

A determination of the structure of liquid Ag_2Te using neutron diffraction and isotopic substitution and its comparison to Ag_2Se

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 7311

(<http://iopscience.iop.org/0953-8984/12/33/301>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 06:39

Please note that [terms and conditions apply](#).

A determination of the structure of liquid Ag_2Te using neutron diffraction and isotopic substitution and its comparison to Ag_2Se

A C Barnes[†], M A Hamilton[†], U Beck[†] and H E Fischer^{‡§}

[†] H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK

[‡] Institut Laue–Langevin, Avenue des Martyrs, F-38042 Grenoble, France

Received 8 May 2000

Abstract. The partial structure factors and pair distribution functions for liquid Ag_2Te have been measured using the method of neutron diffraction and isotopic substitution. The partial structure factors are consistent with a melt in which the predominant interactions are ionic in nature and in which the small Ag^+ ions are highly disordered and move rapidly through a more ordered Te^{2-} sub-structure. A detailed comparison has been made between the structure of this liquid and that of liquid Ag_2Se . It is observed that the main structural features of the two liquids are similar but a significant difference is observed in $S_{\text{AgAg}}(Q)$. The differences in the electronic properties of the two liquids are discussed in light of these results.

1. Introduction

The silver chalcogenides Ag_2X ($X = \text{S}, \text{Se}$ and Te) are materials of considerable fundamental and technological interest in both their solid and liquid states. In their solid phases they are all fast-ion conductors at moderate temperatures (Ag_2S (452 K), Ag_2Se (406 K) and Ag_2Te (423 K)) due to the motion of Ag^+ ions through the chalcogenide lattice (Kobayashi 1990). However, unlike the similarly structured silver halides they also show a significant electronic conductivity (Hasegawa 1985). The significant electronic conductivity is also maintained in the liquid phase (Dancy 1965, Schnyders *et al* 1997). However, liquid Ag_2Se and Ag_2Te show quite different behaviour in their electronic properties in the liquid phase. Ag_2Se and Ag_2Te both melt directly from their fast-ion phases at temperature of ~ 1173 and ~ 1223 K respectively. Ag_2Te has a conductivity of $\sigma = 250 \Omega^{-1} \text{cm}^{-1}$ at 1273 K and has a positive temperature coefficient of conductivity $d\sigma/dT$. In contrast Ag_2Se at 1273 K has a conductivity of $\sigma = 400 \Omega^{-1} \text{cm}^{-1}$ yet shows a negative temperature coefficient of conductivity $d\sigma/dT$. In both cases the thermopower and conductivity data for these liquids suggest that they are both narrow definition liquid semiconductors (as described by Enderby and Barnes (1990)) with a conductivity gap $\Delta E \sim 0.0$ eV. In a detailed study of the electronic properties of liquid Ag_2Se Ohno *et al* (1994) conclude that the electron mobility is unusually high when compared with that of Ag_2Te —a conclusion supported by the Hall effect measurements of Glazov *et al* (1986). The reason for the high mobility is not clear but it has been suggested (Fortner *et al* 1995) that the high ion mobility in the solid may be responsible in a manner outlined by

§ Current address: Laboratoire LURE, Batiment 209d, Centre Universitaire Paris-Sud, BP 34, 91898 Orsay Cedex, France.

Table 1. Neutron scattering parameters used in the data analysis.

| Isotope | \bar{b} (fm) | σ_a (at 0.7 Å) | |
|-------------------|-----------------|-----------------------|--------------------|
| | | (barns) | σ_s (barns) |
| ^{nat}Ag | 5.97 ± 0.04 | 24.6 ± 0.2 | 4.99 ± 0.03 |
| ^{107}Ag | 7.64 ± 0.04 | 14.6 ± 0.5 | 7.44 ± 0.09 |
| ^{109}Ag | 4.19 ± 0.03 | 35.4 ± 0.4 | 2.55 ± 0.06 |
| ^{nat}Te | 5.80 ± 0.03 | 1.58 ± 0.02 | 4.31 ± 0.10 |
| ^{122}Te | 3.8 ± 0.2 | 0.97 ± 0.12 | 1.83 ± 0.16 |

Ramasesha (1982) and Huberman (1974). In a recent paper (Barnes *et al* 1997) we reported detailed measurements of the structure of liquid Ag_2Se at the partial structure factor level and compared the results with molecular dynamics (Rino *et al* 1988) and *ab initio* molecular dynamics simulations (Kirchhoff *et al* 1996). The results supported the belief that the material can be broadly understood as a molten salt of Ag^+ and Se^{2-} ions with some screening of the bare charges due to the mobile electrons. The agreement between the experiment and the computer simulations was excellent apart from $S_{\text{AgAg}}(Q)$, that showed significant differences when compared to the computer simulations. It was suggested that the differences in $S_{\text{AgAg}}(Q)$ and the dynamics of the Ag^+ ions in the liquid may be significant when trying to understand the electronic properties.

In this paper we present results of a neutron diffraction and isotopic substitution experiment to determine the partial structure factors of liquid Ag_2Te . This is an important material to compare with Ag_2Se as its electronic behaviour is more ‘normal’ yet the main difference between the two materials is the slightly larger ion size of the Te^{2-} ion. In a future paper we will consider the Ag^+ dynamics, as determined by coherent quasi-elastic neutron scattering for both of these liquids.

2. Experimental procedure

An experiment to measure the partial structure factors of liquid Ag_2Te at 1273 K was carried out using the D4B diffractometer at the High Flux Beam Reactor at the Institut Laue–Langevin France. Three isotopically labelled samples ($^{109}\text{Ag}_2$ ^{nat}Te , $^{nat}\text{Ag}_2$ ^{nat}Te and $^{107}\text{Ag}_2$ ^{122}Te) with a mass of 2 g were prepared by mixing the pure elements in a quartz tube and mixing the samples at 1350 K for 24 hours. After cooling, the samples were transferred to thin walled quartz tubes with an internal diameter of 3 mm and a wall thickness of 0.5 mm. The experimental method and data corrections applied to the sample scattering were identical to those employed for the experiment on liquid Ag_2Se reported in a previous paper (Barnes *et al* 1997). These samples, as in the case of liquid Ag_2Se , showed a tendency to form small bubbles when melted and a similar renormalization procedure of the data was used to bring the calculated $F(Q)$ values to their correct high Q limits. In all cases this correction was less than 5% on the initially determined $F(Q)$ values and was consistent with the estimated bubble volume in the sample. The incident neutron wavelength was 0.7 Å and the values of the bound scattering length b , absorption cross-section σ_a and scattering cross-section σ_s used in the data analysis are given in table 1. The neutron scattering lengths and cross-sections for silver and tellurium were taken from Koester and Knopf (1980) and Koester *et al* (1986) respectively. The thermal absorption cross-section of ^{122}Te was taken from Mughabghab (1984). The number density of the sample was taken as 0.036 Å^{-3} as determined self consistently from the scattering data.

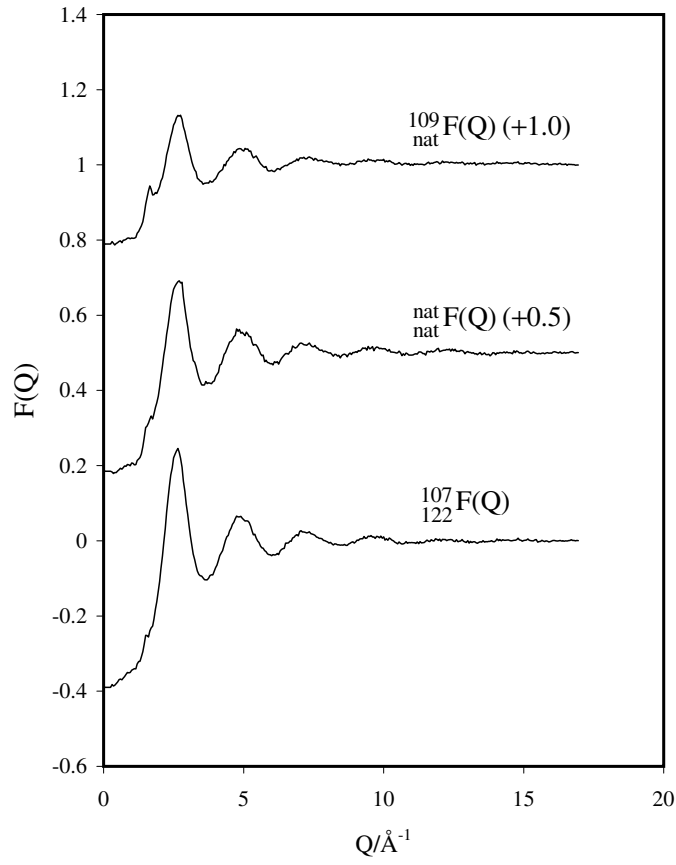


Figure 1. The fully corrected experimental total structure factors for liquid Ag₂Te.

3. Experimental results

Figure 1 shows the three total structure factors ($F(Q)$) obtained after the experimental data corrections. The errors on the data are of the order of 0.05 barns per point and are indicated by the statistical noise in the figure.

The scattering matrix for this isotopic combination is

$$\begin{pmatrix} {}^{nat}F(Q) \\ {}^{109}_{nat}F(Q) \\ {}^{107}_{122}F(Q) \end{pmatrix} = \begin{pmatrix} 0.158 & 0.037 & 0.154 \\ 0.078 & 0.037 & 0.108 \\ 0.259 & 0.016 & 0.130 \end{pmatrix} \begin{pmatrix} S_{AgAg}(Q) - 1 \\ S_{TeTe}(Q) - 1 \\ S_{AgTe}(Q) - 1 \end{pmatrix}.$$

The inverse of this matrix that gives the partial structure factors is

$$\begin{pmatrix} S_{AgAg}(Q) - 1 \\ S_{TeTe}(Q) - 1 \\ S_{AgTe}(Q) - 1 \end{pmatrix} = \begin{pmatrix} -22.2 & 16.9 & 12.3 \\ 129.0 & 140.0 & 36.7 \\ 60.7 & -51.4 & 21.6 \end{pmatrix} \begin{pmatrix} {}^{nat}F(Q) \\ {}^{109}_{nat}F(Q) \\ {}^{107}_{122}F(Q) \end{pmatrix}.$$

This matrix has a normalized determinant $|A_n| = 0.015$ (Edwards *et al* 1975) that is slightly smaller than that obtained in the case of liquid Ag₂Se but still sufficient to obtain reasonable quality partial structure factors. A previous experiment on liquid TlSe (Barnes *et al* 1998) with

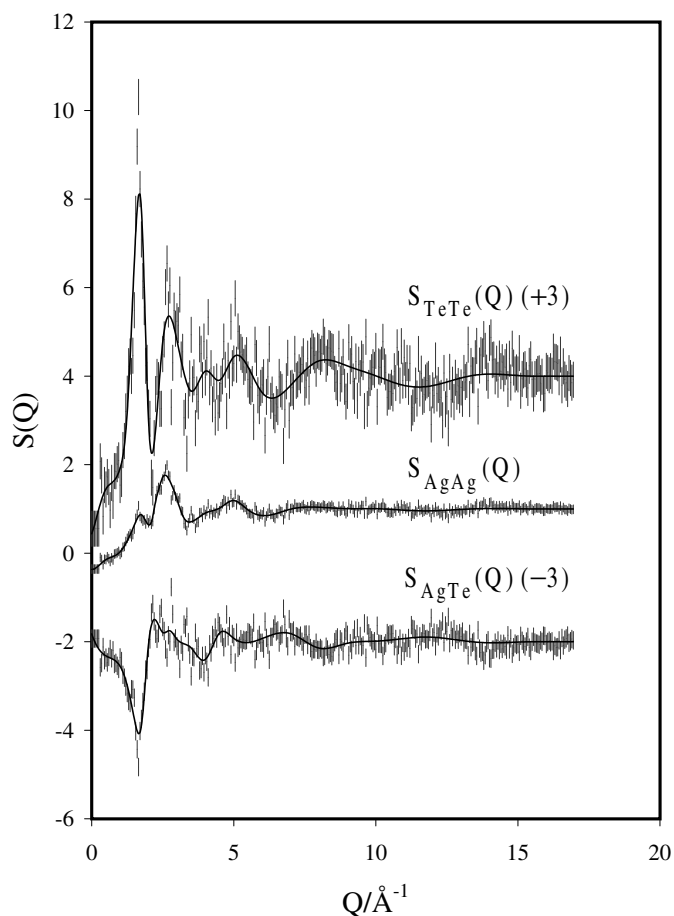


Figure 2. The experimental partial structure factors $S_{TeTe}(Q)$, $S_{AgAg}(Q)$ and $S_{AgTe}(Q)$. The error bars indicate the statistical errors on the data points. The solid lines are the smoothed $S(Q)$ obtained by using a cubic spline fit to the data points.

$|A| = 0.005$ was at the limit of the D4B statistics although the newer generation of instruments (D4C (at the ILL) and GEM (at ISIS, UK)) may see this figure approach closer to $|A| = 0.002$. Figure 2 shows the partial structure factors of liquid Ag_2Te as obtained from the total structure factors by direct use of the inverse matrix above. The measured partial structure factors fully satisfy the sum rules and inequality relations given by Edwards *et al* (1975). The relatively poor statistical accuracy of $S_{TeTe}(Q)$ is a direct consequence of the conditioning of the inverse matrix above. Figure 3 shows the inversion of the total structure factors into the corresponding Bhatia–Thornton structure factors (Bhatia and Thornton 1970). In this case it can be noted that as the scattering lengths of natural Ag and natural Te are almost the same so ${}^{nat}F(Q)$ is a direct measurement of $S_{NN}(Q)$.

Figure 4 shows the partial radial distribution functions obtained from the partial structure factors shown in figure 2. The grey line is the direct Fourier transform of the raw partial structure factors and the solid black line that obtained after Fourier transform of the partial structure factors fitted with a cubic spline. Each of these oscillates around the correct low r limit confirming a satisfactory inversion procedure. A summary of the pertinent structural features for liquid Ag_2Te (this work) and a comparison with liquid Ag_2Se (Barnes *et al* 1997) is given in table 2.

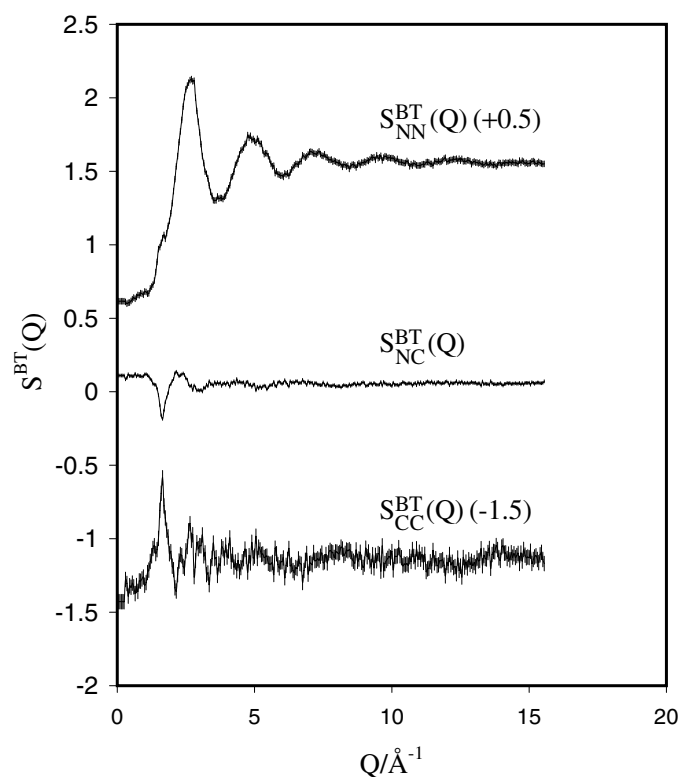


Figure 3. The experimental Bhatia–Thornton partial structure factors $S^{BT}(Q)$.

Table 2. Interatomic distances and coordination numbers in liquid Ag_2Te (this work) and liquid Ag_2Se (Barnes *et al* 1997). The distance for the first minimum r_{min} in the coordination number calculation is indicated in parentheses.

| $g_{ij}(r)$ | First-peak distance (\AA) | Second-peak distance (\AA) | Coordination number $\bar{n}_i^j(r_{min})$ (\AA) |
|--|---|--|--|
| Ag_2Te | | | |
| $g_{TeTe}(r)$ | 4.83 ± 0.1 | 8.2 ± 0.5 | 10.0 ± 0.5 (5.5) |
| $g_{AgTe}(r)$ | 2.88 ± 0.05 | 6.5 ± 0.3 | 11.3 ± 0.5 (5.0) |
| $g_{AgAg}(r)$ | 2.82 ± 0.05 | 5.2 ± 0.5 | 3.9 ± 0.5 (3.2) |
| Ag_2Se | | | |
| $g_{SeSe}(r)$ | 4.6 ± 0.1 | 8.1 ± 0.3 | 13.0 ± 0.5 (5.3) |
| $g_{AgSe}(r)$ | 2.60 ± 0.05 | 6.2 ± 0.5 | 9.3 ± 0.5 (4.3) |
| $g_{AgAg}(r)$ | 2.80 ± 0.05 | 5.0 ± 0.5 | 5.3 ± 0.5 (3.4) |

4. Discussion

4.1. The comparison between liquid Ag_2Se and Ag_2Te

The structure of liquid Ag_2Te shows close similarities to that of liquid Ag_2Se . Using the same arguments suggested for liquid Ag_2Se (Barnes *et al* 1997) we therefore conclude that this liquid can similarly be understood as an ionic melt of Ag^+ and Te^{2-} ions. However, there are subtle differences in the observed structure of Ag_2Se and Ag_2Te that may be of significance

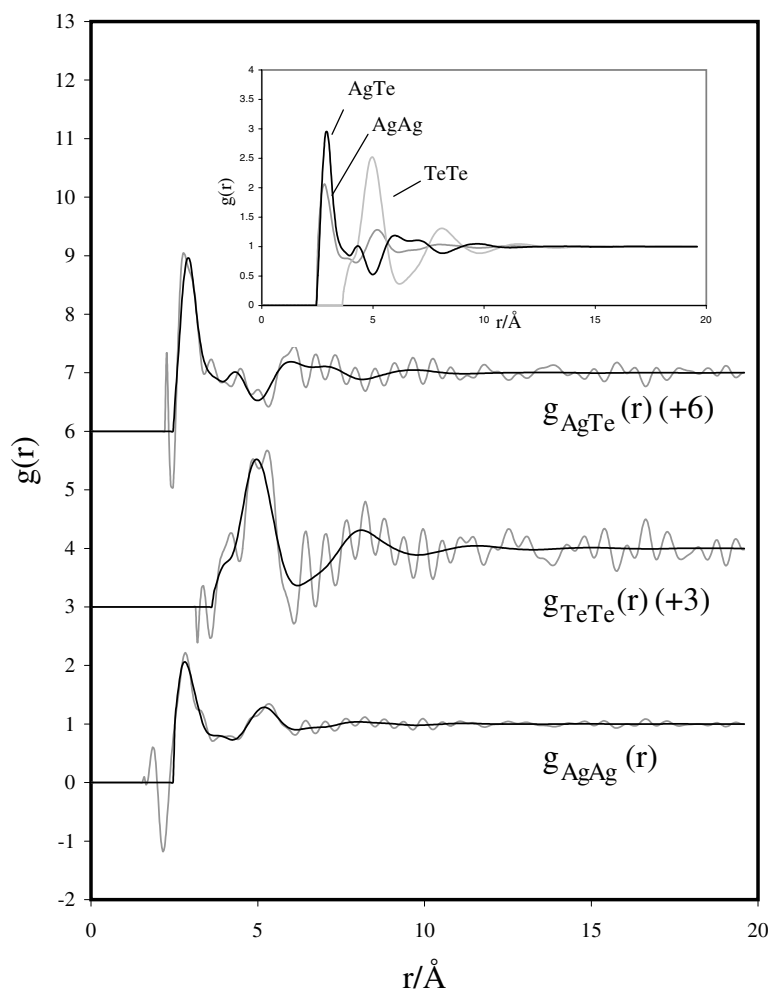


Figure 4. The $g(r)$ obtained from the $S(Q)$ shown in figure 2. The darker lines are the Fourier transforms of the smoothed $S(Q)$, and the lighter lines the Fourier transforms of the unsmoothed $S(Q)$. The inset shows the smoothed $g(r)$ superimposed on the same axis.

in understanding the differences in the electronic properties of the liquids. Figure 5 shows a comparison of the partial structure factors of liquid Ag_2Se previously reported and those of Ag_2Te reported here. It can be seen, apart from the poorer statistical accuracy, that $S_{\text{TeTe}}(Q)$ is very similar to $S_{\text{SeSe}}(Q)$ with a small displacement in the first peak to smaller Q that is consistent with the slightly larger size of the Te^{2-} ion. $S_{\text{AgTe}}(Q)$ and $S_{\text{AgSe}}(Q)$ also show a very close similarity except a suggestion that the oscillations at high Q in the case of $S_{\text{AgTe}}(Q)$ appear to be slightly stronger possibly indicating a stronger real space coordination structure (higher and sharper peaks) in the case of Ag_2Te . A very notable difference is observed in $S_{\text{AgAg}}(Q)$ between the two materials. Both materials show a ‘double peak’ structure, but the first peak is reduced in intensity and the second peak stronger in intensity in the case of Ag_2Te when compared to Ag_2Se . Barnes *et al* (1997) made a detailed comparison between the experimental partial structure factors of liquid Ag_2Se and those obtained by a molecular dynamics simulation (MD) (Rino *et al* 1988) and *ab initio* molecular dynamics simulation

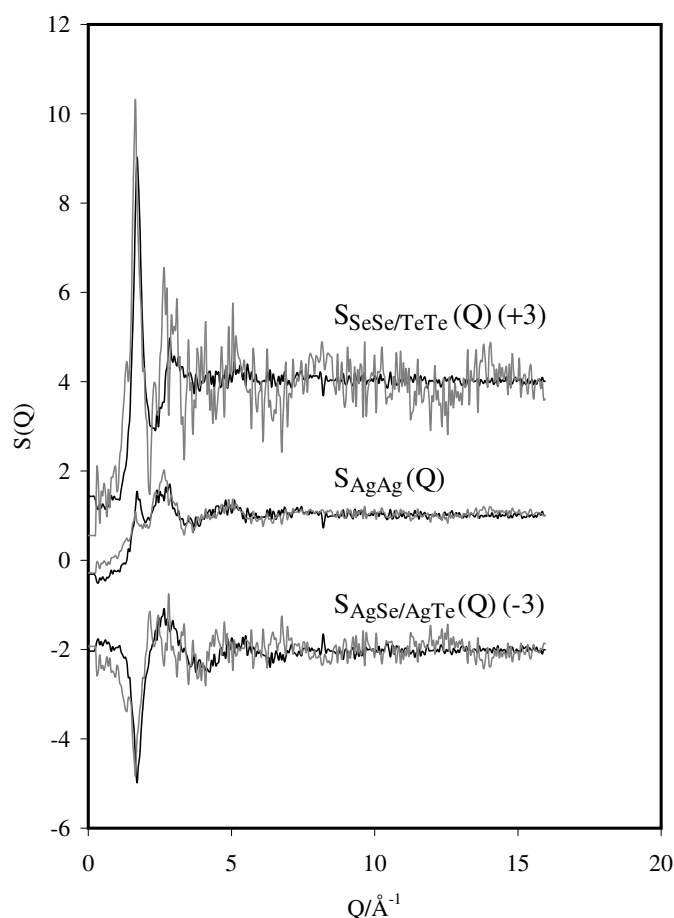


Figure 5. A comparison of the experimental $S(Q)$ for liquid Ag_2Te (lighter lines) with those determined by Barnes *et al* (1997) for liquid Ag_2Se (darker lines).

(AIMD) (Kirchhoff *et al* 1996). It was noted that there was a strong difference between the two simulations in $S_{\text{AgAg}}(Q)$. In the case of the MD simulation this strong double peak was well reproduced whereas in the case of the AIMD simulation it was almost totally absent. From these observations it was concluded that the AIMD simulation failed to reproduce the first peak due to the limited size of the simulation cell—that is this first peak in $S_{\text{AgAg}}(Q)$ originates from correlations on the intermediate length scale. Similarly we argue that the reduction of the height of the first peak in $S_{\text{AgAg}}(Q)$ in liquid Ag_2Te signifies a significant difference in the Ag–Ag structure on the intermediate length scale when compared to Ag_2Se . At the present time we do not know of any computer simulations that have been carried out for liquid Ag_2Te with which to make a direct comparison. A summary of the peak positions and coordination numbers obtained from the data is given in table 2.

Figure 6 shows a comparison of the Bhatia–Thornton structure factors between Ag_2Te and Ag_2Se . These are very similar which again indicates the structure of the two materials is broadly the same. In the case of $S_{NN}(Q)$ (equivalent to the case when all atoms scatter equally i.e. the scattering lengths of the two components are equal) the small shift to smaller Q is consistent with the slightly larger size of the Te^{2-} ion. The $S_{NN}(Q)$ is well defined as it

corresponds almost entirely to the scattering from the sample made from the natural isotopic abundances. However, it is noticeable that the oscillations are much stronger at higher Q in the case of Ag_2Te . Again, this is indicative that the coordination structure is stronger in this liquid. In the case of $S_{NC}(Q)$, it is noticeable that the dip at 1.8 \AA^{-1} is deeper in the case of Ag_2Te . This peak is exactly at the position of the first peak in $S_{AgAg}(Q)$ and accounts for the reduction in its size as observed for $S_{AgAg}(Q)$ in Ag_2Te . In contrast, there is little observable difference in $S_{CC}(Q)$ between the two liquids given the limited statistical accuracy for the Ag_2Te sample.

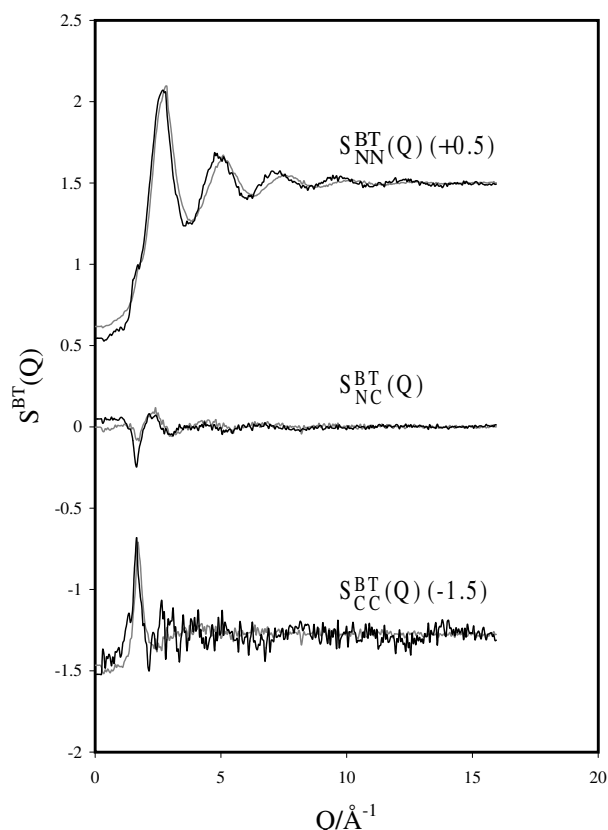


Figure 6. The experimental Bhatia–Thornton $S(Q)$ for liquid Ag_2Te (darker lines) and liquid Ag_2Se (lighter lines). Results for Ag_2Se from Barnes *et al* (1997).

Figure 7 shows a comparison of the partial radial distribution functions of liquid Ag_2Se and Ag_2Te . It can be seen that there is a close similarity between $g_{\text{SeSe}}(r)$ and $g_{\text{TeTe}}(r)$. The movement of the first peak from 4.6 \AA to 4.8 \AA is fully consistent with the change in ion size on changing from Se^{2-} to Te^{2-} (1.91 \AA to 2.11 \AA). The peak also appears slightly sharper in the case of Ag_2Te and accounts for the lower coordination number obtained (there is less overlap with the second shell). However, in the other $g_{ij}(r)$ s there are more noticeable differences. In $g_{\text{AgSe}}(r)$ the first peak occurs at a distance of 2.6 \AA and is noticeably asymmetric with a further shoulder at a distance of 3.8 \AA . In the case of $g_{\text{AgTe}}(r)$ the first peak is further out, again consistent with the larger Te^{2-} ion size. The first peak also appears more symmetric with a further small distinct peak at 4.3 \AA instead of the shoulder observed in $g_{\text{AgSe}}(r)$. This peak

appears to be robust in the Fourier transform and we do not believe it to be an artefact due to termination errors in $S_{\text{AgTe}}(Q)$. The first shell coordination numbers obtained by including this shoulder (in Ag_2Se) and the small peak (in Ag_2Te) give comparable results given the difficulty in defining the first minimum in $g(r)$ in this case. The $g_{\text{AgAg}}(r)$ for the two materials show a marked difference. The first peak occurs at 2.8 \AA in *both* liquids and corresponds closely to the Ag–Ag distance in liquid Ag itself. It appears that the slightly larger ‘anion cage’ of liquid Ag_2Te does not affect this distance. The peak is also sharper and higher in Ag_2Te suggesting that the Ag is more strongly coordinated and/or less mobile in the telluride than in the selenide. The difference is even more marked in the second peak. In the telluride a very distinct peak is observed at 5.2 \AA whereas in the selenide this peak is broader, less well defined and at a closer distance. The Ag–Ag coordination number in Ag_2Se appears slightly higher (5.3 against 3.9) but in both cases the first minimum is relatively shallow such that the coordination number is a poorly defined quantity (we have defined the coordination number by integrating to the first minimum in $g(r)$). Overall for Ag_2Se $g_{\text{AgAg}}(r)$ is less structured suggesting that the Ag^+ ions are more mobile or spread over a larger number of ‘local sites’ than in the case of the telluride. Beyond $\sim 6 \text{ \AA}$, that corresponds to the unit cell of the crystals, the structure in $g_{\text{AgAg}}(r)$ has essentially disappeared in both cases.

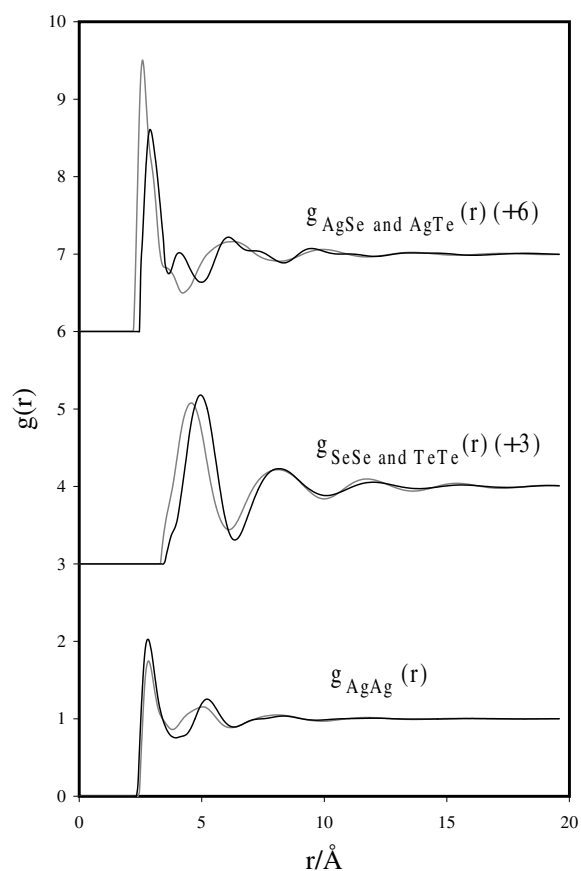


Figure 7. A comparison of the experimental smoothed $g(r)$ for liquid Ag_2Te (darker lines) with those determined by Barnes *et al* (1997) for liquid Ag_2Se (lighter lines).

4.2. The comparison between liquid and γ -Ag₂Te

In the solid state Ag₂Te shows two superionic phases— α -Ag₂Te that exists in the range \sim 410–1000 K and γ -Ag₂Te that exists above \sim 1000 K until it melts at \sim 1223 K (Schneider and Schulz 1993, Kobayashi *et al* 1988). The precise transformation temperatures depend strongly on the stoichiometry of the crystal. Figure 8 shows a comparison of the partial $g(r)$ s of liquid Ag₂Te obtained in this work compared with those of γ -Ag₂Te at 1073 K determined by Keen and Hull (1998) using powder diffraction and reverse Monte Carlo methods. γ -Ag₂Te is a fast ion phase in which the Ag⁺ ions are highly mobile and move through a b.c.c. Te crystalline lattice. It can be seen that there is a remarkable similarity between $g_{AgAg}(r)$ in the liquid and fast ion phases suggesting that the silver structure is largely unchanged on melting. The first shell coordination of Te around Te in $g_{TeTe}(r)$ is also little changed between the liquid and the solid but the effects of the melting of the Te lattice are clearly observed in the loss of structure in $g_{TeTe}(r)$ above 8 Å in the liquid. It is interesting to note that the second peak in $g_{TeTe}(r)$ for the liquid shows a significant shift to smaller r than that of the crystal and is at a distance closer to the shoulder on the left hand peak in the crystalline $g(r)$. In the case of $g_{AgTe}(r)$ there is a good agreement in the height and width of the first peak in $g(r)$ between the liquid and crystal. The second peak at \sim 6 Å is also at a slightly smaller distance than that observed in the crystal. The main distinction between the two $g(r)$ is the small peak observed at \sim 4.3 Å in the liquid. This is totally absent in the crystal data as can be seen in figure 8. As discussed in section 4.1 this could possibly be an artefact in the Fourier transform to $g(r)$. However, it should be noted that a similar shoulder exists to the right of the first peak in $g_{AgSe}(r)$ in liquid Ag₂Se. In the high temperature b.c.c. fast-ion crystal (γ -Ag₂Te) a peak at this distance is not observed experimentally and no Ag–Te correlation at this distance is predicted from the crystal structure (Keen and Hull 1998). In the crystal a distance of 4.3 Å corresponds to a distance somewhere between the trigonal sites at \sim 3.75 Å and the tetrahedral sites at \sim 4.75 Å. Keen and Hull observe that the Ag⁺ ions occupy predominantly the tetrahedral sites with some tendency for the Ag⁺ density to spread toward the trigonal sites in the crystal. Indeed it is the motion of Ag⁺ ions between the tetrahedral and trigonal sites that accounts for the fast-ion motion. On melting γ -Ag₂Te it appears that the local b.c.c. Te structure relaxes to such an extent as to blur the distinction between the trigonal and tetrahedral sites such that the favoured Ag–Te correlation lies somewhere between the mean of the two—i.e. \sim 4.25 Å. Such a distortion would account both for the shoulder observed in $g_{AgSe}(r)$ in liquid Ag₂Se and this small peak observed in $g_{AgTe}(r)$ in liquid Ag₂Te.

4.3. The relationship between the structure and electronic properties of the melt

As described in the introduction liquid Ag₂Se and Ag₂Te show contrasting electronic properties in their liquid phases just after melting, the most notable difference being the change in the sign of the temperature coefficient of the conductivity $d\sigma/dT$, which is negative (and metallic-like) in liquid Ag₂Se. The results presented here confirm the observation of Price *et al* (1993) that the structure of liquid Ag₂Te and Ag₂Se appear very similar at the *total structure factor* level. However, it is clear from these measurements that there are small but significant differences in the partial structure factors of the two materials. This is particularly noticeable in $S_{AgAg}(Q)$ and $g_{AgAg}(r)$ where the silver structure appears to be stronger in the short range (sharper and higher peaks) in Ag₂Te. Both Ag₂Te and Ag₂Se are known to be fast ion conductors in their solid phases before melting. The stronger Ag⁺ coordination (characterized by the higher and sharper peaks in $g(r)$) of the telluride found in this work is suggestive of a slower diffusion mechanism in which the Ag⁺ ions are resident for longer in their near neighbour coordination

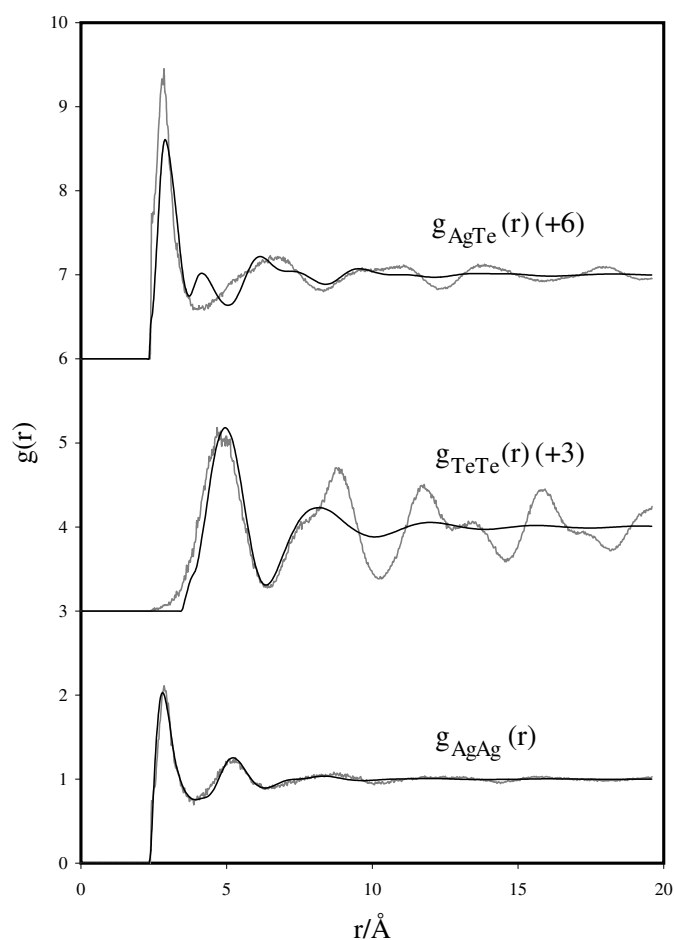


Figure 8. The experimental $g(r)$ for liquid Ag_2Te (darker lines) compared to those determined by an RMC simulation (lighter lines) of total neutron scattering data for $\gamma\text{-Ag}_2\text{Te}$ (data from Keen and Hull 1998).

environment. We are currently in the process of verifying this postulate by directly measuring the diffusion mechanism in both Ag_2Se and Ag_2Te in their fast ion and liquid phases by coherent quasi-elastic neutron scattering experiments. A slower diffusion of Ag^+ in liquid Ag_2Te would be consistent with the suggestion that the unusual electronic properties of these liquids may be linked to the ion motion in the manner outlined by Ramasesha (1982) and Huberman (1974).

5. Conclusions

We have performed measurements of the structure of liquid Ag_2Te to the partial structure factor level using neutron scattering and isotopic substitution. A detailed comparison between liquid Ag_2Se and Ag_2Te shows that the two materials have broadly similar structures with features closely related to that of 2:1 molten salts. The anion–anion structure factor and radial distribution function in both liquids are very similar and the differences can be understood in

terms of the different sizes of the Se^{2-} and Te^{2-} ions. In contrast, the cation–anion and cation–cation partial structure factors and partial radial distribution functions show differences, most notably a stronger short range order in liquid Ag_2Te . We tentatively associate this enhanced short range structure with a decreased mobility of the Ag^+ ions in Ag_2Te . It is suggested that the subtleties in the silver structure and mobility between Ag_2Te and Ag_2Se are responsible for the difference in the electronic properties of the two liquids. Detailed measurements of the silver diffusion in these liquids using coherent quasi-elastic neutron scattering are in progress in order to measure directly the nature of the diffusion mechanism. It would be interesting to see if computer simulations of the structure of liquid Ag_2Te reproduce the observed difference in its structure compared to Ag_2Se .

Acknowledgments

This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC) which we gratefully acknowledge. One of us (MAH) gratefully acknowledges the EPSRC for the award of a PhD studentship. We would also like to thank John Rowden for his help in preparing the samples. We thank Dr Keen and Dr Hull at the Rutherford Appleton Laboratory for kindly sending us their crystallographic data.

References

- Barnes A C, Lague S B, Hamilton M A, Fischer H E, Fitch A N and Doryhee E 1998 *J. Phys.: Condens. Matter* **10** L645
- Barnes A C, Lague S B, Salmon P S and Fischer H E 1997 *J. Phys.: Condens. Matter* **9** 6159
- Bhatia A B and Thornton D E 1970 *Phys. Rev. Lett.* **73** 264
- Dancy E A 1965 *Trans. Met. Soc. AIME* **233** 270
- Edwards F G, Enderby J E, Howe R A and Page D I 1975 *J. Phys.: Solid State Phys.* **14** 3129
- Enderby J E and Barnes A C 1990 *Rep. Prog. Phys.* **53** 85
- Fortner J, Saboungi M-L and Enderby J E 1995 *Phys. Rev. Lett.* **74** 1415
- Glaszov V M, Mamedov S M and Burkhanov A S 1986 *Sov. Phys.–Semicond.* **20** 263
- Hasegawa A 1985 *Solid State Ion.* **15** 81
- Huberman B A 1974 *Phys. Rev. Lett.* **32** 1000
- Keen D A and Hull S 1998 *J. Phys.: Condens. Matter* **10** 8217
- Kirchhoff F, Holender J M and Gillan M J 1996 *Phys. Rev. B* **54** 190
- Kobayashi M 1990 *Solid State Ion.* **39** 121
- Kobayashi M, Ishikawa K, Tachibana F and Okazaki H 1988 *Phys. Rev. B* **38** 3050
- Koester L and Knopf L 1980 *Z. Phys. A* **297** 85
- Koester L, Knopf L and Waschkowski W 1986 *Z. Phys. A* **323** 359
- Mughabghab S F 1984 *Neutron Cross Sections* vol 1, part B (Orlando, FL: Academic)
- Ohno S, Barnes A C and Enderby J E 1994 *J. Phys.: Condens. Matter* **6** 5335
- Price D L, Saboungi M-L, Susman S, Volin K J, Enderby J E and Barnes A C 1993 *J. Phys.: Condens. Matter* **5** 3087
- Ramasesha S 1982 *J. Solid. State. Chem.* **41** 333
- Rino J P, Hornos Y M M, Antonio G A, Ebbjösö I, Kalia R K and Vashishta P 1988 *J. Chem. Phys.* **89** 7542
- Schneider J and Schulz H 1993 *Z. Kristallogr.* **203** 1
- Schnyders H S, Hahn J, Streutker D and Van Zytveld J B 1997 *J. Phys.: Condens. Matter* **9** 10121