PHYSICAL REVIEW B VOLUME 38, NUMBER 13 1 NOVEMBER 1988

Pairing mechanisms in high-T_c superconductors

C. A. Balseiro, A. G. Rojo, E. R. Gagliano, and B. Alascio
Centro Atómico Bariloche, 8400 Bariloche, Rio Negro, Argentina
(Received 12 January 1988)

We study the electronic structure of Cu-O high-T_c superconductors using a tight-binding Hamiltonian with strong intra-atomic and interatomic Coulomb repulsion. We assume that only Cu($3d_{x^2-y^2}$) and O($2p_x$) and O($2p_y$) orbitals are relevant. We solve finite clusters exactly and use a cell approximation to show that the basic assumptions together with quasidegeneracy of p and d energies leads to attractive interactions between holes in the ceramic superconductors.

After several months of intensive experimental and theoretical research on high-T_c superconductors, it seems clear that the electronic properties arise from the Cu-O planes or chains of the structure. Furthermore, transport and magnetic properties[1,2] suggest low carrier concentrations together with strong correlations between them.[3]

Most of the proposed non-electron-phonon mechanisms include high electronic correlations as a starting point.[4-6] In this Rapid Communication we show that high correlations in these materials give rise to pairing between holes due to the electronic polarization of the medium. Our analysis includes what is a common feature of both La-Sr-Cu-O and Y-Ba-Cu-O, viz., Cu-O planes in which O atoms lie between two Cu atoms. We describe the electronic structure of these planes making the two following assumptions: (1) Only the Cu $d(x^2-y^2)$ and O $p(x),p(y)$ orbitals are relevant; (2) strong interatomic and intra-atomic Coulomb interactions.

The simplest Hamiltonian consistent with these assumption reads

$$H=\sum_{i,j,\sigma}\left[E_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+\sum_{\sigma'}U_{ij\sigma\sigma'}n_{i\sigma}n_{j\sigma'}\right]. \tag{1}$$

Here $E_{ii}=E_d(E_p)$, $U_{ii\sigma\bar{\sigma}}=U_d(U_p)$ for i labeling a Cu (O) site. We take only nearest-neighbor matrix elements: namely, $E_{ij}=t$ and $U_{ij\sigma\sigma'}=G$. The operator $c_{i\sigma}^{\dagger}$ creates one electron with spin σ in site i.

The undoped La-Cu-O or stoichiometric Y-Ba-Cu-O correspond to one electron per Cu($3d$) orbital and two electrons per O($2p$) orbitals. Similar versions of Hamiltonian (1) have been used by other authors to describe the electronic properties of high-T_c superconductors. Among others, Emery[7] and Hirsch[8] consider the parameter range in which charge fluctuations in Cu ions are nearly suppressed. In this case an effective Hamiltonian can be written in which the Cu orbitals are eliminated. It is worth noting that this quenching of the Cu charge makes the interatomic Coulomb repulsion G irrelevant. In contrast with this veiwpoint, Baskaran, Zou, and Anderson[9] assume that the O charge fluctuations are negligible, a limit in which G again plays no role.

However, band-structure calculations[10] and spectroscopic experimental evidence[11] indicate that the Cu and O orbitals are nearly degenerate which implies large charge fluctuations in both Cu and O atoms. This seems to be a characteristic shared by three families of ceramic superconductors, namely, Ba-Pb-Bi-O, La-Sr-Cu-O, and Y-Ba-Cu-O. It is in these cases, where charge-transfer excitations of low energy exist, that the interatomic Coulomb repulsion G becomes of fundamental relevance.

In a previous work[12] we reported the study of charge and spin correlations in Cu-O chains described by Hamiltonian (1). We showed that for large intra-atomic correlations ($U_p,U_d > t$) the state with one hole per Cu atom is an insulator. For $(E_p+U_p) < (E_d+U_d)$ the system tends to a $Cu^{2+}O^{2-}$ situation with strong antiferromagnetic correlations between Cu spins. If $(E_p+U_p)\cong(E_d+U_d)$, which is the case of Cu-O planes in these compounds, the spin-spin correlations are partially suppressed, but on the other hand new effects take place. In the semiconducting case (undoped La-Cu-O or stoichiometric Y-Ba-Cu-O) the low-energy charge excitations are excitons. As we show below, when a hole is added to this state polarization effects are important for $G \gtrsim t$. As a result, the motion of the hole is followed by an excitonic cloud giving rise to an "excitonic polaron." In a rather different context it has been argued that such excitoniclike charged clouds can be coupled via phonons to form Cooper pairs.[13]

In what follows we show that within the context of Hamiltonian (1) an attractive interaction between holes arises due to an electronic polarization of the medium. If we want to describe the situation in which charge fluctuations take place in both Cu and O atoms as in the case of these materials, it is not easy to eliminate some degrees of freedom through a canonical transformation. We then resort to the ideas of the real-space renormalization group to write an effective Hamiltonian. This effective Hamiltonian makes evident the existence of an attractive interaction between holes. We proceed as follows. (i) We divide the lattice into cells of three sites each, one Cu and two O atoms (see Fig. 1), and consider only the subspace corresponding to zero, one and two holes per cell. (ii) We calculate the eigenvalues and eigenvectors of the cell Hamiltonian and keep only the lowest-energy states for each number of particles. (iii) We define new cell-fermion operators associated with these states and compute the intercell coupling using standard techniques. This procedure gives the following effective Hamiltonian:

$$H=\sum_{i\sigma}\tilde{\epsilon}n_{i\sigma}+\tilde{U}\sum_{i}n_{i\uparrow}n_{i\downarrow}+\tilde{G}\sum_{(i,j)}n_in_j+\sum_{(ij)}[\tilde{t}a_{i\sigma}^{\dagger}a_{j\sigma}(1-n_{i\bar{\sigma}})(1-n_{j\bar{\sigma}})+\tilde{t}'a_{i\sigma}^{\dagger}a_{j\sigma}n_{i\bar{\sigma}}n_{j\bar{\sigma}}+\tilde{t}''a_{i\sigma}^{\dagger}a_{j\sigma}(1-n_{i\bar{\sigma}})n_{j\bar{\sigma}}], \tag{2}$$

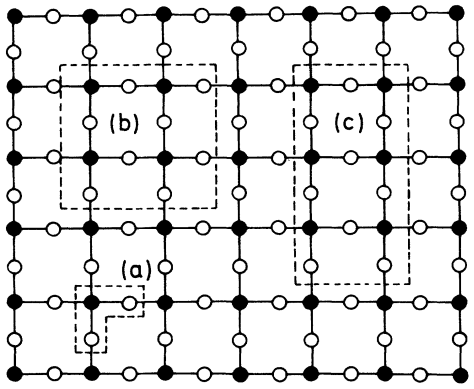

FIG. 1. Cu-O plane structure. (a) Three-sites cluster used in the cell approximation. (b) and (c) Clusters used in finite-size studies.

where i runs over a square lattice and $a_{i\sigma}^{\dagger}$ creates an electron of spin σ in the ith cell: $n_i = n_{i\uparrow} + n_{i\downarrow}$. In terms of the new cell fermion operators, the "one particle" state $a_{i\sigma}^{\dagger}|\mathrm{O}\rangle$ corresponds to one electron per Cu orbital and two electrons per O orbital. The effective intracell Coulomb repulsion $\tilde{U}$ is a large quantity and consequently the one particle per cell state is a Mott insulator. For large U and nearly half filled band the dominant hopping matrix element is $\tilde{t}$. The values of the new parameters, $\tilde{t}$ and $\tilde{G}$, are shown in Fig. 2 as a function of $\Delta = (\epsilon_d + U_d) + 2G - (\epsilon_p + U_p)$. These results correspond to $U_d/2 = U_p = 4t$. The outstanding result concerns the attractive interaction between particles in different cells G. The strongest attractive interaction occurs for values of the parameters which correspond to an effective quasidegeneracy of the d and p orbitals ($\Delta \sim 0$). A simple interpretation of this result can be attained by looking at the highly correlated limit of Hamiltonian (1) ($U_p, U_d \to \infty$). In this limit one valence state of each Cu and O ion can be projected out of the Hilbert space and therefore the system can be regarded as a spinless Fermion lattice as far as the charge degrees of freedom are concerned.[12] We assume that the Cu^{3+} and neutral O are such projected states. In terms of holes we retain the configurations with zero and one hole of each of the ions. Consequently, we find convenient a description in terms of holes. In this highly correlated limit, Hamiltonian (1) can be replaced by the following spinless Hamiltonian.

$$H = \sum_i \Delta_i b_i^{\dagger} b_i + \sum_{(ij)} t_{ij} b_i^{\dagger} b_j + G b_i^{\dagger} b_i b_j^{\dagger} b_j \,. \qquad (3)$$

Here $b_i^{\dagger}$ creates a hole at the ith site, $\Delta_i = \Delta$ ($-\Delta$) for i labeling a Cu (O) site. Having made this approximation we gain simplicity in the description of charge excitations, at the expense of loosing every insight on the spin degrees of freedom. Although we are mainly interested in the properties of the two-dimensional lattice of Fig. 1 we find it instructive to present first some results corresponding to a linear chain of Cu-O atoms described by Hamiltonian (3). In the linear chain, the energy spectrum for $G = 0$ consists of two bands separated by an energy gap $E_g = 2\Delta$. The semiconducting state corresponds to one hole per Cu ion.

The charge-charge correlation function depicted in Fig. 3 makes evident the existence of the excitonic polaron described above. For the case of one hole added to the semiconducting state, this correlation function shows different behaviors for $G = 0$ and $G > t$. For $G = 0$, the O-O correlation function Fig. 3(a) is nearly independent of distance,

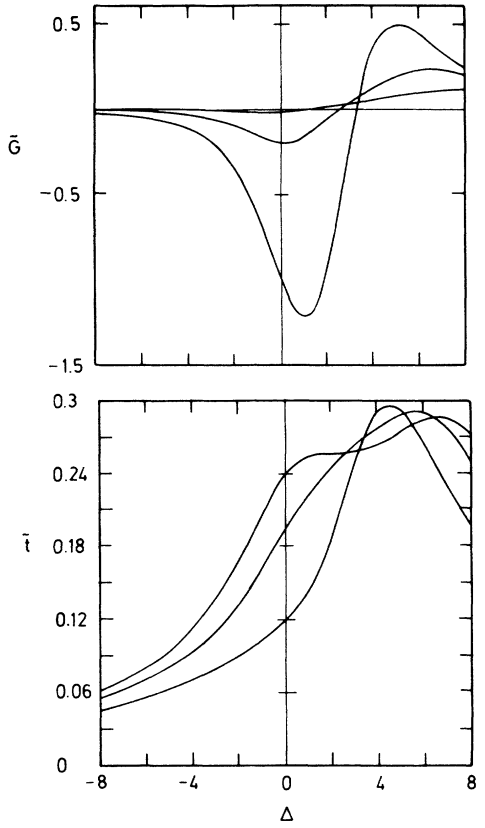

FIG. 2. Effective intracell interaction parameters as a function of Δ.

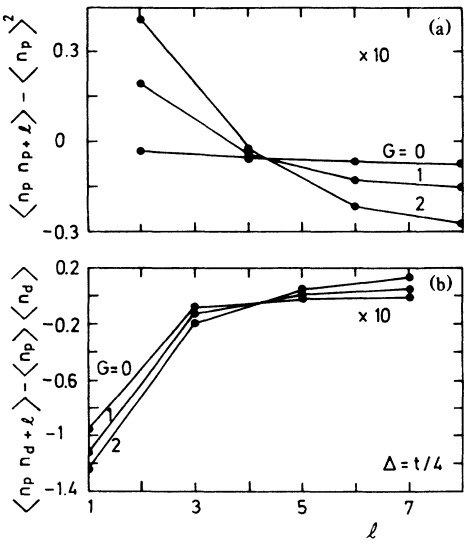

FIG. 3. Charge-charge correlation function as a function of distance. One hole added to a linear chain of sixteen alternating Cu-O atoms. (a) Oxygen-oxygen correlation function. (b) Copper-copper correlation function.

while for $G \geq t$ the correlation function shows a charge excess at near neighbors. In fact, for $G > t$, the added hole goes mainly to O sites and pushes away charge from Cu sites Fig. 3(b), towards the following O atoms. This charge transfer from Cu to O is essentially of excitonic character. For large doping the carrier concentration is large and the picture of excitonic polarons breaks down. In this case our results indicate a metallization of the system.[12]

We now turn our attention to the two-dimensional lattice, in which the $G=0$ spectrum consists of three bands, one bonding separated by a gap from an antibonding and a dispersionless nonbonding band. In the undoped stoichiometric systems the Fermi level lies in the gap; this is a consequence of the large intra-atomic correlations U. However the gap is not given by U but is of structural origin and its value is 2Δ.

For finite G a hole added to the semiconducting state produces, as in the one-dimensional case, a charge redistribution in its vicinity which in turn gives rise to an attractive interaction. Consider Hamiltonian (3) with $t=0$ and $\Delta > 0$, where the attractive interaction can be calculated explicitly. Adding one hole at an O site to the reference state, which consists of one hole per Cu atom, increases the energy by a quantity $\Delta+2G$. If a second hole is added sufficiently far from the first the energy increases again by the same quantity. If however the second hole is added in one of the O sites next to the first, charge can be rearranged so as to give an energy expense of $4\Delta+3G$ [see Fig. 1(d)]. Thus the energy difference between a bound hole-hole pair and two holes far apart is $E_b=2\Delta-G$. If $G < 2\Delta$ no charge redistribution occurs and E_b is zero. If the two holes are added to nth next-nearest neighbor O sites, the same reasoning leads to a binding energy $E_b=2n\Delta-G$.

The above arguments together with the cell approximation make plausible the existence of an attractive interaction between holes in this lattice. Exact diagonalization of finite clusters strongly supports this idea. In what follows we present results corresponding to the two-dimensional lattice of Fig. 1 described by Hamiltonian (3). In order to study the effective interaction between particles we calculate the ground-state energies $E(n)$ for different numbers of particles n in a cluster with periodic boundary conditions. We define the quantity E_b by the expression

$$E_b = E(n+2)+E(n)-2E(n+1)\,, \tag{4}$$

which embodies the effective interaction between particles. This becomes evident if the infinite lattice is thought of as a collection of finite clusters. Equation (4) gives the energy difference between the state with two particles added in the same cluster and the one in which particles are added to different clusters.

If n is equal to the number of Cu atoms, $E_b > 0$ means that when two holes are added to the semiconducting state it is energetically favorable to accommodate them in different clusters. Note that the asymptotic value of (4), as the system size becomes infinite, gives the so-called mass gap in the excitation spectrum of the system with $n+1$ particles. Thus $E_b > 0$ can be interpreted as a precursor of the presence of such a gap. On the other hand, when E_b is negative the lower-energy state is that in which the two extra holes were added to the same cluster. We therefore interpreted $E_b < 0$ as due to an attractive interaction of the two extra particles, $|E_b|$ being the binding energy.

In Fig. 4 we show E_b as a function of G and fixed Δ for the two clusters shown in Fig. 1. E_b is negative for all values of G, vanishing for $G=0$. As G increases E_b remains small up to $G \sim 2\Delta$, where its modulus increases rapidly. The maximum in Fig. 4(a) is a finite-size effect. Such a maximum also occurs in Fig. 4(b) for larger values of G.

We stress that neither the approximations given above, nor the numerical diagonalization leads to an attractive interaction in a simple Cu-O one-dimensional chain.

The presence of an attractive interaction does not necessarily imply a superconducting ground state. A simple two-dimensional model with an attractive nearest-neighbor interaction, as one would obtain from Hamiltonian (8) using the cell approximation, was studied by Scalapino, Sugar, and Toussaint and Gubermatis, Scalapino, Sugar, and Toussaint[14] using Monte Carlo methods. They showed that for the half-filled band case the strong-coupling limit corresponds to a condensation of particles while in the weak-coupling limit pairing is obtained. However the half-filled band is the least favorable situation for pairing due to the structure factor of the super-

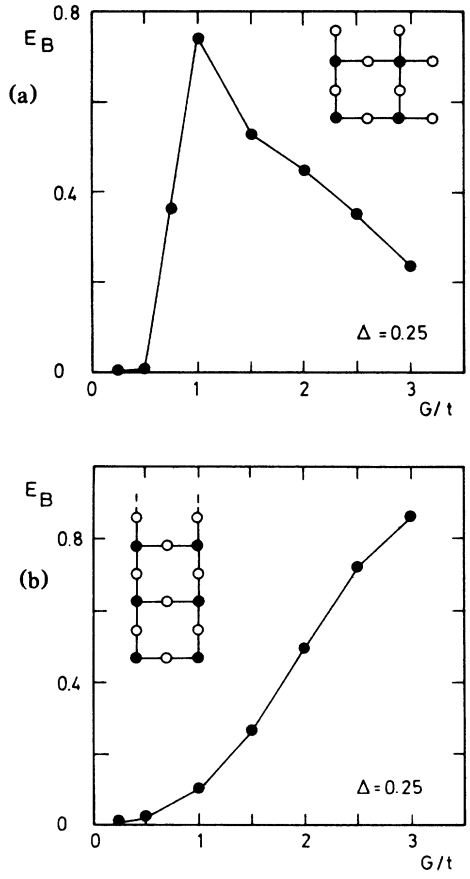

FIG. 4. $|E_b|$ as a function of G for $\Delta=0.25$, as obtained from Hamiltonian equation (3). (a) Square cluster, (b) ladder cluster [see Figs. 1(b) and 1(c)].

conducting order parameter $\Delta(k)$. A mean field solution predicts a critical temperature variation with band filling that shows a maximum for low carrier concentration.[15]

In conclusion, we have shown that the basic assumption regarding the relevant orbitals of Cu and O, strong correlation and quasidegeneracy of p and d energies, lead naturally to attractive interactions between holes in the ceramic superconductors. The results depicted in Fig. 4 clearly show the role of the interatomic interaction G in the pairing force. This fact was first conjectured by Varma, Schmitt-Rink, and Abrahams in Ref. 5.

Note added. After completion of this work, we received a paper by J. E. Hirsch, S. Tang, E. Loh Jr., and D. J. Scalapino[16] containing essentially the same results. We wish to thank J. E. Hirsch for sending us their work before publication.

Two of us (A.G.R. and E.R.G.) are supported by the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

[1]D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinya, and H. E. King Jr., Phys. Rev. Lett. **58**, 2802 (1987).

[2]M. A. Kastner, R. J. Birgeneau, C. Y. Chen, Y. M. Chiang, D. R. Gabbe, H. P. Jenssen, T. Junk, C. J. Peters, P. J. Picone, Tineke Thio, T. R. Thurston, and H. L. Tuller, Phys. Rev. B **37**, 111 (1988).

[3]P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987).

[4]C. M. Varma, S. Schmitt-Rink, and Elihu Abrahams, Solid State Commun. **62**, 681 (1987); in *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 355.

[5]M. Cyrot, Solid State Commun. **63**, 1015 (1987).

[6]A. Khurana, Phys. Today **40** (No. 7), 17 (1987), and references therein.

[7]V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).

[8]J. E. Hirsch, Phys. Rev. Lett. **59**, 228 (1987).

[9]G. Baskaran, Z. Zou, and P. W. Anderson, Solid State Commun. **63**, 973 (1987).

[10]L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987); J. Yu, A. J. Freeman, and J. H. Xu, *ibid.* **58**, 1035 (1987).

[11]A. Bianconi, J. Budnick, A. M. Flank, A. Fontaine, P. Lagarde, A. Marcelli, H. Tolentino, B. Chamberland, C. Michel, B. Raveau, and G. Domezeau, Solid State Commun. **63**, 1009 (1987).

[12]E. Gagliano, A. G. Rojo, C. A. Balseiro, and B. Alascio, Solid State Commun. **64**, 901 (1987).

[13]W. Y. Ching, Yongnian Xu, Guang-Lin Zhao, K. W. Wong and F. Zandiehnadem, Phys. Rev. Lett. **59**, 1333 (1987).

[14]D. J. Scalapino, R. L. Sugar, and W. D. Toussaint, Phys. Rev. B **29**, 5253 (1984); J. E. Gubernatis, D. J. Scalapino, R. L. Sugar, and W. D. Toussaint, *ibid.* **32**, 103 (1985).

[15]H. Fukuyama and K. Yosida, Jpn. J. Appl. Phys. **26**, L371 (1987); M. Foglio and C. A. Balseiro (unpublished).

[16]J. E. Hirsch, S. Tang, E. Loh Jr., and D. J. Scalapino (unpublished).