PHYSICAL REVIEW B VOLUME 39, NUMBER 12 15 APRIL 1989-II

Onset of rigidity in $Se_{1-x}Ge_x$ glasses: Ultrasonic elastic moduli

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(Received 12 September 1988)

The onset of rigidity in $Se_{1-x}Ge_x$ glasses is probed by room-temperature longitudinal and transverse elastic moduli determined by ultrasonic measurements. The longitudinal modulus displays linear behavior with increasing x up to $x=0.3$, corresponding to an average coordination number $\langle r \rangle=2.6$. The transverse modulus displays linear behavior with a slight upturn at $\langle r \rangle=2.4$, saturating beyond 2.5. The onset of rigidity percolation at $\langle r \rangle=2.4$, predicted on the basis of random-network models, is not seen. Other experiments indicate a rigidity threshold near 2.7. The present results are consistent with a departure from random-network models in the form of medium-range structural order.

INTRODUCTION

Se glass is the simplest, stable, twofold-coordinated polymer. As such its mechanical and vibrational properties are interesting. It is thought to consist mainly of tangled chains with some closing on themselves to form rings of various sizes. The chains are linked by covalent bonds and the forces between chains arise from van der Waals interactions. Each bond imposes mechanical constraints on the motion of the atoms to which it is linked. The constraints introduced by van der Waals forces are weak by comparison. Ge atoms, with their fourfold-bonding property, provide a means to crosslink the Se chains. Initially, the added Ge atoms must enter the chains randomly, and in so doing they increase the average number of constraints on each atom. If they continued to go in randomly, without the formation of molecular clusters, eventually a more rigid, random-covalent-network glass with chains linked in all directions would ensue. The system would go over from network-dimensionality one in g-Se to three in g-Ge.

Phillips[1] introduced and Thorpe[2] developed the notion of understanding the mechanical and structural properties of glasses in terms of the average number of mechanical constraints per atom. A system having fewer (more) constraints than the three mechanical degrees of freedom per atom is said to be underconstrained (overconstrained). The constraints are encountered in displacing the atom from equilibrium and depend on the type of bonds involved. In Se and Ge the stretching and bending of bonds provokes restoring forces which are much stronger than those which arise from distorting a dihedral angle. Hence, only stretching and bending constraints are counted. The number of bond-stretching constraints for atoms having r bonds is $r/2$ since each bond is shared by two atoms. The number of bond-bending constraints is $2r-3$, since beyond $r=2$ each new bond introduces two new angles. An underconstrained system admits the displacement of groups of atoms without the provocation of restoring forces and hence has a number of "floppy" modes. (Actually, the weaker forces ignored in counting constraints will come into play so that the floppy modes are shifted from zero to low frequencies.) Mechanically such a system is elastically soft. Ignoring fluctuations from the average ("mean-field" approximation), the fraction of modes which are floppy is given by the number of degrees of freedom per atom, minus the number of constraints per atom divided by the former: $f=2-5\langle r \rangle/6$, where $\langle r \rangle$ is the average number of bonds per atom. [In the $Se_{1-x}Ge_x$ system $\langle r \rangle=2(1+x)$. Thus $f=(1-5x)/3$.] When the number of constraints per atom just equals three, the floppy modes disappear and there is a mechanical threshold to an elastically more rigid system. The above equation shows that this is expected to happen at $\langle r \rangle=\frac{12}{5}$. Detailed computer simulations by Thorpe and co-workers[3] for random glassy alloys show that allowing for fluctuations has very little effect on this mean-field prediction. Furthermore, He and Thorpe[4] have made computer model calculations on the behavior of the elastic moduli to be expected in the vicinity of the threshold for percolation of a rigid cluster. These calculations show a smooth departure from zero, beginning at $\langle r \rangle=2.4$ and rising rapidly thereafter.

Phillips[1,5] has considered the consequences of the constraint model for the structure of glasses. He suggests that a system just at the rigidity threshold is likely to be a chemically ordered, random-covalent-network glass. A multicomponent overconstrained system, on the other hand, may seek relief from large-scale strains by reorganizing chemically into rigid and floppy molecular clusters characterized by the presence of internal surfaces and hence reduced network dimensionality. The natural clusters to be expected would be those present in the associated crystalline modifications.

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This paper presents ultrasonic determinations[6] of the elastic moduli used to make contact with the theoretical work of Ref. 4. The ultrasonic velocities are also used to estimate the Debye-model portion of the vibrational density of states determined by inelastic neutron scattering.[7]

EXPERIMENT

Samples were prepared at the University of Cincinnati with measured starting materials (Ge, 99.9999% and Se, 99.999% from AESAR, Johnson Matthey, Inc.) in 5 or 9 mm internal diameter, evacuated, quartz tubes. They were placed in a vertical furnace and the temperature was slowly raised at 950 °C over one day. The sample tubes were quenched in air horizontally and were replaced flipped over in the oven several times on the second day. On the third day the temperature was slowly lowered to approximately 50 °C above the liquidus temperature and maintained there for another 20 h. Samples with $x<0.3$ were vertically air quenched by removing them from the furnace at this point and allowing them to cool in room air. The $x=0.3$ samples were quenched in a bucket of room-temperature water. This quenching procedure is in accordance with the work of Azoulay *et al.*[8]

At Ohio University cylindrical samples about 5 mm thick were cut from the tubes with a carburundum saw. The cut surfaces were ground parallel and finely polished with 0.5 μm alumina in water. Either quartz or $LiNbO_3$ transducers were used to excite and detect ultrasonic wave pulses in the samples and they were attached with Nonaq stopcock grease or Apiezon N grease. The pulse-echo technique was employed using a Matec model 9000 at resonant frequencies of 10, 15, or 30 MHz. Measurements of both longitudinal and transverse wave velocities were made at 297 K. Sample mass densities were taken from previous measurements[9] in order to convert the measured velocities to longitudinal and transverse elastic moduli defined by $c_L=v_L^2\rho$ and $c_T=v_T^2\rho$. In most samples, a dozen or more well-defined echo pulses were seen from longitudinal waves while only two or three pulses were seen for transverse waves.

RESULTS

The 297-K results are presented in Table I and shown in Figs. 1–3. In Fig. 1 our results for c_L show that to within experimental error there is no significant departure from linearity over the measured range of $\langle r\rangle$ which includes the predicted percolation threshold at 2.4. c_{11} for *c*-Ge is 1289 kbar (Ref. 10) at room temperature and c_L for *g*-Ge is above this. Since the line fit to the data below $\langle r\rangle=2.4$ in Fig. 1 projected to $\langle r\rangle=4$ gives $c_L=327$ kbar, there must be an upturn beyond the range of measurements. The general behavior, then, namely soft moduli in Se-Ge alloys increasing rather suddenly, somewhere beyond $\langle r\rangle=2.7$, is consistent with the present results, but the predicted percolation threshold at 2.4 does not appear in these data. This is shown by the solid line in Fig. 1 which is the prediction of Ref. 4 modified to allow for the "background" elastic properties of the system (presumably arising from forces ignored in the calculation) and normalized to *c*-Ge.

c_T behaves in a similar fashion as seen in Fig. 2 except that there is some indication of a slight upturn around $\langle r\rangle=2.4$ which quickly saturates after 2.5. Again, the prediction of Ref. 4 modified as in the longitudinal case is shown as the solid line.

In Fig. 3 we see the measured sound velocities compared to previous work by Ota *et al.*[11] at 288 K. The transverse velocities are in substantial agreement. In general our longitudinal measurements are systematically lower than theirs by about 3%, more than is to be expected by the temperature difference between the experiments. The reasons for this are unknown. However, the slopes agree in both cases to within experimental error for data below $\langle r\rangle=2.4$. The data are more discrepant beyond $\langle r\rangle=2.5$ where Ref. 11 gives one point at $\langle r\rangle=2.6$ showing a definite upturn.

Also in Table I are shown the coefficients of the ω^2 term in the vibrational densities of states (DOS) calculated from the measured longitudinal and transverse wave velocities. These coefficients are given by $K=(4\pi/h^3N_A)(V_M/v_{\rm av}^3)$ where h is Planck's constant, N_A is

TABLE I. Ultrasonic properties of g-$Se_{1-x}Ge_x$. $\langle r\rangle$ is the average coordination number. The velocities were measured at 297 K by the pulse-echo technique in this work. The mass densities are taken from Ref. 9. The elastic moduli are calculated from the velocities and densities. K is the coefficient of the ω^2 term in the vibrational DOS calculation according to the Debye model using the measured velocities. See the text for details.

$\langle r\rangle$	x	v_L (km/s)	v_T (km/s)	ρ (g/cm^3)	c_L (kbar)	c_T (kbar)	K (10^{-3} states/meV^3)
2	0.00	1.73±0.02	0.85±0.02	4.277	127±3	30.8±1.2	5.92
	0.00	1.75±0.02	0.90±0.02		130±3	34.6±1.2	
2.1	0.05	1.78±0.04	0.95±0.02	4.318	137±9	39.0±2.6	4.52
2.2	0.10	1.88±0.02	1.03±0.02	4.331	152±3	45.9±1.8	3.52
	0.10	1.90±0.02			156±3		
2.3	0.15	1.91±0.02	1.03±0.02	4.339	158±2	46.1±1.8	3.49
2.36	0.18	1.99±0.02	1.07±0.02	4.344	172±3	49.8±1.9	3.09
2.4	0.20	1.97±0.02	1.09±0.02	4.346	168±3	52.0±2.0	2.93
2.44	0.22	2.03±0.02	1.17±0.02	4.348	180±2	59.4±2.3	2.38
2.52	0.26	2.01±0.02	1.21±0.02	4.328	174±3	63.4±2.4	2.18
2.56	0.28	2.08±0.02	1.19±0.02	4.306	186±3	61.4±2.3	2.27
2.6	0.30	2.16±0.02	1.20±0.02	4.277	199±3	61.4±2.3	2.21

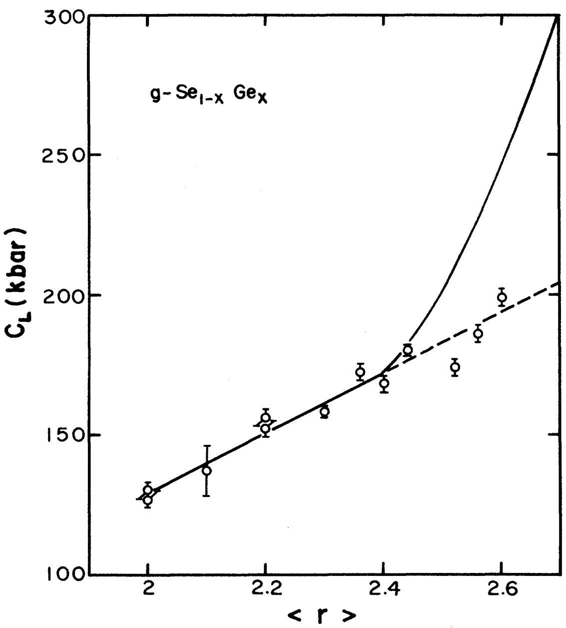

FIG. 1. The measured longitudinal elastic modulus plotted against the average coordination number $\langle r \rangle$ in g-Se$_{1-x}$Ge$_x$. The predicted rigidity threshold is at $\langle r \rangle=2.4$. The solid line is the prediction of Ref. 4 normalized to c-Ge and modified to allow for a background elastic property by fitting a line to the data below 2.4.

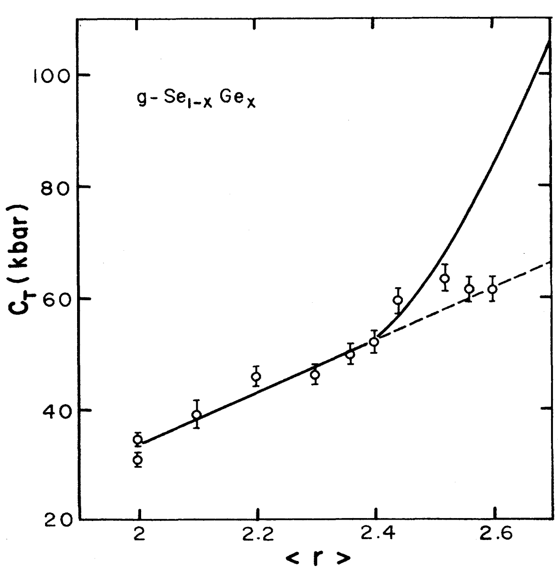

FIG. 2. The measured transverse elastic modulus plotted against the average coordination number $\langle r \rangle$ in g-Se$_{1-x}$Ge$_x$. The predicted rigidity threshold is at $\langle r \rangle=2.4$. The solid line is the prediction of Ref. 4 normalized to c-Ge and modified to allow for a background elastic property by fitting a line to the data below 2.4.

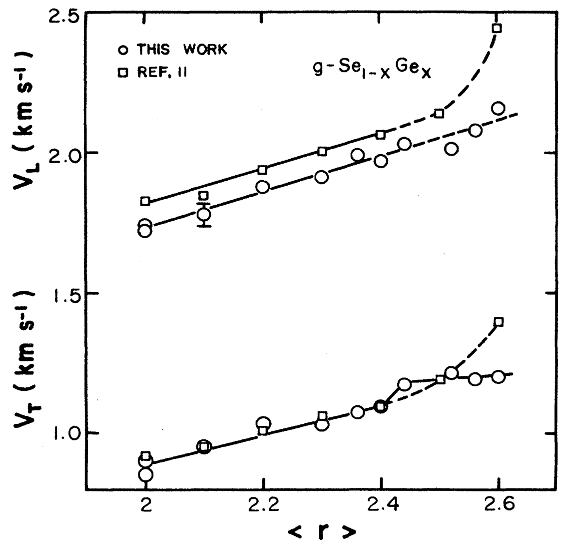

FIG. 3. The measured ultrasonic velocities in km s^{-1} vs average coordination number $\langle r \rangle$ in g-Se$_{1-x}$Ge$_x$ compared to those of Ref. 11. Random error limits in the present experiment are included within the width of the round data symbols. The error bars shown on the $\langle r \rangle=2.1$ data point represent the spread of repeated measurements on several samples. The lines below $\langle r \rangle=2.4$ are linear fits and above $\langle r \rangle=2.4$ are drawn to guide the eye.

Avogadro's number, V_M is the molar volume, and $3/v_{\mathrm{av}}^3=1/v_L^3+2/v_T^3$. They are expressed in units of states/meV^3. The coefficients are normalized to the number of degrees of freedom per atom, i.e., such that the integral of the DOS from zero to the Debye energy is unity.

DISCUSSION

There have been several experimental studies of the rigidity threshold in glasses in addition to Ref. 11. Recently Halfpap and Lindsay[12] made room-temperature ultrasonic measurements on two sets of Se-As-Ge alloy glasses extending beyond the $\langle r \rangle$ range of the present work. They reported experimental difficulties which rendered their measurements considerably less precise than those in Ref. 11 or in the present work. Moreover, they report the presence of 6–8 % O content in some of their samples which we note could lead to inaccurate representations of $\langle r \rangle$ values. Nevertheless, a comparison is useful since these authors interpret their data as evidence for rigidity percolation close to $\langle r \rangle=2.4$ whereas, as we shall see, this and other work points to a higher threshold.

Their c_L results for the low-As-concentration series (more comparable to our Se-Ge) quantitatively agree with ours to within experimental error from $\langle r \rangle=2.1$ to 2.6. Beyond 2.6 their data show a sudden 30% jump and saturation up to $\langle r \rangle=2.9$. The Se data point of Ref. 12, in agreement with Ref. 11, lies above ours. This leads to a slope in the region between $\langle r \rangle=2.0$ and 2.3 which is distinctly flatter than in both the present work and in that of Ref. 11. The high-As-concentration series of Ref. 12 also shows a flatter initial slope and saturation setting in at $\langle r \rangle = 2.5$ with soft elastic moduli persisting to 3.0.

The c_T results for the low-As-concentration series of Ref. 12, except for the pure Se point, lie below those of the present work (and of Ref. 11) and show a gradual increase in slope up to $\langle r \rangle = 2.6$. Beyond 2.6 there is a 30% jump and saturation. Their results for the high-As series are very close to those of the low-As series except there is no jump at 2.6, just saturation at relatively soft values up to $\langle r \rangle = 3.0$.

The main differences, then, between the results of Ref. 12 and the present work over the common range of measurement may be summarized by stating that to within error bars they were at liberty to fit the data between $\langle r \rangle = 2.0$ and $\langle r \rangle = 2.3$ with a line of zero slope whereas we were constrained by our error bars to fit it with a line of nonzero slope, in agreement with the work of Ref. 11 (as demonstrated in Fig. 3). Moreover, this nonzero slope has the physically reasonable interpretation that forces, neglected in the theory, namely dihedral angle and interchain forces, give rise to a "background" elastic property. Here we remark that the inclusion of these forces overconstrains the system even at pure Se. Hence, strictly speaking, there is no threshold to rigidity. There is only a transition between softer elastic properties governed by these weaker forces and harder elastic properties governed by covalent forces. Nevertheless, one might expect from the Phillips[5] argument that the $\langle r \rangle$ value for this gentler transition, calculated for a random network, would occur at the percolation value of 2.4.

A study by Tanaka[13] of the bulk moduli of Ge-As-S glasses shows the same sort of result. There is a gradual rise with nonzero slope below $\langle r \rangle = 2.4$. The slope below 2.4 is nearly the same as that seen in Se-Ge glasses in Fig. 5 of Ref. 11. Beyond $\langle r \rangle = 2.4$ there is a saturation and then a sharp rise beyond 2.7. (Tanaka comments that a plausible reason for the discrepancy between the threshold predicted by theory and the higher one seen in the experiment lies in the medium-range structural order neglected in the theory.)

Duquesne and Bellessa[14] made a study between 1 and 100 K of both sound velocity and attenuation at frequencies around 100 MHz in Se-Ge glasses. Their alloys were rather widely spaced but showed no evidence of a threshold at $\langle r \rangle = 2.4$ in c_T. (Measurements of moduli at low temperatures presumably avoid anelastic effects, but since the internal friction is less than 0.005 in these glasses ultrasonic measurements at room temperature in the present work may be expected to give essentially the relaxed moduli. In any case, there is no discrepancy in the trends seen in both cases.)

Another approach to the threshold question is by experiments to measure the fraction (f) of the modes which are floppy. Kamitakahara *et al.*[7,15] present inelastic neutron scattering measurements of the vibrational DOS for the Se-Ge glassy-alloy series. This provides the most direct evidence for the existence of floppy modes and their alloying behavior. There is a well-defined peak at low frequencies which rapidly tends to disappear as Ge concentration is increased. The fraction of modes under this peak is found to be about $\frac{1}{3}$ in Se and is followed as a function of $\langle r \rangle$. Again, f does not go to zero at $\langle r \rangle = 2.4$ but decreases more slowly, persisting even through $GeSe_2$.

As indicated in Table I, the coefficient of the ω^2 term in the DOS, calculated from the present measurements, decreases monotonically with increasing $\langle r \rangle$. This is associated with the nonzero slope of elastic constants as functions of $\langle r \rangle$ mentioned above and is in accord with the behavior seen in neutron scattering by Kamitakahara *et al.*[15]

Boolchand and Enzweiler[16] made ^{119}Sn Mössbauer studies at several compositions, x, in $(Ge_{0.99}Sn_{0.01})_x Se_{1-x}$ of the recoil-free fraction f_0 extrapolated to $T = 0$ K. They analyzed them to extract the zero-point mean-square displacement $-(\lambda/2\pi)^2 \ln(f_0)$ of the Sn atoms that are tetrahedrally coordinated to four Se near neighbors. λ is the Mössbauer γ-ray wavelength. Though a less direct measure of the floppy-mode fraction than the DOS provided by neutron measurements, the results are interesting. As $\langle r \rangle$ increases there is a sharp decline in $-(\lambda/2\pi)^2 \ln(f_0)$ with a break in slope at $\langle r \rangle = 2.4$ to a more gentle decline persisting at least to $\langle r \rangle = 2.7$. This result is consistent with the previous[17] ^{129}I Mössbauer site intensity ratios I_B/I_A probing the anion-site chemistry and with the behavior seen in the transverse elastic modulus in the present work which also shows a small departure at 2.4. The softer, transverse waves should be expected to give the dominant contribution to $-(\lambda/2\pi)^2 \ln(f_0)$.

Duquesne and Bellessa[18] looked for threshold phenomena in Se-Ge glasses in several measured parameters: the magnitudes of the internal friction peaks, the slopes of the linear temperature variation of velocity of ultrasonic waves, and the densities of tunneling defects. In all cases their measurements showed a decreasing trend as $\langle r \rangle$ increases from 2 at Se, but no disappearance at 2.4. Similarly, Gilroy and Phillips[19] plotted the normalized magnitude of the internal friction peaks against $\langle r \rangle$ and showed decline to zero near $\langle r \rangle = 2.7$.

In sum, there are floppy modes and soft elastic moduli in $Se_{1-x}Ge_x$ glasses. These modes and soft moduli persist beyond the percolation threshold at $\langle r \rangle = 2.4$ calculated on the basis of an unstrained random-network model. This latter point has been established independently by many workers. The absence of the percolation threshold at $\langle r \rangle = 2.4$ and its shift to somewhere near 2.7 requires an explanation. One possibility is the existence of internal strains in the bulk glasses, especially those prepared by air cooling or water quenching, namely those having $\langle r \rangle > 2.5$. Tang and Thorpe[20] showed that the rigidity percolation threshold for a three-dimensional random covalent network under increasing tension is raised continuously to larger $\langle r \rangle$ values and eventually saturates. For this explanation to work for our and other's samples, the internal strains would have to be significantly tensile and to dominate the effects of the unstrained regions such as to give a threshold near 2.7. It seems unlikely that this would be so for the Se-Ge, Se-As-Ge, and S-As-Ge samples prepared and studied independently in several laboratories by different workers.

A second possibility is that Se-Ge glasses, except for very low Ge concentrations, cannot really be described by a random network. Evidence[21–23] has been presented for the existence of medium-range structural order in the form of molecular clusters. If, for example, mechanically rigid fragments embodied in Ge-rich molecular clusters were to form below $\langle r \rangle = 2.4$, the surrounding material would be Ge poor and hence softer. In this way, soft elastic properties could persist beyond $\langle r \rangle = 2.4$. Where the transition to harder elastic properties would occur would depend upon the structure of the clusters. The onset of rigidity presumably would be different for the percolation of clusters of network-dimensionality three than if the clusters were fragments of network-dimensionality two.

CONCLUSIONS

We have measured the room-temperature velocities of longitudinal and transverse waves by the pulse-echo technique in $Se_{1-x}Ge_x$ glasses in the range $x=0$ to $x=0.3$, which corresponds to $\langle r \rangle = 2$ to $\langle r \rangle = 2.6$. The longitudinal elastic modulus in this region increases linearly in $\langle r \rangle$ with no threshold to rigidity at 2.4. The transverse elastic modulus shows a slight upward departure from linearity around 2.4 and saturation beyond 2.5. The behaviors of both moduli depart substantially from theoretical predictions (modified to include "background" elastic properties) of rigidity percolation based on an unstrained, random covalent network. Taken together with other work, these results support the existence of floppy modes and a rigidity threshold beyond 2.6, probably near 2.7. The shift in the position of the threshold is consistent with the presence of medium-range structural order arising from chemical clustering.

ACKNOWLEDGMENT

The work at the University of Cincinnati was supported by NSF Grant No. DMR-85-21005.

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