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Structural study of superionic phase of AgI

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Abstract. A detailed analysis of the x-ray scattering intensity of α -AgI has been carried out by an anomalous scattering technique. The two partial interference functions $S_{ij}^{\text{dif}}(Q)$ for Ag–Ag and Ag–I pairs were estimated using the newly developed theoretical equations of the intensity. The partial distribution functions for I–I, Ag–I and Ag–Ag pairs in this work are consistent with the results obtained from molecular dynamics by Vashishta and Rahman. The intensities of Debye lines were also explained satisfactorily in terms of pair distribution function for Ag–I pairs.

1. Introduction

Various properties of solid fast-ion conductors (often called superionic conductors) such as α -AgI have been extensively studied (see for example, Mahan and Roth 1976) because of their unusually high ionic conductivity. Diffraction patterns for these materials are characterised by the coexistence of Debye peaks and liquid-like diffuse patterns. The Debye peaks are caused by the periodic array of anions (Strock 1934, 1936). A number of diffraction studies concerning the diffuse patterns have been reported (Hoshino 1957, Suzuki and Okazaki 1977, Sakuma *et al* 1977). These previous methods for analysing the observed intensity data seem inadequate because the liquid-like diffuse pattern is attributed to only cation–cation pairs and thus the contribution from anion–cation pairs has been neglected *ab initio* (see for example Sakuma 1978). However, the two components due to cation–cation and cation–anion pairs have been considered more realistically by Tsuchiya *et al* (1978, 1979) in an analysis of liquid-like diffuse patterns from both a theoretical and an experimental point of view.

The main aims of this work are to apply our newly developed theoretical equations to the diffraction pattern for α -AgI type superionic conductors and to present information about the distribution function of cation–cation and cation–anion pairs in α -AgI.

2. Diffraction pattern for Ag-chalcogenide type superionic conductors

Tsuchiya *et al* (1978) have shown that the anion–cation interference function is one of the components in the diffuse patterns of a superionic conductor such as α -Ag₂S. However, a few points in this paper were semiquantative and incorrect. Recently, a more detailed

study of the diffraction pattern has been made to illustrate the basic ideas of a previous paper (Tsuchiya *et al* 1979). In what follows, a brief summary of the essential points is given.

The observed coherent x-ray scattering intensity for a polycrystalline or powdered sample can be written as:

$$I^{\text{coh}}(\mathbf{Q}) = \langle F(\mathbf{Q}) F^*(\mathbf{Q}) \rangle \quad (1)$$

where

$$F(\mathbf{Q}) = \sum_{a=1}^{N_a} f_a \exp(i \mathbf{Q} \cdot \mathbf{r}_a) + \sum_{c=1}^{N_c} f_c \exp(i \mathbf{Q} \cdot \mathbf{r}_c). \quad (2)$$

The asterisk indicates the complex conjugate, $\mathbf{Q}$ is the scattering vector, N_a and N_c are the numbers of anions and cations, respectively, f_i is the atomic scattering factor of the atom i , $\mathbf{r}_a$ and $\mathbf{r}_c$ represent the positions of an anion and a cation respectively, and $\langle \rangle$ represents the configurational average for the system. Substituting (2) into (1) we obtain:

$$\begin{aligned} I^{\text{coh}}(\mathbf{Q}) = & \left\langle f_a f_a^* \sum_{a=1}^{N_a} \sum_{a'=1}^{N_a} \exp i \mathbf{Q} \cdot (\mathbf{r}_a - \mathbf{r}_{a'}) \right\rangle \\ & + \left\langle f_a f_c^* \sum_{a=1}^{N_a} \sum_{c'=1}^{N_c} \exp i \mathbf{Q} \cdot (\mathbf{r}_a - \mathbf{r}_{c'}) + \text{cc} \right\rangle \\ & + \left\langle f_c f_c^* \sum_{c=1}^{N_c} \sum_{c'=1}^{N_c} \exp i \mathbf{Q} \cdot (\mathbf{r}_c - \mathbf{r}_{c'}) \right\rangle. \end{aligned} \quad (3)$$

where cc indicates the complex conjugate. The first bracket yields only Debye given by

$$N_a f_a f_a^* + (N_a + N_c)^2 C^2 f_a f_a^* \delta_{\mathbf{Q}, \mathbf{G}} \quad (4)$$

where C is the concentration of anions and is equal to $N_a/(N_a + N_c)$, $\delta_{\mathbf{Q}, \mathbf{G}}$ is the Kronecker symbol, and $\mathbf{G}$ is the reciprocal lattice vector specified by the anion lattice. Using the radial distribution function between anion and cation pairs, $g_{ac}(|\mathbf{r}_c - \mathbf{r}_a|)$, the second bracket in equation (3) can be transformed as follows:

$$\begin{aligned} & (N_a + N_c)^2 C(1 - C) f_a f_c^* \delta_{\mathbf{Q}, \mathbf{G}} \langle \exp(-i \mathbf{Q} \cdot \boldsymbol{\rho}) \rangle \\ & + f_a f_c^* N_a N_c \frac{4\pi}{V} \int_0^\infty [g_{ac}(r) - 1] \frac{\sin Qr}{Qr} r^2 dr + \text{cc} \\ & = (N_a + N_c)^2 C(1 - C) \delta_{\mathbf{Q}, \mathbf{G}} [f_a f_c^* \langle \exp(-i \mathbf{Q} \cdot \boldsymbol{\rho}) \rangle + f_a^* f_c \langle \exp(i \mathbf{Q} \cdot \boldsymbol{\rho}) \rangle] \\ & + (N_a + N_c) C(1 - C) (f_a f_c^* + f_a^* f_c) [S_{ac}(\mathbf{Q}) - 1] \end{aligned} \quad (5)$$

where V is the volume of sample and $S_{ac}(\mathbf{Q})$ denotes the interference function between anion and cation pairs. $S_{ac}(\mathbf{Q})$ is transformed from the averaged partial pair distribution function between anion-cation pairs $g_{ac}(r)$ in the following form:

$$S_{ac}(\mathbf{Q}) = \frac{4\pi(N_a + N_c)}{V} \int_0^\infty [g_{ac}(r) - 1] \frac{\sin Qr}{Qr} r^2 dr + 1 \quad (6)$$

Here we have assumed that the distribution of cations is isotropic, so the probability that a cation is found at the position $\mathbf{r}$ from an anion depends only on the radial distance r . The term $\langle \exp(i \mathbf{Q} \cdot \boldsymbol{\rho}) \rangle$ and its complex conjugate denote the configurational average of cation distribution in the unit cell.

In a similar way, the interference function between cation pairs $S_{cc}(Q)$ can be obtained from the last bracket of equation (3):

$$N_c f_c f_c^* + (N_a + N_c)^2 (1 - C)^2 f_c f_c^* \delta_{Q, G} \langle \exp(-iQ \cdot \rho) \rangle \langle \exp(iQ \cdot \rho) \rangle + f_c f_c^* (N_a + N_c)^2 (1 - C)^2 [S_{cc}(Q) - 1] \quad (7)$$

where $S_{cc}(Q)$ is related to the averaged partial pair distribution function between cation pairs $g_{cc}(r)$ and is similar to equation (6). We obtain the final expression for the observed total interference function:

$$I^{\text{coh}}(Q)/(N_a + N_c) [C f_a f_a^* + (1 - C) f_c f_c^*] = \frac{(N_a + N_c)}{C f_a f_a^* + (1 - C) f_c f_c^*} [C f_a + (1 - C) \langle \exp(iQ \cdot \rho) \rangle f_c] \times [C f_a^* + (1 - C) \langle \exp(iQ \cdot \rho) \rangle f_c^*] \delta_{Q, G} + \left(1 + \frac{C(1 - C)(f_a f_c^* + f_a^* f_c)[S_{ac}(Q) - 1] + (1 - C)^2 f_c f_c^*[S_{cc}(Q) - 1]}{C f_a f_a^* + (1 - C) f_c f_c^*} \right). \quad (8)$$

The first term of equation (8) contributes to the Debye peaks and the second to the diffuse scattering.

If the thermal vibration is taken into account, the expression for the total interference function is readily obtained by replacing f_i by $f_i \exp(-B_i Q^2/16\pi^2)$, in which B_i is the Debye-Waller factor for atom i , so long as the thermal vibrations of the atoms are independent from one another and its mean square displacement from the lattice point is small. In a real crystal of an Ag chalcogenide type superionic conductor, however, it is more appropriate to include the vibrational effect of the cation to the partial distribution function, $g_{ij}(r)$ and $\langle \exp(-iQ \cdot \rho) \rangle$ because the hopping time and residence time at any site of a cation have been reported to be of comparable order of magnitude (Boyce *et al* 1977). As a first approximation, the atomic scattering factor of an anion f_a would be replaced by $f_a \exp(-B_a Q^2/16\pi^2)$ to analyse the diffuse haloes of x-ray intensity patterns.

It is noteworthy that the expression for the weighting factor of each partial interference function $S_{ij}(Q)$ is the same as the one obtained for a liquid binary alloy. Therefore, the observed diffuse patterns can be decomposed into anion-cation and cation-cation partial interference functions by the standard technique which is frequently applied to the structural study of amorphous materials and liquid alloys.

3. Experimental procedures

The AgI samples were prepared following the procedure described by Suzuki and Okazaki (1977). The basic arrangements for measurements of x-ray scattering intensity and correction of the observed intensity data were almost identical to those described previously (Waseda and Masumoto 1975) and will not be described here. The step scan width ($\Delta 2\theta$) was 0.02° for Debye peaks and 0.4° for the diffuse pattern. The sample was kept at $170 \pm 3^\circ\text{C}$ in a purified dry argon atmosphere. The accumulated counts, varying from 4×10^4 at low angles to 8×10^4 at high angles, were chosen to keep the counting statistics approximately uniform. The normalisation procedure used to obtain the structure factors was identical to that used in previous work on liquid metals and amorphous

solids (Waseda and Tamaki 1975, 1976). The errors in the normalisation were less than 1% according to the usual method first proposed by Rahman (1965).

4. Experimental results and analysis of data

The x-ray diffraction patterns obtained by the use of both Mo- K_α and Cu- K_α radiations show a combination of Debye lines and diffuse scattering. A typical example of an x-ray scattering intensity obtained by using Mo- K_α radiation is shown in figure 1. This figure shows a clear distinction between the Debye lines and the diffused liquid-like pattern. The relative intensities of the Debye lines are tabulated in table 1. These relative intensities are inconsistent with those expected for a typical bcc lattice, which suggests that the coherent scattering from Ag-I and also Ag-Ag pairs has contributed to these Debye lines. Similar behaviour was found in the results of Cu- K_α radiation.

The liquid-like components $S^{\text{dif}}(Q)$ were separated from the total interference functions obtained by Mo- K_α and Cu- K_α radiations, and are shown in figure 2. For example, the values of $S^{\text{dif}}(Q)$ at $Q = 2.50 \text{ \AA}^{-1}$ are 1.178 for Mo- K_α and 1.265 for Cu- K_α radiations, respectively. The two curves are significantly different, as indicated by the error bars in their set of figure 2. This is related to the presence of the diffuse scattering intensities due to the pairs of both Ag-I and Ag-Ag (hereafter denoted as the partial interference functions $S^{\text{dif}}_{\text{Ag-Ag}}(Q)$ and $S^{\text{dif}}_{\text{Ag-I}}(Q)$). Based on the data of $S^{\text{dif}}(Q)$ in figure 2, the partial interference functions are estimated with the standard technique of x-ray anomalous scattering (Waseda and Tamaki 1975). The values of $\Delta f'$ and $\Delta f''$ used in this work are tabulated in table 2 (Cromer and Liberman 1970). The two partial interference functions obtained for the pairs Ag-Ag and Ag-I are shown in figure 3. The vertical lines denote the fluctuations due to the experimental uncertainty, as discussed by

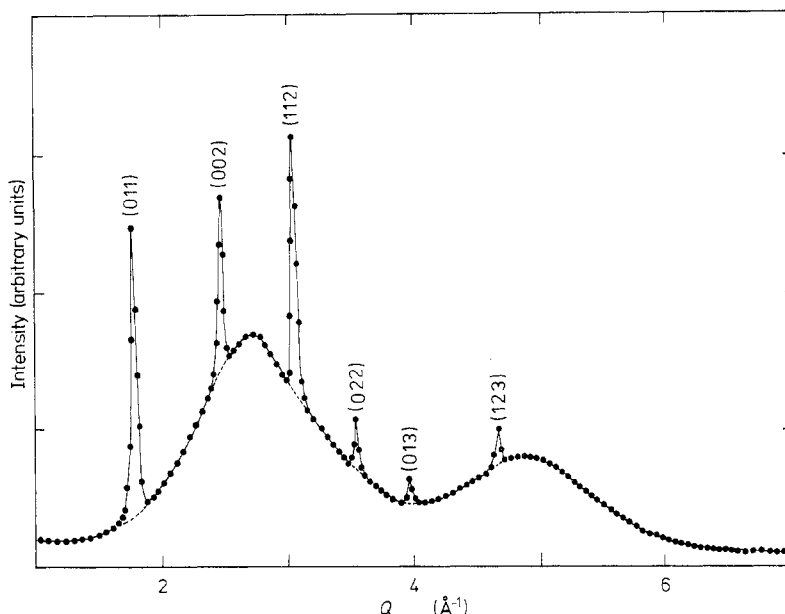
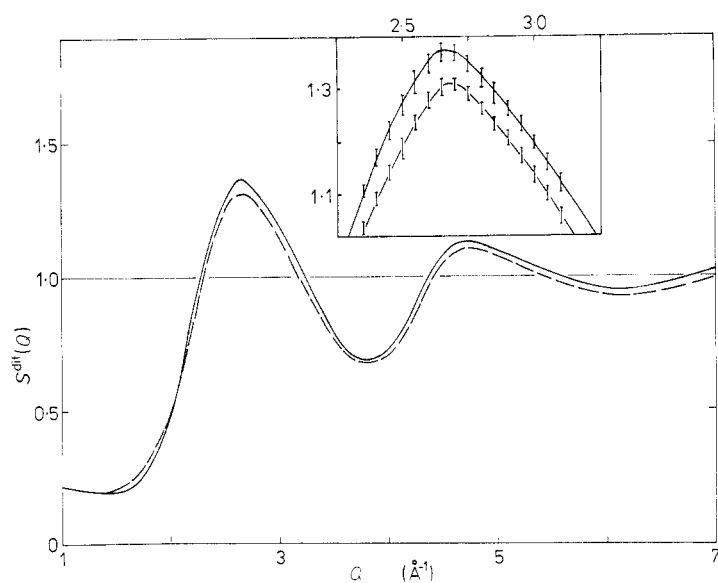


Figure 1. The x-ray scattering intensity of α -AgI by Mo- K_α radiation at 170°C.

Table 1. Observed and calculated intensities of Debye lines.

$d(\text{\AA})$	hkl	I/I_1	I_{cal}/I_1
3.586	(110)	100 (I_1)	99.78
2.533	(200)	63	60.97
2.069	(211)	85	87.02
1.792	(220)	12	10.74
1.602	(310)	4	3.51
1.463	(222)	—	1.46
1.357	(321)	9	6.19
1.267	(400)	—	1.91

**Figure 2.** The diffuse scattering component $S^{\text{dif}}(Q)$ of the total interference function of α -AgI. Full curve, Cu- K_α ; broken curve, Mo- K_α .**Table 2.** Anomalous scattering factors for Ag and I ions (Cromer and Liberman 1970).

	Mo	Cu
Radiation wavelength ($\text{\AA}$)	0.7093	1.5405
Ag $\Delta f'$	-1.085	-0.060
Ag $\Delta f''$	1.101	4.282
I $\Delta f'$	-0.726	-0.579
I $\Delta f''$	1.812	6.835

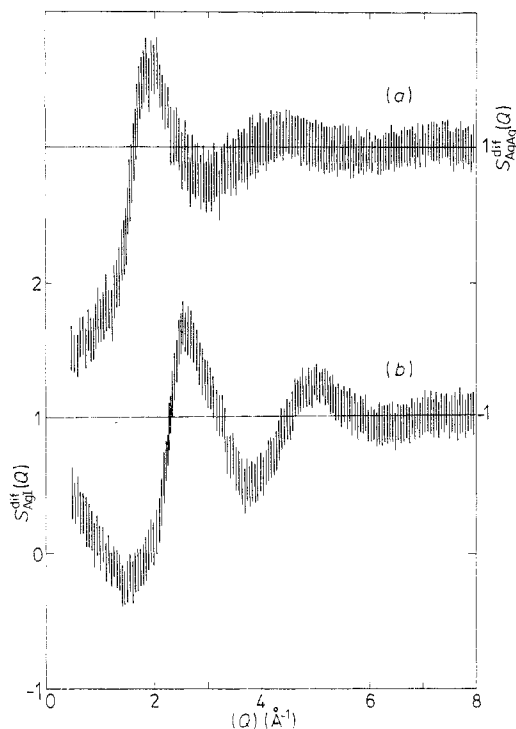


Figure 3. The partial interference functions $S_{ij}^{\text{dif}}(Q)$ for (a) Ag-Ag pairs and (b) Ag-I pairs in α -AgI.

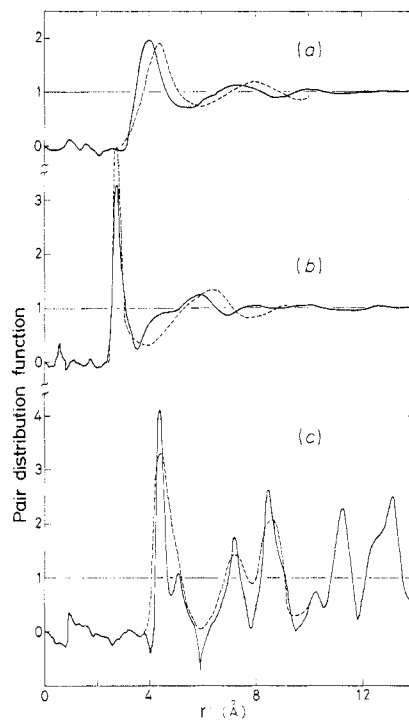


Figure 4. The partial pair distribution functions $g_{ij}^{\text{dif}}(r)$ for (a) Ag-Ag, (b) Ag-I and (c) I-I pairs. Full curves, present results; broken curves, molecular dynamics calculation by Vashishta and Rahman (1978).

Waseda and Tamaki (1975). These are of the order of ± 0.2 . The general form is similar to that of liquid metals and alloys; that is, the structure factor is characterised by small oscillations about unity after the usual first peak. However, the position of the first peak of the Ag-I correlation is situated nearly at the first minimum of the Ag-Ag correlation. This feature is similar to the case reported for α -Ag₂S (Tsuchiya *et al* 1978) and molten salts (Page and Mika 1971, Edwards *et al* 1975, Mitchell *et al* 1976).

The derivation of the partial pair distribution function for liquid metals and alloys $g_{ij}(r)$ (i.e., the average distribution of j atoms at a radial distance r from atom i at the origin) is given by

$$g_{ij}(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty Q [S_{ij}(Q) - 1] \sin Qr dQ. \quad (9)$$

In the present case, $S_{ij}^{\text{dif}}(Q)$ should be used instead of $S_{ij}(Q)$ and then the partial pair distribution functions $g_{ij}^{\text{dif}}(r)$ can be derived from the experimental results using equation (9). These are shown in figure 4 together with the results of molecular dynamics obtained by Vashishta and Rahman (1978). By using these data, the coordination numbers of Ag-I and Ag-Ag pairs are found to be 4.3 and 12.3, respectively. These results are consistent with the above discussion for the characteristic structure of α -AgI.

Next, we consider the intensities of Debye lines, which are represented by the first

term of equation (8). If the thermal vibration of anions is taken into account, the intensities of the observed Debye lines may be given as follows:

$$I_{\text{obs}}(Q) = j(Q)(N_a + N_i)[Cf_a \exp(-BQ^2/16\pi^2) + (1 - C)\langle \exp(-iQ \cdot \rho) \rangle f_c] \\ \times [Cf_a^* \exp(-BQ^2/16\pi^2) + (1 - C)\langle \exp(iQ \cdot \rho) \rangle f_c^*] \delta_{Q, G} \quad (10)$$

where $j(Q)$ is the multiplicity of the BCC lattice of iodine. To calculate the intensities, $\langle \exp(-iQ \cdot \rho) \rangle$ and $\langle \exp(iQ \cdot \rho) \rangle$ must be estimated. Since the effect of the correlation among Ag ions is automatically involved in the experimental pair-distribution function between Ag and I ions, it may be reasonable to assume that the distribution of Ag ions is determined by the pair distribution, $g_{\text{Ag-I}}^{\text{dif}}(\rho)$ as follows:

$$\langle \exp(iQ \cdot \rho) \rangle = \frac{1}{\Omega} \int_{\Omega} g_{\text{Ag-I}}^{\text{dif}}(\rho) \exp(-iQ \cdot \rho) d\rho \quad (11)$$

where Ω denotes the volume of the BCC iodine unit cell and ρ is the distance between an Ag ion and its nearest I ion. The Q dependence of $\langle \exp(-iQ \cdot \rho) \rangle$ thus calculated is given in figure 5. Using these values, the intensities of Debye lines are calculated as a function of the Debye-Waller factor of iodine, B . The results are tabulated in table 1 and are plotted in figure 6 together with the residual index R , which is defined as follows:

$$R = 100 \sum_i |I_{\text{obs}}^i - I_{\text{cal}}^i| / \sum_i I_{\text{obs}}^i \quad (12)$$

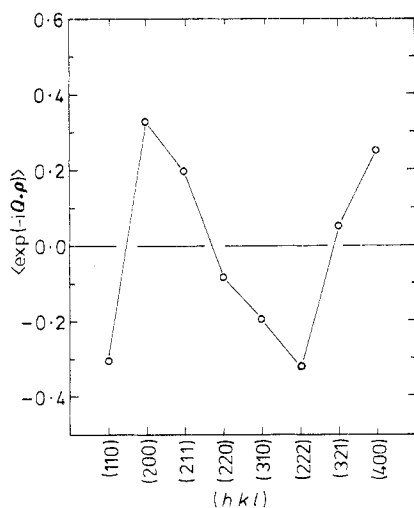


Figure 5. The wavenumber dependence of $\langle \exp(-iQ \cdot \rho) \rangle$; only the $\langle \cos(Q \cdot \rho) \rangle$ term has a non-vanishing value due to the symmetry of the distribution of Ag ions.

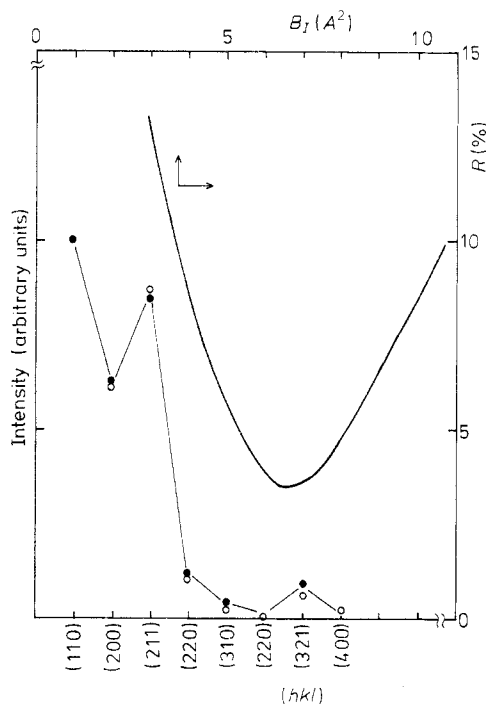


Figure 6. Comparison of the calculated and the observed Debye peak intensities, and the residual index R as a function of Debye-Waller factor of iodine. ●, observed intensity; ○, calculated intensity.

The Debye–Waller factor corresponding to the minimum value of R (3.55%) is $6.5 \text{ \AA}^2$ which is in good agreement with the results of neutron diffraction on powdered AgI (Wright and Fender 1977).

By subtracting the calculated contribution of Ag–I and Ag–Ag pairs from observed intensities of Debye lines, we have calculated the partial pair distribution function between iodine ions using the Fourier transformation. The result is plotted in figure 4.

As shown in figure 4, the present results essentially agree with those obtained by molecular dynamics (Vashishta and Rahman 1978) though the phase difference between experimental and calculated $g_{\text{Ag–Ag}}(r)$ is fairly large.

5. Discussion and conclusion

In previous reports on the diffraction study of the α phase of noble metal chalcogenides (Hoshino 1957, Suzuki and Okazaki 1977, Sakuma *et al* 1978, Sakuma 1978), the diffuse patterns were attributed to only cation–cation pairs and the contribution from cation–anion pairs was neglected *ab initio*. The present results clearly improve upon their inadequate treatment of the diffuse patterns. These results show that both anion–cation and cation–cation interference functions contribute to the liquid-like diffuse patterns. Nevertheless, the present results do not contradict the recent analyses of the intensities of Debye lines in terms of anharmonicity of vibrations (Hoshino *et al* 1977, Cave *et al* 1977), in which the constituent atoms are fixed at the lattice points and have large thermal vibrations due to an effective anharmonic potential. Thus, the distribution functions between Ag–I and Ag–Ag pairs are averaged and may have a liquid-like profile.

The interatomic distance between a silver ion and an iodine ion is estimated from the present partial radial distribution function to be $2.75 \pm 0.01 \text{ \AA}$. This value is about 2.8% less than the value of $2.83 \text{ \AA}$ expected in the case where a silver ion occupies the centre of the tetrahedral site (the lattice constant is $5.070 \text{ \AA}$). EXAFS data (Boyce *et al* 1977, Hayes *et al* 1978) suggest that the Ag–I correlation peaks could be divided into two Gaussian peaks with $r = 2.77\text{--}2.78 \text{ \AA}$ and $r = 2.93 \text{ \AA}$. Our result for the position of the nearest neighbour site is very close to the former of these. However, the resolution of x-ray diffraction measurements is limited so the two possible nearest-neighbour distances given above cannot be distinguished. Therefore, our results are not inconsistent with those of EXAFS measurements.

We have quantitatively confirmed that the liquid-like diffuse pattern in the x-ray diffraction pattern of the superionic phase of AgI consists of both Ag–Ag and Ag–I interference functions, which can be separated from the observed intensity data using the x-ray anomalous scattering technique. The calculated three partial pair distributions are in good agreement with the results obtained by molecular dynamics. The intensities of Debye lines have also been satisfactorily explained in the framework of the present formulation.

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