Migration and correlation in highly defective systems: Fast-diffusion in lithium oxide

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Abstract

The high-temperature superionic phase of lithium oxide is characterized by a high concentration of Frenkel defects and a diffusion mechanism involving several types of atomic jumps. We have calculated the tracer-correlation factor and analyzed the migration paths of the Li ions obtained by molecular dynamics (MD). A kinetic Monte Carlo code, simulating the lithium vacancy diffusion, has been developed and used to predict the correlation factor as a function of the atomic fraction of defects. There is a good agreement with the result directly obtained by MD. The analysis of the jump paths shows that the direct exchange between a vacancy and a migrating atom is the main part of the diffusion mechanism. The other atomic jumps, although complex, mostly imply vacancies. The Li^+ fast-diffusion proceeds by a vacancy mechanism involving several jump types.
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1. Introduction

The understanding of the fast-diffusion mechanism is an important step for a good description of the superionic phase existing in ionic compounds with fluorite or antifluorite structure. The lithium oxide is a fast diffusor at high temperature. Its structure has the antifluorite type and the lattice consists in a simple-cubic array of lithium ions with a spacing $a/2$, where the oxygen ions occupy alternating cube centers.

Initially, the technological interest in lithium oxide as blanket material for fusion reactors has led to complement the experimental studies of the high-temperature disorder and diffusion. Since the superionic conduction in Li_2O is associated with thermally induced cationic Frenkel pairs – meaning equal atomic fractions of vacancies and interstitials – the theoretical studies have been developed to calculate the formation and migration enthalpies of vacancies

and interstitials [1–6]. The recent development of nano-composites has initiated a renewed interest for the studies of these defects (see for example the review of Heitjans and Indris [7]). The first theoretical investigations [1–6] and the recent ones involving an ab initio approach [8] are mainly static calculations of point defect properties. The values of the activation enthalpy for diffusion deduced from these studies are generally too small to be compared to the results of the experiments [1,3,9–11]. The discrepancies have pointed out the need to investigate this problem by molecular dynamics (MD) [6,12–14]. The conclusion of most of the theoretical studies is in favor of the vacancy mechanism but the non-collinear interstitialcy option is also proposed [12,15]. The lack of certainty about the diffusion mechanism could indicate a complex situation and thus requires a study involving at the same time the nature, the concentration and the migration of the defects.

In our previous study [16] we have chosen to use the MD approach to calculate the activation enthalpy for diffusion. In a first step, we have shown that the main part of the cationic Frenkel pairs – responsible for the high-temperature

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dynamic disorder – recombines very quickly and only a small fraction of them contributes to the fast diffusion. The diffusion occurs by discrete jumps of cations between regular sites. The coexistence of several kinds of jumps results in an effective migration enthalpy in good agreement with the experimental values. The features of the different jumps are clearly in favor of the vacancy mechanism.

To ascertain the nature of the diffusion mechanism we have pursued in this work the MD study to calculate the tracer-correlation factor and performed a detailed analysis of the migration paths. Most of the studies concerning highly defective systems and investigating the diffusion mechanism imply jumps towards nearest-neighbors, especially when the correlation factor is calculated and gives a clue for the defect controlling diffusion (see for example the review of Allnatt and Lidiard [17]). The complexity of superionic Li_2O is due not only to the high defect concentration but also to the existence of several kinds of jumps involving mainly first neighbors and to a lesser extent second and third neighbors [16]. Indeed, the correlation factor has already been calculated for mixed jumps of a vacancy [18] but without including the concentration of defects. No theoretical description is available to sort out from our results the nature and the contribution of the defect(s) involved in this diffusion process. We thus computed by MD the tracer-correlation factor as a function of the atomic fraction of defects and compared it to the values we obtained using the kinetic Monte Carlo method simulating vacancy diffusion and including the three jump lengths.

In the MD simulations of this work, we used an interatomic potential [19], which was fitted to the results of ab initio calculations using density functional theory. The results previously obtained with this model [16] are in good agreement with experimental data and in particular the temperature-evolution of the atomic fraction of Frenkel defects is well reproduced. The atomic trajectories were analyzed in order to examine the atomic migration paths and understand the role of the vacancies in the various atomic jumps.

2. Definitions and methods

2.1. Definitions of sites and jumps

The regular lattice sites of the diffusing Li ions are obtained by using the time-averaged positions of the non-diffusing oxygen atoms. An atomic site is defined as a spherical volume centered on a regular lattice site. When this volume is empty there is a vacancy on the site. If a cation does not belong to any atomic site it is an interstitial ion. We also define a cube-center site by the same spherical volume centered on the octahedral site located on each alternate empty cube center (void of oxygen). These spheres are tangent along <1 1 1> with a radius equal to $a\sqrt{3}/8$.

A jump occurs when a cation leaves its initial atomic site, and then enters and remains in another one. A crea-

tion–recombination (CR) is the creation of a Frenkel pair that rapidly recombines. The jumps are defined by their lengths [16]: $a/2$, $a\sqrt{2}/2$ and $a\sqrt{3}/2$ and also by the fact that for the shorter length the atom may or may not travel through the cube-center site. We have observed the four jumps drawn in Fig. 1, where D indicates a direct one and C a jump through the cube-center site.

2.2. Molecular dynamics

The detailed analysis of the cation jumps responsible for the Li-migration has been carried out on equilibrium atomic trajectories computed by MD in the temperature range of the superionic phase. The simulations have been performed in the microcanonical ensemble with the rigid-ion potential chosen in a previous study [16] (P6 of Ref. [19]). The simulated system contains 1500 ions, periodic boundary conditions are employed and the time step is equal to 2×10^{-15} s. The values of the diffusion coefficient D_{Li} of the Li ions have been calculated via the time-dependent mean square displacement and the corresponding Einstein relation [20]. The trajectory durations have been chosen to obtain approximately the same number of jumps. Therefore, the statistical accuracy of the calculations remains comparable whatever the temperature is. The number of jumps per atom ranges from 6 to 9.

2.3. Correlation factor

For a simple mechanism assuming only one type of defect, the correlation factor, f, is defined from the atomic diffusion coefficient, D_{Li}, by the relation (1) [21]

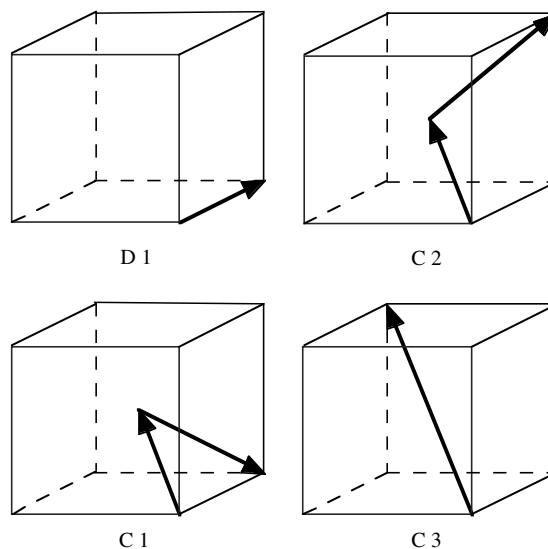$$D_{Li} = f x_{defect} D_{defect} \tag{1}$$

Fig. 1. Definition of the different kinds of jumps drawn in the cationic sublattice cube. Jumps of types 1, 2 and 3 have lengths of $a/2$, $a\sqrt{2}/2$ and $a\sqrt{3}/2$, respectively. Arrows indicate the schematic paths of the jumps.