

A neutron diffraction and isotopic substitution measurement of the structure of liquid Cu₂Se

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

2000 J. Phys.: Condens. Matter 12 9525

(<http://iopscience.iop.org/0953-8984/12/46/301>)

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 06:59

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

A neutron diffraction and isotopic substitution measurement of the structure of liquid Cu_2Se

M A Hamilton[†], A C Barnes[†], U Beck[†], P Buchanan[†] and W S Howells[‡]

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

[‡] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK

Received 1 August 2000, in final form 18 September 2000

Abstract. The partial structure factors and pair distribution functions of liquid Cu_2Se have been determined by neutron diffraction with isotopic substitution. The structure shows characteristics typical of those of an ionic 2:1 melt consisting of Cu^+ and Se^{2-} ions with the cations moving through a more ordered Se^{2-} sub-structure. A detailed comparison has been made with recent results obtained for liquid Ag_2Se . The structure is similar although there is no evidence of the double peak structure in the cation–cation partial structure factor, $S_{\text{CuCu}}(Q)$, as has been found in $S_{\text{AgAg}}(Q)$ for liquid Ag_2Se and, to a more limited extent, for liquid Ag_2Te . There is also less order in the Se^{2-} sub-structure based on a comparison of $S_{\text{SeSe}}(Q)$ and the Bhatia–Thornton concentration–concentration structure factor, $S_{\text{CC}}(Q)$, for the two liquids.

1. Introduction

Copper chalcogenide compounds such as Cu_2Se have a similar conductivity and other properties to the corresponding Silver chalcogenides. However the possible oxidation states of Cu (Cu(I) and Cu(II)) give rise to compounds with a stoichiometry including 2:1 and 1:1. Cu_2S , Cu_2Se and Cu_2Te are liquid semiconductors whereas the corresponding compounds with a 1:1 ratio are more metallic in character. Furthermore both Cu_2S and Cu_2Se have superionic phases prior to the melting transition (Boyce and Huberman 1979) in which the cation is the mobile species in a cubic anion sub-lattice. Ag_2S , Ag_2Se and Ag_2Te (Kobayashi 1990) also have superionic phases but the higher polarizability of Ag^+ results in a correspondingly higher ionic mobility.

The room temperature form of Cu_2Se is tetragonal (Rhalfs 1936) and at 122°C it undergoes a first-order phase transition to the superionic phase. The structure of the superionic phase and the distribution of the mobile cations have been investigated by single crystal neutron diffraction (Oliveria *et al* 1988). The structure of this phase is based on an FCC anion lattice, space group $Fm\bar{3}m$, with the Cu^+ ions in interstitial sites between the tetrahedral and octahedral positions. Barnes and Enderby (1988) report measurements of the conductivity and thermopower for the liquid state of CuSe and Cu_2Se and at two compositions in between. The conductivity is a minimum at the 2:1 composition ($\sigma = 160 \Omega^{-1} \text{cm}^{-1}$) with a positive temperature dependence as expected for a narrow definition liquid semiconductor (Enderby and Barnes 1990). The values of σ and S that were obtained are in good agreement with those of Glazov *et al* (1985). Barnes and Enderby (1988) have also determined the structure of liquid CuSe to the partial structure factor level using neutron diffraction with isotopic substitution. The structure is not

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

Isotope	b_{coh} (fm)	σ_a (barns at 1.8 Å)	σ_s (barns)
^{nat}Cu	7.718 ± 0.004	3.78 ± 0.02	8.01 ± 0.04
^{65}Cu	10.61 ± 0.19	2.17 ± 0.03	14.5 ± 0.5
^{63}Cu	6.43 ± 0.15	4.50 ± 0.02	5.20 ± 0.2
^{nat}Se	7.970 ± 0.009	11.7 ± 0.2	8.31 ± 0.06
^{76}Se	12.2 ± 0.1	85.0 ± 7.0	18.7 ± 0.3

simply ionic as some of the anions form pairs with a distance of 2.40 Å. $S_{CuCu}(Q)$ and $S_{SeSe}(Q)$ and the corresponding real space functions are seen to be similar.

In this paper we present a determination of the structure of liquid Cu_2Se and make a detailed comparison with results that are already available for liquid Ag_2Se (Barnes *et al* 1997). Both Ag_2S (Ohno *et al* 1990) and Ag_2Se (Ohno *et al* 1994) have a highly unusual electronic conductivity in that the temperature dependence is *negative* as expected for a liquid metal rather than positive as for a liquid semiconductor. Furthermore in both cases there is a peak in the conductivity at stoichiometry that is highly unusual. It has been suggested that there is a link between the high ionic mobility in these systems and the anomalous electronic properties (Fortner *et al* 1995). In contrast Ag_2Te has more ‘normal’ properties (Schnyders *et al* 1997) and a detailed comparison of both the structure and dynamics with those of Ag_2Se has already been made in order to investigate possible reasons for this behaviour (Barnes *et al* 2000, Hamilton *et al* 2000). The present results represent an extension of this investigation of the origin of this striking behaviour. The technique of neutron diffraction with isotopic substitution has been used to obtain the partial structure factors and pair distribution functions of Cu_2Se . Favourable isotopes of Cu are available and can be combined with the Se isotopes that have been used previously.

2. Experimental procedure

The measurements reported here were carried out using the SANDALS liquids and amorphous materials diffractometer at the ISIS pulsed spallation neutron source in the UK. Three isotopically labelled samples of Cu_2Se were prepared in the following compositions: $^{63}\text{Cu}_2^{76}\text{Se}$, $^{65}\text{Cu}_2^{nat}\text{Se}$ and $^{nat}\text{Cu}_2^{nat}\text{Se}$. The coherent scattering lengths and scattering cross-sections that were used for Cu and Se are given in table 1. The values for Cu and Se were obtained from Sears (1992) and Koester *et al* (1980) respectively. The samples were prepared by mixing the pure elements and reacting them in silica tubes at 1200 °C for 24 hours. For the experiment the samples were powdered and contained in thin walled silica tubes. Given the high melting temperature of Cu_2Se ($T_m = 1130$ °C), that is close to the softening temperature of silica, the tubes were held and supported by closely fitting vanadium tubes in order to avoid any deformation of the sample containers. Each sample was run for a total of 12 hours with multiple scans performed in order to demonstrate repeatability. The sample was heated using a furnace that consisted of a 0.04 mm thick cylindrical vanadium heating element with several concentric heat shields. Data was also collected for the empty container at 1150 °C, the empty furnace, the instrument background and for a standard vanadium rod of similar dimensions to the sample. The results were corrected for absorption, multiple scattering and inelastic scattering and normalized according to the ATLAS routines (Soper *et al* 1989).

As with previous measurements of molten alloys containing group VI elements the high Q limit of the corrected total structure factors or $F(Q)$ s did not oscillate about the correct value

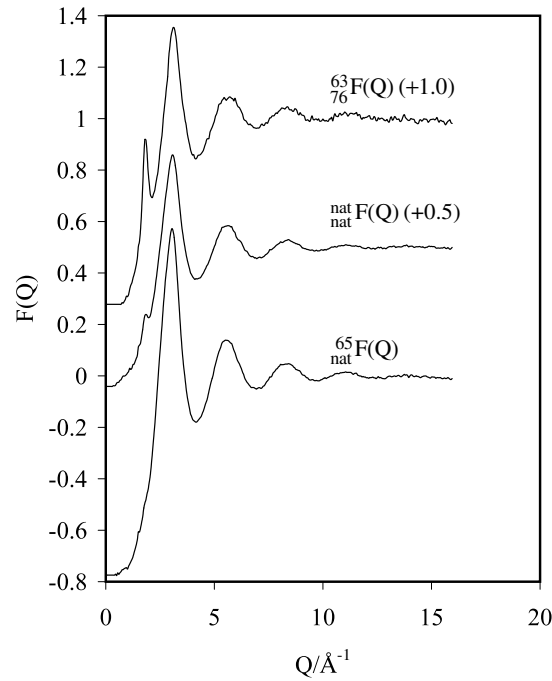


Figure 1. The fully corrected experimental total structure factors for liquid Cu₂Se.

due to the formation of bubbles in the sample. The number of scattering nuclei is therefore uncertain and the $F(Q)$ s were scaled to the theoretical high Q limits. This scaling was less than or equal to 5% of the expected high Q limit. Furthermore a small peak at 1.6 Å in the total pair distribution function indicated some residual structure from the SiO₂ containers and the container subtraction was therefore modified in order to remove any such peak. The additional subtraction in each case was small and amounted to less than one per cent of the container scattering. The procedures for the scaling of the $F(Q)$ s and the subtraction of an additional fraction of the container scattering were as for the results for liquid Ag₂Se described in Barnes *et al* (1997).

The $F(Q)$ for each isotopic composition can be expressed as a weighted combination of the Faber–Ziman partial structure factors according to the following matrix,

$$\begin{pmatrix} {}^{nat} F(Q) \\ {}^{65}_{nat} F(Q) \\ {}^{63}_{76} F(Q) \end{pmatrix} = \begin{pmatrix} 0.265 & 0.071 & 0.273 \\ 0.5 & 0.071 & 0.376 \\ 0.184 & 0.165 & 0.349 \end{pmatrix} \begin{pmatrix} S_{CuCu}(Q) - 1 \\ S_{SeSe}(Q) - 1 \\ S_{CuSe}(Q) - 1 \end{pmatrix}. \quad (1)$$

The units are barns. The inverse of this matrix allows the $S_{ij}(Q)$ to be determined,

$$\begin{pmatrix} S_{CuCu}(Q) - 1 \\ S_{SeSe}(Q) - 1 \\ S_{CuSe}(Q) - 1 \end{pmatrix} = \begin{pmatrix} -22.119 & 12.139 & 4.259 \\ -62.077 & 24.781 & 21.963 \\ 41.103 & -18.152 & -9.795 \end{pmatrix} \begin{pmatrix} {}^{nat} F(Q) \\ {}^{65}_{nat} F(Q) \\ {}^{63}_{76} F(Q) \end{pmatrix}. \quad (2)$$

The conditioning of this matrix, a measure of the effect of experimental errors on the inversion, is given by the normalized determinant (Edwards *et al* 1975), which in this case is $|A_n| = 0.016$. This is not as good as for the NDIS measurements of Ag₂Se by Barnes *et al* (1997) of 0.029 but is comparable to the more recent measurements of Ag₂Te (Barnes *et al* 2000).

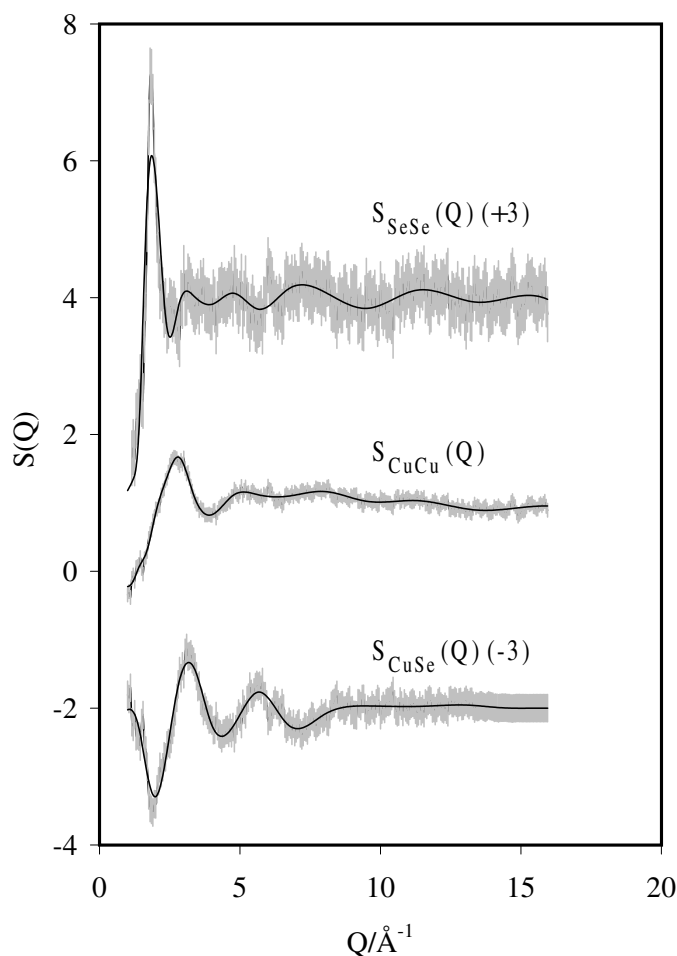


Figure 2. The experimental partial structure factors $S_{SeSe}(Q)$, $S_{CuCu}(Q)$ and $S_{CuSe}(Q)$.

3. Results

Figure 1 shows the fully corrected and normalized experimental total structure factors for the three isotopic compositions of Cu_2Se . The poorer statistical accuracy of the $^{63}\text{Cu}_2^{76}\text{Se}$ sample is due to the high absorption cross-section of ^{76}Se (table 1). The Faber–Ziman partial structure factors that are obtained by inversion of these $F(Q)$ s according to the inverse scattering matrix (equation (2)) are shown in figure 2. The results below $Q = 1 \text{ \AA}^{-1}$ have been truncated in the $S_{ij}(Q)$ because of the unreliability of the results for $^{63}\text{Cu}_2^{76}\text{Se}$ at low Q due again to the high absorption cross-section of ^{76}Se . For time-of-flight measurements longer wavelength neutrons, that correspond to scattering at low Q values, are highly absorbed and a small error in the absorption correction will thus have a large effect. An alternative representation of the results in terms of the Bhatia–Thornton partial structure factors (Bhatia and Thornton 1970) is given in figure 3. The number–number partial structure factor, $S_{NN}(Q)$, is independent of the particular scattering nucleus and is equivalent to a measurement in which the scattering length of each component is equal. This is very nearly the case for $^{nat}\text{Cu}_2^{nat}\text{Se}$ and so $S_{NN}(Q)$ is determined with good accuracy. The pair distribution functions obtained by Fourier transform

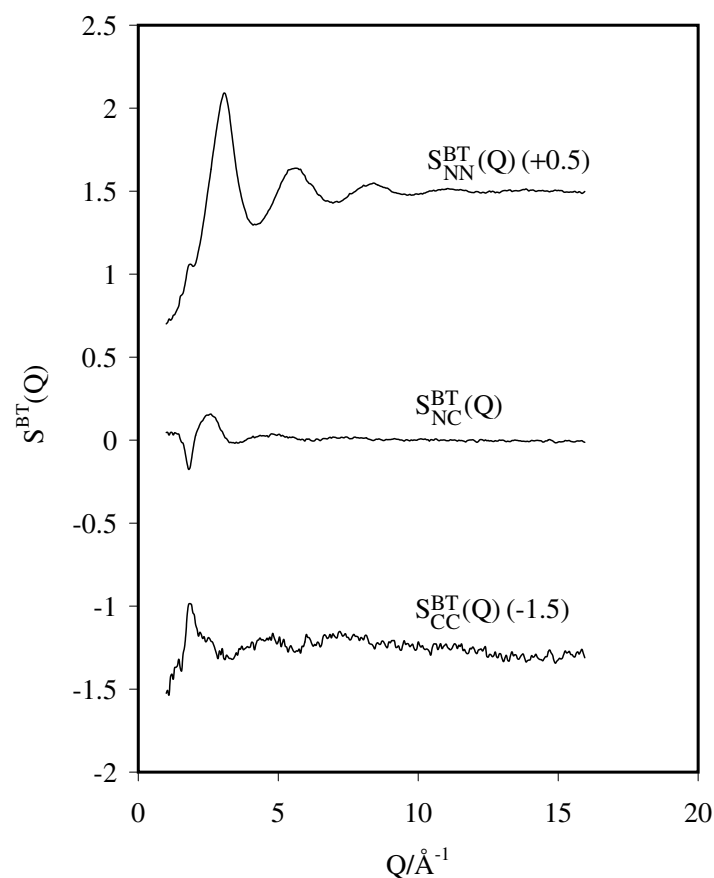


Figure 3. The experimental Bhatia–Thornton partial structure factors $S^{BT}(Q)$.

Table 2. Interatomic distances and coordination numbers in liquid Cu_2Se and Ag_2Se (data from Barnes *et al* 1997).

$g_{ij}(r)$	First-peak distance (Å)	Second-peak distance (Å)	Coordination number $\bar{n}_i^j(r_{min})$ (Å ⁻³)
Cu_2Se			
$g_{\text{SeSe}}(r)$	4.2 ± 0.1	7.2 ± 0.5	14.4 ± 0.5 (5.6)
$g_{\text{CuSe}}(r)$	2.44 ± 0.05	7.1 ± 0.5	6.1 ± 0.5 (3.2)
$g_{\text{CuCu}}(r)$	2.70 ± 0.05	4.7 ± 0.5	7.8 ± 0.5 (3.7)
Ag_2Se			
$g_{\text{SeSe}}(r)$	4.6 ± 0.1	8.1 ± 0.3	13.0 ± 0.5 (5.3)
$g_{\text{AgSe}}(r)$	2.60 ± 0.05	6.2 ± 0.5	9.3 ± 0.5 (4.3)
$g_{\text{AgAg}}(r)$	2.80 ± 0.05	5.0 ± 0.5	5.3 ± 0.5 (3.4)

of the Faber–Ziman $S_{ij}(Q)$ with an atomic number density of 0.05 \AA^{-3} are given in figure 4. A summary of the atomic distances and mean coordination numbers obtained from the $g_{ij}(r)$ is given in table 2. The mean coordination number has been obtained by integrating over $g(r)$ to the first minimum. The $S_{ij}(Q)$ and $g_{ij}(r)$ fully satisfy the inequality conditions of Edwards *et al* (1975) and oscillate about the correct low r limits respectively.

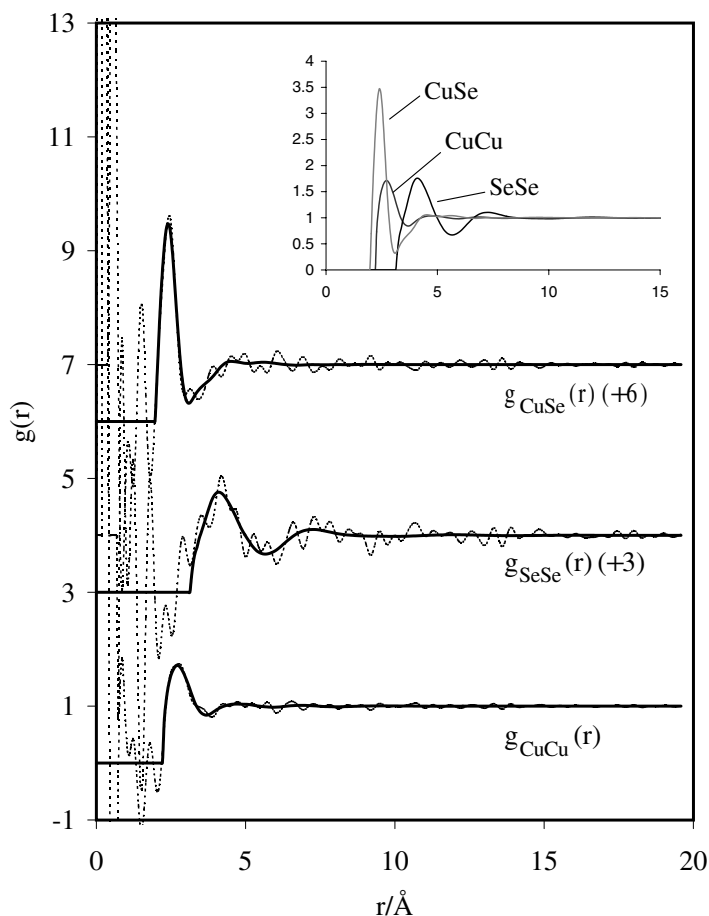


Figure 4. The $g_{ij}(r)$ obtained from the $S_{ij}(Q)$ shown in figure 2. The solid lines are the Fourier transforms of the smoothed $S_{ij}(Q)$, and the dashed lines the Fourier transforms of the unsmoothed $S_{ij}(Q)$. The inset shows the smoothed $g_{ij}(r)$ superimposed on the same axis.

4. Discussion

4.1. The structure of liquid Cu_2Se

The partial structure factors that have been obtained (figure 2) show features that are characteristic of an ionic melt with a strong, but narrow, peak in $S_{SeSe}(Q)$ at $\sim 1.8 \text{ \AA}^{-1}$ and a corresponding dip in $S_{CuSe}(Q)$ at the same value of momentum transfer. This is due to charge ordering and is a clear indication of ionic properties (Edwards *et al* 1975). The low Q limits cannot be reliably determined from these results due to some uncertainty with the data below $\sim 1 \text{ \AA}^{-1}$ but are tending to the values expected for an ionic liquid that follows the conditions for electroneutrality (Bhatia 1977, Rovere and Tosi 1986). Despite the poor quality of the results at low Q it is considered that there is no evidence of a first sharp diffraction peak (FSDP) as seen in network forming melts such as $GeSe_2$ (Penfold and Salmon 1991). The absorption cross-section of ^{76}Se is particularly high and the total structure factor for $^{63}Cu_2^{76}Se$ is the origin of the poor results at low Q . It is this $F(Q)$ that has the greatest contribution to $S_{SeSe}(Q)$ and it is therefore suggested that this is the least well determined of the $S_{ij}(Q)$. $S_{SeSe}(Q)$ is

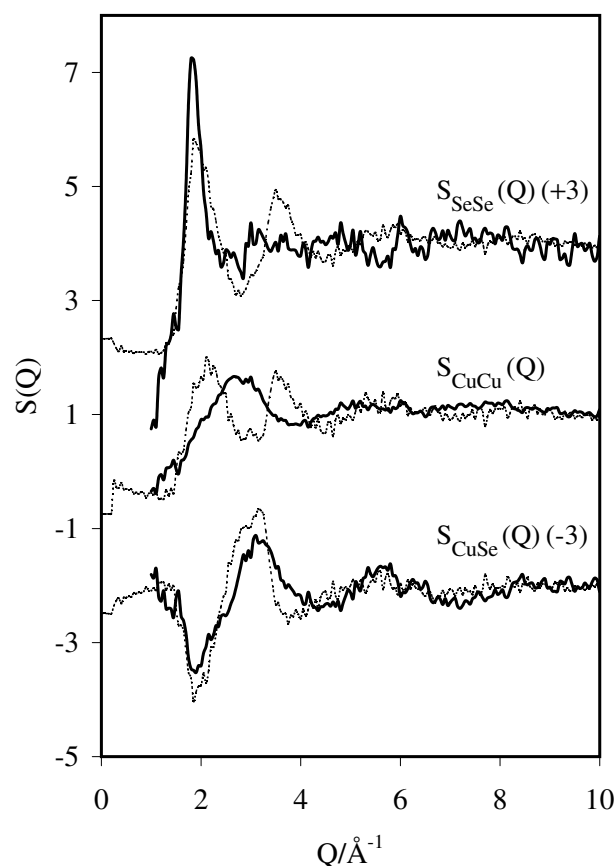


Figure 5. The partial structure factors for liquid Cu_2Se (solid lines) and liquid CuSe (dashed lines: Barnes and Enderby 1988).

dominated by a strong first peak and relatively weak subsequent oscillations. The first peak in $g_{\text{SeSe}}(r)$ occurs at 4.2 \AA with a less well defined second peak at 7.2 \AA . The mean coordination number for $g_{\text{SeSe}}(r)$ is close to 14, which is that of a BCC lattice. However this is a composite number including the nearest and next nearest distances—the distinction between the FCC and BCC like arrangement is strongly dependent on the r range considered. A number close to that of an FCC or BCC arrangement therefore indicates that the Se^{2-} sub-structure in the liquid is closely related to that of the superionic phase from which it melts. This is as found by Barnes *et al* (1997) in the case of liquid Ag_2Se . The cation–cation structure factor has no feature at $\sim 1.8 \text{ \AA}^{-1}$ and a single broad principal peak at 2.8 \AA^{-1} —this distance is close to that found in liquid Cu. There is only a shallow minimum in $g_{\text{CuCu}}(r)$ and a small indication of a second peak at 4.7 \AA . This is consistent with the picture of a melt that is related to the superionic phase from which it melts and in which the Cu^+ ions are mobile and disordered. The first peak in $g_{\text{CuSe}}(r)$ is at 2.44 \AA which is close to that expected given the ionic radii of Cu^+ (0.60 \AA) and Se^{2-} (1.98 \AA). Given the significant effect of composition on the conductivity of binary liquid semiconductors it is interesting to compare the structure of such materials at more than one stoichiometry. We therefore include a comparison with these results and those obtained for liquid CuSe by Barnes and Enderby (1988). For liquid Cu_2Se $S_{\text{CuCu}}(Q)$ and $S_{\text{SeSe}}(Q)$ are very

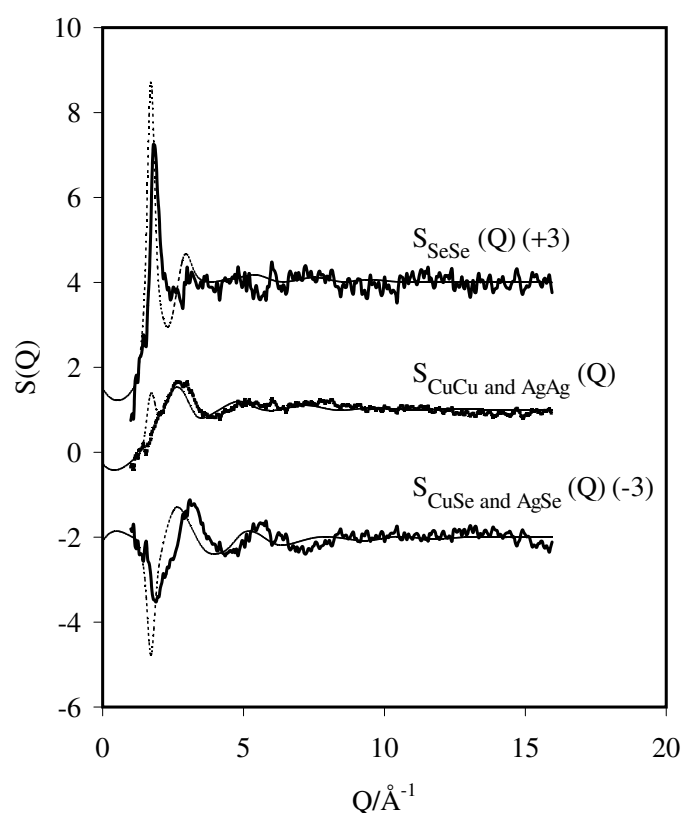


Figure 6. A comparison of the experimental $S_{ij}(Q)$ for liquid Cu_2Se (solid lines) with those determined by Barnes *et al* (1997) for liquid Ag_2Se (dashed lines).

different but in the case of liquid CuSe they are similar (figure 5). The changes in structure on moving from CuSe to Cu_2Se can be understood in terms of the addition of Cu and the loss of the anion (Se_2) pairing. This progressively removes the shorter-range peak at $\sim 2.4 \text{ \AA}$ in $g_{\text{SeSe}}(r)$ and broadens and merges the peaks in $g_{\text{CuCu}}(r)$. The differences in the structure are therefore not unexpected.

4.2. Comparison with liquid Ag_2Se

A direct comparison of the Faber–Ziman $S_{ij}(Q)$ for liquid Cu_2Se and liquid Ag_2Se (Barnes *et al* 1997) is given in figure 6. In general the structures are similar other than the shift in peak position due to the difference in size between Cu^+ (0.6 \AA) and Ag^+ (1.00 \AA). On closer inspection there is a significant difference between the $S_{ij}(Q)$ in that the double peak structure at low Q that is found in $S_{\text{AgAg}}(Q)$ for liquid Ag_2Se is not seen in $S_{\text{CuCu}}(Q)$ for liquid Cu_2Se . Indeed there is no evidence at all of such a peak in $S_{\text{CuCu}}(Q)$. There is a difference in the height of the first peak in $S_{\text{SeSe}}(Q)$ for the two liquids and some evidence of less ordering in liquid Cu_2Se as indicated by the height of the first peak in $S_{\text{CC}}(Q)$ (figure 7) and the less sharp peaks in $g_{\text{SeSe}}(r)$ (figure 8). A comparison of $g_{\text{CuSe}}(r)$ and $g_{\text{AgSe}}(r)$ shows that the asymmetry in the first peak, that is present in the results for Ag_2Se , does not exist in the case of Cu_2Se . For ionic systems such as these the structure of the melt is closely related to that of the phase from which it melts (Enderby and Barnes 1990). In this case the asymmetry in the first peak of

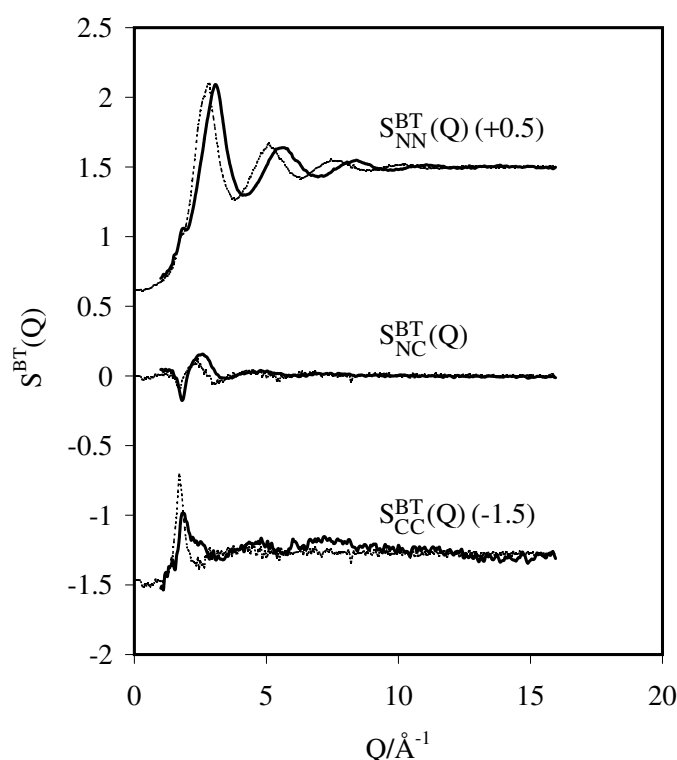


Figure 7. The experimental Bhatia–Thornton $S_{ij}(Q)$ for liquid Cu_2Se (solid lines) and liquid Ag_2Se (dashed lines). Results for Ag_2Se from Barnes *et al* (1997).

$g_{\text{AgSe}}(r)$ indicates that the Ag^+ ions occupy two different interstitial positions, the tetrahedral and octahedral, in the BCC superionic phase prior to melting. In contrast the Cu^+ ions occupy only one type of site situated between the tetrahedral and octahedral positions with a Cu–Se distance of ~ 2.4 Å, which agrees with the distance found for the FCC superionic phase by Oliveria *et al* (1988). This Cu–Se distance compares favourably with that reported for liquid Cu_2Se of 2.52 Å (Barnes and Enderby 1988). A comparison of the experimental Faber–Ziman $S_{ij}(Q)$ for liquid Cu_2Se that have been measured here with those calculated for liquid Ag_2Se by Kirchhoff *et al* (1996) in an *ab initio* molecular dynamics simulation (figure 9) shows similar structural features differing only with the effect of the ion size. Indeed it is seen that overall the features in $S_{ij}(Q)$ are in better agreement with the experimental results for liquid Cu_2Se than with those for liquid Ag_2Se . It would be useful to make a comparison with high quality computer simulations of liquid Cu_2Se .

4.3. Comparison with other 2:1 melts

Recent NDIS results have allowed a comparison of the partial structure factors for several binary 2:1 liquids that are considered as ionic. It is also interesting to make a general comparison with the trends in the partial structures for materials that have more covalent properties in the melt and that tend to form network glasses if quenched. A typical example is given by GeSe_2 and it is observed that there is a clear first sharp diffraction peak at ~ 1 Å $^{-1}$ in the total structure factors measured for both the liquid (Penfold and Salmon 1991) and the glass (Petri *et al* 2000).

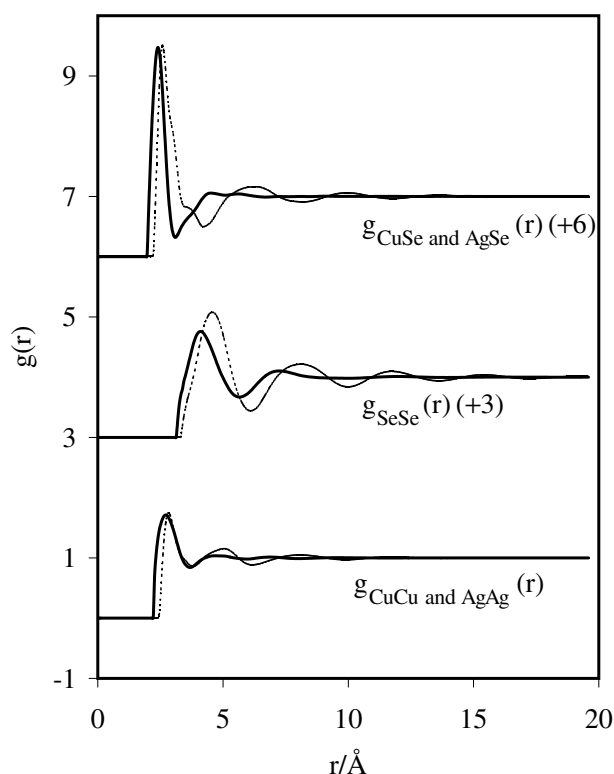


Figure 8. A comparison of the experimental smoothed $g_{ij}(r)$ for liquid Cu_2Se (solid lines) with those determined by Barnes *et al* (1997) for liquid Ag_2Se (dashed lines).

There is also evidence of such a peak in measurements of the total structure factors of Ga–Se alloys (Lague 1996). These materials are also characterized by strong oscillations in the partial structure factors out to high Q values. A peak at $Q \sim 1 \text{ \AA}^{-1}$ is also seen in ZnCl_2 (that is often thought of as ionic material) with the main contribution to it in $S_{CC}(Q)$ (Salmon 1992). Indeed the partial structure factor information for molten ZnCl_2 has now led to it being more commonly considered as a network forming liquid in which covalent interactions are strong. In contrast liquid SrCl_2 (that is believed to be strongly ionic) has no first sharp diffraction peak and has $S_{ij}(Q)$ (McGreevy and Mitchell 1982) that are similar in character to those of liquid Cu_2Se observed in this work. From these observations it appears that liquid Cu_2Se shows no features associated with network forming liquids and hence little evidence of any covalency.

It is the first peak in the cation–cation structure factor that shows the most significant contrast between the various 2:1 liquids for which results are available. Indeed recent NDIS results for liquid Ag_2Te show some evidence of this peak but with a much lower intensity than in liquid Ag_2Se (Barnes *et al* 2000). It is therefore particularly interesting that the current results show no evidence of such a peak. A comparison between the cation–cation partial structure factors for the three liquids is given in figure 10. The suggestion that the highly unusual electronic properties of liquid Ag_2Se and Ag_2S are linked to the high ionic mobility indicates that there should be significant differences in the distribution and dynamics of the cations in these materials if compared to systems that show more normal behaviour. Indeed recent results for liquid Ag_2Te have shown that there are significant differences in both the

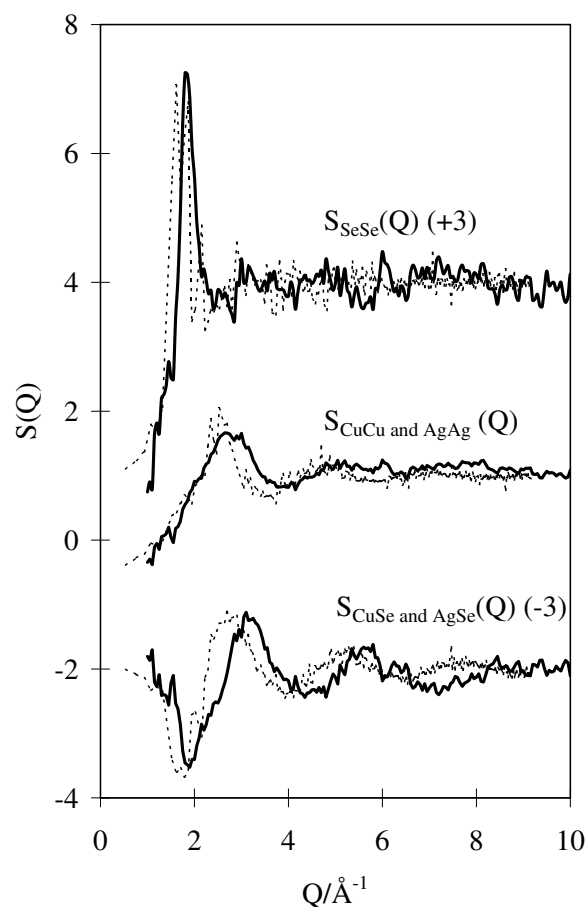


Figure 9. A comparison of the $S_{ij}(Q)$ for liquid Cu_2Se (solid line) with those calculated in an *ab initio* molecular dynamics simulation of liquid Ag_2Se by Kirchhoff *et al* (1996).

structure and dynamics if compared to Ag_2Se (Hamilton *et al* 2000). The present results for liquid Cu_2Se show differences in the structure that are consistent with those observed in Ag_2Te . It is clear that the structure of these binary materials must be considered at the partial structure factor level in order to make such differences apparent. The Cu halides also have superionic phases and it has been shown that $g_{\text{CuCu}}(r)$ for the liquid in the case of CuBr (Allen and Howe 1992) and CuCl (Page and Mika 1971, Eisenberg *et al* 1982) is relatively featureless. Waseda *et al* (2000) also report measurements of the structure of liquid CuBr and CuI using anomalous x-ray scattering coupled with reverse Monte Carlo techniques. They also report an essentially featureless $g_{\text{CuCu}}(r)$ for liquid CuBr but a more prominent first peak in $g_{\text{CuCu}}(r)$ for liquid CuI. However the poor statistical accuracy and RMC fit for CuI cast some doubt on the result for liquid CuI. Minicucci and Di Cicco report careful EXAFS measurements of the structure of liquid CuBr. This technique is very sensitive to the short range structure in the liquid and the authors find the first peak in $g_{\text{CuBr}}(r)$ is higher and narrower than that found by Allen and Howe (1992) but with a comparable coordination number. This they attribute to the statistical noise on the NDIS partial structure factors that leads to a broadening of the peaks in $g(r)$ when the data have been smoothed before Fourier transformation. For $g_{\text{CuCu}}(r)$

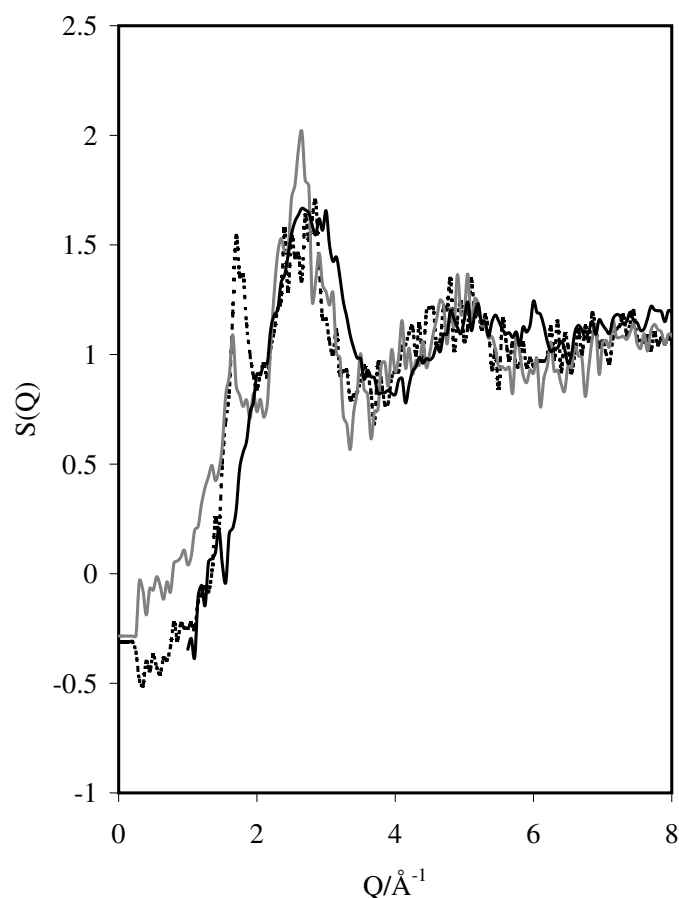


Figure 10. A comparison of the cation–cation partial structure factors for liquid Cu_2Se (dark line), liquid Ag_2Se (dashed line: Barnes *et al* 1997) and liquid Ag_2Te (light line: Barnes *et al* 2000).

they do not see a strong signal in the Cu edge EXAFS and they are unable to refine $g_{\text{CuCu}}(r)$. This is also consistent with little ordering in $g_{\text{CuCu}}(r)$ (that would result in a strong EXAFS signal). The metal-metal partial pair distribution functions $g_{MM}(r)$ for the liquid Ag and Cu chalcogenides have significant structure (figure 10). This can be understood in terms of the increased number of mobile ions packed into essentially the same size anion lattice due to the 2:1 stoichiometry. Benmore and Salmon (1994) make a similar comparison with CuI and CuCl based on a determination of $g_{MM}(r)$ for the glassy superionic conductor $\text{Ag}_2\text{As}_3\text{Se}_4$. Their results also showed significantly more structure in $g_{MM}(r)$ than the Cu halides. Such a featureless $g(r)$ is seen as an indication of the superionic nature of the Cu halides and is in contrast to the shallow first minimum and small second peak in $g(r)$ for the Ag and Cu chalcogenides.

5. Conclusions

The partial structure factors and pair distribution functions for liquid Cu_2Se have been determined by neutron diffraction with isotopic substitution. The results indicate that liquid

Cu₂Se can be considered as a 2:1 ionic melt consisting of Cu⁺ and Se²⁻ ions. A detailed comparison with results for liquid Ag₂Se shows a considerable amount of similarity but with significant differences in the cation–cation partial structure factor. $S_{CuCu}(Q)$ shows no evidence of the first peak at $\sim 1.8 \text{ \AA}^{-1}$ as found for liquid Ag₂Se and to a lesser extent Ag₂Te. It is with this particular $S_{ij}(Q)$ that the greatest contrast has been found for the three liquids. The similarities with the *ab initio* molecular dynamics simulation of Ag₂Se indicate that a comparable simulation of liquid Cu₂Se would give good results and such a simulation would be useful in furthering the understanding of the properties of this liquid. Given the importance of the ion mobility to the properties of such liquids it would be useful to measure the ion dynamics using a technique such as quasi-elastic neutron scattering. In the case of Cu₂Se this would allow a comparison with the QENS results that have already been obtained for Ag₂Se and Ag₂Te.

Acknowledgments

This work was funded by the UK Engineering and Physical Sciences Research Council to whom we are grateful. One of us (MAH) would like to thank the EPSRC for the award of a PhD studentship. Many thanks also to John Rowden and Brian Stockford for assisting us with the manufacture of the sample containers. Finally we greatly appreciate the efforts of the staff at ISIS, in particular John Dreyer, in order to give us the required sample environment.

References

- Allen D A and Howe R A 1992 *J. Phys.: Condens. Matter* **4** 6029
Barnes A C and Enderby J E 1988 *Phil. Mag.* **58** 497
Barnes A C, Hamilton M A, Beck U and Fischer H E 2000 *J. Phys.: Condens. Matter* **12** 7311
Barnes A C, Lague S B, Salmon P S and Fischer H E 1997 *J. Phys.: Condens. Matter* **9** 6159
Benmore C J and Salmon P S 1994 *Phys. Rev. Lett.* **73** 264
Bhatia A B 1977 *Liquid Metals 1976* (Bristol: Institute of Physics)
Bhatia A B and Thornton D E 1970 *Phys. Rev. B* **2** 3004
Boyce J B and Huberman B A 1979 *Phys. Rep.* **51** 189
Edwards F G, Enderby J E, Howe R A and Page D I 1975 *J. Phys. C: Solid State Phys.* **8** 3483
Eisenberg S, Jal S F, Dupuy J, Chieux P and Knoll W 1982 *Phil. Mag. A* **46** 195
Enderby and Barnes 1990 *Rep. Prog. Phys.* **53** 85
Fortner J, Saboungi M-L and Enderby J E 1995 *Phys. Rev. Lett.* **74** 1415
Glazov V M, Mamedov S M and Burkhanov A S 1985 *Sov. Phys.–Semicond.* **19** 1218
Hamilton M A, Barnes A C, Howells W S and Fischer H E 2000 *J. Phys.: Condens. Matter* submitted
Kirchhoff F, Holender J M and Gillan M J 1996 *Phys. Rev. B* **54** 190
Kobayashi M 1990 *Solid State Ion.* **39** 121
Koester L, Knopf K and Waschkowski W 1980 *Z. Phys. A* **296** 43
Lague S 1996 *PhD Thesis* University of Bristol
McGreevy R L and Mitchell E W J 1982 *J. Phys. C: Solid State Phys.* **15** 5537
Minicucci M and Di Cicco A 1997 *Phys. Rev. B* **56** 11 456
Ohno S, Barnes A C and Enderby J E 1990 *J. Phys.: Condens. Matter* **2** 7707
———1994 *J. Phys.: Condens. Matter* **6** 5335
Oliveria M, McMullan R K and Wuensch B J 1988 *Solid State Ion.* **28–30** 1332
Page D I and Mika K 1971 *J. Phys. C: Solid State Phys.* **8** 895
Penfold I T and Salmon P S 1991 *Phys. Rev. Lett.* **67** 97
Petri I, Salmon P S and Fischer H E 2000 *Phys. Rev. Lett.* **84** 2413
Rhalfs P 1936 *Z. Phys. Chem. B* **31** 157
Rovere M and Tosi M P 1986 *Rep. Prog. Phys.* **49** 1001
Salmon P S 1992 *Proc. R. Soc. Lond. A* **437** 591
Sears V F 1992 *Neutron News* **3** 26
Soper A K, Howells W S and Hannon A C 1989 *ATLAS RAL Report* RAL-89-046

- Schnyders H S, Hahn J, Streutker D and Van Zytveld J B 1997 *J. Phys.: Condens. Matter* **9** 10 121
Waseda Y, Kang S, Sugiyama K, Kimura M and Saito M 2000 *J. Phys.: Condens. Matter* **12** A195