Rigidity Percolation and Molecular Clustering in Network Glasses

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^{129}I Mössbauer spectra of g-Ge_xSe_{1-x} alloys display a local maximum in the site-intensity ratio $I_B/I_A(x)$ at the critical composition $x = x_c = 0.23 \pm 0.02$. This observation is consistent with the realization of mechanical critical behavior in a covalent network glass recently predicted by Phillips and Thorpe. We identify x_c with the onset of percolation of a specific molecular fragment based on the layered form of c-$GeSe_2$.

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Phillips[1] and independently Thorpe[2] have predicted that when the average coordination number $\langle m \rangle$ of a three-dimensional covalent network in mechanical equilibrium equals an optimal value of 2.4, a condition for mechanical critical behavior exists. In undercoordinated ($\langle m \rangle < 2.4$) networks, the number N_c of interatomic forces (bond-bending and bond-stretching) per atom visualized to act as constraints is less than the network dimensionality $N_d(=3)$, the number of degrees of freedom per atom. Under a shearing force such undercoordinated networks easily deform and thus possess a finite number of zero-frequency modes $f = N_d - N_c$. In overcoordinated networks ($\langle m \rangle > 2.4$), N_c exceeds N_d, and in general such networks contain macroscopic rigid domains. When $\langle m \rangle = 2.4$, $N_c = N_d$, and $f = 0$, the system is at the mean-field vector percolation threshold. This model represents the mathematical realization of the intuitive idea that a glass is a frozen liquid of very high viscosity, because a liquid is conventionally regarded as having no resistance to shear at zero frequency, while the high viscosity of the glass ($\sim 10^{15}$ times that of a normal liquid) reflects the proximity of the material to the percolation of mechanical rigidity.

Binary Ge_xSe_{1-x} glasses offer an attractive test system for these ideas because the coordination numbers m of Ge and Se are respectively 4 and 2 over the composition range $0 < x < \frac{1}{3}$. The ease of preparing bulk glasses by water quenching and the flexibility of tuning $\langle m \rangle = 2(x+1)$ of the glass network by merely changing the alloy composition x is convenient in practice. Theoretically, the threshold composition x_c^t corresponding to complete satisfaction of mechanical critical behavior is given by $2.4 = 2(x_c^t + 1)$, i.e., $x_c^t = 0.20$. We have studied these binary glasses in the range $0 < x < \frac{1}{3}$ by use of ^{129}I Mössbauer emission spectroscopy. The application of this method to probe the morphological structure of network glasses is discussed elsewhere.[3,4] In the present work we show that the Mössbauer site-intensity ratios studied as a function of x provide dramatic evidence of threshold behavior at $x = x_c = 0.23(2)$. This behavior is found to correlate well with molar volumes[5] and Raman-mode frequencies,[6] both studied as a function of x by previous workers. The present microscopic experiments provide new insights into the nature of the spontaneously rigid domains prevailing in the overconstrained ($x > x_c$) networks. These domains are identified with assemblies of specific molecular clusters described later. It appears that the phenomenon of molecular clustering in overcoordinated glassy networks is a general property of covalent glasses and, furthermore, the experimentally realized mechanical thresholds usually occur in the slightly overconstrained regime ($N_c > N_d$) predicted by the simple count of constraints N_c in the mean-field theoretical descriptions.[1,2]

Figures 1 and 2(a) summarize the principal results. Mössbauer emission spectra of g-$Ge_x(Te_{0.01}Se_{0.99})_{1-x}$ alloys in the range $0 < x < \frac{1}{3}$ exhibit in general two types of chemically inequivalent ^{129}I sites (Fig. 1) which are characterized by nuclear quadrupole couplings of $-890(10)$ MHz (site A) and $-1385(10)$ MHz (site B). The origin of these Mössbauer sites has been discussed previously.[3,4] Specifically, site B is identified with an I-Se σ bond resulting from a Te

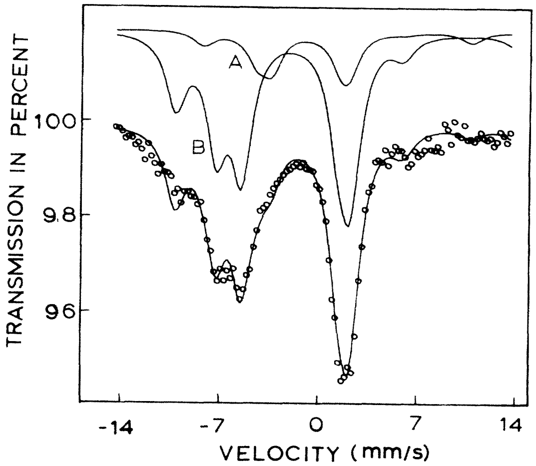

FIG. 1. ^{129}I Mössbauer emission spectrum of g-$Ge_x(Se_{0.99}Te_{0.01})_{1-x}$ alloy at $x = 0.20$ showing presence of the two chemically inequivalent ^{129}I sites A and B with the ratio $I_B/I_A = 4.0 \pm 0.3$. A random cross-linked network model would require the ratio I_B/I_A to be an order of magnitude smaller. See Fig. 2(a).

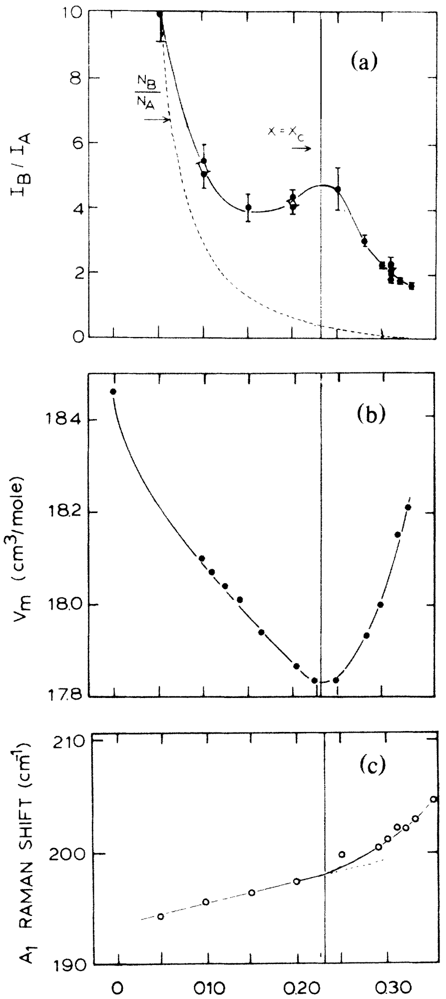

FIG. 2. Mössbauer site-intensity ratio $I_B/I_A(x)$ studied as a function of x in g-$\mathrm{Ge}_x(\mathrm{Se}_{0.99}\mathrm{Te}_{0.01})_{1-x}$ alloys. The I_B/I_A systematics reveal a peak centered at the critical composition $x = x_c = 0.23(2)$. At $x = 0$ (i.e., g-Se) only B sites are observed (Ref. 3) corresponding to $I_B/I_A \rightarrow \infty$. The dashed curve represents a theoretical plot of the site population ratio $N_B/N_A(x)$ based on a random cross-linked chain model. See Ref. 8 for details. (b) Molar volumes of g-$\mathrm{Ge}_x\mathrm{Se}_{1-x}$ alloys as a function of x, taken from the work of Feltz, Aust, and Bleyer (Ref. 5). (c) A_1 Raman-mode frequencies of $\mathrm{Ge(Se}_{1/2})_4$ tetrahedra in g-$\mathrm{Ge}_x\mathrm{Se}_{1-x}$ alloys as a function of x, taken from the work of Murase *et al.* (Ref. 6).

parent site that is twofold coordinated either to Se near neighbors or to a Se and a Ge near neighbor. This is a point discussed elsewhere.[3,4] Site A, on the other hand, represents an I-Ge σ bond which results from a Te parent that is twofold coordinated to Ge near neighbors. The site-intensity ratio $I_B/I_A(x)$ deduced from a standard deconvolution of the spectra is plotted as a function of x in Fig. 2(a). Several significant features of the I_B/I_A trend can be observed. We note, for example, that although $I_B/I_A(x)$ ratio declines steadily with x in the range $0 < x < 0.15$, this trend is qualitatively interrupted once x exceeds 0.15. Specifically, we observe a broad peak centered at $x = 0.23 \pm 0.02$. Furthermore, the ratio $I_B/I_A(x)$ is found to extrapolate[3,4] to a finite value of 1.60(5) at the stoichiometric composition $x = \frac{1}{3}$.

One of the more popular descriptions of the present glasses consists of a *random* cross-linked chain network.[7] In this model Ge atoms are visualized to act as cross links between Se rings or chains. The cross-linking process continues with x, until at $x = \frac{1}{3}$, a fully polymerized random network of tetrahedral $\mathrm{Ge(Se}_{1/2})_4$ units is formed as the natural description of the stoichiometric GeSe_2 glass. We have calculated the expected x variation of the Mössbauer-site population ratio $N_B/N_A(x)$ for this model by use of statistical mechanics and have plotted the results[8] of this calculation in Fig. 2(a) as the dashed curve. As anticipated, $N_B/N_A(x) \rightarrow \infty$ at $x = 0$ since only B sites are possible in a Se glass, while $N_B/N_A(x) \rightarrow 0$ at $x = \frac{1}{3}$ since only A sites are possible in a GeSe_2 network where each Se site acts as a bridge between $\mathrm{Ge(Se}_{1/2})_4$ units. In the composition range $0 < x < 0.10$, the cross-linked chain model appears to be qualitatively correct. At $x > 0.10$ the $I_B/I_A(x)$ trend is, however, qualitatively incompatible with the $N_B/N_A(x)$ trend based on such a model.

To visualize the structural implications of the Mössbauer-spectroscopy results at $x > 0.10$, it is instructive to recall that in these experiments one makes use of the oversized chalcogen Te (covalent radius 1.36 Å) to probe Se sites (covalent radius 1.16 Å) of the network. In an easily deformable network, Te probe atoms can be expected to almost randomly[8] replace available Se sites (A or B) since the local bonding requirements of the oversized probe are met with little or no strain accumulating in the bonds. However, in a network made up of a domain structure, where each domain represents a spontaneously rigid cluster of tetrahedral units, the oversized Te probe atoms can be expected to exhibit widely different site preferences. Specifically, probe atoms can be expelled from the rigid cluster interior either to the cluster surface or even possibly to the intercluster region so as to minimize strain. We visualize the domains in the present glasses to consist of molecular fragments of the layered form of GeSe_2 whose edges have been reconstructed (Fig. 3) to have Se-Se topological defects.[9] In such clusters, we have already noted [3,4] that Te site-preference energies favor surface or edge Se site occupation over interior Se sites by a factor of 13 or more. In Fig. 2(a), the mild increase in $I_B/I_A(x)$ leading to the peak at $x_c = 0.23$ provides a signature of such molecular clusters *nucleating* in the network. Specifically, tetrahedral $\mathrm{Ge(Se}_{1/2})_4$ units prevailing at $x > 0.10$ begin to coalesce progressively in a *nonran-*

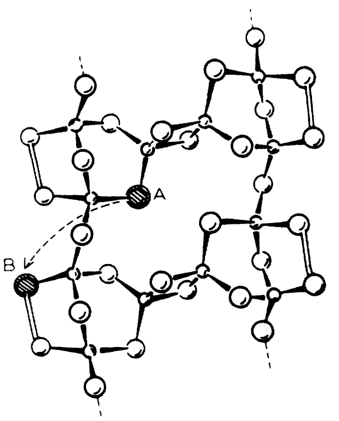

FIG. 3. Molecular fragment of the layered form of *c*-$GeSe_2$ whose edges have been reconstructed to have Se-Se bonds, following Bridenbaugh *et al.* (Ref. 9). The cluster has natural provision for interior (A) and edge (B) Se sites observed in the spectrum of Fig. 1. The oversized Te probe atoms selectively replace the Se edge sites because this replacement strain relieves the Se-Se dimer bond.

dom fashion to nucleate the layerlike molecular fragment of Fig. 3. In this compacted fragment the tetrahedra link in two ways: These either share an edge or a corner. The corner-sharing tetrahedra form a chain (Fig. 3). The chains are laterally coupled by a pair of edge-sharing tetrahedra to form a ladder. In the composition range $0.10 < x < 0.22$ we visualize Te probe atoms to be rapidly expelled (see Fig. 3) from the cluster interior (where only A sites occur) to cluster edge sites (where only B sites occur). This results in a selective transfer of probe atoms from A to B sites and thus qualitatively reverses the I_B/I_A trend. In this composition range the molecular clusters are probably ribbonlike, i.e., small in lateral extent (two corner-sharing chains) but long in the other dimension. Once $x > 0.24$, the precipitous drop in I_B/I_A [Fig. 2(a)] is understood in terms of the ribbonlike clusters growing in lateral dimension. We are suggesting that the adjacent clusters fuse with Ge atoms cross linking the cluster edges, and leading to cluster-size growth from a two-corner–sharing chain at $x = 0.23$ to a six- or eight-corner sharing chain at $x = \frac{1}{3}$. Such growth reduces the surface-to-volume ratio of Se sites in the clusters which is tracked by the ratio I_B/I_A. These ideas lead to a totally different structure of $GeSe_2$ glass as composed of large molecular clusters having a lateral extension of six to eight corner-sharing chains for which independent evidence was provided earlier[4] from ^{119}Sn Mössbauer spectroscopy. The extremum in $I_B/I_A(x)$ at $x_c = 0.23$ reflects a maximum in the reconstructed internal surface area of the glass network. Physically this situation corresponds to a threshold between *homogeneous nucleation* and subsequent *growth* of the clusters once the clusters contact or percolate at x_c.

The mechanical critical behavior at $x_c = 0.23 \pm 0.02$ described here correlates exceedingly well with results of several other experiments reported in other laboratories. Notably, molar volumes (V_m) of these glasses reported by Feltz, Aust, and Bleyer[5] also display [Fig. 2(b)] a threshold behavior at $x_c = 0.23 \pm 0.02$, the same composition. Ge cross linking of quasi 1D Se chains leads to a progressive densification of the network as $\langle m \rangle$ increases linearly. The abrupt reversal of this trend signaled by a change in slope dVm/dx at $x = x_c$ can be understood in terms of van der Waals–mediated intercluster repulsion (lone-pair repulsion) which leads to growth of free volume once the clusters percolate. Murase and Fukunaga[6] recently noted in Raman scattering that the x variation of the A_1 mode frequency [see Fig 2(c)] switches from linear at $0 < x < x_c$ to a superlinear behavior at $x_c < x < \frac{1}{3}$, with $x_c = 0.23 \pm 0.03$. The symmetric stretch (A_1 mode) of $Ge(Se_{1/2})_4$ tetrahedral units apparently undergoes a blue shift on account of intertetrahedral couplings as the network is locally compacted in the layered geometry of the molecular clusters. The linear blue shift of the A_1-mode frequency at $x < x_c$ is merely a reflection of the growing number of tetrahedra that are present in the nucleated clusters. At $x > x_c$, this fraction grows more rapidly as the molecular clusters percolate and overwhelm the bulk of the network. Perhaps most remarkable is the similarity between the composition dependences of I_B/I_A [Fig. 2(a)] and several kinetic measurements of activation energies for glass relaxation as well as the viscosity of the supercooled liquid.[10,11] These show an abrupt quenching of relaxation by bond breaking (as found in Se) for $0.10 < x < 0.16$ which means that the "the structure is blocked up in its native state,"[11] which we explain by formation of the clusters shown in Fig. 3.

In conclusion, we have presented microscopic evidence for structural changes that are consistent with the Phillips-Thorpe model for mechanical critical behavior in a binary covalent network glass. The Mössbauer experiments are insightful because these provide a link between the strictly mechanical aspects emphasized by theory and the structural aspects probed by experiments. We identify the spontaneously rigid domains as the reconstructed $GeSe_2$-like molecular clusters. The success of the present microscopic experiments stems largely from the use of an oversized isovalent probe atom that is an unusually sensitive gauge of network rigidity through site occupancy. Macroscopic experiments employing ultrasonic attenuation,[12] on the other hand, have been surprisingly less informative, probably because van der Waals forces coupling the floppy chains at $x < x_c$ are not much weaker than the intrachain covalent forces and do support phonon propagation in these heterogeneous materials. One is struck by the small but systematic difference between the observed ($x_c = 0.23$) and the theoretically predicted ($x_c^t = 0.20$) critical compositions. This result is of interest because it is quite similar in character to the one documented earlier[13] on the $Ge_{1-y}Sn_ySe_2$ ternary. In those experiments the average number of constraints per atom (N_c) of the network were tuned to N_d by cation alloying. One found that the observed mechanical critical composition of $y_c = 0.35$ is again somewhat different from the theoretically predicted[14] composition $y_c^t = 0.40$. In both of these experiments, the simple count of constraints in the mean-field approach obviously underestimates N_c because the mechanical threshold in real glasses is found to occur in the slightly overconstrained regime ($N_c > N_c$). This may reflect incomplete mechanical configurational as well as thermal equilibration arising from the nucleation and arrested growth of submicrocrystalline clusters.[15]

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