Ag$^+$ dynamics in the superionic and liquid phases of Ag$_2$Se and Ag$_2$Te by coherent quasi-elastic neutron scattering

Ag^+ dynamics in the superionic and liquid phases of Ag_2Se and Ag_2Te by coherent quasi-elastic neutron scattering

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Abstract
The atomic motion of Ag^+ ions in superionic and liquid Ag_2Se and Ag_2Te has been investigated by coherent quasi-elastic neutron scattering. The presence of a Q-dependent broadening of the quasielastic peak indicates that the Ag^+ ion is mobile in the superionic phase of both materials. This motion takes place within a body-centred cubic sub-lattice of Se^{2-} or Te^{2-} ions respectively. Two Lorentzian components were required in order to fit the quasi-elastic broadening: a narrow peak that is attributed to the diffusion of the cations, and a much broader and less intense component that may be due to a localized motion of these ions. An asymmetry in the quasi-elastic peak indicates the presence of a low-energy excitation as reported for other superionic materials. The widths of the narrower Lorentzian showed the characteristic de Gennes narrowing at Q values close to the maximum in $S_{AgAg}(Q)$. A comparison of the widths of the quasi-elastic peak for the two liquids indicates a similar Ag^+ diffusion coefficient but a difference in the mechanism of diffusion. The results for liquid Ag_2Te indicate a jump-diffusion mechanism in comparison to those for Ag_2Se that follow Fick's law.

1. Introduction

Initial studies of the liquid semiconductors Ag_2S and Ag_2Se suggested that they are highly unusual as indicated by the observation that the temperature dependence of the conductivity is *negative* for both systems (Enderby and Barnes 1990). This is very unusual for liquids with a conductivity in the range considered for narrow definition liquid semiconductors. Further measurements of the conductivity and thermopower as a function of both temperature and composition for all the systems Ag–X (X = S, Se or Te) have been made and a previously unreported local maximum was observed in the conductivity at the stoichiometric composition

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in Ag_2S (Ohno *et al* 1990) and Ag_2Se (Ohno *et al* 1994) but *not* in Ag_2Te (Schnyders *et al* 1997). This peak is seen to be strongly temperature dependent and is at a maximum at close to the melting transition. Consideration of the results for the thermopower and magnetic susceptibility indicate that this unexpected increase in the conductivity is due to an enhancement of the carrier mobility (Ohno *et al* 1994).

It has been suggested that this enhancement of the carrier mobility may be linked to changes in the structure or alternatively, as these systems all have superionic phases prior to the melting transition, it may be due to interactions between the charge carriers and highly mobile ions. The striking contrast between the conductivity results for Ag_2Se and Ag_2Te indicate that clues to this behaviour lie in a detailed comparison of the properties of these two materials. Ag_2Se has a single superionic phase prior to the melting transition in which the Se^{2-} ions form a BCC sub-lattice (Kobayashi 1990). The Ag_2Te system has two superionic phases. At lower temperature up to $802\,^{\circ}C$ the Te^{2-} ions form an FCC lattice and at higher temperature up to the melting transition at $950\,^{\circ}C$ the sub-lattice is BCC (Schneider and Schulz 1993).

A detailed study of the structures of liquid Ag_2Se (Barnes *et al* 1997) and Ag_2Te (Barnes *et al* 2000) has been carried out at the partial structure factor level using the technique of neutron diffraction with isotopic substitution. A comparison of the results indicates that the melts are similar and ionic in character but with significant differences in the cation distribution. In particular, although the twin-peak structure of $S_{AgAg}(Q)$ at low Q for Ag_2Se is reproduced in the results for Ag_2Te, the first peak is much weaker and the second correspondingly stronger for the telluride. In real space this is seen as a deeper first minimum in $g_{AgAg}(r)$ and as a better defined and more intense second peak for Ag_2Te. This indicates that the mobile Ag^+ ions are more constrained in liquid Ag_2Te and have a correspondingly higher structural order.

The significant differences between $S_{AgAg}(Q)$ for these materials suggests there may be differences in the silver motion between them. It is therefore of particular interest to determine the time-dependent behaviour of the mobile ions. In this paper coherent quasi-elastic neutron scattering results for both systems are presented to determine whether these differences in the time-averaged cation distribution are indeed reflected in the dynamics.

2. Coherent scattering measurements of dynamics

In a neutron scattering experiment the dynamic structure factor can be written as a combination of the self and distinct parts (Hansen and McDonald 1986),

$$S(Q, \omega) = S_S(Q, \omega) + S_D(Q, \omega) \tag{1}$$

The self-part of the dynamic structure factor gives information about the single particle motion and it is therefore this quantity that is required in order to determine the motion of the Ag^+ ions. However the partial differential cross-section, the quantity that is measured in a scattering experiment, consists of a combination of the total and the self parts of the dynamic structure factor weighted by the coherent and incoherent scattering lengths of the system (see table 1 for these quantities for Ag, Se and Te),

$$\frac{d^2\sigma}{d\Omega\,d\omega} = \frac{k_f}{k_i} N[b_{coh}^2 S(Q, \omega) + b_{incoh}^2 S_S(Q, \omega)]. \tag{2}$$

Here k_i and k_f are the incident and final wavevectors of the neutron and N the number of scattering nuclei. For the self-part of the dynamic structure factor a solution can be found to Fick's law of diffusion that has the form (Egelstaff 1992)

$$S_S(Q, \omega) = \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2} \tag{3}$$

For constant Q this is a Lorentzian with a full-width at half maximum of $2DQ^2$ and a plot of the widths against Q^2 should give a straight line of slope $2D$. Here D is the chemical diffusion coefficient (Ross 1992). If the values of (r, t) measured in an experiment are similar to the characteristic length and time of a diffusive step, as at larger Q, the nature of the diffusive steps must be considered. A model of jump diffusion gives (Egelstaff 1992)

$$S_S(Q, \omega) = \frac{1}{\pi} \frac{f(Q)}{\omega^2 + [f(Q)]^2} \tag{4}$$

where the width at half-maximum for a continuous and random distribution of jump lengths is

$$F(Q) = \frac{1}{\tau} \left[1 - \frac{1}{1 + Q^2 L^2} \right]. \tag{5}$$

In the limit of small Q equation (4) reduces to that for continuous diffusion given by equation (3). Equation (5) is the result derived by Chudley and Elliott (1960) with τ the characteristic jump time and L the jump distance.

If the scattering is entirely coherent then there is no direct measurement of $S_s(Q, \omega)$ as can be seen from equation (2). However Sinha and Ross (1988) have derived a method of calculating the ion motion from the coherent scattering function $S(Q, \omega)$ for light particles diffusing via interstitial sites in a crystal lattice. This method allows for interactions between the diffusing particles and the lattice. They conclude that the coherent scattering from a system of diffusing particles also gives a Lorentzian shape to $S(Q, \omega)$ but with a Q-dependent width that is equivalent to a modified Chudley–Elliott model where

$$S(Q, \omega) = \frac{1}{\pi} \frac{|a(Q)|^2 c(1 - c) f(Q)}{\omega^2 + [f_{coh}(Q)]^2}. \tag{6}$$

Here $a(Q)$ is a form factor that is related to $S(Q)$ and the interactions between the diffusing particles and the lattice (see Sinha and Ross 1988 for details) and therefore the widths that are observed are approximately related to those in the incoherent case if scaled by $S(Q)$,

$$f_{coh}(Q) \sim \frac{f(Q)}{S(Q)}. \tag{7}$$

The width of $S(Q, \omega)$ therefore narrows near the maximum in $S(Q)$ as explained by de Gennes (1959). The widths for the coherent case using equations (5) and (7) should therefore have a Q-dependence based on a modified form of the solution to Fick's law,

$$f_{coh}(Q)S(Q) \sim DQ^2 \tag{8}$$

or for the Chudley–Elliott result,

$$f_{coh}(Q)S(Q) \sim \frac{1}{\tau} \left[1 - \frac{1}{1 + Q^2 L^2} \right]. \tag{9}$$

In the limit of small Q these equations will still give the correct chemical diffusion coefficient (Sinha and Ross 1988).

3. Experimental procedure

The dynamics of Ag+ in Ag_2Se and Ag_2Te were measured in separate quasi-elastic neutron scattering (QENS) experiments using the IN6 time-of-flight spectrometer at the Institut Laue–Langevin in Grenoble, France. The scattering was measured in the solid superionic phase just before melting and in the liquid phase. For Ag_2Te the measurements for the superionic phase were in the higher temperature BCC form. The incident neutron wavelength in both cases was 5.1 Å giving an energy resolution of 109 μeV. The energy resolution of the instrument was

determined by measuring the scattering from a vanadium standard of similar dimensions to the sample. This also allowed normalization of the scattered intensity. The samples of Ag_2Se and Ag_2Te were prepared by mixing of the pure elements and reacting them at $\sim 1100\,°C$ in silica containers. The powdered samples were contained in a niobium cylinder with a diameter of ~ 5 mm and the data were corrected for absorption and container scattering using the standard ILL routine INX. The effect of multiple scattering in the quasielastic region is small (Johnson 1974) especially given the high absorption cross-section of the samples at this wavelength relative to the scattering cross-section (see table 1). The spectra were grouped to improve statistics and interpolated to constant Q using the routine INGRID (Rieutord 1990).

Table 1. Neutron scattering lengths and cross-sections for Ag, Se and Te. Data for ^{nat}Ag from Sears (1992), Se from Koester *et al* (1980) and Te from Koester *et al* (1986).

Isotope	b_{coh} (fm)	b_{incoh} (fm)	σ_a (barns at 1.8 Å)	σ_s (barns)
^{nat}Ag	5.922 ± 0.007	0.58	63.3	4.99
^{nat}Se	7.97 ± 0.02	0.46	11.7	8.31
^{nat}Te	5.80 ± 0.03	-0.37	4.32	4.31

4. Results

The quasi-elastic broadening showed a clear Q dependence; however only a limited region of Q–ω space was accessible to neutrons of this incident wavelength. The resulting $S(Q, \omega)$ were analysed using the Bayesian fitting routine QUASILINES (Sivia *et al* 1992), that allows the most likely number of Lorentzian components to be determined. Figure 1 shows, as an example, a section through $S(Q, \omega)$ for Ag_2Te in the high-temperature superionic phase including the elastic peak and the residual. The quasielastic broadening is clear. Figure 2 shows the same data but with a fit that includes the quasielastic broadening. The function fitted was

$$S(Q, \omega) = \left[A_0 \delta(\omega) + \sum_{i=1}^{N} A_i \frac{f(Q)_i}{\pi(\omega^2 + f(Q)_i^2)} \right] \otimes R(\omega) + B(\omega) + \sigma(\omega). \quad (10)$$

Here $R(\omega)$ is the energy resolution function of the instrument, which is convoluted with a number of Lorentzians, N, of width $f(Q)$ and a delta function that represents the elastic scattering from the sample. Added to this is a background term $B(\omega)$ and a further term to represent statistical noise $\sigma(\omega)$. The energy range of the fit was chosen to be $-1.5 < E$ (meV) < 1.5. A single Lorentzian was assumed to account for the quasi-elastic broadening as expected from the solution to Fick's diffusion law (Egelstaff 1992). However a Bayesian fitting procedure gives evidence of a second Lorentzian component. This peak has low intensity and its inclusion makes little difference to the properties or interpretation of the behaviour of the primary quasi-elastic peak. The full widths at half maximum of the narrower Lorentzian fit for each temperature are plotted against Q^2 in figures 3 and 4 for Ag_2Se and Ag_2Te respectively. The values of these widths show no significant dependence on the energy range over which the fit was performed. The characteristic de Gennes narrowing at the higher Q values that is due to correlation effects between different atoms can also be observed. The narrowing occurs at close to the first maximum in $S_{AgAg}(Q)$. Figures 6 and 7 show the widths modified according to equation (7) by multiplying by $S_{AgAg}(Q)$ (see figure 5). In both cases the cation–cation structure factor for the liquid was used. This has been obtained by neutron diffraction with isotopic substitution (Barnes *et al* 1997, 2000) and the limitations of this technique result

in the statistical noise that is observed. The use of the partial structure factor for the liquid is justified by recent results that indicate that there is little change in the structure of these materials between the superionic phase just before melting and the liquid at this temperature (Hamilton 2000). The dashed curve indicates a least-squares fit to the data in order to extract the diffusion coefficient according to Fick's law. The Q dependence of the widths for liquid Ag$_2$Te is quite different and has been fitted using the Chudley–Elliott model. The diffusion coefficients obtained by a least-squares fit and the model parameters for liquid Ag$_2$Te are given in table 2. The second Lorentzian component was of lower amplitude than the narrower peak but was much broader. The width had little Q dependence but was dependent on the energy range of the fit due to its high correlation with the background.
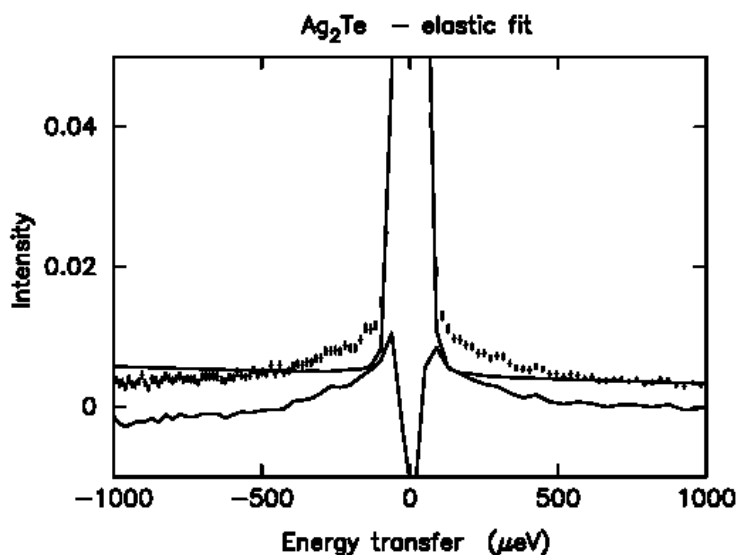

Figure 1. A section at constant Q through $S(Q, E)$ for superionic Ag$_2$Te (γ-phase) showing the elastic peak and the residual.

Table 2. Diffusion coefficients and model parameters for Ag$_2$Se and Ag$_2$Te.

System	Temp. (°C)	D (10^{-9} m^2 s^{-1})
Ag$_2$Te	900	6.5 (±0.5)
	1000	7.6[a] (±0.5) $L = 2.9 \pm 0.1$ Å $\tau = 1.15$ ps
Ag$_2$Se	850	3.4 (±0.5)
	950	4.1 (±0.5)

[a] D is determined from the low-Q limit in figure 7.

5. Discussion

5.1. Dynamics in Ag$_2$Se and Ag$_2$Te

There is a clear Q-dependent broadening of the elastic scattering in both the superionic (see figure 1) and liquid phases of Ag$_2$Se and Ag$_2$Te. This indicates that there are mobile ions within these materials. It is assumed that the Ag$^+$ ions are much more mobile than the Se^{2-}/Te^{2-} ions
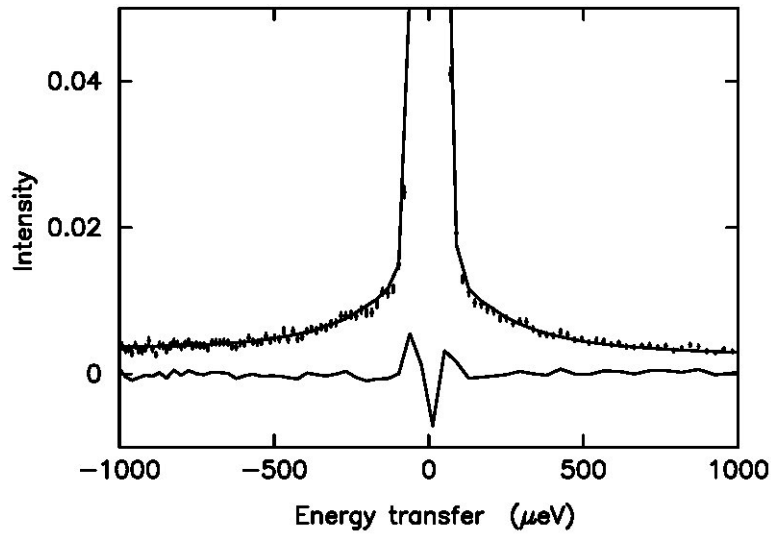
Figure 2. The corresponding fit (using equation (10)) and residual for superionic Ag_2Te.
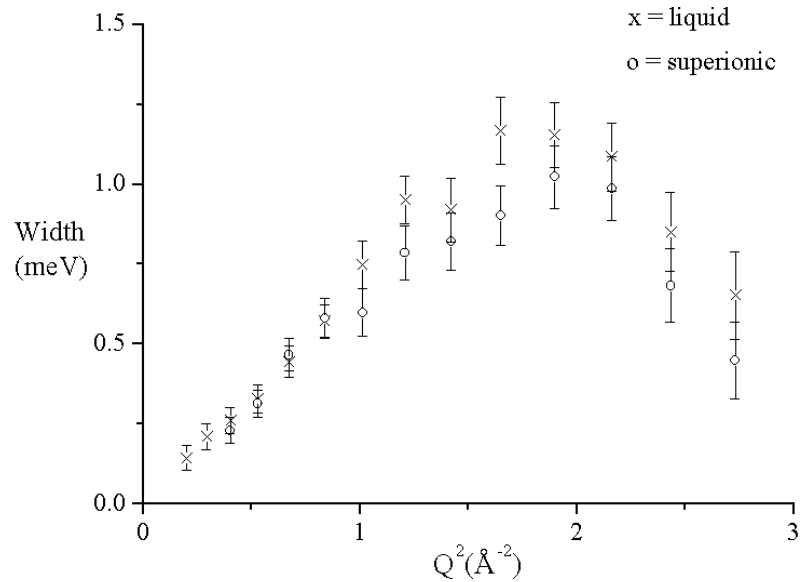

Figure 3. The widths of a single Lorentzian fit to $S(Q, E)$ for liquid ($\times$) and superionic ($\bigcirc$) Ag_2Se plotted against Q^2. At the higher Q values as the first maximum in $S(Q)$ is approached the widths decrease—this is de Gennes narrowing.

due to the difference in size and our knowledge of the fast-ion phase. Indeed recent results for the partial structure factors of superionic Ag_2Se indicate almost complete cancellation of the Bragg scattering that is observed in the case of $S_{AgAg}(Q)$ (Hamilton 2000). Therefore the quasi-elastic broadening is assumed to be entirely due to the mobile Ag^+ ions.

The Bayesian fitting routine gives the most likely number of Lorentzian components as two for all Q values. There is virtually no incoherent scattering from these systems (table 1)
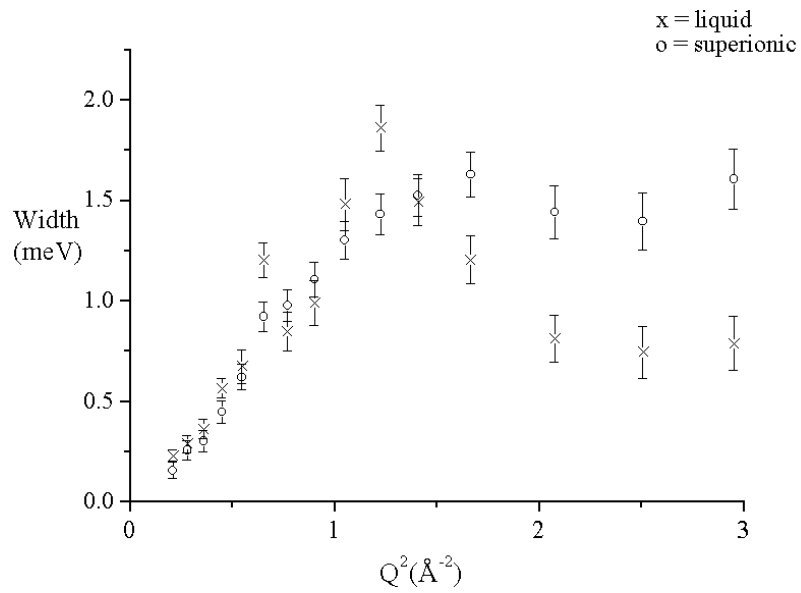
Figure 4. The widths of a single Lorentzian fit to $S(Q, E)$ for liquid ($\times$) and superionic ($\bigcirc$) Ag$_2$Te plotted against Q^2. The trend at higher Q shows de Gennes narrowing.
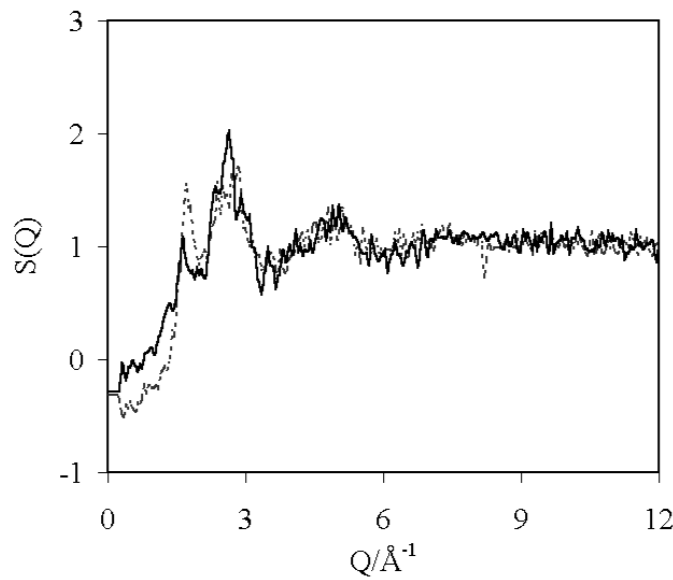

Figure 5. A comparison of $S_{AgAg}(Q)$ for liquid Ag$_2$Te (solid curve) and liquid Ag$_2$Se (dashed curve). The results are from Barnes *et al* (1997, 2000) and have been obtained by neutron diffraction with isotopic substitution.

and so it is the total dynamic structure factor that has been measured. The narrower Lorentzian fit to the data showed the expected 'de Gennes' narrowing of the quasielastic peak at Q values approaching the first peak in $S_{AgAg}(Q)$. In order to interpret the results in terms of the theory developed for the self-part of the dynamic structure factor, or in other words that due
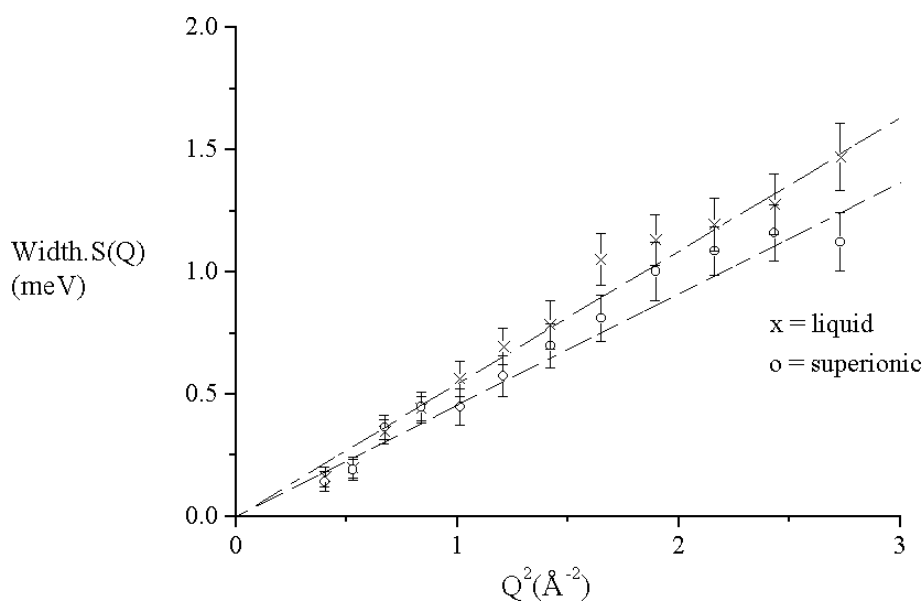
Figure 6. The widths for Ag_2Se from figure 3 multiplied by $S_{AgAg}(Q)$ for liquid Ag_2Se. The dashed line is a least squares fit to the liquid ($\times$) and superionic ($\bigcirc$) results and is Fick's law.

to incoherent scattering, it is necessary to multiply the observed widths by $S_{AgAg}(Q)$ (Skold 1967, Sinha and Ross 1988). The widths following scaling by the relevant $S(Q)$ (figure 5) are shown in figures 6 and 7 for Ag_2Se and Ag_2Te respectively. The measured $S(Q)$s have errors, particularly in the Q range that is considered here, and these errors are magnified as Q^2 so the deviations from the linear behaviour that are observed in figure 6 are not considered as an indication that a linear fit is not appropriate. In the case of Ag_2Se the trend for both the superionic and liquid phases follows that for simple diffusion. A least squares fit to the data with the width proportional to DQ^2 indicates that Fick's law is applicable. The diffusion coefficient for the liquid is seen to be slightly larger than that for the superionic phase. The value obtained here for the liquid ($D_{Ag} = 4.1 \pm 0.5 \times 10^{-9}$ m^2 s^{-1}) is in broad agreement with that obtained in the *ab initio* molecular dynamics simulation of Kirchhoff *et al* (1996) of $D_{Ag} = 6.4 \times 10^{-9}$ m^2 s^{-1}. This behaviour is also observed for the results from superionic Ag_2Te. The measured diffusion coefficient of $D_{Ag} = 6.5 \pm 0.5 \times 10^{-9}$ m^2 s^{-1} (present work) is a little larger than that reported for an MD simulation of $D_{Ag} = 6 \times 10^{-9}$ m^2 s^{-1} by Kobayashi *et al* (1988). In contrast the widths for *liquid* Ag_2Te show a quite different behaviour that can be understood reasonably well by the Chudley–Elliott model of jump diffusion (Chudley and Elliott 1960). Here the jump distance has been fixed and taken to be the nearest neighbour distance in the experimentally determined $g_{AgAg}(r)$, which is ~ 2.9 Å. In this case the small Q limit gives a small increase in the observed diffusion rate for liquid as compared to superionic Ag_2Te.

The broader peak found by the Bayesian fitting routine had several times the width and was of much lower intensity than the narrower component. The width of this broader Lorentzian was of the order of 5 ± 2 meV. The large estimated error is due to the variation of the measured width with the energy range of the fit and the increasing effect of multiple scattering with increasing energy transfer. There was little Q dependence to this peak suggesting that it may be due to a localized motion of the Ag^+ ions as has been reported in previous measurements on superionic Ag_2Se (Hoche *et al* 1983).
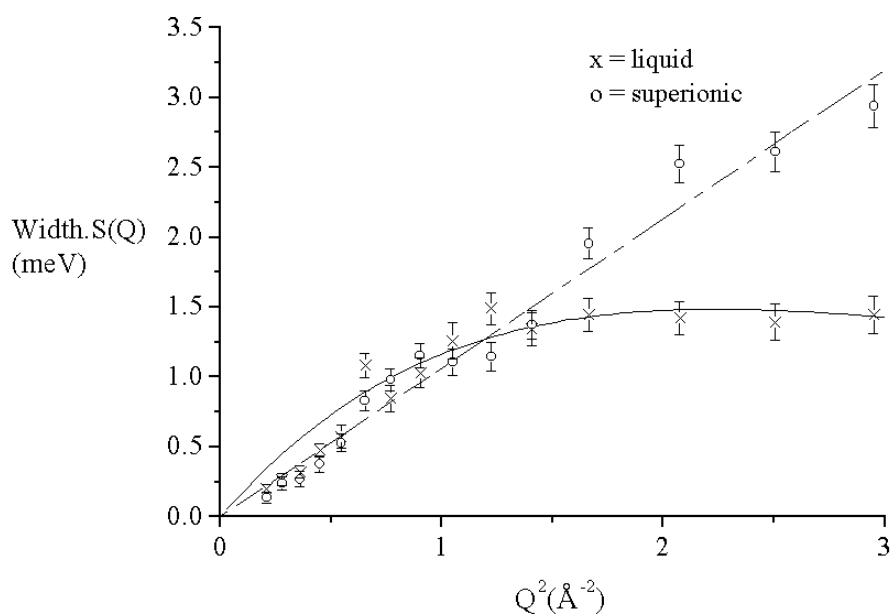
Figure 7. The widths for Ag$_2$Te from figure 4 multiplied by $S_{AgAg}(Q)$ for liquid Ag$_2$Te. The dashed line is a least squares fit to the superionic results (O) with Fick's law. The curve is the Chudley–Elliott model fitted to the results for the liquid ($\times$).

The quasi-elastic peak is asymmetric—more noticeably at the higher Q values. A low-energy excitation with comparable energy ($\sim$2 meV) has been reported in several cases, such as for Ag$_2$S (Grier *et al* 1984) and AgI (Eckold *et al* 1976), for Ag-conducting materials prior to the superionic transition. After the transition this feature is seen not as a distinct peak but as a broad contribution to the quasielastic peak. By the principle of detailed balance this produces an asymmetry as observed in the present results for the case of Ag$_2$Se and Ag$_2$Te.

5.2. Comparison between liquid Ag$_2$Se and Ag$_2$Te

The interest in the ion distribution and dynamics of the Ag$^+$ ions in these materials has been prompted by the observation of unusual electronic properties in Ag$_2$Se, including a peak in the conductivity, that are not observed in Ag$_2$Te. It is therefore of particular interest that there appears to be a marked difference in the mechanism of diffusion. Figure 8 displays the modified widths for liquid Ag$_2$Se and liquid Ag$_2$Te. Those for liquid Ag$_2$Se follow a linear, Fick's law, relationship. In contrast the Q dependence of the widths for liquid Ag$_2$Te is quite different and conforms more to the Chudley–Elliott model of jump diffusion. This is observed in the differences in $S_{AgAg}(Q)$ for the two liquids and to the fact that the broadening of the quasielastic line at higher Q values is quite different in the case of liquid Ag$_2$Te. The differences that have been observed between $S_{AgAg}(Q)$ (Barnes *et al* 2000) are consistent with the contrasting mechanism of diffusion. The crystalline order of superionic Ag$_2$Te allows continuous diffusion. The increase in disorder that is associated with the melting transition results in a change to a jump diffusion behaviour. Of interest here is that such a change is not observed in the case of Ag$_2$Se. The Ag$^+$ ions in liquid Ag$_2$Te are more highly ordered as would be expected if they are considered to jump between discrete sites. The mobile ions in

liquid Ag_2Se are more randomly distributed and this is consistent with a continuous diffusion of ions between interstitial sites.
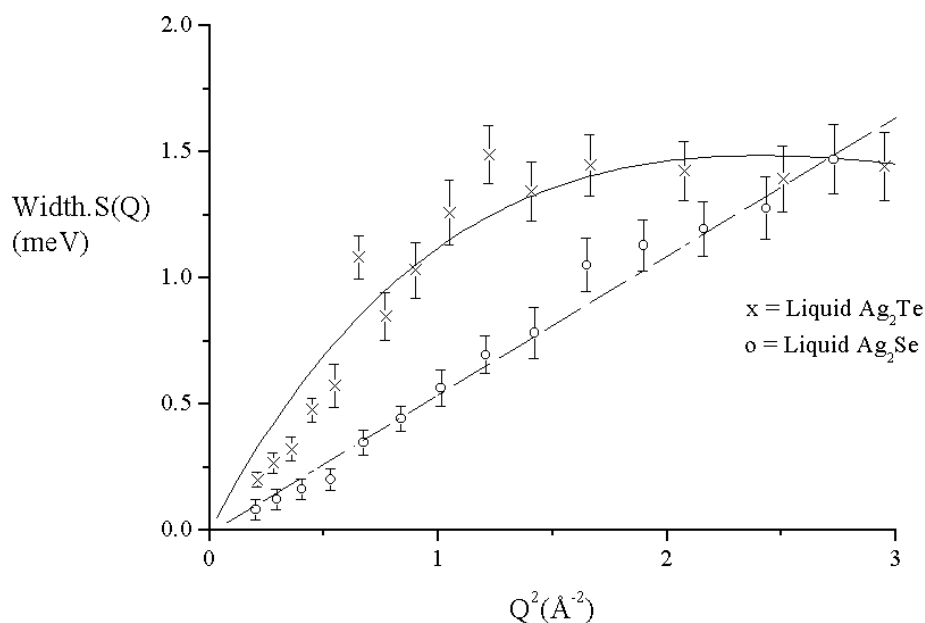

Figure 8. A comparison of the modified widths for liquid Ag_2Se ($\bigcirc$) and liquid Ag_2Te ($\times$). The lines are as in the previous figures.

5.3. The effect of Ag^+ dynamics on the electronic properties

The suggestion by Huberman (1974), Ramasesha (1982) and, more recently, by Fortner *et al* (1995) that mobile ions have an effect on the electronic properties of superionic materials such as Ag_2S and Mg_3Bi_2 has resulted in a detailed comparison of liquid Ag_2Se and Ag_2Te. The differences in the distribution and motion of the Ag^+ ions between these materials suggest that the difference in the conductivity is indeed linked to the ionic mobility. It is difficult at this stage to understand how such an interaction takes place but Ramasehsa's model includes an attraction between the mobile ions and the electrons that lowers the total free energy. In other words the creation of mobile ions has the effect of reducing the band gap and favours the creation of charge carriers.

Both the measurements of the structure and the present results show that the mobile ions in liquid Ag_2Te are more ordered when compared to liquid Ag_2Se. Ramasesha has also suggested that the interaction with the charge carriers has the effect of reducing the cation–cation repulsion. In general it is expected that the mobility of the ions will be reduced following the melting transition as the sub-lattice breaks down. From the present results this is the case for Ag_2Te but not for Ag_2Se. This may indicate that there is a larger effective interaction between the mobile ions and electrons in the case of liquid Ag_2Se. This would result in a lower cation–cation repulsion and the difference in the diffusion mechanism that is observed.

It has been postulated elsewhere (Barnes *et al* 1997) that at higher temperature the properties of Ag_2Se will become more 'normal' as the mobility of the ions decreases.

This would be seen as a change in the mechanism of diffusion and therefore a change of the Q-dependence of the widths to that predicted by the Chudley–Elliott model.

6. Conclusions

There is a clear Q-dependent broadening of the elastic scattering in both superionic and liquid Ag_2Se and Ag_2Te—this indicates that there is diffusion of Ag^+ ions in both these materials in the superionic phase. The 'de Gennes' narrowing that is observed due to the coherent nature of the scattering can be approximately accounted for by multiplying the observed widths by $S_{AgAg}(Q)$. The modified widths indicate that the diffusion in superionic and liquid Ag_2Se and superionic Ag_2Te follows Fick's law and is therefore considered to be continuous. In contrast the results for liquid Ag_2Te indicate that a jump diffusion model is more appropriate. This observation is consistent with the differences that have been observed in the structure of the two liquids that have been reported elsewhere. The difference in the dynamics of these materials is another indication that the unusual electronic properties of these materials may be linked to the high ionic mobility.

Acknowledgments

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