Rigidity Percolation in the Germanium-Arsenic-Selenium Alloy System

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We have measured the elastic constants of two series of glasses in the Ge-As-Se system. Each series consisted of samples whose compositions were chosen to produce an average atomic coordination ($\langle r \rangle$) which ranged from 2 to nearly 3. Different local structures were produced by our making one series much higher in As content than the other. Despite this difference both series exhibited evidence of rigidity percolation near $\langle r \rangle = 2.4$.

The connection between the structure of amorphous materials and their dynamical properties is poorly understood. Until recently no quantitative predictions had been made. Since 1983 Thorpe and co-workers,[1-3] developing an idea first advocated by Phillips,[4] have advanced the simple topological approach of constraint counting to the point that quite testable predictions of elastic-constant behavior can be made.

Consider a network of N atoms, n_r of which have r bonds per atom. If the number of degrees of freedom, $3N$, exceeds the sum of the bond-length ($r/2$ per atom) and bond-angle ($2r - 3$ per atom) constraints, then the excess degrees of freedom are zero (i.e., low) energy or "floppy"[1] modes. The density of floppy modes, ρ_f, is the number of floppy modes divided by N:

$$\rho_f = \frac{3\sum_r n_r - \sum_r n_r [(r/2) + (2r - 3)]}{\sum_r n_r} = 6 - \tfrac{5}{2}\langle r \rangle ,$$

where $\langle r \rangle = \sum_r r n_r / \sum_r n_r$ is the average number of bonds per atom. This mean-field result should apply to a poorly cross-linked material consisting mainly of chains of divalent atoms. If the degree of cross-linking is increased, rigid regions with no floppy modes will form. At some point as the number and size of the rigid regions grows they will begin to contact one another and a percolation transition will occur. This simple calculation suggests that percolation should occur when $\rho_f = 0$ and $\langle r \rangle$ is 2.4. Simulations on a three-dimensional network of twofold-, threefold-, and fourfold-coordinated atoms indicate that a distinct increase in the elastic constants C_{11} and C_{44} begins to occur between 2.35 and 2.45[3] in good agreement with the mean-field prediction.[1] The crucial result of this simulation is that *the rigidity percolation is independent of atomic composition and therefore local structure.*

While the binary alloys $Ge_x Se_{1-x}$ display various anomalies near $\langle r \rangle = 2.4$[5] it is possible that they are chemical effects peculiar to the stoichiometry corresponding to this coordination. Furthermore, the elastic properties of this (or any other) glass system do not appear to have been measured across the proposed

percolation-transition region. By measuring the elastic constants of a ternary system we overcome both of these objections. The germanium-arsenic-selenium alloys are good glass formers over a very large range of compositions as is shown in Fig. 1. Because atoms of these elements are of similar size and form highly directional, short-range covalent bonds, it is easy to apply constraint-counting arguments to these glasses. We are unaware of any reports of ring formation or similar behavior which would complicate the picture of a connected network in the compositions corresponding to $\langle r \rangle$ near 2.4. We prepared two series of glasses as indicated in Fig. 1. The high-As-content series has samples with as much as 43% As while the maximum As concentration in the low-As series is 9%. Thus for any given $\langle r \rangle$ the local structure for the two series is quite different.

Four grams of high-purity Aldrich Gold Label powders (60–200 mesh) were placed in 6-mm-i.d. sili-
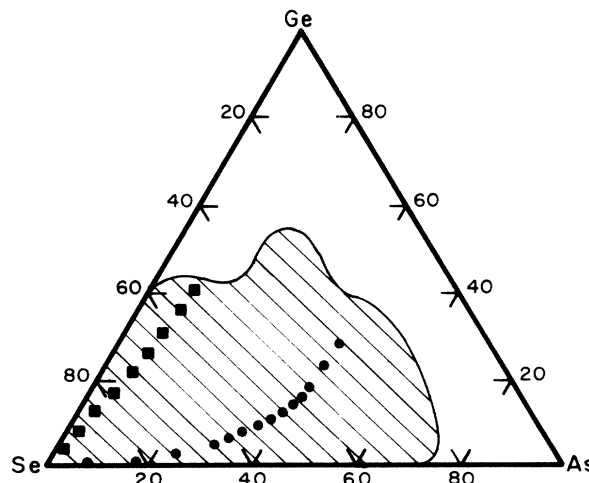

FIG. 1. Phase diagram for the Ge-As-Se system. The shaded part of the phase diagram shows the glass-forming region (Ref. 6). The high- (circles) and low- (squares) As-content compositions are as indicated. $\langle r \rangle$ increases monotonically in each series from lower left to upper right.

ca tubes which were then evacuated to $\sim 10^{-5}$ Torr and sealed. The tubes were rapidly heated to 900 °C in a rocking furnace and held there for 24 to 72 h. The samples were quenched at about 15 °C/min through the melting point and glass transition. Some high-Se-content samples were quenched from 600 °C to reduce the formation of bubbles. This rather low quench rate was necessary to prevent shattering of the glasses. A diamond wafering saw was used to cut 5-mm slices from the tubes which were then ground and polished with water and alumina. Subsequent analysis revealed only minor oxidation of the surface.

Because the quench rate was small, some effort was expanded to verify the amorphous nature of the samples. All samples were a uniform silver-grey in appearance and no signs of phase separation or crystallization were visible under an optical microscope. Differential thermal analysis indicated a second-order transition for 10-mg samples which had been powdered under acetone and dried prior to sealing in aluminum pans. An electron-microprobe analysis revealed no phase separation on a 2-μm scale and produced fringe patterns typical of amorphous materials. Si is soluble in As and the samples containing 30% or more As etched the silica tubes. The microprobe analysis indicates that for the four most highly connected samples in the high-As series the O content is (6-8)%. We assume that, in small amounts, Si will be chemically identical to Ge in the network.

These materials are opaque at 514.5 nm and Bril-

louin scattering could not be used to determine the sound speeds. It was just possible to make pieces of the alloys large enough to allow a variation of McSkimin's ultrasound-pulse-overlap method to be used. A pair of gate pulses were sent at a clock frequency, f_{clock}, to an Arenberg rf generator. The resulting coherent rf pulses were directed to an X- or AC-cut quartz transducer bonded to the sample with Nonaq stopcock grease or Salol, respectively. A time sufficient to allow the echo train to die out would pass before the next pair of rf pulses were generated. This technique allowed measurements to be made with many samples of marginal quality. The bulk of the error in these velocities arises from an uncertainty of when the echo from the first pulse was correctly overlapped with one from the second pulse. Because of the broken nature of the samples, the echoes did not al-
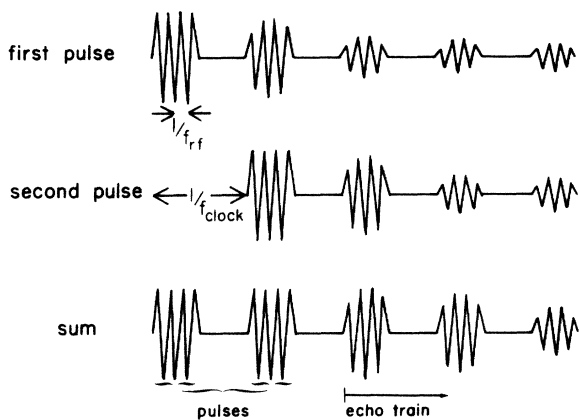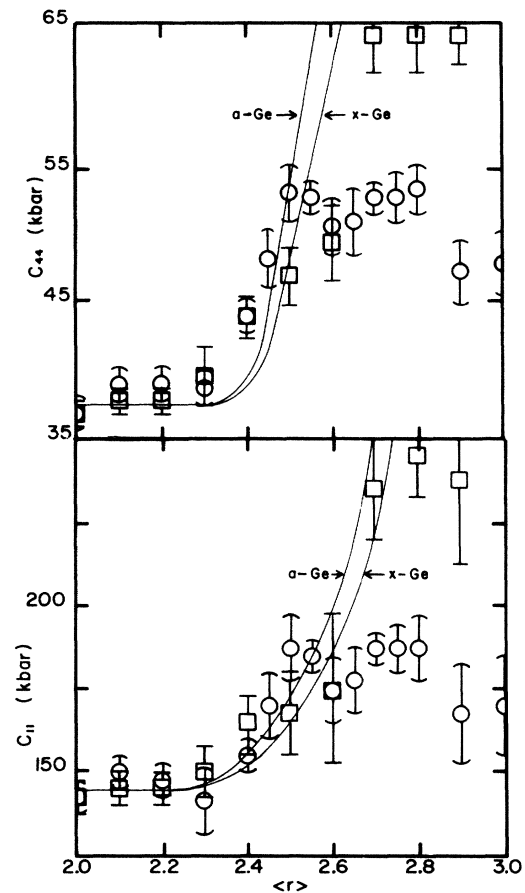
FIG. 2. When the first echo from the second pulse exactly overlaps the second echo from the first pulse, $1/f_{\text{clock}}$ is the time required for the sound pulse to cross the sample twice. To slip the second echo train past the first by one period of the rf wave requires a fractional change in the clock frequency of $\Delta f_{\text{clock}}/f_{\text{clock}} = f_{\text{clock}}/f_{\text{rf}}$. This was usually (1-3)%. Because the second pulse could be suppressed and the echoes from the first pulse were not affected by changes in f_{clock}, it was possible to use pulse widths as large as 2 μs with clock frequencies as high as 300 kHz.

FIG. 3. C_{44} (upper) and C_{11} (lower). Elastic constants are plotted vs $\langle r \rangle$ for the low- (squares) and high- (circles) As series of glasses. The compositions of the samples can be read off of Fig. 1. Solid lines are taken from He and Thorpe (Ref. 3) as outlined in the text. We note that the elastic constants cited for amorphous Ge (Ref. 7) are greater than those found in crystalline Ge (Ref. 8). The curves on this plot should be viewed with some caution.

ways have clearly defined edges or centers. While a unique feature could usually be found to aid in our correctly overlapping the two echoes, an error of one or even two periods of the 15-MHz rf signal is quite possible. This led to errors of as much as 5% in sound speed (10% in C_{11} and C_{44}), far greater than normal for ultrasound experiments (see Fig. 2).

Figure 3 shows our results. The most important feature is the increase in the elastic constants near $\langle r \rangle = 2.4$. He and Thorpe[3] calculate the dependence of C_{11} and C_{44} on $\langle r \rangle$ using a 512-atom diamond lattice supercell ($\langle r \rangle = 4$), cutting bonds at random to reduce $\langle r \rangle$ but not allowing any single-bonded atoms. In order to compare our experimental data with the calculation of He and Thorpe we set the $\langle r \rangle = 2$ value of the elastic constants equal to our measured values for pure selenium. The subsequent calculated points were scaled by a multiplicative factor chosen so as to make the $\langle r \rangle = 4$ values equal to the measured values for either amorphous[7] or crystalline[8] Ge. In He and Thorpe's model, the elastic constants fall to zero as $\langle r \rangle \rightarrow 2$; clearly, noncentral forces, not accounted for in their calculation, contribute significantly. The inclusion of dihedral-angle forces will introduce some slope into the curve below $\langle r \rangle = 2.4$[9] and this could improve the fit to the data in this region. Between $\langle r \rangle = 2.3$ and 2.5 the agreement is reasonable. At $\langle r \rangle = 2.4$ one sample has 5% As and the other 30%; the nearly identical behavior of these structurally dif-

ferent materials is strong evidence for the existence of a rigidity percolation transition in these glasses.

Above $\langle r \rangle = 2.6$ the elastic constants of the two series of glasses no longer track each other and differ dramatically from Thorpe's prediction. We believe that the explanation of this behavior can be found in a breakdown of the continuous network. Thus, in addition to demonstrating the success of constraint counting at low coordinations, these data also show where such arguments become invalid as chemical ordering begins to dominate topological considerations in this system. We intend to explore this more fully in a future paper.

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