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Monte-Carlo analysis of tracer diffusion mechanisms in $YBa_2Cu_3O_{6+c}$

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Abstract. A method for estimating, *via* the Monte-Carlo simulation, the most often realized diffusion mechanisms in 2D ordered structures is presented. Taking as an example the diffusion of oxygen ions in 123 – YBCO high temperature superconductor we propose several diffusion mechanisms and show to what extent they depend on the temperature and concentration of the diffusing particles. Our results are compared with the ones proposed earlier on the basis of energy arguments. We find also additional trajectories, different from those earlier reported in that system.

PACS. 02.70.Lq Monte-Carlo and statistical methods – 66.10.Cb Diffusion and thermal diffusion – 74.72.Bk Y-based cuprates

1 Introduction

Although the diffusion of adatoms on metal surfaces has been studied for a long time (see *e.g.* [1]), the details are still not clear. Theoretical investigations are, in general, based on the lattice gas model. Sadiq and Binder [2] presented an in-depth analysis of diffusion mechanisms in ordered 2D structures. They restricted themselves to repulsive interactions between nearest neighboring (NN) and next-nearest neighboring (NNN) sites. They were also interested mostly in the low temperature regime. In this work we investigate the mechanisms of tracer diffusion in anisotropic systems. Taking as an example the ortho - 1 phase of the ASYNNNI model we present a method for estimating the most probable diffusion mechanism and we show also how this mechanism depends on the temperature and concentration of the diffusing particles.

Salomons and de Fontaine [3] and LaGraff and Payne [4] studied the diffusion of oxygen ions within the basal plane of $YBa_2Cu_3O_{6+c}$ (123 – YBCO) type high temperature superconductor using the ASYNNNI model. Several possible mechanisms of tracer diffusion have been proposed on the basis of energy arguments [2–4]. However, neither the role of oxygen content nor oxygen ordering in the basal plane of $YBa_2Cu_3O_{6+c}$ in determining its critical temperature and other physical properties is not yet clear; for a recent review see [5]. In fact, the oxygen concentration and ordering may be an important factor in determining the magnetic and/or electronic properties, like the existence of Cooper pair-like systems [6,7]. In the same temperature range, *i.e.*, about 300 K, an anomalous effect also occurs in the normal state Hall coefficient [8], as well as in the concentration dependence of the diffusion coefficient of oxygen in the basal plane [9–11]. Other anomalous features at such temperatures have been observed also in thermal transport properties, like the thermal conductivity [12].

Therefore it seems interesting to study the mechanisms of oxygen diffusion in the basal plane of $YBa_2Cu_3O_{6+c}$ in the temperature range above the T_c within a strict framework and numerical means. It should be however mentioned that the method presented below is not restricted to $YBa_2Cu_3O_{6+c}$ but can be applied also to other systems, like, *e.g.*, diffusion of oxygen on the W(110) surface.

2 The model

The ASY(mmetric) N(ext) N(earest) N(eighbor) I(sing) model was introduced in [3]. The interaction of a given particle to its NN is V_1, the interaction to a NNN when mediated by another atom is V_2 and a direct one to a NNN is V_3 [13]. A site i can be either empty ($t_i = 0$) or occupied by an oxygen ion ($t_i = 1$). Hence the Hamiltonian can be written as [3]

$$\mathcal{H} = \sum_{\mathrm{NN}} V_1\, t_i t_j + \sum_{(\mathrm{NNN})_1} V_2\, t_i t_j + \sum_{(\mathrm{NNN})_2} V_3\, t_i t_j. \quad (1)$$

In the case of 123 – YBCO, the particle is an oxygen ion. We take $V_1 = 0.19$ eV; the V_2 ($= -0.159$ eV) interaction is mediated by a Cu atom and the direct one

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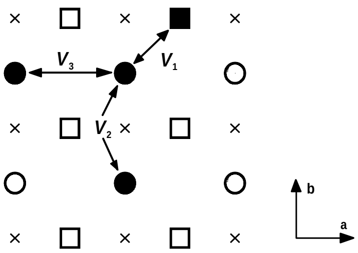


Fig. 1. The 123 – YBCO *ab*-plane structure; circles denote the O(1) sublattice, *i.e.*, "oxygen chains", squares - the O(5) sublattice, *i.e.*, the "empty" sublattice. Full symbols denote occupied sites. Crosses are copper atoms.

with a NNN is $V_3 = 0.054$ eV [13]. In so doing the 2D square lattice splits into two, mutually interpenetrating sublattices, conventionally denoted by O(1) and O(5) (Fig. 1).

Denoting the number of lattice sites by A, and the number of particles by N, we define the coverage, θ, as

$$\theta = N/A, \qquad \theta \in [\,0\,,\,1\,]. \tag{2}$$

It will be useful to introduce also a sublattice density

$$c = 2\,\theta, \qquad c \in [\,0\,,\,2\,]. \tag{3}$$

The phase diagram of the ASYNNNI model has been determined in [3]. Around the density $c = 1$ the model exists, in a large interval of temperatures, in the ortho-1 (OI) phase. In the ideal ortho-1 phase (low temperatures and $c = 1$), all lattice sites of the O(1) sublattice are filled by oxygen ions and all sites in the O(5) sublattice are empty. We have therefore a c (2×2) structure.

We have investigated the system within the range $c \in [0.875, 1.125]$ out of which detailed data are presented for three concentrations c around the stoichiometic one, $c = 0.9$, 1.0, 1.1. Such a choice encompasses three different regions, – vacancies in the O(1) sublattice for $c < 1$, completely filled O(1) sublattice and completely empty O(5) sublattice in the ground state at $c = 1$, and single ions (defects) in the O(5) sublattice for $c > 1$. Notice that for $c = 1$ one oxygen vacancy still exists in the unit cell square.

The model was investigated at two temperatures $T = 650$ K ($k_{\mathrm{B}}T \approx 0.06$ eV) and $T = 1000$ K ($k_{\mathrm{B}}T \approx 0.08$ eV), well inside the stability region for the ortho-1 phase. At the investigated concentrations it has been previously found that the system organizes itself into long chains of occupied sites in the O(1) sublattice [3,4]. Empty sites in the filled O(1) lattice, or additional ions appearing in the O(5) sublattice, are called point defects.

We have used the standard Monte-Carlo method with Kawasaki dynamics (conserving the number of particles) and Metropolis algorithm. A particle has been allowed to jump to one of its NN (provided it was empty) with the probability given by

$$P_{i\to j} = \frac{t_i}{\theta}(1 - t_j)\mathrm{e}^{-\beta \Delta E}, \tag{4}$$

where ΔE is the (positive) change of the energy of the system caused by the jump and $\beta = (k_{\mathrm{B}}\,T)^{-1}$.

For computer simulations we have used $L \times L$ ($L = 56$) square lattice with periodic boundary conditions. For verifying finite size effects a lattice with $L = 140$ has been used as well. Typically we have run the program for 400 kMCS and averaged over 10 initial configurations.

3 The method

The basic quantity characterizing the mobility of the particles is the average jump frequency

$$\nu = n/N, \tag{5}$$

where n is the average number of all jumps performed by the N particles present in the system, in unit time. This is the same quantity as used by Sadiq and Binder [2] in their analysis of diffusion mechanisms. Since it is a global average, it can not yield detailed information about migration of individual atoms.

It is the aim of the present paper to specify the notion of a jump frequency in order to account for different possible paths. Our investigations are based on the following assumptions:

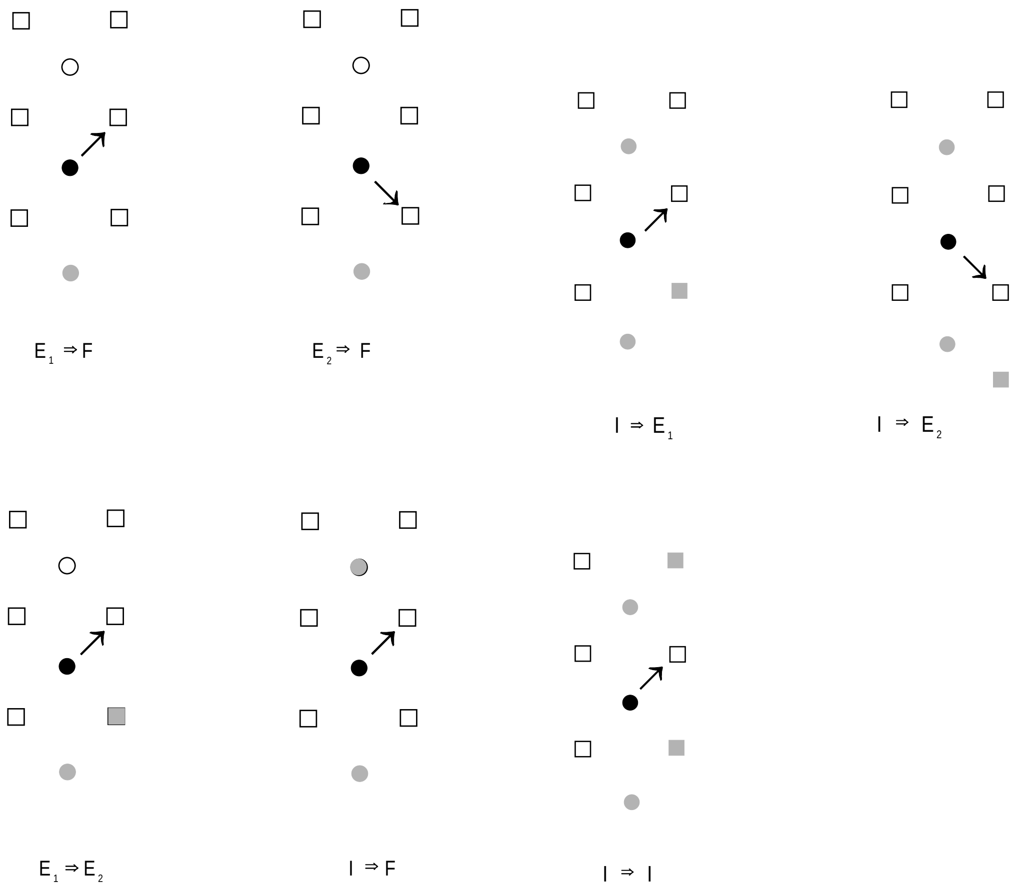
1. There are two interpenetrating sublattices. One is filled up with particles having low energies, the other is empty. Let us recall that in $\mathrm{YBa_2Cu_3O_{6+\mathit{c}}}$ and in the OI phase, the sublattice O(1) is the filled one and O(5) – the empty one. To get into the latter a particle has to overcome an energy barrier.
2. Jumps from the filled sublattice are called *fundamental.* They characterize the type of the diffusion process.
3. Jumps from the second sublattice are called *auxiliary.* Their frequency determines the effectiveness of the diffusion process.
4. A *fundamental* jump and the subsequently following sequence of auxiliary jumps define a diffusive trajectory.
   The mechanism of the diffusion is determined by the preferred diffusive trajectory. Preference is based on the lowest energy cost. Since in our model only jumps to NN are allowed, the sequence of auxiliary jumps is reduced to just one jump.

LaGraf and Payne [4] proposed three *fundamental* jumps:

1. from the interior (I) of a chain,
2. from an end of a chain. If after the move the particle does not interact any longer with the other particles of the chain the jump is called E_1,
3. from an end of a chain, but after the move the particle still interacts with the particles of the chain; this is an E_2 jump,

However to these we add the fourth possibility that the jumping particle did not interact at all with any particle *before* the jump, – it was free (F). This seems a trivial case except that an additional information, not present in [4], occurs due to the situation found *after* the jump. Indeed the jumping particle:

1. can still be free (F),



(a) (b)

Fig. 2. Some fundamental (from the O(1) sublattice) jumps. The starting point of the moving particle is the black circle, occupied sites are shaded. Circles and squares have the same meaning as in Figure 1.

2. can glue together two chains into a single one, thus becoming an internal particle (I),
3. can move to the end of a chain with which it did not previously interact (E_1),
4. can stick to the end of a chain with which it already interacted (E_2).

Examples of fundamental jumps are shown in Figure 2, where the moving particle is marked in black, occupied sites are shaded, empty ones are white. Double arrows (like ⇒) indicate hops from the O(1) sublattice. In a similar way all auxiliary jumps, *i.e.* from the empty O(5) sublattice, can be ordered. They will be marked by single arrows (like →). Any jump can be now classified as belonging to one of 16 possible (4 initial × 4 final states) jumps. We may define the jump frequency for a given type of a jump ($i \rightarrow f$) as

$$F_{i\rightarrow f} = \frac{n_{i\rightarrow f}}{n}, \tag{6}$$

where n is the total number of jumps per unit time, and $n_{i\rightarrow f}$ is the number of jumps of a given type. Analogously the frequency of auxiliary hops, $A_{i\rightarrow f}$, may be defined. The frequencies F and A have been recorded during the simulations.

On the basis of the fundamental and auxiliary jumps possible trajectories of a diffusing particle may be constructed. In principle the trajectories may be of arbitrary length but the complexity of the counting grows rapidly with the length of the trajectory. Hence we had to restrict ourselves to two jumps only. The four basic trajectories are, see Figure 3

S - movement on a straight line,
B - back and forth displacements,
Z - zigzag along the O(1) chains,
N - zigzag normal to the O(1) chains.

During the simulations we have also recorded the frequency of particular trajectories, defined, like in equation (7) by

$$T_k = \frac{M_k}{M}, \quad (k = B, Z, N, S) \tag{7}$$

where M_k is the number of realized trajectories of type k and M is the total number of observed trajectories.

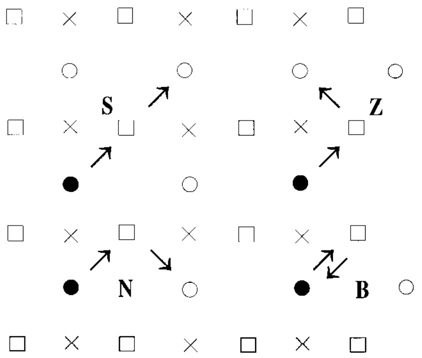


Fig. 3. Examples of basic (B, Z, N, S) trajectories.

4 Results

In the simulations the system was first allowed to relax for *ca.* 50 to 200 kMCS. Afterwards the simulations were carried out for another 400 kMCS.

The frequency of the fundamental and auxilliary jumps, is shown in Tables 1 and 2 respectively for the three chosen concentrations ($c = 0.9$, 1.0, 1.1) and two temperatures ($T = 650$ K and $T = 1000$ K). Jumps contributing to less than 5% have been omitted from the Tables. One should notice the symmetry obtained after averaging over many hops

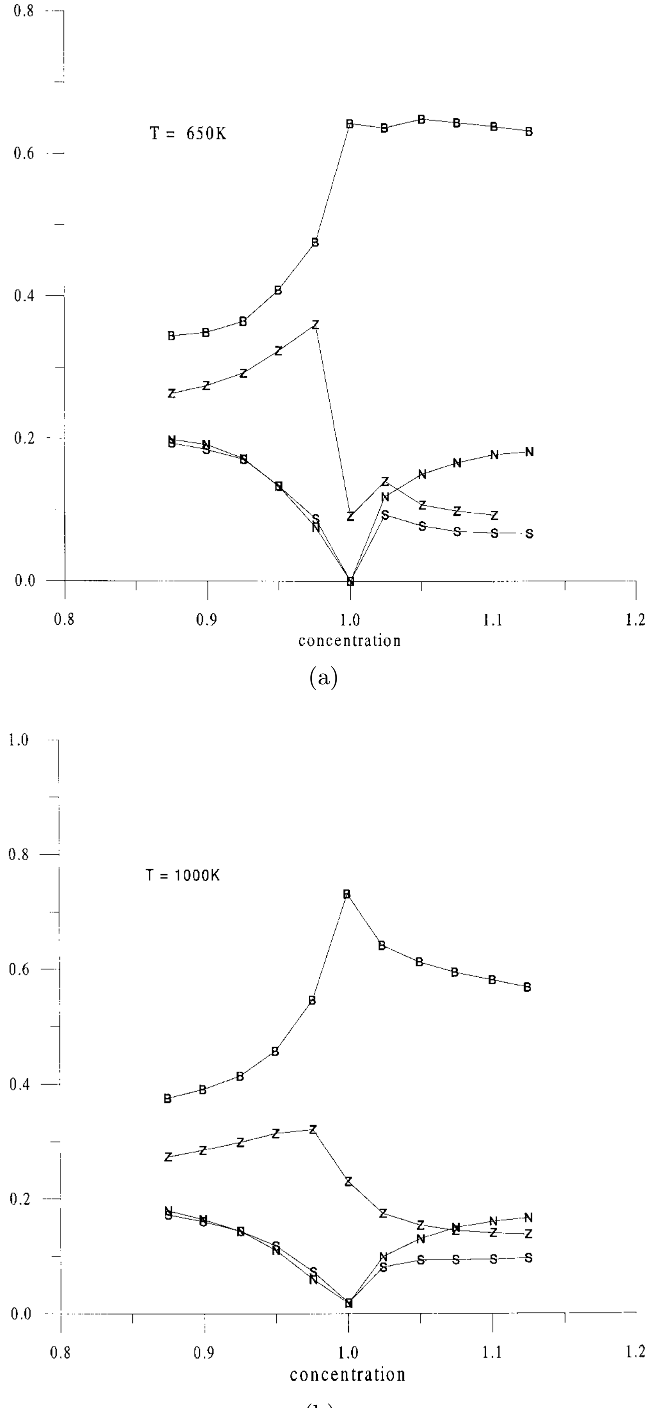
$$F_{i\to f} = A_{f\to i}, \tag{8}$$

and valid for all c and T. Frequencies of the four trajectories recorded during the simulations *versus* concentration of the oxygen ions are shown in Figure 4a for $T = 650$ K and in Figure 4b for $T = 1000$ K, respectively.

It is quite clear that in each case most of the particles move along the B trajectory, hence they do not contribute to the diffusion.

Leaving aside the B trajectories we may now, with the help of the Tables and of Figure 4 construct possible mechanisms for self-diffusion. Let us remark that our data indicate that the diffusion patterns may be sensitive both to the temperature and concentration.

For the concentration $c = 0.9$ and low temperatures it follows from the Tables that there are many free particles, while from Figure 4a that the dominant trajectory is of the Z type. The most probable diffusion mechanism is then the one proposed by LaGraff and Payne [4] as shown in Figure 5a. The S trajectories may be realized by the $E_1 \Rightarrow F \rightarrow E_1$ sequence shown in Figure 5b. The equivalent N trajectory is realized if the empty site on the right chain O(1) in Figure 5b is not above but below the temporarily occupied O(5) site. This mechanism requires however more vacancies in the O(1) sublattice and moreover they should come in pairs. We propose it as an additional mechanism, to the one suggested in [4]. In principle other mechanisms, like $E_1 \Rightarrow F \rightarrow F$, corresponding to a S or N trajectory, are possible. They would require however still more vacancies in the O(1) sublattice, hence they may play a role only at concentrations lower than $c = 0.9$.



(a)

(b)

Fig. 4. Percentage of realized B, Z, N and S trajectories at a) $T = 650$ K, b) $T = 1000$ K. For additional explanations see the text.

At the highest temperature the number of hops to and from a free (F) site decreases but the $F \Rightarrow I$ jumps appear, meaning that pairs of defects (• ○ •) are formed in the O(5) sublattice. Therefore apart from the trajectories present at 650 K, there is another possible one, of the Z type, shown in Figure 5c.

Table 1. Percentage of *fundamental* jumps of a given type. Jumps contributing less than 5% are not shown.

c	0.9		1.0		1.1	
T[K]	jump	percentage	jump	percentage	jump	percentage
650	$E_1 \Rightarrow F$	58.60	$I \Rightarrow F$	78.36	$I \Rightarrow E_2$	58.73
	$F \Rightarrow F$	26.58	$E_1 \Rightarrow E_2$	21.45	$I \Rightarrow I$	26.44
1000	$E_1 \Rightarrow F$	42.17	$I \Rightarrow F$	51.03	$I \Rightarrow E_2$	42.12
	$F \Rightarrow F$	18.89	$E_1 \Rightarrow E_2$	20.83	$I \Rightarrow I$	18.84
	$F \Rightarrow I$	12.14	$I \Rightarrow E_2$	10.73	$I \Rightarrow F$	12.25
	$E_1 \Rightarrow E_2$	7.94	$E_1 \Rightarrow F$	10.72	$E_1 \Rightarrow E_2$	7.99

Table 2. Percentage of *auxiliary* jumps of a given type. Jumps contributing less than 5% are not shown.

c	0.9		1.0		1.1	
T[K]	jump	percentage	jump	percentage	jump	percentage
650	$F \rightarrow E_1$	58.59	$F \rightarrow I$	78.37	$E_2 \rightarrow I$	58.74
	$F \rightarrow F$	26.57	$E_2 \rightarrow E_1$	21.46	$I \rightarrow I$	26.44
1000	$F \rightarrow E_1$	42.21	$F \rightarrow I$	51.04	$E_2 \rightarrow I$	42.09
	$F \rightarrow F$	18.88	$E_2 \rightarrow E_1$	20.82	$I \rightarrow I$	18.83
	$I \rightarrow F$	12.15	$E_2 \rightarrow I$	10.83	$F \rightarrow I$	12.27
	$E_2 \rightarrow E_1$	7.94	$F \rightarrow E_1$	10.75	$E_2 \rightarrow E_1$	8.1

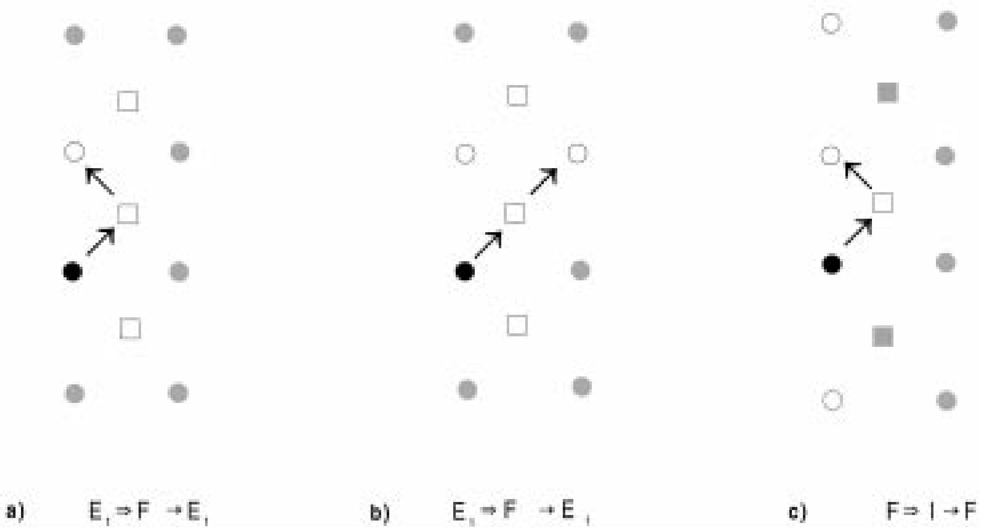

a) $E_1 \Rightarrow F \rightarrow E_1$ b) $E_1 \Rightarrow F \rightarrow E_1$ c) $F \Rightarrow I \rightarrow F$

Fig. 5. Diffusion mechanisms for $c = 0.9$. Symbol explanations as in Figure 2; a) the mechanism proposed in [4], b) additional trajectory at low T, c) trajectory proposed for high T.

For $c = 0.9$ at higher and lower temperatures the dominant mechanism is the Z type trajectory ($E_1 \Rightarrow F \rightarrow E_1$) proposed in [4] and shown in Figure 5a. We have found that at least one mechanism (of the N or S type) at low T and one more (of the Z type) at high T, are also possible.

In the case of $c = 1.0$ and low T there are just two types of fundamental ($I \Rightarrow F$, $E_1 \Rightarrow E_2$) and auxilliary ($F \rightarrow I$, $E_2 \rightarrow E_1$) jumps. There is a preference for the Z type trajectories, hence the dominant mechanism should be the synchronous interchange (motion) of two particles (Z or N trajectories) shown in Figure 6a and originally proposed, for $c = 1.0$, by Salomons and de Fontaine [3]. This mechanism does not require any alterations in the stoichiometry. If however some oxygen ions are displaced from the O(1) into the O(5) sublattice, then other S or N type single particle trajectories ($I \Rightarrow F \rightarrow I$) are also possible (see Fig. 6b). Their role is greater at high T, where the perfect ordering within the sublattices is destroyed, as seen in Figure 4 following an increasing number of the N and S trajectories. Other

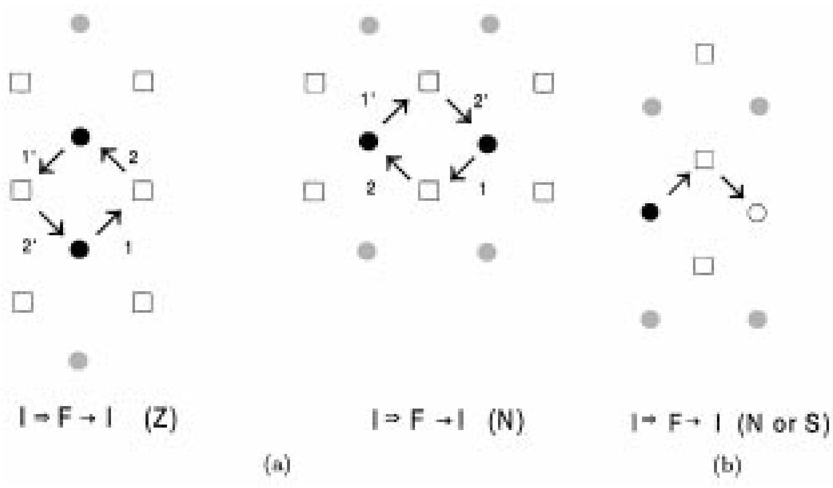


Fig. 6. Diffusion mechanisms for $c = 1.0$; a) the mechanism proposed in [3] as a Z and N type trajectories for a simultaneous motion of two particles, marked here by two black circles, b) additional mechanisms proposed by us for a single particle motion.

trajectories constructed from the $I \Rightarrow E_2$ and $E_1 \Rightarrow F$ and equivalent auxilliary jumps are possible at high T. They require the appearance of a pair of vacancies in the O(1) sublattice, hence they mainly contribute to diffusion at high temperatures.

It follows from the observed trajectories that the deviations from the ideal arrangement of both sublattices are not large. The increase of the Z, N and S trajectories connected with such deviations is about 2%, as follows from Figure 4. The system shows, also at high T, strong correlations among the oxygen ions, mostly *via* the Cu atoms. This is seen from the fact that from the three basically equivalent trajectories shown in Figure 6a, the Z has been the most often recorded one.

Notice that the concentration $c = 1$ is very special, since more than 3/4 of the trajectories belong to the B class. Then at low temperatures there is almost only one contributing mechanism to the diffusion, *i.e.* the Z trajectory. This highly restricted mechanism may be the fundamental reason for the appearance of the $V - \Lambda$ transition in the anomalous dependence of the diffusion coefficient on concentration, observed in [10].

For $c = 1.1$ at low temperatures again the major contribution comes from just two types of jumps $I \Rightarrow E_2$ and $I \Rightarrow I$. The dominating trajectory is the N one, being nearly twice more frequent than the seemingly equivalent S trajectory. We are unable to explain this asymmetry. Possible mechanisms leading to the N (or S) trajectory are $I \Rightarrow E_2 \rightarrow I$ (Fig. 7a) or $I \Rightarrow I \rightarrow I$ (Fig. 7b). The great number of the former sequences (see Tab. 1) indicates that the point defects in O(5) are isolated. At high T we have observed an increased number of jumps from the inside of the O(1) chains, leaving isolated vacancies behind thus favoring the Z trajectories, as shown in Figure 7c.

One should keep in mind that our data only points out to some highly probable diffusion patterns but does not determine them unequivocally nor forbids complicated patterns to be expected when longer jump sequences are to be considered.

5 Concluding remarks

We have investigated a method, based on the Monte-Carlo simulation technique, for determining possible diffusion mechanisms of particles on an incompletely filled 2D plane. We have recorded during the simulations the frequency of occurence of particular jumps (fundamental and auxiliary) as well as sequences of the successive jumps. On that basis we propose several mechanisms for oxygen diffusion within the basal CuO plane and for the ortho-1 phase of $YBa_2Cu_3O_{6+c}$ near the 3/4 filling concentration range, *i.e.* near $c = 1.0$.

There have been several papers [3,4] dealing with diffusion mechanisms in 123 – YBCO, but the authors have not discussed the role of the temperature. Here we have been able to show in what precise range of the parameters c and T the suggested mechanisms are to be valid. We have shown which ones are dominating at "low (650 K) temperatures", and the most often probable (short) trajectories. We have found that there are more possible fundamental and auxiliary jumps at higher temperatures than there are at low ones, as one would expect. This indicates that the diffusion mechanisms are sensitive to both temperature and concentration of oxygen vacancies. The mechanisms found by us require, in general, fulfillment of some conditions, like *e.g.* the presence of vacancies ordered in a special way in the O(1) sublattice. Since we have "observed" such trajectories in the simulations, that means that the conditions are met, and such pairs of vacancies occur in the system.

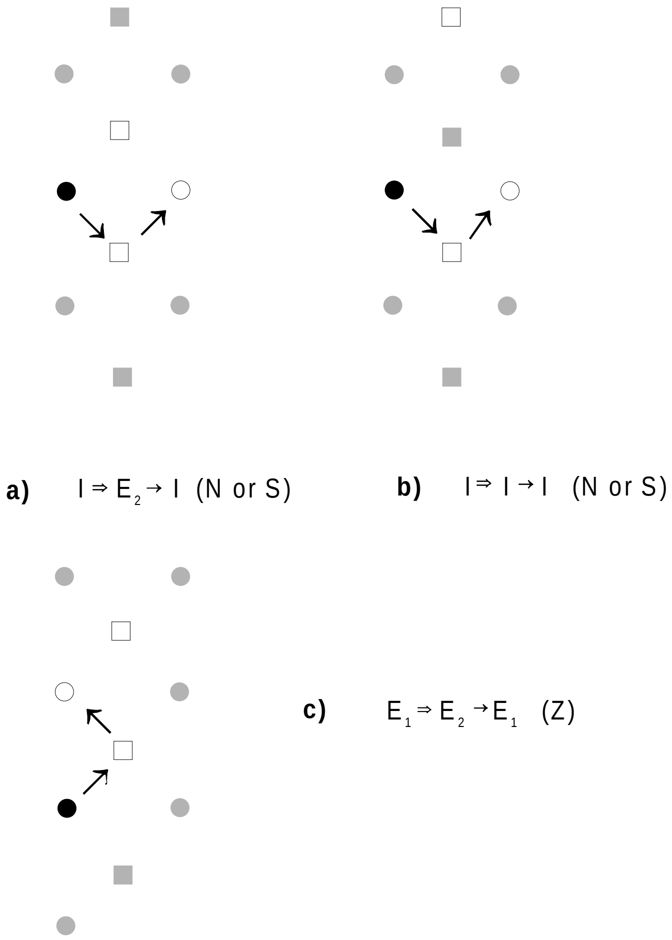


Fig. 7. Possible trajectories for $c = 1.1$; a) and b) at $T = 650$ K temperatures, and c) at $T = 1000$ K.

Since we have considered here jumps of the oxygen ions to NN sites only, we could not comment on the NNN hopping mechanisms proposed by Rothman *et al.* [14]. Moreover the simulations have been made for specific interaction parameter V_1, V_2, V_3 values. Even though such values differ from author(s) to author(s) (and even within our own investigations), we have chosen values which are considered to be the best ones and are the most widely accepted. Large modifications in the relative values could modify the respective ranks of trajectories. Of course some situations are improbable from the experimental point of view from the start.

It is possible to use the method presented above to find possible mechanisms of oxygen diffusion also in the OII phase of $YBa_2Cu_3O_{6+c}$. There will be many more possible trajectories, hence the analysis will be more complex. In principle, the method may also be used in examining jumps to NNN neighbors [10]. This however would require considering non-symmetric energy barriers (anisotropy effects). The problem would lead to much more complex simulations. Introducing the same barriers for jumps to all NN does not yield interesting results since a diffusing particle has to wait longer for any jump if a symmetric barrier is raised. This is simply equivalent to scaling the time. Considering jumps to apical sites, which would require a 3D model, would permit investigation of the role of such trajectories. They are sometimes claimed to be very important [15].

In conclusion, we have found that there is more than a single mechanism of diffusion in a quasi-ordered system like $YBa_2Cu_3O_{6+c}$. The kind of mechanism depends on the concentration, and to a lesser extent, on the temperature. In particular, for $c > 1$ the mechanisms proposed by us for low and for high temperatures, are different from those presented in [3,4].

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References

1. R. Gomer, Rep. Prog. Phys. **53**, 917-1002 (1990); A.G. Naumovets, Yu.S. Vedula, Surf. Sci. Rep. **4**, 365-434 (1985); J.Ph. Bouchaud, A. Georges, Phys. Rep. **195**, 127 (1990).
2. A. Sadiq, K. Binder, Surf. Sci. **128**, 350 (1983).
3. E. Salomons, D. de Fontaine, Phys. Rev. B **42**, 10152 (1990); Phys. Rev. B **41**, 11159 (1990).
4. J.R. LaGraf, D.A. Payne, Physica C **212**, 470 (1993).
5. A.A. Aligia, J. Garces, in *Theory and Applications of the Cluster Variation and Path Probability Methods*, edited by J.L. Moran Lopez, J.M. Sanchez (Plenum Press, New York, 1996) and references therein.
6. M. Ausloos, F. Gillet, Ch. Laurent, P. Clippe, Z. Phys. B **84**, 13 (1991).
7. V.J. Emery, S.A. Kivelson, Physica C **209**, 594 (1993); Nature **374**, 434 (1995).
8. S. Sergeenkov, M. Ausloos, M. Mehbod, J. Phys.-Cond. Matter **6**, L373 (1994).
9. A. Pękalski, M. Ausloos, Physica C **226**, 188 (1994).
10. M. Ausloos, A. Pękalski, Phys. Rev. B **52**, 4577 (1995).
11. A. Pękalski, K. Skwarek, Phys. Rev. B **54**, 4315 (1996).
12. B.M. Terzijska, R. Wawryk, D.A. Dimitrov, Cz. Marucha, J. Rafalowicz, Cryog. **32**, 60 (1992).
13. P.S. Sterne, L.T. Willie, Physica C **162**, 223 (1989).
14. S.J. Rothman, J.L. Routbort, U. Welp, J.E. Baker, Phys. Rev. B **44**, 2326 (1991).
15. M.S. Islam, R.C. Baetzold, J. Mat. Chem. **4**, 299 (1994).