

Mean-field phase diagram of a two-band t - J model for CuO_2 layers

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We study the mean-field phase diagram of a two-band t - J model. Upon varying the doping and the values of the parameters, we identify solutions with different magnetic structure without spin long-range order. A first-order transition occurs between a uniform (rotationally-invariant) and a dimerized (non-rotationally-invariant) Fermi-liquid phase. A second transition (of the second order for low doping and of the first order for larger doping) takes place between the dimerized Fermi liquid and an insulating fully dimerized phase. We also find an instability region of negative compressibility where a phase separation occurs. At zero doping we find a Slater-to-charge-transfer-insulator transition where the compressibility vanishes together with the band dispersion. The results agree with those obtained in the $J=0$ case and in the single-band Hubbard model at the Brinkman-Rice transition.

The discovery of the high-temperature (high- T_c) superconducting oxides¹ has triggered a renewed interest in the study of strongly correlated electron systems. The phenomenology of these materials is very rich. These systems exhibit a magnetic, a metal-insulator transition (MIT), and a superconducting transition.

The high- T_c oxides are characterized by the presence of CuO_2 layers forming nearly two-dimensional structures, which are believed to be the essential ingredients for the understanding of their superconducting and magnetic properties. Anderson proposed² that the superconductivity in these systems is connected with the breakdown of Fermi-liquid (FL) theory. In this context the two-dimensional Hubbard model together with some of its generalizations, the single-band infinite- U Hubbard model with magnetic coupling (t - J model), have received considerably attention. Exotic non-FL phases, i.e., the flux phases, have been conjectured and studied away from half-filling.³ The possibility of a phase separation⁴ into undoped regions with antiferromagnetic order and hole-rich regions has been investigated.

Experimental evidence⁵ indicates that the holes introduced in the system upon doping mostly reside on oxygen sites, but the issue of whether the single-band t - J model contains the essential physics of the copper oxide planes is still controversial. There is a region of parameters in which the low-energy properties of a realistic copper oxide Hamiltonian is described by a single-band t - J model. In other regions of parameters the physics of the two-band Anderson Hamiltonian cannot be described in terms of a single-band model. When the hybridization is weak and the oxygen-oxygen overlap is large one has heavy-fermion behavior. It has been pointed out⁶ that adding oxygen sites to the t - J model allows for an insulating dimerized (i.e., non-FL) phase at finite doping if the magnetic exchange is larger than the hybridization energy.

In this paper we investigate the phase diagram of a two-band t - J model of the CuO planes allowing for dimerized (non-FL) phases and phase separation. We study the $N=\infty$ limit of a model treated by several authors.^{6,7,9} The presence of a coupling-independent expansion parameter $1/N$ is particularly relevant in the present context where a large variety of physical behaviors can arise depending on the values of the parameters. Within this approach the mean-field solutions are exact in the $N=\infty$ limit regardless of the value of the couplings and provide reliable qualitative information on the competition, origin, and interplay of the different physical mechanisms.

The Hamiltonian describing p and d orbitals is given by

$$\begin{aligned}
 H = & -\frac{2t}{\sqrt{N}} \sum_{k,\sigma} \gamma_k (d_{k,\sigma}^\dagger p_{k,\sigma} + \text{H.c.}) + \varepsilon_d^0 \sum_{i,\sigma} d_{i,\sigma}^\dagger d_{i,\sigma} \\
 & + \varepsilon_p \sum_{i,\sigma} p_{i,\sigma}^\dagger p_{i,\sigma} + U_{dd} \sum_i d_{i\uparrow}^\dagger d_{i\downarrow}^\dagger d_{i\downarrow} d_{i\uparrow} \\
 & + \frac{J}{N} \sum_{\langle i,j \rangle, \sigma, \sigma'} d_{i\sigma}^\dagger d_{i\sigma'} d_{j\sigma'}^\dagger d_{j\sigma} .
 \end{aligned} \tag{1}$$

We work in a hole representation in which the vacuum state is the $3d^{10}$ configuration for the copper and the $2p^6$ for the oxygen. The $d_{i,\sigma}$ ($d_{i,\sigma}^\dagger$) operators are annihilation (creation) operators for holes in the Cu atoms, while $p_{i,\sigma}$ ($p_{i,\sigma}^\dagger$) are the corresponding operators on the O sites. ε_p , and ε_d^0 are the bare atomic levels on O and Cu, respectively. After taking the infinite- U_{dd} limit, σ takes values from 1 to N , $1/N$ being the expansion parameter of the theory. Equation (1) aims to simulate the CuO_2 plane where, to be specific, we assume one orbital per Cu site with $d_{x^2-y^2}$ symmetry strongly hybridized to a bond in combination of $p_{x,y}$ orbitals on O sites via a hopping term $t\gamma_k$ where $\gamma_k^2 = \sin^2(k_x/2) + \sin^2(k_y/2)$. In this model

we neglect any O-O overlap so that the nonbonding combination of p_x, p_y orbitals can be factorized out and only the bonding and antibonding combinations need to be taken into account. U_{dd} describes the strong Hubbard repulsion on Cu sites while the corresponding U_{pp} is set equal to zero. J represents the superexchange coupling between the nearest-neighbor copper electrons generated by virtual charge fluctuations on oxygen sites [$J \sim t^4/(\epsilon_p - \epsilon_d^0)^3$]. If this superexchange term were not included in the model (1), it would naturally arise⁷ at $1/N^2$ order. Since we limit ourselves to a $N = \infty$ study we explicitly introduce this term in the Hamiltonian in order to obtain the physics of the magnetic coupling already at mean-field level.

Since from experiments U_{dd} is the largest energy in the problem we set it to infinity. We then implement the local constraint $n_{d_i} \leq 1$ by means of the slave-boson approach⁸ with the standard replacement of the d and d^\dagger operators:

$$d^\dagger \rightarrow d^\dagger b, \quad d \rightarrow b^\dagger d; \quad b_i^\dagger b_i + \sum_{\sigma} d_{i\sigma}^\dagger d_{i\sigma} = q_0 N.$$

The last condition is implemented by Lagrange multiplier field λ_i , while q_0 , originally equal to $1/N$, is taken to be an independent parameter to generate a controlled $1/N$ expansion. Only at the end of the calculation q_0 is set equal to $\frac{1}{2}$ and $N=2$. In mean-field approximation, i.e., in the limit $N \rightarrow \infty$, the effective Hamiltonian reads

$$\begin{aligned} H_{\text{MF}} = & -2tr_0 \sum_{k,\sigma} \gamma_k (d_{k,\sigma}^\dagger p_{k,\sigma} + \text{H.c.}) + \epsilon_p \sum_{i,\sigma} p_{i,\sigma}^\dagger p_{i,\sigma} \\ & + \sum_i \lambda \left[\sum_{\sigma} d_{i,\sigma}^\dagger d_{i,\sigma} + N r_0^2 - N q_0 \right] \\ & + \sum_{\langle i,j \rangle, \sigma} \Delta_{i,j} d_{i,\sigma}^\dagger d_{j,\sigma} + \frac{N}{J} \sum_{i,j} |\Delta_{ij}|^2, \end{aligned} \quad (2)$$

where for simplicity we have set $\epsilon_d^0 = 0$ and where the classic fields $\Delta_{i,j} = (J/N) \sum_{\sigma} \langle d_{i,\sigma}^\dagger d_{j,\sigma} \rangle$ have been intro-

duced in order to decouple the quartic term. It is worth noting that any other (anomalous) decoupling is of higher order in $1/N$.

The $N = \infty$ case is given by the static uniform limit $b = \langle b_i \rangle \equiv \sqrt{N} r_0$ and $\lambda = \langle \lambda_i \rangle$ of the corresponding fields and is determined by minimizing the free energy for various possible mean-field configuration of the Δ 's. In the mean field $\lambda = \epsilon_d - \epsilon_d^0$ is a shift of the bare Cu level while r_0 is a hopping renormalization which controls the width of the bands. $r_0 \neq 0$ allows for the hybridization between the p and d bands and corresponds to a nonvanishing residue in the single-particle Green function. If $r_0 = 0$ there is no p - d mixing and the quasiparticle residue is zero. With $J=0$, this model has been studied in Ref. 9, where a Brinkman-Rice transition was found at half-filling for $t/(\epsilon_p - \epsilon_d^0) \sim 0.3$. With finite J , at zero doping this model has been studied in Ref. 10, where it was shown to exhibit several magnetic (dimer, flux, and uniform) phases without spin long-range order. In particular the dimer solution has the lowest energy and therefore we here consider its generalizations for finite doping as good representatives of magnetically correlated mean-field solutions.

In the uniform phase we set $\langle d_i^\dagger d_{i\pm x} \rangle = \langle d_i^\dagger d_{i\pm y} \rangle = \Delta$ while the dimerized solutions for arbitrary value of doping are given by $\langle d_i^\dagger d_{i+x} \rangle = \Delta_1$, $\langle d_i^\dagger d_{i\pm y} \rangle = \Delta_2$, $\langle d_i^\dagger d_{i-x} \rangle = \Delta_3$ (here i has to be chosen on a sublattice). In this latter case the isotropy of the system has explicitly been broken, allowing for a different amplitude for the Δ fields in the different directions. The mean-field free energy per spin and per copper site is written as

$$\begin{aligned} F = & \frac{\Delta_1^2 + 2\Delta_2^2 + \Delta_3^2}{2J} + \lambda(r_0^2 - q_0) \\ & + \frac{T}{N_{\text{sites}}} \sum_k \ln \{ 1 + e^{[\mu - E^i(k)]/T} \}, \end{aligned} \quad (3)$$

with $E^i(k)$ representing the eigenvalues of the Hamiltonian matrix

$$\begin{pmatrix} \epsilon_d + (\Delta_1 + \Delta_3)\cos(k_x) + 2\Delta_2\cos(k_y) & -i(\Delta_1 - \Delta_3)\sin(k_x) & -2tr_0\gamma_k & 0 \\ i(\Delta_1 - \Delta_3)\sin(k_x) & \epsilon_d - (\Delta_1 + \Delta_3)\cos(k_x) - 2\Delta_2\cos(k_y) & 0 & -2tr_0\gamma_{k+G} \\ -2tr_0\gamma_k & 0 & \epsilon_p & 0 \\ 0 & -2tr_0\gamma_{k+G} & 0 & \epsilon_p \end{pmatrix}.$$

This expression holds for both the dimer and the uniform (when $\Delta_1 = \Delta_2 = \Delta_3 = \Delta$) solutions. k varies in the reduced Brillouin zone and $G = (\pi, \pi)$ has been introduced to take care of the doubling of the unit cell.

The minimization of the mean-field free energy with respect to r_0 , λ , and Δ_i leads to five self-consistency equations. Solving numerically these equations together with the equation for the chemical potential μ , which fixes the average number of particles per unit cell per spin n to the value $(1 + \delta)/2$ (δ is the doping), yields the set of mean-field parameters (r_0, λ, Δ_i). Varying the doping and

the coupling values of the Hamiltonian one obtains different mean-field solutions.

The phase diagram. Figures 1(a) and 1(b) describe the phase diagram of the system $J=0.2$. In Fig. 1(a) we vary t and the doping δ , keeping $\epsilon = \epsilon_p - \epsilon_d^0 = 2$, i.e., $\epsilon/J = 10$, fixed. In Fig. 1(b) we fix $t = 0.5\sqrt{2}$, i.e., $t/J = 2.5\sqrt{2}$, and vary ϵ .

Three different phases are present in both cases. For small values of $W \equiv \epsilon/t$ the system has uniform Δ and is a normal FL (UFL). There is no magnetic long-range order and the quasiparticles are mixtures of copper spin

and oxygen charge. When W increases a first-order phase transition takes place to a phase with finite dimerization $\Delta_i \neq \Delta_j$. This phase is metallic ($r_0 \neq 0$) away from half-filling but has magnetic (dimer) long-range order (MD). This phase is analogous to the itinerant magnetic phases with the dimerization playing the role of magnetic long-range order. For larger values of W a second phase transition to an insulating dimer phase (ID) takes place. The copper spins form a perfect dimer. In the renormalized band description this is described by flat d bands. The holes go to the oxygen sites and are very weakly scattered by the inert magnetic background. In the mean-field theory this fact is reflected by a zero-hybridization order parameter ($r_0 = 0$). If there is oxygen dispersion this phase would be metallic. In the absence of oxygen dispersion we have an insulator even away from half-filling and the transition to the MD phase is a MIT. This phase is realized in magnetic semiconductors, where the magnetic order of the magnetic moments prevents the Kondo effect. The phase diagram of the system is determined by the interplay between the hybridization energy t , the charge-transfer energy $\epsilon_p - \epsilon_d^0$, the magnetic exchange energy J , and the kinetic energy of each hole, which [for $t < (\epsilon_p - \epsilon_d^0)$] is given by $t^2/(\epsilon_p - \epsilon_d^0)$. When J is small the phase diagram can be understood as follows. The transition between the UFL and the MD takes place when the magnetic energy J is comparable to the total kinetic energy of the holes $\sim \delta t^2/(\epsilon_p - \epsilon_d^0)$. The transition between the ID and the MD takes place at small doping when the magnetic energy J is comparable with the kinetic energy per hole $t^2/(\epsilon_p - \epsilon_d^0)$. The system becomes insulating because it can be energetically advantageous to

lose the kinetic energy in order to gain the magnetic exchange energy forming a perfect dimer ($\Delta_1 = J/2$; $\Delta_2 = \Delta_3 = 0$). This transition is expected to be disfavored by increasing doping since the system becomes less correlated. This situation is made more apparent in the first phase diagram [Fig. 1(a)] where the increasing δ when one moves to the right has to be compensated by the decreasing of t , when one moves upwards in the $(\epsilon/t) - \delta$ plane. As a result, even for large doping, it is possible to find a sufficiently small t such that the total kinetic energy loss is smaller than the magnetic gain, making the MIT possible. This MIT is of the second order for small δ and becomes of the first order for larger doping $\delta > 0.18$. For small fixed δ , decreasing t , the bands become continuously flat and λ increases in such a way that the upper d -like band gets superimposed to the ϵ_p level while the lowest d band lies below, separated by a gap of value J . In this situation the completely filled lower d band characterizes the freezing of the charge degrees of freedom on the Cu holes, while the δ holes due to doping partially fill the oxygen level. For larger doping the band interplay is such that the transition is of the first order. In this case, the transition is from a configuration having the holes in well-dispersed bands into the above-described perfectly dimerized configuration.¹¹

The uniform phase is a Fermi liquid with antiferromagnetic correlations. On the other hand our $N = \infty$ approximation does not identify unambiguously the physical nature of the magnetic phases. In particular the dimerized insulator can equally well represent an insulating antiferromagnet or a spin-singlet liquid of holes on the copper sites underlying holes on the oxygen levels. Indeed, although we chose a particular dimer solution, other choices would have been equally acceptable due to the energy degeneration of the various dimer configurations. In fact it is possible to show that small clusters of dimers can be continuously rotated without energy cost, and therefore the seeming long-range order of our solution could be a feature of the mean-field treatment. It is possible that the mean-field ID becomes a quantum liquid of Cu spin singlets once fluctuations are taken into account. Alternatively the ID phase can be thought to mimic an antiferromagnet with localized moments on the Cu sites.¹²

Phase separation. The analysis of the chemical potential as a function of doping identifies in both phase diagrams a region where the compressibility $\kappa \equiv (d\mu/dn)^{-1}$ is negative. This is a signature of a thermodynamic instability leading to a phase separation. Two different attitudes can then be taken. On the one hand, one can include in the model long-range interactions among the holes. This would stabilize the system, preventing phase separation and keeping the validity of the above-described phase diagrams. On the other hand, one can keep the model in Eq. (1) unchanged (with no long-range forces) and accept the presence of the phase separation. To connect this latter case with real systems one has to assume that the background of O^{2-} also separates to compensate for any charge imbalance. Evidence for this has been reported in oxygen-doped La_2CuO_4 .¹³

We have determined the phase separation region

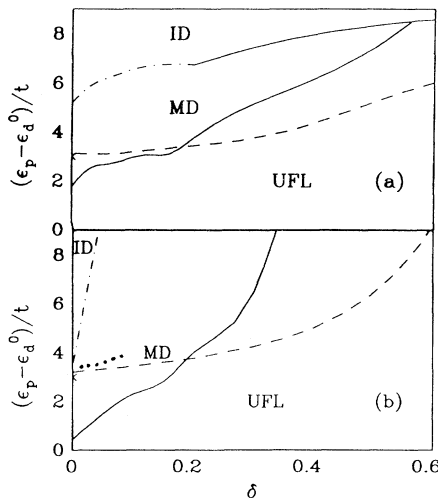


FIG. 1. Phase diagram at $J=0.2$ for various values of ϵ/t and δ . In (a) $\epsilon \equiv \epsilon_p - \epsilon_d^0 = 2$ is fixed and t varies. In (b) $t = 0.5\sqrt{2}$ is fixed while ϵ is changed. UFL: uniform Fermi liquid; MD: metallic dimer; ID: insulating dimer. The solid lines indicate first-order phase transitions while dot-dashed lines indicate second-order phase transitions. The dashed line is the phase separation line. The dotted line in (b) is the phase separation line when $J=0.05$. The crosses in (a) and (b) show the SCITIT.

[which, in Figs. 1(a) and 1(b), is the one above the dashed line] using a standard Maxwell construction. We find that the region of parameters available to the MD phase is strongly reduced, while the ID phase is always unstable at finite doping. Therefore at small t 's or at large ε and finite δ the system will create regions in the space with a perfect insulating dimerization at half-filling and other hole-rich regions in the UFL phase (or in the MD phase if the ε/t ratio is small). Also shown in Fig. 1(b) is the phase separation region, delimited by a dotted line, for a smaller value $J=0.05$ of the superexchange coupling and for small doping.

An analogous phase separation has been discussed⁴ in the single-band t - J model. Hence, phase separation is not a feature of the $N = \infty$ approximation or of the particular (dimer) symmetry chosen for the magnetically correlated mean-field solution, but a generic feature of doped quantum magnets. Contrary to our result, a phase separation at small doping is always found in the single-band t - J model because it corresponds to our $\varepsilon/t \gg 1$ limit,⁹ whereas we can also study the region where the doped system is stable ($\varepsilon \sim t$). Since the charge-transfer energy ε in our model plays the role of U in the Hubbard model our result suggests that no phase separation would occur in a small- U single-band t - J model.

The insulator-insulator transition. At zero doping, when the ratio W reaches a critical value $W_c \sim 3$, the hybridization order parameter which measures the dispersion of the bands ($\sim r_0^2$) goes continuously to zero. This transition is not a MIT because at $\delta=0$, even when r_0^2 is different from zero, the system is already insulator if $\Delta_1 \neq \Delta_2 \neq \Delta_3$. In fact a gap opens between the lowest mainly d bands because of the doubling of the unit cell and the chemical potential lies in the middle of the gap. A similar situation arises in the theory of the AFM Slater insulators. The phase transition which takes place when $W \rightarrow W_c$ can be viewed as a Slater-to-charge-transfer-insulator transition (SCTIT). This transition shares many features with the MIT studied by Brinkman and Rice in the Hubbard model. Here W plays the role of the ratio U/t in the Hubbard model. We calculated both numerically and analytically the behavior of r_0^2 , μ , and κ in the proximity of the SCTIT, finding

$$\kappa \sim r_0^2 \sim \frac{(W_c - W)}{W_c}$$

if $W \rightarrow W_c^-$, and

$$\kappa \sim \frac{(W - W_c)^{1/2}}{W_c}$$

If $W \rightarrow W_c^+$. It should be noticed that the critical behavior of $\kappa^{-1} \equiv d\mu/dn$ is determined by the singular dependence of the level renormalization λ on the doping: below the transition ($W < W_c$) λ crosses smoothly the $\delta=0$ axis, while it becomes discontinuous [$\lambda(\delta=0^+) \neq \lambda(\delta=0^-)$] above the transition. It is therefore natural to expect a divergency of $d\lambda/dn$ at the transition, so that $d\mu/dn \sim (\partial\mu/\partial\lambda)d\lambda/dn = \infty$. We also

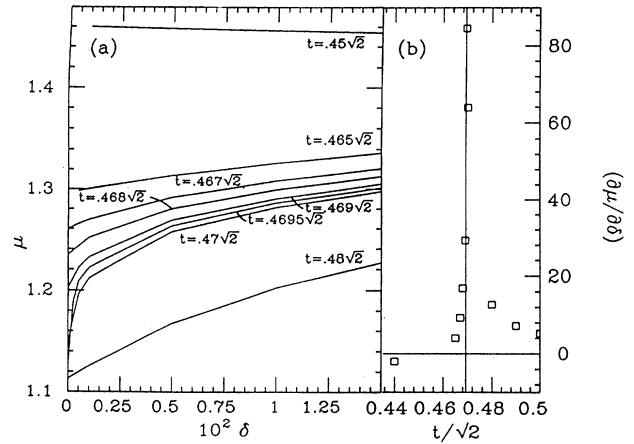


FIG. 2. (a) Chemical potential as a function of the doping. (b) Inverse compressibility divergency across the SCTIT as $\delta=0^+$.

checked that, close to the SCTIT, $\lambda(\delta)$ is odd with respect to the point $\bar{\varepsilon}=(\varepsilon+J)/2$ so that $(d\lambda/dn)_{\delta=0^-} = -(d\lambda/dn)_{\delta=0^+}$. The results are in agreement with those obtained in Ref. 14 for a $J=0$ two-band infinite- U Hubbard model and with the well-known behavior in the single-band finite- U Hubbard model at the Brinkman-Rice transition. The different power appearing in κ for the two cases $W < W_c$ and $W > W_c$ is an indication that the transition cannot be simply interpreted in terms of a standard Landau-Ginzburg mean-field model with W playing the role of the temperature. Figure 2(a) reports numerical calculations for μ as a function of doping for various values of W . κ^{-1} is reported in Fig. 2(b): it diverges at the transition and becomes negative in the phase separation region slightly above SCTIT.

For finite oxygen-oxygen overlap the phase separation occurs between two phases, both having finite hole concentration.

We finally comment on possible implications of our analysis on pairing mechanisms involving magnetic correlations.^{15,16} One can interpret the ID phase in terms of an insulating layer of localized spins on copper underlying a FL of holes¹² in the oxygen band. Assuming a Kondo-like coupling of the mobile holes to the localized spins, some authors have proposed that the holes in the oxygen band will have a pairing tendency in order to reduce the frustration on the antiferromagnetically correlated substrate.

A different scenario can arise if the Kondo coupling is strong. In this case the holes in the oxygen band are bound to the copper spin singlets, and the single-band picture² can be more appropriate. It is believed that the ground state in this region of small doping is not of the FL type,² but does not have magnetic long-range order.

None of these pictures is realized in the large- N limit of our model. In fact, without invoking long-range forces, our model does not allow for the simultaneous presence of the magnetic substrate (ID) and of holes in the oxygen

band: it rather prefers to separate in an insulating perfected magnetic phase with no holes in the oxygen band and a FL phase with copper-oxygen hybridization.

On the other hand the appearance of a phase separation in the large- N limit suggests that the effective forces among the holes have some kind of attractive tail. Whether this attractive tail will lead to superconductivity

(rather than to phase separation) at finite N is an open problem which needs further theoretical investigation.

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¹J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 188 (1986).

²P. W. Anderson, in *Frontiers and Borderlines in Many Particle Physics*, International School of Physics "Enrico Fermi," (North-Holland, Varenna, 1987).

³P. Lederer, D. Poilblanc, and T. M. Rice, *Phys. Rev. Lett.* **63**, 1519 (1989).

⁴V. J. Emery, S. A. Kivelson, and H. Q. Lin, *Phys. Rev. Lett.* **64**, 475 (1990).

⁵N. Nücker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer, and Z. X. Zhao, *Phys. Rev. B* **39**, 6619 (1989).

⁶C. Castellani and G. Kotliar, *Phys. Rev. B* **39**, 2876 (1989).

⁷A. Houghton, N. Read, and H. Won, *Phys. Rev. B* **37**, 3782 (1988).

⁸P. Coleman, *Phys. Rev. B* **29**, 3035 (1984).

⁹G. Kotliar, P. A. Lee, and N. Read, *Physica C* **153-155**, 538 (1988).

¹⁰I. Affleck and B. Marston, *Phys. Rev. B* **37**, 3774 (1988).

¹¹This scenario is different from the one presented in Ref. 6, where the FL-ID transition turned to be of the first order. This difference is a consequence of the simplifying assumption

$\gamma_k = \gamma_{k+G}$ made in Ref. 6 and which, due to band interplay, posed a lower bound to r_0^2 to that the $r_0=0$ limit could not be reached continuously. Moreover in Ref. 6 the $\epsilon \gg t$ limit was considered and therefore the insulator-insulator transition (see below) could not be studied.

¹²The fact that this system is insulating is a consequence of our simplifying assumption of vanishing overlap between oxygen orbitals. If this last assumption were released, the p levels would acquire a dispersion and because of the δ holes in them the system would no longer be insulating, the p holes forming a Fermi liquid on this oxygen band. The stabilizing presence of J would, however, keep the d bands flat.

¹³D. Jorgensen *et al.*, *Phys. Rev. B* **38**, 11 337 (1988); M. Hundley *et al.* (unpublished).

¹⁴G. Kotliar, *Int. J. Mod. Phys. B* **1**, 711 (1988).

¹⁵A. Aharony, R. J. Birgenau, A. Coniglio, M. A. Kastner, and H. E. Stanley, *Phys. Rev. Lett.* **60**, 1330 (1988).

¹⁶C. Castellani, C. Di Castro, and M. Grilli, *Physica C* **153-155**, 1659 (1988).