



# Surface effects on atomic diffusion in a superionic conductor: A molecular dynamics study of lithium oxide

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## ARTICLE INFO

Available online 29 August 2012

### Keywords:

Lithium oxide  
Superionic conductor  
Surface  
Frenkel defect  
Vacancy  
Molecular dynamics  
Diffusion mechanism

## ABSTRACT

The changes induced by a surface in the atomic diffusion in  $\text{Li}_2\text{O}$  are studied by molecular dynamics, using a rigid-ion potential model fitted to *ab initio* data. The properties of the {111} surface are investigated plane by plane at a temperature selected in the superionic phase. The Frenkel defect atomic-fraction and the lithium-ion migration are enhanced mainly in the topmost two planes. The equality of the interstitial and vacancy atomic-fractions found in the bulk is not observed in these planes. The surface migration predominantly occurs by two types of nearest-neighbor atomic jumps via a vacancy mechanism. A geometrical model of the atomic jump-frequency profile allows us to estimate the reduction of the vacancy migration-energy at the surface. We also find a spontaneous  $1 \times 2$  reconstruction of the {110} surface.

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## 1. Introduction

Lithium oxide is a material of technological interest in the fields of fusion reactors or power electronic devices and its superionic behavior at high temperature is a motivating property.  $\text{Li}_2\text{O}$  is characterized by its antifluorite structure and a high amount of Frenkel defects at high temperature. It is interesting to see how its properties, in particular the ionic conductivity, are modified at a surface.

The structural and stability properties of lithium oxide surfaces have been investigated in theoretical studies based on empirical potentials [1,2], Hartree–Fock [3–5] or density-functional theory (DFT) [6] approaches. These studies provide the formation energies of {111} and {110} surfaces calculated at 0 K temperature, and as predicted by Tasker [7], they find that the {111} surface is the most stable one. The lattice dynamics calculations of Taylor et al. [2] performed in the non-superionic phase show that the quasiharmonic free-energy of the {111} surface varies very slightly with temperature.

Most of the experimental and theoretical studies of point defect properties, diffusion and ionic conductivity in lithium oxide have been carried out in the bulk. Nevertheless, there exist a few studies concerning the surfaces [6] and nanocrystalline composites [8–11]. In their DFT study at 0 K temperature, Islam et al. calculated the Frenkel defect and the cation vacancy formation-energies and the Li migration energies associated with some possible diffusion pathways. With respect to the bulk, they concluded that in the {111} surface the

defect concentration is larger and the migration barriers are lower. They also suggested that the most likely migration mechanism follows a zigzag pathway through sites belonging to the two topmost planes. But, at high temperatures, other migration pathways than those envisaged at  $T=0$  K can occur. To our knowledge, such theoretical data on the motion and vibrations of surface lithium-ions do not exist.

The results of the molecular dynamics (MD) simulations reported in this paper have been obtained with an interatomic potential [12] fitted to the results of *ab initio* calculations based on DFT. This model proved convenient to reproduce experimental data, in particular the temperature evolution of the atomic fraction of Frenkel defects [13]. We have shown that the bulk diffusion occurs by discrete jumps of the cations between regular sites. The coexistence of several kinds of jumps results in an effective migration-enthalpy of 0.53 eV in good agreement with experimental values. The results were in favor of a vacancy mechanism and this conclusion was corroborated by the calculation of the tracer-correlation factor [14].

In the present study, we first investigate the structural properties of the  $\text{Li}_2\text{O}\{111\}$  and {110} surfaces at  $T=0$  K, including the reconstruction of the {110} surface. Static calculations require some extrapolations to explain the high temperature behavior. We have chosen the MD technique so that the system spontaneously finds its equilibrium state. We address the relationship between the fast diffusion and the surface by studying the dynamical properties of point defects at  $\text{Li}_2\text{O}\{111\}$  surface in the superionic phase. The quantities are calculated plane by plane as a function of the distance to the terminal plane of the surface. We thus obtain the profiles of vacancy and interstitial atomic-fractions, of atomic vibration-amplitudes, and of frequencies for all spontaneous atomic jumps.

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## 2. Definitions and methods

### 2.1. Surfaces geometry

The antifluorite structure of  $\text{Li}_2\text{O}$  can be described as a simple-cubic lattice of lithium ions with spacing  $a/2$ , where the oxygen ions occupy alternating cube centers. According to the classification of Tasker [7], the surface of ionic crystals may be of three types. Type 1 consists of neutral planes whereas type 2 has charged planes arranged symmetrically without a dipole moment perpendicular to the surface. The type 3 surface is charged and there is a perpendicular dipole moment. We investigated the type 2  $\{111\}$  surface with a terminating cation-plane, and the type 1  $\{110\}$  surface. The stacking sequence of the  $\{111\}$  surface, showing the M (Li) and D (O) planes, is described in Fig. 1. The atomic structure of the  $\{110\}$  surface is illustrated in Fig. 2 together with a  $1 \times 2$  reconstruction. In the reconstructed structure, the trench faces are  $\{111\}$  oriented.

### 2.2. Rigid-ion model

The rigid-ion model (RIM) used has been derived from *ab initio* calculations (P6 of Ref. [12]) and chosen for a previous study of atomic diffusion mechanisms [13,14]. The validation process of this model has yielded results, which compare rather favorably with the corresponding experimental data such as elastic moduli and temperature evolution of the lattice parameter and thermal vibrations [12]. The experimental temperature evolution of the vacancy atomic-fraction is also well reproduced by this model [13]. A complex migration-process of the cation was described and the resulting effective migration-enthalpy is in

good agreement with the experimental data [13]. The critical temperature associated with the superionic phase transition, given by this model, has been evaluated close to 1475 K. Comments have to be added concerning the ability of the RIM to describe the situations studied in the present paper. Indeed, this potential has been fitted to results related to bulk  $\text{Li}_2\text{O}$ . The integrated electronic density that we computed in our *ab initio* calculations [12] suggests that the nominal charges namely  $-2$  and  $+1$  for O and Li, respectively, can be used in the bulk. Since there is only a small variation of these ion charges between the bulk and the surface [4], we have chosen to keep the bulk values. As usual, the Ewald method has been used to calculate the coulombic contributions. In addition, RIM means that the ions are treated as point charges that cannot be polarized. A full description might require to account for the electronic polarizability (as in a shell model for instance). At high temperatures with Li ions quickly migrating, this polarizability probably plays a minor role in dynamical behavior as shown by the bulk properties successfully obtained [13] with this RIM. In addition, since we are interested in checking to what extent the dynamical properties are affected by a surface, it is suitable to use the same potential as in the bulk.

### 2.3. Molecular dynamics

MD computations have been carried out in the microcanonical ensemble to generate 10 equilibrium trajectories of 0.2 ns. The average temperatures (one for each equilibrium trajectory) range between 1322.9 K and 1324.8 K and belong to the superionic phase appearing at about 1100 K. The temperature associated with these trajectories is the average of the 10 average values. It equals 1324 K and all the

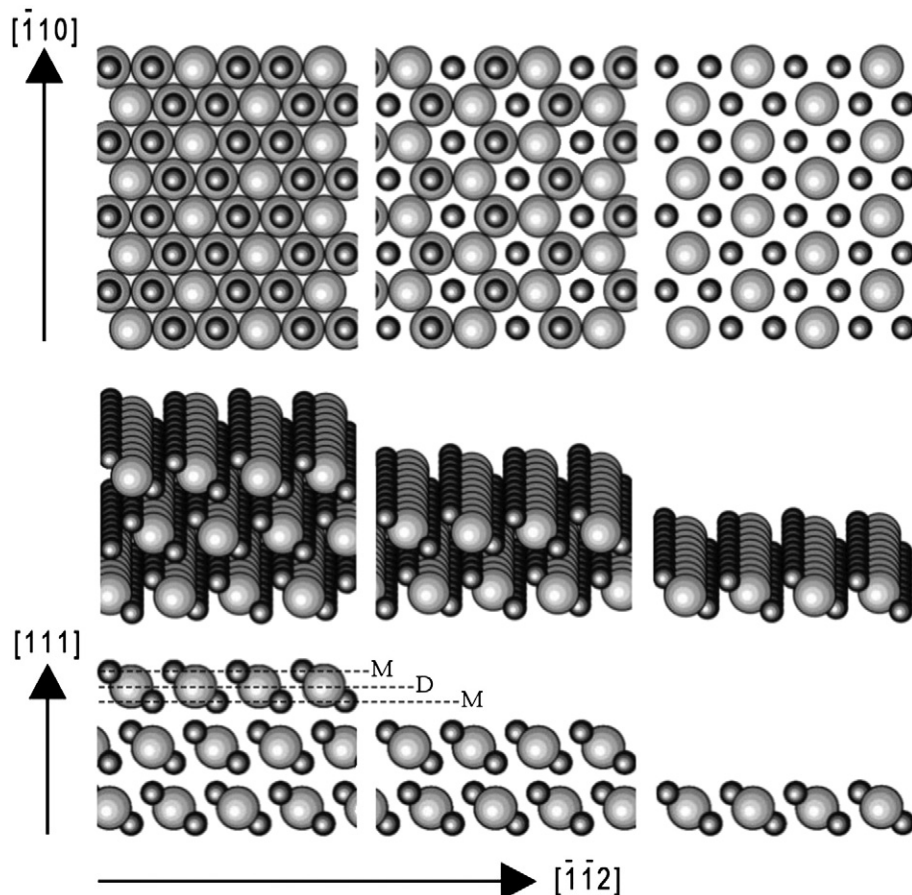


Fig. 1. Top, oblique and side views of the  $\text{Li}_2\text{O}\{111\}$  surface. Li ions, small spheres; O ions, large spheres. M, D, M refer to the monovalent (Li), divalent (O), monovalent (Li) stacking sequence. To clarify the atomic positions in the different planes, the three views are drawn with 9, 6 and 3 atomic planes.

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