Atomic Correlations and Intermediate-Range Order in Molten and Amorphous $GeSe_2$

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Interatomic potentials consisting of two- and three-body covalent forces are proposed for $GeSe_2$. Using these in molecular-dynamics simulations, the nature of intermediate-range order is investigated. All the features in $S(q)$, including the first sharp diffraction peak (FSDP), are in agreement with experiments. The FSDP arises from Ge-Ge and Ge-Se correlations between 4–8 Å and the anomalous decrease in its height on cooling is due to frustration enhanced by increased density. The statistics of edge-sharing tetrahedra and rings are also discussed.

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The structure of binary chalcogenide glasses has been widely studied by neutron and x-ray diffraction measurements.[1-9] These experiments[10] reveal many similarities in the static factor $S(q)$ when expressed in terms of the dimensionless quantity $Q=qr_0$, where r_0 is the bond length. The most celebrated structural feature in these glasses is the first sharp diffraction peak (FSDP) observed between 1.0 and 1.5 $Å^{-1}$, which is believed to be a signature of intermediate-range correlations. Although the chemical constituents and topologies of these glasses are widely different, the dimensionless quantity Q for the FSDP is nearly constant (2.3) in all of these systems.[10]

In amorphous $GeSe_2$ the FSDP is observed at 1.0 $Å^{-1}$. Neutron and x-ray scattering experiments reveal that this peak persists in the molten state and in fact its height at 1100 K is the same as in the low-temperature glass.[1,5] The other peaks in $S_n(q)$, as expected, have smaller amplitudes in the molten state than in the glass. So the key questions are (i) what is the nature of the correlations that give rise to the FSDP at 1.0 $Å^{-1}$, and (ii) why are these intermediate-range correlations so strong in the molten state? Related to these structural issues is the question of the connectivity of the glassy network: In other words, what is the population of edge and corner-sharing $Ge(Se_4)_{1/2}$ tetrahedra and what is the statistics of rings?

We have investigated these issues using the molecular-dynamics (MD) method with interparticle potentials, which are the sums of two-body (V_2) (Ref. 11) and three-body (V_3) (Ref. 12) terms,

$$V=\sum_{i<j} V_2(r_{ij})+\sum_{i<j<k} V_3(\mathbf{r}_{ij},\mathbf{r}_{jk},\mathbf{r}_{ik}) , \tag{1}$$

$$V_2=\frac{H_{ij}}{r^{\eta_{ij}}}+\frac{Z_iZ_j}{r}-\frac{\frac{1}{2}(\alpha_iZ_j^2+\alpha_jZ_i^2)}{r^4}e^{-r/r_{4s}} , \tag{2}$$

$$V_3=B_{jik}f(r_{ij},r_{ik})[\cos\theta_{jik}-\cos\bar{\theta}_{jik}]^2 , \tag{3}$$

where θ_{jik} is the angle between $\mathbf{r}_{ij}$ and $\mathbf{r}_{ik}$; Z_i and α_i are the effective charge and the electronic polarizability of the ith particle. We take $\alpha_{Ge}=0$, $\alpha_{Se}=7$ $Å^3$, $r_{4s}=4.43$ Å, $\eta_{Ge\text{-}Ge}=11$, $\eta_{Ge\text{-}Se}=9$, and $\eta_{Se\text{-}Se}=7$. For Ge and Se the effective charges are $+4Z$ and $-2Z$, respectively, where $Z=0.33e$. Out of six possible three-body interactions, the two involving the Se-Ge-Se and Ge-Se-Ge angles are the most important. For these we choose $\bar{\theta}=109.4°$ and 94°, respectively, and $B_{Se\text{-}Ge\text{-}Se}/B_{Ge\text{-}Se\text{-}Ge}=\frac{1}{4}$. The range of three-body interactions is taken to be 3 Å. The strengths of the steric repulsion H_{ij} are determined from the condition of zero pressure in the molten state. The calculated melting temperature is close to the experimental value (1020 K).

Molecular-dynamics calculations are performed on a system of 648 particles in a cubic cell with periodic boundary conditions. To assess finite-size effects, we have also simulated a system of 5184 particles in a cell whose edge is 55.02 Å in the liquid and 53.75 Å in the glass corresponding to experiment number densities $\rho_L=3.114\times10^{22}$ and $\rho_G=3.338\times10^{22}$ cm^{-3}, respectively. Starting with an initial configuration in which the particles are on a cubic lattice, we heat the system gradually to 2000 K and equilibrate for a long time so that it loses memory of the initial lattice configuration. The liquid at 2000 K is cooled to 1500 K and then to 1100 K. Each of these molten states is equilibrated for 30000 MD time steps. At 1100 K the self-diffusion constant is small ($\sim10^{-6}$ cm^2/sec), indicating that the system is close to freezing. This liquid is quenched to form glasses at 900, 600, 300, and 0 K. After quenching, each system is relaxed for 30000 time steps. Subsequently the partial pair-distribution functions, static structure factors, bond-angle distributions, and the ring statistics are calculated using MD trajectories over 60000 time steps.

From partial pair-distribution functions $g_{\alpha\beta}(r)$ in Fig. 1, we find that Ge-Se and Se-Se bond lengths are 2.30 and 3.75 Å and the corresponding full widths at half maximum are 0.15 and 0.50 Å. The nearest-neighbor

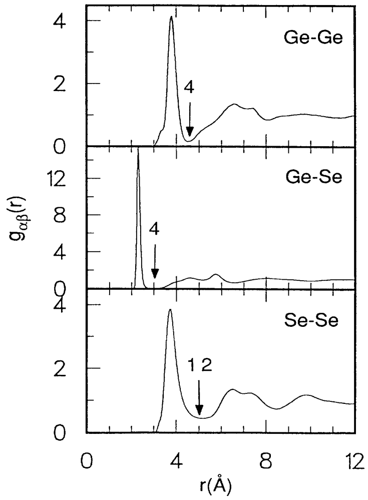

FIG. 1. Pair-distribution functions in a-GeSe$_2$ at 300 K. Arrows indicate coordination numbers.

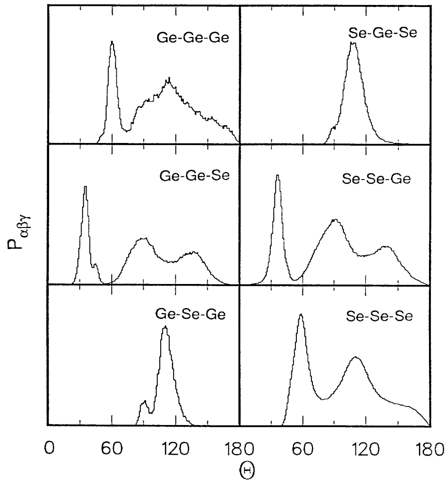

FIG. 2. Bond-angle distributions in a-GeSe$_2$ at 300 K.

(nn) Ge-Se and Se-Se distances are slightly larger in the molten state. Diffraction experiments[5] in a-GeSe$_2$ indicate that Ge-Se and Se-Se bond lengths are 2.37 and 3.80 Å, respectively. From $g_{\text{Ge-Se}}(r)$ we also find that each Ge has four Se nn and that each Se has two Ge nn.

Let us further examine the short-range order through bond-angle distributions $P_{\alpha\beta\gamma}(\theta)$ shown in Fig. 2. The Se-Ge-Se distribution has a peak at 106°, Se-Se-Ge at 36°, and Se-Se-Se at 59°. Combined with the nn coordinations of Ge and Se, these peaks indicate that the system consists of slightly distorted Ge(Se$_4$)$_{1/2}$ tetrahedra. These tetrahedra are also present in the molten state, although with somewhat larger distortions.

The connectivity of Ge(Se$_4$)$_{1/2}$ tetrahedra can be ascertained through the statistics of n-fold rings[13] and the remaining bond-angle distributions. In Fig. 2 the distribution for Ge-Se-Ge angles displays a peak around 111° and also a smaller peak around 88°. From atomic configurations we determine that the latter arises entirely from Ge-Se-Ge angles in edge-sharing tetrahedra (twofold rings). In the glass, 32% of the tetrahedra are edge bonded in contrast to 50% in the crystalline phase. The statistics of rings in the crystalline state[14] and in the glass for 10 configurations are listed in Table I. In the crystal, only twofold, threefold, eightfold, and ninefold rings are present whereas in the glass we find all rings from twofold to twelvefold and a large number of them are threefold, sixfold, sevenfold, and eightfold. The number of eightfold rings containing edge-sharing tetrahedra (40) is most significantly reduced compared to the crystal (432).

Figure 3 shows the experimental and MD results for the neutron static structure factor $S_n(q)$ in the molten and glassy states. In both phases the calculated peak positions and peak heights are in good agreement with the experiments.[5] From the MD results for partial static structure factors in Fig. 4, we find that the first peak in $S_n(q)$ arises from Ge-Ge and Ge-Se correlations. X-ray experiments on GeTe$_2$-GeSe$_2$ glasses reveal that the FSDP grows as Te is replaced by the weaker scatterer Se so as to enhance the Ge contributions.[15] Differential anomalous x-ray scattering experiment also indicates

TABLE I. Distribution of rings in crystalline and glassy GeSe$_2$ for 216 Ge.

Ring size	2	3	4	5	6	7	8	9	10	11	12
Crystal											
Ge[a]	0	216	0	0	0	0	216	216	0	0	0
Ge[b]	108	108	0	0	0	0	432	0	0	0	0
Total rings/Ge	0.50	1.50	0	0	0	0	3.00	1.00	0	0	0
Glass											
Ge[a]	0	201	84	80	142	159	120	75	23	7	1
Ge[b]	70	57	40	38	47	55	40	22	10	4	0
Total rings/Ge	0.324	1.195	0.574	0.546	0.875	0.991	0.741	0.449	0.153	0.051	0.005

[a] Atoms which share corners only.

[b] Atoms which share edges.

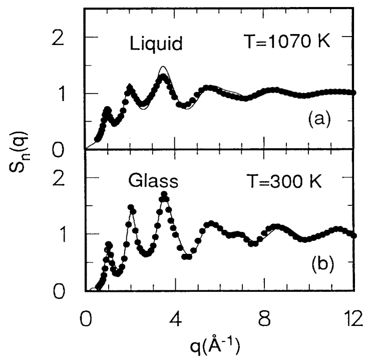

FIG. 3. Neutron static structure factor in glassy and molten $GeSe_2$. Continuous curve is MD and solid circles are from neutron experiment (Ref. 5).

that Ge correlations are responsible for the first peak.[4] Figure 4 also reveals that the second peak in $S_n(q)$ is mainly due to Se-Se correlations since the anticorrelation in Ge-Se is canceled by Ge-Ge and Se-Se correlations. On the other hand, all three correlations contribute to the third peak in $S_n(q)$. These conclusions are supported by anomalous x-ray scattering experiments.[4]

To determine the range of correlations responsible for the FSDP, we have performed calculations in which the correlations are truncated at various distances r_m. This is done by setting $g_{\alpha\beta}(r)=1$ beyond r_m and then the partial and total static structure factors are calculated. For $r_m > 8$ Å the height of the FSDP is affected only slightly, but for 4 Å $< r_m <$ 8 Å it almost disappears. This establishes that intermediate-range correlations between 4 and 8 Å are responsible for the FSDP.

Finally let us discuss the anomalous thermal behavior of the FSDP.[16] As Fig. 3 shows, in both experiments and MD simulation the height of the FSDP is nearly the same in the liquid (1100 K) and in the glass (300 K). In contrast, the other peaks in $S_n(q)$ show the expected broadening and a decrease in their heights on heating. To understand this behavior, let us remember that cooling from 1100 to 300 K results in a 7% increase in the density of the system ($\rho_G/\rho_L=1.07$). To illustrate the effect of temperature alone, we form a glass at 300 K from the melt at 1100 K while keeping the density fixed at ρ_L. The structure factors of this lower-density glass [Fig. 5(b)] and that in the molten state [Fig. 3(a)] show that the heights of all the peaks in $S_n(q)$ increase on cooling. On the other hand, Fig. 5 indicates that the FSDP is higher in the low-density glass (ρ_L) than in the glass with the correct experimental density ρ_G. One possible reason for this behavior may be that an increase in the density enhances the frustration associated with the packing of $Ge(Se_4)_{1/2}$ tetrahedra. Since the length scale for this packing is beyond 4 Å, it is the FSDP that is affected more than the other peaks in the structure factor. The decrease in the height of the FSDP due to larger density offsets the increase resulting from cooling alone. As a result, the height of the FSDP in the molten state is nearly the same as in the glass at 300 K. Figure 5 also shows that the heights of the second and third peaks are lower in the lower-density glass (ρ_L) than in the glass with density ρ_G. Thus, both the decrease in the temperature and the accompanying increase in the density tend to increase the heights of these peaks.

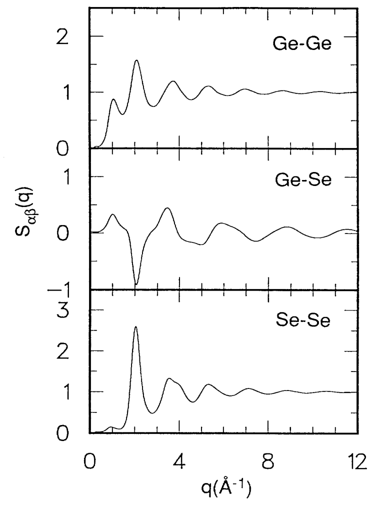

FIG. 4. Partial structure factor in a-$GeSe_2$ at 300 K.

In conclusion, the proposed interaction potential satisfactorily describes the structural features associated with the short- and intermediate-range order including anomalous temperature dependence of the FSDP in $GeSe_2$. Within this framework it is also possible to study the issues related to rigidity percolation and mechanical properties of binary covalent glasses.[7,8]

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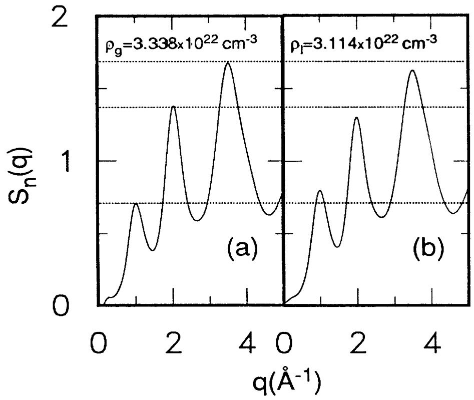

FIG. 5. $S_n(q)$ for a-$GeSe_2$ at 300 K (a) at the glass density ρ_G and (b) at the liquid density ρ_L.

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