GROUND STATE OF THE ATOMIC STRUCTURE OF $YBa_2Cu_3O_{6+x}$

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We study the ordering of O atoms in $YBa_2Cu_3O_{6+x}$ using a two-dimensional Ising model. We assume a screened Coulomb repulsion between any two O ions of the CuO_x planes, but the interaction between second-neighbor O ions with a Cu ion in between is reduced by a factor f. We construct the symmetry independent atomic configurations which enable us to compare the energy of a large number of structures. We obtain a rich x-f phase diagram, which for screening lengths larger than ~1Å and low values of f, contains structures compatible with all the diffraction patterns so far observed. The ground state consists of structures composed of linear CuO chains for $f < 0$, or x near 0.5 and $f < 1$, while for $f = 1$ simple lattices of nearly hexagonal symmetry of O ions, or vacancies added to the $x = 1$ structure dominate.

PACS numbers: 74.70.Vy, 74.60.Mj, 81.30.Hd

I - INTRODUCTION

An important feature of the high Tc superconductors resides in the subtle changes in the superconducting temperature Tc caused by small compositional variations[1,2]. It is of crucial importance to determine to what extent these changes are related to modifications in the atomic structure, since the understanding of this phenomenon could lead to the development of stable or metastable materials with higher Tc.[3,4]

In $YBa_2Cu_3O_{6+x}$, as x is varied, plateaus in Tc (Ref.2) and number of carriers deduced from Hall measurements[5] are observed. On the other hand, structures that differ in the arrangement of O atoms in the CuO_x planes[6] were reported to exist for different values of x at low temperatures. The simplest ones are the tetragonal phase for x = 0 and the orthorhombic phase for x = 1 (Ref.6). For x = 1/2, the unit cell is doubled[7,8]. More complex structures were observed for x = 1/8 (Refs.9,10), x = 7/8 (Refs.10,11), x near 3/5 (Ref.12), and x near 2/3 (Ref.13). The latter two and those of x = 1 and x = 1/2 are composed of linear Cu-O chains. For brevity we shall call them CS. At present, there is controversy on which of these structures are stable and which of them are metastable. From their observations and by comparison with other systems, Alario Franco et al.[10] suggest that a family of different stable ordered phases may be a better representation of the system. Reyes Gasga et al.[14], cooling at constant stoichiometry find that the phase of x = 1/2 is stable, while other CS seem to be metastable. However, evidence of phase separation into x ~ 0.7 and x = 1 (Refs.15,16) and into 0.55 and 0.75 (Ref.17) points towards the stability of another phase, at least, between x = 1/2 and x = 1.

Most theoretical treatments of the ordering of O atoms are based on an Ising model for one of the CuO_x planes. These planes of variable O content are those perpendicular to the c axis that bisect the shortest Ba-Ba distance[6]. The parameters of these models were chosen according to two different points of view: 1) Two or three arbitratry parameters of magnitude equal or less than 0.1 eV (Refs. 18-23). 2) Comparatively large screened Coulomb repulsions[24,25]. In addition to the x = 0 and x = 1 phases (which are easy to explain), the first point of view was used to obtain the x = 1/2 structure as the ground state for the corresponding composition[19], and to explain the high temperature thermodynamics[18,20-23], although the good fit of the phase diagram is rather fortuitous[23]. The existence of other CS structures has been proposed to come from spinodal decomposition[26], but this theory was shown later to be inconsistent[27]. However, recent Monte Carlo calculations[27,28] obtained the x = 2/3 structure as transient. In any case, these theories cannot explain the observed diffraction patterns for x = 1/8 and x = 7/8, which have been shown to be consistent with the second point of view[24,25]. The following facts point towards the Coulomb repulsion being dominant: a) the number of carriers is very low[5], suggesting a screening length of several Å (Ref. 29), b) the variations of the lattice parameters and distances between atoms with x, are explained in terms of Coulomb energies[30,31], c) the crystal structure and parameters of $YBa_2Cu_3O_{6+x}$ and La_2CuO_4 are explained very well using empirical Atom-Atom potentials that include Coulomb interactions[31], d) it is practically impossible to increase x from 1, suggesting a very large nearest-neighbor O-O repulsion[32], e) the observed structures

for x = 1/8 and x = 7/8 (Refs.9-11) show that the O-O interactions are still important at distances of order of 11 Å, f) considering only the Madelung energy, several important properties of this and other high-Tc compounds can be explained[33-35] and g) direct[36] and constrained density-functional[37,38] calculations give values between 1 to 3 eV for the Coulomb repulsion U_{pd} between electrons in nearest- neighbors Cu and O atoms.

The shortcoming in the works of Refs.24 and 25, is that they cannot reproduce the observed CS for x = 1/2, x near 3/5 and x near 2/3 (which were not known by the authors). However, this drawback is removed if also the effects of Cu-O electronic repulsion U_{pd} and Cu-O charge transfer are taken into account. Using a modification appropriate to CuO_x planes of an extended two-band Hubbard model that leads to excitonic pairing in CuO_2 planes[39,40] (and also in BiO_3 systems[40,41]) we have shown that these effects lead to a tendency of the system to order in chains, which competes with the direct O-O repulsion[42]. In the next section we will present a simple argument to show that this tendency can be accounted for by reducing the second-neighbor O-O repulsion if a Cu is in between. Combining exact results in finite clusters and perturbation theory in the hopping, it was shown[42,43] that the above mentioned extension of the two-band Hubbard model explains not only the tendency to order in chains, but also the metal-insulator transition at x = 1/2 (Refs. 5,44,45) hole count in CuO_2 planes[5] and number of Cu and O holes[46].

Using the model described in the next section, the main features of the thermodynamics are also reproduced[42,47], but there is an important difference with the results obtained using the

above mentioned first point of view due to the larger magnitude of the Coulomb interactions: the tetragonal phase almost avoids occupancy of nearest-neighbor O-O atoms (as suggested earlier[30-32]). This reduces considerably its energy at a low cost of entropy for $x = 1/2$, leading to a comparatively low orthorhombic - tetragonal transition temperature T_0 and to important correlations of the latter phase, which remind the $x = 1$ orthorhombic structure[42,47]. The following facts provide evidence of such correlations: a) direct perturbed-angular-correlation measurements[48], b) There is a discontinuity in the slope of the resistivity vs x curve at $x = 0.5$ (probably associated with the metal-insulator transition[5,44,43]), but no change of slope at T_0(Ref.45), and c) ^{18}O diffusion experiments[49] show no break in the Arrhenius plot at T_0.

Here we show that using a screened Coulomb O-O repulsion, reduced for second neighbors if a Cu ion is in between, all the observed diffraction patterns can be explained. The model is described by essentially two parameters: the screening length λ and the reduction factor f. The model is equivalent to a planar Ising model with interactions of range λ, all antiferromagnetic, i.e. competing if $f > 0$ (x and the O chemical potential μ play the role of the magnetization M and magnetic field B respectively). Therefore it is of intrinsic interest in addition to its relevance for high Tc systems.

The model and the method used to solve it are described in sections II and III respectively. Section IV contains the results, section V the comparison with experiment, and section VI a discussion. A short summary of the results has been presented

earlier[42].

II - MODEL

We call n_i (0 or 1), the atomic occupation number at position i of the sublattice of all possible O positions of the CuO_x plane. We assume that this lattice is square, i.e. we neglect the small orthorhombic distortion and take the lattice parameter $b = a$. Calling ε_o the binding energy of a single O atom of the plane of interest, the Hamiltonian can be written in the form:

$$H = \varepsilon_o \sum_i n_i + \frac{1}{2} \sum_{i,j} V_{ij} n_i n_j \qquad (1)$$

where

$$V_{ij} = V_b = f \frac{A}{b} e^{-b/\lambda} \qquad \text{if} \quad \vec{R}_i - \vec{R}_j = \pm \vec{b} \ ,$$

$$V_{ij} = \frac{A}{|\vec{R}_i - \vec{R}_j|} e^{-|\vec{R}_i - \vec{R}_j|/\lambda} \qquad \text{otherwise.} \qquad (2)$$

A is a constant of order $\sim e^2$ if real rather than formal charges are used[50]. In real systems, Cu-O covalency[50] and promotion of holes to O atoms as x is increased, should decrease A. The screening length λ should also decrease with x, particularly after $x = 1/2$ due to the increase in the number of carriers[5,43]. This is confirmed by oxygen K soft x-ray emission measurements[51]. Both effects decrease the derivative of the free energy with respect to x, i.e. the O chemical potential. Here we take parameters independent of x. The ground state depends only on x, λ and f. The fact that $f < 1$ in $YBa_2Cu_3O_{6+x}$ is a consequence of Cu-O charge transfer, Cu intra- and Cu-O inter-atomic electronic

repulsions[42,43]. A simple argument can be given for $x \leq 1/2$: let us assume first that all O ions are -2. For $x = 0$ all Cu ions of the CuO_x plane (Cu(1) in the notation of Ref.6) are +1, the rest are +2 (Refs.46,52). When O atoms are added, they take the electrons from the highest coordinated Cu(1) ions to minimize the Cu-O nearest-neighbor interaction (Cu^{+3} is almost forbidden because of intratomic correlations[53]). If the added x O atoms do not have common nearest-neighbor Cu ions, they take the electrons from their 2x nearest-neighbor 3-fold coordinated Cu(1) ions (we remind the reader that each Cu(1) ion has always two bridging out of plane O(4) neighbors[6]). When two O ions have a common Cu neighbor, the latter is 4-fold coordinated and an extra energy (in comparison to 3-fold coordination) is gained when an electron is taken from it. If all O ions were -2, another electron should be taken from a 2-fold coordinated Cu ion and the energy gain is lost. However, when covalency is taken into account, this 2-fold coordinated Cu ion remains nearly +1 or intermediate valent at the expense of O holes in O(4) atoms or CuO_2 planes and this results in an energy gain ΔE. This energy should be substracted from the direct O-O screened- Coulomb repulsion to obtain the effective interaction V_b of Eq.(2) (Ref.42). The value of ΔE depends strongly on model parameters, particularly on the Cu-O repulsion U_{pd} of the extended two-band Hubbard model. Realistic calculations[42,43], which also explain other electronic properties, give values of the order of 1 eV.

A similar argument could be used to argue that the first-neighbor O-O repulsion is also reduced by ΔE. However, this repulsion is so large[30-32] that in any case nearest-neighbor O

atoms are avoided in the ground state.

III - METHOD OF SOLUTION

Due to the nature and large number of relevant interactions in our model, the method of geometrical inequalities[54] and the cluster method[55], which are in general useful in finding the ground state of Ising models, are not suitable for our case. Monte Carlo calculations[25,27,28] present difficulties at low temperatures: the "simulated annealing" procedure is characterized by extremely slow kinetics and complete ordering is almost never obtained[25,28]. For these reasons Monte Carlo methods were used to justify some of the observed structures as transient or metastable, with the dubious assumption that the Glauber or Kawasaki dynamics chosen has some similarity with the O dynamics in the real system.

In view of the above mentioned difficulties, we have directly compared the energy of a large number of configurations. This method was used earlier in $YBa_2Cu_3O_{6+x}$ (Ref. 19). In our case the studied configurations inlude all the so far observed or proposed superstructures. Also, since the computer time increases with the number of relevant interactions, which in turn increases quadratically with the screening length λ, it was necessary to reduce all possible configurations to those which are not equivalent by symmetry. Otherwise the calculation would have had to be restricted to $\lambda << a$ or a much lower number of configurations. Disregarding the structures with nearest-neighbor O atoms, which are obviously unfavorable for $x \leq 1$, the set of calculated structures include the following subsets: a) all structures whose

unit cell or a multiple of it is a rectangle of largest side $\leq 3a$ and area $\leq 8a^2$, b) all structures with a unit cell 1 x n, i.e. those composed of full and empty chains (CS) for $1 \leq n \leq 8$, c) all simple lattices of O ions with $x \geq 1/8$ and d) all structures with $1/2 \leq x \leq 7/8$ formed substructing simple lattices of O ions from the x = 1 structure. To obtain one and only one representative of all structures that are equivalent by symmetry, we used a group-theoretical method developed by one of us for finite clusters[56], which was expanded to take into account periodic boundary conditions. It can be briefly described by the following steps: 1) one of the possible unit cells considered is chosen, 2) the set of all possible O sites of the unit cell is divided into subsets which are generated by application of the point group G operations to a site, 3) within each subset, all nonequivalent subconfigurations C_i are constructed, 4) from all subconfigurations C_i and C_j belonging to two different subsets, all the possible subconfigurations of the union of both subsets are obtained only once combining C_i and g C_j, where g is one operation representative of those of a doble coset in the $G_i \backslash / G_j$ doble coset decomposition of G, (G_k is the symmetry group of the subconfiguration C_k) 5) the procedure is iterated until all subsets are considered, and 6) structures that are equivalent due to translational symmetry to previous ones are disregarded. To illustrate the power of the method, note that for a unit cell $2\sqrt{2}$ x $2\sqrt{2}$ (with 16 possible O positions), there are $2^{16} = 65536$ possible configurations. We find that only 997 are nonequivalent and after disregarding those with nearest-neighbor O atoms, only 35 structures remain.

It might happen that the ground state for particular values of the parameters is out of the set of structures we have considered. We believe that if this were the case for not too large screening lengths, the ground state structure and its energy would be very similar to our result and would not change the trends of our conclusions. This is the case of the structure of Fig.3 b), which we included because we suspected that it should have lower energy than a similar 2 x 3 structure. The difference of energy was actually very small. Our cluster variation method calculations[42,47] at very low temperatures detected an unexpected ground-state structure only in one case ($x = 0.5$, $\lambda = 1$, $f = 0.6$), but this was a consequence of cutting off the interactions beyond the fifth O neighbors.

IV - RESULTS

For an arbitrary value of x, the ground state of the system is found to consist of a mixture of two phases with two neighboring compositions x_i, x_{i+1} with $x_i < x < x_{i+1}$, that correspond to two structures i and i + 1. These structures can be classified into 4 different types represented in Figs.1 to 4 respectively. Briefly they can be identified as 1) "chain" structures (CS), 2) nearly "hexagonal" structures (HS), 3) "pair" (or small-chainlet) structures (PS) and 4) others. In the wide region of parameters studied, types 1 and 2 are the most frequent and type 4 is very rare. In the following we explain in more detail this classification.

1) CS: structures of minimum energy among those of unit cell 1 x n (composed of full and empty chains) and composition x = m/n

with m and n integers (see Fig. 1). Khachaturyan and Morris proposed similar structures to be originated in spinodal decomposition[26]. They are the ground state for f large and negative.

2) HS: as found earlier by Aligia, Rojo and Alascio[24,25], these structures predominate for f = 1. They can in turn be divided into two groups: a) for $x \leq 2/3$ and $x = 1$, structures of minimum energy among the simple lattices of O ions for a given composition (see Fig. 2 a) to d)). These structures are in general the smallest possible deformation of a perfect hexagonal simple lattice (type p6m) with the same O concentration. This hexagonal structure would minimize the energy if the O ions could be placed in any position of the plane instead of a square lattice. It also reminds the vortex structure of type II superconductors[57] and, in fact, when the positions of the vortices are restricted to a lattice, structures of this type are predicted[58] for magnetic fields corresponding to x = 2/5, 2/3 and 1 (Fig. 2 b) and d) correspond to Fig. 1 a) and b) of Ref. 58). The basic vectors of the O lattice define the structure. These vectors are listed in Table I. Note that for most of these structures, at least one of the basic vectors contains $\vec{a}$ or $\vec{b}$ a half integer number of times. This means that as far as the main diffraction peaks are concerned[24], these structures would be identified as "tetragonal". The x = 1 structure can also be classified as a CS. b) for $2/3 < x < 1$, structures of minimum energy for a given composition, among those obtained adding a simple lattice of O vacancies to the x = 1 structure. The fact that the latter is a square lattice implies that these structures have the same form as in a)[24]. In fact, it can be shown that if A is a simple lattice of O ions, B is any O

structure built on this lattice and A-B is the structure obtained from A substracting the O atoms in the positions of B, the energy per unit cell of A-B can be calculated as:

$$e_{A-B} = \frac{x_A - 2x_B}{x_A} e_A + e_B \qquad (3)$$

Therefore, for fixed A and x_{A-B}, minimizing e_{A-B} reduces to minimizing e_B. An example of this structure is shown in Fig.2) e) and the basic vectors of these structures for $x \leq 7/8$ are given in Table I.

3) PS: these structures appear at the threshold of stability between CS and HS. In general, they are built from pairs of second-neighbor O atoms (or O vacancies added to the $x = 1$ structure) with a Cu in between (see Fig.3). In two cases (Fig.3 c)) the basic unit of the structure is the shortest linear chain containing 3 O atoms (or the O atoms replaced by vacancies). Some structures of these type were proposed by Alario Franco et al.[10]: the structures of Fig. 3 a) are the same as those of Fig.3 c) and 3 g) of Ref.10. Similarly, our Fig. 3 c) corresponds to Figs.3 d) and 3 f) of Ref.10.

4) In the range of parameters investigated ($f \leq 1$, $\lambda \leq 10a_o$, where $a_o = a/\sqrt{2}$ is the lattice parameter of the O sublattice), we found only three structures that do not belong to the previously described types. The most frequent of them is the one shown in Fig.4. Another one is built adding vacancies to the structure of Fig.2 c), suggesting a generalization of the constructing procedure used for type 2 b) (see Fig.2 e)) for large λ. The three structures appear only for large values of λ and $f \sim 1$. This is

due to the fact that within our model with constant A and screening length λ, for a given composition, segregation into neighboring phases implies also a segregation of ionic charges. As the screening by mobile carriers is reduced (λ is increased), this segregation becomes energetically unfavorable and the system prefers structures with increasingly larger unit cell and composition nearer to the given one. To describe accurately the academically interesting regime $\lambda \gtrsim 10a_o$ and $f \sim 1$, a larger number of possible structures have to be considered.

In Fig.5, we show the x - f phase diagram for different values of λ. The regions $0 < x < 1/8$ and $7/8 < x < 1$ are empty because we have not considered structures with these compositions. The phase diagram is dominated by CS and HS. The transition from one type of structure to the other for given composition, happens at values of f which roughly correspond to the equality between V_b (see Eq.(2)) and the largest interaction between O atoms (or additional vacancies if x is larger than 2/3) different from V_b in the corresponding HS. The value of this interaction decreases for $x \to 0$ or $x \to 1$ and is maximum for $x = 1/2$ (compare the length of the basic vectors different from $\pm \vec{b}$ in Fig.2). This explains that for intermediate values of f the CS are stable within an interval of values of x which has its midpoint around $x = 1/2$. For some values of f, the only stable CS is the one with $x = 1/2$. The above mentioned interval grows with decreasing f. The transition between CS and HS is mediated by PS: when the first two have the same energy, the latter is usually the ground state. This is not apparent in Fig.5 for x near 1/8 or 7/8 because in these cases the size of the unit cell of the PS is larger than the maximum size

which we have considered in our set of structures.

For different values of λ the same qualitative behaviour is obtained (compare the three parts of Fig.5). As λ increases two main effects can be observed: a) the values of f for which the transition between CS and HS takes place increase. This can be understood on the basis of the rough explanation of the transition given above. b) the number of different structures increases due to the larger cost of energy involved in the segregation of ionic charges, as explained above.

V - COMPARISON WITH EXPERIMENTS

From the density of carriers[5], one expects a screening length $\lambda \sim 2a_o$ where $a_o = a/\sqrt{2}$ for $YBa_2Cu_3O_7$ and increasing for decreasing x. An exagerated lower bound for λ is $\sim 0.4a_o$ (Ref.29). The reduction factor of the second-neighbor O-O interaction with a Cu in between f, is more difficult to estimate due to the sensitivity of $\Delta E = (1/f-1)V_b$ to the electronic parameters[43], and the uncertainty on the exact values of the O charges, but one expects $0 \lesssim f < 1$. Thus Fig.5 covers a fairly realistic range of parameters. The fact that in real systems A and λ decrease with x, and f also varies, affects the relative stability of the different phases against segregation, but the trends are clear: stable "chain" structures (CS) are expected for compositions around $x = 1/2$. The most stable CS is the experimentally observed[7,8] for $x = 1/2$. Some authors suggest that it would be the only stable CS (apart from the $x = 1$ phase)[14]. Instead, for x near 0 or 1 the structures shown in Fig.2 (HS) dominate for most values of f. The structure shown in Fig.2 a) and that obtained from it replacing

the O atoms by vacancies added to the x = 1 structure, are consistent with the experimental observations for x = 1/8 and 7/8 of a unit cell multiple of $2\sqrt{2}$ x $2\sqrt{2}$ (Refs.9- 11). The slightly different structures proposed in these works (basic vectors (2,2) and (2,-2) instead of those of Table I or Fig.2 a)), have a slightly higher energy (for example, the difference is $2.7\times10^{-4}A/a_o$ for $\lambda = 10a_o$, $6.6\times10^{-5}A/a_o$ for $\lambda = a_o$ and $6.0\times10^{-7}A/a_o$ for $\lambda = 0.4a_o$), and could be favored at moderate temperatures, since a greater entropy is expected.

Concerning the observed CS for x near 2/3, the stability of which is currently under debate, our results for sufficiently low values of f predict stable structures that are quite consistent with the experimental observations, in particular for x = 2/3 (Ref.13) and x = 3/5 (Ref.12). For the latter composition, the predicted CS has the unit cell shown in Fig.1 d). In addition to the main diffraction peaks of the primitive unit cell[24], this structure should present less intense peaks at wave vectors (n/5, 0,0) in units of $2\pi/a$, with the intensity for m = 2,3 being 6.86 times larger than for m = 1,4, which is consistent with the observed diffuse streaking[12]. Note however that the CS for the similar compositions 5/8 and 4/7 (Fig.1 e) and c)) would produce diffraction patterns difficult to distinguish from the previous ones within the experimental resolution. As shown in Fig.6, a mixture of equal quantities of the three structures, oriented paralelly, produces a diffraction pattern very similar to the experimentally observed[12].

For CS, a 1-x dependence of the number of Cu^+ is expected[43,46,52]. Thus, the x-ray absorption experiments of Ref.

46, together with the structural evidence[7,10,59], suggest a transition from HS to CS at $x \sim 0.35$ for increasing x. This fact can be used to determine f and then a change from CS to HS near $x \sim 0.7$ is predicted neglecting the x dependence of the parameters. In fact, a new jump in the amount of Cu^{+} at this value of x has been reported[60], and several experiments suggest a phase transition[15-17]. Also a minimum in the resistivity[2,45] and changes in the temperature[61] and O pressure[32,62] dependence of x are observed.

In the comparison with experiment one should take into account that the structural properties are determined by the number of O atoms in the relevant planes, while the number of holes in the structure is determined by the total number of O atoms per unit cell, and the metal-insulator transition and other properties depend on both quantities[42,43]. The differences between both O concentrations and the nominal O content are affected by O present in grain boundaries and near surfaces and interfaces[63] and by some loss of bridging O(4) atoms[64] specially for low values of x.

VI - DISCUSSION

We have studied a two-dimensional Ising model to represent the possible oxygen positions of the CuO_x planes of $YBa_2Cu_3O_{6+x}$, which are the relevant ones for the structure. We have assumed a screened Coulomb interaction between any two O ions[24,25], but that between second-neighbor interactions with a Cu ion in between was reduced by a factor $f < 1$. We have given a simple argument to show that this reduction factor is due to charge transfer effects

induced by Cu-O Coulomb repulsion. The fact that $f < 1$, the hole count, the metal-insulator transition at $x = 0.5$ and the number of Cu^{+} are qualitatively explained in Ref.43 and briefly in Ref.42 using the same extended Hubbard model that leads to excitonic pairing in CuO_2 planes[39,40].

For realistic values of the screening length λ and a range of positive but small values of f, all the so far observed diffraction patterns[6-13] can be explained in terms of the ground state of the model for the compositions $x = 0$, 1/8, 1/2, 3/5 (or some mixture of 4/7, 3/5 and 5/8), 2/3, 7/8 and 1. Models based on arbitrary, comparatively smaller parameters[18-23] cannot account for the experimental observations at $x = 1/8$ and 7/8 and other structures could only be obtained as metastable. Evidence in favor of the dominant role of Coulomb energies was summarized in the introduction. Note that estimations of the magnitude of the O-O interactions based on the x dependence of O desorption rates[65] or of the O chemical potential[66,67] are actually underestimations because A and λ in Eq.(2) decrease with x, since the concentration of carriers and the number of O holes increase in the metallic phase[5,51,43].

Results presented elsewhere[42,47] using the 9-point approximation of the cluster variation method, show that for $x = 1/2$ and temperatures much lower than the nearest-neighbor O-O interaction, the system undergoes a transition to a highly correlated tetragonal phase. There is experimental evidence of these correlations[48,49,45]. At higher temperatures the transition takes place for $x \sim 0.65$ almost independently of the temperature[47] in reasonable agreement with experiment[6]. Thus, the most important

aspects of the structural and electronic properties of these systems can be accounted for, at least qualitatively, in terms of strong interatomic correlations.

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Table caption

Basic vectors that define: a) for $x \leq 2/3$ or $x = 1$, the O lattices of minimum energy b) for $3/4 < x < 1$, the structures of minimum energy among those obtained adding a simple lattice of O vacancies to the $x = 1$ ground state (see Fig.2). The unit vectors are $(1,0) = \vec{a}$, $(0,1) = \vec{b}$ (Fig.2 a)). In case b), interchanging $\vec{a}$ and $\vec{b}$ a different structure with the same energy (within our model) is obtained.

Table I

x	$\vec{V}_1$	$\vec{V}_2$
1/8	(1,3)	(-2,2)
2/15	(3,5)/2	(3,-5)/2
1/7	(3,5)/2	(5,-1)/2
2/13	(1,5)/2	(5,-1)/2
1/6	(-1,5)/2	(5,-1)/2
2/11	(1,2)	(5,-1)/2
1/5	(1,2)	(2,-1)
2/9	(1,2)	(3,-3)/2
1/4	(1,2)	(2,0)
2/7	(1,2)	(3,-1)/2
1/3	(0,2)	(3,-1)/2
2/5	(1,3)/2	(3,-1)/2
1/2	(1,3)/2	(-1,1)
2/3	(0,1)	(3,1)/2
3/4	(2,1)	(0,2)
4/5	(2,1)	(1,-2)
5/6	(2,2)	(1,-2)
6/7	(3,1)	(1,-2)
7/8	(3,1)	(2,-2)
1	(0,1)	(1,0)

Figure captions

1 - Unit cells of structures of minimum energy for given composition x, among those composed of full and empty CuO chains (CS). Crosses denote Cu atoms, full circles represent O atoms, and empty circles denote empty O sites, which if filled complete the structure for $x = 1$. a) example for $x = 1/n$ with $n = 6$, b) $x = 2/7$, c) $x = 3/8$, d) $x = 2/5$, e) $x = 3/7$. The corresponding structures for compositions 1-x are obtained interchanging full and empty circles.

2 - Examples of structures of minimum energy for given O composition among those built with a simple sublattice of O atoms, or O vacancies on the $x = 1$ structure (HS). a) $x = 1/8$, b) $x = 2/5$, c) $x = 1/2$, d) $x = 2/3$, e) $x = 3/4$. Symbols as in Fig. 1. The basic vectors that define the structure according to Table I are indicated. Dashed lines show a possible choice of unit cell.

3 - Structures denoted by PS in the text, which are the ground state of the system for particular values of the parameters: a) $x = 1/4$, b) $x = 1/3$, c) $x = 3/8$, d) $x = 2/5$, e) $x = 1/2$. Symbols as in Fig. 1. Interchanging full and empty circles in a) to d) the corresponding structures for compositions 1-x are obtained.

4 - Ground state of the system for $\lambda = 4a/\sqrt{2}$, $f = 1$ and $x = 5/8$. Dashed and dotted lines show possible choices of the unit cell. Symbols as in Fig. 1.

5 - Ground state of the system as a function of composition x and

reduction factor f of the repulsion between second-neighbor O ions with a Cu in between, for different values of the screening length λ: top $\lambda = 0.4a_o$, middle $\lambda = a_o$, bottom $\lambda = 4a_o$ where $a_o = a/\sqrt{2}$ is the minimum distance between two possible O positions. The structures are uniquely determined by their type (denoted by different lines) and composition. Dotted line CS (Fig.1), dashed line: HS (Fig.2 and Table I), full line PS (Fig.3) and dotted-dashed line: Fig.4. The structure for x = 1 can also be classified as a CS.

6 - Diffraction pattern of a mixture of equal parts of paralelly oriented CS (see Fig.1) with x = 4/7, 3/5 and 5/8, along the (q,0,0) direction, excluding the peaks at q = 0 and q = 1 in units of $2\pi/a$. All peaks have been broadened with a half-width of 0.03.

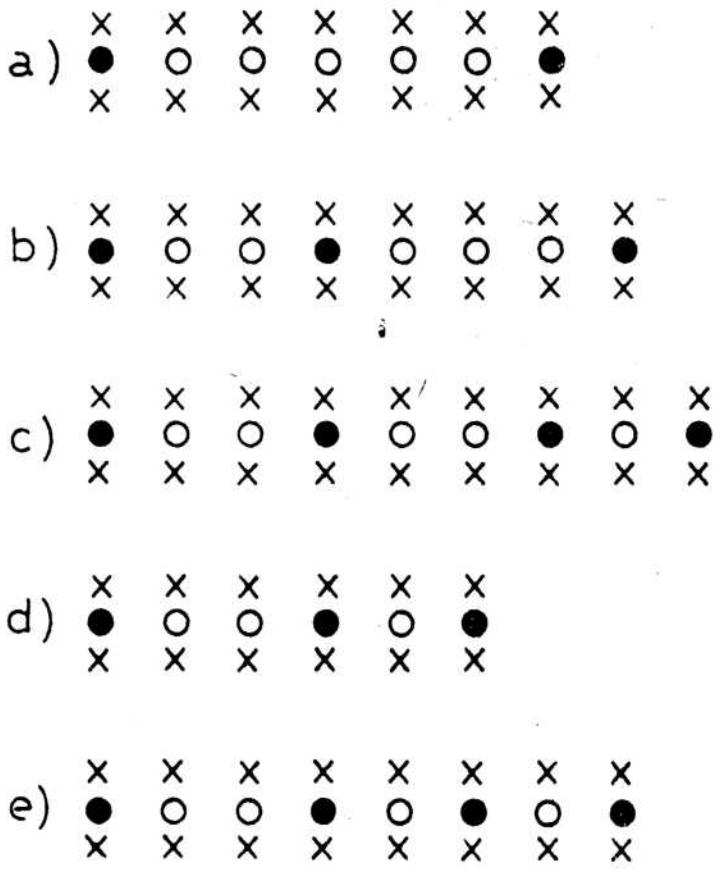

Fig. 1

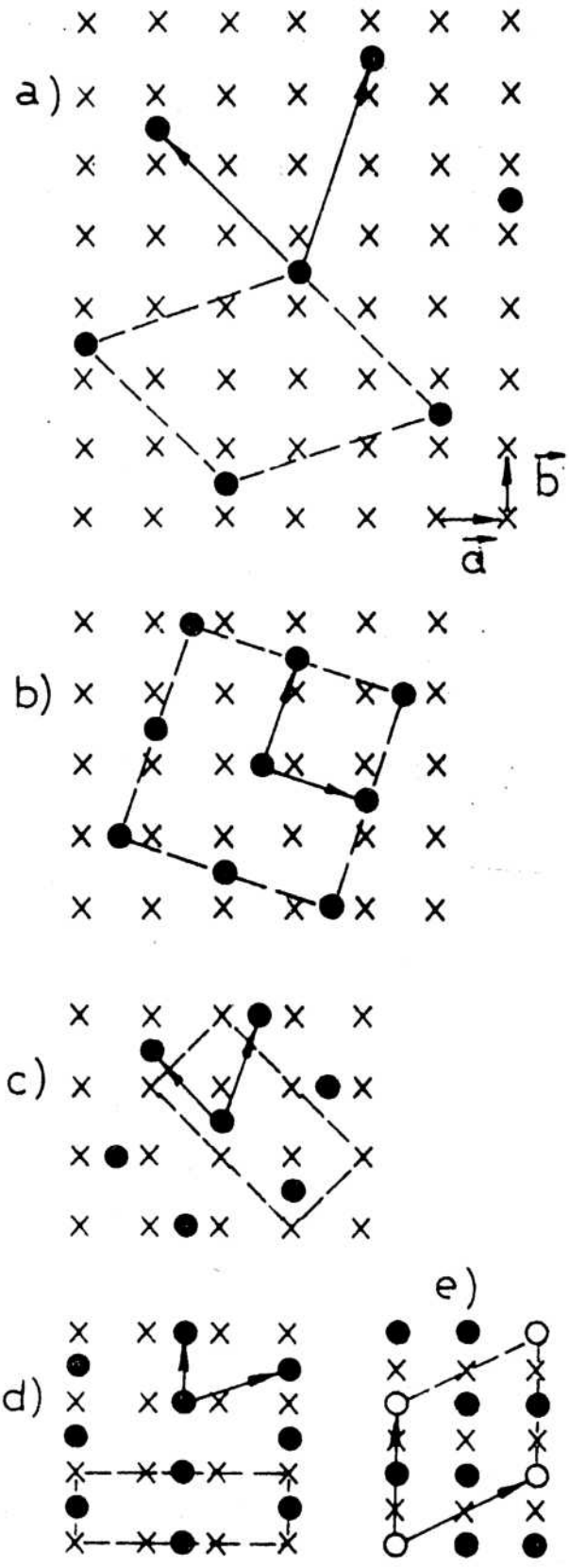

Fig. 2

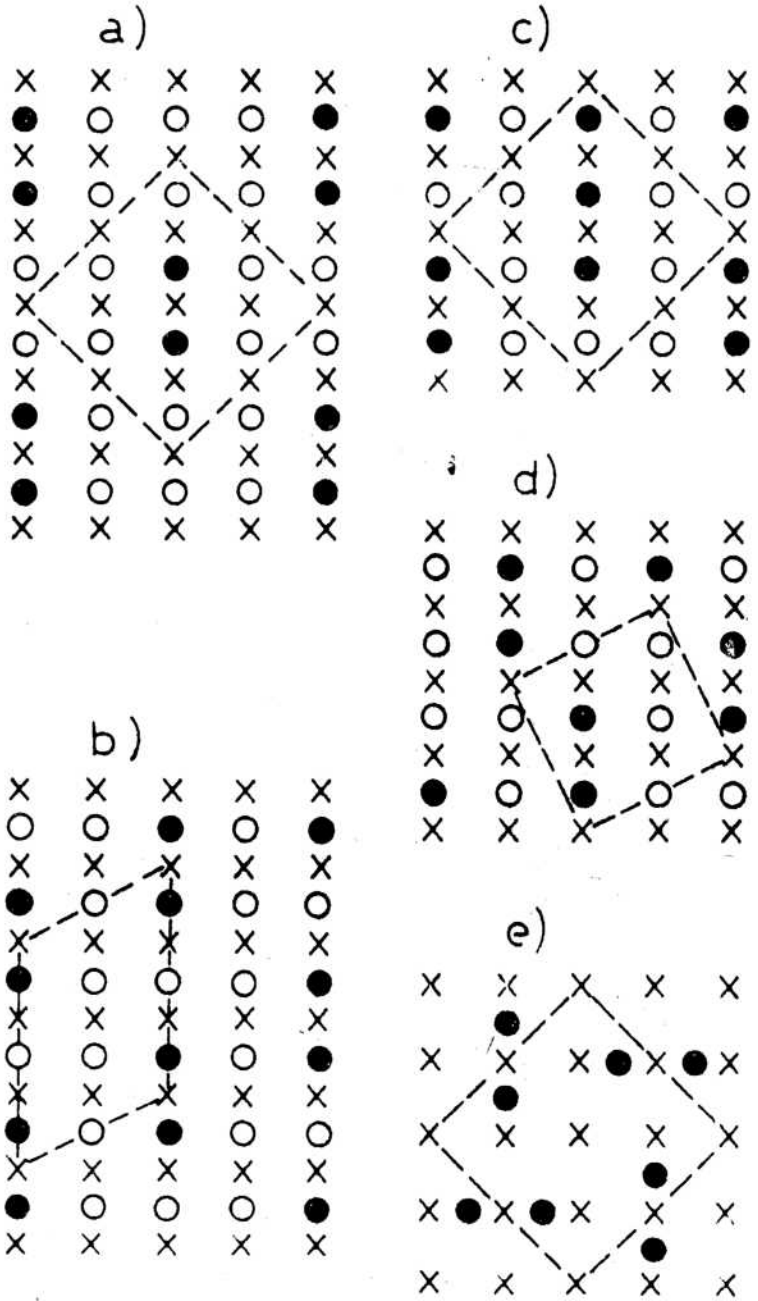

Fig. 3

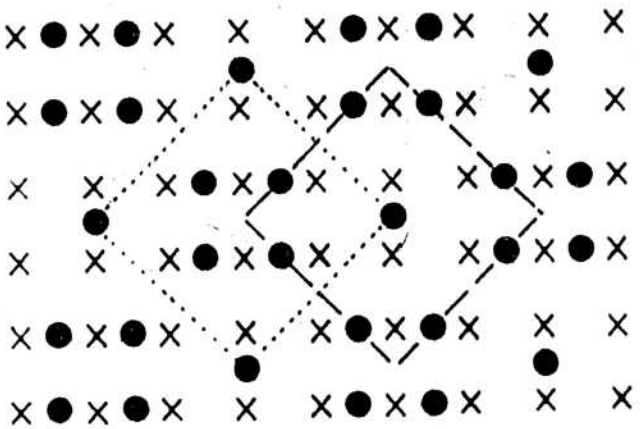

Fig. 4

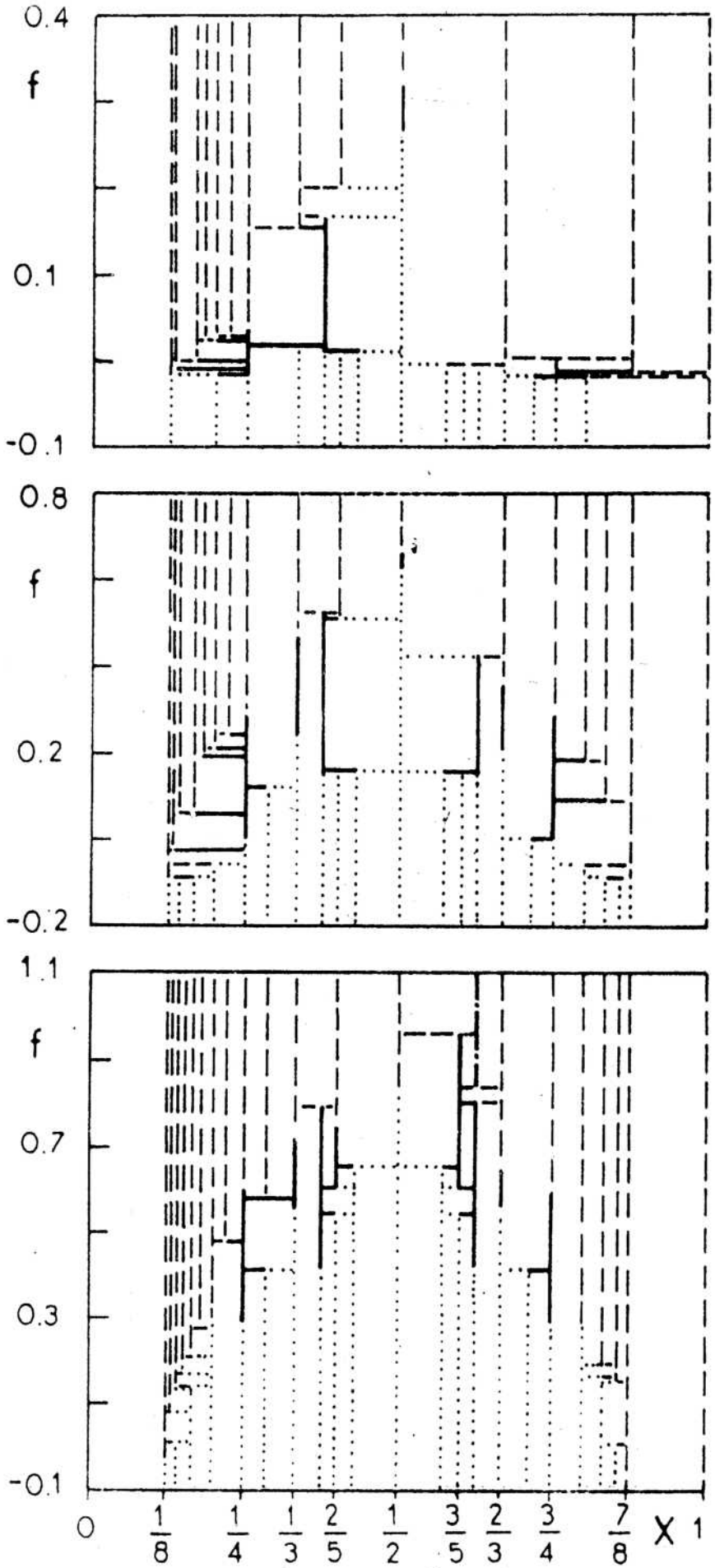

Fig. 5

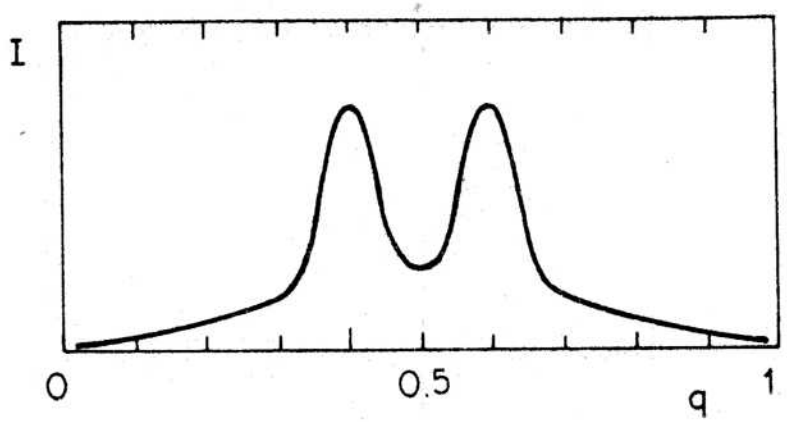

Fig. 6