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# Residence time and density distribution of silver ions in $\alpha$-$Ag_2Te$ by molecular-dynamics simulation

F. Tachibana
*Information Processing Center, Niigata University, Niigata 950-21, Japan*

M. Kobayashi
*Department of Physics, Niigata University, Niigata 950-21, Japan*

H. Okazaki
*General Education Department, Niigata University, Niigata 950-21, Japan*

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A silver-ion diffusion in $\alpha$-$Ag_2Te$ is investigated by a molecular-dynamics method introducing a polyhedron analysis. The microscopic picture for the diffusion process of silver ions is obtained by studying the ratio of the residence time of silver ions in octahedra, $\tau_O$, to that in tetrahedra, $\tau_T$. The temperature dependence of $\tau_O/\tau_T$ is expressed as the Arrhenius formula with an activation energy of 0.18 eV.

## I. INTRODUCTION

Recently we have applied a molecular-dynamics (MD) method to the study of silver diffusion in the superionic conductor $Ag_2Te$.[1] We have calculated the structure and dynamical properties, such as the radial distribution functions, density distribution of Ag ions, self-diffusion coefficient of Ag ions, ionic conductivity, Haven's ratio, and activation energy for ionic diffusion and have shown that these quantities were in good agreement with experiments.

In this paper we perform further studies on the diffusion process of the Ag ion in $\alpha$-$Ag_2Te$ by making use of a MD method. To obtain microscopic information on the diffusion process of Ag ions, we introduce a polyhedron analysis method. The anion fcc sublattice is divided into tetrahedra and octahedra, and cations diffuse among these polyhedra. A detailed study of the diffusion mechanism is conducted by calculating a residence time in each polyhedron.

The simulation method is the same as that in the previous paper.[1] The calculation is performed for a 324-particle system, which is composed of 3×3×3 fcc cubes. In order to avoid surface effects, periodic boundary conditions are imposed on the system. We use the following interaction potentials constructed with two terms, a soft-core repulsive potential and a Coulomb potential,

$$\phi(r_{ij}) = A(\sigma_i+\sigma_j)^n/r_{ij}^n + z_i z_j e^2/r_{ij} , \tag{1}$$

where $A$ is the repulsive strength, $\sigma_i$ and $z_i$ are the ionic radius and the effective valency of the $i$th ion, respectively. $r_{ij}$ is the distance between the $i$th and $j$th ions, and $e$ is the elementary charge.

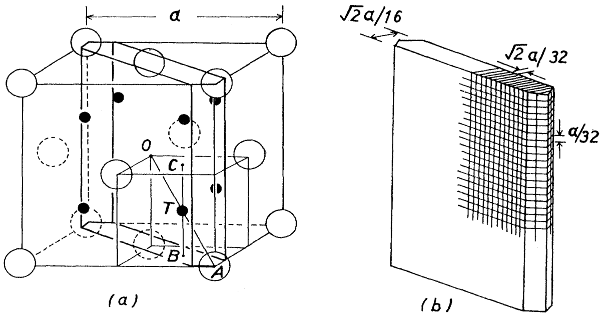
The establishment of the values of the parameters were given in the previous paper[1] and are as follows,

$$\sigma_{Te}=2.21\ \text{Å},\quad \sigma_{Ag}=0.65\ \text{Å} ,$$
$$A=0.1\ \text{eV},\quad z_{Te}=-2z_{Ag}=-1.1 ,$$
$$n=7 .$$

The Ewald method is used to calculate the Coulombic force, and the electrostatic energies are tabulated to reduce the time needed for calculations.[2] For the calculation of average quantities of interest, 12 000 time steps in units of $0.93\times10^{-14}$ s are performed.

## II. SILVER DENSITY DISTRIBUTION

The fcc tellurium lattice is used as a reference frame to study the distribution of silver ions in the unit cell. The most interesting region is the (110) plane of the lattice. We consider a block of thickness $\sqrt{2}a/16$ ( $=0.58$ Å, $a$ the lattice constant). This is shown by bold lines in Fig. 1(a) and is divided into 32×32 rectangular pieces of dimension $(\sqrt{2}a/32)\times(a/32)$, as shown in Fig. 1(b). The number of Ag ions included in each piece is calculated and is averaged over time. Points $T$ and $O$ are the tetrahedral and octahedral sites, respectively. The densi-



(a) (b)

FIG. 1. Antifluorite structure. Open circles show the fcc anion lattice sites and solid circles, the tetrahedral sites. Points $O$ and $B$ (equivalent to $C$) denote the octahedral site and midpoint of the neighboring two tetrahedral sites, respectively. The calculation of Ag-ion density on the (110) plane is carried out in the region surrounded by the bold lines.

ty distributions of Ag ions on the (110) plane and $(\frac{1}{4}00)$ plane at 850 K have been shown in the previous paper.[1] Here we investigate the temperature dependence of the Ag-ion density along the lines *A-T-O* and *B-T-C* in Fig. 1(a). The results are shown in Fig. 2, which shows that the Ag-ion density at the tetrahedral site, $\rho_T$, decreases markedly with increasing temperature, while that at the octahedral site, $\rho_O$, increases slightly with increasing temperature. The Ag-ion density at point *B* (or *C*) is almost zero for any temperatures. These results show that a Ag ion does not move from one tetrahedral site to another directly, but moves to its neighboring tetrahedral site through the vicinity of the octahedral site. This result is similar to the experiments of Sakuma and Saitoh.[3] They have shown that, in a unit cell at 250 °C, 5.18 Ag ions distribute on eight tetrahedral sites with equal probabilities with a strong unharmonic oscillation and remaining 2.82 Ag ions distribute on 32 $(f)$ sites which are located at $x=0.422l$ from the octahedral site, $l$ being a distance between a tetrahedral and an octahedral site.

One of us, Okazaki,[4] has explained the Haven's ratio of $\alpha$-$Ag_2Te$ by the caterpillar mechanism theory[5] of a Ag ion under the assumptions that the Ag ions are statistically distributed on the 12 available sites (eight tetrahedral sites and four octahedral sites) and that they jump along the zigzag lines consisting of alternating tetrahedral and octahedral sites in the (110) plane. The Ag-ion distribution obtained by the present work supports his assumption.

$Ag_2Te$ has essentially an antifluorite structure, as discussed in the above paragraph. Thus, it is interesting to compare the results of $Ag_2Te$ with those of fluorite-type superionic conductors, such as $CaF_2$, $PbF_2$ and $SrCl_2$, obtained by MD calculations. Rahman[6] performed a MD calculation for $CaF_2$, assuming a Kim-Gordon potential[7] as the short-range repulsion. Gillan and co-workers investigated anion diffusion in $CaF_2$,[8,9] $SrCl_2$,[10] and $PbF_2$,[11,12] assuming a Born-Mayer-Huggins potential. Recently Kaneko and Ueda[13] applied the a softcore potential to study the influence of their potential on anion diffusion in $CaF_2$. In any case, their simulation studies suggest that mobile anions do not occupy octahedral sites in the superionic phase and that diffusion occurs by direct jumps between the tetrahedral sites. For example, in $PbF_2$ (Ref. 11) 92% of the anion jumps occur in the [100] direction, 8% in the [110], and less than 1% in the [111]. Both in $SrCl_2$ (Ref. 10) and $CaF_2$,[13] more than 80% of the jumps occur in the [100], about 10% in the [110], and only a few percent in the [111] direction.

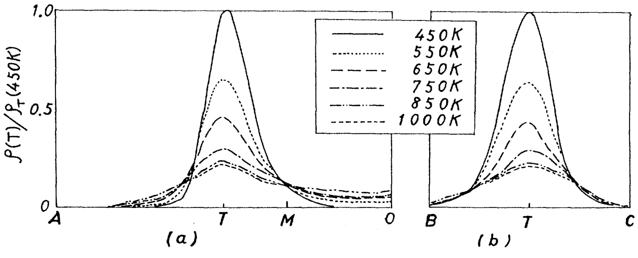


FIG. 2. Temperature dependence of the Ag-ion density along the lines *A-T-O* and *B-T-C*, normalized by the density at the *T* site at $T=450$ K. The lines *A-T-O* and *B-T-C* are shown in Fig. 1.

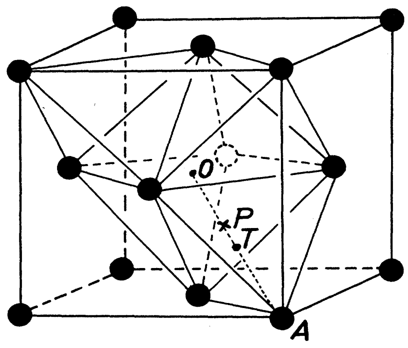


FIG. 3. Tetrahedra and octahedra in fcc anion sublattice. Points *O* and *T* denote the octahedral site and tetrahedral site, respectively. Point *P* lies on the triangular interface sharing a tetrahedron and an octahedron. The distance $\overline{AP}$ is two-thirds of $\overline{AO}$.

It should be noticed that there is a great difference in the effective size of mobile ions between $Ag_2Te$ and fluorite-type materials. Let us consider the ratio $\gamma$ of the ionic radius of an immobile ion to that of a mobile ion. If we use the values of the ionic radii by Pauling, the ratio $\gamma$ is about unity for $PbF_2$, $SrCl_2$, and $CaF_2$ and 1.6 for $Ag_2Te$. For the present MD calculations we take $\gamma=3.4$. A high value of $\gamma$ will offer a space which is available for diffusion. Furthermore, the mass ratios of these materials are $m_{Ag}/m_{Te}=0.845$, $m_F/m_{Pb}=0.092$, $m_{Cl}/m_{Sr}=0.405$, and $m_F/m_{Ca}=0.474$. Then it is reasonable to say that the difference in both the ratio $\gamma$ and mass ratio give an influence on the dynamical properties of these materials: diffusing path, ionic conductivity, etc. These discussion have been given in the previous paper[1] and also by Kaneko and Ueda.[13]

There is a peculiar point (denoted by *M* in Fig. 2) at which the Ag density keeps a constant value for several temperatures. It is interesting that the point *M* is very close to the point *P* shown in Fig. 3, which is the center of the triangle sharing the tetrahedron and octahedron.

## III. POLYHEDRON ANALYSIS AND RESIDENCE TIME

For a microscopic study of silver-ion diffusion, we introduce a polyhedron analysis, which divides the fcc sublattice into tetrahedra and octahedra. As shown in Fig. 3, each tetrahedron shares faces with four octahedra, while each octahedron shares faces with eight tetrahedra. The tetrahedra and octahedra share edges with each other. Thus a cation inside a tetrahedron diffuses into an octahedron through the triangular interface shared by them.

In the previous paper,[1] we have calculated the mean-square displacement (MSD) for Te and Ag ions at several temperatures. It is shown that the MSD of Ag ions increases with time, whereas that of Te ions remains nearly constant, and also that the value of the self-diffusion

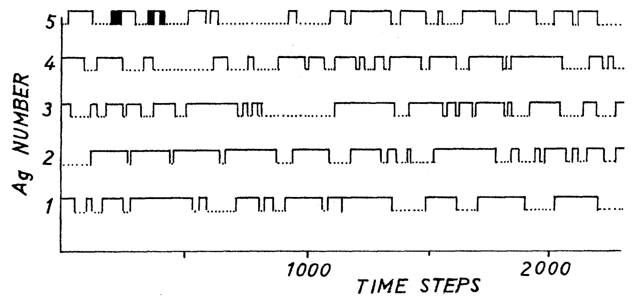


FIG. 4. Trace of the diffusion of a Ag ion for 2500 time steps at 850 K. Solid and dashed lines mean that each Ag ion resides in a tetrahedron and in an octahedron, respectively.

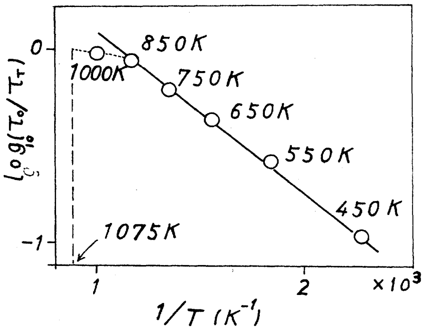


FIG. 6. Plots of $\log_{10}(\tau_O/\tau_T)$ vs $1/T$. From the gradient of the straight line, "activation energy" $\Delta\varepsilon$ is estimated as 0.18 eV.

coefficient of the Ag ion obtained by the MSD agrees well with experimental one, which gives a large liquidlike self-diffusion coefficient. From the MSD of ions and the density distribution of Ag ions derived in the preceding section, it is clarified that a Ag ion moves from a tetrahedron into its neighboring octahedron through the triangular interface between them and vice versa. That is, a diffusion path of a Ag ion is composed of alternating tetrahedra and octahedra.

In Fig. 4, the diffusion traces at 850 K are shown for several Ag ions which are picked up randomly. The solid line and the dashed line show that a Ag ion is in a tetrahedron and in an octahedron, respectively. We see that the residence time in tetrahedra is relatively longer than that in octahedra. There are a few blackened areas in Fig. 4. In these sections a Ag ion vibrates frequently between a tetrahedron and its nearest-neighbor octahedron in an extremely short time interval.

Next we calculate the sum of the residence time of the $i$th Ag ion in the tetrahedra, $\tau_T(i)$, and also that in the octahedra, $\tau_O(i)$, in all time steps $\tau$ [that is, $\tau=\tau_T(i)+\tau_O(i)$]. In Fig. 5, the distributions of $\tau_T(i)/\tau$ are shown for six temperatures. When the mean values of $\tau_T(i)$ and $\tau_O(i)$ are denoted as $\tau_T$ and $\tau_O$, respectively, it is found that $\tau_T > \tau_O$ and $\tau_T$ decreases with increasing temperature.

When we denote the probability that a Ag ion is found in the tetrahedra as $p_T$ and in the octahedra as $p_O$, respectively, the ratio $p_O/p_T$ is equal to $\tau_O/\tau_T$ and is proportional to $\exp(-\Delta\varepsilon/k_BT)$. Here $\Delta\varepsilon$ denotes the potential difference between $O$ and $T$ sites. As shown in Fig. 2, the change of cation density is monotonic along the $T$-$O$ line. Then the potential difference $\Delta\varepsilon$ may be regarded as nearly the "activation energy" for ionic conduction.

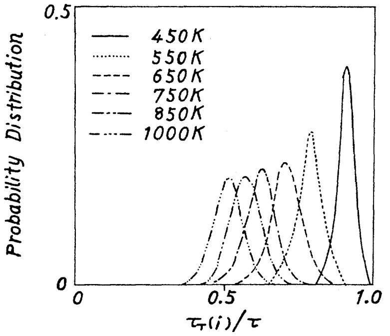


FIG. 5. Probability distribution that each Ag ion resides in tetrahedra in all time steps $\tau$ at six temperatures.

In Fig. 6, $\log_{10}(\tau_O/\tau_T)$ versus $1/T$ is shown at six temperatures. From the gradient of the straight line in the figure, the value of $\Delta\varepsilon$ is estimated as 0.18 eV, which is almost the same as that derived from the temperature dependence of the diffusion constant.[1] This value is in good agreement with the experimental value, 0.14 eV.[14]

In Fig. 6, the value of $\log_{10}(\tau_O/\tau_T)$ at 1000 K deviates from the other five values. Since tetrahedral sites are more stable positions for cations than octahedral sites in an anion fcc sublattice, the ratio $\tau_O/\tau_T$ cannot exceed unity as far as Ag ions diffuse in fcc framework even if the ratio extremely approaches unity with increasing temperature. When we extrapolate to a high-temperature region with a dashed line in Fig. 6, the value of $\log_{10}(\tau_O/\tau_T)$ becomes 0 at 1075 K. Unexpectedly, this temperature agrees with that of the structural phase transition of $Ag_2Te$ from fcc to bcc. Thus, if the MD calculation is performed under the condition which permits a structural phase transition, i.e., if the constant-volume

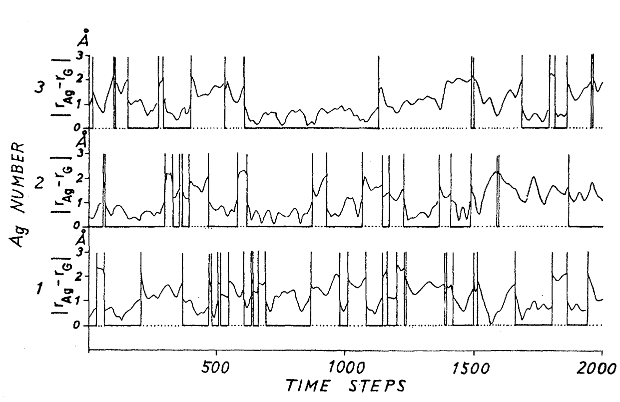


FIG. 7. Traces of the distance between the Ag ion in a polyhedron and the center of gravity of its polyhedron in 2000 time steps. Solid and dashed lines on the abscissa mean that the Ag ion is in a tetrahedron and in an octahedron, respectively.

condition is replaced by the constant-pressure one, all values of $\log_{10}(\tau_O/\tau_T)$ at six temperatures may be put on a straight line which has a more gentle slope than that shown in Fig. 6. However, in any case, the study of a structural phase transition is impossible within the framework of the usual MD technique in which a constant volume of a system is fixed. Then it is inappropriate to refer to the physical properties near 1000 K by our method.

In order to see the microscopic behavior of a Ag ion in a tetrahedron and an octahedron, we calculate the distance between the Ag ion in a polyhedron and the center of gravity of its polyhedron. In Fig. 7, the distance $|\mathbf{r}_{\mathrm{Ag}}-\mathbf{r}_G|$ is shown for several Ag ions in 2000 time steps at 850 K. Here $\mathbf{r}_{\mathrm{Ag}}$ is the coordinate of the Ag ion in a polyhedron and $\mathbf{r}_G$ is that of the center of gravity of its polyhedron. The full line and the broken line on the abscissa show that the Ag ion is in a tetrahedron and in an octahedron, respectively. From this figure, it is clarified that a Ag ion stays in each polyhedron with vibrational motion for hundreds of time steps and the distance $|\mathbf{r}_{\mathrm{Ag}}-\mathbf{r}_G|$ in a tetrahedron is relatively shorter than that in an octahedron.

To summarize, the microscopic picture for the diffusion process of Ag ion in $\alpha$-$Ag_2Te$ has been obtained by studying the ratio of the residence time of Ag ion in octahedra to that in tetrahedra. The temperature dependence of the ratio has been expressed as the Arrhenius formula and has given us 0.18 eV to the value of the activation energy for ionic conduction.

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