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2000 J. Phys.: Condens. Matter 12 A195

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Partial structural functions of molten copper halides CuX (X = Br, I) estimated from the anomalous x-ray scattering measurements

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Received 13 September 1999

Abstract. The three partial structural functions of molten copper halides CuX (X = Br, I) have been estimated from anomalous x-ray scattering (AXS) measurements coupled with the reverse Monte Carlo (RMC) simulation technique. For both cases of molten CuBr and CuI, the Cu–Cu partial structure factor of $a_{\text{CuCu}}(Q)$ was found to be rather structureless and the closest Cu–Cu distance was significantly smaller than that for X–X, indicating like-ion penetration into the first unlike-ion coordination shell, similar to the molten CuCl case. We then suggest a disordered close packing of anions where Cu ions meander so as to take a strongly disordered distribution by penetrating through the tetrahedral holes.

1. Introduction

The structural properties of molten copper halides have been studied since Page and Mika (1971) reported a pioneering investigation of the partial structural functions on molten CuCl by neutron diffraction with the isotope substitution technique. The most significant feature of their results is that the partial structural functions for Cu–Cu pairs is fairly structureless and different from those found in molten alkali halides. Eisenberg *et al* (1982) repeated the measurements on molten CuCl and also obtained the structureless feature of the Cu–Cu pairs. By using the neutron diffraction technique, Allen and Howe (1992) determined three partial structural functions of molten CuBr, indicating that the particular feature of the Cu–Cu pair correlation function is common in molten copper halides. Several theoretical attempts have been so far reported for interpreting such a characteristic structural feature of molten salts including copper (e.g. Gillan 1976). Although a definite conclusion is not established yet, it has been suggested that such a similarly structureless cation–cation correlation should be present for other molten salts exhibiting superionic behaviour (Ginoza *et al* 1987). Then, it is not too much to say that copper iodide CuI, which is known as one of the superionic conductors, must also have a structureless cation–cation correlation in the molten state.

The main purpose of this work is to present the three partial structural functions in molten copper halides CuX (X = Br, I) estimated from anomalous x-ray scattering measurements with synchrotron radiation. The anomalous x-ray scattering (hereafter referred to as AXS) method (Waseda 1984), by utilizing the so-called anomalous dispersion effect near the absorption edge, is well recognized as one reliable way for obtaining the partial structural functions of

disordered materials. The availability of the intense white x-rays from a synchrotron radiation source has greatly improved both acquisition and quality of the AXS data by enabling the use of an energy in which the AXS is the greatest.

2. Fundamentals of the AXS measurements

The atomic scattering factor is expressed by $f(Q, E) = f^0(Q) + f'(E) + if''(E)$, where Q and E are the wavevector and the incident energy, respectively; $f^0(Q)$ corresponds to the scattering factor of the atom at energies sufficiently far from the absorption edge, and $f'(E)$ and $f''(E)$ are the real and imaginary parts of the anomalous dispersion terms. When the incident energy is set to the lower energy side of the absorption edge, E_{abs} , of a specific element A in a binary system, the variation, $\Delta i_A(Q, E_1, E_2)$, between intensities, $I(Q, E_1)$ and $I(Q, E_2)$, measured at the incident energies of E_1 and E_2 , respectively, is attributed to the change in the real part of anomalous dispersion terms of A.

$$\begin{aligned} \Delta i_A(Q, E_1, E_2) &\equiv \frac{\{I(Q, E_1) - \langle f^2(Q, E_1) \rangle\} - \{I(Q, E_2) - \langle f^2(Q, E_2) \rangle\}}{c_A \{f'_A(E_1) - f'_A(E_2)\} W(Q, E_1, E_2)} \\ &= \frac{c_A \Re\{f_A(Q, E_1) + f_A(Q, E_2)\}}{W(Q, E_1, E_2)} (a_{AA}(Q) - 1) \\ &\quad + \frac{c_B \Re\{f_B(Q, E_1) + f_B(Q, E_2)\}}{W(Q, E_1, E_2)} (a_{AB}(Q) - 1) \end{aligned} \quad (1)$$

$$W(Q, E_1, E_2) = \sum_{k=A,B} c_k \Re\{f_k(Q, E_1) + f_k(Q, E_2)\} \quad (2)$$

where $E_{\text{abs}} > E_2 > E_1$ and c_k is the atomic fraction of constituent k ; $a_{ij}(Q)$ denotes the Faber–Ziman type partial structure factor; \Re means the real part of the values in the brackets. The quantity of $\Delta i_A(Q, E_1, E_2)$ contains two partial structure factors, $a_{AA}(Q)$ and $a_{AB}(Q)$ in an A–B binary system. Similarly, $\Delta i_B(Q, E_3, E_4)$ contains $a_{BB}(Q)$ and $a_{AB}(Q)$. Then, in order to obtain the three partial structure factors, the following set of linear equations should be solved:

$$\begin{pmatrix} \Delta i_A(Q, E_1, E_2) \\ \Delta i_B(Q, E_3, E_4) \\ i(Q, E_5) \end{pmatrix} = \begin{pmatrix} \frac{c_A \Re\{f_A(Q, E_1) + f_A(Q, E_2)\}}{W(Q, E_1, E_2)} & \frac{c_B \Re\{f_B(Q, E_1) + f_B(Q, E_2)\}}{W(Q, E_1, E_2)} & 0 \\ 0 & \frac{c_A \Re\{f_A(Q, E_3) + f_A(Q, E_4)\}}{W(Q, E_3, E_4)} & \frac{c_B \Re\{f_B(Q, E_3) + f_B(Q, E_4)\}}{W(Q, E_3, E_4)} \\ c_A^2 f_A^2(Q, E_5) & 2c_A c_B f_A(Q, E_5) f_B(Q, E_5) & c_B^2 f_B^2(Q, E_5) \end{pmatrix} \times \begin{pmatrix} a_{AA}(Q) - 1 \\ a_{AB}(Q) - 1 \\ a_{BB}(Q) - 1 \end{pmatrix}. \quad (3)$$

The ordinary term, $i(Q, E_5)$, is obtained at the energy, E_5 , far from the absorption edges of the constituents. The normalized determinant suggested by, for example, Edwards *et al* (1975) is considered one way for indicating the conditioning of the matrix expressed by weighting factors in equation of (3). The normalized determinants are 0.084 for CuBr and 0.120 for CuI at $Q = 50 \text{ nm}^{-1}$, respectively. Similar numerical values are recognized at all Q -values and this condition is comparable to the corresponding value of 0.03 for molten NaCl by using the neutron isotopic substitution technique (Edwards *et al* 1975).

The AXS measurements for molten copper halides CuX ($X = \text{Br, I}$) were carried out with synchrotron radiation on BL-7C with an Si(111) double-crystal monochromator covering

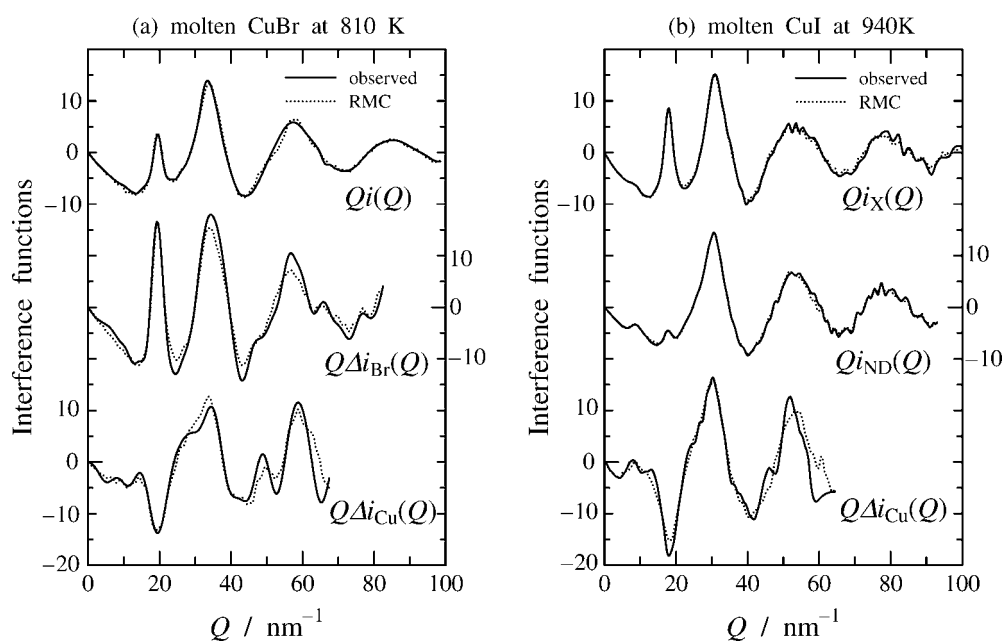


Figure 1. (a) The ordinary interference function of molten CuBr at 810 K, $Q_i(Q)$ and the environmental interference functions $Q\Delta i_{\text{Br}}(Q)$ and $Q\Delta i_{\text{Cu}}(Q)$; (b) the ordinary interference functions of molten CuI at 940 K, $Q_{iX}(Q)$ for x-ray and $Q_{iND}(Q)$ for neutron diffraction (Shirakawa *et al* 1991), and environmental interference function $Q\Delta i_{\text{Cu}}(Q)$ for Cu. Solid lines correspond to the experimental data. Dotted lines denote values calculated by the RMC simulation technique.

the energies ranging from 4 to 21 keV at the Photon Factory, Tsukuba, Japan. The scattering intensities were measured by a solid state detector in the symmetrical transmission geometry using a devised quartz cell. The accumulated counts of intensity, varying from 5×10^5 at low angles to 1×10^5 at high angles, held counting statistics approximately uniform. The experimental uncertainties in the interference functions do not exceed 1.0%. Other details of the experimental set up have been already reported (Saito *et al* 1997) and are not duplicated here. The atomic number densities of molten CuBr and CuI are 36.3 and 28.2 nm^{-3} , respectively, which are calculated from the values of molar volume (Inui *et al* 1991).

3. Results and discussion

Figure 1(a) shows the environmental interference functions of molten CuBr at 810 K, $Q\Delta i_{\text{Cu}}(Q)$ for Cu and $Q\Delta i_{\text{Br}}(Q)$ for Br, which are obtained from the measurements at incident energies of 8.680 keV ($f'_{\text{Cu}} = -3.06$), 8.955 keV ($f'_{\text{Cu}} = -5.58$), 13.170 keV ($f'_{\text{Br}} = -3.37$) and 13.445 keV ($f'_{\text{Br}} = -5.82$). These four energies correspond to 300 and 25 eV below the Cu K (8.980 keV) and Br K (13.470 keV) absorption edges, respectively. The ordinary interference function of $Q_i(Q)$ estimated from the scattering profile at the single energy of 17 keV is also illustrated in this figure. On the other hand, figure 1(b) gives the environmental interference functions of molten CuI at 940 K, $Q\Delta i_{\text{Cu}}(Q)$ for Cu, together with the ordinary interference functions $Q_{iX}(Q)$ measured at 17 keV. The AXS measurement at the K absorption edge (33.167 keV) for I is not readily available in the synchrotron radiation source presently used, because of significantly lower x-ray flux without any insertion devices in such an energy

region. For this reason, the conventional neutron diffraction result by Shirakawa *et al* (1991) including the present author (MS) was employed in the CuI case as the third interference function data, $Q_{iND}(Q)$.

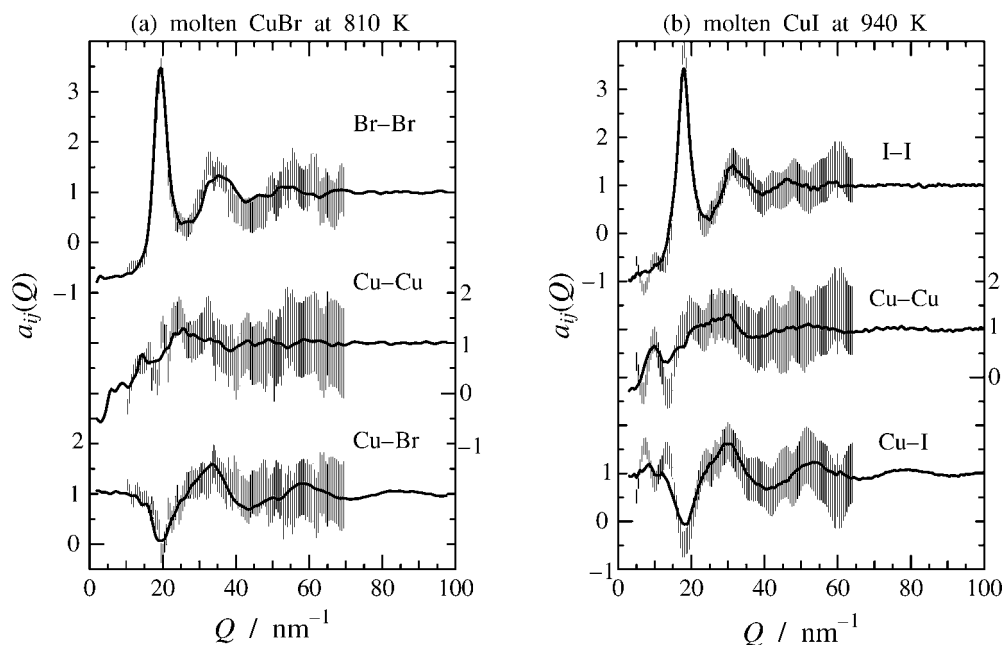


Figure 2. The partial structure factors (a) for molten CuBr at 810 K and (b) for molten CuI at 940 K. Solid lines correspond to the values calculated by the RMC simulation technique.

Figure 2(a) shows the three partial structure factors $a_{ij}(Q)$ of molten CuBr, where the vertical lines denote the uncertainty estimated from the experimental data by solving the simultaneous linear equation of (3). The numerical solutions of the simultaneous linear equations appear to be ill-conditioned at several Q values. Such behaviour is mainly due to the experimental uncertainty caused by the relatively small difference between the anomalous dispersion terms at the two energies and the unpredictably large fluctuation in the numerical solution of equation (3) when the pivot of the matrix is close to zero. At the present time, such small experimental errors cannot always be avoided. However, the reverse Monte Carlo (hereafter referred to as RMC) simulation technique (McGreevy and Pusztai 1988) might be one way to reduce this inconvenience. For this reason, we employed the RMC method in a way essentially identical to that described by McGreevy and Pusztai with an initial configuration of 1728 particles in a cubic box of size $L = 3.624$ nm. The three calculated interference functions were compared to the experimental results and such a comparison was continued with further iteration until a reasonable convergence was obtained, so as to reproduce the three independent interference functions (dotted lines in figure 1(a)). The resultant partial structure factors obtained by the RMC simulation technique are illustrated by the solid lines in figure 2(a). The agreement of present AXS data for molten CuBr with previous results by the neutron isotopic substitution technique (Allen and Howe 1992) are, in the present authors' view, rather surprisingly good. The partial structure factors determined through this procedure with the RMC simulation are considered to be the least conditions necessary for explaining the three independent experimental results of figure 1, although they might not be sufficient conditions for a full explanation. By applying the same data processing, the three partial

structure factors of molten CuI are estimated and they are given in figure 2(b). It can be found that both of the molten salts exhibit similar behaviours except for the peak positions in accord with the anionic size effects. The profiles of $a_{XX}(Q)$ and $a_{CuX}(Q)$ appear to agree with those of simple ionic liquids such as molten alkali halides, by observing that the first valley of $a_{CuX}(Q)$ is located at a Q value where the principal peak in $a_{XX}(Q)$ is situated. In contrast, the partial structure factor of $a_{CuCu}(Q)$ for cation–cation pairs was found to be rather structureless. Moreover, a small pre-peak located at $Q \sim 10 \text{ nm}^{-1}$ is clearly recognized in $a_{CuCu}(Q)$ of both molten CuBr and CuI. Such pre-peaks are considered to be particular density fluctuations mainly associated with the Cu distribution. It should be noticed that the pre-peak profiles are found to become pronounced with increasing anion size or decreasing ionicity, chloride, bromide and iodide in this order. Such behaviour suggests that the highest degree of local cation density fluctuation is quite likely in the molten CuI case.

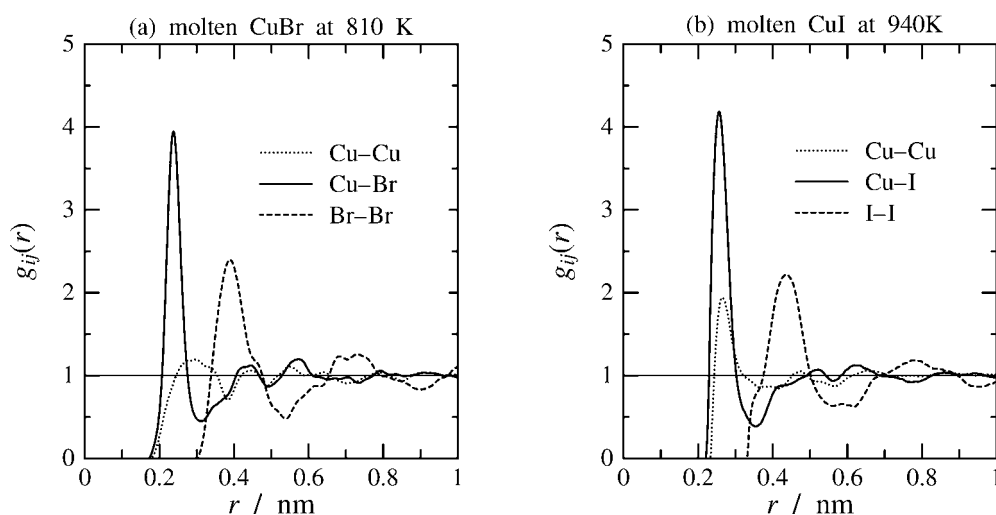


Figure 3. The partial pair distribution functions (a) for molten CuBr at 810 K and (b) for molten CuI at 940 K.

Figure 3 shows the resultant partial pair distribution functions $g_{ij}(r)$ of molten CuBr and CuI. In both cases, the closest Cu–Cu distance is significantly smaller than that for the anion–anion pair, indicating like-ion penetration into the first unlike-ion coordination shell. This characteristic penetration may be interpreted by a decrease in the coulombic repulsion force interacting between Cu ions arising from the reduced charge transfer between unlike ions. It could be suggested that the like-ion penetration of molten CuI is rather more pronounced than the molten CuBr case, although a definite comment about such different behaviour of two copper halides cannot be certainly identified yet from the present results alone. This particular penetration behaviour has also been discussed in terms of the small size effect of Cu ions and the high polarizability of the halide ions (Madden 1999), although this is not well coincident with the results of molten CuCl (Page and Mica 1971, Eisenberg *et al* 1982) and LiCl (McGreevy and Howe 1989), where Cu ions approach more closely than the smaller size of Li ions. The peak positions and the coordination numbers estimated are summarized in table 1, together with the values of the corresponding crystalline phases of zincblende type structure. The coordination numbers for X–X pairs are found to be 11.4 for molten CuBr and 10.2 for molten CuI. On the other hand, the coordination numbers for Cu–X pairs are found to be 3.1 for molten CuBr and 3.1 for molten CuI. When considering a perfect fcc lattice of

anions, the values of N_{+-} of anions around a cation located at a tetrahedral site are four with $r_{--}/r_{+-} = 1.63$ and at an octahedral site six with $r_{--}/r_{+-} = 1.41$, respectively. The values of r_{--}/r_{+-} for molten CuBr and CuI are 1.62 and 1.66, respectively, which are no closer to the octahedral case than the tetrahedral one, although these values are affected, more or less, by thermal vibration of ions in the molten state. Consequently, the present authors maintain the view that the structure of molten copper halides of CuX may be a disordered close packing of anions where the Cu ions take a strongly disordered distribution by meandering through essentially tetrahedral holes.

Table 1. Summary of structural parameters in molten CuBr and CuI.

	Molten CuBr (810 K)				Molten CuI (940 K)			
	Cu-Br		Br-Br		Cu-I		I-I	
	r (nm)	N	r (nm)	N	r (nm)	N	r (nm)	N
Present work	0.245	3.1	0.398	11.4	0.262	3.1	0.436	10.2
Values in the crystalline state	0.247	4	0.403	12	0.266	4	0.435	12
r_{--}/r_{+-}	1.62				1.66			

4. Concluding remarks

The partial structural functions of molten CuBr and CuI have been determined by the AXS method. The results indicate that the particular structureless correlation of Cu-Cu pairs appears to be a common feature in molten halide salts including copper. The present results also show the capability of the AXS method for estimating the partial structural functions of binary liquids. The scarcity of absolutely high accuracy for experimental data still prevents us from obtaining the direct solutions with sufficient reliability of the simultaneous linear equations of equation (3). Nevertheless, the present authors believe that the reverse Monte Carlo simulation technique is one way to reduce such difficulty by providing information in the sense of a necessary condition at best. It would be interesting to extend this approach to other molten salts, so that its usefulness and validity might be tested on a rather wider base.

Acknowledgments

The authors wish to express their gratitude to Professor M Nomura, Photon Factory, High Energy Accelerator Research Organization, for his help on the AXS measurements (proposal No 98G266).

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