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A neutron diffraction study on the structure of molten GeSe$_2$: the Ge coordination environment

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Abstract. The first-order difference method of neutron diffraction is applied to molten GeSe$_2$ at 784 ± 3 °C. The results show that Ge correlations contribute to the first sharp diffraction peak of the total structure factor, give a nearest-neighbour distance $\bar{r}_{GeSe} = 2.40 \pm 0.02$ Å and give an average coordination number of 3.7 ± 0.2 selenium atoms around a germanium atom.

The purpose of this paper is to present the first results on the structure of molten GeSe$_2$ using the isotropic substitution method of neutron diffraction. The work is made possible by the recent measurement of the germanium isotope scattering lengths by Koester *et al* (1987) and forms part of a comprehensive study on the structure of liquid and glassy GeSe$_2$ at the partial pair-distribution function level. Information at this level is important for understanding the physical properties of the GeSe$_2$ melt such as its low electrical conductivity σ (≈ 0.3 Ω^{-1} cm^{-1} just above the melting point), positive gradient of σ with respect to temperature (Andreev *et al* 1976) and high viscosity compared to other melts in the Ge–Se binary system (Laugier *et al* 1977, Borisova 1981). Moreover, there is a long-standing controversy regarding the structure of liquid and glassy GeSe$_2$ which reflects two different philosophies concerning the overall subject of bulk-quenched covalently bonded glass structure. On the one hand, does GeSe$_2$ form a chemically ordered continuous random network (COCRN) in which each germanium atom has four selenium nearest neighbours and each selenium atom has two germanium nearest neighbours (Tronc *et al* 1973, Nemanich *et al* 1983)? On the other hand, does the structure comprise fragments of the layers present in the high-temperature crystalline form of GeSe$_2$, which are modified by the formation of Se–Se dimers—the 'outrigger raft' model of Phillips and coworkers (Bridenbaugh *et al* 1979, Phillips 1981)? Furthermore, partial pair-distribution function information is also important for the development of realistic inter-atomic potentials (Iyetomi *et al* 1989, Vashishta *et al* 1989a, 1989b).

In a neutron diffraction study on molten GeSe$_2$ the coherently scattered intensity can be represented by the total structure factor

$$F(k) = c_{Ge}^2 b_{Ge}^2 (S_{GeGe}(k) - 1) + 2c_{Ge} c_{Se} b_{Ge} b_{Se} (S_{GeSe}(k) - 1) + c_{Se}^2 b_{Se}^2 (S_{SeSe}(k) - 1)$$

where c_α and b_α are, respectively, the atomic fraction and coherent scattering length of species α, and k is the scattering vector. The partial structure factors $S_{\alpha\beta}(k)$ are related to the partial pair-distribution functions $g_{\alpha\beta}(r)$ through

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2 r n_0} \int_0^\infty k(S_{\alpha\beta}(k) - 1) \sin(kr) \, dk$$

where n_0 (= 0.03114 Å^{-3}, Ruska and Thum 1976) is the total number density of the sample. Hence Fourier transformation of $F(k)$ gives

$$G(r) = c_{Ge}^2 b_{Ge}^2 (g_{GeGe}(r) - 1) + 2c_{Ge} c_{Se} b_{Ge} b_{Se} (g_{GeSe}(r) - 1) + c_{Se}^2 b_{Se}^2 (g_{SeSe}(r) - 1).$$

If diffraction experiments are made on two samples that are identical in every respect, except that the germanium is enriched with ^{70}Ge, the difference between the resultant $F(k)$ functions gives the first-order difference function $\Delta_{Ge}(k)$. On transforming to real-space and on substituting for the c_α and b_α, $\Delta_{Ge}(k)$ becomes

$$\Delta G_{Ge}(r)/b = (0.035 \pm 0.002)(g_{GeGe}(r) - 1) + (0.062 \pm 0.004)(g_{GeSe}(r) - 1).$$

The complexity of correlations associated with the total $G(r)$ functions is reduced since $g_{SeSe}(r)$ is eliminated. The average number of species α in the range $r_1 \leqslant r \leqslant r_2$ around an atom of species β placed at the origin of coordinates is obtained from the expression

$$\bar{n}_\alpha^\beta = 4\pi c_\alpha n_0 \int_{r_1}^{r_2} g_{\alpha\beta}(r) \, r^2 \, dr.$$

^{N}Ge^{N}Se$_2$ and ^{70}Ge^{N}Se$_2$ samples, where N denotes the natural isotopic composition, were made prior to the diffraction experiments by mixing elemental ^{N}Ge (99.9999%, Aldrich Gold Label) or ^{70}Ge (96.75% enrichment, Oak Ridge) with ^{N}Se (99.9999%, Aldrich Gold Label) in silica ampoules. The sample filled ampoules were evacuated to a pressure of ~10^{-5} Torr for 12 h, sealed and slowly heated in a rocking furnace to a temperature of 1050 °C where they were held for $\approx$100 h. The samples were then cooled slowly to room temperature and transferred to annealed (at 950 °C), evacuated, sealed and matched cylindrical silica tubes of internal radius 2.8 mm and wall thickness 0.4 mm ready for the diffraction experiments. The latter were made using the D4B instrument at the Institut Laue–Langevin, Grenoble. The instrument employed two 64-cell multi-detectors and an incident wavelength of 0.7038 Å.

The complete diffraction experiment comprised the measurement of an empty cylindrical vanadium heater at room temperature; the samples contained in silica cells in the heater at 784 ± 3 °C (the melting point of GeSe$_2$ is at 742 ± 2 °C, Ipser *et al* 1982); an empty silica cell in the heater at 784 °C; a vanadium rod of radius 3 mm for normalisation purposes; a cadmium bar of radius 3 mm for the background correction at low angles; and nothing placed at the sample position. The data analysis followed along the lines described by Salmon (1988) with the low angle background correction being made after Bertagnolli *et al* (1976).

$\Delta_{Ge}(k)$ is illustrated in figure 1 and shows that there is a significant contrast between the ^{N}Ge^{N}Se$_2$ and ^{70}Ge^{N}Se$_2$ $F(k)$ functions. Of particular note is the peak at 0.98 ± 0.1 Å^{-1} occurring at the position of the first sharp diffraction peak (FSDP) in the $F(k)$ functions (Uemura *et al* 1978, Susman *et al* 1988). Clearly this feature is associated with germanium pair-correlation functions, an observation that was also made for glassy GeSe$_2$ using the anomalous x-ray scattering method (Fuoss *et al* 1981). This indicates structural similarities between the liquid and glassy states.

$\Delta G_{Ge}(r)$ is given in figure 2 and was obtained both by direct Fourier transformation of $\Delta_{Ge}(k)$ and by a maximum entropy method (Soper 1989). The first peak located at 2.40 ± 0.02 Å can be associated with Ge–Se correlations on the basis of a comparison
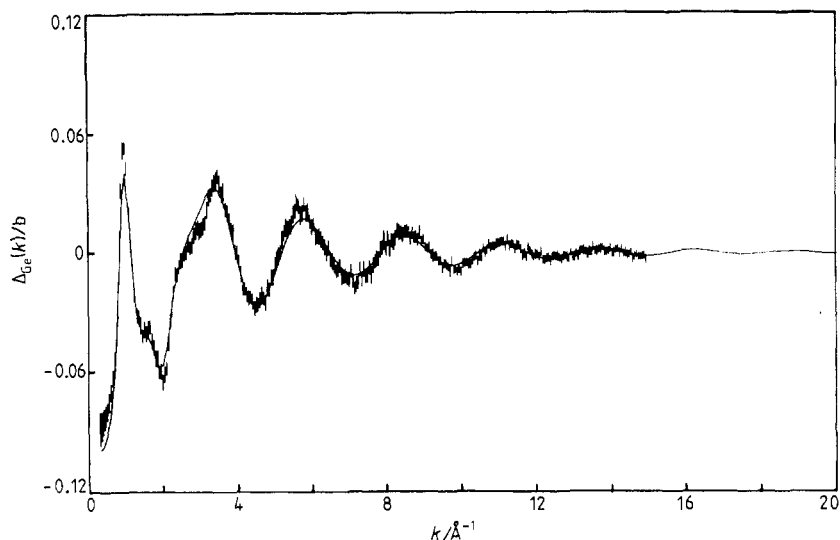
Figure 1. The first-order difference function $\Delta_{Ge}(k)$ for molten $GeSe_2$ at 784 °C. The bars represent the errors on the experimental data and the full curve is the Fourier transform of the $\Delta G_{Ge}(r)$ given by the full curve in figure 2.
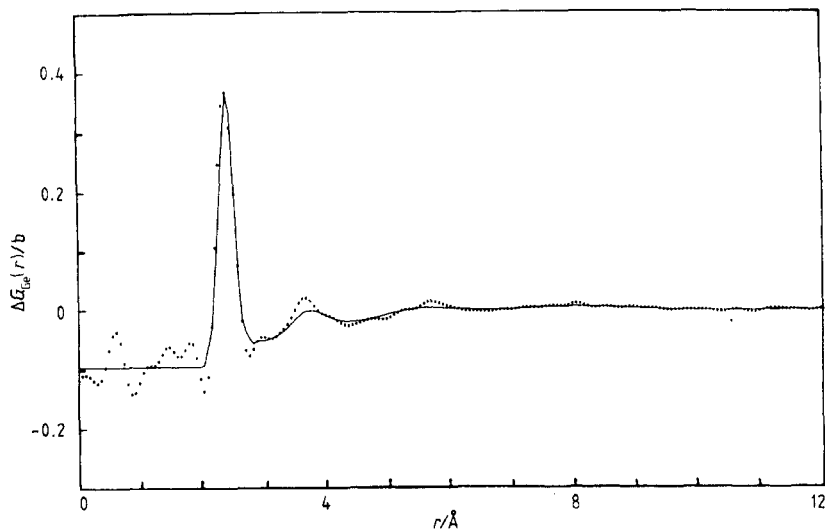
Figure 2. $\Delta G_{Ge}(r)$ for molten $GeSe_2$ at 784 °C. The points give the results of Fourier transforming the $\Delta_{Ge}(k)$ represented by the bars in figure 1 and the line gives the maximum entropy solution.

with the crystal structure of the high temperature $GeSe_2$ phase (Dittmar and Schäfer 1976). With this assignment a coordination number of $\bar{n}_{Se}^{Ge} = 3.7 \pm 0.2$ is obtained by integrating $\Delta G_{Ge}(r)$ over the range $2.09 \text{ Å} \leqslant r \leqslant 2.82 \text{ Å}$. A similarly defined feature, located at 2.38 ± 0.02 Å or 2.37 ± 0.02 Å, also occurs in the $G(r)$ functions obtained for

the ^{N}Ge^{N}Se$_2$ and ^{70}Ge^{N}Se$_2$ $G(r)$ samples. Its integration over the same r-range gives a coordination number of $\bar{n}_{Se}^{Ge} = 3.8 \pm 0.2$ i.e. the presence of Se–Se correlations in the $G(r)$ functions does not substantially alter the results obtained from $\Delta G_{Ge}(r)$ for the first peak region. The data are therefore consistent with an essentially fourfold coordination of Ge by Se and there is no evidence in support of strong Ge–Ge or Se–Se correlations in the first peak region. However, their presence cannot, on the basis of the present data, be entirely ruled out. For example, $\Delta G_{Ge}(r) > \Delta G_{Ge}(0)$ at the minimum after the first peak in figure 2 which implies the existence of further Ge–Se and/or Ge–Ge correlations at this distance.

$\Delta G_{Ge}(r)$ is further characterised by pronounced intermediate range order (IRO) extending to ≈ 8 Å, in accord with the presence of a FSDP in the $\Delta_{Ge}(k)$ of figure 1. A detailed analysis of the correlations within this region awaits a full partial pair-distribution function analysis.

In summary, the present data represents a first step in understanding the structure of liquid and glassy GeSe$_2$ at the $g_{\alpha\beta}(r)$ level through neutron diffraction experiments. The data will provide a test on the accuracy to which the $S_{\alpha\beta}(k)$ can be obtained from a *full* partial structure factor analysis. This follows since the construction of $\Delta_{Ge}(k)$ does not involve any scaling of the total $F(k)$ functions and hence systematic errors in the $F(k)$ that result, for example, from the container and heater correction procedures are reduced or essentially eliminated when $\Delta_{Ge}(k)$ is formed (Soper *et al* 1977). For the present samples this statement holds true since their total scattering and absorption cross-sections are similar and hence the attenuation corrections on both of the $F(k)$ functions are comparable. The low electrical conductivity of the liquid is consistent with a strong covalent character to the Ge–Se bond. The correlations giving rise to the IRO will have a bearing on the high viscosity and glass forming ability of the GeSe$_2$ melt.

Acknowledgments

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