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Electronic structure and diffusion paths of Ag ions in rocksalt structured AgI

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Abstract

The electronic structure and diffusion paths of Ag ions in the rocksalt structured phase of AgI (rs-AgI) are studied based on the full-potential linear-muffin-tin-orbital (FP-LMTO) method. Ag ions in the rs-AgI start to migrate along the ⟨111⟩ direction due to the low energy barrier, as is well known in the cases of AgBr and AgCl. The high ionic conductivity in rs-AgI might be expected from the viewpoint of the empirical overlap parameters between Ag 4d electrons and halogen p electrons.

Keywords: Rocksalt structured AgI; Electronic structure; Superionic conductor; Frenkel defect; FP-LMTO method

1. Introduction

AgI is known as a typical superionic conductor [1]. The superionic phase of AgI appears at 420 K. The value of the ionic conductivity is as high as about 1 Ω^{-1} cm^{-1}. This value is comparable to that of liquid electrolytes. The structure of superionic conductor α-AgI possesses a bcc lattice of iodine ions, while Ag ions are distributed over 42 crystallographic sites: 6(b) octahedral, 12(d) tetrahedral, and 24(h) trigonal. The ion diffusion paths of Ag ions between tetrahedral sites have been shown to occur in the ⟨110⟩ direction, i.e., via the trigonal sites. The ambient pressure data for AgI showed that the sample was initially a mixture of the wurtzite and the zincblende structured phases (AgI-II and AgI-II′, respectively) [2]. In the Phillips scale [3,4], AgI has the ionicity $f_i = 0.770$. This is very close to the critical value $f_c = 0.785$ which marks the idealized boundary between compounds with fourfold-coordinated structures (zincblende, wurtzite) and those with sixfold coordination (rocksalt). Furthermore, AgI might be expected to transform from the zincblende to the rocksalt under hydrostatic pressures. The structural changes of silver halides induced by hydrostatic pressures were investigated using angle-dispersive X-ray diffraction with an image-plate device [2]. Available experimental evidences indicate that the transition from fourfold to sixfold coordination occurs. For pressures between 0.4 and 10 GPa, a rocksalt-structure phase of fcc AgI is stable at room temperature [1]. This fact is in contrast to the fact that other silver halides AgF, AgCl, and AgBr adopt the octahedrally coordinated rocksalt structure at ambient pressure and temperature.

It was indicated that Frenkel defects dominated the electrical conductivities in AgCl and AgBr [5]. It is considered that Frenkel defects dominate also in rs-AgI. According to the results of the molecular dynamics (MD) simulations of AgI under hydrostatic pressures, the gradual onset of the highly conducting state is accompanied by an increasing fraction of dynamical Frenkel defects, a peak in the specific heat and anomalous behavior of the lattice expansion [6]. The measurement of the electrical conductivity of rs-AgI showed the value of the ionic conductivity was approximately 1 Ω^{-1} cm^{-1}, i.e., only slightly less than the electrical conductivity in the α phase [1]. Thus there are two solid electrolyte phases in AgI: α phase and high temperature part of the fcc phase. The main difference between the two is that the iodine sublattice is a body-centered cubic for the α phase, while it is a face-centered cubic for the fcc phase. The conductivity is somewhat lower in the fcc phase than

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in the bcc phase and, in fact, most solid electrolytes that have the fcc structure have lower conductivities than those that have the bcc structure.

Kleppmann et al. [7,8] introduced the quadrupolar deformabilities of Ag ions in order to elucidate the mechanism of the ionic conductivities and the phonon dispersion relations in silver halides. Also, they estimated the decrease of the activation energies owing to the Ag deformabilities, which are ΔE (AgBr) ~ −0.37 eV and ΔE(AgCl) ~ −0.22 eV. These results compare favorably with the differences of the activation energy between alkali halides and silver halides of about 0.3 ~ 0.4 eV. They suggested that the quadrupolar deformabilities of Ag ions led to the decrease of the activation energies for ionic conductions in silver halides.

In this paper, we investigate the mechanism of ionic conductivity in rs-AgI on the basis of the electronic structure theory. We study the electronic structure and the variations of the total energies along ion diffusion paths using the FP-LMTO method. We will discuss the origin of the superionicity by comparing the results conducted by making use of the empirical overlap parameters between Ag 4d electrons and halogen p electrons.

2. Calculation method

Band calculations are carried out using the full-potential linear muffin-tin-orbital program LMTART, where the local density approximation (LDA) is used [9]. In this calculation, the space is divided into muffin-tin spheres and the interstitial region. Within the muffin-tin spheres, the charge density and potential are expanded using spherical harmonics, and in the interstitial region they are expanded in plane waves. The initial charge density is taken as a superposition of the neutral atomic charge densities. The total energy is estimated as the sum of the following terms: $E_{tot} = T_{val} + T_{cor} + E_{el} + E_{xc}$ where T_{val} and T_{cor} are the kinetic energies of the valence and core electrons and E_{el} is the electrostatic energy including electron–electron, electron–nucleus and nucleus–nucleus interactions and E_{xc} is the exchange energy. The convergence is assumed if the self-consistent total energy difference between subsequent iterations is less than 10^{-6} Ry. The density of states (DOS) is calculated using the tetrahedron method, where 6 × 6 × 6 division in the k-space is used. Details of the calculation methods are described in Ref. [9].

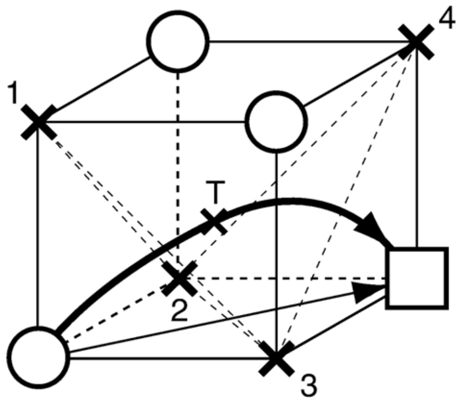

Fig. 1. Schematic view of ion diffusion paths. Two arrows show ion diffusion paths from the octahedral site to the cation vacancy. The bold arrow shows a Ag ion starts to migrate along the ⟨111⟩ direction toward the cation vacancy via the center of the tetrahedron, while the thin arrow shows a Ag ion starts to migrate directly toward the cation vacancy.

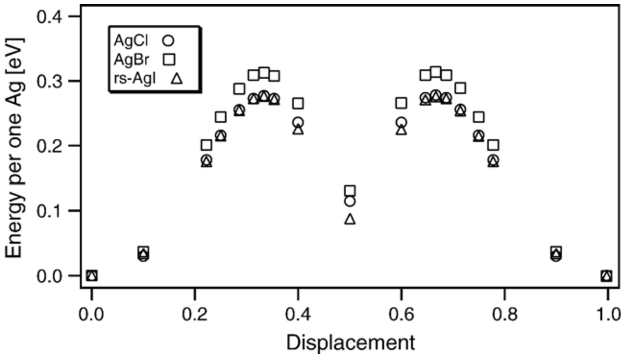

Fig. 2. Total energy variations for AgCl, AgBr and rs-AgI along the bold arrow shown in Fig. 1.

3. Results and discussion

Recently, many studies along the spirit of this study have been done to elucidate the mechanism of the ionic conduction. For example, the electronic structure of the ternary silver compound Ag_3SI was studied in order to clarify the microscopic origin of the structural phase transition and the fast ionic conduction [10]. The electronic structure and the Li diffusion paths in the lithium doped lanthanum titanate were also studied [11].

At first, we evaluate the energy required for the phase transition from the zincblende structure to the rocksalt-structure phase fcc AgI. We estimate the value varying the lattice constant of the rocksalt-structure phase fcc AgI until the total energy difference becomes zero. The ambient pressure data for AgI showed that the sample was initially a mixture of the wurtzite and the zincblende structured phases (AgI-II and AgI-II′, respectively) [2]. However, we adopt the zincblende structure when we estimate the value of the total energy. If we take a lattice constant of the rocksalt-structure phase fcc AgI as about $a = 6.32$ Å, the energy difference becomes zero between that of the rocksalt-structure phase fcc AgI and that of the zincblende

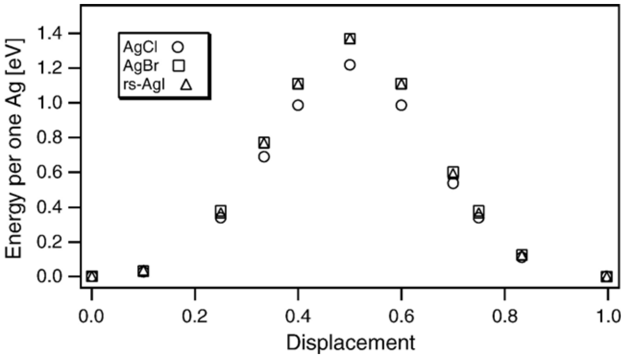

Fig. 3. Total energy variations for AgCl, AgBr and rs-AgI along the ⟨110⟩-axis.