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Model of oxygen diffusion in $YBa_2Cu_3O_{6+x}$ with next-nearest-neighbor hopping: A Monte Carlo study

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To the antisymmetric next-nearest-neighbor Ising (ASYNNNI) model of oxygen diffusion in $YBa_2Cu_3O_{6+x}$ we have added a possibility for an oxygen atom to jump not only to a nearest neighbor but also to a next-nearest-neighbor site through a jump remaining in the *ab* plane. The usual Monte Carlo simulation procedure has been used to calculate the tracer diffusion coefficient which turns out to be less sensitive to the oxygen content than in the standard ASYNNNI model, as found out in experiments. The Arrhenius plots show nearly linear behavior. We have also calculated the average energy per particle in the system. This when plotted as a function of oxygen concentration yielded some information about possible phase transitions in the system. At low temperatures the diffusion is probably taking place along the copper-oxygen chains whereas for higher temperatures and low concentration of oxygen, interchain diffusion as well as reorientation of short oxygen chains is also possible.

I. INTRODUCTION

The problem of oxygen diffusion in $YBa_2Cu_3O_{6+x}$ (YBCO)-type superconductors has received much attention, both from a theoretical and experimental point of view.[1] The problem is interesting since it may contribute to the understanding of superconducting properties of materials like YBCO, but also it poses general questions concerning diffusion in anisotropic media.[2] Neither the experimental nor the theoretical situation in describing oxygen diffusion in YBCO-type crystals is completely clear, as has been shown recently in a series of papers by Rothman *et al.*[3,4] and by LaGraff and Payne.[5]

The main points raised in those papers are the following.

(i) The tracer diffusion coefficient seems to depend only weakly (if at all) on the concentration of oxygen ions. However, the chemical diffusivity is found to depend on it.

(ii) The tracer diffusion, confined to the *ab* plane, is strongly anisotropic, at least around $T=300°C$, but the anisotropy diminishes with the temperature. If the crystal is twinned then the diffusion looks isotropic.

(iii) The Arrhenius plot is a straight line, with uncertainty factor of 2, over the temperature range 300–800 °C; hence the moves of the oxygen ions are not correlated.

(iv) The mechanism of the diffusion is not clear. Rothman *et al.*[3] suggest that only the atoms at the end of the oxygen chains in the *ab* plane move along the rows of O(5) sites (for notation see Fig. 1). Therefore the diffusion, at least in the Ortho-I phase, is via the O(5) to O(5) jumps and has an interstitial character. LaGraff and Payne[5] also present an energy-based analysis of possible diffusion mechanism in the different phase of YBCO. They argue that because of the uncertainty factor in the Arrhenius plots of Rothman *et al.*,[3] correlation effects cannot be ruled out, and that a possible cause of the correlations is the interaction between oxygen defects. There is no measurement of the correlation factor.

(v) None of the existing theoretical models account for all features of the diffusion in YBCO.[6] In particular the antisymmetric next-nearest-neighbor (ASYNNNI) lattice gas model of Salomons and de Fontaine[7] yields tracer diffusion coefficients which are strongly concentration dependent. For a more complete review of existing theoretical models of oxygen diffusion in YBCO and their weak points see Refs. 1, 4, and 6.

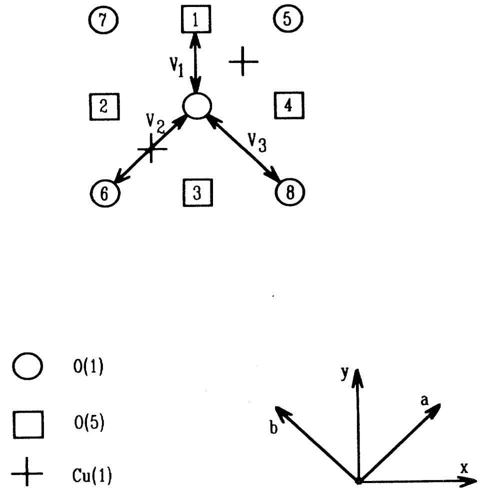

FIG. 1. Arrangement of ions and interactions on a YBCO plaquette in the basal (*ab*) plane.

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The aim of the present paper is to introduce an extension of the ASYNNNI model by taking into account the possibility, neglected in the earlier works,[5,7,8] that an oxygen ion may jump not only to an empty nearest-neighbor (NN) site but also to an empty next-nearest-neighbor (NNN) one. Such a possibility has been already suggested in the analysis given in Refs. 3 to 6. We neglect, however, the possibility of an oxygen ion in a CuO plane to go over a Cu site, either around it or by jumping onto an empty NN O(4) site and then coming

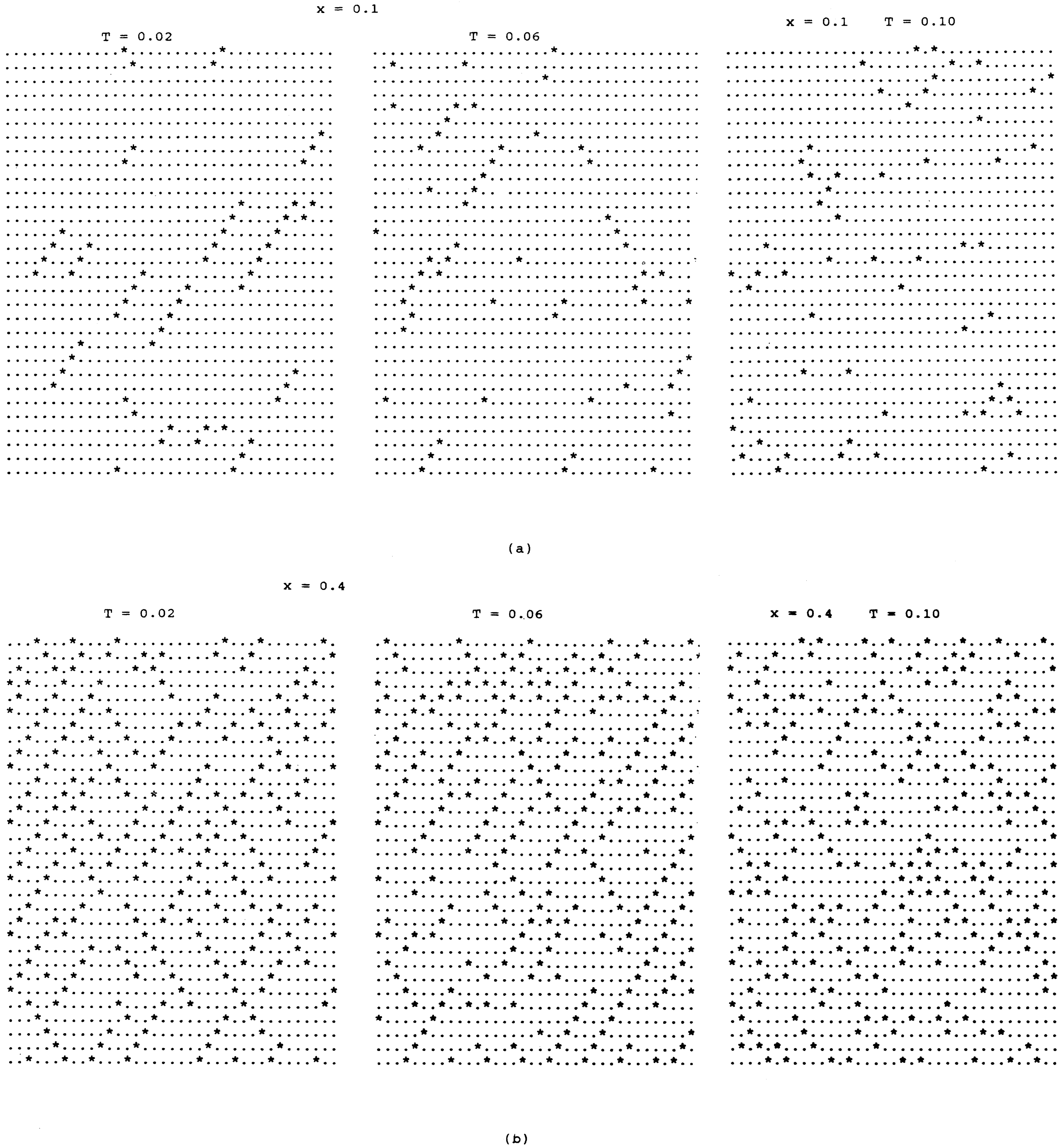
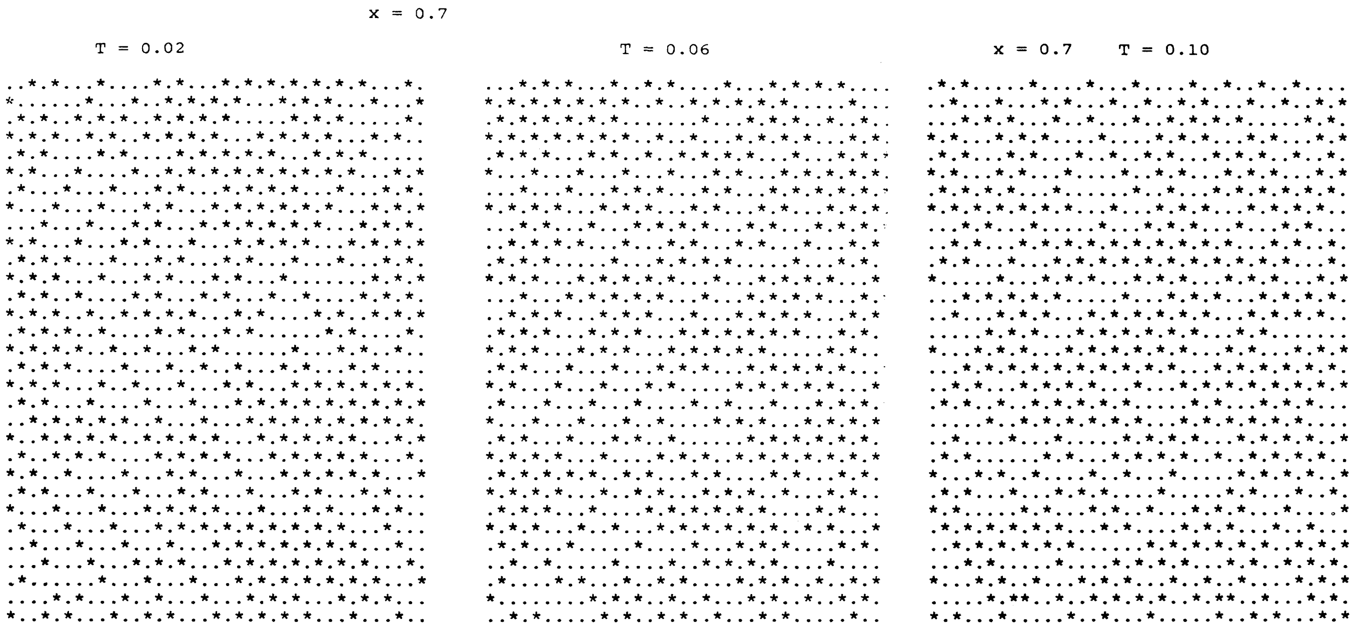


FIG. 2. Initial (after 1 kMCS) configurations at three different temperatures T in eV and concentrations, x, of oxygen ions. Only occupied (*) and empty (·) oxygen sites are shown.



(c)

FIG. 2. (*Continued*).

back to the CuO plane, when a NN or NNN site is vacant.

Using the Kawasaki dynamics and the standard Metropolis algorithm we calculate the tracer diffusion coefficient as a function of the temperature and the concentration of oxygen ions in the *ab* plane. From that data the Arrhenius plots are made. We present the analysis of the average energy of an oxygen ion as due to its interaction with NN and NNN. From the analysis of the diffusion coefficients and the moves of individual particles (oxygen ions) during the simulation we deduce possible mechanisms of oxygen ion diffusion at different concentrations and temperatures.

II. MODEL

We use the standard ASYNNNI model[7] on the square lattice where an oxygen ion interacts with its NN through the bond potential $V_1=0.38$ eV, with its NNN indirectly via a Cu atom with $V_2=-0.13$ eV and directly to NNN with $V_3=0.06$ eV (see Fig. 1). The values of the interaction constant come from Ref. 5.

For simulations we have taken the Monte Carlo method with the standard Metropolis algorithm. The initial configuration was prepared in the following way. For a given concentration, oxygen ions were placed randomly on the lattice sites. In physical terms it means that both the O(5) and O(1) sites were initially occupied. Due to that oxygen chains may appear as well along the O(5)-O(5) as along the O(1)-O(1) lines. We may therefore expect to get a system with chevronlike patterns and twins, even at low temperatures and in the Ortho-I phase. One Monte Carlo step (MCS) consists in N_x (equal to the number of particles) random picks of a particle to move. We let the system evolve during some initial time, usually 1 to 2 kMCS, before the quantities of interest were recorded. The configurations obtained after that initial time are shown in Fig. 2.

In the Monte Carlo procedure a randomly picked O atom has a chance to be shifted to an empty site into one of its four NN or into one of its two NNN (see Fig. 1). It seems to us that a jump over a Cu atom is highly unlikely and therefore in our approach such jumps are forbidden. Allowing for such jumps, although physically interesting, would change a two-dimensional (2D) problem into a 3D one and it would introduce two additional, experimentally unknown, parameters into the model. The allowed moves to a NNN site may thus represent either a O(5) to O(5) or O(1) to O(1) jump in the CuO plane alone. Possible NN moves are either O(1) to O(5) or vice versa, also in the CuO plane. It is, however, not certain whether the NNN jumps require more energy than the NN ones. Therefore we have decided to include an additional parameter into the model—an energy Q which an atom should overcome to realize a move to a NNN. The particular value of Q is yet unknown to us. The diffusion coefficient dependence on the oxygen concentration has been compared for zero and nonzero values of Q.

As usual, a site occupied by an oxygen ion to move is randomly picked. The initial energy is calculated as the sum of its interactions to NN and NNN,

$$E_i=V_1\sum_{j=1}^{4}t_j+V_2\sum_{j=5,6}t_j+V_3\sum_{j=7,8}t_j\ , \tag{1}$$

where $t_j=0,1$ is the occupation variable for the oxygen ion. Then one of the allowed sites for a jump is randomly chosen and the energy after moving the O atom there is calculated according to the same principle.

If the chosen site for the jump happens to be one of the NNN, the final energy, E_f, is increased by adding Q to it. If the difference $\Delta E = E_f - E_i < 0$, the move is realized, otherwise a random number $r \in [0,1]$ is generated and if $r < \exp(\Delta E/kT)$, then the atom is shifted, otherwise it stays in place.

We have calculated the tracer diffusion coefficients along the Ox and Oy axes and in the following used their combination:

$$D_+ = \frac{1}{2}(D_x + D_y) \; . \tag{2}$$

One should note that we consider a rigid square lattice free of stresses and thus free of orthorhombic distortions. Such a system does not support twins. In order to improve the situation, an extra term should be included in the Hamiltonian (see, e.g., Ref. 9 and references therein). Since we deal here only with the tracer diffusivity, we drop the usual asterisk differentiating the tracer and chemical diffusion coefficients.

We have used a 51×51 grid and the simulations were in general run for 5 kMCS with thermalization for 1 kMCS. In some cases, especially at low temperatures, we checked the results by extending the runs to 10 kMCS or to 40 kMCS on a smaller (37×37) lattice, but there was no significant difference. Each data point for D results from an average over at least 7 MC runs.

III. RESULTS

A. The diffusion coefficient

Our aim was to introduce into the ASYNNNI model[5] an ingredient which would likely decrease the dependence of D on the oxygen concentration, x. Figure 3 shows the $\ln D_+$ versus x curves for both models—with and without the possibility for a NNN jump for an O atom. As can be seen, the inclusion of the possible NNN moves decreases greatly, but not completely, the dependence of D_+ on x.

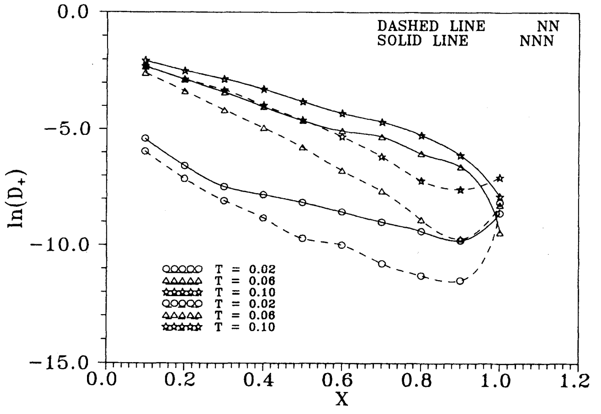


FIG. 3. Diffusion coefficient $\ln D_+$ versus x for our model (with NNN jumps) (solid line) and the model with NN jumps only (dashed line). Temperature is in eV.

A more detailed presentation of the variation of the D_+ versus x curves with T is shown in Fig. 4 for the case of $Q = 0$ and for our model only. Clearly the dependence is different at low ($T = 0.02$ and 0.04 eV) temperatures than at higher T. In particular at $T = 0.02$ and for x close to 1 we observe a change of the behavior of $\ln D_+$. Its value increases with x, whereas for higher T it decreases. We have already remarked this feature in an earlier study[6] and attributed to it a concentration dependent change in the diffusion mechanism in systems containing chevronlike patterns. At low T and close to $x = 1$ the only diffusion mechanism is the interstitial diffusion (as proposed, e.g., in Refs. 3 and 5). At higher T creation of Frenkel pairs, i.e., O(5) to O(1) jumps with possible reorientation of a local chevron pattern, is also possible, a phenomenon which reduces the diffusion.

In Fig. 5 we show the effect of the barrier Q on the diffusion coefficient. The choice of the value $Q = 0.1$ was arbitrary. The barrier seems to slow down the diffusivity without changing the character of the dependence of the diffusion coefficient on T and x. It is therefore logical to use in the following the $Q = 0$ case, for which the system reaches faster its stationary state.

B. The Arrhenius plot

The $\ln D_+$ versus the dimensionless inverse temperature $\tilde{\beta} = V_1/kT$, i.e, the so-called Arrhenius plot, is presented in Fig. 6 for several values of the concentration x of oxygen ions in the basal plane. The data points fall almost on a straight line, indicating only weak correlations. The activation energy, E_a, estimated from that plot depends on the oxygen concentration and has a maximum at $x = 0.5$, similar to what has been already reported in Refs. 7 and 8. There is a point worth noticing. At low ($x \approx 0.2$) concentrations, the deviation from the straight line behavior on the Arrhenius plot occurs at high T. The reasons might be that at low x the oxygen ions are separated one from another by rather long distances and unless the mobility is large the ions will not meet and interact. Since the curvature of the Arrhenius plot marks correlation effects between oxygen ions, we

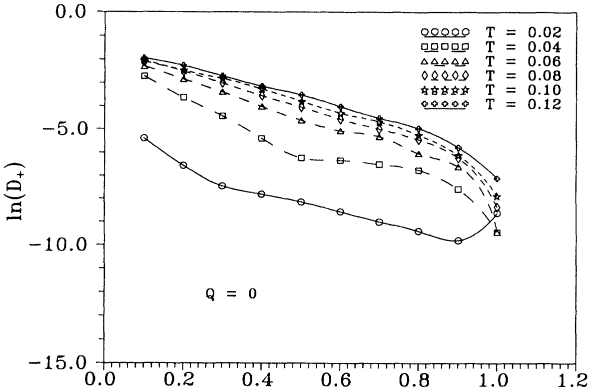


FIG. 4. Diffusion coefficient $\ln D_+$ versus x for our model and five temperatures (in eV), $Q = 0$.

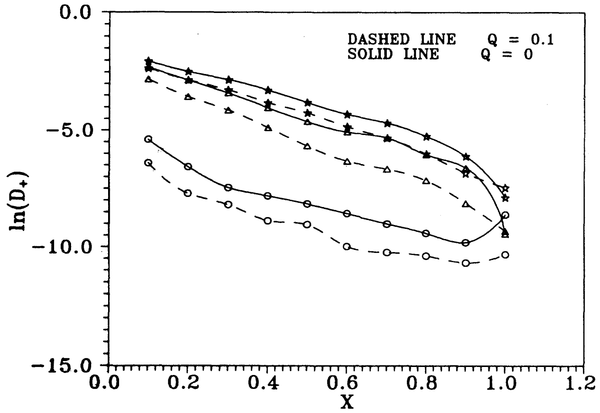


FIG. 5. Diffusion coefficient $\ln D_+$ versus x for $Q=0$ (solid line) and $Q=0.1$ (dashed line).

decided to check the correlations in a more quantitative manner, namely by assuming the simplest correction to the Arrhenius law, i.e.,

$$D_+ = D_+^0 e^{-\tilde{\beta}\hat{E}_a - \tilde{\beta}^2 K} , \tag{3}$$

where $\hat{E}_a = E_a / V_1$ and K is a temperature independent but concentration dependent quantity to be determined such that

$$\ln D_+(x,T) = a_0(x) + \tilde{\beta} a_1(x) + \tilde{\beta}^2 a_2(x) . \tag{4}$$

It turns out that the best fit is obtained with a fifth order polynomial in x for the a's. Although we recover the dependence of D_+ on x and T found in simulations, such a fit works only till $x=0.7$. Attempts to fit the data above that value would require higher order terms in the expansion.

C. Mean energy $\langle E \rangle$

Another quantity which could be useful in analyzing the ordering of this system is the mean energy, $\langle E \rangle$, of interactions of each particle with its NN and NNN. It is simply the E_i energy defined by Eq. (1) averaged over all particles and time steps. The value of $\langle E \rangle$ has been checked as a function of time and lattice size. The error bars on $\langle E \rangle$ are for, e.g., $T=0.04$ eV less than 4.

Figure 7 shows the representative curves at several temperatures. Two points should be noticed: first, the deep minimum of $\langle E \rangle$ moves with T from $x \approx 0.35$ at $T=0.02$ to $x \approx 0.5$ at $T=0.06$ and then disappears. There is also a less pronounced minimum around $x=0.9$ which remains quasistable with T. Secondly, at low x the effect of temperature is much greater.

At low x, $\langle E \rangle \approx 0$ indicates that oxygen ions are mostly isolated . A negative $\langle E \rangle$ implies that clusters will be formed by ions linked mainly via V_2 (negative) interactions. For higher x, the system becomes more dense and on average an oxygen ion has more occupied NN and NNN sites. The interaction with the neighbors being positive and negative gives again a value of $\langle E \rangle$ close to zero. A dense system is of course more stable with respect to an increase of T; therefore, the changes of $\langle E \rangle$ with T are smaller at high x than at low x.

Attributing a minimum of $\langle E \rangle$ to some kind of order in the system (not necessarily long range order) we observe that the described behavior of the minima is indeed similar to the boundary of the (T,x) phase diagram.[7]

IV. CONCLUDING REMARKS

We have presented results coming from MC simulations for the tracer diffusion coefficient in a system where the oxygen ion jumps are possible to NN and NNN sites. On the basis of the obtained results the following conclusions can be made.

(i) The tracer diffusion coefficient for such moves depends more weakly on x now than when the NNN jumps are excluded.[7,8]

(ii) In the present case the system is multidomained and therefore the anisotropy of the diffusivity is rather small, e.g., at $x=0.4$ the ratio D_+/D_- varies from 6.75 at $T=0.02$ to 2.5 at $T=0.12$. Appearance of chevronlike patterns in the system could be the result of the initial conditions—placing randomly the oxygen ions not only on O(1) sites. The configurations, after 1 kMCS from the deposition of ions on the lattice, are shown for several x and T in Fig. 2. It is seen that at low x and low T the oxy-

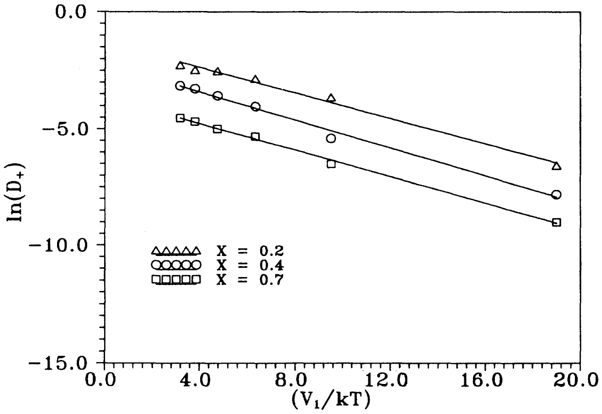


FIG. 6. The Arrhenius plots for several concentrations x.

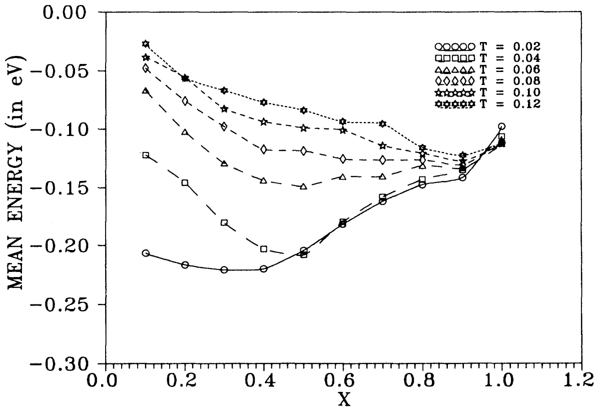


FIG. 7. Configurational energy $\langle E \rangle$ versus x.

gen ions tend to form short chains which grow with oxygen concentration. This tendency of forming chains with x-dependent length agrees with the reasoning presented in Ref. 5. The general pattern of the configurations will remain the same till the end of the simulations.

The orientation of the chains is random, especially at low to intermediate ($x=0.4$) concentration. Randomness gives rise to the appearance of chevronlike patterns. At higher x, e.g., $x=0.7$, the system becomes better ordered and there are less chevron patterns, even at higher T.

To get highly anisotropic diffusion in the *ab* plane, one should have a twinned system which could be achieved by adopting different initial conditions than the ones used here: the oxygen ions should be put on the O(1) sites only or by including a strain energy in the Hamiltonian.[9]

(iii) The Arrhenius plots are nearly straight lines.

(iv) Simulations indicate that, at least at higher concentrations, the diffusion is taking place along the copper-oxygen chains, i.e., O(5)-O(5) or O(1)-O(1). At low concentrations vacancy diffusion O(1)-O(5) is also an important mechanism.

(v) The assumption of strictly 2D model seems thus *a posteriori* valid, but inclusion of oxygen jumps around or over Cu ions could still improve the picture.

In conclusion, we hope that by adding the possibility of NNN hopping for O ions we brought the ASYNNNI model closer to the real $YBa_2Cu_3O_{6+x}$ system which it is supposed to describe.

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