

Microscopic Structure of Liquid GeSe₂: The Problem of Concentration Fluctuations over Intermediate Range Distances

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A first-principle molecular dynamics study on liquid GeSe₂ yields structural properties in good agreement with detailed neutron scattering data. The short range order is accurately described by a variety of bonding configurations, in which regular tetrahedra coexist with an important fraction of homopolar bonds and threefold centers. The first sharp diffraction peak in the total structure factor, which characterizes order over intermediate range distances, is also well reproduced. However, this level of theory does not yield concentration fluctuations over such distances as observed in experiment. [S0031-9007(98)05500-8]

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A first sharp diffraction peak (FSDP) observed in several binary network-forming materials is a manifestation of order occurring over intermediate range distances [1]. This peak is anomalous in a number of ways, and several interpretations have been put forward to explain its structural origin [2–11]. While the FSDP in the total structure factor has been the subject of many investigations, less attention has been devoted to its appearance in the partial structure factors, which have become experimentally accessible only recently via isotopic substitution in neutron diffraction [12,13].

In a molecular dynamics study based on empirical potentials, it was emphasized that the absence of a FSDP in the Bhatia-Thornton [14] concentration-concentration partial structure factor S_{CC} was a general property of binary glasses [15,16]. In the case of liquid and glassy SiO₂, these predictions were indeed confirmed by first-principle molecular dynamics [17]. However, neutron diffraction experiments on liquid GeSe₂ showed that a FSDP also occurred in the S_{CC} structure factor [12] in marked contrast with the theoretical predictions. Subsequently, the appearance of a FSDP in the S_{CC} structure factor was also observed in other disordered systems [18].

The classical molecular dynamics investigations mentioned above provided a description of liquid and glassy GeSe₂ mainly consisting of chemically ordered networks of corner- and edge-sharing tetrahedra [19]. There are, however, experimental indications that chemical order is broken in glassy [20,21] and liquid GeSe₂ [12]. The occurrence of homopolar bonds is further supported by a recent molecular dynamics study [22]. Therefore, it is in order to examine whether an improved description of the structure of liquid GeSe₂ could give rise to a FSDP in the S_{CC} structure factor.

In this Letter we report the results of first-principle molecular dynamics simulations of liquid GeSe₂. Our structural model gives a description of the microscopic

network of unprecedented quality, as evidenced by the comparison with neutron diffraction data. In particular, the FSDP in the total structure factor is correctly reproduced. In liquid GeSe₂ the predominant bonding configuration is the regular tetrahedron. An important fraction of homopolar bonds and miscoordinated atoms are also observed, resulting in a pronounced departure from chemical order. However, in spite of the overall good agreement with the experiment, the level of accuracy of our theory is still insufficient to produce a FSDP in the S_{CC} structure factor.

We perform constant volume first-principle molecular dynamics simulations in which the electronic structure is described within density functional theory and evolves self-consistently during the motion [23]. In our approach, the valence electrons are treated explicitly, whereas norm-conserving pseudopotentials are used to account for core-valence interactions [24]. A generalized gradient approximation (GGA) for the exchange and correlation energy was adopted [25,26]. Our system consists of a stoichiometric composition of 120 atoms in a periodically repeated cubic cell of side 15.7 Å, corresponding to the experimental density of the liquid at $T = 1050$ K. The wave functions are expanded at the Γ point of the supercell on a plane wave basis set defined by an energy cutoff of 10 Ry. This choice leads to converged values for the Se-Ge dimer bond length ($d_0 = 4.01$ a.u.) and vibrational frequency ($\omega = 392$ cm⁻¹), which reproduce the experimental data to within 1% and 4%, respectively. We chose an initial configuration by adapting a crystalline network of tetrahedra to the size of our cell. A fictitious electron mass $\mu_0 = 5000$ a.u. and a time step $\delta t = 0.54$ fs have been used to integrate the equations of motion according to the preconditioning scheme in Ref. [27]. Temperature control is implemented for both ionic and electronic degrees of freedom by using Nosé-Hoover thermostats [28,29]. After a sufficiently long

time period of equilibration, during which the temperature of the system was gradually lowered from 3000 to 1000 K, time averages were taken over a period of 10 ps. The average distance covered by the atoms during the equilibration period (~ 20 Å) is sufficiently extended to ensure that the liquid produced at 1000 K keeps no memory of the initial configuration.

The calculated neutron scattering structure factor shows excellent agreement with the experiment (Fig. 1) [12,30]. In particular, the position and the height of the FSDP are accurately reproduced. This suggests that intermediate range distances are accurately described in our model. A more detailed comparison between theory and experiment is provided by the partial structure factors (Fig. 2). The agreement between theory and experiment is also very good in this case. The peaks at 2 Å⁻¹ and beyond, which define the short range order, are well reproduced. This is particularly striking for the Se-Se structure factor, which carries the smallest experimental errors. A detailed inspection reveals that the second and third peaks in the theoretical Ge-Ge structure factor show a slight shift towards lower wave vectors, but their overall shape agrees with the experimental curve. However, in correspondence to the FSDP, the agreement is only qualitative for each of the partial structure factors. Thus, despite the impressive accord in the total structure factor, the distribution of the FSDP weight in the partial structure factors appears to be different in theory and experiment.

The microscopic structure of disordered GeSe₂ systems has long been contentious [31–35]. Many recently, the observed breakdown of chemical order [12,20,21] has questioned the validity of continuous random network models for describing these materials [36]. Therefore, given the agreement with the experimental data for both the total and the partial structure factors, it is of interest

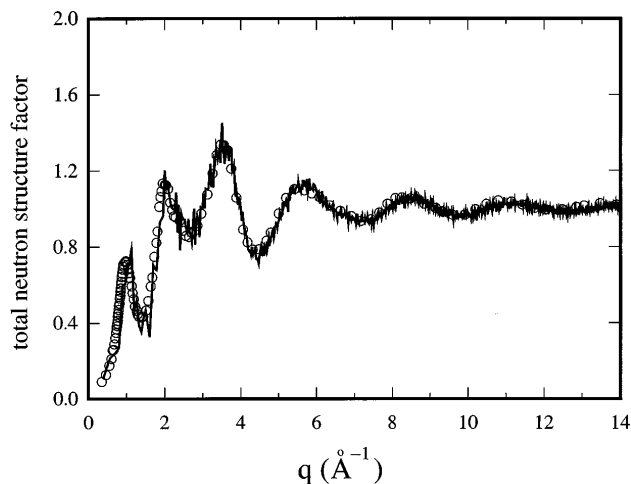


FIG. 1. Calculated neutron structure factor for liquid GeSe₂ compared to experimental data from Ref. [12]. We used scattering lengths of $b_{\text{Ge}} = 8.189$ fm and $b_{\text{Se}} = 7.97$ fm.

to characterize the microscopic structure predicted by our model of liquid GeSe₂. To this end we calculate coordination numbers by using a cutoff radius of 3 Å, corresponding to the minimum in the Ge-Se pair-correlation function. This value is also appropriate to describe nearest neighbor Ge-Ge and Se-Se distances. In the picture which emerges from our calculations fourfold coordinated Ge atoms (63%) and twofold coordinated Se atoms (74%) are still predominant, but coexist with an important fraction of other configurations, such as threefold Se atoms (23%) or undercoordinated Ge atoms (30%). This goes with a substantial disruption of chemical order, which is quantified by 10% of the Ge and 39% of the Se atoms forming homopolar bonds. The Ge fraction is in reasonable agreement with the estimate of 16% derived from Mössbauer spectroscopy for glassy GeSe₂ [21]. Almost all of the Ge-Ge bonds are found in dimers, but in the case of Se more than a fourth of the atoms forming homopolar bonds are part of trimer chains, which recall typical Se motifs. As confirmed by visual inspection (Fig. 3), for such a structure the characterization in terms of corner- and edge-sharing tetrahedra is inappropriate. Nonetheless, we counted that about 45% of the Ge atoms are part of chemically ordered fourfold rings, confirming the value extracted from neutron diffraction data [12]. We also found that a large fraction of Ge atoms (46%) is part of five-fold rings, in which the chemical order is broken only by a Se-Se dimer. This type of structure recalls a subunit of

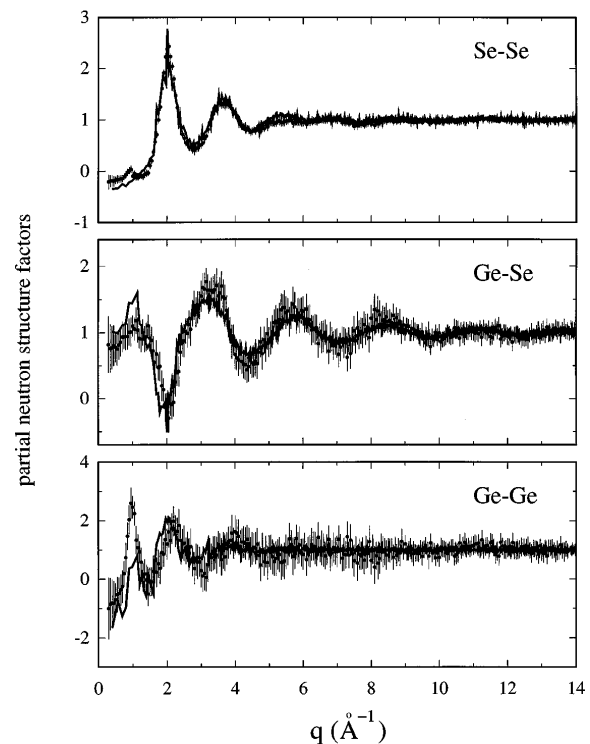


FIG. 2. Faber-Ziman partial structure factors for liquid GeSe₂: theory (solid) and experiment (dots with error bars) [12].

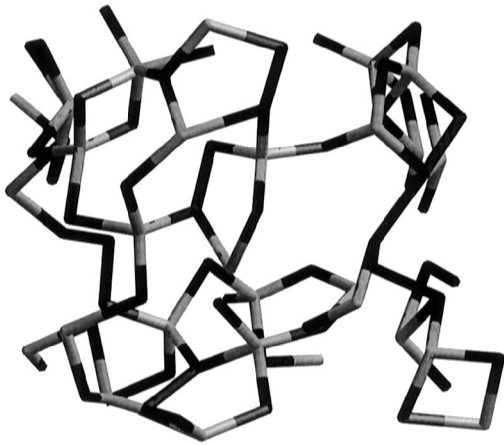


FIG. 3. A snapshot of an instantaneous configuration of liquid GeSe_2 . Black sticks depart from Se atoms and grey sticks from Ge atoms. Two atoms are connected when their mutual distance is smaller than 3 \AA . Some Ge and Se atoms have been removed for clarity.

the “outrigger-raft” model, in which Se-Se dimers terminate crystallinelike layers [32,33]. This structural analysis shows that neither continuous random network nor crystallinelike models [32,33] are adequate to describe disordered GeSe_2 systems.

The Bhatia-Thornton structure factors (Fig. 4) are obtained by taking linear combinations of the partial structure factors in Fig. 2 [14]. The number-number structure factor S_{NN} resembles the total structure factor because the scattering lengths of Se and Ge are very close. Thus, the theoretical description of the FSDP in the S_{NN} structure factor is very good. Differences between the theoretical and experimental curves are now almost completely confined to the S_{CC} structure factor, where a prominent experimental FSDP is contrasted by the absence of any feature in the calculated result. It should be remarked that despite this difference all the other features agree well with the experimental data, suggesting that the absence of a FSDP in the S_{CC} structure factor only marginally affects the short range properties and the appearance of a FSDP in the total structure factor of liquid GeSe_2 .

The absence of a FSDP in the S_{CC} structure factor is in accord with the general predictions in Ref. [15,16]. This fact is even more remarkable considering that the structural description for liquid GeSe_2 obtained here differs radically from that in Ref. [16], which was used to reach those predictions. However, it appears hard to concile this description with the experimental evidence supporting the presence of a FSDP in the S_{CC} structure factor of several disordered systems [18].

By improving the description of the chemical bonding, our work provides a microscopic picture of the structure of liquid GeSe_2 which shows good agreement with neutron diffraction data. This structural model is, nevertheless, still insufficient to explain the physical origin of the

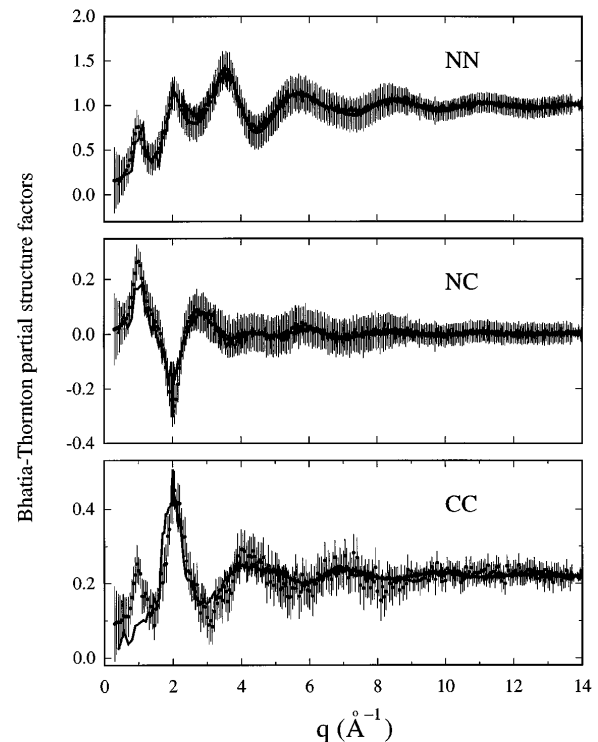


FIG. 4. The Bhatia-Thornton partial structure factors [14] for liquid GeSe_2 : theory (solid) and experiment (dots with error bars) [12].

FSDP in the S_{CC} structure factor observed in the experiment. This defines an important open issue in the physics of disordered network-forming materials.

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