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## Correlation factor of tracer diffusion in $\alpha$ -Ag<sub>2</sub>Te

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**Abstract.** The formula for the correlation factor in tracer diffusion has been derived by a simple and elementary calculation in the case where the diffusion takes place by ions jumping alternately between two kinds of site with equal spacing. The correlation factors for the vacancy and interstitialcy mechanisms are deduced from this formula. The formula has been applied to  $\alpha$ -Ag<sub>2</sub>Te in which Ag ions diffuse by changing alternately between octahedral sites and tetrahedral sites in the anion FCC sublattice.

### 1. Introduction

$\alpha$ -Ag<sub>2</sub>Te is a prototype superionic conductor [1, 2] and is stable between 145 and 802 °C with the FCC structure of Te ions. The FCC structure is divided into two kinds of polyhedron as shown in figure 1: a tetrahedron and an octahedron. Recent results of a molecular dynamics (MD) calculation for  $\alpha$ -Ag<sub>2</sub>Te [3–5] reveal that Ag ions move from a tetrahedron to an octahedron and vice versa through their shared triangular interfaces (see figure 1). No direct movement from tetrahedron to tetrahedron through the edge of the polyhedron takes place. The density distribution of Ag ions on the (110) plane has a maximum at the tetrahedral site (T site) and decreases monotonically towards the octahedral site (O site) [5]. In the octahedron, however, the density of Ag ions is nearly constant and shows no peak at the O site. This suggests that an Ag ion inside the tetrahedron sits at the T site and moves vibrationally with a large amplitude, while an Ag ion inside the octahedron moves diffusively. The above interpretation is consistent with the result of an x-ray diffraction study carried out by Sakuma and Saitoh [6]. They carried out a crystallographic study of  $\alpha$ -Ag<sub>2</sub>Te at 250 °C and interpreted the observed Debye line intensities with a model in which some of the Ag ions, five-eighths, in a unit cell occupy the 8c sites (T sites) and vibrate in an asymmetric anharmonic potential and the remaining Ag ions, three-eighths, are distributed over the 32f sites located near the 4b sites (O sites) and oscillate harmonically with a large amplitude, where 8c, 32f and 4b indicate the multiplicities and codes of the Wyckoff positions in the crystal structure [7]. Considering the situation stated above, we regard the migration of an Ag ion from a tetrahedron to an octahedron (and vice versa) as a jump from a T site to a point (e.g. a 32f site) inside the octahedron (and vice versa). Then the ordinary diffusion theory for solids can be applied to superionic conductors such as  $\alpha$ -Ag<sub>2</sub>Te.

Usually two kinds of mechanism are predominant for diffusion in solids [8–10]. One is the vacancy mechanism and the other is the interstitialcy mechanism. When

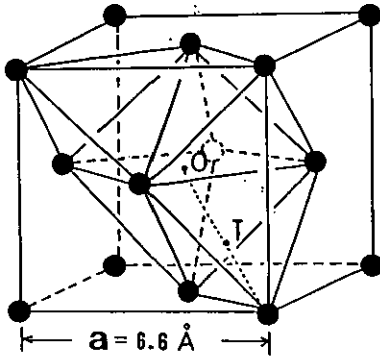


Figure 1. Tetrahedra and octahedra formed by FCC anions. The points T and O denote the tetrahedral site and octahedral site, respectively.

it is considered that the T site is the normal site and the O site is the interstitial site, the interstitialcy mechanism seems to be applicable to  $\alpha\text{-Ag}_2\text{Te}$ . The interstitialcy mechanism is applicable only when the concentration of interstitial ions is so small that interstitial ions are isolated from each other. However, for  $\alpha\text{-Ag}_2\text{Te}$  the concentration of interstitial ions is as large as that of the normal ions, and the normal ions are also as mobile as the interstitial ions. Since there is a strong interaction between mobile ions, there is a strong correlation in all successive jumps between T and O sites.

The correlation factor  $f$  is related to the tracer diffusion coefficient  $D_T$ , its jump frequency  $\Gamma_T$  and the jump distance  $r_T$  by the following equation [8–10]:

$$f = 6D_T/\Gamma_T r_T^2 \quad (1)$$

where the subscript T indicates that the quantities are related to the tracer. In  $\alpha\text{-Ag}_2\text{Te}$ ,  $r_T$  is undefined because of the diffusive motion of Ag ions in the octahedron. If we obtain the expression for  $f$  and the values of  $D_T$  and  $\Gamma_T$ , then  $r_T$  is inversely evaluated using equation (1). In the next section we derive, in a simple and elementary way, the expression for  $f$  for diffusion when the ion jumps alternately between two kinds of site separated by  $r$ . The result is applied to  $\alpha\text{-Ag}_2\text{Te}$  in section 3 using MD data. Some discussion on  $r$  and other parameters is given in section 4.

## 2. Derivation of correlation factor

The correlation factor  $f$  is defined as

$$\langle R_n^2 \rangle = n r^2 f \quad (2)$$

where  $R_n$  is the total displacement vector of a diffusing ion after  $n$  jumps, in which the jump distance in each jump is  $r$ . The angular brackets  $\langle \rangle$  mean the average for many diffusing ions. When the diffusing ion moves alternately between two kinds of site (A site and B site),  $R_n$  is composed of two kinds of jump. We denote a jump from the A site to the B site as an  $\alpha$  jump and from the B site to the A site as a  $\beta$  jump. Then  $R_n$  is expressed when the jump starts from the A site as

$$R_n = r_1^\alpha + r_2^\beta + r_3^\alpha + \dots + r_n' \quad (3)$$

where  $r'_n$  means  $r_n^\alpha$  or  $r_n^\beta$  depending on whether  $n$  is odd or even. When  $|r^\alpha| = |r^\beta| = r$  and  $n$  is even, the mean square  $\langle R_n^2 \rangle$  of  $R_n$  is written as

$$\langle R_n^2 \rangle = nr^2 \left[ 1 + \frac{2}{n} \left( \sum_{i < j}^{\text{odd odd}} \langle \cos \theta_{i,j} \rangle_{\alpha\alpha} + \sum_{i < j}^{\text{odd even}} \langle \cos \theta_{i,j} \rangle_{\alpha\beta} + \sum_{i < j}^{\text{even odd}} \langle \cos \theta_{i,j} \rangle_{\beta\alpha} + \sum_{i < j}^{\text{even even}} \langle \cos \theta_{i,j} \rangle_{\beta\beta} \right) \right] \tag{4}$$

where  $\theta_{i,j}$  is the angle between the two vectors  $r_i$  and  $r_j$ ,  $\langle \cos \theta_{i,j} \rangle_{pq}$  denotes the average of  $\cos \theta_{i,j}$  where the  $i$ th jump and  $j$ th jump are a  $p$  jump and a  $q$  jump, respectively ( $p, q \equiv \alpha$  or  $\beta$ ), and  $\sum^{\text{odd}}$  and  $\sum^{\text{even}}$  denote that the summations are carried out for the odd-number jump ( $\alpha$  jump) and for the even-number jump ( $\beta$  jump), respectively. On comparison of equation (4) with equation (2),  $f$  is equal to the terms in the square brackets on the right-hand side of equation (4).

Considering the relations

$$\langle \cos \theta_{i,j} \rangle = \langle \cos \theta_{i,i+1} \rangle \langle \cos \theta_{i+1,i+2} \rangle \dots \langle \cos \theta_{j-1,j} \rangle \tag{5}$$

$$\langle \cos \theta_{i,i+1} \rangle = \langle \cos \theta_{i+2,i+3} \rangle = \dots \tag{6}$$

and

$$\langle \cos \theta_{i+1,i+2} \rangle = \langle \cos \theta_{i+3,i+4} \rangle = \dots \tag{6'}$$

we have

$$\langle \cos \theta_{i,j} \rangle = \begin{cases} (t_1 t_2)^{(j-1)/2} & \text{for odd } j \\ t_1 (t_1 t_2)^{(j-i-1)/2} & \text{for even } j \end{cases} \tag{7}$$

where  $\langle \cos \theta_{i,i+1} \rangle = t_1$  and  $\langle \cos \theta_{i+1,i+2} \rangle = t_2$ . Using equations (5)–(7), the first term in the parentheses in equation (4) is expressed as follows:

$$\frac{2}{n} \left( \sum_{i < j}^{\text{odd odd}} \langle \cos \theta_{i,j} \rangle_{\alpha\alpha} \right) = \frac{2}{n} \sum_i^{n/2-1} \binom{n}{2-i} (t_1 t_2)^i =_{(n \rightarrow \infty)} \frac{t_1 t_2}{1 - t_1 t_2}. \tag{8}$$

By a similar calculation for the remaining three terms in the parentheses in equation (4), the following expressions are obtained:

$$\frac{2}{n} \left( \sum_{i < j}^{\text{odd even}} \langle \cos \theta_{i,j} \rangle_{\alpha\beta} \right) = \frac{t_1}{1 - t_1 t_2} \tag{9}$$

$$\frac{2}{n} \left( \sum_{i < j}^{\text{even odd}} \langle \cos \theta_{i,j} \rangle_{\beta\alpha} \right) = \frac{t_2}{1 - t_1 t_2} \tag{10}$$

and

$$\frac{2}{n} \left( \sum_{i < j}^{\text{even even}} \langle \cos \theta_{i,j} \rangle_{\beta\beta} \right) = \frac{t_1 t_2}{1 - t_1 t_2}. \tag{11}$$

By substituting equations (8)–(11) into equation (4),  $f$  is finally expressed as

$$f = (1 + t_1)(1 + t_2)/(1 - t_1 t_2). \quad (12)$$

This equation is derived as a special case of the formula given by LeClaire [9]. He considered jumps between sublattice 1 and those between sublattice 2 in addition to those between sublattice 1 and sublattice 2 and gave the formula

$$f = \{(1 + t^{21})(1 + t^{12}) - t^{11}t^{22}\} / \{(1 - t^{11})(1 - t^{22}) - t^{12}t^{21}\} \quad (13)$$

where  $t^{xy}$  is the average of  $\cos \theta$  for jumps between sublattice  $x$  and sublattice  $y$ . In  $\alpha\text{-Ag}_2\text{Te}$ , jumps between T sites and jumps between O sites are not observed; so we obtain equation (12) by putting  $t_{11} = t_{22} = 0$  in equation (13).

From equation (12) is deduced the following equation for the vacancy mechanism by putting  $t_1 = t_2 = t$ :

$$f = (1 + t)/(1 - t) \quad (14)$$

which is also found in [8, 9]. For the interstitialcy mechanism, from equation (12) the equation

$$f = 1 + t \quad (15)$$

can also be deduced [9, 10] by putting  $t_1 = t$  and  $t_2 = 0$  or  $t_1 = 0$  and  $t_2 = t$ , since the tracer jumps from interstitial sites to normal sites are stochastic processes (i.e.  $\langle \cos \theta \rangle = 0$ ) while those from normal sites to interstitial sites are correlated with preceding jumps. Equation (15) is also given in [9].

### 3. Application to $\alpha\text{-Ag}_2\text{Te}$

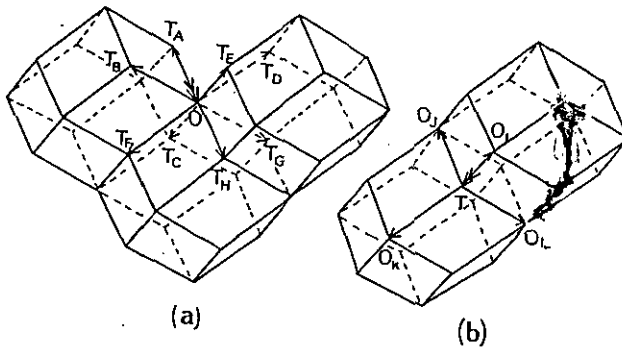
In this section,  $f$ ,  $\Gamma_T$  and  $D_T$  in equation (1) are evaluated utilizing the MD calculation data obtained by the present authors and their co-workers. Here, the description of the MD calculation of  $\alpha\text{-Ag}_2\text{Te}$  is omitted and the readers may refer to previous papers [3, 4].

#### 3.1. Evaluation of $f$

If we consider the crystallographic arrangement of T sites and O sites as shown in figure 2(a) and denote the jump from a T to an O site as an  $\alpha$  jump and a jump from an O to a T site as a  $\beta$  jump,  $t_1$  in equation (12) can be expressed as

$$t_1 = p_A \cos \theta_A + p_B \cos \theta_B + p_C \cos \theta_C + p_D \cos \theta_D \\ + p_E \cos \theta_E + p_F \cos \theta_F + p_G \cos \theta_G + p_H \cos \theta_H. \quad (16)$$

Here  $p_X$  ( $X \equiv \text{A-H}$ ) represents the probability that an Ag ion on an O site jumps to any one of its eight neighbouring T sites.  $\theta_X$  is the angle between the successive two jumps of the Ag ion: an  $\alpha$  jump and a  $\beta$  jump (figure 2(a)). For example when the Ag ion on the O site came from the  $T_A$  site (the double arrow in figure 2(a)) and jumps to the  $T_X$  site (the single arrows in figure 2(a)), the probabilities  $p_A$  to  $p_H$  cited



**Figure 2.** Crystallographic arrangement of T and O sites in  $\alpha\text{-Ag}_2\text{Te}$ . (a) The double arrow shows an  $\alpha$  jump of an Ag ion from a T to an O site and the single arrows show the next  $\beta$  jumps from O to T sites after the  $\alpha$  jump. (b) The double arrow shows a  $\beta$  jump of an Ag ion from an O to a T site and the single arrows show the next  $\alpha$  jumps from T to O sites after the  $\beta$  jump.

**Table 1.** Summary of quantities obtained from the MD work. The meaning of quantities in the first column is given in the text.

Quantity	Value at the following temperatures				
	550 K	650 K	750 K	850 K	1000 K
$p_A$	0.829	0.772	0.695	0.653	0.597
$p_B (= p_C = p_D)$	0.047	0.060	0.077	0.084	0.096
$p_E (= p_F = p_G)$	0.008	0.013	0.019	0.025	0.030
$p_H$	0.006	0.009	0.017	0.020	0.025
$t_1$	-0.862	-0.810	-0.736	-0.692	-0.638
$p_I$	0.313	0.337	0.340	0.331	0.328
$p_J (= p_K = p_L)$	0.229	0.221	0.220	0.223	0.224
$t_2$	-0.084	-0.116	-0.120	-0.108	-0.104
$f$	0.136	0.185	0.255	0.297	0.347
$\langle r \rangle / \tau_0$	0.82	0.88	0.88	0.92	0.95

in table 1 are obtained by the MD simulation. The probability  $p_A$  of the backward jump is much greater than the probabilities  $p_B$  to  $p_H$  in the other directions and decreases with increasing temperature. It is interesting to note that the probability  $p_H$  of a forward jump is the smallest.

In a similar way,  $t_2$  is written as

$$t_2 = p_I \cos \theta_I + p_J \cos \theta_J + p_K \cos \theta_K + p_L \cos \theta_L. \quad (17)$$

The quantities  $p_I$  to  $p_L$  and  $\theta_I$  to  $\theta_L$  have the same meanings as those in equation (16) (figure 2(b)). When an Ag ion on a T site comes from the  $O_I$  site (the double arrow in figure 2(b)), the probabilities  $p_I$  to  $p_L$  in table 1 are found. In this case, the backward jump probability  $p_I$  is slightly greater than the probabilities  $p_J$  to  $p_L$  in the other three directions and is almost constant with variation in temperature. Considering the results given in table 1 we see that an Ag ion in a tetrahedron moves to its four neighbouring octahedra with nearly equal probabilities. However, an Ag ion in an octahedron has a tendency to return to the tetrahedron in which it was previously located. This means that there is a weak correlation in successive jumps

from octahedron to tetrahedron and from tetrahedron to octahedron and there is a strong correlation in successive jumps from tetrahedron to octahedron and from octahedron to tetrahedron.

Substituting the values of  $t_1$  and  $t_2$  into equation (12) the values of  $f$  were evaluated as shown in table 1. The temperature dependence of  $f$  is shown in figure 3.

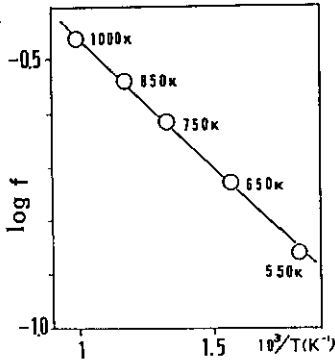


Figure 3. Log  $f$  versus  $1/T$ .

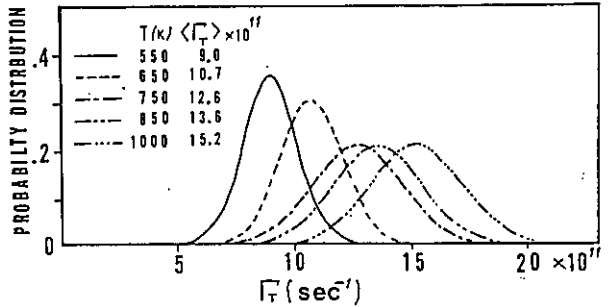


Figure 4. Probability distributions of  $\Gamma_T$  at five temperatures. The average values  $\langle \Gamma_T \rangle$  of  $\Gamma_T$  at each temperature are given in the upper left-hand side of the figure.

### 3.2. Jump frequency and diffusion coefficient

$\Gamma_T$  which appeared in equation (1) is obtained by counting the number of jumps of ions between the tetrahedron and the octahedron in a unit of time. As the values of  $\Gamma_T$  are different from ion to ion,  $\Gamma_T$  has a distribution as shown in figure 4. When we denote the mean value of  $\Gamma_T$  as  $\langle \Gamma_T \rangle$ , the temperature dependence of  $\langle \Gamma_T \rangle$  is expressed by the Arrhenius-type formula

$$\langle \Gamma_T \rangle = \Gamma_0 \exp(-\epsilon_T/k_B T) \tag{18}$$

with  $\Gamma_0 = 16.2 \times 10^{11} \text{ s}^{-1}$  and  $\epsilon_T = 0.06 \text{ eV}$  (figure 5). Here,  $k_B$  and  $T$  represent the Boltzmann constant and temperature, respectively.

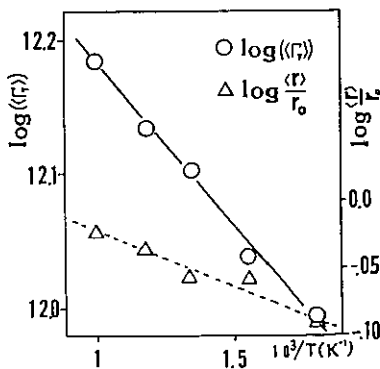


Figure 5. Log  $\langle \Gamma_T \rangle$  and log  $(r/r_0)$  versus  $1/T$ .

The diffusion coefficient  $D_T$  obtained from the MD calculation is expressed by the Arrhenius-type formula

$$D_T = D_0 \exp(-\epsilon_D/k_B T) \quad (19)$$

with  $D_0 = 3.9 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$  and  $\epsilon_D = 0.17 \text{ eV}$ .  $\epsilon_D$  is larger than the experimental value of 0.14 eV obtained by Okazaki [11].

The jump distance  $r$  of a cation may also differ for every jump. By introducing the average  $\langle r \rangle$  of  $r$ , we may consider that the cation diffusion in  $\alpha$ -Ag<sub>2</sub>Te takes place by the jump mechanism with a constant jump distance  $\langle r \rangle$  and a jump frequency  $\langle \Gamma_T \rangle$ , and we can use equations (1) and (2) by putting  $\langle \Gamma_T \rangle$  and  $\langle r \rangle$  instead of  $\Gamma_T$  and  $r_T$ , respectively. Substituting  $\langle \Gamma_T \rangle$ ,  $D$  and  $f$  evaluated by the MD simulation into equation (1), we obtain  $\langle r \rangle$  which is shown in table 1 and figure 5. It is seen from figure 5 that  $\langle r \rangle$  is smaller than the distance  $r_0$  between the T site and the O site and it approaches  $r_0$  as the temperature increases.

#### 4. Discussion

The activation energy  $\epsilon_\Gamma$  of  $\Gamma_T$  in equation (18) is less than the activation energy  $\epsilon_D$  of  $D_T$  in equation (19). The reason is as follows. In diffusion in ordinary solids,  $r_T$  and  $f$  in equation (1) have almost constant values. The temperature dependence of  $D_T$  is subject to that of  $\Gamma_T$ . Therefore,  $\epsilon_D$  is equal to  $\epsilon_\Gamma$ . In the case of  $\alpha$ -Ag<sub>2</sub>Te, the migration of cations in the octahedron is diffusive and it is difficult to specify a stable position of the cation in the polyhedron, so that  $\langle r \rangle$  (and hence  $\langle r \rangle^2$ ) is not constant for all temperatures and has a temperature dependence.  $f$  also has a temperature dependence as shown in figure 3. The temperature dependences of  $\langle r \rangle^2$  and  $f$  are represented by the Arrhenius-type formulae

$$\langle r \rangle^2 = r_0^2 \exp(-\epsilon_r/k_B T) \quad (20)$$

and

$$f = f_0 \exp(-\epsilon_f/k_B T) \quad (21)$$

with  $\epsilon_r = 0.02 \text{ eV}$  and  $\epsilon_f = 0.09 \text{ eV}$ , respectively. By using the MD calculation,  $\epsilon_D$  has been evaluated as 0.17 eV. The sum of the three values  $\epsilon_\Gamma$ ,  $\epsilon_r$  and  $\epsilon_f$  is equal to 0.17 eV. Thus the equation

$$\epsilon_D = \epsilon_\Gamma + \epsilon_r + \epsilon_f \quad (22)$$

is obtained. This relation is also derived by substituting equations (18)–(21) into equation (1).

Recently, Holdsworth *et al* [12] have theoretically analysed the correlated random walk of tracer diffusion between two sublattice systems, composed of two interpenetrating FCC and simple-cubic sublattices resulting in NaCl and CsCl structures, as functions of the ratio of the tracer hopping rate from sublattice 1 to sublattice 2 to the tracer hopping rate from sublattice 2 to sublattice 1 and of the mean ion concentration in a sublattice. They [13, 14] have also carried out Monte Carlo simulations for the systems and have obtained quantitatively good coincidence with the theory. However, their results are not available to apply to the present system since the diffusion of Ag ions takes place between two different sublattices: one is a simple-cubic sublattice formed by T sites and the other is an FCC sublattice formed by O sites. It would be an interesting problem to try to extend their theory to the present system, but this remains as a task for the future.



## 5. Summary

The formula for the correlation factor  $f$  of tracer diffusion has been derived in the case where the diffusing ion jumps alternately between two kinds of site with equal spacing. It has been shown that the expressions for the correlation factors of the vacancy and interstitialcy mechanisms are deduced from the present formula. The formula is applied to the diffusion of Ag ions in  $\alpha$ -Ag<sub>2</sub>Te. In successive jumps of Ag ions from a T to an O site and from an O to a T site, the backward jump probability is greater than the probabilities in the other seven directions, while in successive jumps from an O to a T site and from a T to an O site the backward jump probability is slightly greater than the probabilities in the other three directions. The average  $\langle r \rangle$  of the jump distance is shorter than the distance  $r_0$  between a T site and an O site. It increases with increasing temperature. As the temperature dependences of  $f$  and  $\langle r \rangle$  are expressed by Arrhenius-type formulae, the activation energy of diffusion is expressed as the sum of the activation energies of the jump frequency ( $\Gamma_T$ ), of the correlation factor  $f$  and of the jump distance  $\langle r \rangle$ .

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