IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Structure of two liquid semiconductors $Ag_{1-x}Se_x$ and $Ag_{0.67}Te_{0.33}$

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

1993 J. Phys.: Condens. Matter 5 3087

(http://iopscience.iop.org/0953-8984/5/19/008)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.159
The article was downloaded on 12/05/2010 at 13:19

Please note that terms and conditions apply.

J. Phys.: Condens. Matter 5 (1993) 3087–3094. Printed in the UK

Structure of two liquid semiconductors $Ag_{1-x}Se_x$ and $Ag_{0.67}Te_{0.33}$

David Long Price†, Marie-Louise Saboungi†, Sherman Susman†, Kenneth J Volin†, John E Enderby‡ and Adrian C Barnes‡

† Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA
‡ H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK

Received 12 January 1993

Abstract. Neutron diffraction measurements have been carried out on $Ag_{1-x}Se_x$ and $Ag_{0.67}Te_{0.33}$ alloys to investigate possible structural causes for the differences in electrical transport properties observed in the two alloys. $Ag_{1-x}Se_x$ was measured for three compositions, $x = 0.30$, 0.33 and 0.36, at temperatures just above the liquidus (1045, 915 and 855 °C, respectively), and for $x = 0.33$ at three temperatures (915, 985 and 1045 °C). The $Ag_{1-x}Te_x$ system was measured at only one composition $x = 0.33$, just above the liquidus (985 °C). At the level of the average correlation function, the behaviour of liquid Ag–Se shows no unusual dependence on either concentration or temperature, and the selenium and tellurium alloys show generally similar behaviour. There is no obvious structural connection with the anomalous concentration dependence of the electrical conductivity in $Ag_{1-x}Se_x$ alloys or with the different behaviour in both electronic and ionic conduction observed in the Ag–Se and Ag–Te systems.

1. Introduction

A typical liquid semiconducting alloy is characterized by a drastic decrease of the electronic conductivity σ_e as a function of composition, reaching a minimum of 500 Ω^{-1} cm^{-1} or less near a characteristic stoichiometric composition; the temperature derivative of σ_e is positive and reaches a maximum at the composition corresponding to the minimum σ_e [1, 2]. Recently, highly unusual behaviour in liquid $Ag_{1-x}S_x$ and $Ag_{1-x}Se_x$ alloys near the stoichiometric composition Ag_2X has been revealed by electronic conductivity, thermopower and magnetic susceptibility measurements [3, 4]. In these alloys, σ_e decreases smoothly with increasing x until $x = 0.32$ and then rises to give a sharp peak with $\sigma_e = 250$ and 450 Ω^{-1} cm^{-1} for Ag_2S and Ag_2Se, respectively. Furthermore, $d\sigma_e/dT$ is positive until $x = 0.32$ and takes negative values at $x = 0.33$; these are the only known liquids which combine a low value of $\sigma_e (< 500\ \Omega^{-1}\ \mathrm{cm}^{-1})$ with a negative $d\sigma_e/dT$. On heating up to 1200 °C, the peak in $\sigma(x)$ disappears and $d\sigma_e/dT$ becomes positive, reverting to the typical behaviour.

In contrast, $Ag_{1-x}Te_x$ behaves as a typical liquid semiconductor with positive $d\sigma_e dT$ over the entire range of temperatures and compositions measured [5, 6].

All three alloys exhibit fast ion conduction in the high-temperature solid and liquid phases. The temperature dependence of the ionic conductivity σ_i has measured by Endo *et al* [5] using the residual potential method. Here also there are different behaviours, with $d\sigma_i dT$ positive in Ag_2S and Ag_2Se and negative in Ag_2Te.

The differences in the electrical transport properties, and in particular the anomalous concentration dependence in the electronic conductivity of the sulphur and selenium alloys,

© 1993 US Government

could be due to changes in either the electronic or the atomic structure. To investigate the possibility of an atomic structural component, neutron diffraction measurements have been carried out on $Ag_{1-x}Se_x$ and $Ag_{0.67}Te_{0.33}$ alloys just above their melting points. The Ag–Se system was chosen over the Ag–S in order to avoid the rapid rise of the liquidus line for $x < 0.33$ in $Ag_{1-x}S_x$. $Ag_{1-x}Se_x$ was measured for three compositions, $x = 0.30$, 0.33 and 0.36, at temperatures just above the liquidus (1045, 915 and 855 °C, respectively), and for $x = 0.33$ at three temperatures (915, 985 and 1045 °C). The more typical $Ag_{1-x}Te_x$ system was measured at only one composition, $x = 0.33$, just above the liquidus (985 °C).

2. Experiments

High-purity silver, silver selenide and silver telluride were used as received from the manufacturer for synthesis of the liquid semiconductors. These reactants were not purified further but were stored and subsequently manipulated in a glove box under a dry nitrogen atmosphere. High-purity selenium was further treated to remove the residual surface oxide [7].

Stoichiometric proportions of the starting materials, totalling approximately 16 g for each sample, were charged into previously outgassed, 9 mm OD fused silica ampoules. The samples of Ag_2Se and Ag_2Te were sealed under vacuum and used directly in the experiment as loaded. The sealed ampoules of $Ag_{0.64}Se_{0.36}$ and $Ag_{0.70}Se_{0.30}$ were placed separately into a rocking furnace and slowly brought up in temperature to where the Ag_2Se:(Se, Ag) starting materials had fully reacted to form a homogeneous liquid ($T_{liq} = 789$ °C for $Ag_{0.64}Se_{0.36}$ and 995 °C for $Ag_{0.70}Se_{0.30}$). The furnace was then left in a horizontal position to cool, resulting in a coherent boule of material. This procedure allowed the sample material to remain in the same fused silica ampoule for the diffraction measurements.

Time-of-flight neutron diffraction measurements were carried out at the Special Environment Powder Diffractometer at the Intense Pulsed Neutron Source at Argonne. Diffraction runs were made over 8–12 h for each sample and temperature and over 8 h for the empty silica container at each measurement temperature. A vanadium standard rod and the empty spectrometer were measured for calibration purposes. Data were analysed using standard procedures [7, 8] and combined over a scattering angle range 14–90° and a wavelength range 0.55–1.65 Å using flux weighting.

3. Results

Average structure factors $S(Q)$ are shown for $Ag_{0.67}Se_{0.33}$ (915 °C) and $Ag_{0.67}Te_{0.33}$ (985 °C) in figure 1. These are neutron-weighted averages [7] in which each partial structure factor $S_{ij}(Q)$ is weighted by the factor

$$w_{ij} = (c_i c_j)^{1/2} b_i b_j \Big/ \left(\sum_i c_i b_i \right)^2 \tag{1}$$

where c_i and b_i are the concentration and coherent scattering length of element i; $b_i = 5.98$, 7.97 and 5.80 fm for i = Ag, Se and Te, respectively [1, 9]. The Se alloy structure factor shows a small pre-peak due to chemical ordering [2, 10]. This peak is not observed in the Te alloy, probably because the scattering lengths are too similar. The structure factors of $Ag_{1-x}Se_x$ for $x = 0.30$, 0.33 and 0.36 are shown in figure 2, and those for $Ag_{0.67}Se_{0.33}$ at

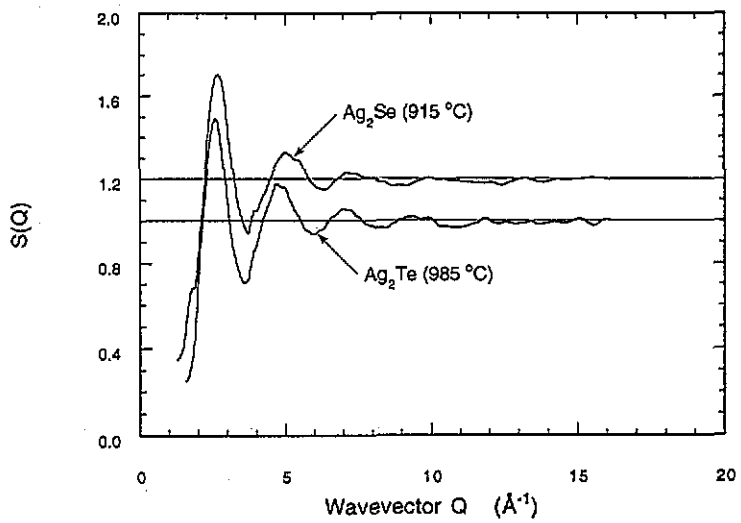

Figure 1. Measured neutron-weighted average structure factors of liquid $Ag_{0.67}Se_{0.33}$ (915 °C); and $Ag_{0.67}$ $Te_{0.33}$ (985 °C) upper curve displaced by 0.2.

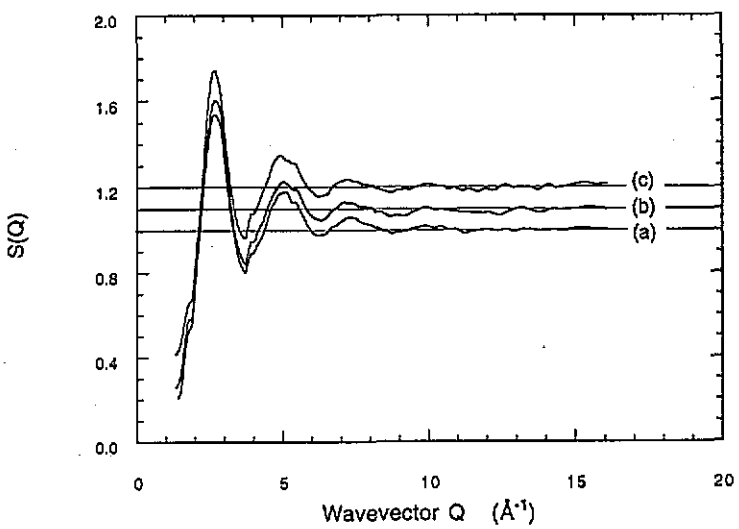

Figure 2. Measured neutron-weighted average structure factor of liquid Ag_xSe_{1-x} as a function of composition: (a) $x = 0.64$ (855 °C); (b) $x = 0.67$ (915 °C); (c) $x = 0.70$ (1045 °C); upper curves displaced successively by 0.1.

$T = 915$, 985 and 1045 °C in figure 3. No dramatic changes with either composition or temperature are observed.

Molecular dynamics (MD) computer simulations of Ag_2Se have been carried by Rino *et al* [11] in order to study the fast ion conduction in the solid and liquid. The simulations were based on model potentials comprising Coulomb interactions, steric repulsion and charge–dipole interactions involving the Se^{2-} ions. The MD $S(Q)$ is compared with the present data at 985 °C in figure 4 and seen to be in reasonable agreement, the main differences being

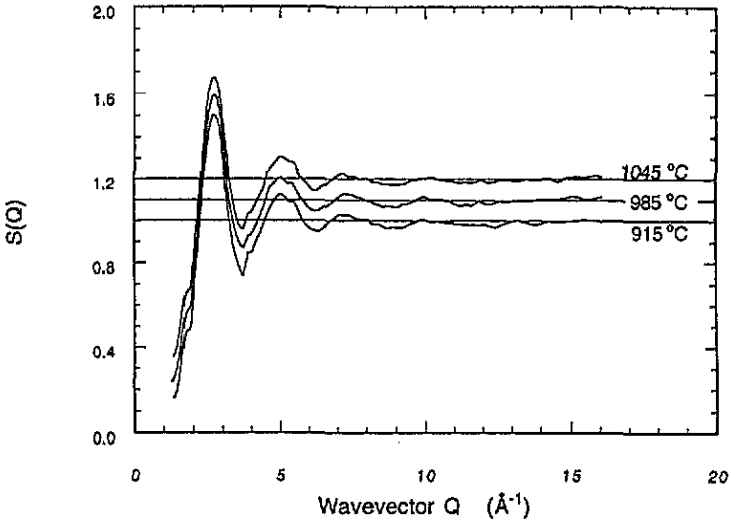

Figure 3. Measured neutron-weighted average structure factor of liquid $Ag_{0.67}Se_{0.33}$ as a function of temperature; upper curves displaced successively by 0.1.

a less pronounced pre-peak and a lower main peak in the MD results. The Ag^+ fast ion diffusion in the simulation is enhanced in the liquid compared with the high-temperature solid and increases further as the melt is heated, in accord with the experimental observation [5]. The value of the Ag^+ diffusion constant is 9×10^{-5} cm^2 s^{-1} at 963 °C, about four times that of Se^{2-}. The ionic conductivity calculated from these numbers is $\sigma_i = 3.7\ \Omega^{-1}$ cm^{-1}, in reasonable agreement with the experimental value [5] of 4.8 Ω^{-1} cm^{-1} at 980 °C.

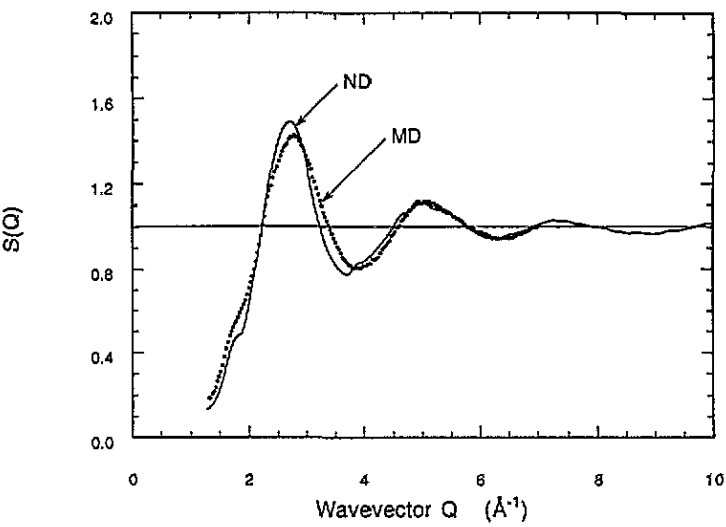

Figure 4. Comparison of molecular dynamics computer simulation ([11], 963 °C) and experimental (985 °C) neutron-weighted average structure factors of liquid Ag_2Se.

Pair distribution functions $g(r)$, also neutron-weighted averages, were obtained by

Fourier transformation of the $S(Q)$ data over the Q range 1–15 Å^{-1}, using the Lorch modification function. Typical results plotted in terms of the total correlation function

$$T(r) = 4\pi\rho r g(r) \tag{2}$$

are shown in figures 5 and 6 for $Ag_{0.67}Se_{0.33}$ (915 °C) and $Ag_{0.67}Te_{0.33}$, respectively. All correlation functions show qualitatively similar behaviour, with an asymmetric peak at $r \sim 2.8$ Å followed by a relatively structureless pattern. Number densities ρ were adjusted to give $g(r) = 0$ at low r and are listed in table 1. For $Ag_{0.67}Se_{0.33}$, both the $S(Q)$ and $g(r)$ data are in good agreement with the previous results of Enderby and Barnes [1].

Table 1. Parameters from fits to $T(r)$ for $Ag_{1-x}X_x$ (X=Se.Te).

X	x	T (°C)	ρ (Å^{-3})	r_1 (Å)[a]	σ_1 (Å)[b]	$Z_{Ag}(X)$[c]	$Z_{Ag}(Ag)$[d]
Se	0.30	1045	0.0307	2.78	0.23	3.1	8.9
Se	0.33	915	0.0419	2.77	0.24	3.5	10.3
Se	0.33	985	0.0407	2.77	0.24	3.45	10.0
Se	0.33	1045	0.0397	2.78	0.25	3.4	9.6
Se	0.36	855	0.0430	2.78	0.24	3.8	11.2
Te	0.33	985	0.0322	2.88	0.19	3.2	5.6

[a] Position of fitted Gaussian in $T(r)$.
[b] Standard deviation width of Gaussian.
[c] Coordination number for X about Ag, calculated from fitted Gaussian.
[d] Coordination number for Ag about Ag, calculated from residuals out to 4 Å.

The partial pair correlation functions $g_{ab}(r)$ obtained from the computer simulation of Ag_2Se [11] are shown in figure 7. The Ag–Se and Se–Se correlation functions have reasonably well defined first peaks centred near 2.7 and 4.3 Å, respectively, and coordination numbers of ~ 4 and ~ 14 Se^{2-} ions about an average Ag^+ and Se^{2-} ion, respectively. These numbers are similar to those found for the high-temperature solid, where the Ag^+ ions occupy mainly tetrahedral sites in the Se^{2-} ion lattice. In contrast, the Ag–Ag correlation is very diffuse (again, like the high-temperature solid) with an almost level, gas-like distribution after a minimum separation of about 2 Å. Somewhat arbitrarily, one can define a coordination number of around ten out to a very shallow valley in $g(r)$ at $r = 4$ Å.

Following [1] and the MD results, we ascribe the first peak in the measured $T(r)$ to Ag–Se or Ag–Te correlations and the residual structure out to 4 Å principally to Ag–Ag correlations. The first peak has a well defined Gaussian shape on the low-r side which are used to fit Gaussian functions, taking account of the r-space broadening introduced by the finite cut-off in $S(Q)$ at $Q = 15$ Å. After subtracting the Gaussian peak, the residual is ascribed to Ag–Ag correlations out to $r = 4$ Å. Values for the fitted parameters and calculated coordination numbers [7] based on these assignments are given in table 1.

It is seen from table 1 that there is little change in the position or width of the first coordination peak with either composition or temperature in $Ag_{1-x}Se_x$ alloys. There is a slight drop in the coordination of Se about Ag with temperature and a significant rise with increasing x. All the coordination numbers are less than four, in contrast with the value of 4–4.5 found in the computer simulations. This may be because of peak is falling off

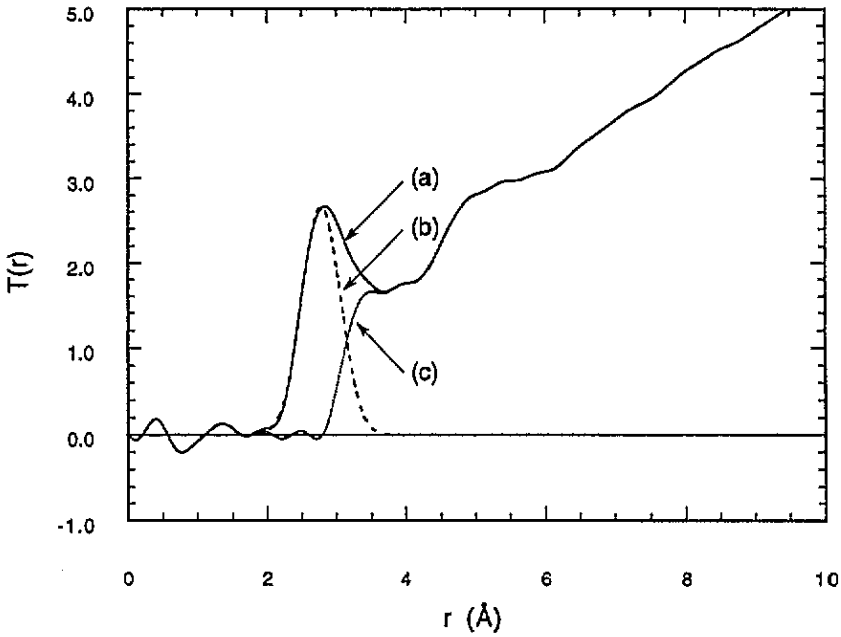

Figure 5. Neutron-weighted average total correlation function of liquid $Ag_{0.67}Se_{0.33}$ (915 °C): (*a*) measured function; (*b*) Gaussian fit to first peak; (*c*) residual.

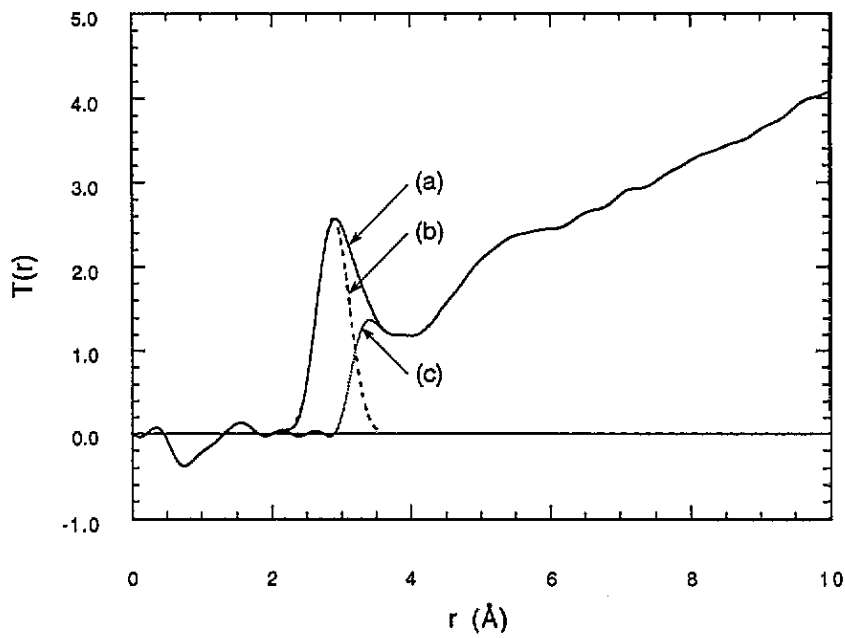

Figure 6. Neutron-weighted average total correlation function of liquid $Ag_{0.67}Te_{0.33}$: (*a*) measured function; (*b*) Gaussian fit to first peak; (*c*) residual.

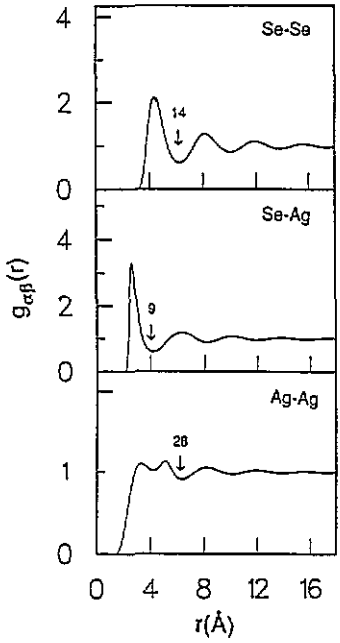

Figure 7. Molecular dynamics partial pair correlation functions of liquid Ag_2Se [11].

more slowly on the high-r side, or may truly reflect a coordination number less than four. Coordination numbers about Ag^+ of around three have been found in fast ion conducting glasses of $GeSe_2$, Ag_2Se_3 and Ag_2Se_3 doped with silver [12–14]. The first coordination shell is further out, and narrower, in $Ag_{0.67}Te_{0.33}$ compared with $Ag_{0.67}Se_{0.33}$.

For the $Ag_{1-x}Se_x$ alloys, Ag–Ag coordination numbers of around ten are obtained from the residuals out to 4 Å, consistent with the MD results. The numbers decrease slightly with increasing temperature and increasing Ag concentration. The Ag–Ag coordination number for $Ag_{0.67}Te_{0.33}$, derived in the same way, is around six.

4. Discussion

The measured structures for $Ag_{1-x}Se_{1-x}$ and $Ag_{0.67}Te_{0.33}$ are consistent with the picture provided by the molecular dynamics computer simulation of Rino *et al* [11]. These indicate a well-defined Ag–Se coordination with the Ag^+ ions in predominantly tetrahedral sites, as in the high-temperature (fast ion conducting) solid. The Ag–Ag correlation is comparatively structureless, consistent with the fast Ag^+ conduction observed experimentally and with the computer simulation. However, a full isotopic substitution study is necessary to determine the precise form for $g_{AgAg}(r)$ and whether there are short metal–metal distances characteristic of liquid semiconductors for which covalent effects are significant.

At the level of the average correlation function, the behaviour of liquid Ag–Se shows no unusual dependence on either concentration or temperature, and the selenium and tellurium alloys show generally similar behaviour. It follows that there is no obvious structural connection with the anomalous concentration dependence of the electrical conductivity in $Ag_{1-x}Se_x$ alloys or with the different behaviour in both electronic and ionic conduction observed in the Ag–Se and Ag–Te systems. A detailed study at the partial correlation function level is required to clarify whether such a connection exists; this work is now in progress.

Acknowledgments

The authors thank the operations staff at the Intense Pulsed Neutron Source for making the experiments possible. This work was supported in part by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contact No W-31-109-ENG-38.

References

[1] Enderby J E and Barnes A C 1990 *Rep. Prog. Phys.* **53** 85
[2] Saboungi M-L, Geertsma W and Price D L 1990 *Ann. Rev. Phys. Chem.* **41** 207
[3] Ohno S, Barnes A C and Enderby J E 1990 *J. Phys.: Condens. Matter* **2** 7707
[4] Ohno S, Barnes A C and Enderby J E 1993 to be published
[5] Endo H, Yao M and Ishida K 1980 *J. Phys. Soc. Japan* **48** 235
[6] Okada T, Kakinuma F and Ohno S 1983 *J. Phys. Soc. Japan* **52** 3526
[7] Susman S, Volin K J, Montague D G and Price D L 1990 *J. Non-Cryst. Solids* **125** 168
[8] Price D L, Misawa M, Susman S, Morrison T I, Shenoy G K and Grimsditch M 1984 *J. Non-Cryst. Solids* **66** 443
[9] Sears V F 1986 *Neutron Scattering (Methods of Experimental Physics 23)* ed K Sköld and D L Price Part A (Orlando, FL: Academic) p 521
[10] Price D L, Moss S C, Reijers R, Saboungi M-L and Susman S 1989 *J. Phys.: Condens. Matter* **1** 1005
[11] Rino J P, Hornos Y M M, Antonio G A, Ebbsjö I, Kalia R K and Vashishta P 1988 *J. Chem. Phys.* **89** 7542
[12] Dejus R J, Susman S, Volin K J, Montague D G and Price D L 1992 *J. Non-Cryst. Solids* **143** 162
[13] Penfold I T and Salmon P S 1990 *Phys. Rev. Lett.* **64** 2164
[14] Benmore C J and Salmon P S 1993 to be published