Monte Carlo studies of oxygen ordering in the $YBa_2Cu_{3-x}A_xO_{7-\delta}$ systems (A = Ga,Al)

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Monte Carlo simulation with constant oxygen concentration (Kawasaki dynamics) of a lattice-gas model with anisotropic interaction is used to explore the effects of thermal quenching on oxygen ordering in the basal plane of $YBa_2Cu_3O_{7-\delta}$ and related systems. The oxygen structure factor is calculated for various quenching conditions and for different oxygen concentrations. The growth of the orthorhombic domain is monitored through the $\mathbf{q}$ dependence of the oxygen structure factor along the a and b directions. The effect of substituting Ga^{3+} or Al^{3+} ions at Cu(1) chain sites on the oxygen ordering is also discussed within the framework of this model.

INTRODUCTION

Since the discovery of high-temperature superconductivity in the Y-Ba-Cu-O system, many studies have focused on various aspects of the effects of processing the $YBa_2Cu_3O_{7-\delta}$ materials, including phase identification, structure analysis, and superconducting property measurements. It has been shown that the phase responsible for the 92 K superconductivity in the $YBa_2Cu_3O_{7-\delta}$ system is a perovskite-related structure whose major structural feature consists of two-dimensional (2D) CuO_2 planes and Cu-O linear chains.[1-4] In addition to confirming the tetragonal-to-orthorhombic structural phase transition at 700°C in a pure oxygen atmosphere, neutron diffraction measurements have determined the oxygen stoichiometry of the "1:2:3" compound as a function of temperature in thermodynamic equilibrium.[5] The previously mentioned structural phase transition was found to be of the order-disorder type and resulted from the oxygen vacancy ordering along the axis of the unit cell.

Superconducting properties as a function of oxygen content $(7-\delta)$ have been extensively studied by several authors.[6-8] It has been found[9] that the superconducting transition temperature for thermally quenched samples changes from 92 to O K as the oxygen content is varied from 7.0 to 6.5.[9] On the other hand, results on samples obtained by the gettered annealing method at low temperatures[10] show a clear plateau in T_c versus the oxygen-concentration curve. This plateau at $T_c \approx 60$ K is strong evidence for the existence of two superconducting phases in the $YBa_2Cu_3O_{7-\delta}$ system. The plateau at $T_c \approx 60$ K is thought to be related to the appearance of the double-cell orthorhombic structure, which has been seen in several experiments.[11-14] Cluster-variational calculations within a lattice-gas model[12,15] also predict the existence of such a structure. These results suggest that the superconducting properties are extremely sensitive to the oxygen ordering in the basal plane.

In our previous work, we have used a two-dimensional lattice-gas model to study the order-disorder transition in the CuO plane of the $YBa_2Cu_3O_{7-\delta}$ system.[16] Using a model Hamiltonian with isotropic nearest-neighbor and anisotropic next-nearest-neighbor interactions and with a suitable choice of parameters, we were able to fit most of the experimental data[5] satisfactorily. In this paper we explore this model in more detail and report a series of Monte Carlo (MC) simulations for constant oxygen concentration.[17] Three reasons for undertaking such a study are now given.

First, to see if the double-cell orthorhombic structure is indeed stable, we have investigated the low-temperature structure of the CuO plane of the "1:2:3" compound for various oxygen concentrations and thermal cooling rates using Monte Carlo simulations. Since the oxygen concentration is fixed, we have used Kawasaki dynamics in our simulation. Structure factors associated with oxygen ordering along the a and b axes are calculated to identify different types of structures.

Second, in their attempt to explain the oxygen-concentration dependence of T_c,[10] Zaanen *et al.*[18] developed a simple model relating the superconducting properties to the hole concentration in the CuO_2 plane. The latter depends on the oxygen concentration and oxygen ordering in the CuO plane through the electronic structure of the CuO chains formed in the CuO basal plane, these chains acting as a reservoir of holes for the CuO_2 planes. To apply their model to real systems, it is important to know the CuO chain distribution for different oxygen concentrations. We believe that the information obtained from Monte Carlo simulations will be useful for a detailed calculation of the electronic properties of these compounds.

Finally, to elucidate the role of Cu in the CuO chains and CuO_2 planes in the observed superconducting properties, several authors have explored the effects of replacing Cu ions by other cations on the superconducting and structural properties.[19-23] It is now known that the Cu(1) site (the chain site) can be preferentially substituted by nonmagnetic elements Ga or Al. X-ray and neutron diffraction studies indicate that the structure of $YBa_2Cu_{3-x}(Ga,Al)_xO_7$ becomes tetragonal for $x > 0.18$.

Unlike the tetragonal phase of $YBa_2Cu_3O_{7-\delta}$ ($\delta > 0.5$), the tetragonal $YBa_2Cu_{3-x}(Ga,Al)_xO_7$ system is a superconducting with T_c as high as 80 K. The Cu(1) site can also be preferentially substituted by magnetic elements such as Fe and Co.[21–23] The structure of these systems becomes tetragonal at a much smaller value of x compared to the Ga- or Al-doped systems. These transition metal impurities introduce additional complexity into the systems due to their magnetic moments. We generalize the lattice-gas model developed for the $YBa_2Cu_3O_{7-\delta}$ system to include the effect of these substituted impurities and investigate the oxygen ordering using Monte Carlo simulation. For the sake of simplicity we will consider only the case of the Ga- and Al-doped systems in this paper.

THE LATTICE-GAS MODEL

The structure of the CuO plane of $YBa_2Cu_3O_{7-\delta}$ is described as a 2D square lattice consisting of Cu atoms, oxygen atoms, and oxygen vacancies. In the ordered (orthorhombic) phase the oxygen atoms and the vacancies are ordered so that there are linear Cu-O chains parallel to the b axis, as shown in Fig. 1. For a fixed oxygen concentration, the lattice-gas Hamiltonian can be written as

$$H = V_1 \sum_{\langle ij \rangle} n_i n_j + V_2 \sum_{(ij)a} n_i n_j + V_3 \sum_{(ij)b} n_i n_j \ , \qquad (1)$$

where V_1 represents the interaction between two nearest-neighbor oxygen atoms; V_2 and V_3 represent the interactions between two next-nearest-neighbor oxygen atoms either parallel (V_2) or perpendicular (V_3) to the b axis. Assuming the oxygen-oxygen interaction to be predominantly of the screened Coulomb type, we have $V_1 > 0$ and $V_3 > 0$. However due to the presence of the bridging Cu atom, $V_2 < 0$. In our previous work,[16] the values of these parameters were chosen as

$$V_1 = 0.25\text{eV}, \quad V_2 = -0.2\text{eV}, \quad V_3 = 0.1\text{eV} \ . \qquad (2)$$

Using this set of parameters, Monte Carlo simulations in our previous work gave results in excellent agreement with experiments.[16] The orders of magnitude of V_1 and V_3 can be justified by assuming a screened Coulomb type interaction between the oxygen ions. If we assume that there is one mobile hole per unit cell (as is the case in $YBa_2Cu_3O_7$), using both Thomas-Fermi and ion dielectric screening ($\epsilon_0 \approx 7$), we estimate $V_1 \approx 0.3$ eV and $V_3/V_1 \approx 0.4$, which are consistent with the choice of the parameters given in Eq. (2).

From a fit of the experimental value of the oxygen concentration at the orthorhombic-to-tetragonal structural transition temperature[16] and the fact that the ground state of the $YBa_2Cu_3O_{6.5}$ system has a double-cell orthorhombic structure,[13,14] V_2 is found to be negative. The attractive interaction between two oxygen atoms bridged by Cu is primarily due to the transfer of oxygen holes via Cu. Unfortunately there is no satisfactory method to calculate V_2 because it depends not only on the oxygen hole density but on the interaction with the localized spins at the Cu sites. To estimate the order of magnitude of V_2, we consider the CuO chains only and construct a one-dimensional tight-binding model to describe the motion of the oxygen hole. We further assume that the localized spins on the Cu sites are either ferromagnetically or antiferromagnetically ordered. Using values of the parameters from Emery's model,[24] we find that V_2 is negative and is of the order of 0.1 eV. Thus we believe that this lattice-gas model is physically reasonable and the oxygen-oxygen interaction is basically anisotropic and of short-range nature in the "metallic" phase. It is known that the Thomas-Fermi screening length increases with the decreasing of oxygen content which decreases the hole density, and the lattice-gas model with short-range interaction fails to be a good approximation for $\delta \geq = 0.5$ when the system becomes insulating and the interaction becomes long ranged.

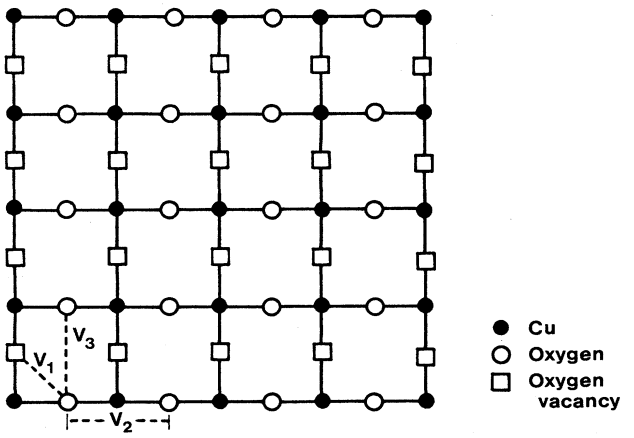

FIG. 1. The ground-state structure of the CuO plane of the $YBa_2Cu_3O_7$ system.

MC SIMULATION OF THERMAL QUENCHING

We have performed Monte Carlo simulations with Kawasaki dynamics using the previously mentioned lattice-gas model (Eq. 1). A 40×40 lattice was used to obtain the "snapshot" of oxygen configurations and to calculate the structure factor of oxygen. The high-temperature configuration was obtained by using MC simulations at $T = 2300$ K (well above the order-disorder phase transition temperature for $\delta = 0$) and the system was equilibrated at this temperature with 10 000 MCS/site (MCS = Monte Carlo steps). The low-temperature data were obtained by either slowly cooling (annealing) with a temperature interval of 100 K or rapidly cooling (quenching) to 300 K. 10 000 MCS/site were used to obtain thermodynamic averages for each temperature. The results are shown in Figs. 2–5.

Figures 2 and 3 show the oxygen configurations of the annealed and the quenched systems at 300 K for the $YBa_2Cu_3O_{6.5}$ system. We find that the structure for the annealed sample is a double-cell orthorhombic (II) structure with half of the CuO chains intact and half empty. The structure for the $YBa_2Cu_3O_7$ system as shown in Fig. 1 is referred to as the orthorhombic I structure. The quenched system, on the other hand, shows very small

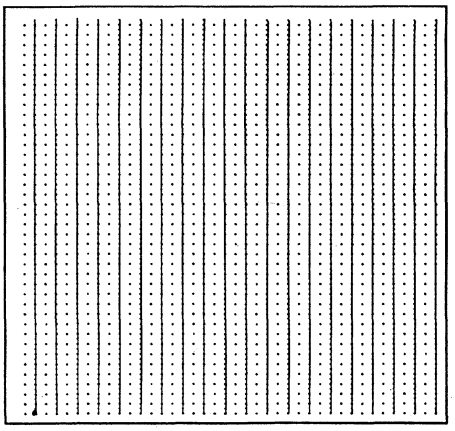

FIG. 2. Oxygen configuration of the annealed $YBa_2Cu_3O_{6.5}$ system.

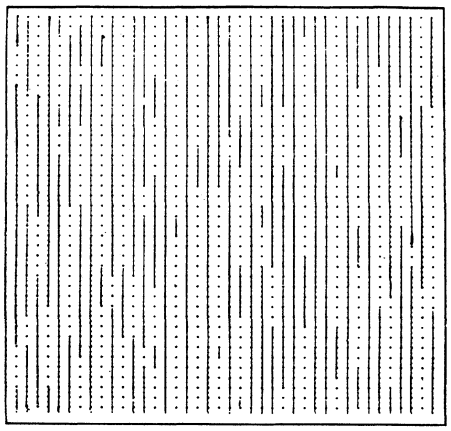

FIG. 4. Oxygen configuration of the annealed $Yba_2Cu_3O_{6.7}$ system.

domains of orthorhombic structure, with CuO chains oriented along the *a* and *b* directions. The overall symmetry is, however, tetragonal as indicated by the structure factor along the *a* and *b* directions.

The difference between the structures of quenched and annealed systems has also been studied for the oxygen concentration 6.7. Since this oxygen concentration is not appropriate for either the I structure or the II structure, new structural features arise. Typical oxygen configurations and the structure factor for the $YBa_2Cu_3O_{6.7}$ compound at 300 K are shown in Figs. 4 and 5 and Figs. 6 and 7, respectively. From these results we find that the low-temperature structure for the annealed system (Fig. 4) is a highly degenerate one. Instead of a single domain of ordered structure or a two-domain structure which is phase separated into I and II domains, we find long Cu-O chains "intercalated" into each other so that one sees a mixture of structure with I and II symmetry as indicated by the calculated structure factor (Fig. 6) as well as the "snapshots" of the oxygen configurations (Fig. 5). From the width of the diffuse peak at $(\pi,0,0)$ along the *a* axis [Fig. 6(b)] we estimate the coherence length of II structure along the *a* axis to be about 5–6 unit cells corresponding to about 20–25 Å, which agrees very well with the experimental results.[13,14] It is also shown, both by the oxygen structure factor calculation and the "snapshots" of the oxygen configuration that the average Cu-O chain length depends sensitively on the thermal history of the sample. This may in turn, as indicated by Zaanen *et al.*,[18] affect the hole density in the CuO_2 plane, and the superconducting transition temperature T_c. The quenched system like $YBa_2Cu_3O_{6.5}$ shows short chains in both the *a* and *b* directions and the overall symmetry is tetragonal, as seen in the structure factor for both the *x* and *y* (i.e., *b* and *a*) directions (Fig. 7).

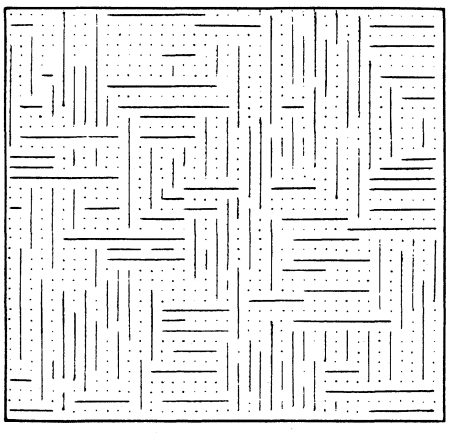

FIG. 3. Oxygen configuration of the quenched $YBa_2Cu_3O_{6.5}$ system.

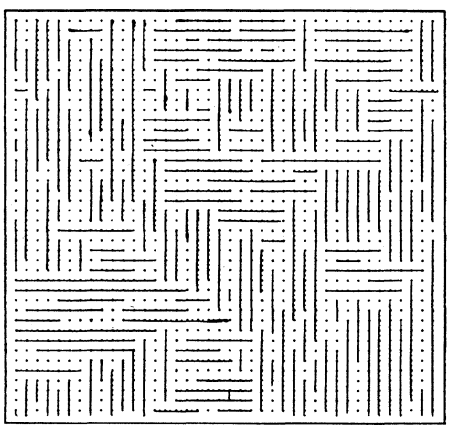

FIG. 5. Oxygen configuration of the quenched $Yba_2Cu_3O_{6.7}$ system.

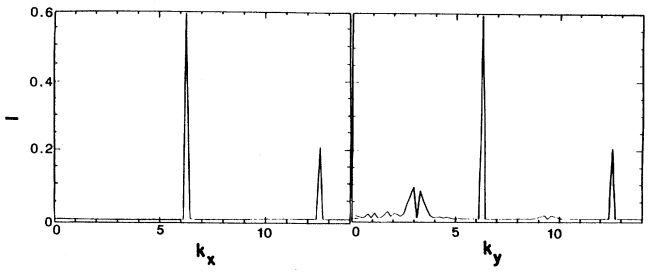

FIG. 6. Oxygen structure factor of the annealed $YBa_2Cu_3O_{6.7}$ system (wave vector **k** is in units of $1/a$).

SUBSTITUTION EFFECT

When a divalent or monovalent Cu ion is substituted by a trivalent M (M=Ga or Al) ion, holes on the oxygen sites will tend to localize near the M sites (Fig. 8). This will have two major effects which are (a) the binding energy of the oxygen is increased near the impurity site and (b) the oxygen-oxygen repulsion is increased near the impurity site either due to the increase of the negative charge of oxygen ions or due to the decrease in local screening because of the decrease in the hole density.

Based on this picture, we modify the lattice-gas model of Eqs. (1) to incorporate the effects of the impurities. The Hamiltonian representing the modified system is

$$H=\sum_{\langle ij\rangle} V_{1ij}n_in_j+V_2\sum_{(ij)a} n_in_j+\sum_{(ij)b} V_{3ij}n_in_j+\sum_i E_in_i \ , \quad (3)$$

where

$$V_2=-0.2 \text{ eV} \ , \quad (4)$$

$$V_{1ij}=0.25 \text{ eV}, \quad V_{3ij}=0.1 \text{ eV} \ , \quad (5)$$

if neither site i nor site j are the nearest neighbors of M;

$$V_{1ij}=0.5 \text{ eV}, \quad V_{3ij}=0.2 \text{ eV} \ , \quad (6)$$

if either site i or site j is the nearest neighbor of M;

$$V_{1ij}=1.0 \text{ eV}, \quad V_{3ij}=0.4 \text{ eV} \ , \quad (7)$$

if both sites i and j are the nearest neighbors of M. In addition, the single-site binding energy $E_i=-4$ eV if site i is the nearest neighbor of M and $E_i=0$ otherwise.

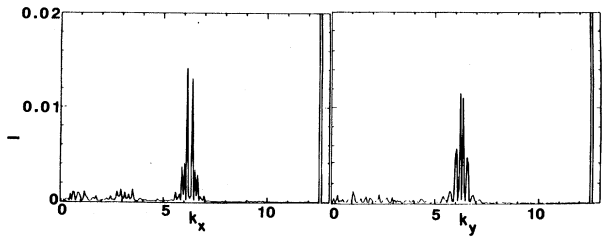

FIG. 7. Oxygen structure factor of the quenched $YBa_2Cu_3O_{6.7}$ system (wave vector **k** is in units of $1/a$).

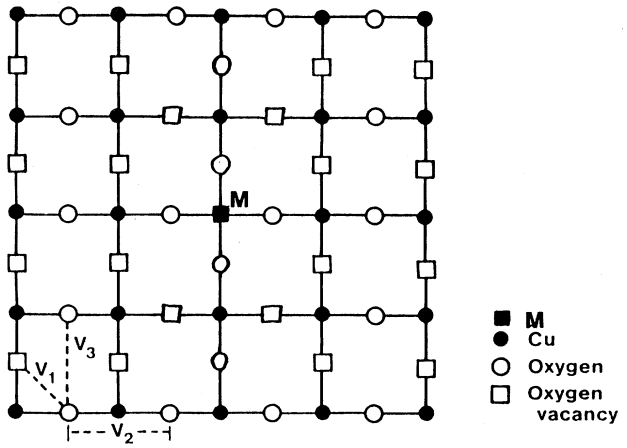

FIG. 8. The structure of the basal plane of the $YBa_2Cu_{3-x}M_xO_7$ system with a single impurity M.

Since the oxygen concentration in $YBa_2Cu_{3-x}(Ga,Al)_xO_{7-\delta}$ is very close to 7, we assume that the oxygen concentration is unchanged for different values of x. We also assume that the impurity M is randomly distributed in the CuO plane. A Monte Carlo simulation with constant oxygen concentration and x is performed on a 60×60 square lattice. For a given configuration of impurity M, 10 000 MCS/site are used to calculate the order parameter S, which is given by the difference in oxygen concentrations p_1 and p_2 in the two sublattices[16] (the circles and squares in Fig. 1):

$$S=\frac{p_1-p_2}{p_1+p_2} \ . \quad (8)$$

For each value of x, S is averaged over 20 configurations of the impurities M. The calculated order parameter S at $T=300$ K is shown as squares in Fig. 9.

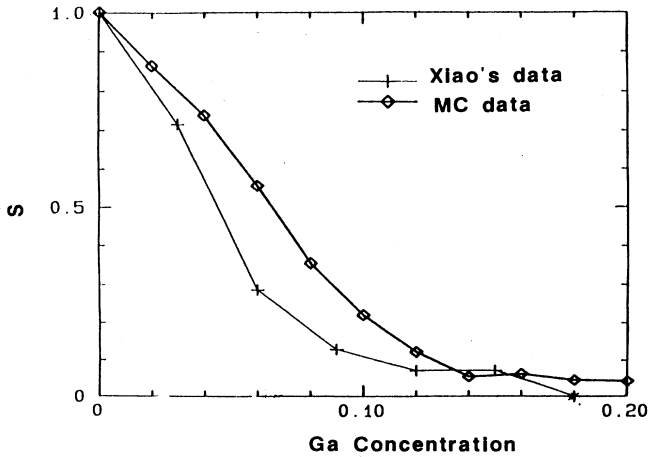

FIG. 9. Oxygen order parameters S of the $YBa_2Cu_{3-x}M_xO_7$ system as a function of the impurity concentration x at 300 K from Monte Carlo simulations and from data of Xiao *et al.* (Ref. 19).

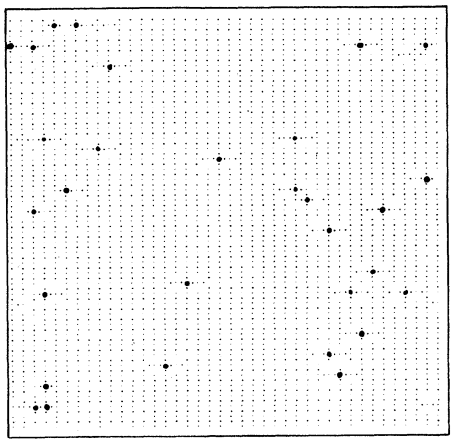

FIG. 10. Oxygen configuration of $YBa_2Cu_{3-x}M_xO_7$ for $x=0.02$ obtained from Monte Carlo simulation at 300 K.

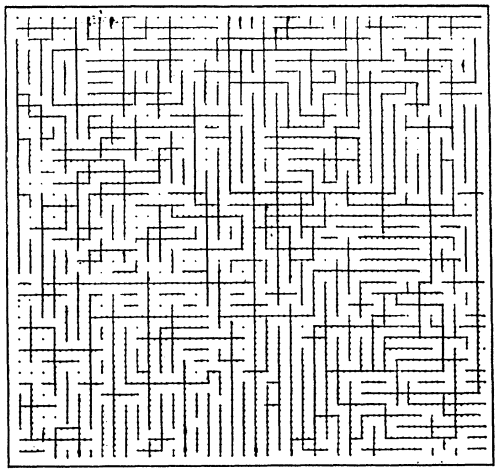

FIG. 11. Oxygen configuration of $YBa_2Cu_{3-x}M_xO_7$ for $x=0.12$ obtained from Monte Carlo simulation at 300 K.

The order parameter deduced from the experiment Xiao *et al.*[18] [assuming that $S=(b-a)/(b+a)$] is also shown in Fig. 9 as crosses. The general agreement is good, thus providing a justification of the basic assumptions behind our modified lattice-gas model. The discrepancy is either due to the long-range effect of the impurity on local oxygen ordering or the fact that the distribution of M is not completely random.

From a "snapshot" of the oxygen configuration of the M-substituted systems we find that local "cross links" are formed around the M sites (Fig. 10). These cross links destroy the Cu-O chain along the b direction and form short Cu-O chains along the a direction. As the concentration of the impurity increases, the number of short Cu-O chains along the a direction also increases (Fig. 11). For $x>0.16$ the system becomes tetragonal. However, unlike the tetragonal phase of the quenched $YBa_2Cu_3O_{7-\delta}$ systems, the length of the Cu-O chains are long enough (due to large oxygen concentration) to produce a large enough density of conducting holes in the CuO_2 plane. This may be the reason why the superconducting transition temperature T_c is still quite high in these Ga- or Al-substituted compounds even though the structure is tetragonal. The above conjecture has to be tested by an actual calculation following the procedure of Zaanen *et al.*[18]

SUMMARY

Monte Carlo simulation of a simple lattice-gas model with anisotropic interaction was performed in order to study the effects of thermal quenching and substitution of the Cu(1) site by trivalent nonmagnetic impurities (Ga,Al) on oxygen ordering in the basal plane of a $YBa_2Cu_{3-x}M_xO_{7-\delta}$ system. We find that the oxygen ordering is very sensitive to the thermal history of the samples. The cooling rate should be slow enough to get long Cu-O chains. The low-temperature structure of the oxygen-deficient system obtained by annealing is shown to be a mixture of I and II structures. The orthorhombic-to-tetragonal transition in Ga-or Al-doped systems is found the be due to short cross-linked CuO chains near these trivalent impurities. We believe that these simulation studies will be helpful in understanding the structure of $YBa_2Cu_3O_{7-\delta}$ systems and provide structural information for detailed calculations of their electronic properties.

ACKNOWLEDGMENTS

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