hole concentrations exceeding those for which the Neel temperature drops to zero, this might be taken as evidence against the description of the stochiometric system as a Slater insulator. However, the existence of short ranged antiferromagnetic order [7,8] and impurity induced disorder does complicate the picture.

Photo-emission experiments show that on doping away from half filling new states appear at energies where one could infer a gap to exist [9,10]. 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. This could be interpreted as impurity states within the insulating gap forming an impurity band and then becoming metallic. However, the fermi-surface crossings of the bands observed in both angle resolved photo-emission experiments [11-13] and high field de Haas-van Alphen measurements [14-15] do agree with calculated electronic structures [16-18] of the ordered materials and any correspondence with the formation of a fermi-surface of disordered impurity bands would be fortuitous. Thus, it seems as if these states at the fermi-level are actually coherent quasi-particle states of the ordered system, so the simple picture of a charge transfer insulator without any further many-body renormalizations is not appropriate. There does exist strong coupling [19-21] and intermediate coupling theories [22] which predict strong quasi-particle peaks at the fermi-level of the doped systems. In one theory the quasi-particle peak is formed from the non-interacting density of states by depressing the intensity away from the fermi-level. This depression is due to the rapidly increasing quasi-particle lifetimes with increasing excitation energy away from the fermi-energy. The states removed from the bands appears in the form of incoherent upper and lower Hubbard bands. As the strength of the Coulomb correlations increase, the variation of the quasi-particle lifetime becomes stronger and the integrated strength of the quasi-particle peak is diminished. In the slave boson theories [19-21], appropriate to strong coupling, the lower Hubbard band is removed to infinity, a narrow quasi-particle peak remains at the fermi-level and an incoherent upper Hubbard band forms just above the fermi-energy. Thus, a qualitative but not quantitative agreement exists between the intermediate and strong coupling theories for sufficiently strong doping.

At the stochiometric composition, the slave boson theory 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 [20-21,23]. In this note, we shall examine the phase diagram of the Oxide superconductors using a realistic parameterization [24] of the Copper and Oxygen bands close to the fermi-level. We shall show that not only does the dispersion associated with the direct overlap between the p orbitals on neighboring Oxygen ions have an important effect on the phase diagram, but also that the sign is of crucial importance in deciding whether the stochiometric system should be a charge transfer insulator or a metal, in the absence of the antiferromagnetic correlations. It is also noted that the effect of the direct p to p overlap and the Coulomb interaction is such that the system avoids nesting of the d portions of the fermi-surface. Using values of the tight binding parameters inferred from band structure calculations [24-26] a phase diagram is obtained for the high temperature superconducting Oxides, as a function of hole or electron doping. With this parameterization this system is found to always be metallic, as the number of holes in the d orbitals remains less than unity for all types of doping. The electronic correlations, as manifested by the mass renormalization or integrated intensity of the quasi-particle peak in the density of states, is calculated as a function of doping, and is found to only exhibit a weak variation that is asymmetric between the cases of electron and hole doping.

In the next section, we shall outline the model and the slave boson mean field theory. In the third section, we shall solve the self-consistency equations for the phase diagram, as a function of electron and hole doping. The resulting fermi-surface, the coherent part of the quasi-particle density of states are calculated. The low temperature limit of the magnetic susceptibility, is given directly by the total quasi-particle density of states at the fermi-level. In the final section we shall summarize our results.

SLAVE BOSON MEAN FIELD THEORY

Following the interpretation of Zaanen, Allen and Sawatzky [5] we consider the relevant low energy ionic states of Copper to be Cu^{++} and Cu^{+}, corresponding to the $3d^9$ and $3d^{10}$ configurations. For the stoichiometric system we assume the Copper ions to be in a $3d^9$ configuration and the Oxygen ions to be in a $2p^6$ configuration. The 10-fold degeneracy of the 3d band is broken by crystal field splitting into a fully occupied 6-fold degenerate t_{2g} band and a partially occupied 4-fold degenerate e_g band. The latter is split due to a Jahn-Teller distortion [27] 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, we only consider the electronic states composed from the Copper d $(x^2 - y^2)$ orbital and the p (x) and p (y) orbitals of the Oxygen ions. The total Hamiltonian for the simplified system is written as

$$H = H_0 + H_I$$

(2.1),

where H_0 represents the one body terms and H_I represents the Coulomb interactions between the electrons. Due to the exponential decay of the overlap of wave functions, we can simplify the Hamiltonian by neglecting tight binding interactions other than with the closest neighbors. Also, we only include the hybridization of the d orbitals with the p (x) orbital of the neighboring Oxygen ions that are collinear with the x axis through the Copper ion. Likewise, for the Oxygen ions collinear with the y axis, only the overlap with the p (y) orbitals need be taken into consideration. The overlap between the d $(x^2 - y^2)$ and the other p (x) and p (y) orbitals on the neighboring Oxygen ions are zero, due to symmetry. We shall also consider the direct overlap, t, of the p (x) and p (y) orbitals of neighboring Oxygen ions. The geometry and the wave functions are depicted in figure 2. The overlap integrals, t', of the p (x) with the p (x), and the p (y) with the p (y) wave functions on neighboring Oxygen atoms are neglected. This approximation decouples
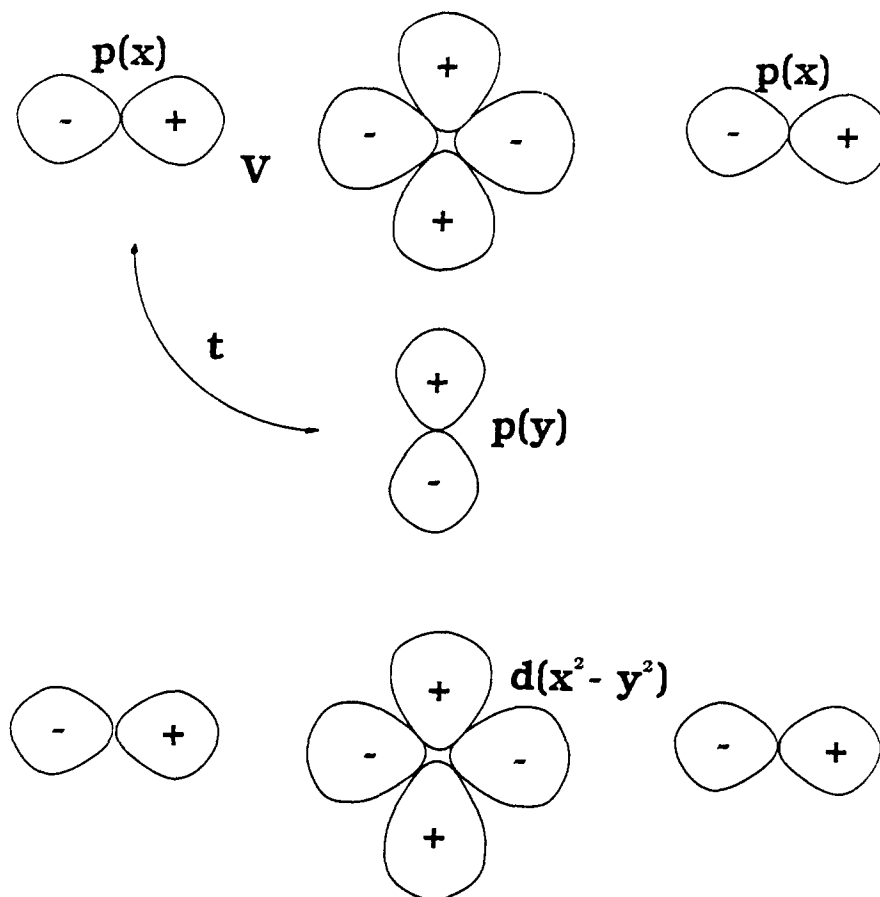

Figure 2.
A schematic picture of the real space structure of the two dimensional Copper Oxide planes. The form of the Copper 3d ($x^2 - y^2$) and the Oxygen p (x) and p (y) orbitals are shown schematically.

a p (x) and a p (y) orbital from interacting with the Copper ions, but the inclusion of a t' term can be shown to have an insignificant affect on our conclusions. The signs of the tight binding parameters can be inferred from the phases of the wave functions [28]. After an appropriate gauge transformation of the wave functions, the kinetic energy terms of the Hamiltonian can be written as,

$$H_0 = \sum_{\underline{k},m} E_p \left(p^+_{x,\underline{k},m} p_{x,\underline{k},m} + p^+_{y,\underline{k},m} p_{y,\underline{k},m} \right)$$

$$+ \sum_{\underline{k},m} E_d \, d^+_{\underline{k},m} d_{\underline{k},m}$$

$$+ \sum_{\underline{k},m} \Big\{ 2 \, V \cos(k_x a/2) \left(p^+_{x,\underline{k},m} d_{\underline{k},m} + d^+_{\underline{k},m} p_{x,\underline{k},m} \right)$$

$$+ 2 \, V \cos(k_y a/2) \left(p^+_{y,\underline{k},m} d_{\underline{k},m} + d^+_{\underline{k},m} p_{y,\underline{k},m} \right) \Big\}$$

$$- \sum_{\underline{k},m} 4 \, t \cos(k_x a/2) \cos(k_y a/2) \left(p^+_{y,\underline{k},m} p_{x,\underline{k},m} + p^+_{x,\underline{k},m} p_{y,\underline{k},m} \right)$$

$$(2.2),$$

where N_s is the number of unit cells in the lattice, a is the linear dimension of the unit cell, and $d^+_{\underline{k},m}$, $p^+_{y,\underline{k},m}$ and $p^+_{x,\underline{k},m}$, respectively, create an electron with spin m, in the Bloch state labeled by wave vector $\underline{k}$ in the bands composed of the d ($x^2 - y^2$), p (y) and p (x) orbitals. The spin index m, is assumed to take on N distinct values. The first term represents the binding energy of the degenerate Oxygen p (x) and p (y) orbitals, and the second term represents the binding energy of the Copper 3d orbital. The third and fourth term represents the hybridization of the d orbital with the p (y) and p (x) orbitals on the neighboring Oxygen ions. The last term represents the direct hopping of electrons between the p (x) and p (y) orbitals on neighboring ions, and its inclusion distinguishes this work from earlier analysis [19-21,23]. The Coulomb interaction between the holes on the same Copper ion is written as,

$$H_I = \sum_{i,m,m'} U_{dd}/2 \, d_{i,m} d_{i,m'} \, d^+_{i,m'} d^+_{i,m}$$

$$(2.3).$$

The corresponding interaction U_{pp} between holes in the orbitals of the same Oxygen ion is calculated to be smaller and has been shown [24] not to appreciably affect the electronic structure, and therefore we shall neglect the latter interaction. Also, the effect coulomb interaction U_{pd} between the p electrons and d holes is estimated to be the smallest parameter in the Hamiltonian.

The infinite U_{dd} slave boson theory projects out the states where more than one hole appears on the same lattice site. This projection is accomplished by introducing a local boson field b_i, at each lattice site, which satisfies the constraint

$$\sum_m d_{i,m} d^+_{i,m} + b^+_i b_i = 1$$

$$(2.4),$$

for each i. Since the boson occupation number has eigenvalues consisting of the non-negative integers, enforcing the constraint has the effect of restricting the number of holes in the d orbital to be zero or unity. The constraint is imposed by introducing the Fourier representation of a Dirac delta function. On evaluating this integral, within the saddle point approximation, this has the effect of renormalizing the d level energy E_d according to the prescription,

$$E_d^* = E_d - \lambda_i$$

$$(2.5).$$

The projection out of configurations with more than one hole eliminates the Coulomb interaction terms in H_I. The transformation of the physical d electron operators into quasi-particle operators has the effect that the hybridization terms in equation (2.2) are modified to,

$$N_s^{-1/2} \sum_{\underline{k},m} \Big\{ 2 \, V \cos(k_x a/2) \left(p^+_{x,\underline{k},m} d_{\underline{k}-\underline{q},m} b_{\underline{q}} + b^+_{\underline{q}} \, d^+_{\underline{k}-\underline{q},m} p_{x,\underline{k},m} \right)$$

$$+ 2 \, V \cos(k_y a/2) \left(p^+_{y,\underline{k},m} d_{\underline{k}-\underline{q},m} b_{\underline{q}} + b^+_{\underline{q}} \, d^+_{\underline{k}-\underline{q},m} p_{y,\underline{k},m} \right) \Big\}$$

$$(2.2'),$$

where the appearance of the slave boson operator ensures that holes are not transferred into d orbitals

already containing one hole. Since the constraint commutes with the Hamiltonian and number operator, the constraint needs only to be imposed just once. It should be noted that, due to the projection, the physical d electron operators are composed of the product of the d quasi-particle operators and the boson operators.

A static part is explicitly separated out from the Fourier Transform of the boson field via the replacement,

$$b^+_{\underline{q}} = B^+_{\underline{q}} + N_s^{1/2} B^*_{\underline{0}} \, \delta_{\underline{q},0}$$

(2.6).

The static part $B_{\underline{0}}$ is to be chosen such that the boson field satisfies the equations of motion. The mean field approximation consists of neglecting the fluctuating parts of the boson field. The parameters of the Hamiltonian can be rescaled in a manner such that the mean field approximation is expected to be exact in the limit of infinite degeneracy, N. In particular, the boson field, the hybridization and the partial occupation of the d level can be rescaled so that the boson propagators are of the order of 1/N and therefore vanish in the infinite N limit.

At the mean field level, the λ_i are independent of i and the boson amplitude $B_{\underline{0}}$ satisfies the equation

$$\lambda \, B_{\underline{0}} = - 1/N_s \sum_{\underline{k},m} 2 \, V \, (\cos k_x a/2 < d^+_{\underline{k},m} p_{x,\underline{k},m} > + \cos k_y a/2 < d^+_{\underline{k},m} p_{y,\underline{k},m} >)$$

(2.7),

and the average number of d holes is given by

$$1 = \left\{ 1/N_s \sum_{\underline{k},m} < d_{\underline{k},m} d^+_{\underline{k},m} > \right\} + B^*_{\underline{0}} B_{\underline{0}}$$

(2.8).

Since, the projection has removed all the terms other than those quadratic in the fermion operators, and the mean field approximation has replaced the boson field by a complex number, the equations of motion for the quasi-particle electronic Green's functions truncate. The Green's function for the d quasi-particles has the form,

$$G^{dd}(\underline{k},\omega) = \sum_i A^{dd}_i(\underline{k})/(\hbar\omega - E_i(\underline{k}))$$

(2.9),

where $E_i(\underline{k})$ are the dispersion relations for the three hybridized bands and $A^{dd}_i(\underline{k})$ are the d weights. The dispersion relations for the three branches of the hybridized band are given by the expressions

$$E_1(\underline{k}) = 2 \, q^{1/2} \cos \phi/3 + (2 E_p + E_d^*)/3$$

$$E_2(\underline{k}) = 2 \, q^{1/2} \cos(\phi + 2\pi)/3 + (2 E_p + E_d^*)/3$$

and

$$E_3(\underline{k}) = 2 \, q^{1/2} \cos(\phi - 2\pi)/3 + (2 E_p + E_d^*)/3$$

(2.10a),

in which q is given by

$$q = 1/9(E_d^* - E_p)^2 + 1/3[4V^{*2}(\cos^2 k_x a/2 + \cos^2 k_y a/2) + 16t^2\cos^2 k_x a/2 \cos^2 k_y a/2]$$

(2.10b),

and ϕ is given by the solution of the equation

$$q^{3/2}\cos \phi = r$$

(2.10c),

where

$$r = 1/3^3(E_d^* - E_p)^3 + 1/6(E_d^* - E_p)[4V^{*2}(\cos^2 k_x a/2 + \cos^2 k_y a/2) - 32 \, t^2 \cos^2 k_x a/2 \cos^2 k_y a/2]$$

$$- 16 \, V^{*2} t \cos^2 k_x a/2 \cos^2 k_y a/2$$

(2.10d).

In these expressions, the effective value of the hybridization V has been renormalized to $V^* = V B_0$, which

represents the reduction in the probability of a hole hoping into the d shell of a Copper ion due to the probability that it is already occupied by a hole. This effect is similar to the reduction of the band widths or the enhancements of the effective masses found by Brinkman-Rice [29] in their treatment of the localization transition in the Hubbard model. The renormalization of the d level energy to E_d^* from E_d is due to the kinetic energy associated with the virtual hopping of the holes. The d weights of the hybridized bands are given by the expressions,

$$A^{dd}_1(\underline{k}) = 1/3 \left\{ 1 + \right.$$

$$\frac{[(E_d^*-E_p)^2/3^2 - 16t^2\cos k_x a/2 \cos^2 k_y a/2 + q]\sin\phi/3 + 2 q^{1/2}(E_d^*-E_p)/3 \sin2\phi/3}{q \sin \phi} \left. \right\}$$

(2.11),

and the weights for the other two branches of the dispersion relation are obtained by replacing ϕ by $\phi \pm 2\pi$, respectively, in the above expression.

The self-consistency equations simplify to

$$-\lambda\, B^*_{\underline{0}}B_{\underline{0}} = N/N_s \sum_{i,\underline{k}} C_i(\underline{k})\, f(E_i(\underline{k}))$$

(2.12),

and

$$N - 1 + B^*_{\underline{0}}B_{\underline{0}} = N/N_s \sum_{i,\underline{k}} A^{dd}_i(\underline{k}) f(E_i(\underline{k}))$$

(2.13),

in which the $C_i(\underline{k})$ are give by the expressions obtained from

$$C_1(\underline{k}) =$$

$$\left\{ [4V^{*2}(\cos^2 k_x a/2 + \cos^2 k_y a/2)(E_d^*-E_p)/3 - 32V^{*2}t \cos^2 k_x a/2 \cos^2 k_y a/2] \sin\phi/3 \right.$$

$$+ 4V^{*2}(\cos^2 k_x a/2 + \cos^2 k_y a/2) q^{1/2}\sin 2\phi/3 \left. \right\} / (3 q \sin \phi)$$

(2.14),

by making the replacement ϕ to $\phi \pm 2\pi$. The chemical potential μ is found from

$$5N - 1 + \delta = N/N_s \sum_{i,\underline{k}} f(E_i(\underline{k}))$$

$$+ N/N_s \sum_{\underline{k}} \{ f(E_p + 4t \cos k_x a/2 \cos k_y a/2) + f(E_p - 4t \cos k_x a/2 \cos k_y a/2) \}$$

(2.15),

where a positive δ represents the amount of electron doping away from half filling, and a negative δ corresponds to hole doping. The last two terms represent the number of electrons in the p (x) and p (y) bands that are decoupled from the d ($x^2 - y^2$) orbital. For sufficiently small magnitudes of the doping, the chemical potential μ is pinned to the uppermost hybridized band.

ANALYSIS

The self-consistency equation (2.12) also allows for the trivial solution $B_{\underline{0}} = 0$, where the constraint implies that the number of electrons in the d ($x^2 - y^2$) orbitals, per site is unity. In this state the d quasi-particle 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 can not occur as the minimum value of $B_{\underline{0}}$ corresponds to the minimum number of d holes, which in turn implies the maximum occupation of the p orbitals. Since for hole doping, $\delta > 0$, the p bands are completely filled at maximum occupation, the introduction of extra electrons into the d band necessitates a value of $B_{\underline{0}}$ such that $B_{\underline{0}} > \delta > 0$. Thus the localized or incoherent state is restricted to the case of hole doped systems $\delta < 0$, and as we shall show occurs at high temperatures when the bare charge transfer energy $E_d - E_p$ is sufficiently large.

The self-consistency equations can be shown to always have non-trivial 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 which the boson field condensate evaporates and the d states localize is given by the solution of

$$E_d - E_d^* = V^2 2/N_s \sum_{\underline{k}} \left\{ \right.$$

$$\frac{(\cos k_x a/2 + \cos k_y a/2)^2 [\; N \; f(E_p - 4t \cos k_x a/2 \cos k_y a/2) - N + 1 \;]}{(\; E_d - E_p + 4t \cos k_x a/2 \cos k_y a/2 \;)}$$

$$+ \frac{(\cos k_x a/2 - \cos k_y a/2)^2 [\; N \; f(E_p + 4t \cos k_x a/2 \cos k_y a/2) - N + 1 \;]}{(\; E_d - E_p - 4t \cos k_x a/2 \cos k_y a/2 \;)} \left. \right\}$$

(3.1),

where the renormalized d energy level E_d^* is related to the chemical potential, $\mu(T)$, via

$$E_d^* = \mu(T) - k_B T \log_e(N-1)$$

(3.2).

For hole doping any second order instability of the low temperature coherent phase can be inferred from consideration of 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

$$\mu(T) = E_p + k_B T \log_e[\; 4N/-\delta \;] + k_B T \log_e[\sum_{n=0} \{(2n)!/(n!)^4\} (t/k_B T)^{2n}]$$

(3.3),

when $k_B T >> t$, and then would fall within the band

$$\mu(0) = E_p + 4 \; |t| \; (\; 1 + \delta\pi/4N \;)$$

(3.4),

at zero temperature, if the phase transition does not previously occur. As the chemical potential is pinned to the d level at low temperatures, the d level also becomes degenerate with the p bands. When this degeneracy occurs, for some values of $\underline{k}$ the denominator in (2.16) vanishes and the summation diverges logarithmically at low temperatures. Since the summation is restricted to be positive, this implies a minimum of the right hand side of equation (3.1) as a function of T. Therefore one finds that there is 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 first conclusion central to this report can be found by direct consideration of equation (3.1). From inspection of the above equation, one sees that for small values of the doping, where the $\underline{k}$ values associated with the band crossings are close to zero, the sign of t plays an important role. In particular, for positive values of t the denominator of the second term vanishes for $\underline{k}$ values close to the point where the factor $(\cos(k_x a/2) - \cos(k_y a/2))^2$ is minimized, whereas if t is negative the denominator of the first term in the summation is minimized for $\underline{k}$ values close to the point at which the factor $(\cos(k_x a/2) + \cos(k_y a/2))^2$ is also a maximum. This has the effect that the critical temperature T_c is drastically smaller for negative values of t than for positive values of t. An equation for the transition temperature can be derived, in the presence of the p (x) - p (x) and p (y) - p (y) hopping terms t', which has a similar structure to that derived above, except instead of two it has four terms corresponding to the splitting of the branches in the p bands, calculated with $V = 0$. Not only is t' smaller [24] than t, but also the t' terms neither split the degeneracy of the un-hybridized p bands [24-26] at $\underline{k} = 0$, nor change the overall p band width, thus, the above reasoning remains unchanged by the inclusion of t'.

The physical reason for the crucial dependence of the above equation on the matrix element factors is simply that the d level hybridizes with the combination,

$$\cos k_x a/2 \mid p \, x > \; + \; \cos k_y a/2 \mid p \, y >$$

(3.5),

of the p orbitals, which for small $\underline{k}$ values corresponds to the combination of orbitals

$$\mid p \, x > \; + \; \mid p \, y >$$

(3.6),

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. For the opposite case, of negative t, the above combination represents the anti-bonding p orbital at the top of the p band, and due to the closer proximity with the d band the hybridization process is simply much more efficient.

At the stochiometric composition, where $\delta = 0 -$, the dependence of the effective charge transfer energy $E_d^* - E_p$ on temperature implied by (3.2) and (3.3) shows that the critical temperature T_c is restricted to occur in the zero temperature limit. Since the upper band is of predominantly d character, equation (3.1) 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 also strongly depends upon the sign of the p to p hopping matrix element. Since earlier studies of the phase diagram either ignored the p band width altogether [19,23] or introduced it phenomenologically by broadening a dispersionless p level [20,21], the above effect has not been discussed. Again, the above effect can be seen by examining the zero temperature limit of equation (2.16), after the summations over $\underline{k}$ have been performed. For $k = (E_d^* - E_p)/4|t| > 1$, the equation takes the form

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

(3.7),

where K(k) and E(k) are the first and second elliptic integrals [30], and the summations are divergent for $k < 1$. It should be noted that first two terms within the square brackets represents terms odd in t, and that for positive values of t the logarithmic divergences of K(k), which occur when the renormalized d level is energetically degenerate with the top of the p band, exactly cancel. The left hand side of the equation possesses a minimum, as a function of $(E_d^* - E_p)/4|t|$, which implies that the corresponding 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,

$$(E_d - E_p)_c = 4|V| \; - \; (4t)/2 + [(4t)^2 + (4t')^2]/(16V)$$

(3.8),

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

$$(E_d - E_p)_c = \; 4 \, |t| \; + \; 2 \, (\, 1 - 2/\pi \,) \, V^2/|t| \qquad\qquad t > 0$$

$$(E_d - E_p)_c = 4 \, |t| \; + \; 4 \, V^2/\pi|t| \; \log[\, \pi/2 \; |4t/V|^2 \,] \, - \, 2 \, V^2/|t| \qquad\qquad t < 0$$

(3.9).

Using the positive sign for t, the values of $(E_d - E_p)/4t = 1.077$ and $|V|/4t = 0.615$, extracted from tight binding fits to L.D.A. electronic structure calculations [24-26], one concludes that for $\delta = 0$ the high temperature superconducting Oxides ought to be in the coherent phase. In part, this is due to the effect of the p band width in shifting the bare charge transfer energy from $E_d - E_p$ by an amount $4|t|$, which is relatively large [24]. However, the effect of the term U_{pd} that has been neglected in this analysis will tend to stabilize the incoherent phase [31]. A considerable amount of variation may occur between different methods of extracting a set of tight binding parameters from band structures as well as isolating the correlations inherent in L.D.A., but the critical value of the bare charge transfer energy that we find, $(E_d - E_p)_c/4t = 2.1$, is above most of the values to be found in the literature. This conclusion is similar to the results of reference [23], where it was found that the critical ratio of the bare charge transfer energy to V was 6.25 which is rather large compared with the actual values appropriate to La_2CuO_4 compounds. The phase diagram, for $\delta = 0$, is shown in figure 3.
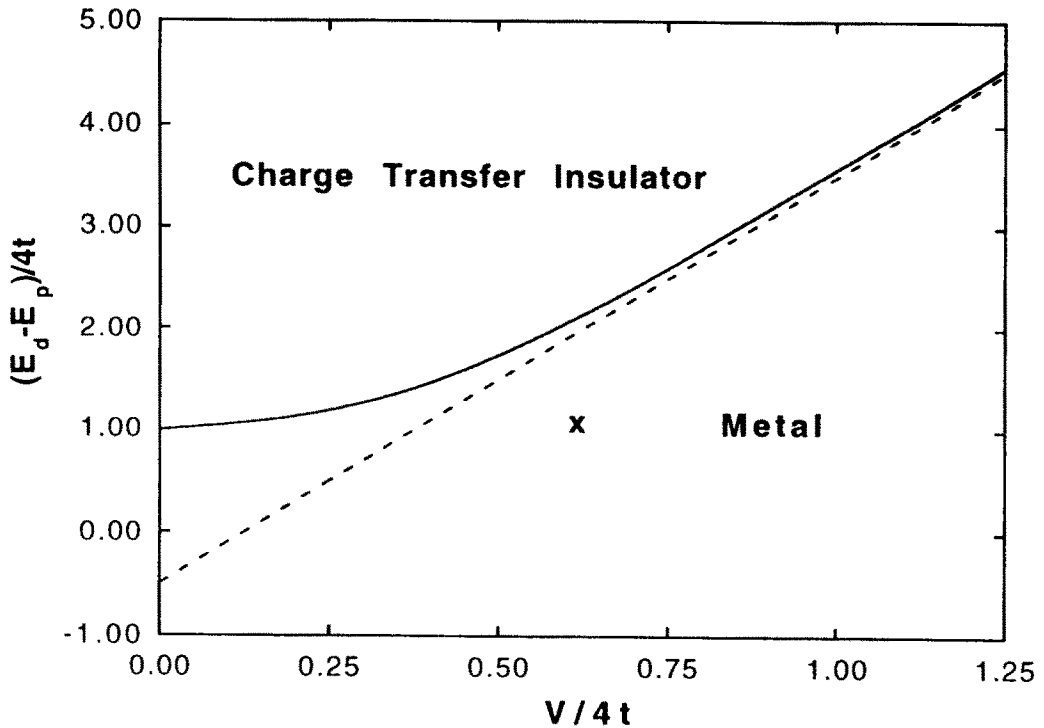
Figure 3.

Further information concerning the nature of the phase boundary, can be found by examining the limit $\delta \to 0 +$ of the electron doped phase, $\delta > 0$. As previously mentioned, this phase is restricted to be metallic, with the effective hybridization matrix element V^* is greater than $\delta^{1/2} V$. Examination of the T = 0 self-consistency equations shows, as expected, that there is always a non-trivial solution for arbitrary δ and bare charge transfer energies. In the limit $\delta \to 0 +$, 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 solving the T = 0 limit of the constraint equation (2.13), is limited to values less than $4|t|(1 + \delta/4N)$ one concludes, in agreement with the work of Doniach and Melo [21], 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 stochiometric system is a charge transfer insulator, when the parameters lay in the region above the phase boundary shown in figure 3. Thus, one is lead to the speculation that the CuO planes ought to be metallic in stochiometric La_2CuO_4, and the observed in insulating behavior is due to the existence of three dimensional antiferromagnetic ordering which opens up a gap at the fermi-surface [2].

An asymmetry in the variation of the electronic correlations, manifested by B_0 or V^*, with electron or hole doping can be inferred from the complete absence of the high temperature state for the electron doped systems, and we concomitant lower limit of $V^* > \delta^{1/2} V$. This leads one to conclude that the low temperature slave boson condensate amplitude or the inverse of the mass enhancement remains relatively larger in the electron doped systems, when compared to the hole doped counterparts with large values of $(E_d - E_p)/V$. This asymmetry is less apparent when the value of $(E_d - E_p)$ is decreased so that the system is further from the transition between the metallic and the charge transfer insulator states. The absence of a significant variation in the slave boson amplitude does not necessarily imply a slow variation of physical quantities such as coefficient of the linear T term in the low temperature specific heat [32], since the quasi-particle density of states does exhibit two dimensional Van Hove singularities which might fall close to the fermi-level for some values of doping. The total quasi-particle density of states at the fermi-

level is shown in figure 4 where it is seen to only have a relatively slow variation with doping. This can be directly compared to the low temperature limit of the experimentally determined magnetic susceptibility [34], which also shows only a relatively slow variation. The results for the susceptibility in this work are found to lie intermediate between the susceptibility inferred from electronic structure calculations [17] and the experimental data [34]. Naively, one might have expected that as the doping is changed from electron

Magnetic Susceptibility
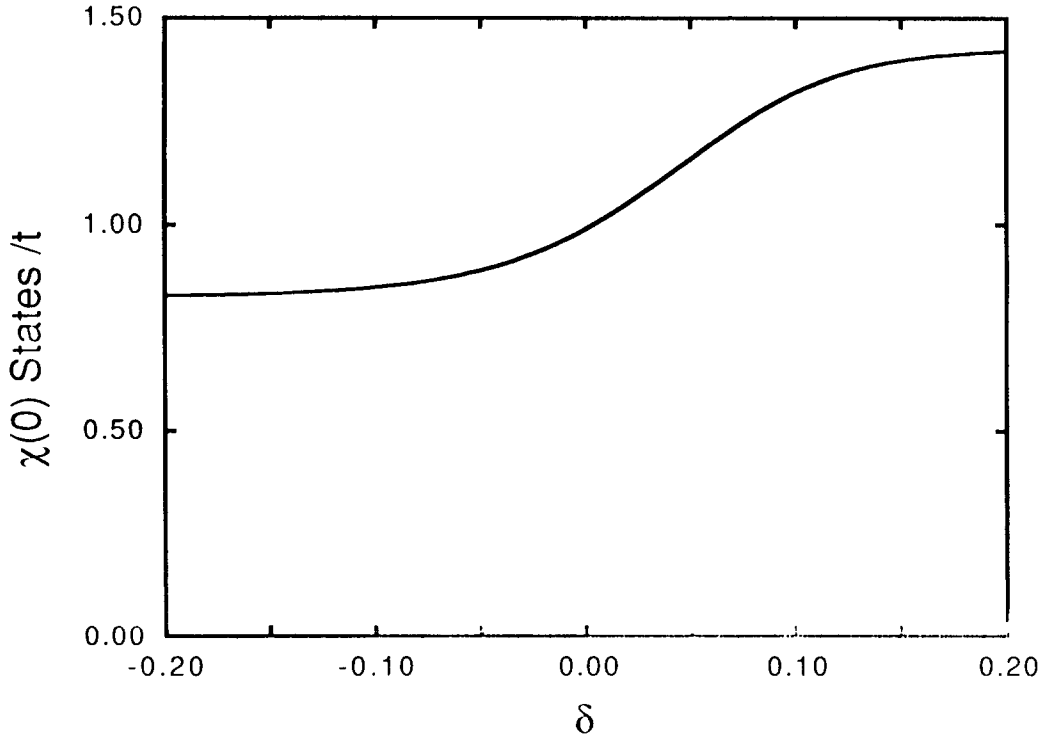
Figure 4.
 The variation of the calculated magnetic susceptibility with doping δ. The susceptibility is given in terms of States per unit t. With t = 0.65 eV, one finds a susceptibility for δ = - 0.1 with magnitude of roughly 3 States /eV, which can be directly compared with the experimentally [34] determined range of values of 4 to 5 States/eV.

to hole type the fermi-surface of the upper band would sweep through the case of perfect nesting, and the density of states may have swept through the associated Van Hove singularity. The total quasi-particle density of states is shown in figure 5, for δ = 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

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

(3.10),

and the highest energy Van Hove singularity is found at

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

(3.11).

Only two of these peaks are below the fermi-energy. This is in contrast to the results of paramagnetic band structure calculations [17], which produce similar structures in the density of states, but where the highest Van Hove singularity lies roughly 0.1 eV below the fermi energy. This discrepancy is due to the effect of the electronic correlations which produces a variation in the renormalization of E_d^*, such as to produce a sheet of non-hybridizing p bands at the fermi-surface in addition to the sheet due to the hybridized d - p bands. The non-hybridizing p states contribute a sheet to the fermi-surface given by the solution of

$$\mu = 4 |t| \cos k_x a/2 \cos k_y a/2$$

(3.12),

and the hybridized p and d sheet is given by the solution

Density of States

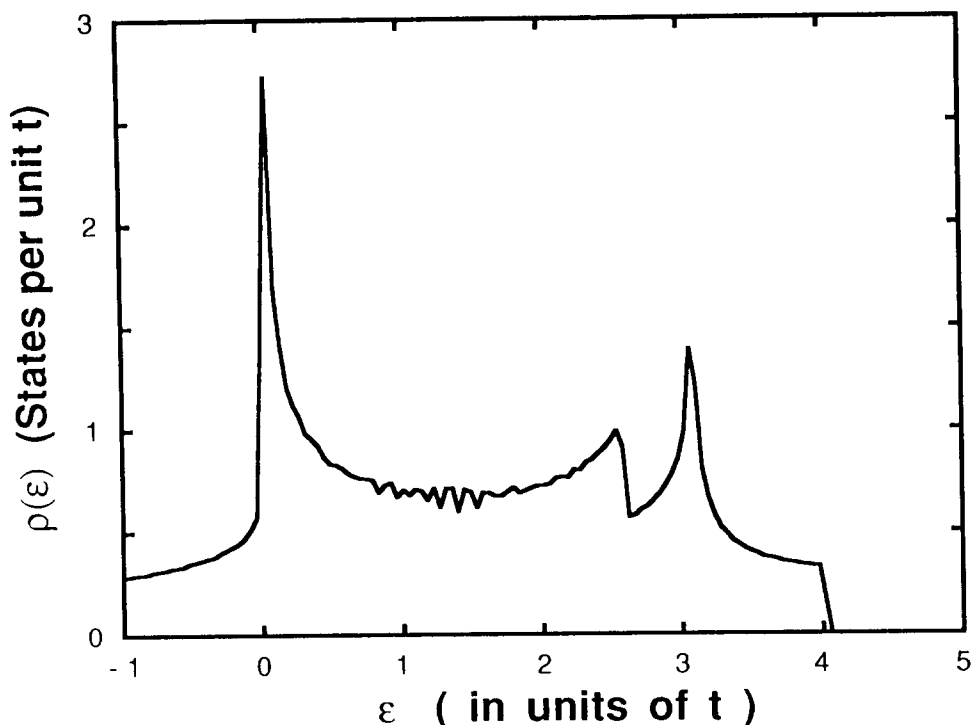ε (in units of t)

Figure 5.

The energy dependence of the quasi-particle density of states. The units are those of quasi-particles 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 $\mu = 3.05$ t. Three structures are seen to lie in the vicinity of the fermi-energy, corresponding to the turning points at (π,π), $(\pi,0)$ and $(0,0)$. Due to the gauge transformation performed on the creation and destruction operators, $(0,0)$ corresponds to the X point and (π,π) is the Γ point in the standard convention.

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

$$(3.13).$$

These sheets of the fermi-surface touch at $k_x = k_y = 2 \cos^{-1}(\mu/4t)$, for positive values of t as seen in figure 6. The degeneracy of the sheets at this point is due to the non-hybridizing nature of the upper band along the lines $k_x = \pm\, k_y$, and will be lifted by the inclusion of the t' terms that were neglected in the above analysis. The effect of the combined variation of both the fermi-energy μ and E_d^* with δ is such that the hybridized d - p portion of the fermi-surface avoids perfect nesting of the fermi-surface. This is accomplished since, for positive t 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. Hence, this explains the relatively smooth variation of the measured high temperature values of the magnetic susceptibility and linear T coefficient in the specific heat with doping.

CONCLUSIONS

The phase diagram of the isolated CuO_2 planes of the high T_c Oxide 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 [35]. Despite this agreement, doubt has been cast on the reliability of the mean field approximation [36] in describing systems with a finite value of N. A study of an exactly soluble atomic system [36] has been performed, for which there is a phase transition as a function of N. Although the restrictive conditions imposed on the
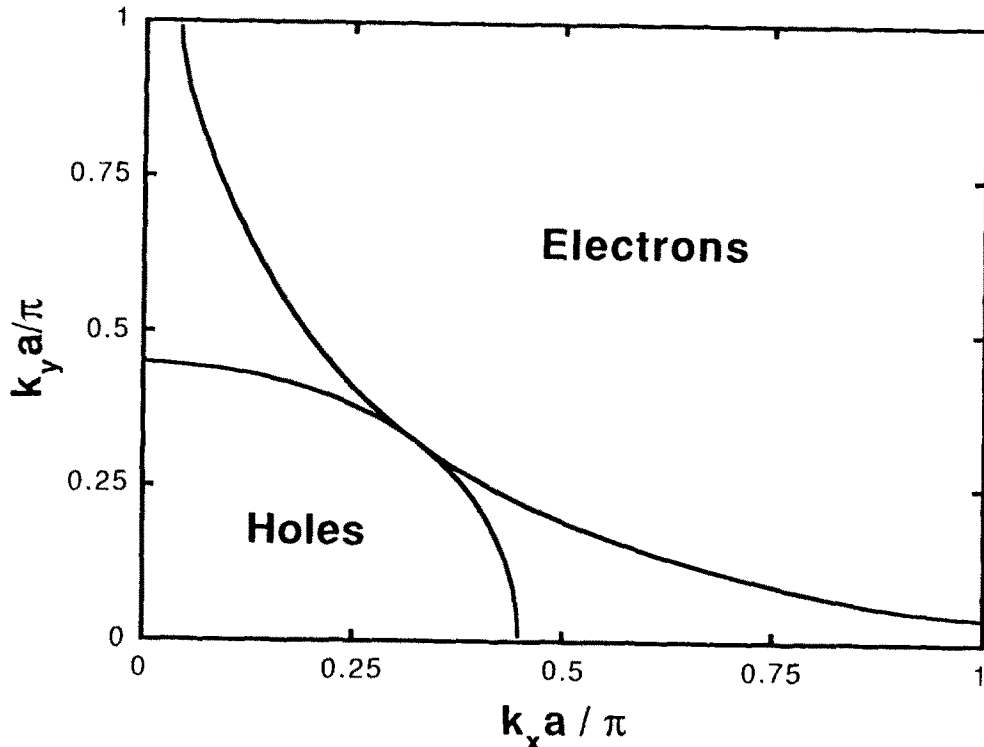
Fermi-Surface

Figure 6.
The sheets of the fermi-surface given by equations (3.12) and (3.13), found with self consistently determined parameters obtained for the stochiometric system. Two pockets of holes are found centered at (0,0). The fermi-surface shows that the states associated with points $(\pi,0)$, $(0,\pi)$ are unoccupied allowing the system to take some advantage of the energy lowering due to the opening up of the hybridization gap.

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 $N \rightarrow \infty$, 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. Since the band width due to direct p - p hopping processes is estimated to be much larger than the hybridization V, this represents a significant factor in determining phase boundaries. The sign of the p-p hopping matrix element, relative to the p-d hybridization matrix elements, also has a strong effect on the positioning of the phase boundaries. For the values obtained by tight binding parameterizations of band structure calculations, one finds that 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 stochiometric composition. The low temperature insulating behavior observed experimentally in the stochiometric systems could be attributed to the opening up of a Slater gap at the fermi-surface, due to the existence of three dimensional magnetic ordering. Thermodynamic properties found above the ordering temperature, such as the linear T term of the specific heat or $Q =$ Q magnetic susceptibility show smooth variations with doping [34], indicative of the absence of either strong variations in many-body correlations or the close proximity of the two dimensional Van Hove singularities in the density of states with the fermi-energy.

ACKNOWLEDGEMENTS

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