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## LETTER TO THE EDITOR

# Integral-equation theory of the origin of medium-range order in molten and vitreous chalcogenides

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**Abstract.** The origin of medium-range order in molten and vitreous  $\text{GeSe}_2$ , signified by the first sharp diffraction peak (FSDP), is examined in terms of interatomic potentials using the integral-equation method. A systematic study of steric and charge-transfer effects shows that the FSDP originates from a combination of the excluded-volume effect and local charge neutrality. These effects are also found to be responsible for a network structure consisting of  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedra. The anomalous temperature dependence of the FSDP can be ascribed entirely to an increase in the density of the system on cooling.

The first sharp diffraction peak (FSDP) observed in diffraction experiments (Uemura *et al* 1975, 1978, Fuoss *et al* 1981, Nemanich *et al* 1983, Feltz *et al* 1985, Fuoss and Fischer-Colbrie 1988, Susman *et al* 1988) on molten and glassy  $\text{GeSe}_2$  has received a great deal of attention in recent years. Yet there is no concrete understanding of the correlations that give rise to this peak. The location ( $\approx 1 \text{ \AA}^{-1}$ ) of the FSDP suggests that it is due to medium-range correlations extending beyond the nearest-neighbour distances. This feature has also been observed in other chalcogenide glasses such as  $\text{SiO}_2$ ,  $\text{GeS}_2$ ,  $\text{SiSe}_2$ , and  $\text{As}_2\text{Se}_3$  (Moss and Price 1985). What is puzzling is that the height of the FSDP in the glassy state has been observed to increase on heating. This is a reversible phenomenon common to many of the systems where this has been investigated.

In this Letter we examine the origin of medium-range order associated with the FSDP. Phillips (1981) has proposed a raft model to describe the atomic-scale structure of amorphous  $\text{GeSe}_2$ . In his model the interlayer correlations, similar to those in the crystalline  $\text{GeSe}_2$ , are responsible for the FSDP. Moss and Price (1985), on the other hand, have shown that the random packing of  $\text{Ge}(\text{Se}_{1/2})_4$  structural units explains all the features in the static structure factor including the FSDP. Neither model is, however, satisfactory since it is not clear which partial correlations give rise to the FSDP. Furthermore, recent x-ray scattering measurement (Fuoss and Fischer-Colbrie 1988) on thin films of amorphous  $\text{GeSe}_2$  gave no evidence of a low-dimensional structure as proposed by Phillips.

In a recent molecular dynamics (MD) study of molten and glassy  $\text{GeSe}_2$  (Vashishta *et al* 1988a,b), the structural and dynamical properties have been examined using two- and three-body covalent interactions. These simulations reveal the existence of  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedra and can explain most of the experimental results including the anomalous temperature dependence of the FSDP.

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The MD calculations suggest that steric repulsion and local charge neutrality effects are mainly responsible for the medium-range order manifested as the FSDP. The purpose of this Letter is to examine these two effects in detail and understand the origin of the FSDP at the atomistic level using the integral-equation approach. The anomalous behaviour of the FSDP is also studied by properly taking into account the effect of the increase in the density on cooling.

To study the steric and charge transfer effects systematically, we consider the following three distinctive models for GeSe<sub>2</sub>:

- (i) mixture of neutral hard spheres,
- (ii) mixture of charged hard spheres,
- (iii) the effective potential for GeSe<sub>2</sub> (Vashishta *et al* 1988b).

The essential features of the two effects are incorporated in model (ii). In model (iii) the effective potential between atoms  $\mu$  and  $\nu$  consists of Coulomb interaction, charge-dipole interaction, and steric repulsion:

$$\varphi_{\mu\nu}(r) = Q_{\mu}Q_{\nu}/r - [\frac{1}{2}(\alpha_{\mu}Q_{\nu}^2 + \alpha_{\nu}Q_{\mu}^2)/r^4] \exp(-r/r_{4s}) + H_{\mu\nu}/r^{\eta_{\mu\nu}}. \quad (1)$$

Here Ge and Se atoms are characterised by effective charges  $4Q$  and  $-2Q$ , respectively;  $Q$  is chosen to be  $0.33e$ . The other parameters in the effective potential are listed below:

$$\begin{array}{lll} \alpha_{\text{Ge}} = 0 & \alpha_{\text{Se}} = 7.0 & r_{4s} = 4.43 \\ H_{\text{Ge-Ge}} = 1.114 & H_{\text{Ge-Se}} = 146.1 & H_{\text{Se-Se}} = 284.1 \\ \eta_{\text{Ge-Ge}} = 11 & \eta_{\text{Ge-Se}} = 9 & \eta_{\text{Se-Se}} = 7 \end{array} \quad (2)$$

where the length and energy are measured in units of  $\text{\AA}$  and  $e^2/\text{\AA}$  ( $=14.40$  eV), respectively. For a discussion of these parameters, see Vashishta *et al* (1988b).

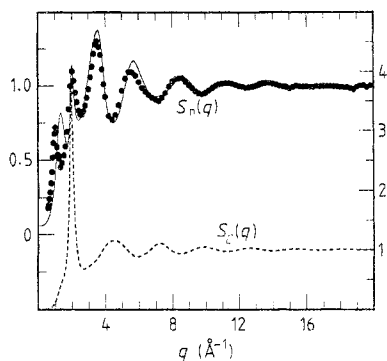
The form of the potential in model (ii) is given by

$$\varphi_{\mu\nu}(r) \begin{cases} \infty & \text{for } r < \sigma_{\mu} + \sigma_{\nu} \\ Q_{\mu}Q_{\nu}/r & \text{for } r > \sigma_{\mu} + \sigma_{\nu} \end{cases} \quad (3)$$

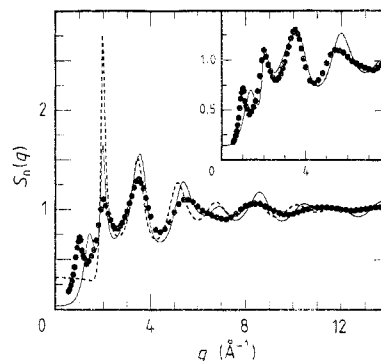
where the effective charges  $Q_{\mu}$  are the same as in model (iii). The ionic radii  $\sigma_{\mu}$  are determined from the bond lengths of Ge–Se ( $2.35$   $\text{\AA}$ ) and Se–Se ( $3.75$   $\text{\AA}$ ) in the glassy (Uemura *et al* 1978, Nemanich *et al* 1983) and crystalline (Dittmar and Schäfer 1976) states:  $\sigma_{\text{Ge}} = 0.475$   $\text{\AA}$  and  $\sigma_{\text{Se}} = 1.875$   $\text{\AA}$ . The potential used in model (i) corresponds to setting  $Q_{\mu} = 0$  in (3).

In the integral-equation approach the correlation functions can be calculated much more easily than with the MD method. Using the Percus–Yevick (PY) scheme (Percus and Yevick 1958) for model (i) and the hypernetted-chain (HNC) scheme (van Leeuwen *et al* 1959, Morita 1960) for models (ii) and (iii), we investigate the structure of disordered GeSe<sub>2</sub> from correlation functions. The HNC method accurately accounts for the long-range nature of the Coulombic interaction (Iyetomi 1984). Analytic solutions (Lebowitz 1964, Ashcroft and Langreth 1967) are available for the PY equation, while the HNC equation is solved numerically using Gillan's method (Gillan 1979, Abernethy and Gillan 1980).

We now consider medium-range order and charge–charge correlation. Figure 1 shows the neutron scattering structure factor  $S_n(q)$  and the charge–charge structure factor  $S_C(q)$  obtained with the effective potential (1) at the experimental density  $\rho = 3.114 \times 10^{22}$   $\text{cm}^{-3}$  and at  $T = 1071$  K, which is just above the melting point ( $1015 \pm 2$  K;



**Figure 1.** Neutron scattering structure factor  $S_n(q)$  and charge-charge structure factor  $S_c(q)$  in molten  $\text{GeSe}_2$ . The full and broken curves represent the HNC results for  $S_n(q)$  and  $S_c(q)$  obtained with the potential (1) at  $T = 1071$  K; the full circles are neutron diffraction results (Susman *et al* 1988) at  $T = 1084$  K. The left-hand and right-hand ordinates are the scales for  $S_n(q)$  and  $S_c(q)$ , respectively.



**Figure 2.** Neutron scattering structure factor  $S_n(q)$  for three hard-sphere models at the same thermodynamic state as in figure 1. The broken and full curves in the main frame are the results for the neutral and charged hard-sphere models, (i) and (ii), with the total packing fraction  $\eta = 0.578$ . The full curve in the inset refers to the results for the modified charged hard-sphere model with  $\sigma_{\text{se}} = 1.7$  Å. The full circles are the experimental data (Susman *et al* 1988) at  $T = 1084$  K.

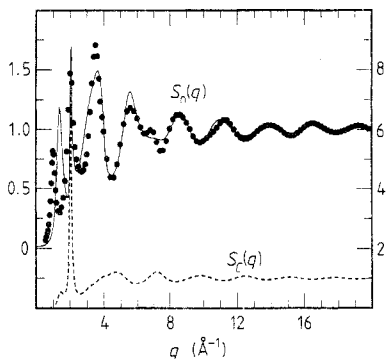
see Ipser *et al* 1982). The results of the HNC calculation are in good agreement with the experimental results (Susman *et al* 1988). The only discrepancy is in the position of the first peak; the experimental peak position is  $1 \text{ \AA}^{-1}$  whereas the calculated position is  $1.3 \text{ \AA}^{-1}$ . The reason for this discrepancy will be discussed later.

Figure 1 shows that the FSDP is a prominent feature in  $S_n(q)$  and not in  $S_c(q)$ . Clearly the FSDP is a feature associated with correlations whose spatial extent is determined by local charge neutrality. This is further supported by the comparison of the  $S_n(q)$  for the charged and neutral hard-sphere models as displayed in figure 2. These and the  $S_n(q)$  in figure 1 establish that the FSDP does not appear in model (i) even though the 'second' and 'third' peaks representing the short-range correlations already exist at their correct positions in that model.

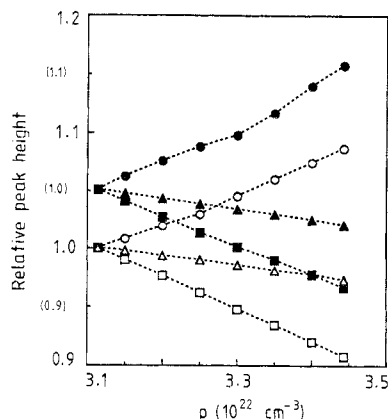
The coordination number for the Ge atom is calculated by integrating the pair-distribution function  $g_{\text{Ge-Se}}(r)$ . In models (i), (ii) and (iii) the coordination numbers are 5.56, 3.64 and 4.42, respectively. Together with the Ge-Se and Se-Se bond lengths, these coordinations indicate the presence of  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedral units in models (ii) and (iii). We have examined Ge-Ge correlations in model (i) and we find that the corresponding coordination number is 1. This suggests that without the Coulombic interaction Ge atoms form dimers. The size of these dimers is only  $2.8 \text{ \AA}$ .

The following picture for the medium-range order associated with the FSDP emerges from the above results. A combination of steric and Coulombic forces gives rise to  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedral units where the charge of a fourfold-coordinated Ge atom is locally compensated by the two-fold-coordinated Se atoms. These neutral units form a network and the correlations over distances characterised by the local charge-neutrality result in the FSDP. The appearance of the FSDP thus does not depend on the minor details in the potential.

Coming back to the discrepancy between the HNC and experimental results, we performed a calculation in model (ii) reducing the Se-Se contact distance from  $3.75 \text{ \AA}$



**Figure 3.** Neutron scattering structure factor  $S_n(q)$  and charge-charge structure factor  $S_c(q)$  in vitreous  $\text{GeSe}_2$ . The full and broken curves represent the HNC results for  $S_n(q)$  and  $S_c(q)$  obtained with the potential (1) at  $T = 300$  K; the full circles are neutron diffraction results (Susman *et al* 1988) at  $T = 10$  K. The scales for  $S_n(q)$  and  $S_c(q)$  are on the left-hand and right-hand sides, respectively.



**Figure 4.** The relative height of the first three peaks in  $S_n(q)$  based on model (iii) as a function of density at fixed temperatures. The height of each peak is normalised to the value at the liquid density. The squares, circles and triangles refer to the values for the first, second and third peaks, respectively. The open and full symbols denote the results at  $T = 1071$  K and  $623$  K, respectively.

to  $3.4 \text{ \AA}$ . This improved the overall agreement with experimental results (this is understandable because the bond length between the Se atoms is determined by a combination of the steric and Coulombic interactions), but the position of the FSDP remains unchanged, as is evident from the inset in figure 2. It therefore appears that the discrepancy is due to residual covalent effects in the form of three-body and higher-order interactions. In the MD simulations with three-body interactions (Vashishta *et al* 1988a), the position of the FSDP is indeed the same ( $1 \text{ \AA}^{-1}$ ) as in diffraction experiments.

The HNC solution for model (iii) was extended much below the melting temperature to  $T = 300$  K. Figure 3 compares the HNC result for vitreous  $\text{GeSe}_2$  at  $T = 300$  K with the diffraction data. The calculated results are in good agreement with the experiment; even the splitting of the fourth peak is found in the HNC calculations. Figure 3 also shows that the FSDP in  $S_c(q)$  is still a small shoulder at such low temperatures.

We now consider the anomalous temperature dependence of the first sharp diffraction peak. In diffraction experiments the change in temperature is accompanied by a change in the density of the system. The MD calculations reveal that the anomalous decrease in the height of the FSDP on cooling is due to an enhancement of frustration in the packing of tetrahedra by the increased density. To see the effect of change in density alone, we show in figure 4 the heights of the first three peaks in  $S_n(q)$  as a function of density in model (iii) at two fixed temperatures. The density dependence of each peak shows a different trend: the height of the FSDP decreases with the increased density whereas the second peak behaves in exactly the opposite manner. The change in the height of the third peak is much less. This result is consistent with the recent x-ray diffraction experiment (Tanaka 1987) on amorphous  $\text{GeS}_2$  under hydrostatic pressure where the increase in pressure (the density increases accordingly) is observed to depress the FSDP. In the HNC calculations, the heights of these peaks decrease, as expected, with an increase in the temperature at a fixed density and the effect of temperature is stronger than that of the density.

In conclusion, we have identified the nature of the medium-range correlations that give rise to the FSDP and have also examined its anomalous temperature dependence in GeSe<sub>2</sub> using the integral-equation method. The HNC calculations reveal that the medium-range order is closely associated with distances over which local charge neutrality prevails.

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