Electronic Properties of High-T_c Superconductors

C. A. Balseiro[(a)] and M. Avignon
Laboratoire d'Études des Propriétés Électroniques des Soides, Centre National de la Recherche Scientifique, BP 166, 38042 Grenoble CEDEX, France

A. G. Rojo and B. Alascio
Centro Atomico Bariloche, 8400 Bariloche, Río Negro, Argentina
(Received 13 October 1988)

We study a generalized Hubbard Hamiltonian which includes the Cu and O orbitals in the CuO_2 planes of high-T_c superconductors. We use the slave-boson technique to account for the intra- and interatomic correlations. In the saddle-point approximation we obtain the metal-insulator phase diagram and conclude that for one hole per unit cell in the CuO_2 plane, La_2CuO_4 is a charge-transfer insulator. Our results show that doping produces a rapid metallization of the system and destroys antiferromagnetic order. Transport properties and the mechanism for superconductivity are briefly discussed.

PACS numbers: 74.65.+n, 74.20.−z, 75.10.Jm

In what concerns the electronic properties of high-T_c superconductors it is accepted that the carriers which play the dominant role for the superconductivity are mainly localized in the CuO_2 planes of these materials. There is also growing experimental evidence which indicates that electronic correlations are large, at least in the Cu sites.[1,2] Also, spectroscopic experiments show that holes added over the stoichiometric compound go mainly to the O sites.[3] For these reasons the conventional band-structure calculations are not adequate for an understanding of the electronic properties of these systems. In particular, they fail in describing the insulating nature of La_2CuO_4.

In searching for a theory of high-T_c superconductivity it is essential to have a good and, if possible, simple description of the reference normal state. Although some attempts have been made to treat the correlation effects in a proper way, they restrict to a range of parameters which do not always correspond to what is now accepted for high-T_c materials.[4-6]

In this Letter we consider a tight-binding Hamiltonian which includes Cu $3d$ and O $2p$ orbitals together with intra- and interatomic correlations. We show that the slave-boson technique in the saddle-point approximation provides the desired description with no restrictions in the parameter range. We derive and generalize the Zaanen, Sawatzky, and Allen (ZSA) phase diagram.[7] Our results are therefore not only applicable to high-T_c materials but are extendible to other transition-metal compounds. The Hamiltonian under consideration is[8]

$$H=\sum_{i\sigma}\epsilon_i n_{i\sigma}+\sum_{\langle ij\rangle\sigma}t_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+\sum_i U_i n_{i\uparrow}n_{i\downarrow}+V\sum_{\langle ij\rangle}n_i n_j, \tag{1}$$

where the index i runs over the sites of CuO_2 two-dimensional lattice in which every O atom lies between two Cu atoms. The operator $c_{i\sigma}^{\dagger}$ creates a hole with spin σ at the Cu $3d_{x^2-y^2}$ (O $2p_x,2p_y$) orbital with i labeling a Cu (O) site. The corresponding parameters $\epsilon_i=\epsilon_p,\epsilon_d$ and $U_i=U_p,U_d$ are the orbital energies and intra-atomic repulsions, respectively, while t_{ij} is the hopping matrix element and V is the interatomic Coulomb repulsion. In Eq. (1), the symbol $\langle ij\rangle$ means that the sum is performed only over nearest neighbors.

We extend to the present case the slave-boson treatment of Ref. 9 in which a single-band Hubbard model was considered. For the purpose we introduce four boson fields per site associated with each occupation state of the p or d orbitals, namely e_i, $s_{i\sigma}$ ($\sigma=\uparrow\downarrow$), and d_i. If the boson number operators ($e^{\dagger}e$, $s^{\dagger}s$, etc.) are viewed as projection operators on different occupation states, the following conditions have to be imposed:

$$e_i^{\dagger}e_i+\sum_s s_{i\sigma}^{\dagger}s_{i\sigma}+d_i^{\dagger}d_i=1\,, \tag{2a}$$

$$c_{i\sigma}^{\dagger}c_{i\sigma}=s_{i\sigma}^{\dagger}s_{i\sigma}+d_i^{\dagger}d_i\,. \tag{2b}$$

Equations (2a) and (2b) are the completeness relation and the charge-conservation condition, respectively. In the combined fermion-boson Hilbert space the Hamiltonian reads

$$H=\sum_{\langle ij\rangle\sigma}tZ_{i\sigma}^{\dagger}c_{i\sigma}^{\dagger}c_{j\sigma}Z_{j\sigma}+\sum_{i\sigma}\lambda_{i\sigma}c_{i\sigma}^{\dagger}c_{i\sigma}+\sum_{i\sigma}(\epsilon_i-\lambda_{i\sigma})(s_{i\sigma}^{\dagger}s_{i\sigma}+d_i^{\dagger}d_i)+\sum_i U_i d_i^{\dagger}d_i$$
$$+V\sum_{\substack{\langle ij\rangle\\ \sigma\sigma'}}(s_{i\sigma}^{\dagger}s_{i\sigma}+d_i^{\dagger}d_i)(s_{j\sigma'}^{\dagger}s_{j\sigma'}+d_j^{\dagger}d_j)+\sum_i\lambda_i'\left[e_i^{\dagger}e_i+\sum_{\sigma}s_{i\sigma}^{\dagger}s_{i\sigma}+d_i^{\dagger}d_i-1\right], \tag{3}$$

where λ_i and λ_i' are Lagrange multipliers introduced to satisfy the constraints of Eq. (2) and $Z_{i\sigma}$ is given by[10]

$$Z_{i\sigma}=(1-d_i^{\dagger}d_i-s_{i\sigma}^{\dagger}s_{i\sigma})^{-1/2}(e_i^{\dagger}s_{i\sigma}+s_{i\bar{\sigma}}^{\dagger}d_i)(1-e_i^{\dagger}e_i-s_{i\bar{\sigma}}^{\dagger}s_{i\bar{\sigma}})^{-1/2}. \tag{4}$$

In the physical subspace defined by Eqs. (2) the Hamiltonian (3) has the same matrix elements as those calculated

for (1) in the original Hilbert space. We evaluate the partition function in the saddle-point approximation (SPA), in which all Bose fields are taken as numbers independent of time. In the paramagnetic state the Lagrange multipliers (λ) and the boson-field mean values are independent of the cell position and spin. In the SPA the free energy per cell for the paramagnetic phase can be written as

$$f=-k_BT\sum_{ak\sigma}\ln[1+e^{-\beta(\epsilon_{ak\sigma}-\mu)}]+U_d d_d^2+2U_p d_p^2+4V\sum_{\sigma\sigma'}(s_{p\sigma}^2+d_p^2)(s_{d\sigma'}^2+d_d^2)$$
$$+\sum_{\sigma}[(\epsilon_d-\lambda_d)(s_{d\sigma}^2+d_d^2)+2(\epsilon_p-\lambda_p)(s_{p\sigma}^2+d_p^2)]$$
$$+2\lambda_p'\left[e_p^2+\sum_{\sigma}s_{p\sigma}^2+d_p^2-1\right]+\lambda_d'\left[e_d^2+\sum_{\sigma}s_{d\sigma}^2+d_d^2-1\right], \quad (5)$$

where $\epsilon_{ak\sigma}$ is the one-electron energy corresponding to band α and wave vector k. The bonding and antibonding bands ($\alpha=1,2$) are given by

$$\epsilon_{ak\sigma}=\tfrac{1}{2}(\lambda_p+\lambda_d)+(-1)^{\alpha}E(\xi) \quad (6a)$$

with

$$E(\xi)=\{\tfrac{1}{4}(\lambda_p-\lambda_d)^2+4q^2t^2[1+\tfrac{1}{2}\xi(k)]\}^{1/2}. \quad (6b)$$

In Eqs. (6), $\xi(k)=\cos(k_xa)+\cos(k_ya)$, and $q=\langle Z_i^{\dagger}Z_j\rangle$. The third band is a dispersionless nonbonding band with $\epsilon_{3k\sigma}=\lambda_p$. In our calculations the density of the ξ's, $\rho(\xi)$, is taken as a constant for $|\xi|<2$. The free energy f must be minimized with respect to the variables d_i, $s_i=s_{i\sigma}$, e_i, and λ_i ($i=p,d$). At $T=0$, for the case of one hole per unit cell, we find either a semiconducting phase characterized by $q=0$ or a metallic phase with $q\neq0$. In Fig. 1 we show the phase diagram obtained in (U_d,Δ) space, where $\Delta=(\epsilon_p-\epsilon_d+2V)/2$ is the charge-transfer energy. Note that Δ not only depends on the energy difference between the Cu and O orbitals but also includes the effect of the interatomic repulsion V as suggested by Varma and Schmitt-Rink.[11] This phase diagram resembles the ZSA phase diagram. For large U_d, by increasing Δ one reaches a metal-insulator boundary at $\Delta^c\approx 2t+2t^2/U_d$. The semiconducting state is of charge-transfer type. In the large-Δ limit, the boundary is at $U_d^{(c)}\approx 8t^2/\Delta$. This limit can be viewed as a Mott transition in the narrow bonding band. For $\epsilon_p>\epsilon_d$, the phase boundary is independent of U_p. In fact, the metal-insulator boundary is obtained as the set of parameters U_d and Δ for which there is an infinitesimal charge transfer δn ($q\to 0$); near this boundary the effect of U_p can be neglected since it is of order δn^2. This seems to be a quite general phase diagram, since we obtain very similar boundaries for different lattice structures if Δ is replaced by $\Delta=(\epsilon_p-\epsilon_d+zV)/2$, where z is the oxygen coordination number of the lattice.

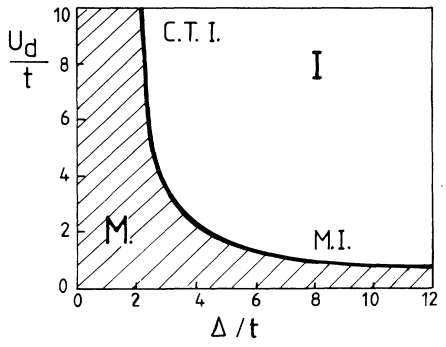

FIG. 1. Metal-insulator phase diagram in the (U_d,Δ) plane. The metallic and insulating areas are denoted by M and I, respectively. The region of the parameters corresponding to a charge-transfer insulator (C.T.I.) and a Mott insulator (M.I.) are indicated.

In the semiconducting phase the mass gap is given by

$$E_g=\left.\frac{\delta E}{\delta n}\right|_{1^+}-\left.\frac{\delta E}{\delta n}\right|_{1^-}, \quad (7)$$

where E is the internal energy and n is the average number of particles per unit cell. The gaps obtained are shown in Fig. 2 for different values of the parameters. For $U_d\to\infty$, $E_g=2(\Delta^2-4t^2)^{1/2}$, which clearly indicates that in the large-U limit the gap is of charge-transfer type. On the other hand, for $\Delta>U_d$ the gap is dominated by U_d (Mott insulator).

For simplicity, we assume that the effect of doping or changing the oxygen content in high-T_c superconductors is to modify the number of holes per unit cell but that it

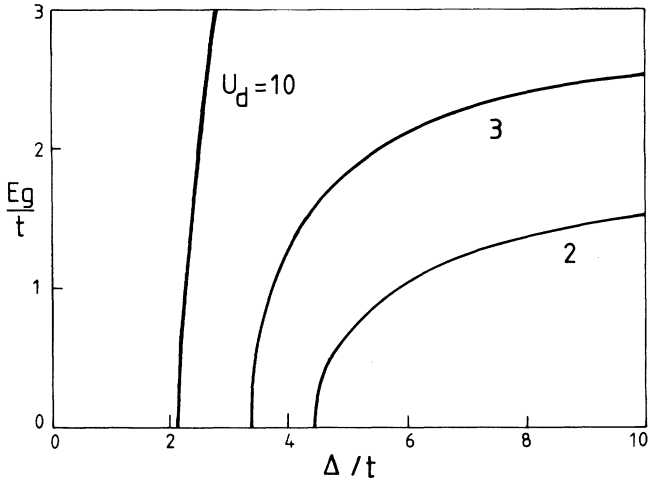

FIG. 2. Mass gap as defined by Eq. (7) as a function of Δ for different values of U_d. The results are independent of U_p.

does not change the microscopic parameters of Hamiltonian (1). We calculate the mass renormalization as a function of doping. The renormalized mass m^* is given by the factor q which in turn renormalizes the hopping matrix element as $m/m^* = q^2 E^0(\xi_F)/E(\xi_F)$, where m is the bare mass and E (E^0) is the energy defined by Eq. (6b) at the Fermi level for the interacting (noninteracting) system.

In Fig. 3 we present results for m^* as a function of doping $\delta = n - 1$, n being the number of holes per unit cell. The results obtained show that in the metallic phase and far from the metal-insulator boundary, $m^* \sim m$ is weakly dependent on doping. In the semiconducting phase the effective mass decreases rapidly with doping, showing a rapid metallization of the system as was previously conjectured from exact diagonalization of small clusters.[8] For a reasonable set of parameters obtained for La_2CuO_4[12] [$t \sim 1.5$ eV, $U_d \sim 6t$, $U_p \sim 3t$, $(\epsilon_p - \epsilon_d)/2 \sim t$, $V \sim 1.5t$] this system lies in the region of charge-transfer semiconductors. However, for this set of parameters the system is close to the metal-insulator boundary and with a change in the parameters within physically reasonable limits one could obtain either a heavy-mass metal or a semiconductor with a gap E_g up to 2 eV.

Within the same framework we study the antiferromagnetic instability. We assume an antiferromagnetic structure in which there is no magnetization of the O atoms and the Cu sublattice is divided in two interpenetrated sublattices. By studying the divergence of staggered susceptibility associated with the proposed magnetic structure, we obtain the phase diagram of Fig. 4. This phase diagram is restricted to $\epsilon = (\epsilon_p - \epsilon_d)/2 > 0.5$. For ϵ small (or negative), the holes tend to localize on O sites and, consequently, the proposed magnetic structure becomes unstable. For $\epsilon \geq 0.5$, the holes are localized mainly on the Cu and the phase diagram is not very sensitive to U_p. In agreement with experimental results, we find that systems close to the stoichiometric situation are antiferromagnetic but a small doping destroys the magnetic long-range order.

We have looked for the temperature dependence of the effective mass in stoichiometric samples. To simplify the calculations we have taken the limit $U_d \to \infty$. In this limit the probability of double occupation at Cu sites d_d^2 is zero. Temperature induces charge transfer from Cu to O. In lowest order in this charge transfer and eliminating λ', the free energy can be written in terms of p_d^2 only. The charge on Cu is then given by

$$\langle p_d^2 \rangle = \frac{\int p_d^2 e^{-\beta f(p_d^2)} dp_d^2}{\int e^{-\beta f(p_d^2)} dp_d^2}, \tag{8}$$

where f is the free energy. Using this expression to calculate the effective mass at low temperatures, we obtain $q(T) = \gamma\sqrt{T}$.

The obtained temperature dependence of q in the limit $U_d \to \infty$ implies that $m/m^* \propto \gamma T$. The prefactor is very small if the system lies well inside the insulating phase but increases and becomes large for insulators lying close to the metal-insulator boundary. Recent experimental results on Y-Ba-Cu-O indicate the effective mass of the carriers are temperature dependent.[13]

The model Hamiltonian (1) has been extensively studied in connection with superconductivity induced by charge-transfer excitations. Varma, Schmitt-Rink, and Abrahams[14] first suggested the importance of the interatomic repulsion V as responsible for the superconductivity in these compounds. Moreover, numerical simulations in small clusters show the existence of pairing in the CuO_2 planes.[8,15] In the present approach the nature of this pairing can be visualized by adding two holes to the charge-transfer insulator. The added holes, which are infinitely massive, are bounded for $V > \epsilon_p - \epsilon_d$.[8] As the doping increases the mass decreases and if this mechanism is not completely inhibited it could give rise to superconductivity.

Finally, let us mention that for the generalized Hamiltonian of Eq. (1) it is not clear how to extend the Gutz-

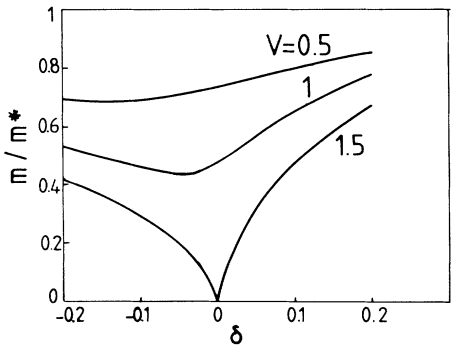

FIG. 3. Effective mass as a function of doping. The parameters are $U_d = 6t$, $U_p = 0$, $\epsilon = t$, and different values of V.

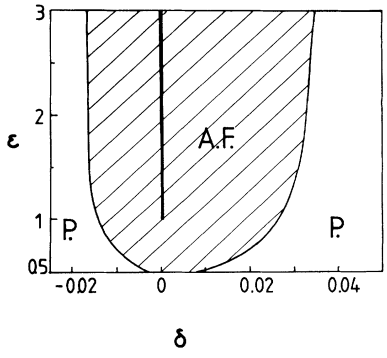

FIG. 4. Magnetic phase diagram in the (ϵ, δ) plane. The hatched area is antiferromagnetic. The thick line at $\delta = 0$ indicates the insulating state. The parameters are $U_d = 6t$, $U_p = 0$, and $V = 1.5t$.

willer approximation (GA) and different approaches have been proposed.[16] Our results with the slave-boson technique are not equivalent to those obtained in these treatments, although they are qualitatively similar. Using the GA as defined in Ref. 17 we obtained a phase diagram similar to that of Fig. 1.

In summary, we presented a slave-boson treatment of a generalized Hubbard Hamiltonian which models the electronic structure of CuO_2 planes. In our treatment all on-site interactions are treated on the same footing. The interatomic repulsion V is considered at a level which corresponds to a Hartree-type approximation. In the saddle-point approximation we derive a metal-insulator phase diagram and study the antiferromagnetic instability and the metallization of the system as a function of doping.

We have shown that for Δ larger than a critical value, the stoichiometric systems are charge-transfer insulators. In this phase the Cu-O planes are highly ionic; however, a small doping produces a rapid metallization. In agreement with experimental results, systems close to stoichiometry are antiferromagnetic but the long-range antiferromagnetic order is rapidly destroyed by doping.

The approach presented here provides a natural framework for the study of high-T_c superconductivity.

One of us (A.G.R.) is supported by the Consejo Nacional de Investigaciones Cientificas y Tecnias, Argentina. We are grateful to D. Mayou for helpful discussions concerning the Gutzwiller approximation. Laboratoire d'Études des Propriétés Électroniques des Solides is associated with Université Joseph Fourier, Grenoble, France.

---

[a]On leave from Centro Atomico, Bariloche, Argentina.

[1]See, for example, *High Temperature Superconductors and Materials and Mechanisms of Superconductivity,* edited by J. Müller and J. L. Olsen (North-Holland, Amsterdam, 1988).

[2]A. Bianconi *et al.*, Z. Phys. B **67**, 307 (1987); in Ref. 1, p. 1761, and references therein.

[3]N. Nücker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Temmermann, Phys. Rev. B **37**, 5158 (1988).

[4]P. W. Anderson, Science **235**, 1196 (1987); G. Baskaran, Z. Zhou, and P. W. Anderson, Solid State Commun. **63**, 973 (1987).

[5]F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).

[6]G. Kotliar, P. A. Lee, and N. Read, in Ref. 1, p. 538; P. J. Hirschfeld *et al.*, Proceedings of the American Physical Society March Meeting, New Orleans, 1988 (unpublished).

[7]J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[8]E. R. Gagliano, A. G. Rojo, C. A. Balseiro, and B. Alascio, Solid State Commun. **64**, 901 (1987); C. A. Balseiro, A. G. Rojo, E. R. Gagliano, and B. Alascio, Phys. Rev B **38**, 9315 (1988); in Ref. 1, Vol. 2, p. 1223.

[9]G. Kotliar and A. Ruckenstein, Phys. Rev. Lett. **57**, 1362 (1986).

[10]The $Z_{i\sigma}$ is introduced to guarantee that the change in the fermion state at site i is followed by the corresponding change in the boson state. The choice of $Z_{i\sigma}$ in not unique. If we impose the condition that in the saddle-point approximation, the exact results are recovered for the noninteracting case, then the choice is restricted and the form of Eq. (4) is a good choice (see Ref. 9 for the Hubbard model).

[11]C. M. Varma and S. Schmitt-Rink, in *Proceedings of the International Conference on Novel Mechanisms of Superconductivity, Berkeley, 1987,* edited by S. Wolf and V. Kresin (Plenum, New York, 1987).

[12]M. Schlüter, in *High Temperature Superconductivity,* edited by R. Nicolsky and R. Escudero (World Scientific, Singapore, 1988).

[13]G. A. Thomas *et al.*, Phys. Rev. Lett. **61**, 1313 (1988).

[14]C. M. Varma, S. Schmitt-Rink, and Eliu Abrahams, Solid State Commun. **62**, 681 (1987); C. M. Varma, in "Towards a Theoretical Understanding of High T_c Superconductors," edited by S. Lundqvist *et al.* (World Scientific, Singapore, to be published).

[15]J. E. Hirsch, S. Tang, E. Loh, Jr., and D. J. Scalapino, Phys. Rev. Lett. **60**, 1668 (1988); see also Ref. 8.

[16]D. Mayou, D. Nguyen Manh, and J. P. Julien (to be published); see also K. Miyake, T. Matsuura, K. Sano, and Y. Nagaoka, J. Phys. Soc. Jpn. Lett. **57**, 722 (1988).

[17]P. Nozières, "Magnétisme et Localisation dans les liquides de Fermi," lecture notes, Collège de France, 1986 (unpublished).