

Neutron inelastic scattering study of Se-As-Ge glasses: A test of the vibrational isocoordinate rule

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Determinations of the generalized neutron vibrational density of states (GVDOS) made on samples of Se-As-Ge glass alloys by neutron inelastic scattering at the NIST Center for Neutron Research are presented. It is observed that up to a certain characteristic vibrational energy the GVDOS are nearly identical for alloys over a broad range of compositions as long as they have the same average coordination number $\langle r \rangle$. In the present work this feature, referred to as the vibrational isocoordinate rule (VIR), is established for samples of Se-As-Ge alloys over the entire glass-forming region with $\langle r \rangle$ ranging from 2.16 through the theoretical rigidity percolation threshold 2.4 up to 3.2. Compositional exceptions to the VIR have been found along and near the Se-As binary alloy line above $\langle r \rangle = 2.4$. [S0163-1829(99)12105-2]

I. INTRODUCTION

Covalent, multicomponent glass alloys having a variety of compositions with the same average coordination number $\langle r \rangle$ (Ref. 1) are called "isocoordinate glasses." Such glasses often display "isocoordinate rules," namely, properties which depend only on $\langle r \rangle$ and not on composition.² These isocoordinate rules are especially evident in the chalcogenide glasses, i.e., made with elements of group VI B: S, Se, and Te.

Examples of isocoordinate rules in chalcogenide glasses involving mechanical and thermal properties are the behaviors of ultrasonic elastic constants,³⁻⁵ hole relaxation in Se-H spectral hole-burning experiments,⁶ and the behaviors of the glass transition temperatures T_g ,^{4,7} dilatometric softening temperatures,⁷ and measures of hardness.^{7,8} Using bond length as a ruler, these behaviors span length scales from the macroscopic (elastic constants, hardness) to tens of bond lengths (spectral hole burning). Similarly, using typical vibrational frequencies as a measure, the glass transition temperature, spectral hole relaxation, and ultrasonic behavior are all long-time-scale phenomena. It is likely that mechanical constraint theories of covalent structures developed by Phillips⁹ and Thorpe¹⁰ lie at the foundation of these phenomena.

It is of interest in this connection to add to the already existing isocoordinate rules the vibrational isocoordinate rule (VIR) which was observed by Kamitakahara *et al.*¹¹ The VIR is that the generalized neutron vibrational density of states (GVDOS) of pairs of isocoordinated glasses are nearly identical up to some characteristic energy, typically about 20 meV. Compared to acoustic measurements, this observation extends the time scale down by seven orders of magnitude and the length scale to a few bond lengths for isocoordinate rule behavior. The exploration of the compositional extent and frequency range of VIR behavior over the glass-forming region of the Se-As-Ge system is the subject of the present study.

The glasses of group VI B chalcogens, either by themselves or in combination with other elements,¹² especially

from groups IV B and V B, present a rich array of glass formers. In particular, the Se-As-Ge alloys, having covalent coordination numbers from 2 to 4, provide an exceptionally broad range for study (see Fig. 1 in which the curved line represents the boundary of the glass-forming region found in the text by Borisova¹²). This system features local structures from rings and chains in Se to quasi-two-dimensional structures along the As-Se binary line,¹³ to three-dimensionally rigid network glasses such as GeSe₂.¹⁴ Glasses of this system have been reported¹² with average coordination numbers ranging continuously from $\langle r \rangle = 2.0$ to 3.2.

Below are described our observations of isocoordinate rule behavior in these glasses. Since there seems to be some variety of methods in the literature, a detailed description of sample preparation and an outline of sample characterization is provided. In connection with displaying values of T_g measured in this work, we plot them along with measurements taken from the literature to display an isocoordinate rule and exceptions to it which turn out to be exceptions to the VIR as

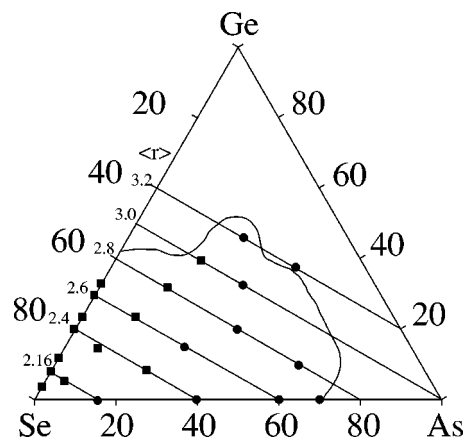


FIG. 1. The ternary glass diagram indicates the sample compositions (circles) which were used for this work in addition to the samples previously measured by Kamitakahara *et al.* (Ref. 11) (squares). The straight lines across the ternary graph represent isocoordinates and the curved line displays the glass-forming region proposed by Borisova (Ref. 12).

TABLE I. A list of the prepared samples, ordered by the average coordination number, is displayed. For each alloy the composition and glass transition temperature based on the point of inflection method are given. The last two columns provide information on the preparation procedure. The numbers need to be interpreted as following. For example, the 2.16 sample was heated slowly from 400 to 820 °C within 4 h, making stops at several intermediate temperatures. The sample was then kept at 820 °C for 2 h and 30 min before it was quenched into ice-water (iw). Other abbreviations: oiw=oil-ice-water, oisw=oil-ice-salt-water, a=amorphous, and c=crystalline.

$\langle r \rangle$	Se	As (at. %)	Ge	T_g (°C)	preparation [°C (h:min)]	quenching/result
2.16	0.840	0.160	0.000	92	400–820 (4:00), 820 (2:30)	iw/a
2.4	0.600	0.400	0.00	196	400–822 (2:30), 822 (4:45)	iw/a
2.6	0.550	0.300	0.150	274	250–750 (4:30), 750 (4:05)	air/a
2.6	0.400	0.600	0.000	135	300–860 (4:50), 860 (3:15), 780 (1:45)	oiw/a
2.7	0.300	0.700	0.000	150	400–850 (2:15), 850 (4:40), 780 (1:00)	oiw/a
2.8	0.400	0.400	0.200	346	143–750 (3:40), 750 (1:20)	air/a
2.8	0.300	0.600	0.100	315	400–820 (2:15), 820 (5:00)	oiw/c
					600–1000(1:30), 1000 (1:20), 822(10:45), 720 (1:00)	oiw/a
3.0	0.325	0.350	0.325	419	600–1050 (0:45), 1050 (11:35), 820 (3:50)	oiw/a
3.2	0.250	0.300	0.450	437	400–800 (3:00), 800 (5:00)	iw/c
					600–1050 (0:10), 1050 (14:50), 750 (5:45)	oiw/c
					820 (0:20)	oiw/a
3.2	0.175	0.450	0.375	445	400–1050 (0:40), 1050 (12:20), 822(1:10)	oisw/c
					822 (2:35)	oisw/a

well. A discussion of neutron scattering results which establish the validity of the VIR over the glass-forming region of these alloys follows. Attention is then turned to the exceptions to the VIR which come in the frequency domain and in the composition domain. The origin of each is examined. Finally, the concept that isocoordinate rules are associated with network connectivity only, and not with network topology or dimensionality, is discussed.

II. EXPERIMENTAL PROCEDURES

A. Sample preparation

The Se-As-Ge alloys were prepared following the descriptions of Susman *et al.*,¹⁵ Azoulay *et al.*,¹⁶ and Halfpap.¹⁷ Several details are pointed out in this section. Quartz ampoules were cleaned in a 25 wt. % hydrofluoric acid (HF aqueous) bath and outgassed until the pressure stabilized to 10^{-7} Torr. All sample handling was performed in a helium-filled glove box (oxygen level: ≤ 5 ppm, water vapor level ≤ 0.05 ppm). The pure elements were treated in the following way. Selenium shot (ALFA, purity 99.999 wt. %) was melted for 2–3 hours in a continuously evacuated ($p \sim 10^{-7}$ Torr) quartz ampoule to remove hydrogen and oxygen as volatile H_2Se and SeO_2 . High purity arsenic (ALFA, purity 99.9999 wt. %) was heated to 350 °C in an evacuated quartz ampoule while the top part of the ampoule was kept at 25 °C. This distills out the volatile oxide contaminants. Even though germanium (ALFA, purity 99.999 wt. %) does not attract oxygen in great amounts on its surface, it was heated under vacuum to 450 °C overnight in order to reduce the oxygen content.

Weighed starting materials usually of the order of grams measured to within 10 mg were loaded into 2-mm thick-walled quartz ampoules, sealed under 10^{-7} Torr dynamic vacuum and transferred to a rocking furnace for further treatment. The duration of heating in the rocking furnace and

post-quench annealing temperatures depended strongly on sample composition. Preparation details are provided in Table I. The ampoules were removed from the furnace and immediately quenched in an ice-salt water mixture covered with peanut oil. The peanut oil coats the hot ampoule as it enters the quench bath and, compared with water, apparently reduces the vapor layer isolating the ampoule from the bath, thus improving thermal contact. It was necessary to use peanut oil for the high arsenic and $\langle r \rangle = 3.2$ samples. For several alloys the heating process had to be repeated as indicated in Table I because of crystallization of the quenched sample. In most instances the unopened ampoule with crystalline material was placed directly back into the furnace for further treatment. Crystalline material can often be distinguished from glassy material by its dull color, black coating, or bubble formation on the surface. Finally, all samples were annealed for 18–20 h at 100 °C below their glass transition temperatures to reduce strains.

B. Sample characterization

Sample characterization was done in three steps: x-ray diffraction (XRD), energy-dispersive x-ray spectroscopy (EDX), and differential scanning calorimetry (DSC). XRD experiments using Cu $K\alpha$ radiation were performed over a range of $2^\circ < 2\theta < 120^\circ$ to check for Bragg peaks and therefore any crystalline structure. Samples exhibiting Bragg peaks were submitted to a modified cycle of heat treatment and quenching until subsequent XRD measurements showed no further Bragg peaks to within the sensitivity of the measurement. The recorded XRD patterns were also monitored for systematic variations of the first sharp diffraction peak (FSDP), a signature of intermediate-range order.

EDX was used to test the homogeneity and stoichiometry of the samples. Several small chunks of one sample batch were polished flat using 0.1 μm alumina powder and mounted within one EDX run. These spectra were then com-

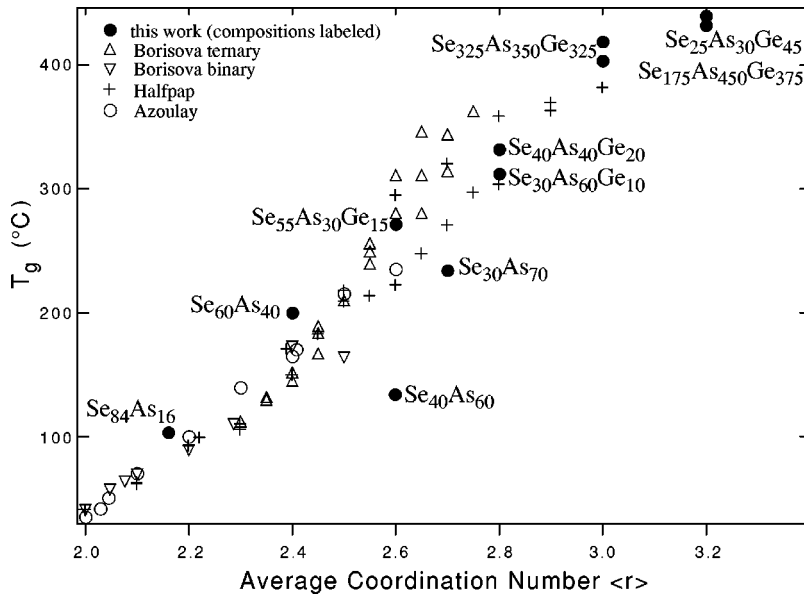


FIG. 2. An example of an isocoordinate rule is the behavior of the glass transition temperature. For underconstrained glasses the glass transition temperatures are independent of composition for isocoordinated alloys. Above the theoretical rigidity percolation threshold of $\langle r \rangle = 2.4$ isocoordinated alloys have a wider spread in T_g . Two exceptions, namely, As_3Se_2 and As_7Se_3 , can be found, with both of them being also outstanding in their GVDOS. Samples used in this work are labeled with their composition. The uncertainty of these T_g 's were found to be $\pm 5^\circ\text{C}$. References for all additional T_g 's: Borisova (Ref. 12), Halfpap (Ref. 25), and Azoulay *et al.* (Ref. 16).

pared to Se, As, and Ge standards. The homogeneity and correct stoichiometry could be verified to within the 3% experimental uncertainty of the spectrometer. The stoichiometries reported in Table I, however, are based on the weights of the starting materials used.

DSC heating measurements were performed on a Perkin Elmer Joel JSM 5300. It has been shown by Mahadevan and Giridhar¹⁸ that for several chalcogenide glasses the glass transition temperatures vary by 30 K for heating rates from 1.25 to 40 K/min. For this reason it is important to note that all scans were performed under the same conditions with a heating rate of 30 K/min. The glass transition temperatures were determined by the point-of-inflection method using the heating curves. Glass transition temperatures versus average coordination numbers are displayed in Fig. 2. This graph is a plot of our T_g along with values for Se-As-Ge glasses found in the literature. Since the data listed are from three sources, differences due to experimental methods and evaluations of the data are to be expected. Figure 2 illustrates the T_g isocoordinate rule. As already pointed out by Tatsumisago *et al.*,⁴ composition-specific variations, i.e., departures from the T_g isocoordinate rule, become particularly noticeable above the theoretical rigidity percolation threshold of $\langle r \rangle = 2.4$. Figure 2 indicates that at higher average coordination numbers (see, e.g., $\langle r \rangle = 3.2$), the isocoordinate rule appears to be in effect again. However, since the glass-forming region for $\langle r \rangle$ values above 2.8 is reduced considerably (see Fig. 1), the validity of the T_g isocoordinate rule cannot be explored over a very wide composition range.

III. NEUTRON TOF EXPERIMENT

Time-of-flight (TOF) neutron inelastic measurements were performed at the Fermi Chopper Spectrometer (FCS) at the National Institute of Standards and Technology (NIST) Center for Neutron Research. In the first run incident neutrons of wavelength 2.435 Å were chosen to provide sufficient intensity, resolution, and a suitable Q range for the use of the incoherent approximation in analyzing the data for the vibrational density of states. The sample container used in this initial Se-As-Ge experiment was an aluminum foil cyl-

inder with dimensions 5.4 cm length by 1.6 cm diameter and 0.07 mm wall thickness. It was placed into an outer aluminum foil container of dimensions 6 cm length by 2 cm diameter and 0.15 mm wall thickness, and the whole assembly was mounted into a 30-cm-diam evacuated Al can. The exposed sample area was defined by a cadmium mask placed on the outer surface of the can. The samples, consisting of chips of dimensions a few mm, were on average 18 g. In subsequent runs, for an improved intensity 4.80 Å incident neutrons were used. The reduced Q range attending this selection had no apparent effect on the spectra. The 4.8 Å spectra are downshifted by about 1 meV at 20 meV compared to the 2.435 Å spectra. This discrepancy remains unresolved. The Al foil container was also changed to an annular cylinder of 2 cm outer diameter having 2 mm sample region thickness to reduce multiple scattering and absorption. A typical sample run lasted 22 to 28 h. The empty container runs were 13 h long and the vanadium run, which was used to calibrate the detectors, took 4 h.

Data were normalized to the scaled incident beam exposure dose as determined by monitor detector counts. The sample scattering intensity for subsequent analysis was obtained by subtracting smoothed empty container data multiplied by the ratio of sample run to empty run monitor counts.

In reducing the data to extract the GVDOS several approximations are thought to be adequate for the qualitative comparisons made in this study. Differences in atomic masses (Se, As, Ge: 78.96, 74.92, 72.61 amu) and in coherent neutron scattering lengths (Se, As, Ge: 7.97, 6.58, 8.185 fm) were ignored. A rough estimate of multiple scattering showed that it did not affect the comparisons of GVDOS made in this work. The GVDOS was obtained in the incoherent approximation as described previously,¹¹ correcting for multiphonon contributions and absorption using MUPHOCOR.¹⁹

IV. EXPERIMENTAL RESULTS AND DISCUSSION

GVDOS determined in this work of Se-As-Ge alloys with average coordination numbers ranging from 2.16 to 3.2 are displayed in Fig. 3 as symbols with lines to guide the eye.

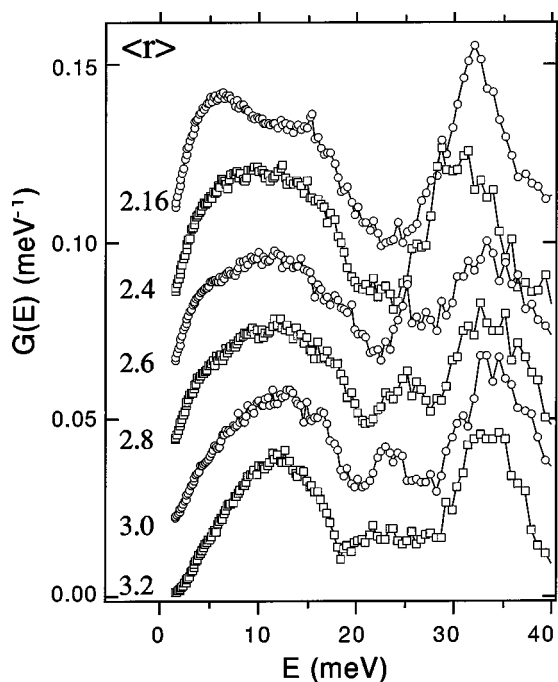


FIG. 3. GVDOS of Se-As-Ge alloys spanning the glass-forming region from $\langle r \rangle = 2.16$ to 3.2 are displayed. Starting from the highest $\langle r \rangle$ value, successive curves are shifted by 0.015 units on the vertical scale. The compositions of these alloys are as follows: $\langle r \rangle = 2.16$, $\text{Se}_{84}\text{As}_{16}$; $\langle r \rangle = 2.4$, Se_6As_4 ; $\langle r \rangle = 2.6$, $\text{Se}_{55}\text{As}_{30}\text{Ge}_{15}$; $\langle r \rangle = 2.8$, $\text{Se}_4\text{As}_4\text{Ge}_2$; $\langle r \rangle = 3.0$, $\text{Se}_{325}\text{As}_{350}\text{Ge}_{325}$; $\langle r \rangle = 3.2$, $\text{Se}_{25}\text{As}_{30}\text{Ge}_{45}$.

The underconstrained glass with $\langle r \rangle = 2.16$ shows the “floppy mode” peak at 5 meV identified earlier by Kamitakahara *et al.*¹¹ With increasing $\langle r \rangle$ value the floppy mode intensity decreases and can be seen in the overconstrained glasses ($\langle r \rangle > 2.4$) as a shoulder in the low-energy regime. This behavior was already observed in Ref. 11 on a different selection of Se-As-Ge alloys.

Figure 4 illustrates the central result of this work, namely, that the vibrational isocoordinate rule holds over most of the glass region: for underconstrained glasses ($\langle r \rangle = 2.16$) as well as for overconstrained ones [$\langle r \rangle = 2.8, 3.2$ (3.0 not shown)]. A review of Fig. 1 shows the very wide range of compositions of the isocoordinate glasses whose spectra are shown here. It should be pointed out that spectra of isocoordinated glasses measured at NIST using 2.435 Å incoming neutrons and the earlier measurements of Kamitakahara *et al.* taken at the Institute Laue Langevin TOF instrument IN4 using 2.2 Å incoming neutrons (different spectrometers, wavelengths, samples made in three different laboratories) are in agreement to within ± 0.25 meV.

Most significant is the comparison in Fig. 5 of Ge_2Se_8 and As_2Se_3 which are isocoordinates terminating the $\langle r \rangle = 2.4$ line. Since it is expected that Ge_2Se_8 is a predominantly three-dimensional (3D) network glass while As_2Se_3 is a predominantly 2D one, it is remarkable to see that the low-energy regions up to 20 meV are nearly identical.

Although the VIR appears to be a strong empirical rule, its theoretical foundation remains obscure. The energy scale for vibrations over the entire glass-forming region is nearly the same: it ends near 40 meV. This reflects the similarity in mass and bond forces among the three elements. Neverthe-

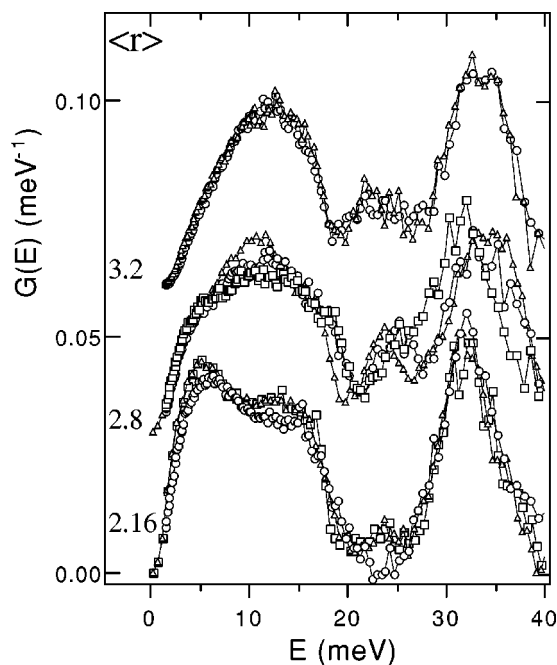


FIG. 4. The VIR is best shown by plotting GVDOS of isocoordinated alloys on top of each other. Data consist of FCS (see Table I) and IN4 (see Ref. 11) measurements. $\langle r \rangle = 2.16$, $\square \text{Se}_{92}\text{Ge}_{08}$, $\triangle \text{Se}_{89}\text{As}_{06}\text{Ge}_{05}$, $\circ \text{Se}_{84}\text{As}_{16}$; $\langle r \rangle = 2.8$, $\triangle \text{Se}_{51}\text{As}_{18}\text{Ge}_{31}$, $\circ \text{Se}_4\text{As}_4\text{Ge}_2$, $\square \text{Se}_3\text{As}_6\text{Ge}_1$; $\langle r \rangle = 3.2$, $\circ \text{Se}_{25}\text{As}_{30}\text{Ge}_{45}$, $\square \text{Se}_{175}\text{As}_{450}\text{Ge}_{375}$. Successive isocoordinated pair curves are shifted by 0.030 units on the vertical scale.

less, there are noticeable and characteristic differences in the GVDOS above ~ 20 meV for different stoichiometric isocoordinates which reflect differences in the short-range order (SRO) of these glasses. One example is in the $\langle r \rangle = 2.4$ data of Fig. 5 where the A_1 mode of $\text{GeSe}_{4/2}$ tetrahedra is evident as a peak near 25 meV in the Se_8Ge_2 (\triangle) spectrum but absent in As_2Se_3 (\circ) in which the SRO about each As is closer to trigonal. From this we conjecture that the broadband below 20 meV is sensitive *only to connectivity and not to network topology* as expressed in the short-range order. This broadband is dominated by modes extending widely over the network and not by modes localized on robust “molecular”

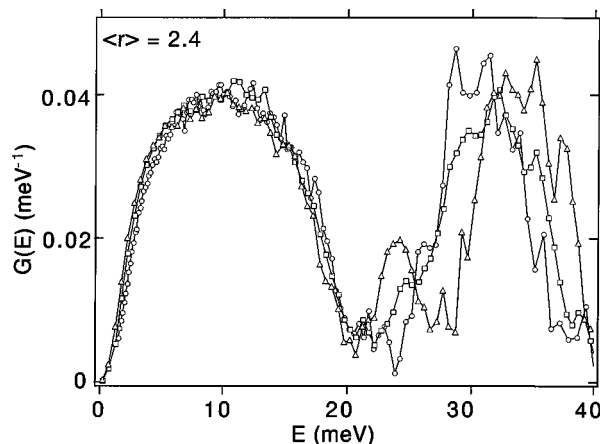


FIG. 5. Three Se-As-Ge alloys of average coordination $\langle r \rangle = 2.4$ are shown. Data consist of FCS (see Table I) and IN4 (see Ref. 11) measurements. $\triangle \text{Se}_8\text{Ge}_2$, $\square \text{Se}_{675}\text{As}_{250}\text{Ge}_{075}$, $\circ \text{Se}_3\text{As}_2$.

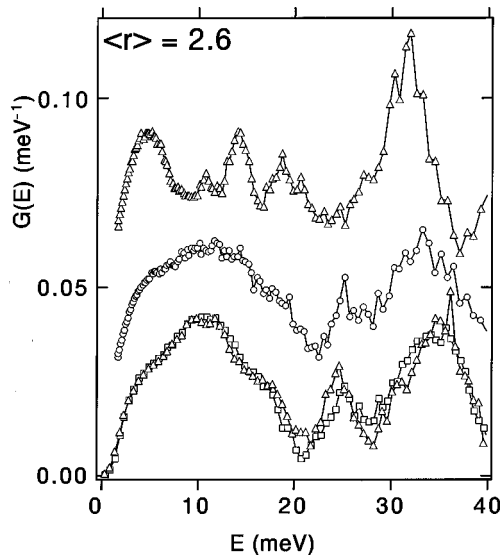


FIG. 6. The bottom curves, $\triangle \text{Se}_7\text{Ge}_3$ and $\square \text{Se}_{63}\text{As}_{14}\text{Ge}_{23}$ (both IN4 data), and the middle one, $\circ \text{Se}_{55}\text{As}_{30}\text{Ge}_{15}$ (FSC data), are isocoordinates at $\langle r \rangle = 2.6$ which follow the VIR. The top curve, As_3Se_2 ($\langle r \rangle = 2.6$) is an exception to the vibrational isocoordinate rule. Starting from the bottom, successive data curves are shifted up by 0.030 units on the vertical scale.

features in the glass such as the tetrahedron giving rise to the A_1 mode. Then the energy at which departure from VIR behavior occurs corresponds to vibrational modes in which local SRO, not just average connectivity, begins to matter. Model calculations are underway to test this point.²⁰ Thus regions of the spectrum displaying exceptions to the VIR are expected to have considerable localized character. As shown below, there are also glass compositions which are exceptions to the VIR even within the first broadband.

The exceptions to the VIR found so far occur along and near the Se-As line beyond $\langle r \rangle = 2.4$. In particular, As_3Se_2 , $\langle r \rangle = 2.6$, displays a peaky behavior in the low-energy region (see Fig. 6). As a direct comparison to As_3Se_2 , three additional 2.6 alloys, which follow the VIR, are also displayed in the lower part of Fig. 6. As_3Se_2 , which was prepared and measured on four separate occasions, always displays the same atypical behavior in the low-energy regime. X-ray, DSC, and Raman measurements performed on portions of samples made in this study show clearly that this alloy is indeed a glass. In particular Fig. 7 displays the x-ray powder patterns of the isocoordinated alloys As_3Se_2 and $\text{Se}_{55}\text{As}_{30}\text{Ge}_{15}$. No Bragg peaks for either sample were observed, demonstrating that the alloys are indeed glassy. Compared to Fig. 6 where the GVDOS of these glasses are very different, Fig. 7 shows that the x-ray patterns are rather similar except for a few subtle differences. There is a noticeable Q shift and narrowing of the FSDP of As_3Se_2 compared to $\text{Se}_{55}\text{As}_{30}\text{Ge}_{15}$. The Raman measurement on As_3Se_2 shows an intense, broad, asymmetric feature centered at $\sim 230 \text{ cm}^{-1}$ and no noticeable peaks at lower frequencies where the neutron results show sharp features at 10.7, 14.1, and $18.6 (\pm 0.1) \text{ meV}$ (86, 114, and 150 cm^{-1} , respectively).

A clue to these departures from the VIR may be discerned from an examination of the equilibrium crystalline phase diagram of $\text{As}_x\text{Se}_{1-x}$,²¹ which indicates that at the composition

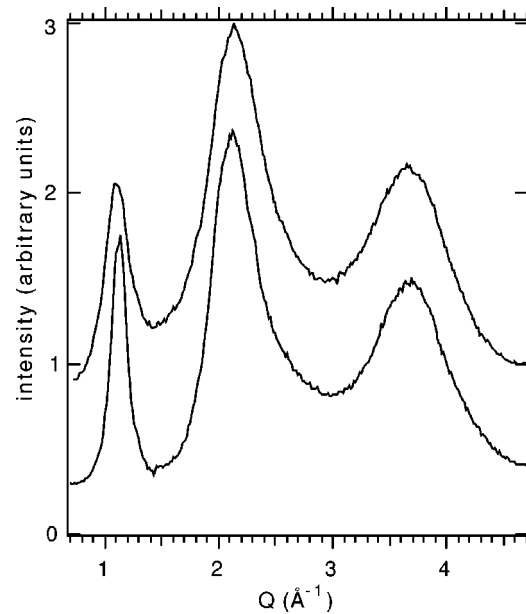


FIG. 7. The x-ray powder patterns of As_3Se_2 (bottom) and $\text{Se}_{55}\text{As}_{30}\text{Ge}_{15}$ (top), both $\langle r \rangle = 2.6$, are compared. The top curve is shifted up by 0.5.

$\text{As}_{60}\text{Se}_{40}$ one expects a slow cooling run along the isopleth to result, beginning at 673 K, in precipitation of pure As followed by freezing at the eutectic temperature (522 K) of a fine mixture of trigonal As and monoclinic As_4Se_4 in the ratio of the eutectic composition (As_4Se_3). Monoclinic As_4Se_4 is a molecular crystal in which these ‘‘cage’’ molecules are weakly bonded to each other by van der Waals forces. It is then reasonable to expect a quench along the same isopleth to result in a ‘‘polymerized’’ network glass containing some fraction of isolated As_4Se_4 molecules and As-rich regions. Raman and infrared²² spectroscopy of crystalline As_4Se_4 exhibit strong sharp lines at the frequencies 134, 190, 207, 240, and 248 cm^{-1} , and weaker features at 92, 104, 109, 114, 136, 144 cm^{-1} . In the range below 180 cm^{-1} this list contains three frequencies (92, 114, and 144 cm^{-1}) which lie near the ones observed in this work.

The phase diagram also exhibits crystalline phases of As_4Se_3 which can be achieved only by long anneals below 400 K. This phase decomposes above that temperature to a solid mixture of trigonal As and monoclinic As_4Se_4 . It is possible, but less likely, to have admixtures of As_4Se_3 in the glass as well. Consequently, of the observed vibrational frequencies²³ of this molecule the lowest ones, 107 and 140 cm^{-1} , are possible candidates for two of the features seen above.

Se_3As_7 with $\langle r \rangle = 2.7$ is also an exception to the VIR as is $\text{Se}_{35}\text{As}_{60}\text{Ge}_{05}$ with the same coordination number. It should be emphasized that these glasses show sharp features at essentially the same frequencies as As_3Se_2 , although these features are beginning to be less evident in the Ge-containing glass $\text{Se}_{35}\text{As}_{60}\text{Ge}_{05}$. VIR behavior is nearly completely recovered for the isocoordinate glass $\text{Se}_5\text{As}_3\text{Ge}_2$.

The fact that the sharp features found in the exceptions to the VIR occur at the same frequencies suggests a common physical origin: the separation in these glasses on a nanoscopic scale of regions containing isolated molecules. If in-

deed this explanation for the exceptions is correct, it would show that *departures from the VIR correspond to departures from connectivity*, and this would support the conjecture that the VIR is an expression of connectivity alone. The verification of the existence of isolated molecular fragments in these glasses and their identification is the subject of current research.

V. SUMMARY

In this work the vibrational isocoordinate rule has been established over the entire region of the Se-As-Ge ternary diagram with the exception of binary Se-As glasses with $\langle r \rangle > 2.4$ and ternary glasses near the Se-As line. We conjecture that the VIR is an expression of network connectivity only and not SRO. Exceptions have been found along and near the Se-As line at $\langle r \rangle = 2.6$ and $\langle r \rangle = 2.7$ which all show the same sharp spectral features. It is suggested that the exceptions to the VIR will find their explanation in departures

from connectivity, namely, the presence of isolated, weakly bound molecules in these glasses displaying characteristically sharp molecular vibrational modes.

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- ¹Here $\langle r \rangle = \sum_{i=1}^n c_i(8 - N_i)$ for an alloy of composition $A = \sum_i A_i c_i$ made of elements A_i , c_i is the atomic fraction of element A_i , and N_i is its group number in the Periodic Table. This equation expresses the “8-N” rule originally proposed by Mott (Ref. 24) which is known to work well for many covalent network glasses (Ref. 13). Covalent network glasses are made of elements in which covalent forces dominate and ionic and other bonding forces may be neglected. For these systems it is sensible to use $\langle r \rangle$ to characterize network connectivity.
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