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Elastic properties of Si_xSe_{1-x} glasses

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Transverse and longitudinal phonons have been studied in Si_xSe_{1-x} glasses over a wide composition range. The results show anomalous behavior at $x=0.33$ consistent with a structural transformation. Above $x=0.33$ our results are consistent with the theory of "rigidity percolation."

Over the past few years there has been an enormous effort to try to understand the properties of noncrystalline materials in terms of their microscopic structure. The problems encountered in such an undertaking are formidable from both the theoretical and experimental standpoints. The loss of translational symmetry precludes the use of many conventional theoretical techniques, while experimentally, many measured properties depend strongly on the preparation techniques (e.g., quenching rates) and numerous characterization probes (e.g., x rays and neutrons) reveal only average properties which are hard to relate unambiguously to microscopic properties.

Because of this state of affairs, it has been extremely valuable to determine features or characteristics that can be explicitly associated with the amorphous state and to develop theoretical models to deal with them. Perhaps the best known of the models in this category is the continuous random network[1] model used to describe the structure of a class of noncrystalline solids.

In a number of recent theoretical articles[2-6] it has been proposed that the elastic properties of certain amorphous systems could be described by a model based on "rigidity percolation." This approach incorporates concepts of under- and over-constrained networks introduced by Phillips.[7,8] In calculations on systems where the average coordination can be varied, it was found[6] that the elastic constants C_{ij} of the material have the following form:

$$C_{ij}=K(r-2.4)^{1.5} . \tag{1}$$

Here K is a constant, r is the average coordination, and 2.4 is the coordination at which percolation occurs. Equation (1) is a fit to the results of simulations and provides a good fit in the range $2.4<r<3.2$; for $r>3.2$ the behavior differs slightly from the simple expression given in Eq. (1). Below $r=2.4$ the model predicts that all elastic constants are zero and consequently that the model becomes structurally unstable.

Given the attractive conceptual simplicity of the model, it is somewhat surprising that very little experimental work has been forthcoming to test the hypothesis. This fact must be traced to the difficulty in finding an appropriate system that can be fabricated over the desired composition range, and that many of these systems are highly reactive and cannot be investigated without considerable precautions. The limited experimental data available does not provide a definitive answer to the problem. The Ge_xS_{1-x} system has been studied using Brillouin scattering by Pelous *et al.*,[9] over the composition range $x=0.1-0.35$, so that the average coordination, given by

$$r=2+2x , \tag{2}$$

covers the critical coordination 2.4. Although a substantial softening is observed as x is decreased, no discontinuity is observed at $x=0.2$. Samples of Ge-As-Se, investigated ultrasonically by Halfpap and Lindsay,[10] indeed show evidence of anomalous behavior at $r\cong2.4$. Work on Ge_xSe_{1-x} by Duquesne and Bellessa[11] show a definite drop in the elastic constants as Se is incorporated into the system but no dramatic change at $r=2.4$. Their results, however, can be reconciled with the theory if it is assumed that when r drops below 2.4 the system has nonzero elastic constants which are independent of concentration. Using ultrasonic techniques, Ito *et al.*[12] have studied three different series of Ge-As-Se samples, none of which show clear anomalies at $r=2.4$.

Here we have chosen to study samples of amorphous Si_xSe_{1-x}. This system has been extensively investigated[13-15] in our laboratory and is well characterized in terms of density[13] and glass-transition temperature;[14] structure has been studied using x-rays,[15] extended x-ray absorption fine structure (EXAFS),[15] and neutron scattering.[15] In this paper, we report the results of an experimental investigation of the elastic properties of Si_xSe_{1-x} glasses over the composition range $x=0.06$ to 0.42. Brillouin scattering is the experimental technique of choice since it enables us to seal the hygroscopic and reactive samples into protective ampoules filled with inert gas. The procedure for synthesizing the purified, homogeneous, isotropic glasses have been described by us elsewhere.[13] However, it is essential to emphasize that once a sample surface has been generated, that it be handled only in a high-quality glove box and that it be encapsulated immediately.

The experiments were carried out using 647-nm radiation with powers as low as a few milliwatts in order to keep the samples from crystallizing due to laser heating. Because most of the sample surfaces were extremely irregular (obtained by simple fracture), and many samples are not transparent to this radiation, we were obliged to work in the backscattering geometry. We use the term

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backscattering in the general sense to indicate that the scattered light emerges through the same surface as that on which the incident light impinges. In the actual geometry used, light was incident at 65° from the surface normal and the collected light was at $\sim -25°$ from the normal. This somewhat unusual geometry was chosen since in perfect backscattering (i.e., $\mathbf{k}_i$ colinear with $\mathbf{k}_s$) the transverse phonons do not couple to the radiation. We stress, however, that even in the geometry used the signal from the transverse modes is *extremely* weak and could not be observed in all samples.

Figure 1 shows the frequency shifts measured in vitreous Si_xSe_{1-x} as a function of Si concentration. The open circles are for longitudinal phonons, the closed circles for transverse. The arrows on the left-hand side are calculated using the elastic constants for pure vitreous selenium,[16] $\rho = 4.285$ g/cm^3 and the refractive index $n = 2.7 \pm 0.2$. The scale on the upper border is the average coordination as given by Eq. (2). The sound velocity (v) is related to the measured frequency shift in wave numbers ($\Delta\nu$) through

$$v = \Delta\nu \frac{c\lambda}{n 2\cos[(\theta_1+\theta_2)/2]} , \tag{3}$$

where c is the velocity of light, λ the laser wavelength (647 nm), n the refractive index, and θ_1 and θ_2 are given by

$$\sin\theta_1 = \frac{1}{n}\sin 65° \tag{4}$$

and

$$\sin\theta_2 = \frac{1}{n}\sin 25° . \tag{5}$$

Although n is not known for these materials, very crude Brewster's angle measurements show that it is in the range 2.5 ± 0.5. It can be easily shown that the cosine term in Eq. (3) only ranges from 0.94 to 0.98 as n changes from 2 to 3. Therefore to within $\sim 2\%$ Eq. (3) can be approximated by

$$nv = \Delta\nu 9.71 \times 10^5 \text{ cm/sec} , \tag{6}$$

with $\Delta\nu$ in cm^{-1}. It is this expression which has been used to generate the scale on the right-hand side of Fig. 1.

The most notable feature in Fig. 1 is the minimum in both the longitudinal and transverse velocities at $x \approx 0.33$. This "anomaly" in sound velocity is consistent with the structural change at this concentration which was inferred in Ref. 13 from density measurements. It is also interesting to note that our data above $x = 0.33$ extrapolate to zero at $x = 0.20 \pm 0.03$ ($r = 2.40 \pm 0.06$) and is thus consistent with Eq. (1) which predicts that the c_{ij} go to zero at $x = 0.2$. Since the starting point for the theoretical model is a fully fourfold-coordinated system from which bonds are then removed, our results for $x > 0.33$ can be considered as a corroboration of the theory. The fact that the elastic constants do not go to zero is not a serious problem since it can be argued that the "phase transition" at $x = 0.33$ preempts the use of the model below this concentration. The exponent governing the dependence of v on $(r - 2.4)$ obtained from our experimental results is ≈ 1 which is to be compared with 0.75 predicted by Eq. (1). This small discrepancy can be attributed to the simplicity of the model which does not include changes in density or bond strengths (i.e., a Si—Si bond is assumed to be the same as a Si—Se bond).

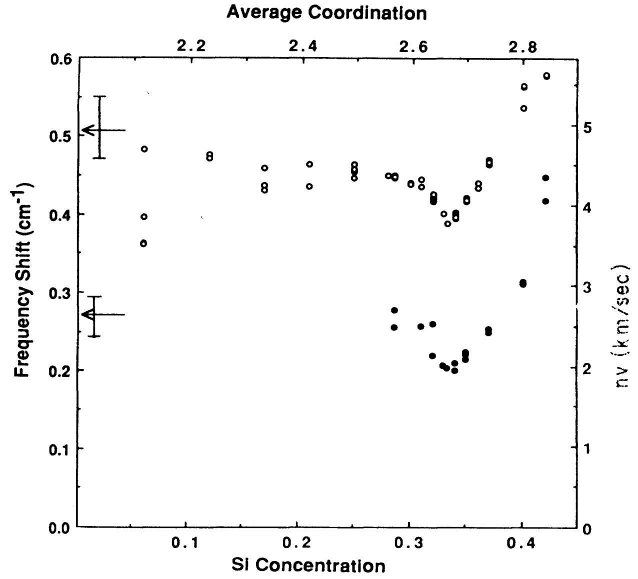

FIG. 1. Brillouin frequency shifts as a function of Si concentration in Si_xSe_{1-x}. Open and closed points correspond to longitudinal and transverse velocities, respectively. The arrows are calculated from literature values for pure amorphous Se.

In spite of the fact that our results on the Si_xSe_{1-x} system can be taken as evidence in favor of the "rigidity percolation" model,[2–6] the overall situation at present is far from clear: Our results are consistent with theory if we assume a preemptive structural change at $x = 0.33$ instead of the predicted collapse at $x = 0.2$; the results of Ref. 10 on Ge-As-Se samples show a clear anomaly at $r = 2.4$ (which corresponds to our $x = 0.2$) where we see no changes; finally the results of Refs. 9 and 12 show no anomalous behavior across the composition ranges investigated.

It is clear from the comments in the previous paragraph that considerably more experimental work is needed before the elastic properties of covalent amorphous systems can be understood. We hope that improved techniques in material fabrication and characterization will make such studies possible.

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