

Oxygen-disorder and correlation effects on the hole concentration and metal-nonmetal transition in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

A. Latgé and E. V. Anda

Instituto de Física, Universidade Federal Fluminense, 24220 Niteroi, Rio de Janeiro, Brazil

J. L. Morán-López

Instituto de Física, Universidad Autónoma de San Luis Potosí, 78000 San Luis Potosí, San Luis Potosí, Mexico

(Received 30 October 1989; revised manuscript received 27 February 1990)

A detailed analysis of the effect that oxygen disorder has on the electronic structure of the highly correlated high- T_c superconductors is presented. The system is modeled by a Hubbard-type Hamiltonian in which the on-site and intersite correlations between oxygen and copper atoms are included. The Green-function formalism is used to calculate the local electronic density of states at the Cu and O sites characteristic of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ as a function of oxygen concentration x and of the cation charge Q . Due to the large electronic interactions, a Mott-Anderson metal-nonmetal transition is obtained, in accordance with the experimental findings. The hole concentration n is calculated for disordered and ordered systems. A plateau in the concentration dependence of n is obtained for $0.45 \leq x \leq 0.75$, only in the ordered system. The correlation functions of the various charge states in Cu and O are also calculated and discussed.

I. INTRODUCTION

The study of the crystallographic structure of high- T_c superconducting materials has been a necessary step in the attempt to understand its superconductive properties. Neutron powder diffraction studies¹ have revealed that the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ system has the structure of an oxygen-deficient perovskite with essentially two active, one-dimensional (1D) and two-dimensional (2D), electronic objects in the unit cell: two CuO_2 planes and a linear chain in the basal plane, which are weakly linked by an oxygen atom. This atom is in a bridge position between two copper atoms [O(4) in the notation of Ref. 1] closer to the chain than to the CuO_2 planes.

Several band-structure calculations of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ using various local-density-functional approximation schemes, reported recently,^{2,3} have been limited to the case in which the material can be considered microscopically as an ordered system ($x=0, 0.5$, and 1). Unfortunately, the transition from the superconducting to the insulating state observed in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ as a function of the oxygen concentration cannot be explained within the context of those theories. However, those calculations have revealed that the main features of the band structure near the Fermi level can be obtained by considering only two electronic orbitals: the d and p orbitals associated to Cu and O, respectively. This fact allows us to use a simple tight-binding model to study the electronic density of states in the vicinity of the Fermi energy.

In a previous work⁴ we used a tight-binding approach, as suggested by the local-density-functional calculations, to study the effect that the disorder, introduced by the oxygen vacancies, has on the electronic density of states of the compound. We were able to establish a correlation between the crystallographic phase (orthorhombic-

tetragonal) and the superconducting properties. However, a severe shortcoming of that study, as well as of the local-density-functional schemes, is that we did not include the electronic interactions of a local highly correlated system. Due to the large intra-atomic electronic repulsion at the Cu and at the O sites, it is generally accepted that the high- T_c ceramics belong to that class of systems. For example, those theories predict a metallic phase for any oxygen concentration ($0 \leq x \leq 1$), a fact that contradicts extensive experimental evidences.⁵ It is now well established that high- T_c superconductors, and in particular $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, suffer a Mott-Anderson metal-nonmetal transition as a function of the oxygen content (self-doping) and of the total charge Q transferred by the cationic elements to the basal and CuO_2 planes. The fact that the density of states at the Fermi level has mainly oxygen character, as has been determined by several experimental measurements,⁶ tends to confirm that those systems are Mott insulators for $x \leq 0.3$.

A proper understanding of superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ requires a detailed analysis of the simultaneous effects that electronic correlations and disorder have on the region near the Fermi level and in particular its influence on the equilibrium interchange of electronic charge (as a function of doping) between the localized linear chain states and the extended states of the CuO_2 planes. It is this equilibrium of charge between the 1D and 2D parts of the system which regulates the dependence of T_c as a function of oxygen content, and which could give an explanation for the reduction of the superconducting transition temperature for samples with the oxygen atoms partially ordered and which are produced by a quenching process.

The purpose of this paper is to treat the highly correlated disordered electronic gas in a simple way but accurate enough to permit an adequate description of the

Mott-Anderson metal-nonmetal transition. Simultaneously we study the charge redistribution between the CuO_2 planes and the chains, associated to the mobile and localized holes, which can eventually give a plausible explanation for the dependence of the critical temperature with doping. The existence of a typical plateau at approximately 60 K (the value of this temperature depends upon the way in which the sample is prepared) for a wide range of oxygen concentration ($0.8 > x > 0.5$) is believed to be related to the number of mobile holes at the CuO planes. The number of total holes can be inferred experimentally by chemical methods,⁷ while the mobile holes can be obtained approximately by Hall measurements.⁸

Although many efforts have been devoted to understand the superconducting properties of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ there are still many open questions. Examples are (i) the understanding of the essential mechanism for superconductivity, (ii) the role of the various oxygen and copper atoms and their electronic charge, and (iii) the spatial ordering of oxygen at low temperatures in the basal plane. There is, as well, a lack of a microscopic model of high- T_c oxides for $T > T_c$, which we believe could help to understand the superconductive phase. In this paper we address some of those questions. The Hamiltonian used is presented in Sec. II. Its solution and the calculation of the local electronic density of states is contained in Sec. III. Finally the results are presented and discussed in Sec. IV. Details of the calculation are given in the Appendix.

II. THE HAMILTONIAN

To describe the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ system we propose a Hubbard type of Hamiltonian, which includes the intrasite Cu and O and the nearest-neighbor intersite O-O and O-Cu electronic repulsions. The Hamiltonian is composed by two contributions: a 2D oxygen [O(2)] decorated copper [Cu(2)] CuO_2 square lattice and a 1D oxygen [O(1)] renormalized-copper [Cu(1)] linear chain in the basal plane. The Cu(1) is renormalized by a strong interaction with its two nearest-neighbor oxygen atoms [O(4)] perpendicular to the basal plane. From neutron-diffraction data one obtains for the distance between the CuO_2 planes and O(4) a value of 2.23 Å, in comparison to the distance between O(4) with the linear chain, which is 1.85 Å. For simplicity we neglected the weak interaction between the O(4) atoms and the CuO_2 planes, which permits us to write the Hamiltonian as the sum of two independent terms:

$$H = H_{\text{chain}} + H_{\text{plane}}, \quad (2.1)$$

which can be written

$$\begin{aligned} H = & \sum_{\beta i \sigma} E_{\beta}^{\beta} p_{i\sigma}^{\dagger} p_{i\bar{\sigma}} + \sum_{\beta \alpha \sigma} E_{\text{Cu}}^{\beta} d_{\alpha\sigma}^{\dagger} d_{\alpha\bar{\sigma}} + U_p \sum_{i\sigma} n_{i\sigma} n_{i\bar{\sigma}} \\ & + U_d \sum_{\alpha\sigma} N_{\alpha\sigma} N_{\alpha\bar{\sigma}} + U_{pd} \sum_{i\alpha\sigma\sigma'} n_{i\sigma} N_{\alpha\sigma'} \\ & + U_{pp} \sum_{ij\sigma\sigma'} n_{i\sigma} n_{j\sigma'} + \sum_{i\alpha\sigma} V_{pd}^{i\alpha} (p_{i\sigma}^{\dagger} d_{\alpha\sigma} + \text{c.c.}), \quad (2.2) \end{aligned}$$

where $n_{i\sigma} = p_{i\sigma}^{\dagger} p_{i\sigma}$, $N_{\alpha\sigma} = d_{\alpha\sigma}^{\dagger} d_{\alpha\sigma}$, and $i(\alpha)$ denotes an

oxygen (copper) atom. The $p_{i\sigma}^{\dagger} (d_{\alpha\sigma}^{\dagger})$ operators create an electron on site $i(\alpha)$ with spin σ at the $p - (d -)$ orbital and β corresponds to the two possibilities; chains or planes. The intrasite (intersite) correlations are denoted by U_p and U_d (U_{pd} and U_{pp}). The matrix element $V_{pd}^{i\alpha}$ corresponds to the hopping between copper at site α and the nearest-neighbor oxygen atoms at site i .

The solution of the many-body Hamiltonian (2.2), describing a system of randomly distributed oxygen atoms ($x < 1$), requires the simultaneous treatment of the disorder and of the electronic correlation. While the many-body effects are essential for both the basal and CuO_2 planes, the disorder is restricted only to the chains in the basal plane. As observed in neutron-diffraction experiments,¹ the oxygen atoms that get in and out of the system come and go mainly to the oxygen sites O(1) and O(5) in the basal plane. Only recently it has been recognized⁹ that also a small amount of oxygen gets in and out of the O(4) sites. Furthermore, the influence of the disorder on the CuO_2 plane will be neglected.

The many-body problem is solved by using the alloy analogy approximation¹⁰ for the intra-atomic repulsion at Cu and O sites, and a Hartree-Fock approach for the smaller intersite O-O and O-Cu repulsions. This approach reduces the electronic correlation problem to a self-consistent solution of a disordered system with two chemical species; single and double occupied atoms. This kind of formalism allows us to include the many-body problem and the oxygen-real-space disorder within the same context. The values used in the calculation, following *ab initio* calculations,¹¹ are $U_d = 9.0$ eV, $U_p = 6.0$ eV, $U_{pd} = 1.8$ eV, $U_{pp} = 0.9$ eV, $E_{\text{O}} - E_{\text{Cu}} = 0.5$ eV, and $V_{pd} = 1.2$ eV. The ratio between the hopping on the basal plane and the corresponding to the O(4) sites is 0.83.

III. THE ELECTRONIC DENSITY OF STATES

To obtain the quantum-mechanical and configurational averages of the relevant physical variables, we adopted the Green-function method. The diagonal Green functions are calculated by applying a real-space renormalization technique,¹² which decimates iteratively the lattice points corresponding to Cu and O sites. At each stage of the decimation, the eliminated degrees of freedom are configurational averaged, preserving the statistical correlations between diagonal and nondiagonal renormalized parameters. We showed in a previous work¹³ that this is a very accurate procedure to calculate the density of states of low coordinated systems, as it is the case of high- T_c ceramics, because the long-range spatial fluctuations are preserved at all stages of renormalization.

A double decimation scheme was employed to guarantee the invariance of the equations of motion corresponding to the original basal plane chain (Cu-O-Cu-O-Cu. . .). This is illustrated in Fig. 1. The existence of the O(4) atoms linked to the copper Cu(1) atoms are taken into account by renormalizing the Cu(1) undressed diagonal Green function. The set of equations of motion for the Green function $G_{\alpha\beta}(w)$, corresponding to a semi-infinite linear chain, is

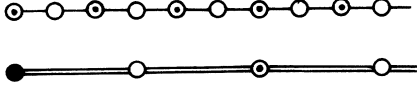


FIG. 1. Double decimation scheme for the one-dimensional chain.

$$G_{00}(w) = g_0^\gamma + g_0^\gamma \bar{V}_{0,1}^{\text{Cu}} G_{10}(w), \quad (3.1)$$

$$G_{10}(w) = g_1^\alpha V_{1,0}^{\text{O}} G_{00}(w) + g_1^\alpha V_{1,2}^{\text{O}} G_{20}(w), \quad (3.2)$$

$$G_{20}(w) = g_2^\beta V_{2,1}^{\text{Cu}} G_{10}(w) + g_2^\beta V_{2,3}^{\text{Cu}} G_{30}(w), \quad (3.3)$$

⋮

where $\bar{V}_{0,1}^{\text{Cu}}$ is an effective hopping element defined in the Appendix and the undressed locators are given by

$$g_i^\lambda = \frac{1}{w - E_i^\lambda}. \quad (3.4)$$

Here, $w = w + i\eta, \eta = 0^+$.

The subindex $i(\alpha)$ is associated to the O(Cu) sites, while λ denotes atoms with one or two electrons. For the sake of simplicity and in order to apply the decimation procedure in a straightforward manner, we describe the CuO_2 planes by a copper-oxygen decorated Bethe lattice. Since this lattice can be constructed by an infinite series of interconnected linear chains at one point, the renormalization technique which solves the 1D problem solves as well the Bethe lattice. The CuO_2 plane is a low coordinated lattice ($2 < Z < 4$) and this approximation does not introduce any significant spurious physical results in the calculations. For the CuO_2 plane, within the Bethe lattice approximation, one can use for the decimation procedure the set of Eqs. (3.1)–(3.3), where the renormalized locators associated to Cu(1) are replaced by the corresponding undressed Green function of Cu(2). The renormalization relations, which result from the decimation process, are given in the Appendix.

As already mentioned, the U_{pd} and U_{pp} terms are treated using the Hartree-Fock approximation. To that aim the diagonal matrix elements of the Hamiltonian are renormalized by the self-consistent procedure, since they depend explicitly on the occupation number $n_{i\sigma}(N_{\alpha\sigma})$ at the O(Cu) sites. To calculate the local density of states at Cu(2) more accurately, as far as disorder is concerned, we considered a cluster of nine atoms (Fig. 2) in an exact way. The cluster is saturated by renormalized surface Green functions generated by the Bethe lattice decimation.

The density of states (DOS) depends on the concentration and more strongly on the oxygen vacancy distribution in the basal plane. Despite the fact that this problem is not completely understood, it is well established that for samples prepared by annealing, the oxygen vacancies order in the basal plane at least for certain values of the oxygen content.^{14,15} We assume the following ordering process: At high temperatures the probability to find an oxygen atom at the O(1) and O(5) sites in the basal plane

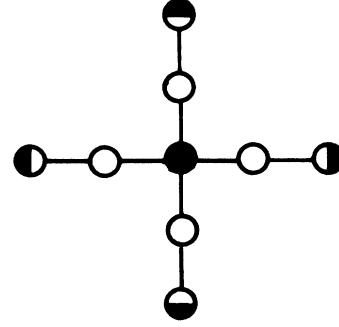


FIG. 2. Cluster of nine atoms used to calculate the electronic local density of states of the CuO_2 plane elements.

is the same (tetragonal phase); upon reducing the temperature and below the critical temperature of the tetragonal to orthorhombic phase transition, the oxygen atoms occupy preferentially the O(1) sites; reducing the temperature further, makes that all the oxygen atoms occupy only sites along the chains of O(1) sites but are randomly distributed; finally, at even lower temperatures, the vacancies in the chain form ordered patterns.

We analyze the effect of the vacancies present in systems with concentrations $x < 1$ by considering two different situations. In the first case, it is assumed that the vacancies appear at random positions along the well established linear chains. This corresponds to a material quenched from the partially ordered phase mentioned above to superconductivity temperatures. Secondly, for the annealed system we adopt the very simple distribution proposed by Zaanen *et al.*,¹⁶ which coincide for certain values of x with the experimental results.^{14,15} Considering two adjacent linear chains we assume that, for the interval $0.5 < x < 1$, one of the chains remains intact, and the other dilutes in such a way as to maintain the oxygen vacancies as far apart as possible. For the particular case in which $x = 0.5$, the basal plane contains only intact chains intercalated with empty chains. Reducing further the oxygen concentration, the chains that at $x = 0.5$ were intact, begin to dilute up to a situation in which, for $x = 0$, all the oxygen atoms are removed from the basal plane.

The dilution of the linear chains produces two effects that have to be taken into account properly. The pres-

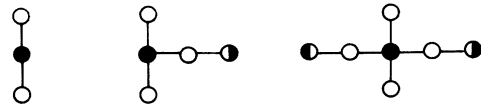


FIG. 3. The three different clusters present in the chains, and for which the Cu(1) is (a) twofold coordinated, (b) threefold coordinated, and (c) fourfold coordinated.

ence of an oxygen vacancy between two copper atoms [Cu(1)], eliminates the link between them, introducing thereby a nondiagonal disorder into the system. On the other hand, as the copper changes its coordination and as a consequence its environment, the diagonal element is renormalized (diagonal disorder) due to a modification of the charge cloud of the neighborhood. The diagonal and nondiagonal disorder have to be treated taking into account the correlation between them. After the decimation procedure of the dilute chain has been carried out, we consider the three different clusters shown in Figs. 3(a), 3(b), and 3(c), for which Cu(1) is twofold, threefold, and fourfold coordinated, respectively. For the case of the quenched system the spatial correlation between vacancies can be neglected and the statistical weight of the three different clusters is, $p_2 = (1-x)^2$, $p_3 = 2x(1-x)$, and $p_4 = x^2$, respectively. On the other hand, the annealed situation has to be analyzed considering four different ranges of concentration. It is easy to show that the probabilities of the various clusters are those given in Table I.

The oxygen atoms at the O(4) positions suffer, as well, a modification in its environmental charge. This effect is reflected on its diagonal matrix element, quantity that depends on the coordination of the Cu(1) to which it is linked. However, as it is discussed in the following, this is not an important effect because its DOS is located far below E_F .

The diagonal matrix elements corresponding to Cu(1), O(4), and O(1) in the three possible configurations are given by

$$E_{\text{Cu}(1)}^{2f} = 4U_{pd}(n_{\text{O}(4)} - 2n_{\text{O}(2)}) ,$$

$$E_{\text{Cu}(1)}^{3f} = E_{\text{Cu}(1)}^{2f} + 2U_{pd}n_{\text{O}(1)} , \quad (3.5)$$

$$E_{\text{Cu}(1)}^{4f} = E_{\text{Cu}(1)}^{2f} + 4U_{pd}n_{\text{O}(1)} ,$$

$$E_{\text{O}(4)}^{2f} = (U_d - 4U_{pd})N_{\text{Cu}(2)} - (8U_{pp} + U_p)n_{\text{O}(2)}$$

$$+ 2U_{pd}N_{\text{Cu}(1)} , \quad (3.6)$$

$$E_{\text{O}(4)}^{3f} = E_{\text{O}(4)}^{2f} + 2U_{pp}n_{\text{O}(1)} ,$$

$$E_{\text{O}(4)}^{4f} = E_{\text{O}(4)}^{2f} + 4U_{pp}n_{\text{O}(1)} ,$$

$$E_{\text{O}(1)}^{4,3f} = (U_d - 4U_{pd})N_{\text{Cu}(2)} - (8U_{pp} + U_p)n_{\text{O}(2)}$$

$$+ 4U_{pd}N_{\text{Cu}(1)} + 8U_{pp}n_{\text{O}(4)} , \quad (3.7)$$

where the index $2f$, $3f$, and $4f$ correspond to the three clusters shown in Figs. 3(a), 3(b), and 3(c), respectively. Furthermore, the diagonal matrix elements for the CuO_2 plane are

$$E_{\text{Cu}(2)} = 0 ,$$

$$E_{\text{O}(2)} = U_d N_{\text{Cu}(2)} - U_p n_{\text{O}(2)} . \quad (3.8)$$

The position of the Fermi level E_F and the occupation numbers are obtained self-consistently by solving the coupled equations:

$$2 \int_{-\infty}^{E_F} [2\rho_{\text{Cu}(2)}(w) + 4\rho_{\text{O}(2)}(w) + 2\rho_{\text{O}(4)}(w)$$

$$+ \rho_{\text{Cu}(1)}(w) + x\rho_{\text{O}(1)}(w)]dw = 9 + Q \quad (3.9)$$

and

$$2 \int_{-\infty}^{E_F} \rho_{\text{local}}(w)dw = n_i , \quad (3.10)$$

where $\rho_i(w)$ is the local density of states of each atom and Q is the cationic charge per unit cell of the non-copper metal atoms, transferred to the planes and chains. $Q=7$ in the case of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The number 2 in front of the integrals results from spin degeneracy. We investigated the electronic behavior of different compounds and in particular the metal-nonmetal transition as a function of the oxygen content and the transferred charge Q .

IV. RESULTS AND DISCUSSION

We show in Figs. 4(a) and 4(b) the total density of states of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ for $x=1$ and 0.7, respectively. The intra-atomic electronic repulsion at the copper and oxygen atoms have split the states into a sort of lower and upper Hubbard bands. However, the correlation gap is more complicated than the one that the Mott-Hubbard model could normally predict. It is a charge-transfer gap existing essentially between the filled upper Hubbard O $2p$ band and the empty upper Hubbard Cu $3d$ band. The Fermi energy falls near the correlation gap. This fact could explain why in the photoemission spectra¹⁷ a DOS is observed at the Fermi level, much smaller than the value obtained in density functional calculations, in which the local strong electronic repulsion at Cu and O sites cannot be included.

We have calculated the LDOS of Cu at the various positions and as a function of the oxygen content (the details of the calculation are given in the Appendix). The results are shown in Figs. 5(a)–5(c) and 6(a) and 6(b). The strong intra-atomic electronic repulsion of Cu, U_d , splits the states far apart from the Fermi level. Otherwise the O(2) and O(1) bands, less split by the electronic repulsion, reveal the predominant oxygen $2p$ character of the states near the Fermi level. This agreement with the

TABLE I. Ordered oxygen-vacancy probabilities.

	$1.00 \geq x \geq 0.75$	$0.75 \geq x \geq 0.50$	$0.50 \geq x \geq 0.25$	$0.25 \geq x \geq 0.00$
P_2	0	$(3-4x)/2$	0.50	$1-2x$
P_3	$2(1-x)$	$2x-1$	$2(0.5-x)$	$2x$
P_4	$2x-1$	0.50	$(4x-1)/2$	0

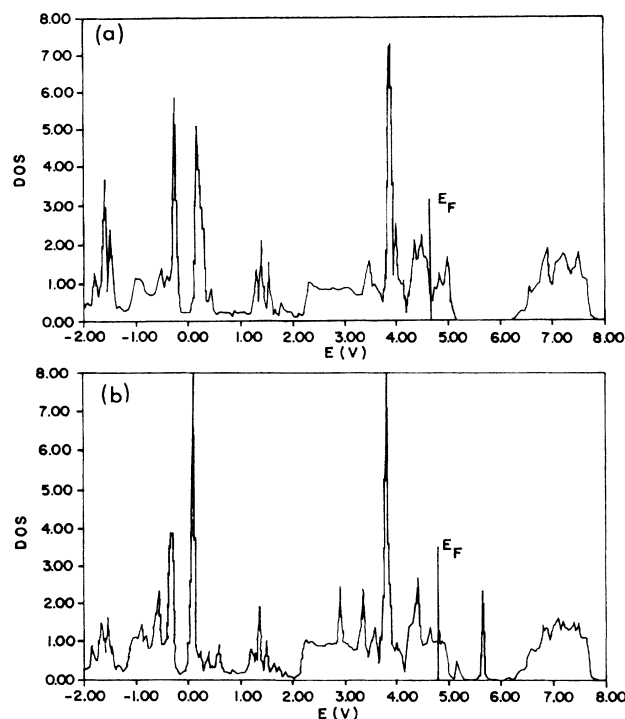


FIG. 4. The total electronic density of states: (a) $\text{YBa}_2\text{Cu}_3\text{O}_7$ and (b) $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$. The energy is given in units of the hopping integral V .

spectroscopy measurements¹⁷ shows the great importance of considering the Hubbard terms to get an appropriate description of the material.

The O(4) atoms, on the other hand, behave as acceptors of two electrons. It is an inert element in the sense that its LDOS is negligible at the vicinity of the Fermi level [see Fig. 5(e)]. However, it plays an important role in reducing locally the available charge of the nearest Cu(1) to which it is strongly bound. This behavior compensates in part the role played by the Y and Ba elements which liberate charge to the electronic active part of the system, however without any significantly local effect. The DOS of Cu(1) and O(1) exhibit a strong dependence upon oxygen content x , due to the direct disorder that the oxygen vacancies introduce into the Cu-O chain. The DOS reduces its dispersion and shrinks its peaks as could be expected to be the case of an increasingly diluted chain. We can predict that the states are spatially localized, since they correspond to a one-dimensional disorder system.

The DOS of the system shows a well defined gap for $x = 1$. This feature is produced by the repulsion of the electronic charge at the copper and oxygen sites. As the number of vacancies increases, the gap is filled by an increasing, however small, amount of states. They correspond to O(1) and Cu(1) Hubbard eigenvalues that are shifted to higher- and lower-energy values respectively, due to changes in the nearest environment of these atoms upon dilution. The oxygen vacancies create twofold and

threefold coordinated copper atoms, which are able to bind electrons more strongly than fourfold coordinated copper atoms, since in those cases the electrons do not suffer the repulsion of the electronic charge at the oxygen sites that are missing. Although, experimentally, it has not been possible to synthesize the compound with $x = 1$, and the gap has not been confirmed, other theoretical approaches¹⁸⁻²⁰ seem to indicate that the gap disappears in that limit.

We treat the interatomic Coulomb repulsion within the context of the Hartree-Fock approximation. This fact is reflected in the diagonal matrix elements of Cu(1) as it is given in Eqs. (3.5)–(3.8). For the case of twofold-

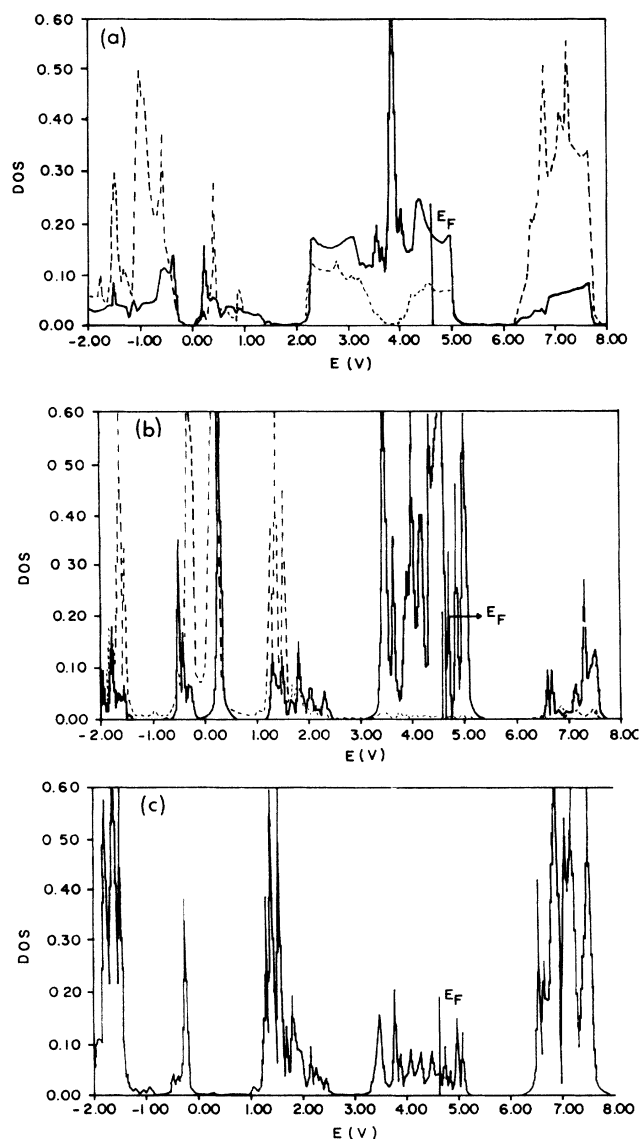


FIG. 5. The local electronic density of states of $\text{YBa}_2\text{Cu}_3\text{O}_7$, at the various Cu and O sites: (a) O(2) (solid line), Cu(2) (dashed line); (b) O(1) (solid line), O(4) (dashed line) and, (c) Cu(1). The energy is given in units of the hopping integral V .

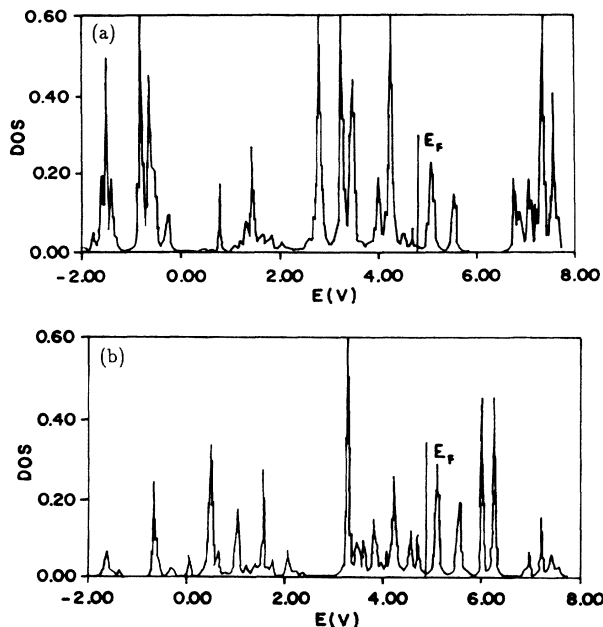


FIG. 6. The local electronic density of states at the elements in the basal plane in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$: (a) O(1) and (b) Cu(1). The energy is given in units of the hopping integral V .

coordinated copper the LDOS lies almost completely below the Fermi level, as it is shown in Fig. 7. However, it is not a passive structural element since the probability of creating it, which requires the existence of two adjacent oxygen vacancies, increases as the oxygen content is reduced. This displacement of the LDOS of twofold-coordinated copper below the Fermi level is very important to understand the reason why it is possible to obtain superconductivity for concentrations smaller than $x=0.5$, as it will be discussed in the following. An equivalent situation occurs for the case of O(4) which changes its environment with dilution by eliminating the electronic repulsion of the nearest oxygen neighbors. However, this situation has no consequences since O(4),

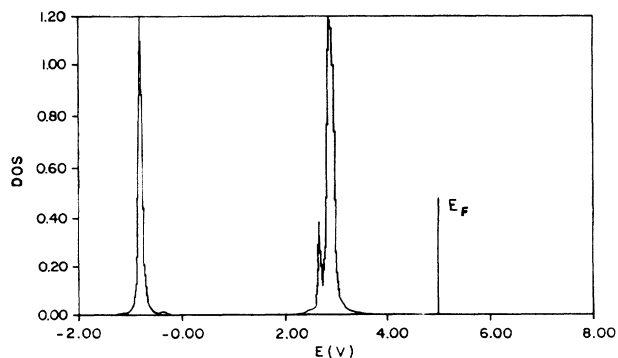


FIG. 7. The local electronic density of states of a twofold coordinated Cu(1) in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$. The energy is given in units of the hopping integral V .

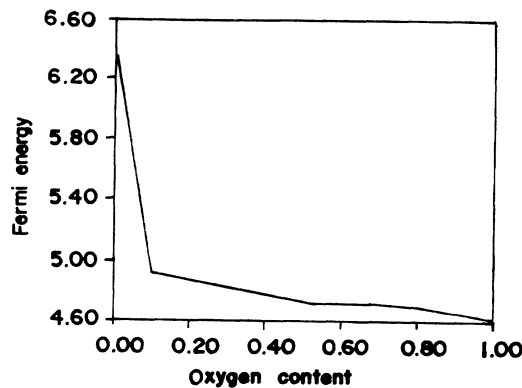


FIG. 8. The Fermi level as a function of the oxygen content.

as already mentioned, is an inert element with its DOS well below the Fermi level, independent of x . For the case of the O(1) atoms, even if a reduction on the oxygen content does not modify the number of its nearest neighbors, the changes on the electronic charge of its environment produces a displacement of the binding energy of an electron sitting on it. The CuO_2 plane is not greatly affected by a change in the oxygen concentration because it maintains its crystallographic structure independent of oxygen content. It suffers an almost rigid shift to lower values of energies as x decreases.

In Fig. 8 we present the dependence of the Fermi energy as a function of the oxygen content. For values of x for which the Fermi level lies at the upper oxygen band the variation is almost linear with a small slope, having a rapid increase as soon as E_F enters into the pseudogap. The E_F do not remain constant due to the fact that the pseudogap is populated by localized states originated in the diluted chains. A more complete comparison between theory and experiment was not possible because to the best of our knowledge a systematic experimental study of the behavior of E_F with x is lacking.

The system suffers a metal-nonmetal transition as a function of oxygen content when the Fermi level goes through the delocalized states of CuO_2 plane [essentially O(2) states] and enters into the pseudogap populated by localized Cu-O states. From this point of view the metal-nonmetal transition is of the Mott-Anderson type.²¹ It is produced by the interplay of the electronic correlation which opens the correlation gap and the disorder which populates it with localized states.

Within the range of solid solubility of the compounds $\text{Y}(\text{La}_y\text{Ba}_{1-y})_2\text{Cu}_3\text{O}_{6+x}$ and $(\text{Y}_y\text{Ca}_{1-y})\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$ the metal-nonmetal transition has been experimentally studied as a function of the oxygen content x and, by changing the concentration y , as a function of the cation charge Q . We analyzed this problem theoretically changing the value of Q in Eq. (3.9).

Figure 9 shows, in the parameter space x versus Q , the theoretical (dashed line) and the experimental results (solid line), separating the insulating from the superconducting phases. As it could be expected the metal-nonmetal transition for these compounds occurs at

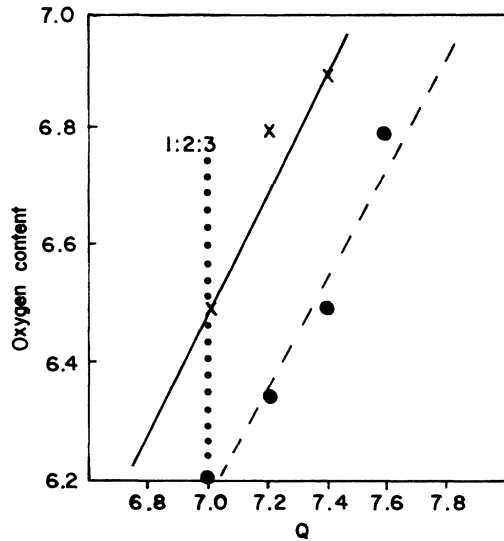


FIG. 9. The metal-nonmetal transition for a series of isostructural compounds. The dashed line corresponds to the theoretical results and the solid line corresponds to experimental results from Ref. 4.

higher values of oxygen concentration as the cationic charge increases. Despite the dispersion that the experimental results have (they depend on the sample preparation), there is a good agreement between theory and experiment. For instance, for the case of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ the metal-nonmetal transition is experimentally verified, depending upon the particular sample, within the range $0.5 < x < 0.2$. A similar behavior can be expected for the other solid solutions.

It is widely recognized that the Cu-oxide superconducting properties depend upon the hole concentration at the CuO_2 planes. In particular, that seems to be the case for $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, since it is believed that the Cu-O chains, being disordered 1D physical objects, do not contribute to superconductivity itself. It is reasonable to think that localized electronic states would not provide an adequate basis for the formation of a mobile Cooper pair. However, the linear chains play an important role as a charge reservoir which control, as a function of oxygen content, the number of holes in the planes. Semiempirical analyses have appeared in the literature²² based on these ideas, explaining qualitatively the equilibrium that could be expected between the electronic charges on the planes and the chains as a function of x and Q . They were able to show that the main variable correlated with T_c in these materials is the charge on the CuO_2 plane.

We calculated the number of holes at the CuO_2 planes as a function of x . It was obtained by taking the difference between the electronic charge of the plane at thermodynamic equilibrium for a fixed value of x and Q and the corresponding value in the case when the Fermi level lies at the edge of the DOS of the CuO_2 plane, immediately before the gap. The number of holes is not

directly obtained from the area of the DOS of the CuO_2 plane, above E_F up to the gap, because due to many-body effects this area changes when the electronic charge is increased in the system. The calculation was done for the statistics corresponding to the random and to the ordered distribution of vacancies (Fig. 10).

For the ordered case, Fig. 11(a) shows the existence of a plateau for the number of holes in the CuO_2 plane for a range of oxygen concentration $0.45 < x < 0.75$, which coincide with experimental measurements of the Hall carriers and the critical temperature, as a function of the oxygen content. On the other hand, for the random vacancy distribution case [Fig. 11(b)], the dependence of the hole number with x is almost linear. This is also consistent with experimental results, which indicate that for a nonequilibrium-prepared sample, the plateau is much less pronounced and in some cases almost negligible.²³ These results emphasize the importance of the sample preparation to understand the dependence of the superconducting transition temperature with the oxygen concentration.

In terms of the preceding discussion there is a crucial difference between the ordered and the random oxygen vacancy statistics in the range $0.45 < x < 0.75$. As it is shown in Fig. 10, the probability of having twofold-coordinated copper is larger for the ordered than for the disordered case, and remains constant for $0.25 < x < 0.5$. A similar behavior follows the probability of fourfold-coordinated copper for $0.5 < x < 0.75$. The observed plateau for the ordered-oxygen configuration is the result of the pinning of the Fermi level in the interval $0.45 < x < 0.75$. The rapid increase of $\text{Cu}^+(3d^{10})$ for the ordered distribution of vacancies provides a mechanism of pinning the E_F . The local DOS of these atoms is completely below E_F , pushing it to lower energies and compensating the opposite effect produced by the self-doping when x is reduced.

For the situation in which the vacancies are randomly distributed along the chains those effects are not important because the number of twofold and fourfold-coordinated Cu are monotonic functions of x (see Fig. 10). For the case of a sample with a random distribution of vacancies, the dependence of the hole number with x is almost linear, but shifted with respect to the result that

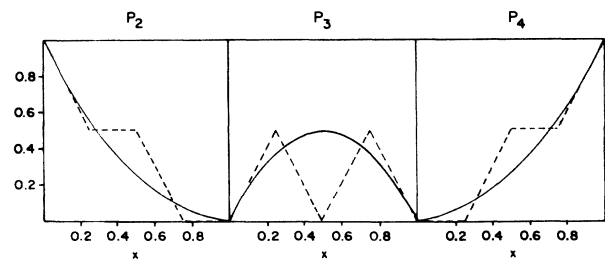


FIG. 10. Diagrams of the oxygen-vacancy probabilities. The solid lines correspond to the random distribution, while the dashed line corresponds to the ordered case given in Table I.

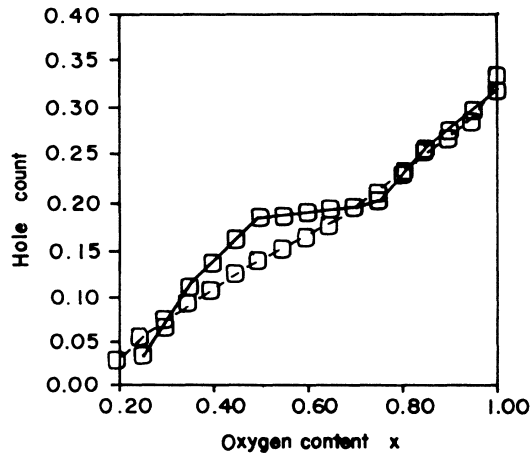


FIG. 11. Number of holes on the CuO_2 plane as a function of the oxygen content for the following: (a) an ordered vacancy distribution and (b) a random case.

one obtains by assuming that the oxygen states are responsible for the holes, leaving the copper state with an invariant charge in a configuration Cu^{2+} . It is easy to show that under that assumption the number of holes on the planes is given by

$$n_h^{\text{plane}} = \frac{2(2x-1)}{4x+1}. \quad (4.1)$$

This difference is due, to some extent, to the existence of Cu^+ in the sample. According to Eq. (4.1), the system becomes insulator (zero number of holes) at $x=0.5$. This contradicts the fact that superconductivity and metallic behavior above T_c for samples with $x \geq 0.3$, has been observed. In our model, the number of holes belonging to the CuO_2 plane goes to zero at $x=0.2$. This behavior is due to the drastic changes in the DOS of the chains upon dilution. As the oxygen concentration is reduced, the number of states available to be filled below E_F increases, reducing thereby the self-doping concentration necessary for the insulating state.

The plateau obtained for $0.45 < x < 0.75$, in the ordered situation, is produced by the statistics assumed. We do not obtain similar behavior near $x=1$ because in that range all the probabilities depend linearly on the concentration. A similar plateau has been obtained assuming the same statistics on the ordering of the vacancies in the chain and using a model without correlation.¹⁶ However in our case the pinning of E_F is a consequence of the Coulomb repulsion which locates the DOS of the twofold coordinated copper below E_F .

The determination of the valence states of Cu (Cu^{3+} , Cu^{2+} , and Cu^+) in the superconductive ceramics and their role in superconductivity have given inconclusive results.^{24,25} We calculated within our model the probability of getting the three different charge states for the oxygen and copper atoms in the planes and along the chains as a function of the oxygen content.

The correlation function $\chi_2^i = \langle n_{i\sigma} n_{i\bar{\sigma}} \rangle$ gives the proba-

bility of two electrons being at the same site i . χ_2^i can be obtained by integrating the imaginary part of the diagonal Green function associated to double occupation:

$$\chi_2^i = \langle n_{i\sigma} n_{i\bar{\sigma}} \rangle = -\frac{i}{\pi} \int_{-\infty}^{E_F} \text{Im} \langle \langle n_{i\sigma} c_{i\bar{\sigma}}; c_{i\bar{\sigma}}^+ \rangle \rangle dw. \quad (4.2)$$

The correlation functions χ_1^i and χ_0^i , corresponding to the case of simple (Cu^{2+} and O^-) and zero occupation (Cu^{3+} and O) can be obtained directly from the relations:

$$\begin{aligned} \chi_2 + 2\chi_1 + \chi_0 &= 1, \\ 2\chi_1 + 2\chi_2 &= 2\langle n_i \rangle. \end{aligned} \quad (4.3)$$

The first equation indicates that there is an atom at each site independent of its state of charge, and the second establishes the balance of charge at each atom. The results obtained for the correlation functions in the CuO_2 planes and in the chains are shown in Figs. 12 and 13, for the cases of ordered and disordered distributions of vacancies in the basal plane. As it was already mentioned, the $\text{O}(4)$ atoms behave as inert elements in the system. They are always in the O^{2-} state of charge, independent of the oxygen content and of the statistics considered. Electron energy-loss spectroscopy experiments²⁶ have been carried out to obtain information about the character of the electronic holes. The conclusion drawn was that the number of holes in the $\text{O}(4)$ sites should be much smaller than the number in the other three oxygen sites.

The situation for the $\text{O}(2)$ atoms is similar. There is a small change in the contribution of the various states of charge as a function of x , reducing the number of oxygen

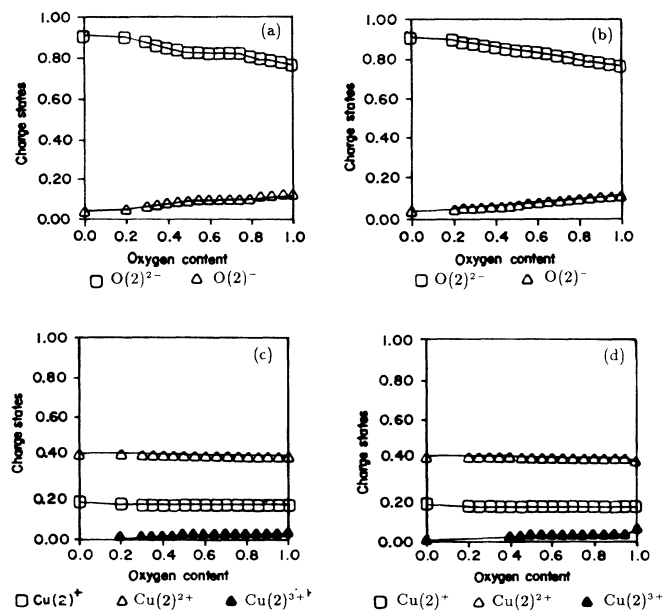


FIG. 12. Probability of the charge states for the plane elements. (a) and (c) correspond to an annealed sample, while (b) and (d) correspond to a quenched sample.

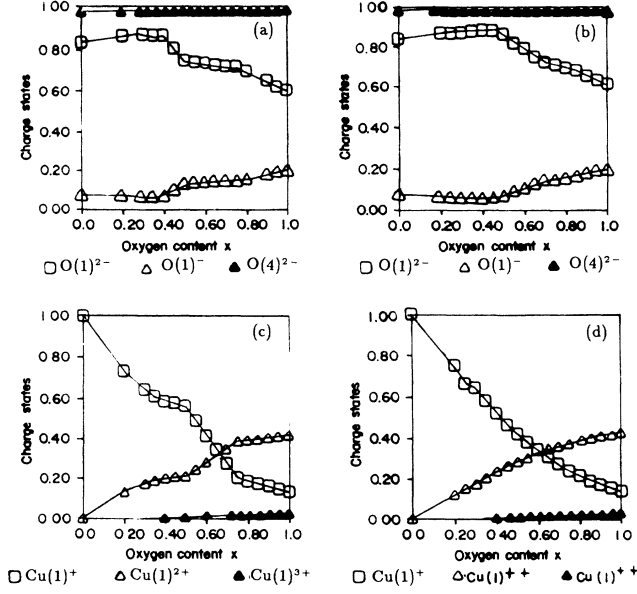


FIG. 13. Probability of the charge states for the chain elements. (a) and (c) correspond to the annealed sample, while (b) and (d) correspond to the quenched sample.

atoms with one electron and increasing the number of double charge state as x increases. In Cu(2), independently of the vacancy statistics, there is a constant ratio between Cu^{2+} and Cu^+ , approximately equal to 2. This coincides very well with x-ray photoemission spectroscopy measurements,²⁴ which suggest that the ground state of copper is 30–40% of d^{10} and 60–70% d^9 .

The weight of the Cu^{3+} configuration that we obtained is almost negligible for Cu(1) and Cu(2) for all values of x . The result that Cu is never Cu^{3+} in these compounds is still a matter of controversy, although several spectroscopic measurements tend to confirm that result.

In contrast to the elements of the CuO_2 plane, the state of charge of Cu(1) and O(1), depend sensitively on x . The results are shown in Fig. 13. In the range of x for which the number of holes is constant in the CuO_2 plane, there is a significant increase in the weight of Cu(1), reflecting

the increasing influence of twofold-coordinated copper.

In summary, we have proposed a model to study the main electronic properties of the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ compounds which treats the effects of disorder and electronic correlation within the same context. The model was able to evidenciate the oxygen 2p character of the states near the Fermi level, the Mott-Anderson-type metal-nonmetal transition and, in particular, to reproduce the experimental observed *plateau* for the number of holes in the CuO_2 plane for a range of oxygen content in the case of an ordered oxygen-vacancy distribution. This fact could be understood as a consequence of the increase of the twofold coordinated copper atoms in this range of oxygen concentration, which pins the Fermi level. The calculation confirmed the negligible contribution of Cu^{3+} to the state of charge of copper, while Cu^{2+} and Cu^+ participate with 30 and 70 %, respectively, in agreement with experimental results.

To understand the correlation between the superconductive properties of these materials and the orthorhombic-tetragonal phase transition it is necessary to incorporate another active d orbital just to be able to include in the basal plane oxygen occupation along and perpendicular to the chains. A more accurate treatment of correlation and disorder and the inclusion of another d orbital in the model will be the subject of a subsequent work.

ACKNOWLEDGMENTS

This work was partially supported by Dirección General de Investigación Científica y Superación Académica de la Secretaría de Educación Pública through Grant No. C89-08-0081, by Consejo Nacional de Ciencia y Tecnología through Grant No. P228CCOX880186, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and by Financiadora de Estudos e Projetos (FINEP) from Brazil.

APPENDIX

By decimating the Green functions corresponding to the decorated semi-infinite linear chains shown in Fig. 1 we obtain the following renormalization relation for the diagonal Green function and the effective hopping terms between Cu and O nearest-neighbor atoms

$$\bar{g}_i^\lambda = \sum_{c_{i+1}^\alpha c_{i+2}^\beta} \frac{\bar{g}_i^\lambda c_{i+1}^\alpha c_{i+2}^\beta}{g_i^\lambda \bar{V}_{i,i+1} g_{i+1}^\alpha V_{i+1,i}^O},$$

$$\bar{V}_{i,i+a} = \sum_{c_{i+1}^\alpha c_{i+2}^\beta} \frac{\bar{V}_{i,i+1} g_{i+1}^\alpha V_{i+1,i+2}^O + 2g_{i+2}^\beta V_{i+2,i+3} c_{i+1}^\alpha c_{i+2}^\beta}{1 - g_{i+1}^\alpha (V_{i+1,i+2}^O + 2g_{i+2}^\beta V_{i+2,i+3}^{\text{Cu}} + V_{i+1,i} g_i^\gamma \bar{V}_{i,i+1})},$$

$$V_{i,i+3}^{\text{O}(\text{Cu})} = V_{i,i-3}^{\text{O}(\text{Cu})} = \sum_{c_{i-1}^\alpha c_{i-2}^\beta c_{i+1}^\gamma c_{i+2}^\delta} \frac{D_{i,i-1,i-2,i-3}^{\text{O}(\text{Cu})\alpha\beta}}{N_{i,i+1,i+2,i-1,i-2,i-3}^{\text{O}(\text{Cu})\gamma\lambda\delta\alpha\beta}},$$

where

$$D_{\{i\}}^{\text{O}(\text{Cu})\{\alpha\}} = V_{i,i-1}^{\text{O}(\text{Cu})} g_{i-1}^\alpha V_{i-1,i}^{\text{Cu}(\text{O})} g_{i-2}^\beta V_{i-2,i-3}^{\text{O}(\text{Cu})},$$

and

$$N_{|i|}^{O(Cu)|\alpha} = (1 - g_{i-1}^\beta V_{i-1,i-2}^{Cu(O)} g_{i-2}^\alpha V_{i-2,i-1}^{O(Cu)}) \\ \times (1 - g_i^\gamma) \left[\frac{V_{i,i-1}^{Cu(O)} g_{i-1}^\alpha V_{i-1,i}^{O(Cu)}}{1 - g_{i-1}^\alpha V_{i-1,i-2}^{Cu(O)} g_{i-2}^\beta V_{i-2,i-1}^{O(Cu)}} + \frac{V_{i,i+1}^{Cu(O)} g_{i+1}^\lambda V_{i+1,i}^{O(Cu)}}{1 - g_{i+1}^\lambda V_{i+1,i+2}^{Cu(O)} g_{i+2}^\delta V_{i+2,i+1}^{O(Cu)}} \right],$$

where $\bar{V}_{i,j}$ is the hopping element between the surface atom and its first neighbor and c_i^α is the concentration of atom i . When i corresponds to an oxygen atom of the one-dimensional Cu-O chain, O(1), then

$$c_i^\alpha = \begin{cases} 1-x \\ x(1-n_{O(1)}) \\ xn_{O(1)} \end{cases}$$

for vacancy; single occupation, $\alpha=1$; and double occupation, $\alpha=2$, respectively, while for the other elements [Cu(2), O(2), Cu(1), and O(4)]

$$c_i^\alpha = \begin{cases} 1-n_i \\ n_i, \end{cases}$$

single occupation, $\alpha=1$; and double occupation, $\alpha=2$, respectively.

The n_i are the occupation numbers which are supposed to be independent of spin. The complexity of the renormalization relation is a consequence of the difference between local environments originated by solving the disorder and many-body problem within the same context. The final LDOS is calculated by writing the final Green functions corresponding to the different clusters of Figs. 2 and 3.

- ¹J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, and I. K. Schuller, *Phys. Rev. B* **36**, 3608 (1987).
- ²L. F. Mattheiss and R. D. Hamann, *Solid State Commun.* **63**, 395 (1987).
- ³S. Massida, J. Yu, and A. J. Freeman, *Phys. Lett. A* **122**, 198 (1987).
- ⁴E. V. Anda and J. L. Morán-López, *Proceedings of the First Latinamerican Conference on High Temperature Superconductivity, Rio de Janeiro, 1988* (World Scientific, Singapore, 1988); J. L. Morán-López, *Solid State Commun.* **71**, 923 (1989).
- ⁵Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzari, *Phys. Rev. B* **38**, 7156 (1988).
- ⁶N. Ntcker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Tammernann, *Phys. Rev. B* **37**, 5158 (1988).
- ⁷W. M. Shafer, T. Penney, and B. L. Olson, *Phys. Rev. B* **36**, 4047 (1987).
- ⁸Z. Z. Wang, J. Chayhold, N. P. Ong, J. M. Taraxen, L. H. Greene, W. R. Mckinnon, and E. W. Hall, *Phys. Rev. B* **36**, 7222 (1987).
- ⁹J. D. Jorgensen, H. Shaked, D. G. Hinks, B. Dabrowski, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, K. K. Kwok, L. H. Nunez, and H. Claus (unpublished).
- ¹⁰J. Hubbard, *Proc. R. Soc. London, Ser. A* **285**, 542 (1964).
- ¹¹M. Schluter, M. S. Hybertsen, and N. E. Christensen (unpublished).
- ¹²C.E.T. Gonçalves da Silva and B. Koiller, *Solid State Commun.* **40**, 215 (1983).
- ¹³E. V. Anda and A. Latgé, *J. Phys. C* **21**, 4251 (1988).
- ¹⁴M. A. Alario-Franco, J. J. Capponi, C. Chaillout, J. Chenevas,

- and M. Marezio, in *Proceedings of the Materials Research Society Meeting, Boston, 1987*, edited by M. D. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller, *Materials Research Symposia Proceedings Vol. 99* (Materials Research Society, Pittsburgh, 1988).
- ¹⁵G. Van Tanderloo, H. W. Zandbergen, and S. Amelinckx, *Solid State Commun.* **63**, 289 (1987).
- ¹⁶J. Zaanen, A. T. Paxton, O. Jepsen, and O. K. Andersen, *Phys. Rev. Lett.* **60**, 2685 (1988).
- ¹⁷A. Fujimori, E. Takayama-Huromachi, Y. Uchida, and B. Okai, *Phys. Rev. B* **35**, 8814 (1987).
- ¹⁸H. Eskes and G. A. Sawatzky, *Phys. Rev. Lett.* **61**, 1415 (1988).
- ¹⁹C. A. Balseiro, M. Avignon, A. G. Rojo, and B. Alascio, *Phys. Rev. Lett.* **62**, 2624 (1989).
- ²⁰A. M. Oles and J. Zaanen, *Phys. Rev. B* **39**, 9175 (1989).
- ²¹N. Mott, *Metal-Insulator Transition* (Taylor and Francis, London, 1974).
- ²²T. Penny, M. W. Shafer, and B. L. Olsen, *Proceedings of the Adriatico Research Conference and Workshop: Towards the Theoretical Understanding of High-T_c Superconductors, Trieste, 1988*, edited by S. Lundqvist, E. Tosatti, M. P. Tosi, and Yu Lu (World Scientific, Singapore, 1988), p. 699.
- ²³J. M. Tarascon and B. G. Bagley, *Mater. Res. Soc. Bull.* **14**, 53 (1989).
- ²⁴A. Balzarotti, M. De Crescenzi, N. Motta, F. Patella, and A. Sgarlata, *Phys. Rev. B* **38**, 6461 (1988).
- ²⁵D. Sarma and C. N. Rao, *Solid State Commun.* **65**, 47 (1988).
- ²⁶N. Nücker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer, and Z. X. Zhao, *Phys. Rev. B* **39**, 6619 (1989).