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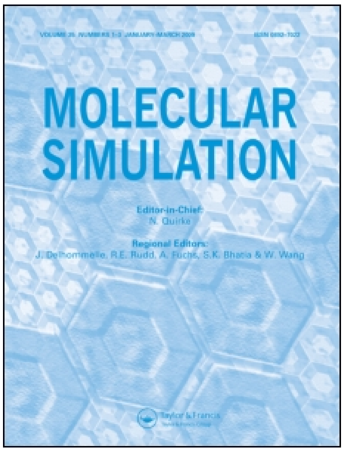

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Anomalous pre-melting volume expansion in AgBr—*ab initio* approach

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Ab initio calculation of silver bromide, AgBr, in the pre-melting region has been performed. The anomalous behavior of the temperature dependence of the volume has been analyzed by Frenkel defect formation. The occupation probability of cation in the interstitial site has been estimated from these considerations. The valence electron density distributions have also been investigated.

Keywords: Pre-melting; AgBr; *Ab initio* calculation; Lattice expansion; Electron density distribution

PACS: 61.72 Bb; 65.40 De; 71.15 Nc

1. Introduction

Noblemetal-halides have been widely studied, which includes a group of substances, i.e. superionic conductors that exhibit high values of ionic conductivity while in the solid state. The mechanism of high ionic conductivity in these materials has been of considerable interest because of their novel physical behavior and technological importance [1]. It is well known that silver iodide is one of the superionic conductors in its alpha phase, i.e. α-AgI, in which silver ions statistically distribute around the iodine bcc cubic. On the other hand, AgBr has a rock salt structure in its solid phase and dose not exhibit high conduction, though it is also one of the silver halides. We have investigated the effect of dissolving AgBr into AgI on the structure, transport properties, and screening effects between anion and cation by molecular dynamics simulations [2,3].

Meanwhile, the results for the ionic transport properties resembled the superionic-like behavior of ions have been found in molecular dynamics simulations of AgCl and AgBr melts [4]. More over, some experimental results, e.g. anomalous lattice expansion [5] and conductivity behavior [6] indicates the anomalous pre-melting phenomena of AgCl and AgBr, which may be interpreted as melting frustrate a transition of them to a superionic phase. The importance of the study of pre-melting behavior of non-superionic noblemetal-halides is strongly suggested by these facts [7]. In this study, we make an approach to the temperature dependence of lattice constant in pre-melting region of AgBr by *ab initio* calculation. The results of electronic density distribution are also shown in later section.

2. Computational procedure

The calculation has been performed in the framework of the local density approximation of the density functional theory (LDA) [8]. The norm-conserving pseudopotentials by Troullier and Martins (TM) [9] are used. The interaction between 4d electrons of Ag and 4p states of Br, i.e. so called p–d hybridization can been taken into account in these procedure. The cut off energy 60 Ry is used for the total energy of plane wave expansion, with a periodic representation of the system in a box under periodic boundary conditions. It has been confirmed that the difference of the total energy to the case using 100 Ry cut off energy is less than 0.015%. For integration in the Brillouin zone, $4 \times 4 \times 4$ Monkhorst and Pack grid was employed [10]. These calculations were performed with the ABINIT code [11].

At first, in order to confirm the propriety of the calculation, the equilibrium lattice constant of AgBr

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in rock salt structure was calculated, which was obtained by the cell optimization result. The obtained lattice constant 5.61 Å, which is very close to the value 5.64 Å in literature [12]. The latter was also calculated using TM pseudopotentials. This fact prompts us to calculate the temperature dependence of the lattice constant of AgBr.

3. Temperature dependence of the volume

The thermal expansion of the crystal lattice has been theoretically explained by the Gruneisen equation. The equation predicts the linear change of the lattice with temperature increase, however the experimental results significantly deviate from the linear change [5]. Lawn [5] explained this disagreement by the defect formation. Andreoni and Toshi [7] showed the Frenkel disorder of cation was formed in the bromine sublattice in the very hot solid. In this study, in order to simulate the temperature dependence of the lattice of AgBr, we have performed the calculation of the total energy of the system in constant temperature condition, i.e. NTV ensemble. Isothermal calculation has been performed using Langevin equation by introducing friction between ions [13] in the ABINIT code. We briefly describe Langevin molecular dynamics procedure as follows. The ionic positions, $\mathbf{r}_j$, evolve according to

$$m_j\ddot{\mathbf{r}}_j = \mathbf{F}_j - \gamma m_j\dot{\mathbf{r}}_j + \varepsilon_j \tag{1}$$

where $\mathbf{F}_j$ is the inter atomic force acting on the jth particle, and m_j stands for ionic mass. The last terms on the right-hand side of (1) are the dissipation and fluctuation force, respectively. The dissipative forces are introduced to remove the heat generated in the system during the *ab initio* procedure, which is defined by the friction coefficient, γ, expressed as,

$$\gamma = \frac{\sum(\mathbf{F}_j\cdot\dot{\mathbf{r}}_j)}{\sum(m_j\dot{\mathbf{r}}_j^2)} \tag{2}$$

These differential equations (1) and (2) are called "Gauss' isothermal" equations of motion [13]. This procedure is one of the methods to keep the temperature of the system constant, as well as the Nosé thermostat. The fluctuation forces are defined by random Gaussian variables, $\boldsymbol{\varepsilon}_i$, which satisfy the following relation:

$$\langle\varepsilon_i^\alpha(t)\rangle = 0 \tag{3}$$

and

$$\langle\varepsilon_i^\alpha(t)\varepsilon_j^\alpha(t')\rangle = 2\gamma m_i k_B T\delta_{ij}\delta(t-t'). \tag{4}$$

The angular brackets denote statistical averages, and α stands for the Cartesian component. The coefficient of T on the right-hand side of (4) insures that the fluctuation–dispersion theorem is obeyed. Inter atomic forces can be obtained from Hellmann-Feynman theorem using the pseudopotential wave functions [13].

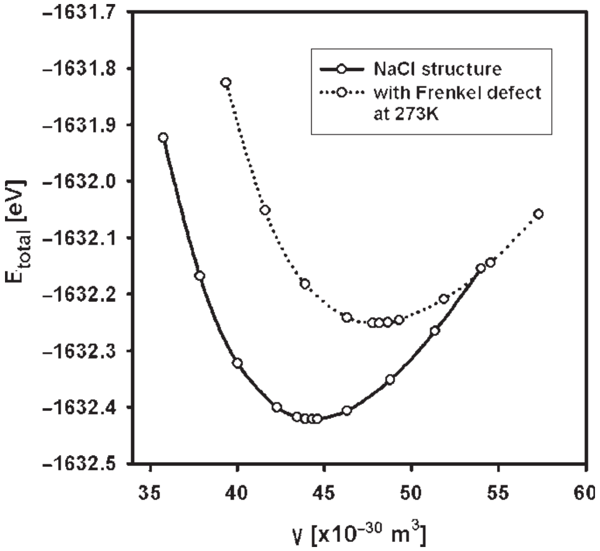

Figure 1. Variation of energy with volume per AgBr pair for two different ionic structure at 273 K.

The calculation has been performed for two different ion arrangements; i.e. the rock salt structure and the structure with a Frenkel defect changing its volume in various temperatures. In calculations we actually used the primitive cell containing eight atoms, i.e. four Ag and four Br, although in literature, the extremely limited number of atoms, e.g. two or three, are sometimes used in the total energy calculation of ionic crystals [14]. The calculated results of the total energy vs. the volume of the unit cell at 273 and 673 K, i.e. just below the melting temperature, are shown in figures 1 and 2, corresponding to pressures between −7.2 and 23.5 Gpa, and −7.8 to 22.2 Gpa, respectively. The structure with Frenkel defect has the minimum energy position in larger volume than the rock salt structure in both temperatures. The difference of the minimum of the total energy of both structures

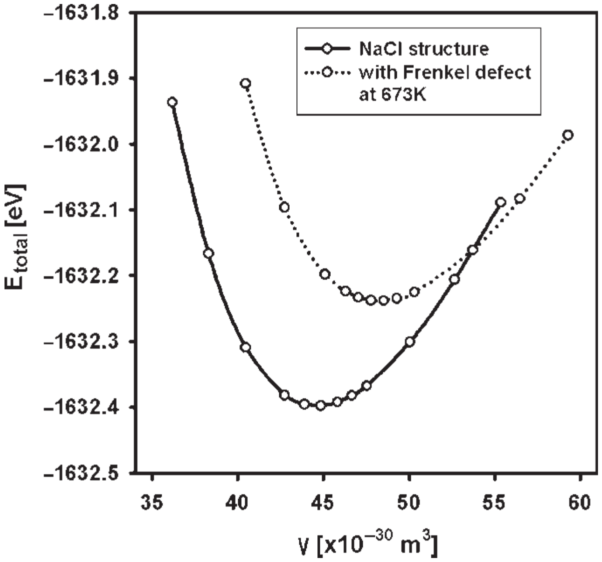

Figure 2. Variation of energy with volume per AgBr pair for two different ionic structure at 673 K.

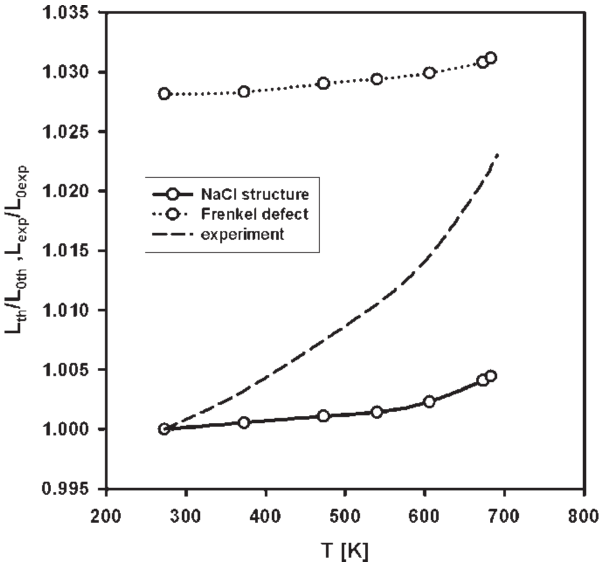

Figure 3. Temperature dependence of relative lattice constant for two different ionic structure with experimental data after Ref.5.

is 0.160(eV) in 673 K. These value are comparable to the enthalpy of migration of interstitials involved the non-collinear paths 0.278(eV) obtained by Aboagye and Friauf [6] using conductivity data. This fact suggests that the defect in the interstitial position is stable in larger volume, and can be easily occupied by migrating cations, that may promote the defect formation in the pre-melting region.

It can be observed that the energy minimum shifts to the larger volume with temperature increase. The obtained temperature dependence of the lattice constant is shown in figure 3 as the ratio to the value of rock salt structure at 273 K with experimental data after Ref.5. As is seen in figure 3, the curve of the experimental lattice change approaches from rock salt structure to that of the structure with defect. This fact means the fraction of the Frenkel defect gains as the temperature increase, which will be discussed in the following section.

4. The ratio of the defect formation

The theory of the lattice distortion in the crystals was developed by Frenkel [15]. In the theory of Frenkel, however, the defect formation of both cations and anions are equally assumed. To apply the theory to the present system AgBr, we modify the theory to the case that the deformation of cation is dominant, which will be summarized as follows.

In order to generalize the theory, we express the equi-charged binary salt as M^+X^-. In the statistical equilibrium state of the crystal, the number of holes N_h, the dislocated atoms N_d should be considered, which origins are from cations. N_h holes and N_d atoms are placed at the lattice site and at the interstitial sites, respectively. In other words, $N_0 - N_d$ cations randomly distribute at $N_0 - N_d + N_h$ sites in the crystal, where N_0 stands for the number of cations, i.e. the half number of the total atoms in the crystal N_t. The change of the volume of the crystal associated with the defect and hole formation is represented as,

$$\Delta V = N_d v_d - N_h v_h \tag{5}$$

where v_h is the volume contraction from the ideal crystal by formation of a hole and v_d is the volume expansion with the occupation by an atom in the interstitial site of the crystal. If the potential energy increase by the formation of one hole and one interstitial atom are expressed by U_h and U_d, respectively, then the additional energy is represented as,

$$\Delta W = N_h U_h + N_d U_d \tag{6}$$

The hole, i.e. the lack M^+ ion with positive charge $+e$, behave like a negative charge $-e$. The condition,

$$N_h = N_d \tag{7}$$

is required to ensure the charge neutrality of the whole crystal. This relation is also represented by the concentrations of holes and dislocated atoms, i.e. their number per unit volume, $n_h = N_h/V$ and $n_d = N_d/V$, respectively. In the case that the condition (7) is not satisfied, the crystal contains a charge per unit volume, as,

$$\rho = e(n_d - n_h) \tag{8}$$

The total free energy of these distortions is expressed as,

$$\begin{aligned} F &= F_d + F_h \\ &= N_d U_d - kT[\log N_0! - \log N_d! - \log(N_0 - N_d)!] \\ &\quad + N_h U_h - kT[\log N_0! - \log N_h! - \log(N_0 - N_h)!] \end{aligned} \tag{9}$$

By the condition of minimizing F and using equation (7), we obtain the relations, as,

$$N_d = N_0 \exp\left(\mu - \frac{U_d}{kT}\right) \tag{10a}$$

$$N_h = N_0 \exp\left(-\mu - \frac{U_h}{kT}\right) \tag{10b}$$

where μ is a Lagrange multiplier. By eliminating N_d and N_h using (7), we obtain

$$\mu = -\left(\frac{U_h - U_d}{2kT}\right) \tag{11}$$

In this case, the surface effect have to be considered where an uncompensated charge $-e$ remains, while a cation migrate into the interstitial of the crystal. If a total charge inside the crystal is,

$$Q = e(N_d - N_h) \tag{12}$$

then a charge $-Q$ remains on the surface of the crystal. These two charges give rise to an electrical field represented as ϕ, which produces an effect to restore the charge neutrality condition. Then the total potential energies for a hole and a dislocated atom are represented as $U_h - e\phi$ and $U_d + e\phi$, respectively. The volume concentration of holes and dislocated atoms are represented, as,

$$n_{\mathrm{d}} = n_0 \exp\left\{-\frac{(U_{\mathrm{d}} + \mathrm{e}\phi)}{kT}\right\} \tag{13a}$$

$$n_{\mathrm{h}} = n_0 \exp\left\{-\frac{(U_{\mathrm{h}} - \mathrm{e}\phi)}{kT}\right\} \tag{13b}$$

where $n_0 = N_0/V$.

The potential ϕ is determined by the Poisson's equation, as,

$$\nabla^2 \phi = -4\pi \frac{\rho}{\varepsilon} \tag{14}$$

Using equations (8), (13a) and (13b), equation (14) is reduced to

$$\nabla^2 \phi = -\left(\frac{4\pi \mathrm{e} n_0}{\varepsilon}\right) \times \left\{\exp\left(-\frac{(U_{\mathrm{d}} + \mathrm{e}\phi)}{kT}\right) - \exp\left(-\frac{(U_{\mathrm{h}} - \mathrm{e}\phi)}{kT}\right)\right\} \tag{15}$$

or,

$$\nabla^2 \varphi = \left(\frac{4\pi \mathrm{e}^2 n_0}{\varepsilon kT}\right) \exp\left(-\frac{(U_{\mathrm{d}} + U_{\mathrm{h}})}{2kT}\right) \{\exp(\varphi) - \exp(-\varphi)\} \tag{16}$$

$$\nabla^2 \varphi = \left(\frac{8\pi \mathrm{e}^2}{\varepsilon kT}\right) n_0 \exp\left(-\frac{(U_{\mathrm{d}} + U_{\mathrm{h}})}{2kT}\right) \sinh \varphi \tag{17}$$

where

$$\varphi = \frac{\mathrm{e}\phi}{kT} - \frac{\mathrm{U_h} - \mathrm{U_d}}{2kT}$$

equation (17) is corresponding to the Debye–Hückel theory, which determines the potential distribution in a solution of an electrolyte with the electrode playing the same role as the crystal surface.

In equation (17), the factor

$$n_0 \exp\left(\frac{-(U_{\mathrm{d}} + U_{\mathrm{h}})}{2kT}\right) \tag{18}$$

indicates the concentration of the pairs of the hole and interstitial atom.

Taking $U_{\mathrm{d}} + U_{\mathrm{h}}$ as W, i.e. the formation energy of the defect pair, and using (5) and (18), the "anomalous" volume change ΔV in lattice volume V due to the volume effect of defects formation is expressed as,

$$\frac{\Delta V}{V} = \left\{\frac{(N_{\mathrm{d}} v_{\mathrm{d}} + N_{\mathrm{h}}(-v_{\mathrm{h}}))}{V}\right\} = \{n_{\mathrm{d}} v_{\mathrm{d}} + n_{\mathrm{h}}(-v_{\mathrm{h}})\} = A \exp\left(\frac{-W}{2kT}\right) \tag{19}$$

where A is constant. If we assume $n_{\mathrm{d}} \sim n_{\mathrm{h}}$, then (19) is written as $\Delta V/V \sim n_{\mathrm{d}}\ (v_{\mathrm{d}} + (-v_{\mathrm{h}}))$. n_{d} is expected in proportion to the occupation probability in the interstitial site, in other words the probability of Frenkel defect formation, $P_{\mathrm{i}}(T)$, which may be expressed as a function of temperature. Therefore, we take $\Delta V/V$ is in proportion to $P_{\mathrm{i}}(T)$. Using obtained volume change in figure 3 with equation (19), we can evaluate the temperature dependence of $P_{\mathrm{i}}(T)$. Lawn [5] took ΔV as the deviation from linear temperature dependence. However, it is clearly observed that the lattice change is not linear even in the case of defect free rock salt structure. Therefore, we take ΔV as the volume change from rock salt structure to that with Frenkel defect obtained by *ab initio* calculation. The possible moving direction and the number of cations in the unit cell have been took into account. The obtained result is shown in figure 4. At 683 K, $P_{\mathrm{i}}(T)$ is estimated 0.020, which is comparable to the value 0.016 at 680 K obtained by Andreoni and Tosi [7]. A and W are also estimated to be 0.202 and 0.271(eV), respectively. The value of W is very close to the enthalpy of migration of interstitials 0.278(eV) calculated by Aboagye and Friauf [6]. The graph of A exp($-$ $W/2kT$) is also shown in figure 4. The agreement with $P_{\mathrm{i}}(T)$ is very well.

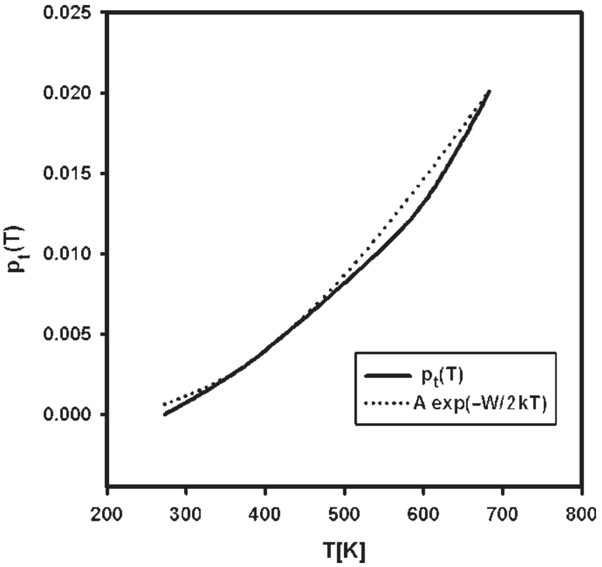

Figure 4. Occupation probability of cations on the interstitial site with fitting line.

5. Valence electron density

The hybridized orbit in noble-metal halides sometimes expressed as p–d hybridization. The electronic feature of AgBr is supposed to affect the structural and transport properties. Then it is of interest to obtain the electron density distribution in the pre-melting region. The calculation has been performed at 673 K for the rock salt structure and that with Frenkel defect. The calculated data are visualized with VENUS [16].

The obtained results of the valence electron distribution for the rock salt structure and that with Frenkel defect at 673 K are shown in figures 5 and 6, respectively. The electron density is also drown on the "sliced" surface (0 1 0) and (0 2 2) in figures 5 and 6, respectively.

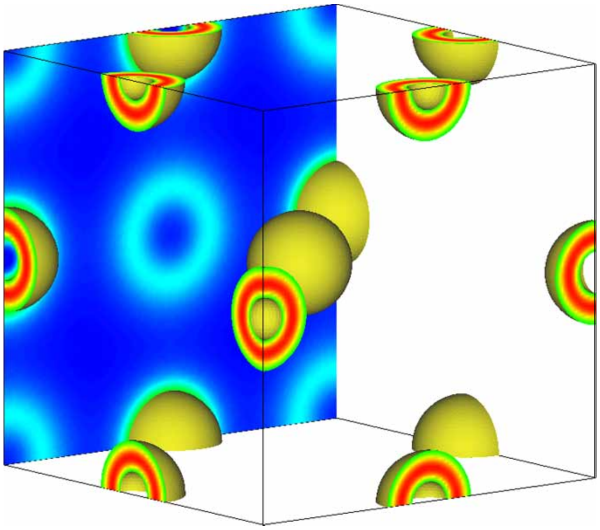

Figure 5. Valence electron distribution in the rocksalt structure.

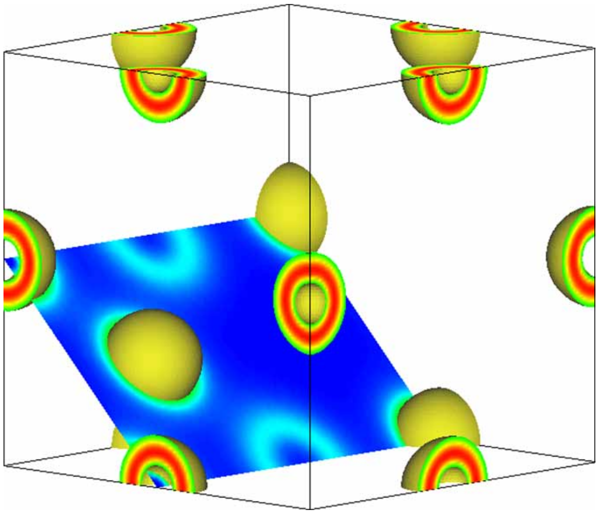

Figure 6. Valence electron distribution in the structure with Frenkel defect.

The density is expressed as grading color; higher density position corresponds to red. The equi-density surfaces are drawn on 0.345 of the maximum density, which surround Ag ions. As is seen in these figures, Ag ions are also surrounded by high density distribution of 4d electrons. In the vicinity of ions, the depletion regions are seen, which means the absence of "core" electrons in the calculation. The overlap of the density distributions is observed between the different kind ions. These features are resembles to the radial distribution and the density distributions on the (1 0 0) plane obtained by Takahashi *et al.* using X-ray diffractometry [17]. As is seen in figure 6, it is very interesting that the electron density overlap between different ions is pronounced especially around the interstitial silver ion, which suggests the formation of the hybridized orbital between them. This fact may cause the stability of interstitial ions and Frenkel defects in the pre-melting region.

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