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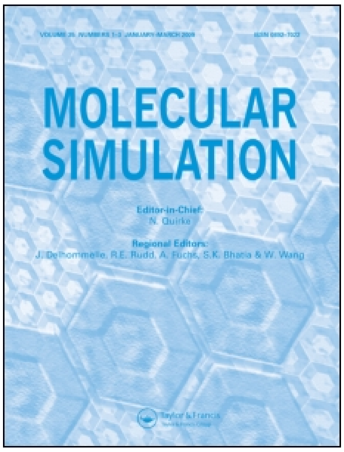

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Molecular Dynamics Simulation of High-*T_c* Superconductors

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MOLECULAR DYNAMICS SIMULATION OF HIGH T_c SUPERCONDUCTORS

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We present the results of MD simulations of oxygen diffusion in $YBa_2Cu_3O_{7-x}$ ($x = 0.09 - 0.27$) at 1350-1500 K employing Born model potentials. No strong stoichiometry dependence of the oxygen diffusion is observed. The variation in the oxygen diffusion coefficients is found to be less than 70% in the x range 0.09-0.27 which is in agreement with experimental data. Changes in stoichiometry are found to cause the redistribution of oxygen, which may be the reason for the lack of a strong stoichiometry dependence of the diffusion coefficient in $YBa_2Cu_3O_{7-x}$. Moreover, we find that the oxygen migration mechanisms in $YBa_2Cu_3O_{7-x}$ are the same in the x range 0.09-0.27: the oxygen vacancies migrate between O(1), O(4) and O(5) sites. The possible oxygen-ion jump paths are observed to be O(1)—O(5), O(1)—O(4), and O(4)—O(5), but not O(5)—O(5).

KEY WORDS: High T_c-superconductors, oxygen diffusion

INTRODUCTION

Molecular dynamics has been extensively used in the study of diffusion processes in both liquids and solids. Few MD studies have however been reported on high T_c superconductors [1-3], where there are, nevertheless, several fundamental and applied problems concerned with oxygen diffusivities. We will discuss in this paper, the application of MD techniques to the study of oxygen diffusion in $YBa_2Cu_3O_{7-x}$ ($x = 0.09 - 0.27$). All the work described is based upon empirically derived pair potential functions which have been successfully employed in modelling structural and defect properties of high T_c oxides. In the next section we will discuss the strategies for MD simulations and for deriving potential parameters by empirical procedures. In later sections we will show how MD provides a powerful technique for determining the diffusion coefficients, activation energies, ion migration paths and ion distributions in these materials. In particular, we shall demonstrate the usefulness of the techniques for investigating diffusion mechanism in the high T_c superconductors.

METHOD

We have used standard microcanonical ensemble MD, employing periodic boundary conditions and an Ewald treatment of the summation of long range Coulomb terms. The accuracy of the simulation as a whole is of course determined by the quality of the interatomic potentials describing the system. In deriving potential parameters for ionic materials two broad strategies are available: first we can fit variable potential parameters to available crystal properties (such as the crystal structure, elastic constants, dielectric constants etc.); secondly we can attempt to calculate ionic interactions directly by theoretical methods. The first approach is used in this work. Because it is extremely expensive in computational terms to use the shell model treatment of polarizability in MD calculations, we used rigid ion models in this study as has been the case in most MD studies of solids. We use Born model potentials with short-range terms of the Buckingham form

$$\Phi = A \exp(-r/\rho) - C/r^6. \tag{1}$$

In deriving our potentials we employed Baetzold's [9] parameters as the starting point but refitted them so that the new rigid ion parameters reproduced the structure of $YBa_2Cu_3O_7$ (see Figure 1). Our model uses formal charge of 3+, 2+ and 2+ for Y, Ba and Cu respectively. All O ions, except O(1), were given a charge of 2− whereas O(1) is assigned a charge of 1−. The potential parameters used in the study are listed in Table 1. This potential reproduces the structure of $YBa_2Cu_3O_7$ with a maximum error in any structural parameter of 5%. It is the best that can be achieved within the pair potential, rigid ion approximation.

We used oxygen compositions corresponding to $YBa_2Cu_3O_{6.91}$, $YBa_2Cu_3O_{6.82}$ and $YBa_2Cu_3O_{6.73}$. In order to simulate $YBa_2Cu_3O_{6.91}$ we took three O(1) out of 32 $YBa_2Cu_3O_7$ units (which comprise 416 atoms) to create three oxygen vacancies before the start of the simulation, and then assigned three of the O(1) species a charge of 2− in order retain electroneutrality. To simulate $YBa_2Cu_3O_{6.82}$ and $YBa_2Cu_3O_{6.73}$ we took six and nine O(1) out of a 32 $YBa_2Cu_3O_7$ unit. The constant volume MD simulations were performed using a (15.22 Å × 15.53 Å × 23.61 Å) box containing 407–413 atoms (depending on the values of x). Newton's equations we're integrated using the leap frog algorithm [10] with a 1 fs time step. Initially a Gaussian distribution of velocities was assigned to all the atoms in the simulation box. Iterative velocity scaling for 15 ps was employed to achieve equilibrium. There then followed a 100 ps production run in order to obtain sufficient trajectories to investigate the migration mechanisms.

The simulations were performed for each composition at temperatures ranging from 1350 to 1500 K. These are, of course, higher than those used in the experimental studies, and are needed to obtain sufficiently high diffusion coefficients to allow accurate study by MD. On comparing with experiment we extrapolate experimental data to the temperatures at which our calculations were performed.

Calculation of the mean square displacement (MSD) of atoms as a function of time leads to a direct measure of the self-diffusion coefficient D, via the following equation [11]:

$$\langle |r(t) - r(0)|^2 \rangle = B + 6Dt, \tag{2}$$

where $|r(t) - r(0)|$ is the displacement of a particle from its initial position; the brackets denote an average over the particles concerned and over time origins; B is a thermal factor arising from atomic vibrations. From the Arrhenius equation

$$D = D_0 \exp(-Q/kt), \tag{3}$$

the activation energy Q and pre-exponential factor D_0 can be obtained.

The calculations were performed on CRAY X-MP and NEC-SX supercomputers using a modified version of the FUNGUS computer code originally developed by Walker [12]. We used molecular graphics techniques in the analysis of the MD trajectories. The molecular modelling package INSIGHT II [13] on a Silicon Graphics workstation was employed in animating the framework trajectories for investigating oxygen diffusion mechanisms.

RESULTS AND DISCUSSION

(1) *Oxygen diffusion coefficients*

Oxygen diffusion in $YBa_2Cu_3O_{7-x}$ has been studied both experimentally [14-21] and theoretically [22-25]. A comprehensive review was given by Rothman *et al.* [20]. But the activation energies for oxygen diffusion reported by different workers clearly show significant scatter (from 0.5 eV to 2.2 eV), and the nature of the oxygen diffusion paths in $YBa_2Cu_3O_{7-x}$ is still controversial. Ronay and Nordlander [24] suggested that oxygen could move interstitially between the O(5) sites (see Figure 1) with an almost zero activation energy for motion. Rothman *et al.* [19, 20] suggested a similar type of mechanism in which an oxygen ion at the end of a row of O(1) sites jumps into an O(5) site, and moves along O(5) sites until it comes to another row end where it attaches itself. Islam's static lattice calculations [25] showed that oxygen diffusion via the O(1)—O(4)—O(1) path was energetically the most favorable, with an activation energy of 0.72 eV.

A second controversy concerns the effect of oxygen partial pressure P_{O_2} (and hence stoichiometry) on oxygen diffusion in $YBa_2Cu_3O_{7-x}$. Some studies [16, 18, 26-28] have suggested that there is, as would be expected, a P_{O_2} (or stoichiometry) dependence of the oxygen diffusion coefficient. In contrast, however, Rothman *et al.* [20] found that there is no strong dependence of the tracer diffusion coefficient on the stoichiometry. Their results , covering a range of x between 0.31 and 0.44, indicate that any change of oxygen diffusion coefficient D with x is by less than a factor of two. Since the concentration of both the oxygen ion vacancies and oxygen ions on O(5) sites increases with decreasing P_{O_2} [29], they propose that the approximate insensitivity of D to P_{O_2} suggests either that the diffusion coefficient is independent of the defect concentrations, or that there is cancellation of two opposing effects influencing the P_{O_2} dependence of D [20].

Our MD studies have yielded valuable insight into both these problems. Thus Figure 2 shows the mean square displacement (MSD) plot for oxygen migration in $YBa_2Cu_3O_{6.91}$ at 1500 K (Curves a, b, and c correspond to the MSD in the *a*−, *b*− and *c*− direction respectively whereas the "total" curve corresponds to the total MSD). The oxygen diffusion coefficients corresponding to $x = 0.09$, $x = 0.18$ and $x = 0.27$ at different temperatures are calculated from the MSD plots and are given in Table 2. We found that the diffusion coefficients for $YBa_2Cu_3O_{6.82}$ are slightly larger than those for $YBa_2Cu_3O_{6.91}$, but the difference is not greater than

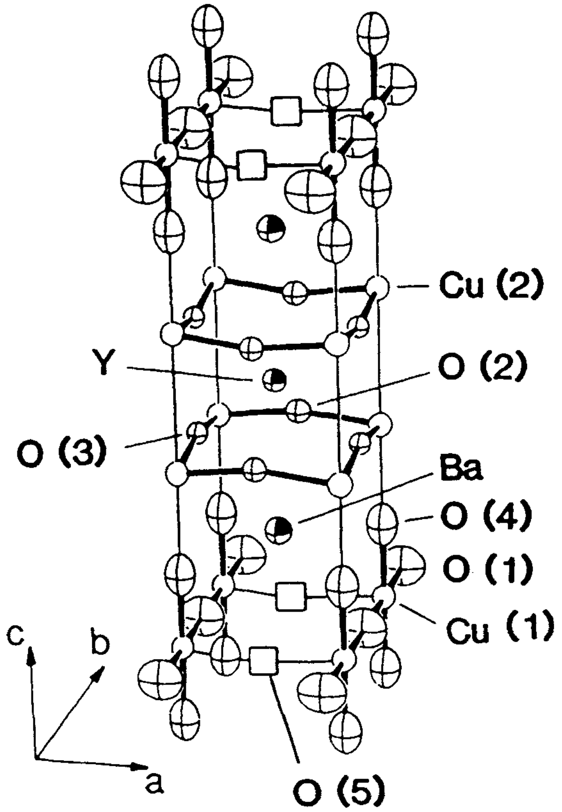

Figure 1 Structure of $YBa_2Cu_3O_7$.

40%, despite the doubling in x. For $x = 0.27$, we find that the oxygen diffusion coefficient actually drops to $4.7 \times 10^{-8}\,cm^2 s^{-1}$, which is not only less than the value at $x = 0.18$ ($7.8 \times 10^{-8}\,cm^2 s^{-1}$) but also less than the value at $x = 0.09$ ($5.6 \times 10^{-8}\,cm^2 s^{-1}$). Thus when x varies by 200% (from 0.09 to 0.27) the largest variation in the oxygen diffusion coefficient is less than 70%. Hence our results suggest that there is no strong stoichiometry dependence of the oxygen diffusion coefficients in the x range of 0.09-0.27, which is in agreement with the experimental results of Rothman *et al.* [20] and earlier theoretical results [26]. We return later to a discussion of the reasons for the lack of strong stoichiometry dependence.

Using our calculated oxygen diffusion data we obtained the Arrhenius plot [ln(D) vs T^{-1}] shown in Figure 3, from which we derive an activation energy of 0.97 eV with $D_0 = 1.4 \times 10^{-4}\,cm^2 s^{-1}$ for $YBa_2Cu_3O_{6.91}$ and an activation energy of 0.96 eV with $D_0 = 1.7 \times 10^{-4}\,cm^2 s^{-1}$ for $YBa_2Cu_3O_{6.82}$. These data are in good agreement with the experimental result which give an activation energy of 0.97 eV with $D_0 = 1.4 \times 10^{-4}\,cm^2 s^{-1}$ for this range of compositions [19, 20]. The similar oxygen diffusion coefficient and activation energy in $YBa_2Cu_3O_{6.91}$ and $YBa_2Cu_3O_{6.82}$ indicate that the oxygen diffusion mechanisms appear to be the same for these two systems.

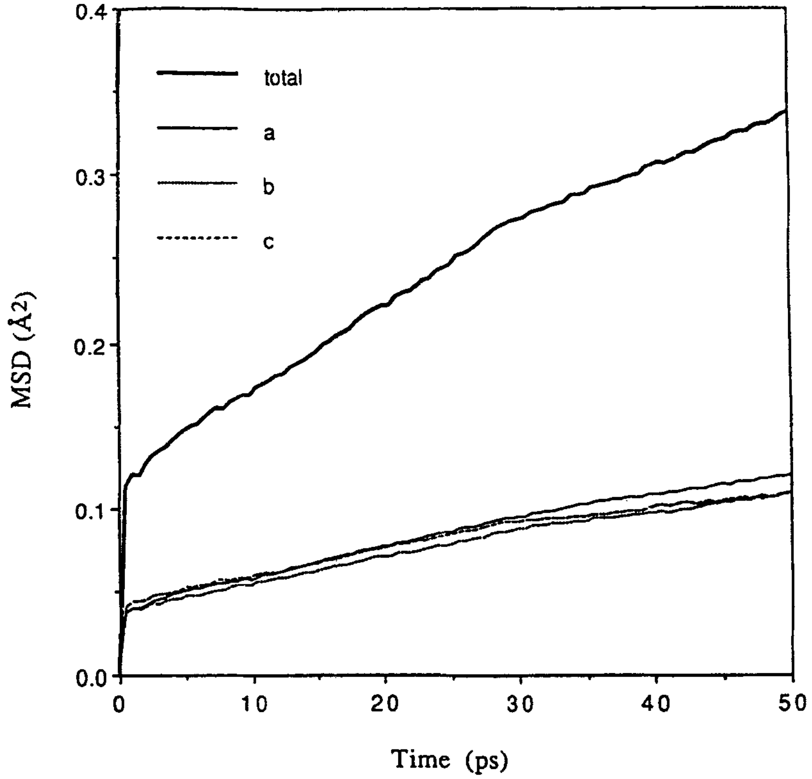

Figure 2 MSD plot for oxygen migration in $YBa_2Cu_3O_{6.91}$ at 1500 K. Curves *a*, *b*, and *c* correspond to the MSD in the *a*−, *b*− and *c*− direction respectively while the "total" curve corresponds to the total MSD.

(2) *Oxygen ion jump paths*

MD methods allow us, of course, to view directly ion migration paths by analysis of MD particle trajectories. Figure 4 shows the *xy* projection of the coordinates of the oxygen ions situated in the Cu(1)-O plane of $YBa_2Cu_3O_{6.91}$ at 1450 K for a duration of 100 ps. Of the eighteen oxygen ions located in this plane, fourteen are situated on O(1) sites and the others on O(5) sites at $t = 0$ (the symbols O1 and O5 denote the initial positions of the oxygen ions). During the simulation, several oxygen ions are observed to jump between sites. The jump paths for these oxygen ions are:

ion A: O(1)—O(5)—O(1)
ions B: O(1)—O(5)
ions C: O(5)—O(1)—O(5)
ion D: O(1)—O(4)—O(1)—O(4)—O(1)—O(4)—O(1)

The rest of the oxygen ions vibrated at their equilibrium sites. Neither O(5)—O(5) nor O(1)—O(1) jumps are observed in this MD simulation.

Table 1 Potential parameters for short range interaction.

	$A(eV)$	$\rho(\AA)$	$C(eV\AA^6)$
$O^{2-}-O^{2-}$	22764.3	0.1490	25.0
$O^{2-}-O^{2-}$	22764.3	0.1490	25.0
$O^{2-}-Cu^{2+}$	3799.3	0.24273	0.0
$O^{2-}-Ba^{2+}$	3115.5	0.33583	0.0
$O^{2-}-Y^{3+}$	20717.5	0.24203	0.0
$O^{-}-O^{-}$	22764.3	0.1490	25.0
$O^{-}-Cu^{2+}$	1861.6	0.25263	0.0
$O^{-}-Ba^{2+}$	29906.5	0.272375	0.0
$Cu^{2+}-Ba^{2+}$	168128.6	0.2558	0.0
$Ba^{2+}-Ba^{2+}$	2663.7	0.2558	0.0

Table 2 Calculated oxygen diffusion coefficients of $YBa_2Cu_3O_{7-x}$.

x	$T(K)$	D	D_a	D_b	D_c
		$(\times 10^{-8} cm^2 s^{-1})$			
0.09	1400	4.5	1.8	1.7	0.96
0.09	1450	5.6	2.2	2.1	1.5
0.09	1500	7.6	2.8	2.5	2.4
0.18	1350	4.4	1.3	1.5	1.6
0.18	1400	5.7	2.6	0.8	2.2
0.18	1450	7.8	3.2	2.3	2.3
0.27	1450	4.7	2.2	1.0	1.5

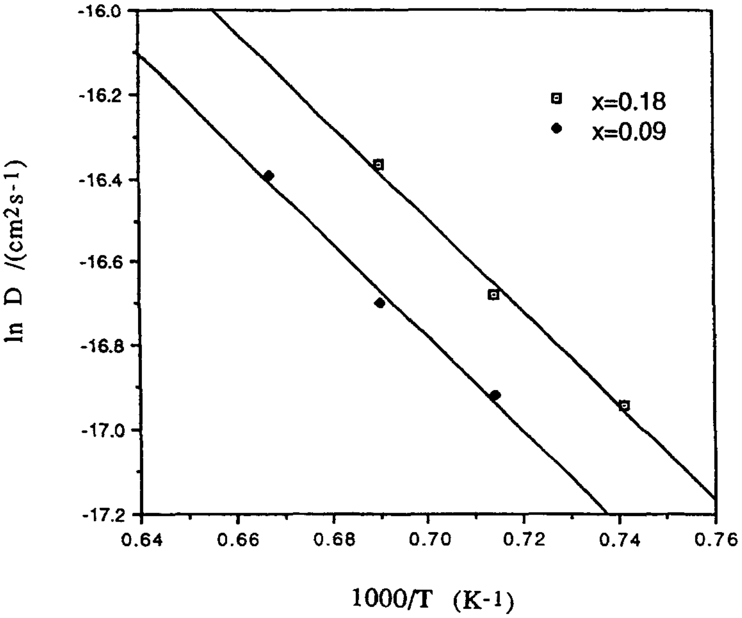

Figure 3 Calculated Arrhenius plot for oxygen diffusion in $YBa_2Cu_3O_{6.91}$ and $YBa_2Cu_3O_{6.82}$.

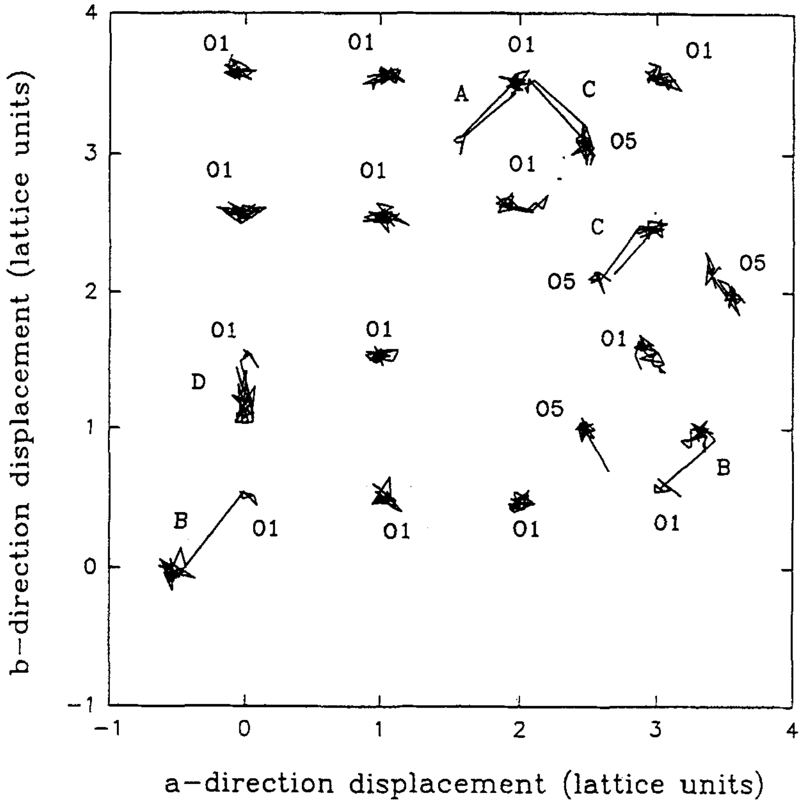

Figure 4 The *xy* projection of the coordinates of the oxygen ions situated in the Cu(1)—O plane of $YBa_2Cu_3O_{6.91}$ at 1450 K for a duration of 100 ps. The jump paths for the oxygen ions are: ions A: O(1)—O(5)—O(1); ion B: O(1)—O(5); ion C: O(5)—O(1)—O(5); and ion D: O(1)—O(4)—O(1)—O(4)—O(1)—O(4)—O(1).

Figure 5 shows the *yz* projection of the O(3) and O(4) coordinates in $YBa_2Cu_3O_{6.91}$ for a duration of 100 ps (simulated at 1450 K). Two unoccupied O(4) sites were observed, but there is no O(3)—O(4) jump. Two oxygen jump paths were noted. That for oxygen ion A is O(5)—O(1)—O(5) and that for oxygen ion B is O(4)—O(5)—O(4). Figure 6 shows the *xz* projection of the O(2) and O(4) coordinates in $YBa_2Cu_3O_{6.91}$ for the same duration and at the same temperature. As with Figure 5, we did not observe the O(2)—O(4) jump although one O(4) vacancy is present. We observed a jump path involving O(4)—O(5) (shown as A) and one between O(5)—O(1) (shown as B).

The *xy* projections of the oxygen coordinates for $YBa_2Cu_3O_{6.82}$ and $YBa_2Cu_3O_{6.73}$ are similar to those for $YBa_2Cu_3O_{6.91}$. Only O(1)—O(5), O(1)—O(4) and O(4)—O(5) jump paths are observed. The *yz* and *xz* projections of oxygen coordinates for $YBa_2Cu_3O_{6.82}$ and $YBa_2Cu_3O_{6.73}$ are also similar to those for $YBa_2Cu_3O_{6.91}$. Only O(1)—O(4) and O(5)—O(4) jump paths are observed.

In summary, we find that $YBa_2Cu_3O_{7-x}$ ($x = 0.09 - 0.27$) has the same jump paths at high temperatures for all compositions studied, these being O(1)—O(5),

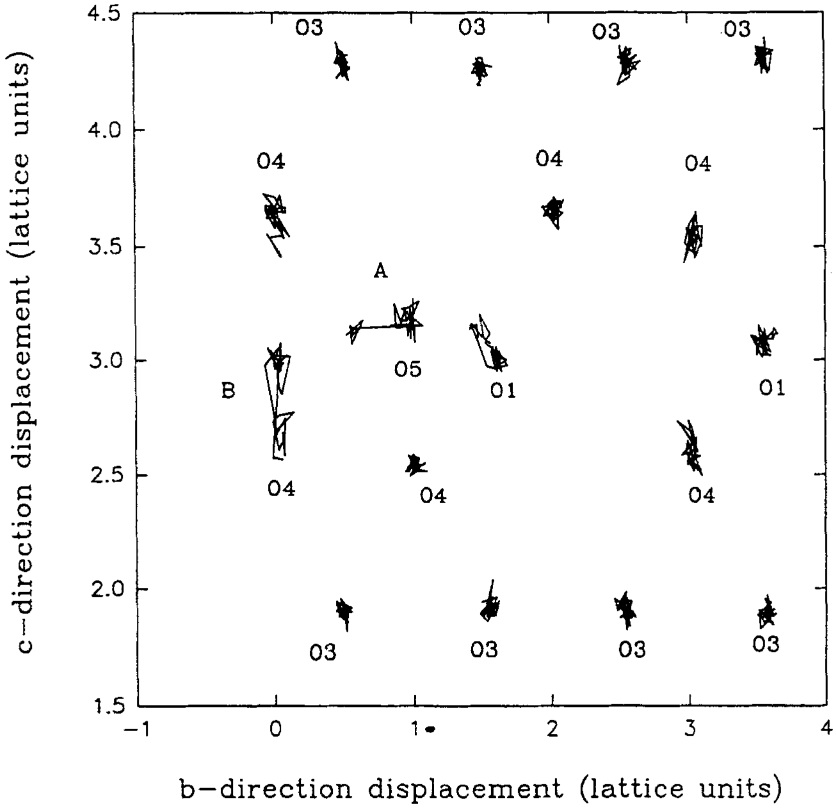

Figure 5 The xz projection of O(4) coordinates in $YBa_2Cu_3O_{6.91}$ at 1450 K for a duration of 100 ps. The jump paths of the oxygen ions are: ion A: O(5)—O(1)—O(5) and ion B: O(4)—O(5)—O(4).

O(1)—O(4) and O(4)—O(5). No O(2)—O(4), O(3)—O(4), and O(5)—O(5) jump paths were observed in any simulation.

(3) *Oxygen distribution*

Change in the oxygen deficiency "x" can change the oxygen vacancy concentration and oxygen vacancy distribution in $YBa_2Cu_3O_{7-x}$. MD simulation is the ideal tool to study this process. To investigate the actual concentration of oxygen vacancies in $YBa_2Cu_3O_{7-x}$ we recorded the oxygen coordinates and counted the oxygen ions situated at O(1), O(4) and O(5) sites at different times ($t = 0, 20, 40, 60, 80$ and 100 ps) at 1450 K. The average fractional oxygen site occupancies and average numbers of oxygen vacancies and interstitials are reported in Table 3. It is interesting to see that the fractional oxygen site occupancy n(O4) is not close to 1, indicating that changes in oxygen stoichiometry cause not only rearrangements of oxygen ions at O(1) and O(5) sites but also of oxygen ions at O(4) sites. This result is in agreement with neutron diffraction results [30]. We also observed that n(O1) + n(O5) > 1 which indicates that some oxygen ion in the Cu(1)—O plane

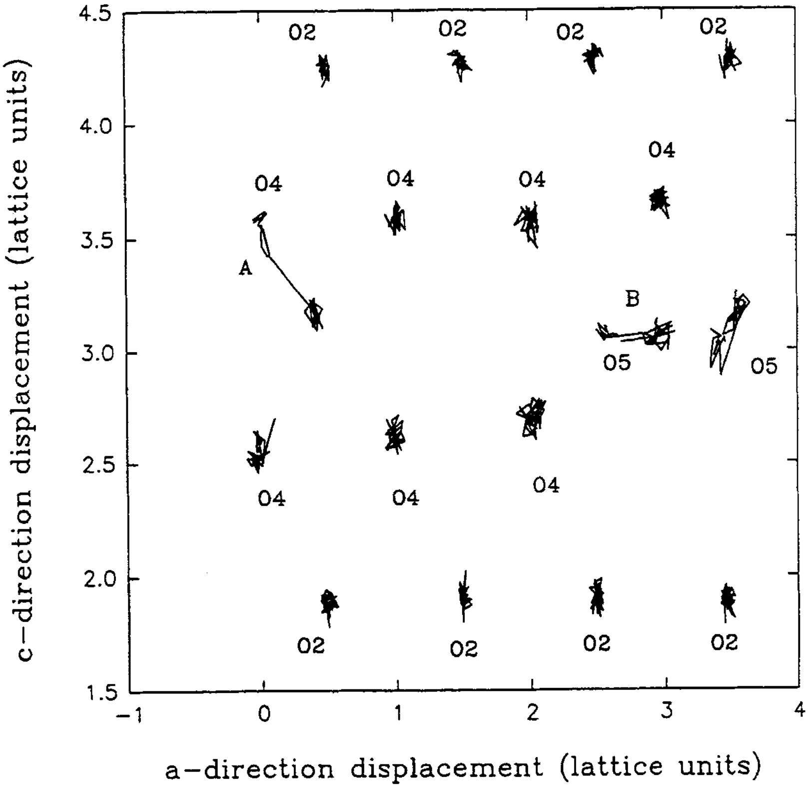

Figure 6 The yz projection of O(4) coordinates in $YBa_2Cu_3O_{6.91}$ at 1450 K for a duration of 100 ps. The jump paths of the oxygen ions are: ion A: O(4)—O(5); ion B: O(5)—O(1).

originate from O(4) sites, as we did not observe O(2)—O(4) and O(3)—O(4) jumps. We found that the total number of "real" oxygen vacancies is much greater than that indicated by the stoichiometry. For example, three oxygen vacancies were introduced into O(1) sites for $YBa_2Cu_3O_{6.91}$. After equilibration we found 17 oxygen vacancies and 14 interstitials. We also found that most oxygen ions at the O(5) site do not originate from the O(1) sites but from the O(4) sites, and that there, are more oxygen vacancies at O(4) sites than at O(1) sites (see Table 3b).

The number of oxygen vacancies and interstitials increases as x increases from 0.09 to 0.18. The concentration of vacancies at the O(1) site, $N(V_{O1})$ increases by about 60% whereas that at the O(4) site $N(V_{O4})$ and the number of occupied O(5) sites $N(O5_I)$ increases by about 26% and 31% respectively (see Table 3b). The total number of oxygen vacancies $N(V_{O1} + V_{O4})$ and total number of defects N(total) increases by about 41% and 34% respectively. When we recall that the oxygen diffusion coefficient at $x = 0.18$ is about larger than 40% larger than the oxygen diffusion coefficient at $x = 0.09$ it appears that the *total* number of oxygen vacancies plays an important role in oxygen diffusion in $YBa_2Cu_3O_{7-x}$.

If we examine the relevant concentrations of different oxygen defects we find that for $YBa_2Cu_3O_{6.91}$ and $YBa_2Cu_3O_{6.82}$:

Table 3 Calculated fractional oxygen site occupancies and numbers of oxygen vacancies and interstials in $YBa_2Cu_3O_{7-x}$.

(a) Fractional oxygen site occupancies

T(K)	x	n(O1)	n(O5)	n(O4)
1350	0.09	0.81	0.34	0.88
1350	0.18	0.78	0.50	0.77
1450	0.09	0.91	0.28	0.86
1450	0.18	0.75	0.48	0.81

(b) Number of oxygen vacancies and interstials

T(K)	x	V_{O1}	$O5_I$	V_{O4}	$V_{O1} + V_{O4}$
1350	0.09	6 (3)	11 (0)	8 (0)	14 (3)
1350	0.18	7 (6)	16 (0)	15 (0)	22 (6)
1450	0.09	3 (3)	9 (0)	9 (0)	12 (3)
1450	0.18	8 (6)	14 (0)	12 (0)	20 (6)

Note: The numbers in parenthese are the defect numbers we introduced before MD calculated.

$$N(V_{O1} + V_{O4}) > N(O5_I) > N(V_{O4}) > N(V_{O1}).$$

But as x continues to increase from $x = 0.18$ to $x = 0.27$, the oxygen distribution changes considerably. At $x = 0.27$, nine oxygen vacancies were introduced into O(1) sites. After equilibration $N(V_{O1})$ is found to be very close to the value we introduced, and $N(V_{O4})$ is close to $N(O5_I)$. Compared to the values at $x = 0.18$, $N(V_{O1} + V_{O4})$ slightly reduced and N(total) reduced by about 18%. The presence of a lower level of "real" vacancies despite the higher oxygen deficiency seems to be the reason why at $x = 0.27$ the oxygen diffusion coefficient is smaller than that at $x = 0.18$.

(4) *Oxygen diffusion mechanisms and their temperature variation*

As we have seen MD techniques can give ion migration paths and distributions, which are essential for a full understanding of the diffusion mechanism. Because we did not observe oxygen ions moving along O(5) sites as suggested by Rothman *et al.* [7], and found that the oxygen ion on the O(5) site can easily jump into the O(1) site, we propose the following oxygen diffusion mechanism in $YBa_2Cu_3O_{7-x}$: at lower temperatures, because of the low occupancy of the O(5) site, oxygen vacancy jumps of the type O(1)—O(4)—O(1) will predominate as static lattice calculations suggested [25]. Because there are very few vacancies on O(2) and O(3) sites and because of the difficulty of O(2)—O(3) or O(3)—O(4) jumps, oxygen jumps in the c-direction will therefore be very restricted. These mechanisms seem able to explain the oxygen diffusion behavior at lower temperatures (i.e. $D_b \gg D_a$ and $D_{ab} \gg D_c$) without invoking O(5)—O(5) jumps. At higher temperatures the O(5) site is more easily occupied so that jumps from the O(1) site to the O(5) site begin to occur with the frequency of those jumps from the O(1) site to the O(4) site. In this case the oxygen diffusion will mainly be via the *ab*-plane rather than via the chain along the *b*-direction. This will result in $D_a \sim D_b$ and $D_{ab} > D_c$ as our simulation results revealed (for detailed discussion see reference 3).

When the oxygen stoichiometry changes the oxygen diffusion coefficient does not show a strong dependence on oxygen stoichiometry as experimental work [20] and our simulations revealed. We find that the change in oxygen stoichiometry causes a significant change in the oxygen distribution. Although the mechanism whereby the oxygen distribution effects oxygen diffusion in $YBa_2Cu_3O_{7-x}$ is still not clear, it appears that oxygen redistribution may play a more important role than stoichiometry in oxygen diffusion in $YBa_2Cu_3O_{7-x}$. In particular, the formation of oxygen vacancies at O(4) sites may be of considerable importance. The participation of the O(4) oxygen in the oxygen diffusion in $YBa_2Cu_3O_{7-x}$ is also discussed in previous studies [31-35]. Earlier theoretical work which reported strong stoichiometry dependence of oxygen diffusion in $YBa_2Cu_3O_{7-x}$, did not consider oxygen vacancy formation at the O(4) site. We suggest therefore that such models be included in future accounts of oxygen diffusion in $YBa_2Cu_3O_{7-x}$.

CONCLUSIONS

We have studied oxygen diffusion in $YBa_2Cu_3O_{7-x}$ ($x = 0.09 - 0.27$) using MD simulations in the temperature range 1350-1500 K. Our results show no strong stoichiometry dependence of the diffusion coefficient: for values of x from 0.09 to 0.27 its variation is less than 70% which is in good agreement with experimental results. We found that all compositions for $YBa_2Cu_3O_{7-x}$ in the range $x = 0.09 - 0.27$ have the same oxygen jump paths: O(1)—O(5), O(1)—O(4), and O(4)—O(5), but not O(5)—O(5). Our investigation of the oxygen distribution in $YBa_2Cu_3O_{7-x}$ shows that there are more O(4) vacancies than O(1) vacancies and that the total number of oxygen vacancies is higher than that expected from the stoichiometry. Change in stoichiometry was found to have a great effect on the oxygen distribution. We propose that oxygen diffusion in $YBa_2Cu_3O_{7-x}$ does not take place by the movement of oxygen ions over O(5) sites between the rows of oxygen ions, but rather by the movement of oxygen ions along the path O(1)—O(4)—O(1) at lower temperatures and by the movement of oxygen ions mainly along the path O(1)—O(5)—O(1) at high temperature. We suggest that redistribution of oxygen may be the reason for the lack of a strong stoichiometry dependence of oxygen diffusion in $YBa_2Cu_3O_{7-x}$.

Acknowledgements

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