A determination of the partial structure factors of liquid TlSe using combined x-ray and neutron diffraction

LETTER TO THE EDITOR

A determination of the partial structure factors of liquid TlSe using combined x-ray and neutron diffraction

A C Barnes†, S B Lague†, M A Hamilton†, H E Fischer‡, A N Fitch§ and E Dooryhee§

† H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK
‡ Institut Laue–Langevin, Avenue des Martyrs, F-38042, Grenoble, France
§ European Synchrotron Radiation Facility, Avenue des Martyrs, F-38043, Grenoble, France

Abstract.   The partial structure factors of liquid thallium selenide, TlSe, have been determined using a combination of two neutron diffraction measurements using isotopic substitution and one x-ray diffraction measurement. We show that the statistical accuracy obtained using this method is considerably higher than that achievable using neutron diffraction and isotopic substitution alone. The results unambiguously show the formation of Se polyanionic species in the liquid.

The method of neutron diffraction and isotopic substitution (NDIS) is extremely powerful for obtaining unambiguous information concerning the local atomic structure in disordered materials (Enderby and Barnes 1990). It has been applied successfully for many years as a method of obtaining the partial structure factors of a wide range of binary liquid and glassy materials. However, despite this success, the number of materials that have been studied using this method is limited due to the relatively few elements with isotopes that have a large enough variation in their neutron scattering lengths. There have also been many studies of liquid structure using x-ray diffraction. However, x-ray scattering by itself gives limited information due to the Q-dependence of the x-ray form factors of the atoms and there is no equivalent to isotopic substitution whereby partial structure factors can be obtained. (In principle the x-ray anomalous scattering technique can be used. However, the limited contrast in x-ray scattering lengths achievable with this technique leads to relatively poor statistical accuracy for the partial structure factors (Waseda 1984) although the outlook is improving with the development of third-generation synchrotron sources.) It is also more difficult to fully correct and normalize x-ray diffraction due to the difficulties of removing the inelastic Compton scattering.

In this work we show how a combination of NDIS and x-ray diffraction can be used to obtain the partial structure factors for a liquid in which NDIS alone is insufficient to provide statistically accurate partial structure factors. The method is equivalent to using the x-ray diffraction pattern as a 'third-isotope' combination in a traditional NDIS experiment.

Liquid $Tl_x Se_{1-x}$ alloys for $1/2 \leqslant x \leqslant 2/3$ have an electronic conductivity characteristic of narrow-definition liquid semiconductors (Enderby and Barnes 1990). For $x = 2/3$ the material is considered as being comprised of essentially Tl^+ and Se^{2-} ions that give rise to a charge-transfer gap in the electronic density of states (Barnes 1993). As selenium is added to Tl_2Se, the conductivity remains low, indicating that the gap in the electronic

density of states remains. Neutron diffraction measurements at the total structure factor level (Lague *et al* 1996) show that this is due to the formation of Se^{n-} ions which preserve the essentially ionic character of the liquid. However, the detailed structure of the selenium-rich alloys cannot be ascertained from these total structure factor measurements alone. A NDIS measurement of the partial structure factors of liquid Tl_2Se was carried out by Barnes and Guo (1994). However, due to the nature of the available isotopes (^{203}Tl, ^{205}Tl (Sears 1992) and ^{76}Se (Koester *et al* 1980)), the statistical accuracy of the partial structure factors obtained was low and strong smoothing procedures were required to obtain the partial $g(r)$s. This reduced the real-space resolution obtainable. We have carried out a similar measurement to obtain the partial structure factors of the equi-atomic liquid TlSe using the same isotope combinations. In this case the Q-independent scattering matrix for the three isotopically labelled samples ($^{N}Tl^{N}Se$, $^{205}Tl^{N}Se$ and $^{203}Tl^{76}Se$, where N represents the natural isotopic composition) can be written in terms of the partial structure factors ($S_{TlTl}(Q)$, $S_{TlSe}(Q)$ and $S_{SeSe}(Q)$) as

$$\begin{pmatrix} {}^{N}_{N}F(Q) \\ {}^{205}_{N}F(Q) \\ {}^{203}_{76}F(Q) \end{pmatrix} = \begin{pmatrix} 0.1929 & 0.1588 & 0.3501 \\ 0.2275 & 0.1588 & 0.3802 \\ 0.1222 & 0.3721 & 0.4264 \end{pmatrix} \begin{pmatrix} S_{TlTl}(Q) - 1 \\ S_{SeSe}(Q) - 1 \\ S_{TlSe}(Q) - 1 \end{pmatrix} \qquad (1)$$

which can be inverted to give the partial structure factors as follows:

$$\begin{pmatrix} S_{TlTl}(Q) - 1 \\ S_{SeSe}(Q) - 1 \\ S_{TlSe}(Q) - 1 \end{pmatrix} = \begin{pmatrix} -125.6 & 106.5 & 8.1 \\ -86.1 & 67.3 & 10.7 \\ 111.1 & -89.2 & -9.4 \end{pmatrix} \begin{pmatrix} {}^{N}_{N}F(Q) \\ {}^{205}_{N}F(Q) \\ {}^{203}_{76}F(Q) \end{pmatrix}. \qquad (2)$$

A measure of the conditioning of this matrix is given by its normalized determinant $|A_n| = 0.005$ (Edwards *et al* 1975). This can be improved marginally (but with the additional cost of an extra isotope) by using a sample of $^{N}Tl^{76}Se$ instead of (or in addition to) the $^{N}Tl^{N}Se$ sample. This improves $|A_n|$ to a value of 0.01. Figure 1 shows the partial structure factors derived from an NDIS experiment on liquid TlSe using the isotope combinations given in equation (1). The measurements were made on the D4B diffractometer at the High Flux Beams Reactor at the Institut Laue–Langevin, Grenoble, France. The data were corrected using the same procedures as were used in the study of liquid Ag_2Se as outlined by Barnes *et al* (1997). The low statistical precision of the partial structure factors obtained in this NDIS experiment is apparent in these figures.

In the case of x-ray diffraction from liquid TlSe there is a large contrast between the x-ray form factors of the high atomic number Tl (81) and selenium (34) atoms (Wilson 1995). By using the x-ray diffraction data in addition to the NDIS data, a considerable improvement can be made in the statistical precision of the partial structure factors obtained. Because of the Q-dependence of the x-ray form factors, the inversion from x-ray/neutron total structure factors must be carried out at each point in Q-space. As an example of the matrix conditioning, the scattering and inverse scattering matrices at $Q = 5$ Å^{-1} are as follows:

$$\begin{pmatrix} {}^{205}_{N}F(Q) \\ {}^{203}_{76}F(Q) \\ {}^{X}F(Q) \end{pmatrix} = \begin{pmatrix} 0.2968 & 0.2072 & 0.4960 \\ 0.1327 & 0.4042 & 0.4631 \\ 0.5184 & 0.0784 & 0.4032 \end{pmatrix} \begin{pmatrix} S_{TlTl}(Q) - 1 \\ S_{SeSe}(Q) - 1 \\ S_{TlSe}(Q) - 1 \end{pmatrix} \qquad (3)$$

which can be inverted to give the partial structure factors as follows:

$$\begin{pmatrix} S_{TlTl}(Q) - 1 \\ S_{SeSe}(Q) - 1 \\ S_{TlSe}(Q) - 1 \end{pmatrix} = \begin{pmatrix} -5.625 & 1.983 & 4.643 \\ -8.290 & 6.105 & 3.184 \\ 8.846 & -3.737 & -4.109 \end{pmatrix} \begin{pmatrix} {}^{205}_{N}F(Q) \\ {}^{203}_{76}F(Q) \\ {}^{X}F(Q) \end{pmatrix} \qquad (4)$$
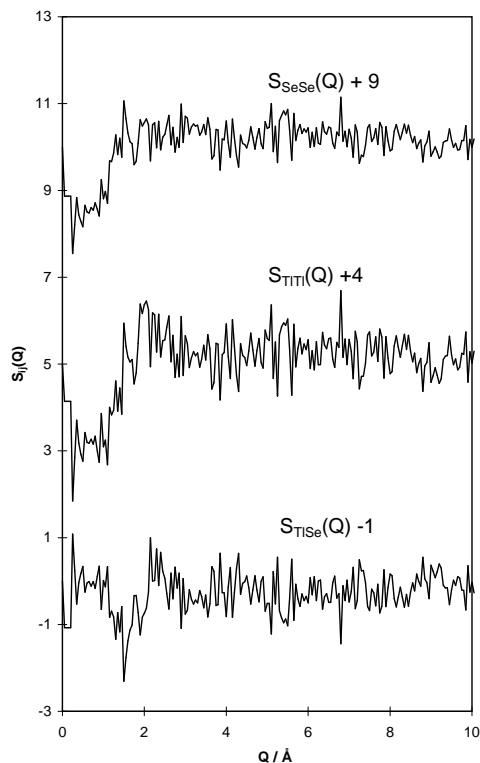
Figure 1. The partial structure factor of liquid TlSe obtained using NDIS with samples of $^{N}Tl^{N}Se$, $^{205}Tl^{N}Se$ and $^{203}Tl^{76}Se$.

where $^{X}F(Q)$ is the x-ray total structure factor. This gives a conditioning figure of $|A_n| = 0.088$ which is typical at all Q-values. The improvement in the statistical precision of the partial structure factors for the same precision in the total structure factors is apparent in the conditioning of this matrix. Figure 2 shows the experimental partial structure factors determined using this sample combination. The improvement in the statistical accuracy of the partial structure factors compared with the NDIS measurement is clear. The x-ray data were taken using the BM16 diffractometer at the ESRF using 38 keV incident radiation. This diffractometer gives results with three key advantages over lower energy x-ray measurements:

(i) high intensities at high energies are attainable, which allows measurements of the transmission through high-atomic-mass samples to be made;

(ii) the existence of high-energy-resolution analysers ($\Delta E \leqslant 5$ eV) that experimentally reject the inelastic Compton scattering are used in the scattered beam;

(iii) high values of Q ($\sim$35 Å^{-1}) are attainable, which leads to higher real-space resolution.

The samples were contained in thin-walled silica capillaries of 0.3 mm diameter which were heated with the instrument hot-air furnace. The data was corrected for the effects of self-attenuation (Paalman and Pings 1962) and the empty-can and background scattering using similar corrections to those applied in the neutron scattering case (Barnes *et al* 1997). Multiple scattering was considered as negligible due to the high absorption of the sample
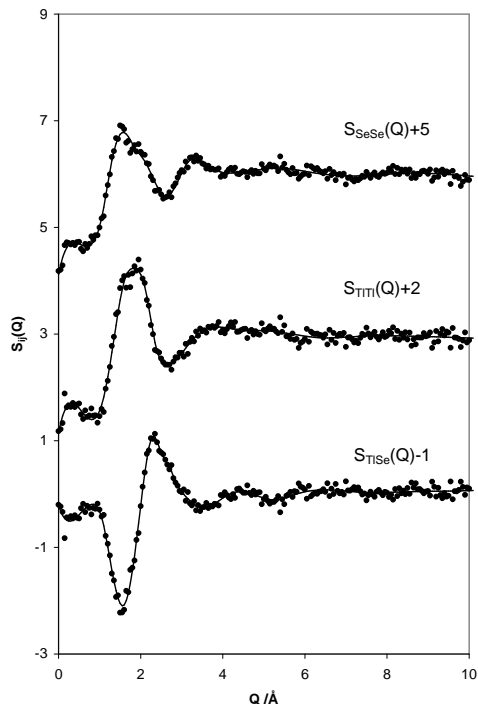
Figure 2. The partial structure factors of liquid TlSe obtained using a combination of neutron diffraction and x-ray scattering data.

and the energy analysis of the detectors. Full details of the data analysis will be given in a later paper.

The raw $S_{ij}(Q)$ obtained by directly inverting the scattering matrix were smoothed using a cubic spline fit as shown in figure 2. The corresponding $g_{ij}(r)$ obtained by Fourier transform of the smoothed $S_{ij}(Q)$ are shown in figure 3.

The $S_{ij}(Q)$ in figure 2 show features closely resembling those of a typical molten salt. Most notable is the sharp dip in $S_{\mathrm{TlSe}}(Q)$ at ~ 1.5 Å^{-1} which is characteristic of chemical ordering in the liquid. Lague *et al* (1996) and Usuki *et al* (1993) have previously reported measurements of the total structure factor of liquid $\mathrm{Tl}_{1-x}\mathrm{Se}_x$ at various compositions. Each of theses authors observes a peak in the total radial distribution function at 2.35 Å which they attribute to the existence of Se polyanions at selenium-rich compositions. In this study the peak at 2.35 Å is only observed in $g_{\mathrm{SeSe}}(r)$ which unambiguously confirms these conclusions. The first peak in $g_{\mathrm{TlTl}}(r)$ and the main peak in $g_{\mathrm{SeSe}}(r)$ both occur at approximately 4 Å. This can be compared with a distance of 4.8 Å for Se–Se and 4.4 Å for Tl–Tl reported by Barnes and Guo for liquid $\mathrm{Tl}_2\mathrm{Se}$. Usuki *et al* also attempted to approximate the partial structure factors of liquid $\mathrm{Tl}_2\mathrm{Se}$ and $\mathrm{Tl}_2\mathrm{Se}_3$ by investigating the changes in the total structure factors of the liquid over a small concentration range. The peaks that we find at 4 Å for both the Tl–Tl and Se–Se correlations are broadly similar to those reported for liquid $\mathrm{Tl}_2\mathrm{Se}_3$. Integration of the first peak in Se–Se yields an Se–Se coordination of 0.5 ± 0.1 which is close to the values of 0.38 and 0.63 reported by Usuki *et al* (1993) and Kameda *et al* (1990) respectively. The coordination number for the main peaks (calculated to the first minimum in $g_{ij}(r)$) are Tl–Tl: 9 ± 1, Se–Se: 10 ± 1 and Tl–Se: 6.0 ± 0.5. These numbers correspond with those typical of molten-salt-like materials.
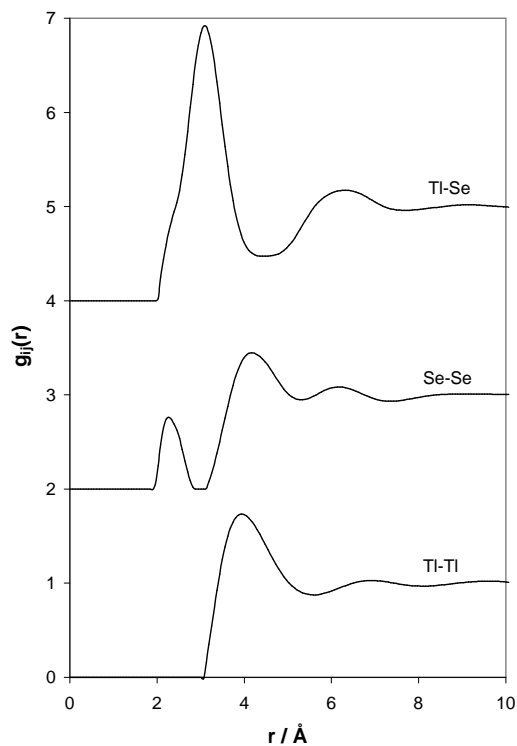
Figure 3. The partial $g_{ij}(r)$ obtained from the partial structure factors in figure 2.

These results clearly demonstrate how accurate x-ray diffraction measurements can be used in combination with NDIS methods to enhance the precision with which partial structure factors of binary liquid systems can be extracted. The availability of diffractometers at synchrotron sources with high energy resolution of the scattered x-ray beam, coupled with high incident intensities and energies has improved the precision with which the x-ray measurements can be made. The technique of combined x-ray/neutron diffraction for measuring the partial structure factors of binary systems outlined here is most effective when the system consists of one light and one heavy element (which provides high contrast in the x-ray form factors), and where the light element has a large contrast in the available isotopic scattering lengths (especially if the scattering length of the light atom is higher than that of the heavy atom).

In principle the accuracy of the data obtained can be improved further by carefully matching the resolution of the neutron and x-ray diffractometers. This is particularly important for materials for which there are relatively sharp diffraction features at small Q (<2 Å^{-1}) where many neutron diffractometers (such as D4B) have poor resolution. For experiments in which there is a smaller contrast between the x-ray and neutron scattering lengths it may also be necessary to verify the precision of the x-ray atomic form factors (for example to take into account the charge state of the scattering species).

References

Barnes A C 1993 *J. Non-Cryst. Solids* **156–8** 675
Barnes A C and Guo C 1994 *J. Phys.: Condens. Matter* **6** A229
Barnes A C, Lague S B, Salmon P S and Fischer H E 1997 *J. Phys.: Condens. Matter* **9** 6159
Edwards F G, Enderby J E, Howe R A and Page D I 1975 *J. Phys. C: Solid State Phys.* **8** 3483
Enderby J E and Barnes A C 1990 *Rep. Prog. Phys.* **53** 85
Kameda Y, Uemura O, Hangai K and Satow T 1990 *J. Non-Cryst. Solids* **117+118** 84
Koester L, Knopf L and Waschkowski W 1980 *Z. Phys.* A **296** 43
Lague S B, Barnes A C, Archer A D and Howells W S 1996 *J. Non-Cryst. Solids* **205–207** 89
Paalman H H and Pings C J 1962 *J. Appl. Phys.* **33** 2635
Sears V F 1992 *Neutron News* **3** 26
Usuki T, Shirakawa Y, Maruyama K and Tamaki S 1993 *J. Non-Cryst. Solids* **156–158** 716
Waseda Y 1984 *Novel Applicatons of Anomalous (Resonance) X-ray Scattering for Structural Characterization of Disordered Materials* (New York: Springer)
Wilson A J C 1995 *International Tables for X-ray Crystallography* vol C (London: Kluwer)