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Structure of liquid Ge_xSe_{1-x} at the stiffness threshold composition

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We investigate by first-principles molecular dynamics the structural properties of liquid $GeSe_4$, i.e., Ge_xSe_{1-x} at $x=0.2$. This composition is very close to the so-called stiffness threshold composition, at which dramatic changes in a series of experimental properties occur. The calculated total neutron structure factor is in very good agreement with experiment. The results show that liquid $GeSe_4$ is a good prototype of a chemically ordered network. It consists of $GeSe_4$ tetrahedra that are connected by either shared Se atoms or Se chains. [S0163-1829(98)52446-0]

Chalcogenide glasses are materials that easily form disordered networks. A widely studied member of this group is Ge_xSe_{1-x}, which easily forms a glass for $x<0.43$.[1] Within this composition range the network structure can be envisaged as follows: for $x=0$ the network consists of Se chains and rings; increasing x results in crosslinking these structures by Ge atoms, which enlarges the rigidity of the network. The number of constraints due to bonds in a network can be counted as a function of composition. A critical composition, x_c, is found when the number of constraints is equal to the number of degrees of freedom in the network.[2] This critical composition constitutes a ''stiffness'' threshold in a mean field sense between an underconstrained, floppy network, and an overconstrained, rigid network.[3] For Ge_xSe_{1-x} this threshold is given by $x_c=0.20$, i.e., $GeSe_4$.[2,3]

A number of experiments have been carried out to confirm the existence of this threshold. Extrema of various physical properties at the threshold have been found: a maximum in the density;[4] a maximum in the transition pressure at which the semiconducting network changes into a metallic crystalline phase;[5] an extremum in the Mössbauer intensity ratio of two different Se sites;[6] a jump in the frequency of the

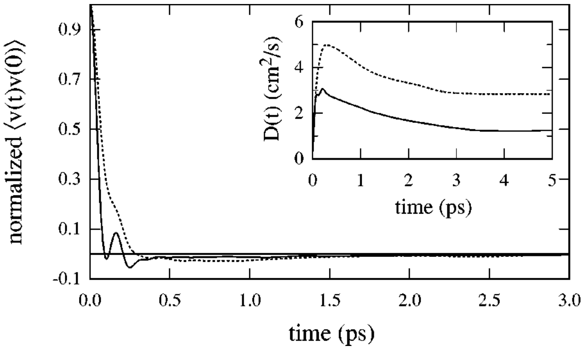

FIG. 1. Single particle velocity-velocity self-correlation function $\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$ of Ge (full line) and Se (dotted line), normalized to the value taken at $t=0$. The inset shows $D(t)$, the time integral of $\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$ for Ge (full line) and Se (dotted line).

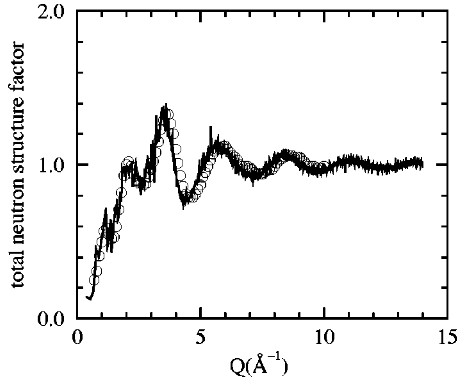

FIG. 2. Calculated total neutron structure factor for liquid $GeSe_4$ (solid line) compared to the experimental results of Ref. 22 (circles).

A_1 mode in the Raman spectrum.[7,8] Experiments indicate that the microscopic structure at the threshold is that of a chemically ordered network.[9] Further knowledge about the microscopic structure is currently based on phenomenological models.[10,11] A detailed determination of the structure at the stiffness threshold composition is an essential prerequisite to understanding the onset of rigidity. Here, we acquire a precise knowledge of the atomic structure of disordered Ge_xSe_{1-x} systems at the stiffness threshold by performing first-principle molecular dynamics simulations of liquid $GeSe_4$. In particular, we address the issue whether $GeSe_4$ is a chemically ordered network.

The calculations are performed with the scheme described in Ref. 12. Ge and Se are modeled by norm conserving, separable pseudopotentials with s and p nonlocal projectors.[13,14] A generalized gradient approximation for the exchange-correlation energy is used.[15] The wave functions are expanded at the Γ point in a plane wave basis with kinetic energy cutoff of 10 Ry. These numbers give converged values for the GeSe dimer bond length, vibrational frequency, and cohesive energy, within 0.5, 0.6, and 2.2%, respectively. The preconditioning scheme of Ref. 16 ($E_p=1$ Ry, $\mu_0=700$ a.u.) allows the use of a timestep of 0.53 fs for temperatures up to 2500 °C. The liquid is modeled by 120 atoms, 24 Ge and 96 Se, in a periodic cubic box of size 16.0 Å, yielding a density equal to the experimental one at 800 °C.[17] The temperatures of both the ions and electronic degrees of freedom are controlled by thermostats.[18,19] As the initial configuration we use the coordinates of a liquid $GeSe_2$ sample,[20] and randomly replace Ge atoms by Se to obtain the correct stoichiometry of $GeSe_4$. The system is heated to $\approx$1700 °C, and then gradually cooled to and equilibrated at 800 °C in a total of 13 ps. The average mean squared displacement of the atoms during this period is 8.7 Å, enough to leave no memory of the initial configuration. Subsequently, 7.2 ps of equilibrium data is gathered.

The single particle velocity-velocity self-correlation function $\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$ (see Fig. 1) decays to zero within $\sim$2 ps, ensuring that the averages taken over 7.2 ps are representative of equilibrium. The self-diffusion coefficients obtained by taking the slope of the mean square displacement vs time in between 2 and 6 ps, yields 1.2 ± 0.2 and $2.5\pm0.3\times10^{-5}$ cm^2/s for Ge and Se, respectively.[21] Within the calculated error bars, these values are the same as those obtained by time integration of $\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$ (Fig. 1, inset); i.e., 1.25×10^{-5} cm^2/s for Ge and 2.8×10^{-5} cm^2/s for Se. This further demonstrates that our simulations reflect the equilibrium behavior of liquid $GeSe_4$ at 800 °C.

The calculated total structure factor for neutron diffraction is compared to the experimental one in Fig. 2.[22] The experimental results, obtained at 600 °C, are for the closest concentration we could find to our composition: $x=0.15$. The agreement between our model and experiment is very good; the position and intensity of the main peaks are accurately reproduced. This is particularly important for the first sharp diffraction peak at $\approx$1.2 Å^{-1}. This peak is a signature of intermediate range order, and is found in many binary networks.[23] The presence of this peak in our model indicates that the intermediate range order in the liquid is well described. There is a small shift between the theoretical and experimental values for high scattering vectors, indicating a slight difference between the theoretical and experimental nearest neighbor bond lengths.

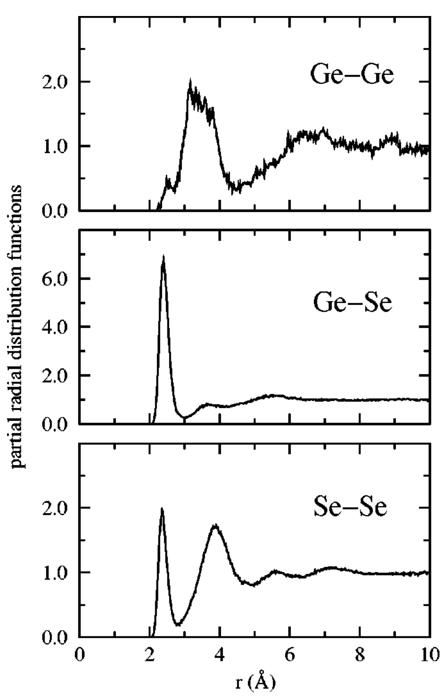

FIG. 3. Calculated partial radial distribution functions for liquid $GeSe_4$.

TABLE I. Total and partial coordination numbers for $GeSe_4$ as predicted by the RCN model, the CON model, and the present work. n_X^{tot} is the total coordination of an atom of species X. n_X^Y is the coordination of an atom of species X by an atom of species Y.

	n_{Ge}^{Ge}	n_{Ge}^{Se}	n_{Ge}^{tot}	n_{Se}^{Ge}	n_{Se}^{Se}	n_{Se}^{tot}
RCN	1.33	2.67	4	0.67	1.33	2
CON	0	4	4	1	1	2
Present work	0.06	3.87	3.93	0.97	1.04	2.01

We first focus on the short range order (SRO), which is described by the nearest neighbor coordination of the constituent species. Atoms are considered to be bonded if their distance is smaller than the first minimum in the corresponding radial distribution function (RDF). Figure 3 shows these RDF's. Integration of the first peaks gives the coordination numbers reported in Table I. The total coordination numbers of Ge and Se are very close to the values predicted by the so-called $8-N$ rule,[24] which gives the coordination number of an atom as a function of its column (N) in the periodic table. For Ge we found, respectively, 7, 86, and 5% of the atoms to be threefold, fourfold, and fivefold coordinated; for Se 5, 89, and 6% are onefold, twofold, and threefold coordinated. Another aspect of the SRO in binary systems is whether there is preferential formation of heteropolar bonds. The structure is a chemically ordered network (CON),[24] if all atoms are coordinated according to the $8-N$ rule and if the number of heteropolar bonds is as large as possible compatibly with the composition. On the other hand, if there is no preference for either homopolar or heteropolar bonds, the structure is a random covalent network (RCN).[24] The difference between these two shows up in the partial coordination numbers, n_X^Y, which denote the coordination of an atom of species X by atoms of species Y. In Table I these numbers are listed for an RCN and a CON of $GeSe_4$, together with the calculated ones. Our liquid $GeSe_4$ is very close to a CON,[25] which implies that the Ge atoms are most likely to be found in $GeSe_4$ tetrahedra, while an amount of the Se atoms will necessarily form homopolar Se bonds.

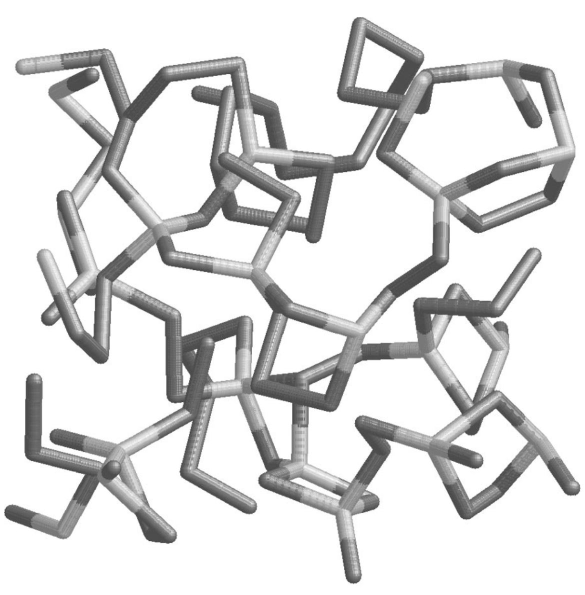

FIG. 4. Snapshot of the liquid $GeSe_4$ model. Light sticks start from Ge atoms, dark sticks from Se atoms.

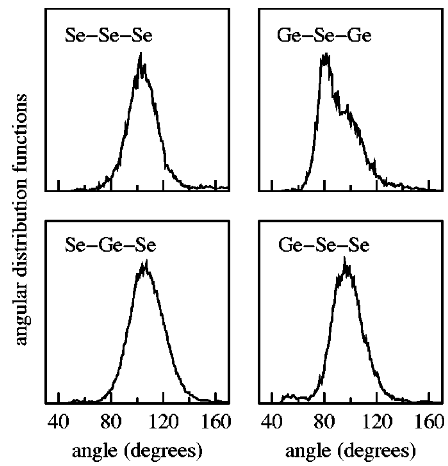

FIG. 5. Angular distribution functions for liquid $GeSe_4$ (arbitrary units).

The fact that our liquid is a CON does not completely determine the SRO in this system. To see this consider a CON of $GeSe_2$. It consists of $GeSe_4$ tetrahedra that are connected by ''shared'' Se atoms. Starting from this structure one can construct a CON of $GeSe_4$ by adding two Se atoms per Ge atom. On the one hand, one could add these Se atoms as separate Se chains, which yields a phase separated structure consisting of $GeSe_2$ and Se. On the other hand, one could also put these Se atoms in between two connected tetrahedra, which yields a structure consisting of $GeSe_4$ tetrahedra connected to each other by homopolar Se bonds. This illustrates a degree of freedom that can be identified as follows. Within the CON there are three different bonding configurations for the Se atoms: one with two Ge bonds (GG), one with two Se bonds (SS), and one with both a Ge and a Se bond (GS). We denote their respective fractions by y_{GG}, y_{GS}, and y_{SS}. At the $GeSe_4$ composition y_{GG} and y_{SS} are necessarily equal and y_{GS} is related to them by the constraint that the sum of the three terms must be equal to one.[26] Hence, within the CON there is one degree of freedom left to distribute the Se atoms over the three possible configurations. The two examples sketched above correspond to two possible extrema: $y_{GG}:y_{SS}:y_{GS}=50:50:0\%$ for the phase separation, and $y_{GG}:y_{SS}:y_{GS}=0:0:100\%$ for the other example. An explicit count of the twofold coordinated Se atoms in our simulation shows that within a 2% errorbar $y_{GG}:y_{SS}:y_{GS}=30:30:40\%$. This shows that in the present calculation $GeSe_4$ tetrahedra are connected both by shared Se atoms (i.e., a GG configuration) and by Se chains (i.e., GS and possibly some SS configurations). A snapshot of this structure is shown in Fig. 4.

The SRO in liquid $GeSe_4$ can directly be compared with that of liquid $GeSe_2$, which has recently been studied within the same approach used here.[20] Contrary to what we found in the present work for liquid $GeSe_4$, the $8-N$ rule was not satisfied in liquid $GeSe_2$ and the structure could not be characterized as a CON. This transition from a CON to a network with broken chemical order as a function of composition has also been found experimentally.[9]

The peaks in the RDF's for distances larger than the nearest neighbor distance are a manifestation of the intermediate range order (IRO) in the system and in particular the Ge-Ge RDF shows correlations between tetrahedra. The shortest connection between two tetrahedra is by means of shared Se atoms. Two configurations occur, the corner sharing (CS), when the tetrahedra share one Se atom, and edge sharing (ES), when the tetrahedra share two Se atoms. These configurations have slightly different Ge distances of ≈3.6 and 3.1 Å, respectively.[27] Hence, the broad peak in the Ge-Ge RDF between 3–4 Å is caused by the presence of both CS and ES tetrahedra. In the present calculation we find 49% of the Ge atoms to be part of chemically ordered fourfold rings, which are characteristic of ES tetrahedra. All the remaining Ge atoms are part of Ge-Se-Ge chains, which are characteristic of CS tetrahedra. Further correlations between tetrahedra are best described by counting ring structures in the network. We find 30% of the Ge atoms to be in fivefold rings containing three Se atoms, and 25% of the Ge atoms to be in sevenfold rings containing four Se atoms. Chemically ordered rings are rare, apart from the fourfold rings present in ES tetrahedra. This preference to form ring structures with broken chemical order shows once more that the connection between tetrahedra is not only by shared Se atoms, but also by Se chains. With respect to the size of the Se chains, we find 20% of the Se atoms to be in Se dimers, 10% in trimers, 14% in 4-mers, and 28% in >4-mers.

Angular distribution functions (ADF's) are shown in Fig. 5, in which the Ge-Ge-Ge and Ge-Ge-Se ADF's have been omitted since the homopolar Ge-Ge bonds seldom occur. Three of these angular distribution functions have a single peak at approximately the same position. The Se-Ge-Se ADF has a broad peak at 107°, close to the expected tetrahedral angle. The Se-Se-Se ADF peaks at 104° in good agreement with the corresponding angle in the trigonal Se crystal (103.3°).[28] The peak at 97° in the Ge-Se-Se ADF characterizes the angle at which Se chains connect to tetrahedra. The small weight in the low-angle region of the Ge-Se-Se ADF is due to the occasional presence of threefold rings. The Ge-Se-Ge ADF has two peaks, one at ~80° and one at ~100°, which describe the connectivity between neighboring tetrahedra. These angles can be ascribed to ES and CS tetrahedra, respectively, and agree well with the Ge-Se-Ge angles in the high temperature phase of crystalline $GeSe_2$,[27] where ES tetrahedra show angles close to 80°, and CS tetrahedra show angles in between 96° and 100°.

In conclusion, we have obtained a microscopic model of liquid $GeSe_4$ which is in very good agreement with neutron diffraction experiments. The liquid is a chemically ordered network. In this network the $GeSe_4$ tetrahedra are connected by both shared Se atoms and Se chains.

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