Direct Evidence for Stiffness Threshold in Chalcogenide Glasses

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Raman scattering in Ge_xX_{1-x} glasses, $X = $ S or Se, reveals that the frequency of A_1 modes of corner-sharing $Ge(X_{1/2})_4$ tetrahedra displays a discontinuous jump between $x = 0.225$ and $x = 0.230$, which coincides with a minimum in the nonreversing heat flow at the glass transition T_g established from modulated differential scanning calorimetry. These results constitute direct evidence for a stiffness threshold at a mean coordination $\langle r \rangle_c = 2.46(1)$, which is well described by mean-field constraint counting procedures. [S0031-9007(97)03283-3]

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A covalently bonded random network progressively stiffens as its connectivity or mean coordination number $\langle r \rangle$ increases. Networks consisting of chains (every atom having two nearest neighbors, $r = 2$), as in elemental S or Se, are mechanically floppy because the number of nearest-neighbor bonding constraints [1] per atom (=2) are less than 3, the degrees of freedom per atom. The reverse is the case for networks composed of tetrahedral units ($r = 4$), such as those of elemental Si or Ge, which are thus intrinsically rigid. In random networks, enumeration of mean-field atomic constraints due to bond stretching and bond bending forces as a function of mean coordination $\langle r \rangle$ reveals [1,2] that the number of zero-frequency (floppy) modes per atom extrapolates linearly to zero when $\langle r \rangle$ increases to 2.40. Thus at a critical mean coordination $\langle r \rangle_c = 2.40$, the number of constraints per atom (n_c) equals [1] the degrees of freedom per atom (n_d), and mean-field theory predicts [2] the onset of rigidity. In the macroscopically rigid region ($\langle r \rangle > \langle r \rangle_c$), numerical simulations [3] in random networks show that elastic constants (C) display a power-law behavior with $\langle r \rangle$, i.e., $C \sim (\langle r \rangle - 2.4)^p$ with $p = 1.40$.

These simple and elegant ideas on mean-field atomic constraints in random networks have attracted particular attention in glass science. Experiments on chalcogenide glasses not only display evidence of a threshold behavior in the electronic [4], thermal [5], vibrational [6,7], and structural [8,9] properties when $\langle r \rangle$ approaches 2.40 with one exception [10], but the glass forming tendency itself appears to be optimized [1,11] when the network becomes mechanically critical, i.e., $n_c = n_d$. In spite of these developments, understanding of the physical nature of the stiffness transition, in network glasses, has remained largely *qualitative*. In this Letter we report Raman scattering and temperature modulated differential scanning calorimetry measurements (MDSC) in binary Ge_xS_{1-x} and Ge_xSe_{1-x} glasses which provide direct evidence for the stiffness threshold near $\langle r \rangle_c = 2.46(1)$ in both glass systems with the local elasticity displaying the anticipated power-law behavior in the rigid regime. The shift of the stiffness transition to a value slightly larger than the mean-field value of 2.40 may be generic for IV-VI glasses, and is shown to be associated with floppiness of chalcogen chain segments in which the bond-bending constraint at chalcogen sites is intrinsically broken.

The binary Ge_xX_{1-x} glass systems, with $X = $ S or Se form homogeneous bulk glasses over wide compositions ($0 < x < 0.43$) and have been the subject of previous Raman [12–14] and Mössbauer [8] spectroscopic investigations from which details of glass molecular structure have evolved. These glass systems are attractive also because stoichiometric chemical compounds occur at compositions ($x = 0$, 1/3, 1/2) far removed from the anticipated stiffness threshold ($x = 1/5$). We have synthesized about 40 glass compositions starting from 99.9999% elemental Ge, Se, and S, sealed in evacuated ($<5 \times 10^{-7}$ Torr) silica ampoules in the desired molar ratio. Melts were homogenized at 1000 °C for at least 48 hours and then equilibrated at about 50 °C above the liquidus for an additional 24 hours before quenching in water. As a check on glass compositions, we measured glass transition temperatures $T_g(x)$ using a TA Instrument Model 2920 MDSC and the results (Fig. 1) show T_g's to increase monotonically with x. Micro-Raman measurements performed in a

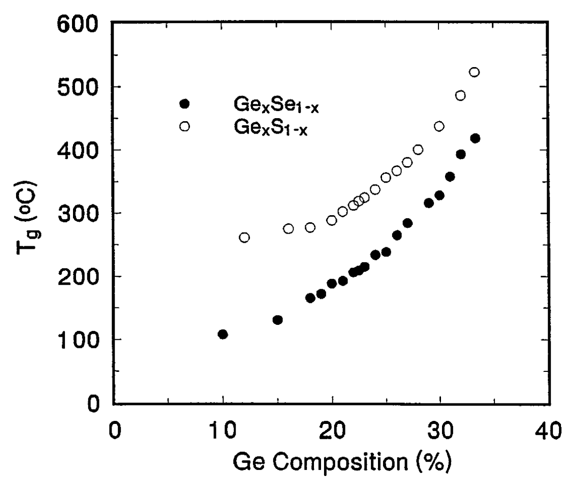

FIG. 1. T_g of Ge_xS_{1-x} glasses (top) from DSC measurements taken at a 20 K/min scan rate, and of Ge_xSe_{1-x} glasses (bottom) from MDSC measurements at a scan rate of 3 K/min and a modulation of ± 1 K/100 sec.

backscattering geometry, using a triple monochromator (ISA, Inc. Model T64000) equipped with a microscope attachment and a CCD detector, showed the glass samples to be homogeneous on a scale of a few microns. A Joule-Thompson refrigerator (MMR Technologies, Inc., Model 2300) was used for low-T measurements. Figure 2 displays Raman spectra observed at selective Ge-Se (Ge-S) glass compositions taken using <1 mW of 647.1 nm (514.5 nm) exciting radiation and a CCD detector.

The A_1 symmetric stretch of corner-sharing (CS) $Ge(X_{1/2})_4$ units gives rise [13,14] to modes at about 200 cm^{-1} for X = Se, and at about 340 cm^{-1} for X = S glasses. We have closely followed the mean frequency $\nu(x)$ of these A_1 modes by least-squares fitting the observed line shapes, and the results are reproduced in Figs. 3(a) and 3(b). We find that $\nu(x)$ increases linearly [12] in the $0.10 < x < 0.225$ composition range, displays

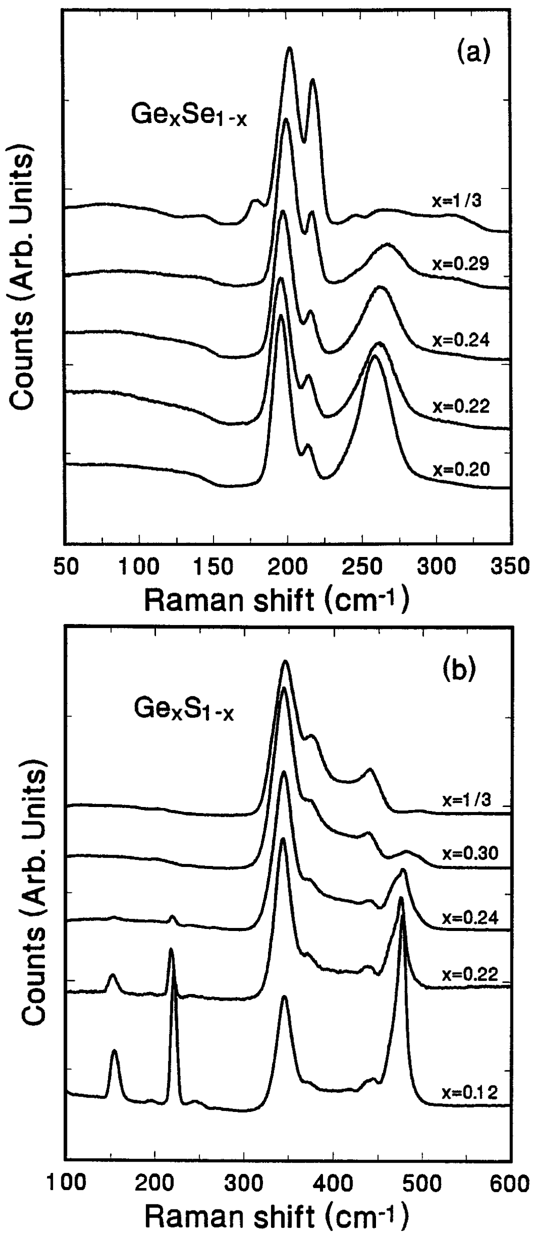

FIG. 2. Raman scattering at selected glass compositions in indicated binaries displaying growth of A_1 mode of CS tetrahedra at the expense of corresponding chain and/or ring modes with increasing Ge content. A typical spectrum is the result of a 10 s integration time and 10 accumulations with a CCD detector. No smoothing of the data was performed.

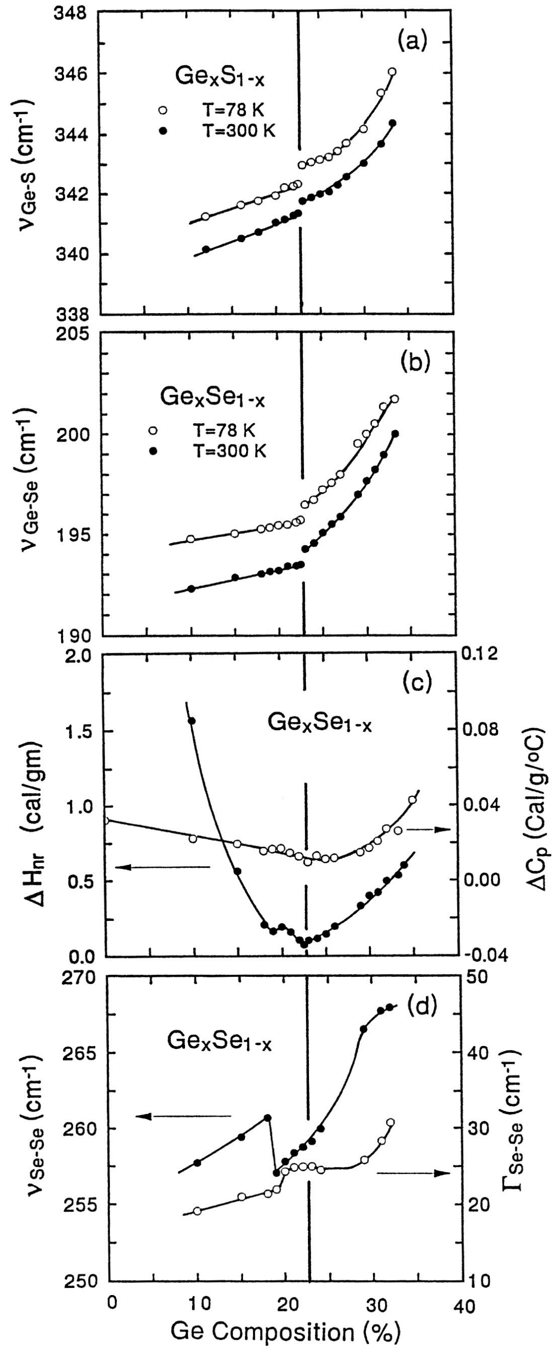

FIG. 3. (a) A_1 mode frequency of CS $Ge(S_{1/2})_4$ units and (b) $Ge(Se_{1/2})_4$ units, (c) relative changes in nonreversing heat flow $\Delta H_{\mathrm{nr}}(T_g)$ (filled circles) and specific heat change $\Delta C_p^{\mathrm{rev}}$ (open circles) from MDSC measurements, and (d) A_1 mode frequency of Se_n chains or rings (filled circles) and mode linewidth (open circles), each studied as a function of Ge concentration x in indicated binary glasses. The lines drawn through data points are to guide the eye.

a discontinuous jump between $x = 0.225$ and $x = 0.230$, and then increases superlinearly at higher x. To characterize the superlinear variation, we have fit ν^2 using the following power law [3]:

$$\nu^2 - \nu_c^2 = A(\langle r \rangle - \langle r \rangle_c)^p. \quad (1)$$

In Eq. (1), the mean coordination of the binary glasses $\langle r \rangle = 2(1 + x)$, since Ge and the chalcogen atoms X are, respectively, 4- and 2-fold coordinated. ν_c is the Raman shift corresponding to $x_c = 0.23$ or $\langle r \rangle_c = 2.46$. The power p, obtained by plotting $\log(\nu^2 - \nu_c^2)$ against $\log(\langle r \rangle - \langle r \rangle_c)$ (see Fig. 4), is $p = 1.29(3)$ and $p = 1.33(1)$ for the S and Se glasses, respectively, at 78 K. At 300 K, somewhat lower values $p = 1.21(2)$ and $p = 1.20(3)$, respectively, are obtained.

In MDSC measurements, one can decompose the total heat flow at T_g into a reversing component (that follows the programmed sinusoidal heating rate) and a nonreversing one. Results on Ge-Se glasses for the nonreversing heat flow $\Delta H_{\rm nr}(T_g)$ and the specific heat change $\Delta C_p^{\rm rev}$ (deduced from the reversing heat flow) are included in Fig. 3(c). Remarkably, while $\Delta C_p^{\rm rev}$ remains largely constant, $\Delta H_{\rm nr}$ shows a well-defined minimum near $x = x_c$ which coincides with the abrupt increase in $\nu(x)$.

The addition of Ge to a Se or S glass serves to cross-link chains of chalcogen X(=S or Se) atoms, promoting formation, first of CS, and then of edge-sharing (ES) $Ge(X_{1/2})_4$ units at the expense of X_n chains, thereby compacting [9] the network and accumulating internal strain. Thus increasing x simulates an external pressure on the network as is corroborated by the similar changes they both produce on the Raman spectra of the chalcogen-rich glasses [12]. In the process S_8 monomers, which are stable at low x, open up to form part of the network backbone [12,14]. This is clearly seen from the extinction of the sharp modes of S_8 units at 158, 218, and 474 cm^{-1}

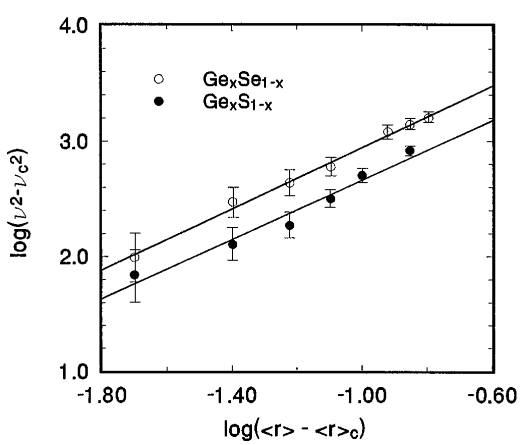

FIG. 4. Plot of $\log(\nu^2 - \nu_c^2)$ against $\log(\langle r \rangle - \langle r \rangle_c)$ gives the power p describing the superlinear variation of elastic constants in the rigid region for Ge-S and Ge-Se glasses. To avoid interference from Ge_2S_6 units that contribute a mode near 340 cm^{-1}, glass compositions near GeS_2 are excluded in the analysis of p.

both with increasing x [Fig. 2(b)], and with application of hydrostatic pressure [12] to a $Ge_{0.15}Se_{0.85}$ glass, for example. A similar indication of the opening up of Se_8 rings to form Se_n chain segments occurs in the Ge-Se glasses near $x \gtrsim 0.19$. Raman active A_1 stretch [14] of Se_8 rings at 250 cm^{-1} and of Se_n chains at 235 cm^{-1}, although partially resolved at low x, merge into a broad mode (at 255 cm^{-1}) with increasing x, until at $x \gtrsim 0.19$, the mode centroid abruptly redshifts by $\sim$4 cm^{-1} and further broadens [Fig. 3(d)]. [S_8 and Se_8 rings present in binary As_xX_{1-x} glasses (X = S or Se) at low x (<0.10), also open up with x as network strain accumulates and the rings become extinct [14] when x approaches 0.27(0.20) for X = S(Se).]

The A_1 mode of $Ge(X_{1/2})_4$ units is a symmetric breathing motion of the 4 chalcogens about the central Ge atom. The *scale* for the underlying mode frequency ν is set by the Ge-Se or Ge-S *bond-stretching force constant and the mass of the chalcogen*. The bridging angle between CS tetrahedra about the chalcogens [15] deviates from $\pi/2$ by about 10°, so that *mode frequency changes* in the glasses derive from *intertetrahedral couplings*. The smallness of the frequency shifts suggest that the A_1 mode is weakly coupled to a few nearby tetrahedra. This is consistent with calculations [15] of the inverse participation ratio of the A_1 mode in *ab initio* molecular dynamics. Furthermore, since CS tetrahedra represent the majority component of the network around $x \sim 0.2$, their vibrational behavior becomes a sensitive gauge of the overall network connectivity in a global sense. The abrupt blueshift of the A_1 mode frequency $\nu(x)$ at $x_c = 0.23$ shown in Figs. 3(a) and 3(b), constitutes *direct evidence* for the *onset of rigidity* in both the glass systems investigated.

Additional support for our interpretation derives from two other observations; (1) the power p characterizing the nonlinear variation of $\nu^2(x)$ at $x > x_c$, and (2) the nonreversing heat flow $\Delta H_{\rm nr}(x)$ minimum at $x = x_c$. (1) Since $\nu^2 - \nu_c^2$ is largely a measure of network elasticity on a local scale, its variation with $\langle r \rangle$ would be well described by the numerical experiments of Ref. [3] which include short-range forces only in simulating the elastic behavior of random networks. The measured values of p in the two glass systems decrease with temperature due to anharmonic effects [16]. The mean value of $p = 1.31(3)$ at $T = 78$ K (Fig. 4) in the two glass systems should be fairly close to the $T \to 0$ K value. It compares well with the numerical prediction [3] of $p = 1.40$. In contrast bulk elastic constants [10] do not display such a power-law behavior because long-range interactions become important [8] at long wavelength. They also alter the functional dependence of elastic constants on $\langle r \rangle$. (2) A minimum in $\Delta C_p^{\rm tot}$ at the stiffness threshold was inferred earlier [5] from DSC measurements, and understood to be the consequence of a strong resistance of the network to structural degradation (minimum fragility) upon heating across T_g. The present MDSC results highlight that the minimum fragility at the stiffness threshold [5] actually derives from a minimum in $\Delta H_{\rm nr}$, while $\Delta C_p^{\rm rev}$ remains nearly constant [Fig. 3(c)] at about 0.02 cal/g/°C. The $\Delta H_{\rm nr}$ variation with $\langle r \rangle$ [Fig. 3(c)] mimics the activation energy E_a ($\langle r \rangle$) for stress relaxation with $\langle r \rangle$ in chalcogenide glasses [17]. These results suggest that when $\langle r \rangle = \langle r \rangle_c$, structural relaxation of the glass network proceeds with minimal enthalpic changes because the miniscule network stress is uniformly spread when the network is mechanically critical ($n_c = n_d$).

The small *but systematic* shift of $\langle r \rangle_c = 2.46(1)$ from the mean-field value, $\langle r \rangle_c = 2.40$, suggests an additional significant feature of network dynamics, namely, the breaking of certain constraints. The floppy chalcogen chain segments connecting the rigid tetrahedral (ES and CS) units must respond to the network stiffening at $x > 0.20$ by locally distorting [as revealed by an abrupt increase in the width of the A_1 mode of Se_n chain Fig. 3(d)]. We speculate that the *bond-angle constraint* at chalcogen atoms in such chain fragments is *intrinsically broken*. For a network possessing a fraction, m_2/N, of 2-fold coordinated atoms with broken bond-angle constraint, the stiffness threshold is given [18] by

$$\langle r \rangle_c = 2.4 + 0.4(m_2/N). \qquad (2)$$

An approximate value [19] of $m_2/N = 0.08(2)$ can be deduced from a random network model [13] of both these glass systems and leads to $\langle r \rangle_c = 2.43(1)$ from Eq. (2) in reasonable accord with present Raman result of 2.46(1) and the earlier [8] Mössbauer spectroscopy result. More reliable estimates of m_2/N will result from inelastic neutron scattering [9] and molecular-dynamic simulations [15] in future and permit a more stringent test of ideas introduced here.

In summary, the present Raman scattering and MDSC measurements on binary Ge-S and Ge-Se glasses reveal a stiffness threshold at a mean coordination $\langle r \rangle$ of 2.46(1), which can be understood well in terms of mean-field constraint theory if the bond-angle constraint at chalcogen atoms in distorted chain fragments is considered to be broken. These ideas would be expected to extend to other IV-VI glass systems (Ge-Te, Si-S, Si-Se). Furthermore, one would expect that in ternary glass systems, such as IV-V-VI glasses (Ge-As-Se), as the content of the group V element in the alloy glasses increases, the concentration of floppy chalcogen chain segments would decrease and vanish at the composition As_2Se_3 ($m_2/N \rightarrow 0$) to lower the stiffness threshold from 2.46 to 2.40.

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[19] $Ge_xSe_{1-x} = x GeSe_a + (1 - x - ax)Se$, the first term comes from CS and ES units as well as isolated tetrahedra(IT) in chalcogen chains, while the second term from Se_n-chain fragments, with the coefficient $1 - x - ax = m_2/N$. By weighting the nine possible CS, ES, and IT configurations with their frequency of occurrence at $x = 0.23$ in a random network model developed in Ref. [13], we obtain $a = 3.07(2)$ and $m_2/N = 0.08(2)$. In this model Raman cross sections of CS, ES, and IT units are *assumed* equal.