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Partial structural functions of binary liquids estimated from anomalous X-ray scattering measurements

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A new apparatus has been built for structural studies of high-temperature liquids using the anomalous X-ray scattering (AXS) method with synchrotron radiation. AXS measurements were made in the asymmetrical reflection mode for a free liquid surface by changing the beam direction using an additional mirror system. The usefulness and capabilities of this new equipment were confirmed by obtaining the individual partial structural functions of liquid $Bi_{30}Ga_{70}$ alloy.

Keywords: anomalous X-ray scattering method; partial structural functions; Bi–Ga liquid alloy.

1. Introduction

Two possible diffraction geometries exist for applying the anomalous X-ray scattering (AXS) method using synchrotron radiation to liquid samples. One is a transmission mode and the other is a reflection mode. Since each mode has its own advantages, the better diffraction geometry should be chosen by consideration of the physicochemical properties of the liquid samples of interest. Recently, we reported a successful determination of partial structural functions for molten CuBr (which has a relatively small mass absorption coefficient and a high vapor pressure) by the AXS method in transmission geometry with a quartz sample cell (Saito *et al.*, 1997). On the other hand, reflection geometry is needed with liquid metals and alloys, for which the mass absorption coefficient is large and the vapor pressure is low. To the best knowledge of the present authors, utilization of reflection geometry with a synchrotron radiation source has been quite limited on a worldwide level. This prompted us to build a new apparatus that is suitable for structural studies of high-temperature liquids with large mass absorption coefficients and low vapor-pressure components by applying the AXS method with synchrotron radiation.

The main purpose of this paper is to describe a new experimental technique for determining the partial structural functions, using liquid $Bi_{30}Ga_{70}$ alloy as an example.

2. Fundamentals of the AXS method

The atomic scattering factor is expressed as $f(Q,E) = f^0(Q) + f'(E) + if''(E)$, 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 low-energy side of the absorption edge, $E_{\rm abs}$, 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 E_1 and E_2, respectively, is attributed to the change in the real part of the anomalous-dispersion terms of A:

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

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

where $E_{\rm abs} > E_2 > E_1$ and c_k is the atomic fraction of the k constituent; $a_{ij}(Q)$ denotes the Faber–Ziman type partial structure factor; $\Re$ means the real part of the values in the brackets. The quantity $\Delta i_A(Q, E_1, E_2)$ 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 equations should be solved:

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

The ordinary term, $i(Q, E_5)$, is obtained at the energy E_5, far from the absorption edges of the constituents.

3. Experimental

The AXS measurements were carried out with synchrotron radiation on beamline 7C at the Photon Factory, Tsukuba, Japan. The measurements were made in the asymmetrical reflection mode with a beam-direction-changing mirror system.

Fig. 1 shows a schematic diagram of the experimental set-up in the asymmetrical reflection mode for a free liquid surface of $Bi_{30}Ga_{70}$ alloy. The high-temperature chamber is mounted on the center of the diffractometer (left side of the figure). The liquid $Bi_{30}Ga_{70}$ alloy sample was heated to a temperature of 590 K, 55 K above its critical temperature, in a rectangular graphite crucible [(30×20) mm^2 $\times$ 3 mm depth] under a highly purified argon atmosphere.

A schematic of the X-ray optics is also given in Fig. 1. A monochromatic horizontal X-ray beam is first diffracted downward through a Bragg angle $2\varphi(E)$ by a W/Si multilayer mirror ($2d$ = 4.05 nm). The multilayer mirror is set on a stage that rotates

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to adjust the angle φ and also translates along a 600 mm long translation stage. The translation stage itself is mounted on the arm of a separate rotation axis, 2φ. The individual rotations φ and 2φ and the translation stage are synchronously controlled so that the beam diffracted by the W/Si multilayer mirror passes just through the center of the 2φ axis. Concentric with the 2φ axis is another rotation, ω. A flat fused quartz mirror, coated with Pt, is mounted at the center of the ω axis. Therefore, the X-ray beam diffracted by the multilayer mirror is totally reflected by the flat fused quartz mirror through the angle ω. Throughout a specific X-ray energy region, this mirror system can keep the final emitted-beam direction constant; that is, a glancing angle α is maintained. The W/Si multilayer mirror always faces downward. The Pt-coated quartz mirror, however, faces upward when $2\varphi(E)$ is larger than α and downward when $2\varphi(E)$ is smaller than α. If the critical angle for total reflection from the Pt-coated mirror, $2\omega_c(E)$, is larger than $|2\varphi(E) - \alpha|$, it is possible to adjust the final emitted-beam direction without any significant loss of the intensity. As an example, the beam direction could be kept constant through an energy range from 8.5 to 15 keV, with sufficient incident intensity, when the glancing angle α was chosen as 3.0°.

4. Structural study of liquid $Bi_{30}Ga_{70}$ alloy by the AXS method

Fig. 2 shows the environmental interference functions $Q\Delta i_{\mathrm{Bi}}(Q)$ and $Q\Delta i_{\mathrm{Ga}}(Q)$ which were obtained from the measurements at incident energies of 10.0682 keV ($f'_{\mathrm{Ga}} = -3.17$), 10.3432 keV ($f'_{\mathrm{Ga}} = -5.67$), 13.126 keV ($f'_{\mathrm{Bi}} = -10.51$) and 13.401 keV ($f'_{\mathrm{Bi}} = -15.30$). These energies correspond to 300 and 25 eV below the Ga K (10.3682 keV) and Bi L_{III} (13.426 keV) absorption edges, respectively. The ordinary interference function $Qi(Q)$, estimated from the scattering profile at an energy of 15.0 keV (which corresponds to an energy away from either edge), is also illustrated in Fig. 2. Fig. 3 shows the three partial structure factors for liquid $Bi_{30}Ga_{70}$ alloy, where the vertical lines denote the uncertainty estimated from the experimental data by solving the simultaneous linear equation (3), given above. The numerical solutions of the simultaneous linear equations appear to be ill-conditioned at several Q values, frequently giving some physically unreasonable behavior in the resultant radial distribution functions. Such behavior is mainly due to the experimental uncertainty caused from 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 (Stantson, 1961). At the present time, such small experimental errors cannot always be avoided. However, the reverse Monte Carlo (RMC) simulation technique (McGreevy & Pusztai, 1988) might be one way to reduce this inconvenience. We used the RMC method in a way essentially identical to that described by McGreevy & Pusztai with an initial configuration of 6750 atoms, of which 2025 atoms represent Bi and the remaining atoms Ga in a cubic box of size L = 5.5032 nm. We defined the following statistics for the calculation:

$$\chi^2 = \sum_{m=1}^{n} \{i(Q_m) - i^c(Q_m)\}^2/\sigma^2(Q_m) + \sum_{\alpha} \sum_{m=1}^{n'} \{\Delta i_\alpha(Q_m) - \Delta i^c_\alpha(Q_m)\}^2/\sigma^2_\alpha(Q_m). \quad (4)$$

It included one total interference function and two environmental interference functions. The three interference functions calculated 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 of $Q\Delta i_{Bi}(Q)$, $Q\Delta i_{\mathrm{Ga}}(Q)$ and $Qi(Q)$ (dotted lines in Fig. 2). The solid lines in Fig. 3 illustrate the resultant partial structure factors obtained by the RMC simulation technique, which reconstruct the three interference functions.

It was found that the RMC partial structure factor $a_{\mathrm{GaGa}}(Q)$ of the Ga–Ga pair has an asymmetry in the first peak and corresponds rather closely to that of pure liquid Ga [broken line in

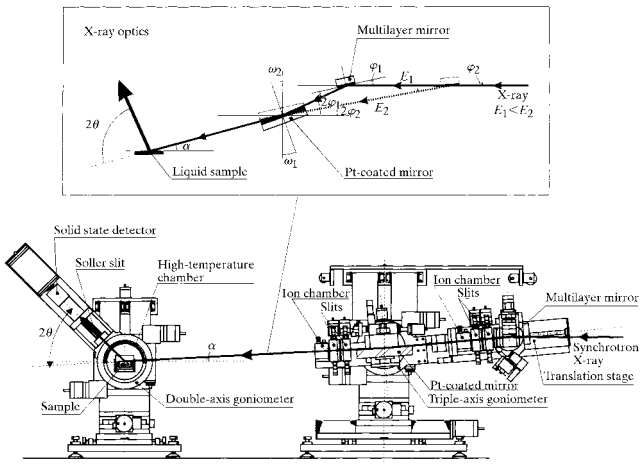

Figure 1
Schematic diagram of the AXS experimental set-up for a free liquid surface sample in the asymmetrical reflection mode. The inset contains a schematic of the beam-direction-changing X-ray optics, which uses a W/Si multilayer mirror and a flat fused quartz mirror coated with Pt.

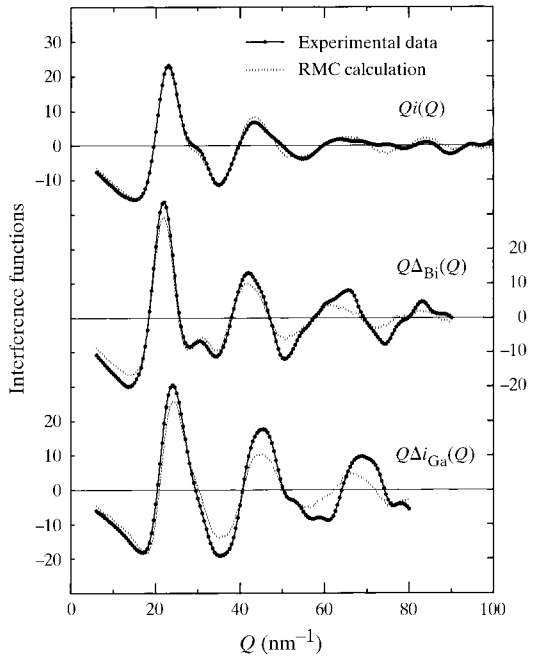

Figure 2
The ordinary interference function $Qi(Q)$ and the environmental interference functions $Q\Delta i_{\mathrm{Bi}}(Q)$ and $Q\Delta i_{\mathrm{Ga}}(Q)$ of the liquid $Bi_{30}Ga_{70}$ alloy at 590 K. Solid lines correspond to the experimental data. Dotted lines denote values calculated by the RMC method.

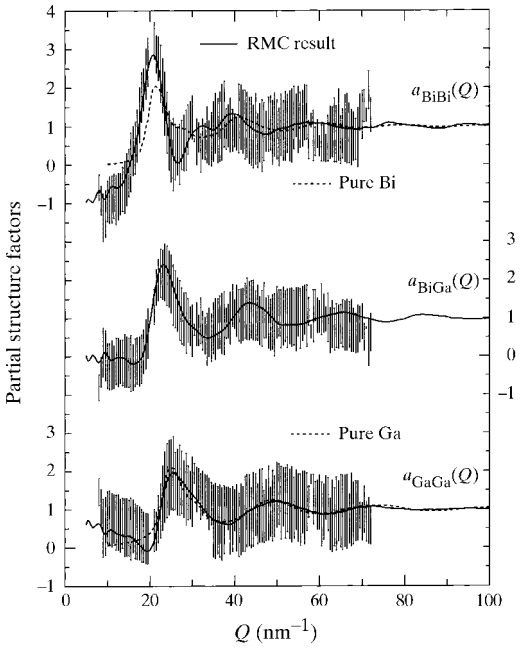

Figure 3
Three partial structure factors for liquid $Bi_{30}Ga_{70}$ alloy at 590 K. Solid lines correspond to the values calculated by the RMC method. Broken lines indicate the structure factors of pure Bi and Ga for comparison.

Fig. 3 (Waseda, 1980)]. The partial structure factor of the unlike atom pair $a_{BiGa}(Q)$ has maxima that lie in between those of the two like-atom pairs. The partial structure factor $a_{BiBi}(Q)$ of the Bi–Bi pair is characterized by a small hump near $Q = 32$ nm^{-1} on the low-Q side of the second peak, as well as no subsidiary hump on the higher-Q side of the first peak. Such behavior differs remarkably from that of pure liquid Bi (Waseda, 1980) and this may be attributed to a particular feature of the liquid $Bi_{30}Ga_{70}$ alloy.

5. Concluding remarks

It is quite satisfying that a reflection-mode AXS measurement with synchrotron radiation for a free liquid surface sample could be realized with a triple-axis goniometer utilizing the combination of a W/Si multilayer mirror and a flat fused quartz mirror coated with Pt. The present result shows the capabilities of the new apparatus and the utility of anomalous X-ray scattering measurements for estimating the partial structural functions of a binary liquid. Although the insufficient absolute accuracy of the experimental data still prevents us from obtaining exact solutions of the simultaneous linear equations from the AXS measurements alone, we believe that the reverse Monte Carlo simulation technique is one useful way to reduce such difficulties. The obtained partial structural functions for liquid $Bi_{30}Ga_{70}$ alloy in this work provide a step forward for obtaining a direct link between the atomic scale structure and characteristic properties. Thus, it would be interesting to extend the AXS measurements to the estimation of partial structural functions for various other liquids.

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