Vibrational densities of states and network rigidity in chalcogenide glasses

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Vibrational spectra have been measured by neutron scattering for a series of Se-Ge and Se-As-Ge glasses, spanning a wide range in composition and, consequently, in network connectivity. Low-frequency "floppy" modes arising from underconstrained atomic configurations have been observed, in qualitative agreement with recent theories of the dynamics of network glasses. The number of floppy modes was found to depend only on the average coordination number $\langle r \rangle$. There is some indication of a rigidity percolation threshold at $\langle r \rangle \approx 2.4$, but the effect in the vibrational densities of states is not dramatic. The wave-vector dependence of the scattering at low vibrational energies (≈ 2 meV) is acoustic-phonon-like. Specific heats C calculated from the measured densities of states show a strongly composition-dependent bump in C/T^3 near 4 K, in accord with experiment.

I. INTRODUCTION

The vibrational spectra of amorphous solids bear a close relationship to their atomic-scale structure, and to their mechanical and thermal properties. The Se-As-Ge alloy system is particularly interesting in this regard, having covalent coordination numbers varying from 2 to 4 along the series, with local structure from polymer-chain-like selenium to three-dimensionally rigid network glasses, and having an exceptionally broad range of glass-forming compositions. Since the atomic masses and covalent bond strengths among the constituents are very close, this system affords a good arena for studying variations in glassy properties governed by local bonding and network considerations.

Recent theories have provided a framework for making comparisons of the properties of these glasses. The theories are based on the concept of constraint counting, in which the average atomic coordination number $\langle r \rangle$ plays an important role. For the glass $Se_{1-x-y}As_xGe_y$, the average coordination number is given by

$$\langle r \rangle = 2(1-x-y) + 3x + 4y \ .$$

Phillips[1] and Thorpe and co-workers[2,3] have shown that, when the number of degrees of freedom in a random network exceeds the number of mechanical constraints imposed by the covalent bonding (ignoring the effects of smaller forces), the system allows displacements of groups of atoms with no change in energy. That is, there are certain modes which have zero frequency. In the presence of the small residual interactions, the zero-frequency or "floppy" modes acquire finite frequencies. But one expects that their number will still be largely governed by constraint-counting arguments which give the "floppy" mode fraction as the number of excess degrees of freedom divided by the total number of degrees of freedom.

Perhaps the most interesting result of the constraint-counting theories is the prediction of an elastic rigidity threshold at the average coordination number ($\langle r_c \rangle = 2.4$) for which the number of degrees of freedom exactly equals the number of constraints and the number

of floppy modes goes to zero. The existence of such a threshold was predicted within a mean-field theory[1,2] and subsequently confirmed in a computer simulation[3] of bond depletion on a diamond structure.

The applicability of the theory to Se-As-Ge glasses involves the premise that details in the network bonding are secondary and that the mechanical and vibrational behavior are governed at low energies by the average coordination number $\langle r \rangle$. The array of twofold, threefold, and fourfold coordinated atoms are distributed in the real glasses in a very nonrandom fashion. One would never arrive at a chemically ordered covalent random network of $Ge(Se_{1/2})_4$ tetrahedra, for example, simply by deleting bonds completely randomly from an initially tetrahedrally bonded diamond structure. The question is whether, in spite of such chemically governed tendencies and the unspecified role of residual interactions not considered by constraint counting, real materials exhibit floppy modes which are determined by the average coordination number $\langle r \rangle$.

Regardless of the applicability, or lack thereof, of the theories, the neutron-scattering experiments on Se-As-Ge glasses reported here are directed toward the general question of the nature of the vibrational modes in disordered systems. To what extent can they account for the observed thermodynamic properties, especially specific heat? To what extent are the modes harmonic vibrations,

and are there indications of modes of special character, perhaps extremely anharmonic ones indicating even more unusual atomic motions at lower frequencies and characteristic temperatures? Can some connection be made with the very low-temperature properties of glasses?

II. EXPERIMENTAL METHODS

Two sets of glassy samples were prepared, one at the University of Cincinnati and the other at Arizona State University, as summarized in Table I. In both cases, the glasses were quenched from the melt, using procedures described previously.[4] Most of the neutron-scattering data were obtained at room temperature on the IN4 thermal-neutron time-of-flight (TOF) spectrometer at the high-flux reactor of the Institut Laue-Langevin (ILL), Grenoble, France. Energy-gain spectra were observed using a 12.5-meV incident neutron beam. Typically, counts were accumulated for about 6 h on 10-g samples. Some additional data at low temperature were taken on a triple-axis spectrometer at the National Institute of Standards and Technology, but they are not shown here.

The vibrational density of states (VDOS) $g(\hbar\omega)$ is obtained by integrating the TOF data weighted by the sine of the scattering angle between the angular limits set by the detectors. In the incoherent approximation, the one-phonon expression arising from such an integral is

$$\left[\frac{d\sigma}{d\hbar\omega}\right]\Big|^{(1)} = [\hbar^2\bar{\sigma}(Q_{max}^4 - Q_{min}^4)G(\hbar\omega)]/\{8\pi k_0^2\hbar\omega[\exp(\hbar\omega/kT)-1]\overline{M}\} \, , \tag{1}$$

containing several factors. Most important to us is the generalized VDOS,

$$G(\hbar\omega) = \sum_i \alpha_i g_i(\hbar\omega) \, ,$$

where

$$\alpha_i = (c_i\sigma_i/M_i)/\sum_j (c_j\sigma_j/M_j) \, ,$$

σ_i is the thermal neutron total bound cross section for atoms of species i, c_i is the atomic concentration, and M_i

TABLE I. The compositions and average coordination numbers $\langle r \rangle$ of the glasses in this study. The Se-Ge glasses are from the University of Cincinnati and the Se-As-Ge glasses are from Arizona State University.

Se-Ge	$\langle r \rangle$	Se-As-Ge	$\langle r \rangle$
Se	2.0		
$Se_{96}Ge_4$	2.08	$Se_{89}As_6Ge_5$	2.16
$Se_{92}Ge_8$	2.16	$Se_{773}As_{114}Ge_{113}$	2.35
$Se_{88}Ge_{12}$	2.24	$Se_{675}As_{250}Ge_{75}$	2.4
$Se_{80}Ge_{20}$	2.4	$Se_{63}As_{14}Ge_{23}$	2.6
$Se_{77}Ge_{23}$	2.46	$Se_{51}As_{18}Ge_{31}$	2.8
$Se_{70}Ge_{30}$	2.6	$Se_{395}As_{210}Ge_{395}$	3.0
$GeSe_2$	2.67		

the atomic mass. $g_i(\hbar\omega)$ is the partial VDOS for species i averaged over all modes of frequency ω and weighted by atomic vibrational amplitudes. $\overline{M} = \sum_i \alpha_i M_i$ is an average mass of the scattering atoms. $\bar{\sigma} = \sum_i c_i\sigma_i$ is the average total bound cross section. The maximum and minimum transferred wave vectors are Q_{max} and Q_{min}, and the incoming neutron has wave vector k_0. Other symbols have their usual meanings. $G(\hbar\omega)$ has been corrected for multiphonon contributions with the aid of an iterative procedure embodied in the computer code MUPHOCOR developed at Karlsruhe.[5]

In these glasses, $\alpha_i \approx c_i$ since the scattering lengths and masses of the component elements are quite similar. ($b_i = 0.89$, 0.63, and 0.84×10^{-12} cm and $M_i = 72.6$, 74.92, and 79.0 amu for Se, As, and Ge, respectively.) Then we may take

$$G(\hbar\omega) \approx \sum_i c_i g_i(\hbar\omega) \equiv g(\hbar\omega) \, ,$$

and regard the results as close to the true density of states $g(\hbar\omega)$. In subsequent sections we shall refer to the measured quantity simply as $g(\omega)$. Each $g(\omega)$ function is normalized so that $\int g(\omega)d\omega = 1.0$. A combination of IN4 neutron TOF measurements with the analysis using the Karlsruhe code described here yields VDOS of exceptionally good quality.

III. RESULTS

VDOS for Se-As-Ge glasses, with $\langle r \rangle$ ranging from 2 to 3, are shown in Fig. 1. For pure Se, there is a prominent peak at 5 meV, which we identify as the floppy mode peak. Indeed, the area under this peak, from 0 up to 8 meV, is 0.28, which is close to the value of $\frac{1}{3}$ anticipated from constraint-counting arguments. As $\langle r \rangle$ is increased, the floppy mode peak declines rapidly in intensity but does not change in position. It is clear that the peak does not disappear at the predicted rigidity percolation threshold at $\langle r_c \rangle = 2.4$ but persists as a shoulder to higher $\langle r \rangle$ and is still evident at $\langle r \rangle = 3$. A more detailed comparison of the experiment with theoretical predictions, and with the results of other experiments, will be made later in the text.

Other features are also evident in the VDOS. The Se spectrum, which is very similar to that previously obtained by Gompf,[6] contains, in addition to the floppy mode peak, a broad shoulder extending to 19 meV, followed by a gap and a sharp peak at 31 meV. The shoulder and sharp peak can be regarded, respectively, as the bond-bending and bond-stretching vibrations, each with about $\frac{1}{3}$ of the total spectral weight. As the Ge concentration is increased, a feature arises in the gap, at about 24 meV or 194 cm^{-1}. This feature has been identified in detailed Raman scattering[7-9] studies as an A_1 mode and arises from vibrations of Se atoms with their cross-linking Ge neighbors. It will be discussed later.

Returning to the low-frequency behavior, we have found that the spectra for Se-Ge and Se-As-Ge glasses with the same average coordination number give virtually identical results for frequencies up to about 15 meV. That is to say, the floppy mode behavior, and indeed the
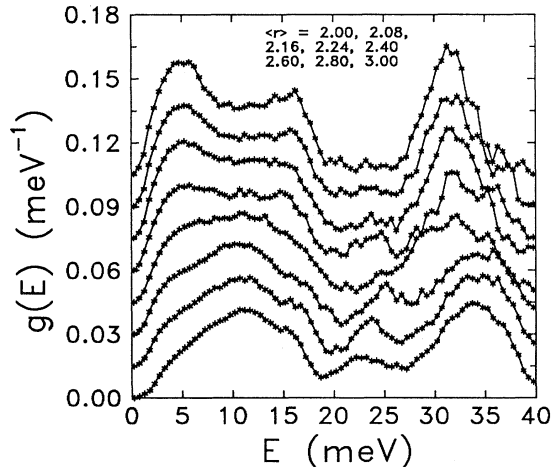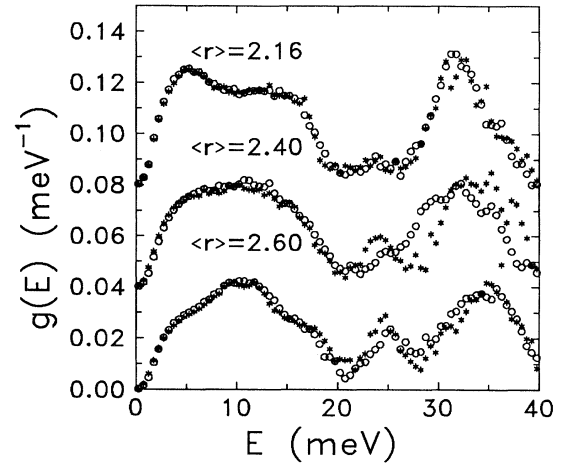

FIG. 2. VDOS comparing pairs of alloy glasses having the same $\langle r \rangle$ value. $\langle r \rangle = 2.16$: $*$, $Se_{92}Ge_{08}$; $\circ$, $Se_{89}As_6Ge_{05}$; $\langle r \rangle = 2.40$: $*$, $Se_{80}Ge_{20}$; $\circ$, $Se_{675}As_{250}Ge_{075}$; $\langle r \rangle = 2.60$: $*$, $Se_{70}Ge_{30}$; $\circ$, $Se_{63}As_{14}Ge_{23}$. Starting from the bottom, successive data set pairs are shifted up by 0.04 units.

shape of the bottom half of each spectrum, are functions only of the mean coordination $\langle r \rangle$ and not of Ge and As concentrations individually (Fig. 2). In contrast, the bond-stretching peak near 30 meV shows significant variation with composition for the same $\langle r \rangle$. Likewise, the A_1 mode region varies with composition at the same $\langle r \rangle$, the structure becoming washed out for higher As content. This is particularly evident at $\langle r \rangle = 2.4$, for which the ternary sample has the largest relative As content of the samples.

IV. DISCUSSION

A. Relevance to the concept of rigidity percolation

The computer simulations of Cai and Thorpe[10] involved removing bonds on a diamond structure of atoms linked by a Keating potential. In their first model no dihedral angle forces were included, so that in locally underconstrained regions, modes of zero frequency (the "floppy" modes) appeared when the average coordination number was lowered sufficiently through bond removal. These modes can then be conveniently counted and are dynamically quite separate from other, ordinary, vibrational modes.

In Se-Ge and Se-As-Ge glasses, the presence of residual interactions, such as forces opposing dihedral angle modulation, and interchain coupling apart from As or Ge linkages, raise the floppy modes to finite frequencies. In addition, they produce a dynamical mixing, so that the low-frequency normal modes are some mixture of floppy modes and acoustic-phonon-like modes. This makes a direct comparison of the VDOS to this first Cai-Thorpe simulation somewhat problematic.

In their second model, Cai and Thorpe extended the simulation to include residual interactions. Otherwise,
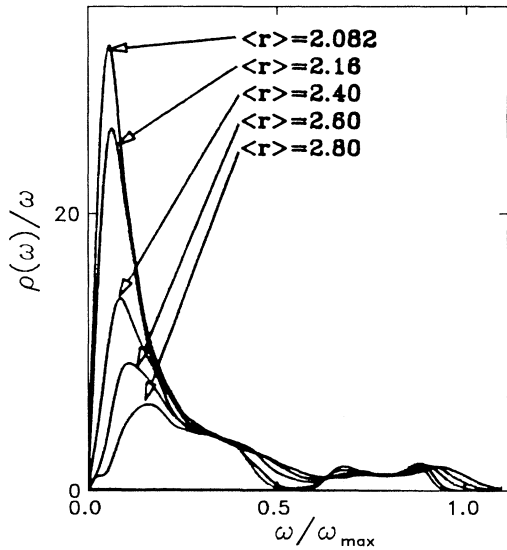

FIG. 1. VDOS for Se-As-Ge alloy glasses. Starting from the bottom ($\langle r \rangle = 3.00$), successive curves have been shifted up to 0.015 units on the vertical scale. The top curve ($\langle r \rangle = 2.00$) is for pure Se glass. The other alloy glasses in order are $\langle r \rangle = 2.08$, $Se_{96}Ge_4$; $\langle r \rangle = 2.16$, $Se_{89}As_{06}Ge_{05}$; $\langle r \rangle = 2.24$, $Se_{88}Ge_{12}$; $\langle r \rangle = 2.40$, $Se_{675}As_{250}Ge_{075}$; $\langle r \rangle = 2.60$, $Se_{63}As_{14}Ge_{23}$; $\langle r \rangle = 2.80$, $Se_{51}As_{18}Ge_{31}$; and $\langle r \rangle = 3.00$, $Se_{395}As_{210}Ge_{395}$. The peak at ≈ 5 meV is identified as the "floppy" mode peak.

FIG. 3. VDOS calculated for $Se_{1-x}Ge_x$ alloy glasses by Cai and Thorpe, Ref. 10, plotted as $g(\omega)/\omega$ vs ω/ω_{max}.

delineate the trends. The neutron data give a somewhat flat dependence with just a hint of a break closer to $\langle r \rangle = 2.3$ than 2.4. The theoretical dependence of $\langle 1/\omega \rangle$ on average coordination $\langle r \rangle$ shows a gentle break near 2.4, but the effect is a much less pronounced one than would be expected in a simple Keating potential calculation. While it cannot be said on the basis of the neutron data alone that there is such a break, the correspondence with theory would suggest that there is one. The gentle break in even the theoretical dependence implies that the residual interactions have reduced the prominence of the rigidity percolation threshold, making it rather difficult to detect in physical property measurements on Se-based glasses.

A more dramatic effect is seen in $\langle 1/\omega \rangle$ derived from Mössbauer measurements.[11] The latter involve a Sn substitution for Ge as the Mössbauer nucleus. Most probably, the Sn acts like a mass defect whose atom-specific vibrational spectrum is enhanced in the floppy mode region, thus making the break at 2.4 in Fig. 5 more pronounced.

The effects on lower-frequency properties, such as sound velocities, are even more radically diminished. Originally He and Thorpe[12] used a Keating potential

the calculation is similar, involving random bond depletion on a diamond structure. The results, shown in Fig. 3, bear a rather good qualitative resemblance to the experimental data of Fig. 4. In both Figs. 3 and 4, the densities of states $g(\omega)$ are displayed in the form $g(\omega)/\omega$, which emphasizes the low-frequency, few meV, region. The area under these curves is the first inverse moment $\langle 1/\omega \rangle$ which can be regarded as a measure of the floppy mode intensity, permitting the comparison shown in Fig. 5.

In the first place, the correspondence between theory and experiment is, quantitatively speaking, not very close, so that we have chosen to replot the neutron-derived results by themselves, in order to more clearly

FIG. 4. VDOS measured for Se-As-Ge alloy glasses in this work plotted as $g(E)/E$ vs E. Top curve: $\langle r \rangle = 2.00$; bottom curve: $\langle r \rangle = 3.00$. The alloys corresponding to various $\langle r \rangle$ values are as indicated in Fig. 1.
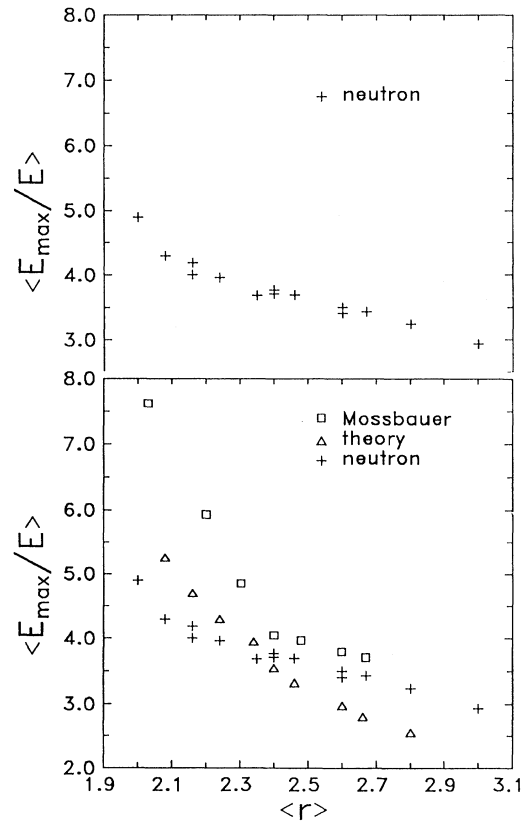
FIG. 5. The first inverse moment of the VDOS for Se-As-Ge glasses normalized to $E_{max} = 40$ meV. Theory is from Ref. 10, Mössbauer results are from Boolchand et al., Ref. 11. According to simple constraint-counting arguments the rigidity threshold occurs at $\langle r_c \rangle = 2.4$.
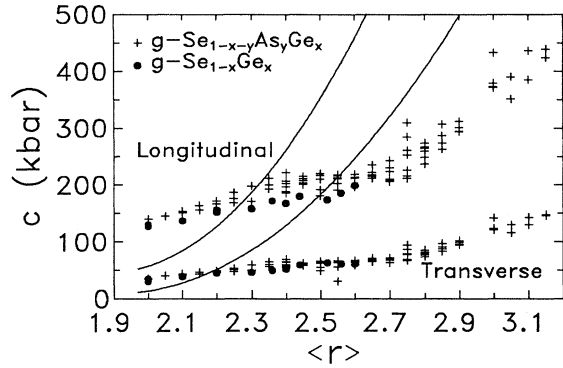
FIG. 6. Room-temperature longitudinal and transverse ultrasonic elastic constants for chalcogenide glasses vs average coordination number, $\langle r \rangle$. ○: g-$Se_{1-x}Ge_x$, Ref. 13; +: g-Se-As-Ge, Ref. 14. The groups of points, for example, at $\langle r \rangle = 2.7$, are not random scatter in the data but rather represent distinct compositions all having the same $\langle r \rangle$ value. The theory of Ref. 10 is represented by the solid curves. No transition is evident at $\langle r \rangle = 2.4$.

FIG. 8. VDOS measured for Se-As-Ge glasses plotted as $g(E)/E^2$ vs E to compare with that estimated from the ultrasonics results of Fig. 6. The latter, represented as solid circles along the vertical axis, are, from the top, for $\langle r \rangle = 2.00$–3.00 in the order shown in the figure. The peaks around 2 meV are important in determining the position of the bump in the specific heats in Fig. 10.

simulation to predict a clear onset of rigidity at $\langle r_c \rangle = 2.4$ in the elastic moduli. Ultrasonic data measured on g-$Se_{1-x}Ge_x$ (Ref. 13) and also recent extensive measurements on g-Se-As-Ge (Ref. 14) show no evidence of a signature of rigidity percolation in this particular property at 2.4 (Fig. 6). The data on g-Se-As-Ge glasses having the same $\langle r \rangle$ value represent different alloys and not random scatter in the data. For example, the data at $\langle r \rangle = 2.7$ have increasing As concentration in going from top to bottom. There is a noticeable change in slope, especially in the longitudinal elastic modulus, beginning near $\langle r \rangle = 2.7$ which is probably associated with chemical ordering ($GeSe_2$ has $\langle r \rangle = 2.67$), but this is not predicted by the theory which relies on a bond-depleted diamond lattice. The second Cai-Thorpe calculation which includes residual forces does not accurately reproduce the
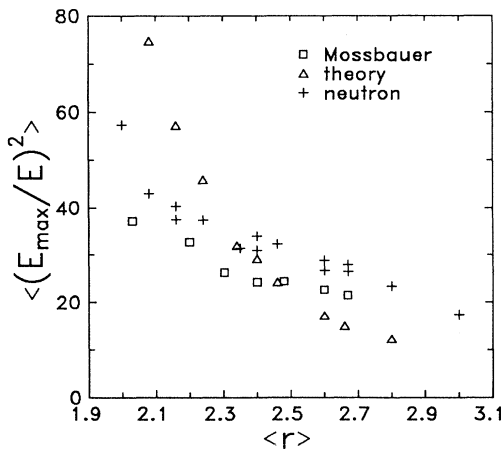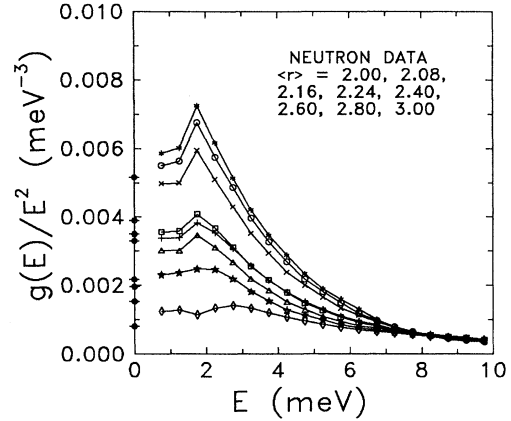
data either, showing a much steeper concentration dependence than is observed (Fig. 6), but it is in qualitative accord in not predicting an effect of rigidity percolation on the elastic constants at $\langle r_c \rangle = 2.4$.

We also note that, taking the second inverse moment $\int d\omega\, g(\omega)/\omega^2$, tends to eliminate any suggestion of the threshold, as shown in Fig. 7. This moment emphasizes modes that are generally lower in frequency than the floppy modes.

The correspondence between the neutron data for $g(\omega)/\omega^2$ and the same quantity determined from the elastic constants for the same or nearly the same alloys is shown in Fig. 8. Extrapolations of the neutron data to the vertical axis lie systematically above the solid points derived from the data of Fig. 6 for the corresponding $\langle r \rangle$ values. This provides a hint that there may be a frequency region between the acoustic regime and the "floppy" mode regime in which there are other modes (e.g., those associated with two-level states), but the uncertainties in the experiments do not permit one to firmly draw such a conclusion. It would be interesting to follow the VDOS to lower frequencies in these glasses with higher resolution to investigate this issue.

B. Comparisons with Raman spectra and previous neutron measurements

The VDOS we have measured display excellent correspondence with Raman spectra[7–9] but the strengths of various features are, as might be expected, somewhat different. The dominant features in Raman scattering, the A-type modes around 24 meV = 194 cm^{-1} are relatively weak in the densities of states. Figure 9 compares the Raman spectrum for $GeSe_2$ glass from Ref. 7 with our neutron-derived density of states. The Raman data, which are of higher resolution, show a multiplet structure whose major components are an A_1 mode and a so-called
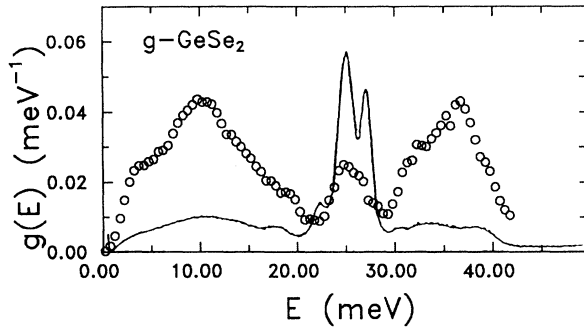

FIG. 7. The second inverse moment of the VDOS for Se-As-Ge glasses normalized to $E_{max} = 40$ meV. Theory is from Ref. 10. Mössbauer results are from Ref. 11.

FIG. 9. Comparison of the GeSe$_2$ VDOS with the normalized Raman spectrum of Sugai, Ref. 7.

A_1 companion mode. There is a hint of resolution into these two components in the spectrum shown in Fig. 9.

The nature of the A_1 mode has been confirmed in the recent extensive neutron measurements of Walter et al.[15] on GeSe$_2$. They present a plot of the wave-vector dependence of the scattering at the A_1 mode energy along with a calculation for the same based on the breathing mode of the Ge(Se$_{1/2}$)$_4$ isolated tetrahedral molecule and find excellent agreement. Somewhat improved resolution and statistics and a similar analysis might shed light on the vibration patterns involved in the more controversial A_1 companion mode. Above 7 meV, the lowest energy for which Walter et al. present data, the two neutron results for $g(\omega)$ on g-GeSe$_2$ are in good agreement.

C. Low-temperature specific heats

Specific heats can be calculated from our data as integrals over the densities of states. The results are compared with experimentally measured values[16,17] for the specific heats in Fig. 9. When one considers that the densities of states were measured at room temperature, with the lowest measured energies at about 0.75 meV, the correspondence is remarkably good. No fitting parameters are involved, even on the vertical scale. The experimental specific heats show maxima in C/T^3 at about 4 K, followed by a gradual drop. The maximum is most prominent, and the drop largest, for Se glass, with the other glasses displaying maxima at roughly the same temperature, but with a more gradual drop beyond the maximum. The presence of such maxima is a general feature of the specific heat of glasses in the 1–50 K range, and is found here to be sensitive in position and size to the peak in $g(\omega)/\omega^2$ seen in Fig. 8. The only feature that is not well reproduced by the calculations is the drop that occurs in the experimental specific heats below 4 K. This discrepancy is an artifact of the extrapolation of the lowest-frequency data in Fig. 8 straight across to the vertical axis, which, as noted above, would force an ω^2 dependence above that estimated from acoustic data. Evidently, this extrapolation is not really accurate and/or the modes of lowest energy have substantial anharmonicity. Higher-energy modes ($E > 0.5$ meV) can be expected to have a small, "normal" anharmonicity. A more accurate calculation of specific heat in this low-temperature regime must await detailed VDOS measurements at low frequencies.

D. Q dependence of low-energy scattering

At a given excitation frequency ω and wave vector Q, the coherent one-phonon scattering function can be written as

$$S(Q,\omega) \sim f_B g(\omega)\omega^{-1} \left\langle \left| \sum_j b_j \exp(-W_j)\exp(i\mathbf{Q}\cdot\mathbf{R}_j)(\mathbf{Q}\cdot\mathbf{\varepsilon}_{sj})M_j^{-1/2} \right|^2 \right\rangle ,$$

where f_B is a Bose factor, $g(\omega)$ is the VDOS and b, W, R, and M denote the neutron scattering length, Debye-Waller exponent, position, and mass of atom j. Apart from the prefactors, this expression differs from the elastic scattering function

$$S(Q,0) \sim \left| \sum_j b_j \exp(-W_j)\exp(i\mathbf{Q}\cdot\mathbf{R}_j) \right|^2$$

in that it involves atomic masses and the eigenvector ε_{sj} in mode s for the jth atom. The angular brackets imply an orientational average over directions of $\mathbf{Q}$ and an average over all modes s with the same frequency ω. For acousticlike modes, one expects the eigenvectors to vary slowly from atom to atom so that, for the terms contributing the most important correlations in $S(Q,0)$, the quantity $(\mathbf{Q}\cdot\mathbf{\varepsilon}_{sj})$ is nearly constant and can be pulled out from the sum. Then one expects $S(Q,\omega)$ to be nearly proportional to $Q^2 S(Q,0)$. The actual data will contain multiphonon terms which are expected to provide a background varying smoothly with Q. Shown in Fig. 11 is $S(Q,\omega)$ shifted and scaled to compare with $Q^2 S(Q,0)$ for 2-meV excitation energy in glassy Se, i.e., about half-way
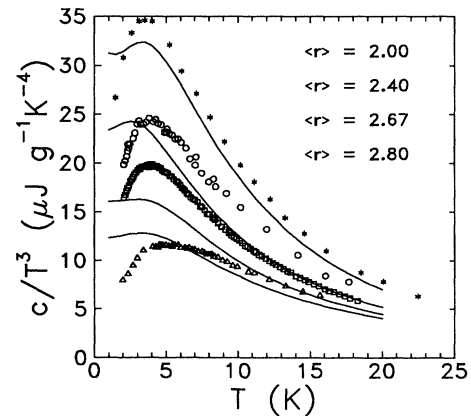

FIG. 10. Specific heat for several $\langle r \rangle$ values calculated from the measured VDOS and compared with experiment. Top curves, $\langle r \rangle = 2.0$, neutron: Se, thermal: Se, Ref. 16. $\langle r \rangle = 2.40$, neutron: Se$_{675}$As$_{250}$Ge$_{075}$, thermal: Se$_{80}$Ge$_{20}$. $\langle r \rangle = 2.67$, neutron: GeSe$_2$, thermal: GeSe$_2$. Bottom curves, $\langle r \rangle = 2.80$, neutron: Se$_{51}$As$_{18}$Ge$_{23}$, thermal: Se$_{60}$Ge$_{40}$. The thermal data of the lower three curves are from Ref. 17.
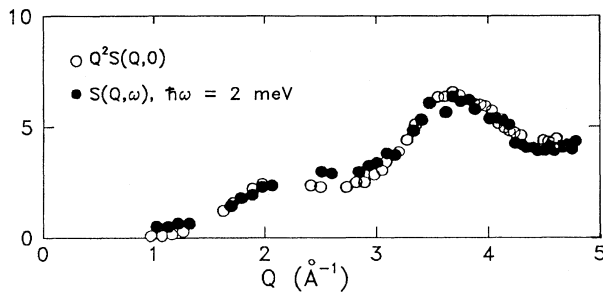
FIG. 11. $S(Q,0)Q^2$ compared with $S(Q,\omega)$ for $\hbar\omega=2$ meV in Se glass. For acoustic vibrations the structure factors are expected to be similar.

below the maximum in the floppy mode peak. The agreement indicates that modes at this energy do not depart significantly from acoustic behavior. Similar results have been found for several of the Se-As-Ge alloys in this energy region.

V. SUMMARY

We find that the variation in network connectivity in Se-As-Ge glasses has an effect on low-frequency vibrational modes which appears to be completely determined by the average coordination number $\langle r \rangle$. In particular, the number of floppy modes due to underconstrained atomic configurations, as measured by $\langle 1/\omega \rangle$, is a smooth function of $\langle r \rangle$. The existence of a rigidity per-colation threshold at $\langle r \rangle =2.4$ is consistent with the data, but its effect on vibrational properties is not dramatic. There is a good correspondence of the neutron data with Raman scattering, ultrasonic elastic moduli, and specific-heat measurements. Excitations observed near 2 meV in glassy Se-As-Ge, about half-way up the floppy mode peak, have scattering properties like those expected from acoustic phonons.

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