A Simple Model for Oxygen Conduction in Some Perovskite Compounds

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A simple model for oxygen ion conduction in perovskite compounds is proposed. The potential for an oxygen ion is calculated as the sum of the long range Coulomb potential and short range repulsive potential in a cubic lattice. The activation energy is estimated as the difference in the values of potential at the barrier and at the stable site. When appropriate conditions are satisfied, the activation energy has a minimum as a function of lattice constant in accordance with recent experiments.

1　Introduction

Some perovskite oxides containing lanthan in A-site are known to be oxygen ion conductors and expected as promising electrolyte materials for solid oxide fuel-cells [1,2]. Recently Nomura et al. have reported experimental results on the relation between ionic conductivity and lattice constants in $LaM^{III}O_3$ based perovskite mixtures [3].

According to their report, the replacement of ions in B-site from Al to Ga, Sc, In or Lu increases lattice parameters depending on the increase of the ionic radius of each replacing ions as shown in Table 1. They have shown the ionic conductivity and the activation energy as functions of free volume in the lattice (Fig.1). The free volume is defined as the free space unoccupied by atoms in the lattice and is calculated using ionic radii. Nomura et al. have found that the free volume increases with the increase of the radius of the B-site ion, Ga ion gives a maximum in ionic conductivity and the maximum of ionic conductivity corresponds to the minimum of the activation energy.

To explain main features of their experimental results of ionic conductivity, we here propose a very simple model of the activation energy for ionic motion in these oxides. We consider a cubic lattice composed of metallic ions and oxygen ions with vacancies of the latter. When one oxygen site happens to be vacant, an oxygen ion in the adjacent site is able to move to the vacancy overcoming the potential barrier and contributes to the conductivity. We evaluate the potential as the function of lattice parameter and show a possibility of the existence of

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Table 1. Crystal structures of $La_{0.9}Sr_{0.1}M^{III}O_{3-d}$ [3].

Substance	Crystal structure	Lattice Parameters			Volume/formula
		a (Å)	b (Å)	c (Å)	(Å³)
$La_{0.9}Sr_{0.1}AlO_{3-d}$	hexagonal	5.362	—	13.147	54.54
$La_{0.9}Sr_{0.1}GaO_{3-d}$	orthorhombic	5.504	5.520	7.737	58.76
$La_{0.9}Sr_{0.1}ScO_{3-d}$	orthorhombic	5.688	5.809	8.080	66.73
$La_{0.9}Sr_{0.1}InO_{3-d}$	orthorhombic	5.735	5.930	8.216	69.86
$La_{0.9}Sr_{0.1}LuO_{3-d}$	orthorhombic	5.835	6.014	8.367	73.40
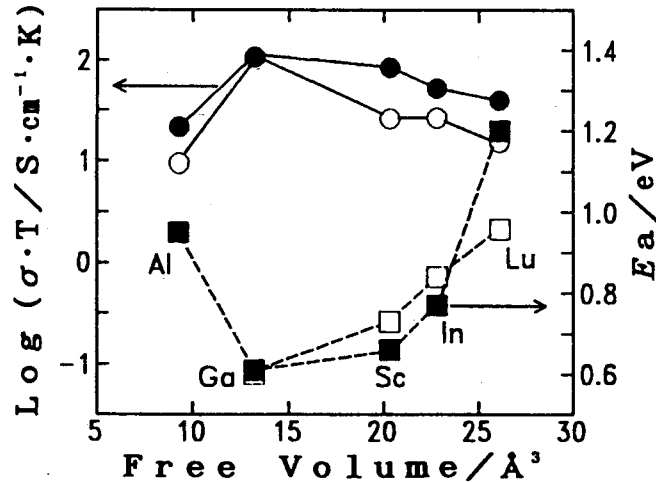
Fig.1 Conductivity vs. free volume (in air (●) and in N_2 (○)), and activation energy vs. free volume (in air (■) and in N_2 (□)) for $La_{0.9}Sr_{0.1}M^{III}O_{3-d}$[3].

a minimum in the activation energy which is given as the difference of potential between a stable site and the barrier.

2 Model

We consider a body centered cubic lattice with the corners occupied by metallic ions and body centers occupied by oxygen ions (Fig.2). The oxygen ions in the lattice feel the short range repulsive force from metallic ions and the long range Coulomb force from metallic ions and oxygen ions.

The Coulomb potential is calculated by summing up the contributions from all atoms except one oxygen vacancy through the Ewald method. The repulsive potential is assumed to be written in the form,

$$\text{repulsive potential} = \sum_{n.n.} \exp(-2r/a_0). \tag{1}$$

Here a_0 is a lattice constant and r is the distance between the lattice points and an oxygen ion moving from one stable site to the vacant site in the next cell. Summation is taken over the nearest neighbors of the original site and the next site.
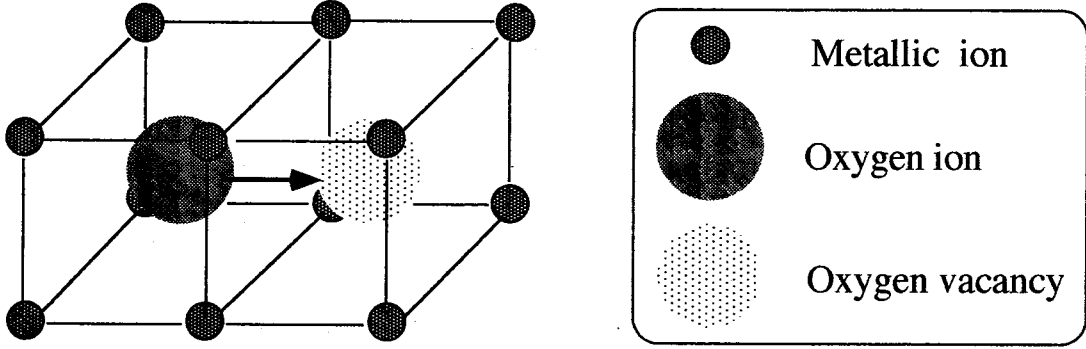
Fig.2 Simple Model of Oxygen Conduction

The activation energy is estimated by the difference between the potential at the stable oxygen site and the potential barrier. The potentials at each site is the sum of these two contributions.

$$\text{total potential} = \text{Coulomb potential} + \text{repulsive potential}$$

$$= \frac{ZZ'e^2}{4\pi\varepsilon} \sum \frac{1}{r} + f \sum_{n.\ n.} \exp\left(-2r/a_0\right), \tag{2}$$

$$\text{activation energy} = (\text{total potential})_{\text{barrier}} - (\text{total potential})_{\text{stable site}}. \tag{3}$$

Here, f is a constant factor expressing the ratio of two potentials.

3 Results and Discussions

Total potential is calculated for various values of lattice parameter. Some examples of them are shown in Fig.3. The value of the factor f is fixed at 90 and the lattice parameter varies from 1.0 to 1.4. The abscissa is the position of the oxygen ion measured from the stable position. The activation energy can be obtained as the difference between the peak value and the minimum value.

The values of the activation energy are shown in Fig.4 as a function of lattice parameter for the various values of factor f. The activation energy has a minimum when the value of f is in some range: For larger or smaller values of f, it is a monotonous function. The order of magnitude of the activation energy is in agreement with experiments.

At first sight, the activation energy defined here seems to be a monotonously decreasing function of the lattice constants. Though our model is simple and primitive, it is clearly shown that there exists a possibility of having a minimum in the course of expansion in accordance with experimental results. It is also clear that, for more serious comparison with experiments, we have to take into account the exact lattice structure of perovskite instead of the cubic lattice and valence dispersion of metallic ions.
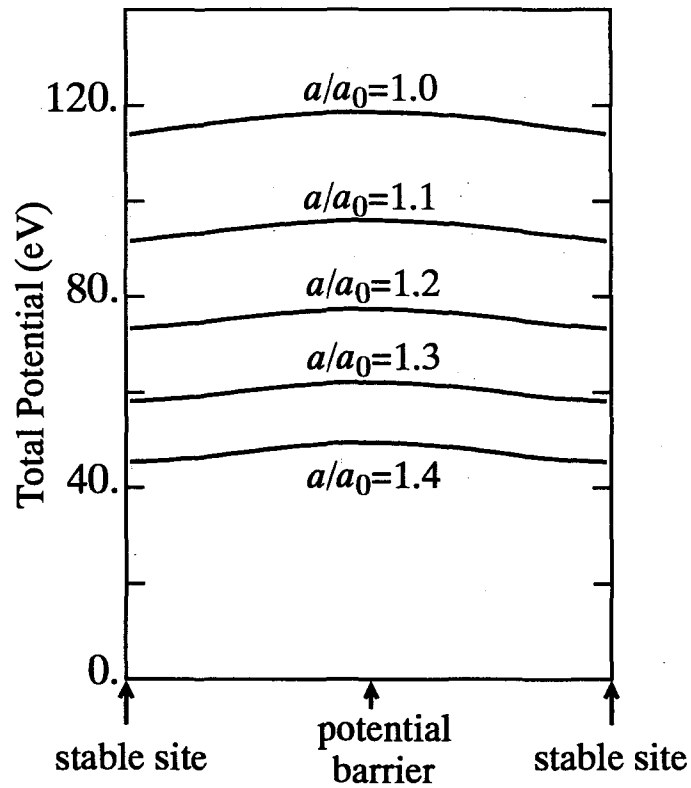
Fig.3 Total potential on the oxygen path. f is fixed at 90.
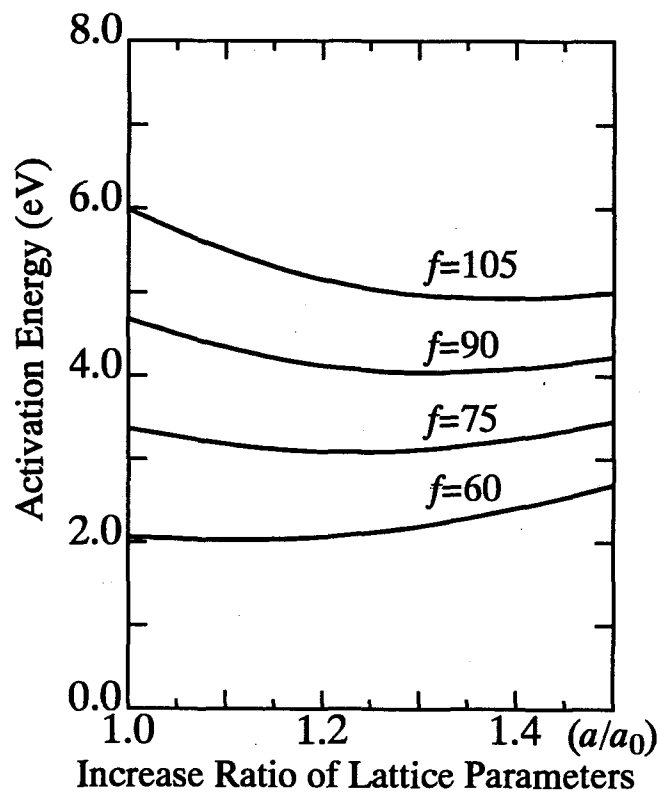Lattice constants are increased from a/a_0=1.0 to 1.4.

Fig.4 Activation energy vs. lattice parameters.

Acknowledgments

References

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