

DIFFUSE SCATTERING OF SUPERIONIC PHASE OF CuAgSe

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The diffuse scattering pattern of high temperature phase of CuAgSe was investigated by X-ray powder diffraction measurements at 523 K. The wide and strong peak of diffuse scattering appeared around $2\theta\sim 35^\circ$. There were two contributions to the oscillatory diffuse scattering, one was the short range order of cations. The other was the correlation between thermal displacements of anion–cation and cation–cation pairs. The theoretical treatments of the diffuse scattering including the correlations among the thermal displacements of atoms were described.

Keywords: CuAgSe, diffuse scattering, superionic conductors, X-ray diffraction

Introduction

In recent years, superionic materials have been studied much because of their application to the electrochemical devices such as batteries, fuel cells and gas sensors [1]. There has been much interest in the structure and the diffuse scattering of superionic conductors, which show unusual high ionic conductivity in the high temperature phase [2]. It is well known that diffuse scattering contains information about short range order and thermal vibrations of atoms in a solid sample. Anomalously strong and oscillatory diffuse scattering from crystalline superionic conductors has been studied in X-ray and neutron scattering experiments. The theoretical treatment including the disordered arrangements of cations and the correlations among the thermal displacements of atoms has been applied to the diffuse scattering [3, 4].

In this paper, the diffuse scattering of superionic phase of CuAgSe is inspected by X-ray powder diffraction measurements at 523 K. Numerical calculations of diffuse scattering intensities have been made on the crystal structure of CuAgSe [5, 6].

Experimental

Stoichiometric quantities of copper, silver and selenium were weighted and enclosed in a pyrex tube in vacuum condition and melted at 733 K for 1 day. After solidification, it was annealed at 623 K for 2 days and then 333 K for 3 days. The obtained compound was crushed to a fine powder and then the sample was enclosed in a pyrex tube again and kept at 623 K for

1 day. After that, it was gradually cooled to room temperature. The X-ray diffraction pattern of CuAgSe was measured with powder sample at 523 K. X-ray diffraction data were collected using Cu- K_α radiation monochromatized with a PG 002 reflection for 10 s per step at 0.05° intervals over the 2θ range from 10° to 90° by a step-scan mode. The observed X-ray diffraction pattern, where the corrections of air scattering, fluorescent X-rays and background noise were performed, was given in Fig. 1. Several Bragg lines and a large diffuse scattering were found in Fig. 1. The wide and strong peak of the diffuse scattering appears around $2\theta\sim 35^\circ$. In addition to the strong peak, a very weak second peak of the oscillatory diffuse scattering could be observed around $2\theta\sim 75^\circ$.

Structure of high temperature phase of CuAgSe

From the intensity analysis of Bragg lines of CuAgSe at 523 K, the cubic system of the space group denoted

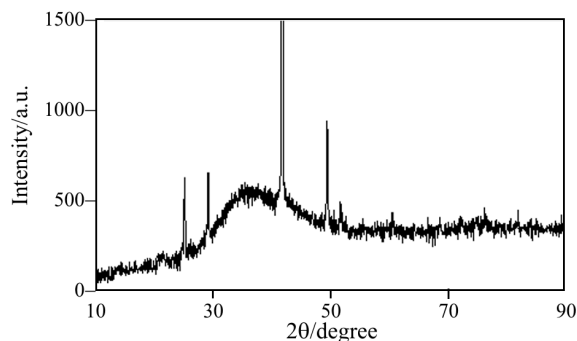


Fig. 1 Observed intensities of CuAgSe at 523 K by the Cu- K_α X-ray diffraction measurement

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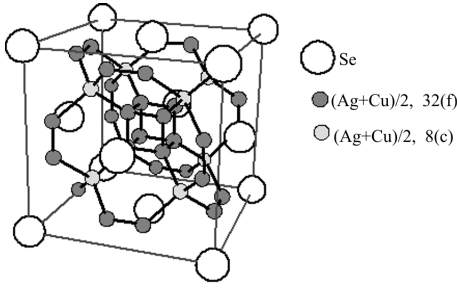


Fig. 2 Atomic arrangement in the unit cell of CuAgSe at 523 K

by $Fm\bar{3}m$ with disordered arrangement of copper and silver ions was found to be most plausible. The lattice constant at 523 K is $a=6.109\pm 0.001$ Å. The atomic positions in the unit cell of superionic phase of CuAgSe were illustrated in Fig. 2. The number of atoms and the atomic positions are as follows

$$\begin{aligned} &(000, 0\ 1/2\ 1/2, 1/2\ 0\ 1/2, 1/2\ 1/2\ 0)+ \\ &4\ \text{Se in } 4(a) \quad \quad \quad 000, \\ &m(\text{Cu+Ag})/2\ \text{ in } 8\ (c) \quad 1/4\ 1/4\ 1/4, 3/4\ 3/4\ 3/4, \\ &(8-m)\ (\text{Cu+Ag})/2\ \text{ in } 32\ (f) \\ &\quad \quad \quad xxx, x\bar{x}\bar{x}, \bar{x}x\bar{x}, \bar{x}\bar{x}x, \bar{x}\bar{x}\bar{x}, \bar{x}x\bar{x}, x\bar{x}\bar{x}, x\bar{x}\bar{x}. \end{aligned}$$

The number of cations distributed on the 8(c) sites (m), the position of 32(f) sites for cations (x) and the three thermal parameters for anions and cations ($B_{\text{Se}}, B_{\text{cat}(c)}, B_{\text{cat}(f)}$) were determined as $m=5.4$, $x=0.4$, $B_{\text{Se}}=3.0$ Å², $B_{\text{cat}(c)}=1.8$ Å², $B_{\text{cat}(f)}=6.6$ Å².

Analysis of diffuse scattering and discussion

The diffuse scattering of α -AgI was discussed by the disordered arrangements of Ag and vacancy [7]. In the case of the superionic phase of CuAgSe, a more complicated theoretical treatment with disordered arrangement of Cu, Ag and vacancy is needed. The background intensity I of scattered X-rays by CuAgSe crystal consists of two terms: the incoherent scattering term and the diffuse scattering (coherent scattering) term which is the focus of this paper. The general expression of the diffuse scattering term I_d can be written as

$$I_d = k \sum_s \sum_{s'} e^{iQ \cdot (R_s - R_{s'})} \left\langle \Delta F_s \Delta F_{s'}^* \right\rangle \quad (1)$$

where k is a constant depending on the experimental conditions which is proportional to the polarization factor. R_s is the position vector of the s^{th} site in the crystal and summation is taken over the unit volume of the crystal. ΔF_s is defined as the deviation of the structure factor at the s^{th} site from the mean structure factor. The deviation of the structure factor is due to the disordered structure and the statistical displacement

of atoms from their mean positions caused by thermal vibration. The diffuse scattering intensity I_d is composed of four contributions: the contribution from anion-anion pairs (I_{aa}), anion-cation pairs (I_{ac}), cation-anion pairs (I_{ca}) and cation-cation pairs (I_{cc}). The contribution from anion-anion pairs, i.e. between selenium atoms, in which Se atom has the statistical displacement caused by thermal vibration, can be written as

$$I_{aa}^{s=s'} = k \sum_{s(\text{Se})} f_{\text{Se}} f_{\text{Se}}^* (1 - e^{-2M_{\text{Se}}}), \quad (2)$$

$$I_{aa}^{s \neq s'} = k \sum_{s(\text{Se})} \sum_{s'(\text{Se})} f_{\text{Se}} f_{\text{Se}}^* (e^{-2M_{\text{Se}}(1-\lambda_{\text{Se-Se}})} - e^{-2M_{\text{Se}}}) e^{iQ \cdot (R_{s(\text{Se})} - R_{s'(\text{Se})})} \quad (3)$$

where f_{Se} is the atomic scattering factor of selenium atom. $\text{Exp}(-M_{\text{Se}})$ is the Debye-Waller factor of selenium atoms. The correlation among the thermal displacements between atom A and B is shown as

$$\lambda_{A-B} = \frac{2 \langle \Delta r_{s(A)} \Delta r_{s'(B)} \rangle}{\langle (\Delta r_{s(A)})^2 \rangle + \langle (\Delta r_{s'(B)})^2 \rangle} \quad (4)$$

The contribution from anion-cation pairs, in which cation has the disordered arrangement in addition to the statistical displacement caused by thermal vibration, can be written as

$$I_{ac} = k \sum_{s(\text{Se})} \sum_{s'(ci)} p_{ci} f_{\text{Se}} f_{ci}^* \left\{ \begin{array}{l} e^{-(M_{\text{Se}}+M_{ci})(1-\lambda_{\text{Se-ci}})} \\ -e^{-(M_{\text{Se}}+M_{ci})} \end{array} \right\} e^{iQ \cdot (R_{s(\text{Se})} - R_{s'(ci)})} \quad (5)$$

where subscript ci means the i^{th} cation and f_{ci} is atomic scattering factor of i^{th} cation. f_{ci} is either $f_{\text{Cu}}, f_{\text{Ag}}$ or 0, whereas p_{ci} is the probability of finding the cation- i in any sites, which is equal to the ratio of the number of cation- i to the number of sites in the crystal. In case of ordered arrangement, p_{ci} is equal to 1. $\text{Exp}(-M_{ci})$ is the Debye-Waller factor for cation- i . The contribution from cation-anion pairs can be written as

$$I_{ca} = k \sum_{s(ci)} \sum_{s'(\text{Se})} p_{ci} f_{ci} f_{\text{Se}}^* \left\{ \begin{array}{l} e^{-(2M_{\text{Se}}+M_{ci})(1-\lambda_{\text{ci-Se}})} \\ -e^{-(M_{\text{Se}}+M_{ci})} \end{array} \right\} e^{iQ \cdot (R_{s(ci)} - R_{s'(\text{Se})})} \quad (6)$$

From the analysis of Bragg lines of CuAgSe, it is known that cations are distributed at 8(c) and 32(f) positions, so the contribution from cation-cation pairs can be written as

$$I_{cc}^{s=s'} = k \sum_{s'(ci)} \sum_i v_i \left\{ \begin{array}{l} p_i (|f_{\text{Ag}}|^2 + |f_{\text{Cu}}|^2) \\ -p_i^2 |f_{\text{Ag}} + f_{\text{Cu}}|^2 e^{-2M_i} \end{array} \right\} \quad (7)$$

$$I_{cc}^{s \neq s'} = k \sum_{i,j} \sum_{s^{(ci)}} \sum_{s'^{(ci)}} \left\{ \begin{array}{l} P_i \alpha_{ij} |f_{Cu} + f_{Ag}|^2 \\ (e^{-(M_i+M_j)(1-\lambda_{ij})}) \\ -\delta e^{-(M_i+M_j)} \\ +P_i \gamma |f_{Cu} + f_{Ag}|^2 e^{-(M_i+M_j)} \end{array} \right\} e^{iQ(R_{s^{(ci)}} - R_{s'^{(ci)}})} \quad (8)$$

where the probability functions α and β are introduced. α gives the probability of finding an atom at a site apart by a distance r from a site occupied by an atom, and β is the probability of finding an atom at a site apart by a distance r from a vacant site. Subscript i and j in the above two equations refer to the positions of 8(c) and 32(f) sites of cations. δ and γ in Eq. (8) are equal to $2(p_i+p_j-2p_i p_j)$ and $(2p_i \alpha_{ij} - \beta_{ij}) - 2p_i(2p_j \alpha_{ij} - \beta_{ij})$, respectively.

Expression for above equations can be simplified in the case of powder samples, it can be written

$$I_{aa}^{s=s'} = kN_0 n_{Se} f_{Se} f_{Se}^* (1 - e^{-2M_{Se}}) \quad (9)$$

$$I_{aa}^{s \neq s'} = kN_0 n_{Se} f_{Se} f_{Se}^* \sum_r Z_r S_r (e^{-2M_{Se}(1-\lambda_{Se-Se})} - e^{-2M_{Se}}) \quad (10)$$

$$I_{ac} = kN_0 n_{Se} \sum_r \sum_i Z_r S_r P_{ci} f_{Se} f_{ci}^* (e^{-(M_{Se}+M_{ci})(1-\lambda_{Se-ci})} - e^{-(M_{Se}+M_{ci})}) \quad (11)$$

$$I_{ca} = kN_0 \sum_r \sum_i n_{ci} Z_r S_r P_{ci} f_{ci} f_{Se}^* (e^{-(M_{Se}+M_{ci})(1-\lambda_{ci-Se})} - e^{-(M_{Se}+M_{ci})}) \quad (12)$$

$$I_{cc}^{s \neq s'} = kN_0 n_c \sum_j v_j \left\{ \begin{array}{l} P_j (|f_{Ag}|^2 + |f_{Cu}|^2) \\ -P_j^2 |f_{Ag} + f_{Cu}|^2 e^{-2M_j} \end{array} \right\} \quad (13)$$

$$I_{cc}^{s \neq s'} = kN_0 n_c \sum_r \sum_{i,j} Z_r S_r \left\{ \begin{array}{l} P_j \alpha_{ij} |f_{Cu} + f_{Ag}|^2 \\ (e^{-(M_i+M_j)(1-\lambda_{ij})}) \\ -\delta e^{-(M_i+M_j)} \\ +P_i \gamma |f_{Cu} + f_{Ag}|^2 \\ e^{-(M_i+M_j)} \end{array} \right\} \quad (14)$$

S_r is equal to $\sin[(4\pi r \sin\theta)/\lambda]/[(4\pi r \sin\theta)/\lambda]$, N_0 is the number of the unit cell in unit volume, n corresponds to the number of atoms per unit cell, and Z_r is the number of sites at a distance r belonging to the s' type neighbor around s type site. v_c and v_f are equal to 8/40 and 32/40, respectively. Assuming that the distribution between Cu and Ag is random, the following relations were used

Table 1 Interatomic distances r (Å), the number of nearest neighboring sites Z , the correlation among the thermal displacements of atoms λ and the probability function α in CuAgSe at 523 K. 8(c) and 32(f) are the atomic positions of cations. p_{8c} and p_{32f} are equal to 5.4/8 and 2.6/32, respectively

	r	Z	λ	α
8(c) – 32(f)	1.582	4	–	0
8(c) – 32(f)	2.499	12	–	0
8(c) – Se	2.645	4	0.7	–
8(c) – 8(c)	3.055	6	0.7	0.37
8(c) – 32(f)	3.158	12	0.7	0.04
8(c) – 32(f)	3.702	4	0	p_{32f}
32(f) – 32(f)	1.222	3	–	0
32(f) – 8(c)	1.582	1	–	0
32(f) – 32(f)	1.723	3	–	0
32(f) – 32(f)	2.114	1	–	0
32(f) – 8(c)	2.499	3	–	0
32(f) – 32(f)	2.590	3	–	0
32(f) – Se	2.590	3	0.7	–
32(f) – 32(f)	2.865	3	0.7	0.04
32(f) – 8(c)	3.158	3	0.7	0.37
32(f) – 32(f)	3.562	12	0	p_{32f}
32(f) – 8(c)	3.702	1	0	p_{8c}
32(f) – 32(f)	3.763	12	0	p_{32f}
32(f) – Se	3.763	3	0	–
Se – 32(f)	2.590	24	0.7	–
Se – 8(c)	2.645	8	0.7	–
Se – 32(f)	3.763	24	0	–

$$\beta_{r(v-Cu)} = \beta_{r(v-Ag)},$$

$$\alpha_{r(Cu-Cu)} = \alpha_{r(Ag-Ag)} = \alpha_{r(Cu-Ag)} = \alpha_{r(Ag-Cu)}$$

where v means a vacant site, k is proportional to the polarization factor $(1+\cos^2 2\theta \cos^2 2\epsilon)/2$, where 2ϵ is the Bragg angle for a pyrolytic graphite monochromator. There are some relations among short range order parameters

$$\beta_{r(v-j)} = \frac{(p_j - 2p_i \alpha_{r(i-j)})}{(1 - 2p_i)}$$

$$\alpha_{r(i-j)} = \left(\frac{p_j}{p_i} \right) \alpha_{r(j-i)}$$

Using the values of the interatomic distances which are calculated from the atomic positions, the short range order and the correlations among thermal displacements of atoms in Table.1, the diffuse scattering intensity I was calculated from Eqs (9–14). The obtained results are shown in Figs 3 and 4. It is found

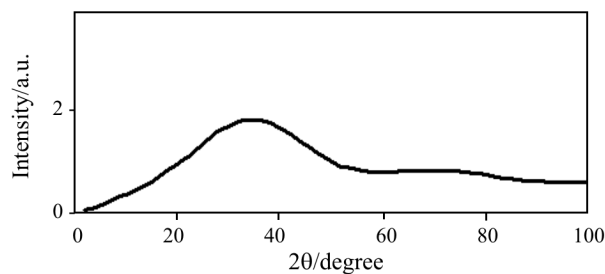


Fig. 3 Calculated diffuse background intensity of CuAgSe at 523 K

that the profile of diffuse scattering in Fig. 1 almost corresponds to the calculated profile in Fig. 3. The strong diffuse scattering around $2\theta \sim 35^\circ$ in Fig. 1 is related to the maximum values of cation-cation part of Eq. (14) and cation-anion and anion-cation part ($I_{ca} + I_{ac}$) in Fig. 4. The intensity of these parts has maximum values around $2\theta \sim 35^\circ$. The oscillating scheme of cation-cation part above $2\theta \sim 35^\circ$ is cancelled by that of anion-cation and cation-anion part as shown in Fig. 4. Therefore, the diffuse scattering intensity does not show clear peak from 55 to 90° in Fig. 1. The $s=s'$ term of cations (Eq. (13)) and that of anions (Eq. (9)) have a monotonous function in Fig. 4. Especially the cation term has a very large intensity and gives strong diffuse scattering intensity over the whole scattering angle, whereas the anion term has small intensity especially for small scattering angle. Most of the intensity of cation part is produced by the disordered arrangement of Cu and Ag atoms. The $s \neq s'$ term of anions (Eq. (10)) have no contribution to the total intensity because its value was zero over the whole scattering angle. The small contribution from anion-anion part can be understood as a consequence of ordered positions of anions (Se atoms) in the crystal of CuAgSe. The large intensity of $s=s'$

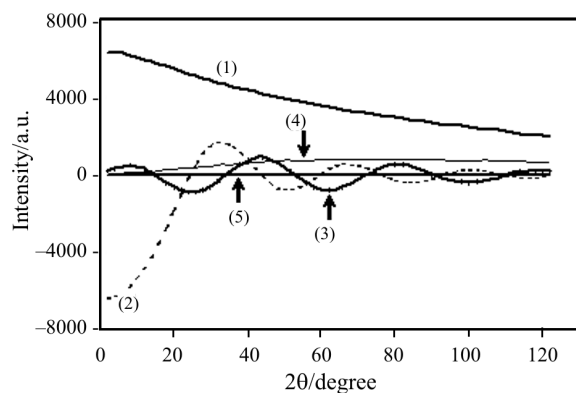


Fig. 4 Calculated intensity of (1) cation-cation ($s = s'$) term, (2) cation-cation ($s \neq s'$) term, (3) cation-anion and anion-cation term, (4) anion-anion ($s = s'$) term, (5) anion-anion ($s \neq s'$) term

term of cations part (Eq. (13)) at small scattering angle is cancelled by that of Eq. (14) as shown in Fig. 4.

It is known that the statistical distribution of cations and the short interatomic distances between cations play an important role of an atomic diffusion in α -AgI, α -Ag₃SI and α -Cu₂Se. In case of superionic phase of CuAgSe, all Cu and Ag ions are statistically distributed on the 8(c) and 32(f) sites and the smallest interatomic distances of these sites are 1.2~1.5 Å. The path connecting these nearest neighboring 8(c) and 32(f) sites could be an easiest channel of cation movement in the superionic phase of CuAgSe.

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