Structure of Covalently Bonded Glass-Forming Melts: A Full Partial-Structure-Factor Analysis of Liquid $GeSe_2$

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The first full partial-structure-factor analysis of molten $GeSe_2$ is made using the method of isotopic substitution in neutron diffraction. It is shown that the melt comprises roughly equal numbers of edge- and corner-sharing tetrahedra which give rise to a highly connected or network liquid. Concentration fluctuations extend over distances characteristic of the intermediate-range order, contrary to the results obtained from recently developed effective potentials for covalently bonded glass-forming melts. The problem as to whether or not $GeSe_2$ forms a chemically ordered continuous random network is examined.

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In this Letter we address the problem of the structure of covalently bonded glasses and the melts from which they are formed by investigating molten $GeSe_2$ using the method of isotopic substitution in neutron diffraction. The $GeSe_2$ system has been widely studied and may be regarded as a generic glass-forming binary material. In particular, there are two features of its structure that are typical of many covalently bonded disordered materials. The first is the occurrence of a first sharp diffraction peak (FSDP) in the total structure factor $F(k)$ measured by diffraction methods which, unlike the other peaks, does not decrease in height as the glassy material is melted [1]. The second is the appearance in Raman spectra of a companion mode A_1^c to the symmetrical breathing mode A_1 that is associated with $Ge(Se_{1/2})_4$ tetrahedra [2]. In $GeSe_2$, at least, the A_1^c mode survives the melting transition [3].

How these features arise from the structure of the material remains a subject of controversy [4,5]. This results from the intrinsic difficulties of working with disordered systems and the nature of existing structural information. Conventional diffraction experiments, for example, yield only the $F(k)$ functions [1], while extended x-ray-absorption fine-structure experiments give information that is limited to short-range correlations [6]. The anomalous x-ray scattering method has been applied to glassy $GeSe_2$ [7] but the extraction of the full set of partial structure factors, $S_{\alpha\beta}(k)$, was not possible and the range of scattering vectors was restricted to $0.5 \lesssim k \lesssim 10$ Å^{-1}. Molecular-dynamics simulations of the molten and glassy states have also been made [8], but these calculations are limited by the accuracy of the effective potentials that are used and by the extent of existing experimental information used for comparison with the simulation results.

In view of the importance of $GeSe_2$ as a model for glass-forming covalently bonded network liquids and the recent measurement of the coherent scattering lengths of the Ge isotopes we have made a *full* $S_{\alpha\beta}(k)$ analysis of molten $GeSe_2$ at $784 \pm 3\,°C$ (mp of $742 \pm 2\,°C$) using the neutron-diffraction method [9]. The object is to enable a better test of the physics of this system by providing *experimental* partial pair-distribution functions $g_{\alpha\beta}(r)$ that contain information on *both* the short- and intermediate-range order (IRO). A central question regarding models for $GeSe_2$ [4,5] is the extent to which its molten and glassy states retain a memory of the crystal structure.

The $F(k)$ function for molten $GeSe_2$ measured by the neutron-diffraction method is given by

$$\begin{aligned} F(k) = {} & c_{\mathrm{Ge}}^2 b_{\mathrm{Ge}}^2 [S_{\mathrm{GeGe}}(k) - 1] \\ & + 2c_{\mathrm{Ge}} c_{\mathrm{Se}} b_{\mathrm{Ge}} b_{\mathrm{Se}} [S_{\mathrm{GeSe}}(k) - 1] \\ & + c_{\mathrm{Se}}^2 b_{\mathrm{Se}}^2 [S_{\mathrm{SeSe}}(k) - 1] \,, \end{aligned}$$

where c_α and b_α are, respectively, the atomic fraction and coherent scattering length of species α and the (Faber-Ziman) $S_{\alpha\beta}(k)$ are related to the $g_{\alpha\beta}(r)$ through the usual expressions [9]. The weighting factors of the $S_{\alpha\beta}(k)$ in the equation for $F(k)$ can be changed by isotope enrichment. Hence diffraction experiments on three samples that are identical in every respect, except their isotopic composition, will give three $F(k)$ functions which can then be solved to reveal the individual $S_{\alpha\beta}(k)$. In the present case these samples were ${}^{N}\mathrm{Ge}{}^{N}\mathrm{Se}_2$ giving ${}^{N}_{N}F(k)$, where N denotes the natural isotopic abundance, ${}^{70}\mathrm{Ge}{}^{N}\mathrm{Se}_2$ giving ${}^{70}_{N}F(k)$, and ${}^{73}\mathrm{Ge}{}^{76}\mathrm{Se}_2$ giving ${}^{73}_{76}F(k)$. The coherent scattering lengths were $b({}^{N}\mathrm{Ge}) = 8.189(3)$ fm, $b({}^{70}\mathrm{Ge}) = 9.93(10)$ fm, $b({}^{73}\mathrm{Ge}) = 5.20(4)$ fm, $b({}^{N}\mathrm{Se}) = 7.970(9)$ fm, $b({}^{76}\mathrm{Se}) = 12.04(10)$ fm, and a measure of the conditioning of the set of simultaneous equations used to obtain the $S_{\alpha\beta}(k)$ is given by the determinant of the normalized weighting-factor matrix $|A|_n = -0.01$ [9]. The diffraction experiments were made using the D4B instrument at the Institut Laue-Langevin, Grenoble, and are described elsewhere [10].

The measured $F(k)$ functions were of high statistical precision which enabled their direct solution to give the $S_{\alpha\beta}(k)$ illustrated in Fig. 1. In view of the systematic errors that can accompany such a procedure it was ensured that the data satisfy several self-consistency criteria. It was checked that the $S_{\alpha\beta}(k)$ satisfy the usual sum-rule and inequality relations [9] and that the Ge partial structure factors can be reconstituted to give the difference function $\Delta_{\mathrm{Ge}}(k) \equiv {}^{70}_{N}F(k) - {}^{N}_{N}F(k)$. This is important

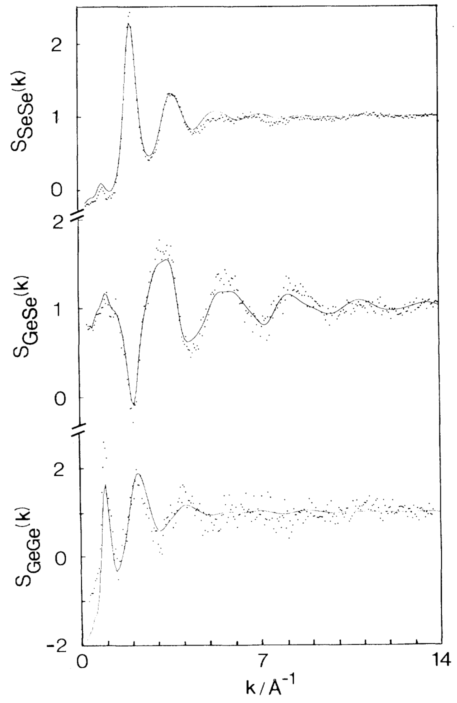

FIG. 1. The measured $S_{\alpha\beta}(k)$ for liquid GeSe$_2$ (dots) and the ME fits (solid curves) corresponding to the dashed curves in Fig. 2.

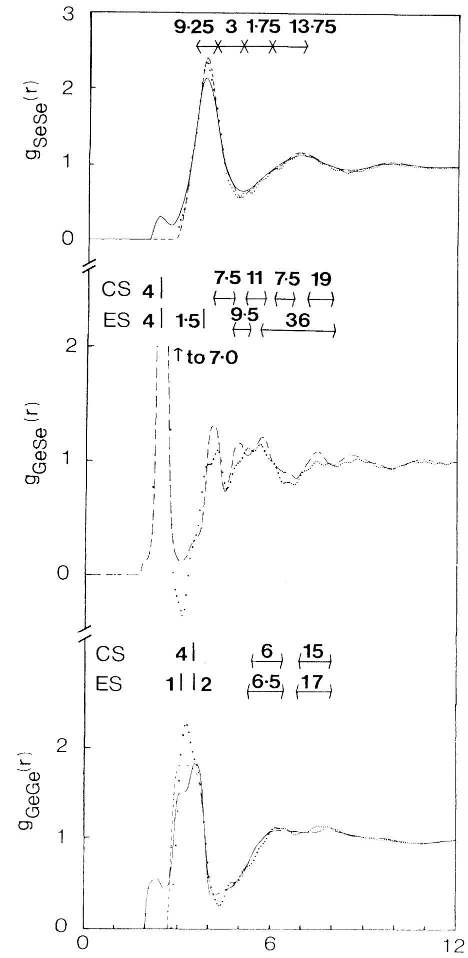

FIG. 2. The $g_{\alpha\beta}(r)$ for liquid GeSe$_2$ obtained from the data of Fig. 1 by direct FT (dotted curves) and by the ME method. In the latter, homopolar bonding was either forbidden (dashed curves) or was allowed (solid curves) (see text). Vertical bars show the positions, or horizontal arrows show the spread of positions, of neighbors in the HT crystalline phase of GeSe$_2$; the adjacent numerals are the corresponding coordination numbers. Since the coordination environment of a Ge atom has a marked dependence on whether it occupies an edge- or corner-sharing (ES or CS) site the two cases have been distinguished for $g_{GeSe}(r)$ and $g_{GeGe}(r)$.

since several types of systematic error are reduced or essentially eliminated when $\Delta_{Ge}(k)$ is formed [10] and the $S_{Ge\beta}(k)$ functions are the least well conditioned of the set of three. The $S_{\alpha\beta}(k)$ reveal, when weighted to reconstruct the $F(k)$ functions, that the major contribution to the FSDP at $k=0.98(2)$ Å^{-1} arises from $S_{GeGe}(k)$.

The $g_{\alpha\beta}(r)$ were obtained by direct Fourier transformation (FT) of the $S_{\alpha\beta}(k)$ and by a maximum-entropy (ME) method [11] in which homopolar bonding was forbidden since the Ge-Se bond energy is relatively large. They are compared in Fig. 2 (dotted and dashed curves) with the structure of the high-temperature (HT) crystalline GeSe$_2$ polymorph [12] which is the phase that coexists with the liquid at the melting point. The discrepancy between the FT and ME results does not substantially affect the following discussion wherein the average coordination number $\bar{n}_\alpha^\beta$ of species β around species α in the range $r_1 \leq r \leq r_2$ is deduced from the $g_{\alpha\beta}(r)$ through the expression given in Ref. [10].

The first main peak in $g_{SeSe}(r)$ at 3.80(2) Å shows a broad distribution of Se-Se distances which is comparable with the crystal structure. Its integration over the range $2.76 \leq r \leq 4.91$ Å gives $\bar{n}_{Se}^{Se}=10.3(5)$ [13]. The first intense peak in $g_{GeSe}(r)$ at 2.42(2) Å is followed by marked IRO correlations extending to ≈ 12 Å. Integration of the first peak from 2.09 Å to the first minimum gives $\bar{n}_{Ge}^{Se}=3.6(3)$ which, together with the ratio $r_{GeSe}/r_{SeSe}=0.635$, supports the presence of distorted tetrahedra in the melt (the ideal ratio for tetrahedral units is $\sqrt{3/8}=0.612$). Furthermore, the edge-sharing (ES) Ge crystal site has Se neighbors in the range $4.6 \lesssim r \lesssim 5.3$ Å, whereas the corner-sharing (CS) Ge crystal site has Se neighbors in the range $4.0 \lesssim r \lesssim 4.8$ Å. The peak in $g_{GeSe}(r)$ at ≈ 4.1 Å is therefore attributed to predominantly CS tetrahedra, while the one at ≈ 4.9 Å arises from the presence of both ES and CS tetrahedra. The first main peak in $g_{GeGe}(r)$ occurs in the range $2.7 \leq r \leq 4.4$ Å and its integration gives $\bar{n}_{Ge}^{Ge}=3.3(6)$. The small value of the low-r limit in this integration is consistent with the presence of ES tetrahedra in the melt, and the $\bar{n}_{Ge}^{Ge}$ value indicates comparable numbers of ES and CS sites. This follows since in the crystalline state each ES or CS Ge atom has, respectively, three or four nearest-neighbor Ge atoms and there are *equal* numbers of ES and CS sites giving $\bar{n}_{\mathrm{Ge}}^{\mathrm{Ge}}=3.5$. $g_{\mathrm{GeGe}}(r)$ also reveals IRO correlations beyond ≈ 4.5 Å and it is found, by truncating $g_{\mathrm{GeGe}}(r)$ at progressively lower-r values and noting the effect on the k-space data, that the FSDP in both $S_{\mathrm{GeGe}}(k)$ and ${}^{N}_{N}F(k)$ arises from these correlations.

The present experimental work lends support to several aspects of the molecular-dynamics and integral-equation calculations made by Vashishta and co-workers [8]. There are, however, significant differences between experiment and theory. For example, the use of effective two-body potentials for molten $\mathrm{GeSe_2}$ fails to predict the correct position for the FSDP, seriously underestimates the proportion of ES tetrahedra present in the melt (only $\sim 5\%$), and does not give the correct $\bar{n}_{\mathrm{Ge}}^{\mathrm{Ge}}$. The introduction of three-body effects helps to relieve some of these problems, but major differences still remain. This is most readily seen by forming the concentration-concentration structure factor $S_{CC}(k)$ [14] which, to the extent that the liquid can be regarded as comprising solely ionic species, becomes the charge-charge structure factor $S_{ZZ}(k)$ with the imposition of overall charge neutrality,

$$\frac{S_{CC}(k)}{c_{\mathrm{Ge}}c_{\mathrm{Se}}} \equiv 1+c_{\mathrm{Ge}}c_{\mathrm{Se}}[S_{\mathrm{GeGe}}(k)+S_{\mathrm{SeSe}}(k)-2S_{\mathrm{GeSe}}(k)] = S_{ZZ}(k)\,.$$

Vashishta and co-workers did not find a FSDP in this function from any of their calculations on $\mathrm{GeSe_2}$ [8(a)] and attributed this to the absence of charge-density fluctuations at distances corresponding to the IRO correlations. Indeed, they regarded this feature as *generic* for network glasses and melts [8(b)]. However, as demonstrated in Fig. 3, $S_{CC}(k)$ displays a FSDP at 0.96(2) Å^{-1} which is *comparable* in magnitude to the remaining features and arises predominantly from the Ge-Ge IRO. This is the first observation of a FSDP in $S_{CC}(k)$ for a glass-forming network melt and its occurrence is related to the chemical ordering of the Ge-Se network at distances characteristic of the IRO. The present results therefore challenge the premise that "*the absence of a FSDP in $S_{ZZ}(k)$ is independent of the interaction potential used to describe the system, or the particular detail of the connectivity of the system, or the theoretical scheme used to carry out the calculations*" [8(b)].

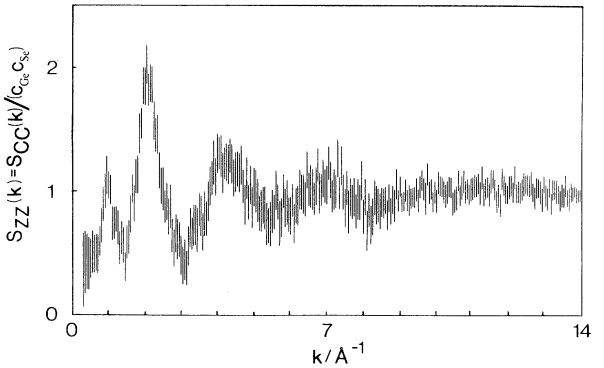

FIG. 3. $S_{ZZ}(k)$ for liquid $\mathrm{GeSe_2}$ derived from the measured $S_{\alpha\beta}(k)$ by the formula in the text. The vertical bars display the statistical errors.

In view of the controversy in the literature [4,5] between the different models for disordered $\mathrm{GeSe_2}$ the ME method was again applied but with the restriction of only heteropolar bonding lifted, i.e., the low-r cutoff distances for $g_{\mathrm{SeSe}}(r)$ and $g_{\mathrm{GeGe}}(r)$ were decreased to those that exist in, respectively, liquid Se and amorphous Ge. The like-atom $g_{\alpha\alpha}(r)$ thus obtained (solid curves, Fig. 2) show small peaks in the low-r region at distances comparable to the Se-Se contact distance in liquid Se [2.30(2) Å, cf. 2.35 Å] and the Ge-Ge contact distance in amorphous Ge [2.33(3) Å, cf. 2.46 Å]. The physical reality of these features is supported, to some extent, by consideration of the real-space representations of the $F(k)$ and $\Delta_{\mathrm{Ge}}(k)$ functions since integration over the same r range as the first main peak in $g_{\mathrm{GeSe}}(r)$, assuming Ge-Se correlations alone, gives slightly higher mean coordination numbers [3.8(2) and 3.7(2)]. Our data therefore appear to be consistent with the occurrence of Se-Se and Ge-Ge contacts and within this framework might be taken as firm evidence in support of the "outrigger-raft" model that has been used to explain the FSDP and A_1^c mode in liquid and glassy $\mathrm{GeSe_2}$ [4]. In this model the layers present in the HT $\mathrm{GeSe_2}$ crystalline phase are fragmented and Se-Se dimers form along the resultant "raft" edges. The Se-rich rafts are then compensated by the occurrence of Ge-Ge contacts, thought to be in the form of isolated or polymerized $\mathrm{Ge_2Se_3}$ units. We, however, reserve judgement on this viewpoint since homopolar bonds will also occur in a *defected* chemically ordered continuous random network (COCRN) model in which well-defined layers need not be present.

A full resolution to this apparent dichotomy requires at least a knowledge of bond-angle distributions; i.e., by how much can the HT $\mathrm{GeSe_2}$ phase bond angles vary as the temperature is raised through the melting point? Our results cannot be used to give this (three-dimensional) information directly since the $g_{\alpha\beta}(r)$ are isotropic functions and covalent forces are important [15]. A method such as the Car-Parrinello approach to *ab initio* molecular-dynamics simulations using density-functional theory [16] is required. The present data will, however, provide a framework for testing the efficacy of such calculations and hence the relative importance of the (quasicrystalline) outrigger raft and COCRN models as extreme descriptions of the melt and glass structure.

In summary, we present the first full *experimental* set of $S_{\alpha\beta}(k)$ for $\mathrm{GeSe_2}$ which is a *covalently* bonded liquid that readily forms a glass by bulk-quenching methods. The results demonstrate the need for a revision of the interatomic potentials that have been used for such systems and provide a benchmark for future theoretical models.

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