

## Defects in a Disordered World: The Structure of Glassy GeSe<sub>2</sub>

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The full set of partial structure factors for the prototypical network glass GeSe<sub>2</sub> was measured using the method of isotopic substitution in neutron diffraction. The basic building block of the network is the Ge(Se<sub>1/2</sub>)<sub>4</sub> tetrahedron in which 34(5)% of the Ge reside in edge-sharing configurations. The intrinsic chemical order of the glass is, however, broken with a maximum of 25(5)% Ge and 20(5)% Se being involved in homopolar bonds at distances of 2.42(2) and 2.32(2) Å, respectively.

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Fundamental to an understanding of the optoelectronic and other physicochemical properties of network glasses is a knowledge of their microscopic structure and hence the type and number of entities which may be regarded as defects. In this context, the structure of the prototypical network glass GeSe<sub>2</sub> has long been the subject of controversy, the scope of the proposed models covering two different philosophies. On the one hand, is the basic structure best described in terms of a chemically ordered continuous random network, as originally proposed by Zachariassen in 1932 [1], in which homopolar or “wrong” bonds may occur accidentally [2–4]? On the other hand, is it best thought of in terms of an aggregate of motifs that maintain a memory of the crystalline phase of the material and in which homopolar bonds exist as an integral part [5–7]?

A first step to solving this puzzle requires definitive experimental information on the full set of partial pair distribution functions,  $g_{\alpha\beta}(r)$ , describing the atomic positions to provide a benchmark for testing the quantitative predictions of the various models for network glasses. Here we meet this outstanding challenge by applying the method of isotopic substitution in neutron diffraction to glassy GeSe<sub>2</sub>. The results give direct evidence for the existence of structural motifs such as homopolar bonds which are not present in the high temperature crystalline phase of this material, HT-GeSe<sub>2</sub>, and provide for an intriguing opportunity to make significant progress on the structure of disordered network materials. Although the presence of homopolar bonds has been inferred from some spectroscopic experiments [5–8], their existence has proved controversial [2,4], and they have not previously been identified by using diffraction [3,9,10] or extended x-ray absorption fine structure [8,11] methods. This results, in part, from the similar neutron scattering lengths for Ge and Se of natural isotopic abundance and their close atomic numbers and sizes.

The three samples required for the diffraction experiments,  ${}^N\text{Ge}{}^N\text{Se}_2$ ,  ${}^{70}\text{Ge}{}^N\text{Se}_2$ , and  ${}^{73}\text{Ge}{}^{76}\text{Se}_2$ , where  $N$  denotes the natural isotopic abundance, were made from  ${}^N\text{Ge}(99.9999\%)$ ,  ${}^N\text{Se}(99.999\%)$ , and highly en-

riched isotopes  ${}^{70}\text{Ge}(99.8\% {}^{70}\text{Ge}, 0.2\% {}^{72}\text{Ge})$ ,  ${}^{73}\text{Ge}(98\% {}^{73}\text{Ge}, 0.3\% {}^{70}\text{Ge}, 0.8\% {}^{72}\text{Ge}, 0.8\% {}^{74}\text{Ge}, 0.1\% {}^{76}\text{Ge})$ ,  ${}^{76}\text{Se}(99.75\% {}^{76}\text{Se}, 0.2\% {}^{74}\text{Se}, 0.05\% {}^{77}\text{Se})$ . The isotopes were freshly separated and immediately sealed under vacuum to minimize the chemical impurity content at  $\leq 0.05\%$ . The samples, whose stoichiometry was determined by mass to be 0.3333(2) Ge: 0.6667(2) Se, were produced identically following a stringent procedure designed to avoid contamination [12]. The components were sealed within silica ampoules (1 mm wall thickness, 4.8 mm internal diameter) and were melted together in a rocking furnace prior to quenching from 850 °C in an ice/salt-water mixture at  $-5$  °C. Small ampoules were chosen to promote the formation of homogeneous glasses: differential scanning calorimetry experiments gave comparable traces with a glass transition temperature of 394(6) °C (onset at 10 °C/min) and no small angle neutron scattering was observed. The as-quenched glasses were held in vanadium cans for the diffraction experiments, which were made using the instrument D4B (Institut Laue-Langevin, Grenoble) with an incident neutron wavelength of 0.7046 Å. The neutron scattering lengths are  $b({}^N\text{Ge}) = 8.185(20)$  fm,  $b({}^{70}\text{Ge}) = 10.0(1)$  fm,  $b({}^{73}\text{Ge}) = 5.09(4)$  fm,  $b({}^N\text{Se}) = 7.970(9)$  fm, and  $b({}^{76}\text{Se}) = 12.2(1)$  fm. The partial structure factors  $A_{\alpha\beta}(Q)$ , where  $Q$  denotes the magnitude of the scattering vector, were obtained by using a careful analysis process wherein strict tests were applied to ensure the reliability of the data sets at each and every step of the procedure [12–14]. For example, the first order difference functions, wherein the Ge-Ge or Se-Se correlations are eliminated by subtracting the appropriately weighted diffraction patterns for two of the samples [12,13], satisfy self-consistency checks which would be disobeyed if the samples had inequivalent compositions [15]. Further, it was confirmed that these difference functions can be replicated by using the measured  $A_{\alpha\beta}(Q)$ .

The  $A_{\alpha\beta}(Q)$  are shown in Fig. 1 and are of high statistical quality. They confirm [3,9] that the first sharp diffraction peak in the measured total diffraction patterns at

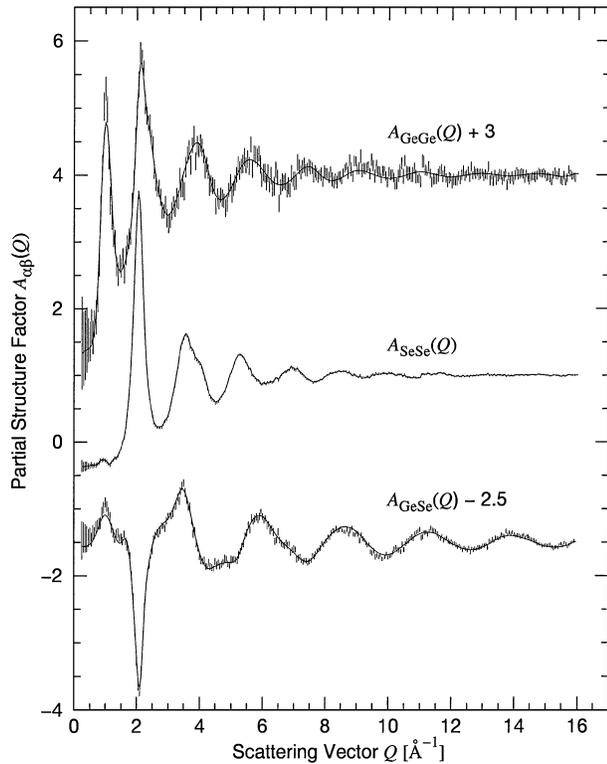


FIG. 1. The measured partial structure factors,  $A_{\alpha\beta}(Q)$ , for glassy  $\text{GeSe}_2$  at  $26(1)^\circ\text{C}$ . The bars represent the statistical errors on the data points and the solid curves are the Fourier transforms of the  $g_{\alpha\beta}(r)$  given in Fig. 2(b). The corresponding reduced  $\chi^2$  values of 0.84, 0.40, and 1.14 for  $A_{\text{GeGe}}(Q)$ ,  $A_{\text{SeSe}}(Q)$ , and  $A_{\text{GeSe}}(Q)$  increase to 1.04, 3.92, and 1.65, respectively, if the defect peaks at low  $r$  in  $g_{\text{GeGe}}(r)$  and  $g_{\text{SeSe}}(r)$  and at  $3.02 \text{ \AA}$  in  $g_{\text{GeSe}}(r)$  are removed.

$Q = 1.00(2) \text{ \AA}^{-1}$ , which is a ubiquitous feature of covalently bonded amorphous solids [16], arises predominantly from the Ge-Ge correlations, i.e., from the real space intermediate range ordering of Ge-centered structural motifs.

An interpretation of the features in the corresponding real-space functions  $t'_{\alpha\beta}(r)$  is complicated by the effects of statistical noise and the finite measurement window function of the diffractometer  $M(Q \leq 15.9 \text{ \AA}^{-1}) = 1$ ,  $M(Q > 15.9 \text{ \AA}^{-1}) = 0$ . Specifically,

$$t'_{\alpha\beta}(r) = \frac{2}{\pi} \int_0^\infty dQ [A_{\alpha\beta}(Q) - 1] M(Q) Q \sin(Qr), \quad (1)$$

where  $t'_{\alpha\beta}(r) = t_{\alpha\beta}(r) \otimes M(r)$ ,  $t_{\alpha\beta}(r) = 4\pi n_0 r \times [g_{\alpha\beta}(r) - 1]$ ,  $n_0$  is the atomic number density of the glass [=  $0.0334(1) \text{ \AA}^{-3}$  [17]],  $\otimes$  denotes the one-dimensional convolution operator, and  $M(r)$  is the real-space representation of  $M(Q)$ . The effect of statistical noise was reduced by using spline-fitted partial structure factors for the Fourier transforms and, to enable those features that are artifacts of  $M(r)$  to be distinguished, the resultant  $t'_{\alpha\beta}(r)$  were fitted by least squares to a sum of Gaussians representing the partial pair correlation func-

tions convoluted with  $M(r)$  [Fig. 2(a)]. The final  $t_{\alpha\beta}(r)$  were then obtained by smoothly merging the Gaussian representation of  $t_{\alpha\beta}(r)$  in the region where the effect of  $M(r)$  is measurable with the  $t'_{\alpha\beta}(r)$  obtained by direct Fourier transformation of the spline-fitted  $A_{\alpha\beta}(Q)$  and by setting the unphysical low- $r$  oscillations to  $-4\pi n_0 r$ . The resultant  $g_{\alpha\beta}(r)$  functions are shown in Fig. 2(b) and,

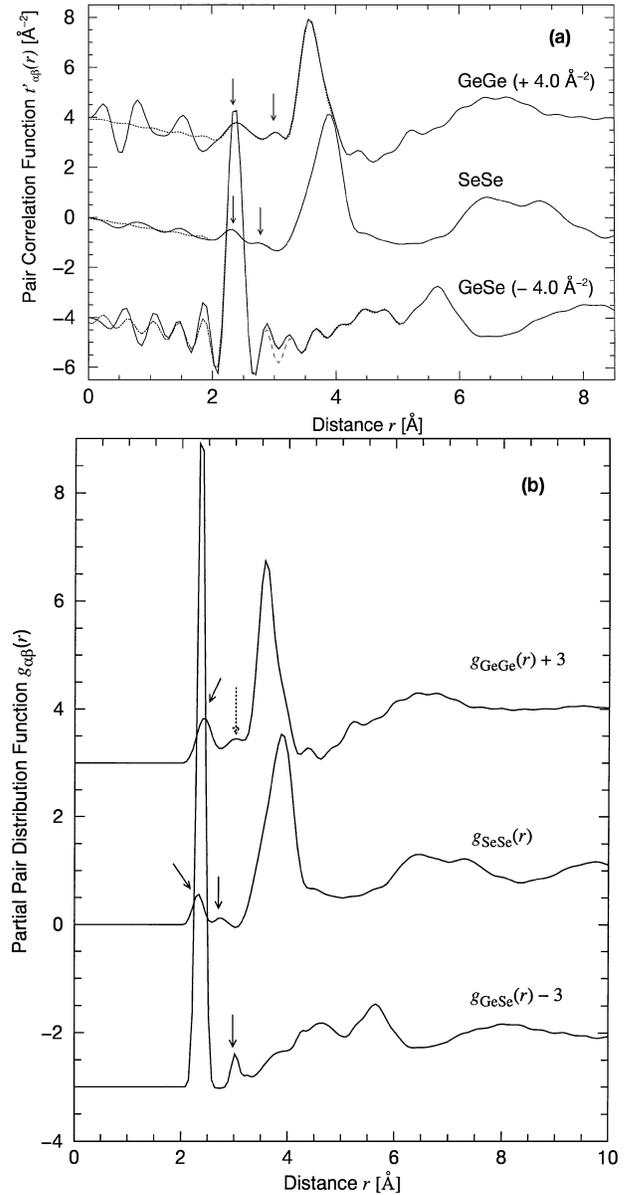


FIG. 2. (a) The  $t'_{\alpha\beta}(r)$  obtained from the  $A_{\alpha\beta}(Q)$  of Fig. 1 using Eq. (1) (solid curves) and the Gaussian fits (dotted curves). The fitted functions are identical to the  $t'_{\alpha\beta}(r)$  at large  $r$  values and the vertical arrows point to the fitted low- $r$  features for the like-atom correlations. The dashed curve shows the effect of omitting the defect peak at  $3.02 \text{ \AA}$  in the Ge-Se correlations. (b) The partial pair distribution functions,  $g_{\alpha\beta}(r)$ , for glassy  $\text{GeSe}_2$  derived from the  $t'_{\alpha\beta}(r)$  in Fig. 2(a). The solid arrows point to the defect peaks and the dotted arrow to the Ge-Ge distance for edge-sharing tetrahedra.

as required, their Fourier transforms give an excellent account of the measured  $A_{\alpha\beta}(Q)$  of Fig. 1.

The main peaks in  $g_{\text{GeSe}}(r)$ ,  $g_{\text{GeGe}}(r)$ , and  $g_{\text{SeSe}}(r)$  at 2.36(2), 3.57(2), and 3.89(2) Å in Fig. 2(b) give Ge-Se, Ge-Ge, and Se-Se coordination numbers of 3.7(1), 3.2(3), and 9.3(3), respectively, which are comparable to those previously measured for the liquid phase [13]. Since the ratio of the Ge-Se:Se-Se distances is 0.607(6), close to the value of  $\sqrt{3/8} = 0.612$  expected for perfect tetrahedral coordination, the results imply that there are a large number of tetrahedral  $\text{Ge}(\text{Se}_{1/2})_4$  structural motifs. These are the basic building blocks of HT- $\text{GeSe}_2$  [18] and appear to be more regular in the glass than in the liquid where the distance ratio is 0.637(6). In HT- $\text{GeSe}_2$  the presence of equal numbers of edge- and corner-sharing  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedra gives two nearest-neighbor Ge-Ge distances at 3.05 and 3.55 Å, the shortest between the centers of edge-sharing motifs. The low- $r$  Ge-Ge peak at 3.02(2) Å is assigned to this distance and the coordination number of 0.34(5) is consistent with 34(5)% of the Ge being in edge-sharing tetrahedra, in accordance with a previous estimate [10].

Importantly, there is clear evidence for a substantial number of defects, i.e., structural motifs that are *not* present in HT- $\text{GeSe}_2$  [18]. For example, the like-atom  $g_{\alpha\beta}(r)$  show Ge-Ge and Se-Se correlations at typical homopolar single bond distances of 2.42(2) and 2.32(2) Å, respectively [12]. These small- $r$  features are required if the real-space representations of the first order difference functions are to be reproduced. Further Se-Se correlations occur at 2.74(2) Å and there are also Ge-Se correlations at 3.02(2) Å. The coordination numbers for the Ge-Ge and Se-Se homopolar bonds are 0.25(5) and 0.20(5), comparable to the values found in the liquid state [13]. When taken together with the Ge-Se coordination number, these values imply that Ge and Se are, within the experimental error, fourfold and twofold coordinated; i.e., they have a full outer shell of eight electrons. If only dimers are formed, then a maximum fraction of 25(5)% of the Ge and 20(5)% of the Se are involved in homopolar bonds. The number of Ge-Ge or Se-Se homopolar bonds is roughly the same at  $0.05(2)N'$ , where  $N'$  is the total number of atoms, and the total number of bonds for  $\text{GeSe}_2$  is  $4N'/3$  if the bonding requirements of Ge and Se are fully satisfied. Hence the ratio of the number of Ge-Ge (or Se-Se) bonds to the total number of bonds in the glass is  $\approx 4\%$  which is in agreement with an estimate based on the law of mass action [19]. Application of the isotopic substitution method has enabled these important structural features to be resolved and thus allows for a test of models for the intrinsic broken chemical order.

As an illustration, in the disputed “outrigger raft” model [5,7] the predominant Ge-centered structural motifs are regular  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedra and  $\text{Se}_{3/2}\text{Ge-GeSe}_{3/2}$  ethanelike dimers. The upper limit of 25(5)% on the

fraction of Ge involved in dimers is then consistent with an estimate of 16(1)% from Mössbauer experiments where Sn was used as a Ge probe [7]. However, the Ge-Se defect peak at 3.02(2) Å, which is necessary to fit  $t'_{\text{GeSe}}(r)$ , does not correspond to an intramolecular distance in ethanelike dimers. This suggests *additional* Ge-centered motifs comprising defected tetrahedra wherein three Se reside at 2.36 Å and another Se at 3.02 Å. The Ge-Se coordination number for the 3.02 Å peak of 0.29(5) then gives a maximum fraction of Ge in the defected tetrahedra of 29(5)% such that the minimum fraction of Ge in regular  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedra is 52(6)%. These fractions are consistent with those found in a recent molecular dynamics calculation [20] and invoke the question as to how such a large number of intrinsic defects can be reconciled with the appearance of pronounced intermediate range atomic ordering.

The present work demonstrates that defects in disordered materials can be identified by the careful use of diffraction methods. It will therefore provide a new stimulus for tackling the basic problem of the structure of this prototypical glass and thereby its atomic dynamics and phenomena such as photostructural change.

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