

Local modes in tetrahedral  $\text{Ge}(\text{S}_x\text{Se}_{1-x})_2$  glasses

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(Received 10 June 1982)

The Raman spectra of melt-quenched  $\text{Ge}(\text{S}_x\text{Se}_{1-x})_2$  glasses are discussed for  $x = 0.25$ . The spectra show well-defined mixed-anion  $A_1$ -like breathing modes of  $\text{GeS}_{n/2}\text{Se}_{(4-h)/2}$  tetrahedra whose frequencies scale roughly with the corresponding modes of  $\text{GeCl}_n\text{Br}_{4-n}$  molecules. Quantitative examination of the scaling factors shows that the scaling in the glass is strongly modified by  $A_1$ - $F_2$  mode-mode interactions produced by the loss of  $A_1$  symmetry and greatly enhanced intertetrahedral interactions.

The molecular structure of many network glasses, such as  $g\text{-SiO}_2$ ,  $g\text{-As}_2\text{Se}_3$ , and  $g\text{-GeSe}_2$ , can be described in terms of building blocks or corner-sharing clusters. When these clusters are tetrahedral, as in glasses of the type  $A^M B_2^N$  with  $M = 4$  and  $N = 6$ , this description is particularly useful because of the great stability and high symmetry of the  $A(B_{1/2})_4$  tetrahedral units. Moreover, when the corner-sharing bond angle  $\theta_B$  is close to  $\pi/2$  Sen and Thorpe showed<sup>1</sup> that the normal vibrational modes of the tetrahedral building blocks are largely decoupled in the glass. This explains the observation by Raman scattering<sup>2-6</sup> of four distinct and well-separated vibrational bands in  $g\text{-GeS}_2$  and  $g\text{-GeSe}_2$  where  $\theta_B$  is close to  $100^\circ$ . These four bands correspond qualitatively to the  $A_1$ ,  $E_2$ , and  $2F_2$  normal tetrahedral vibrational modes which are observed<sup>7</sup> in the analogous gas molecules  $\text{GeCl}_4$  and  $\text{GeBr}_4$ . Raman scattering by the  $A_1$  symmetric breathing mode is particularly strong and narrow in the glass, with a full width at half maximum of  $\Delta\nu_1/\nu_1 = 0.07$ .

While the interactions between tetrahedra are weak, they are still present and because tetrahedra are the basic structural units in so many good glass formers the study of them is of considerable interest. We have found that these interactions can be examined quantitatively by preparing mixed tetrahedra  $\text{GeS}_{n/2}\text{Se}_{(4/2-n/2)}$  in pseudobinary  $\text{GeS}_x\text{Se}_{2-x}$  alloys. The  $A_1$ -like vibrational frequencies  $\nu_1(n)$  of the  $\text{GeS}_{n/2}\text{Se}_{(4/2-n/2)}$  mixed tetrahedra can then be compared with those of the mixed tetrahedral molecules  $\text{GeCl}_n\text{Br}_{4-n}$ , respectively, which have parallel mass defects. The mixed tetrahedra sensitively probe cluster interactions. We have developed a one-parameter theory of  $\nu_1(n)$  for  $n = 0, 1, 2$ , and 3 which constitutes the first realistic and quantitative model of cluster interactions in a glass-forming material.

The techniques of sample preparation and Raman scattering used have been described previously.<sup>6,8</sup> In particular, the homogeneity of the pseudobinary melt-quenched glass alloys was examined by differential thermal analysis, and no evidence was found for

phase separation or stoichiometry. The Raman spectrum taken at  $-190^\circ\text{C}$  for  $g\text{-GeS}_{0.5}\text{Se}_{1.5}$  is shown in Fig. 1, graph A. This spectrum is superficially similar to that of  $g\text{-GeSe}_2$ , apart from the additional peaks at 218, 232, and 248  $\text{cm}^{-1}$  which lie on the high-frequency side of  $\nu_1(0) = 203 \text{ cm}^{-1}$ , which is the  $A_1$  peak of  $\text{Ge}(\text{Se}_{1/2})_4$  clusters.

To determine the origin of these additional peaks one might attempt to grow single crystals of  $\text{GeS}_x\text{Se}_{2-x}$  alloys. However, the unit cells of the crystalline forms of these materials are large and complex, with 48 or 72 atoms/unit cell, and other workers<sup>9</sup> have encountered difficulties in growing large single crystals of the related glass former  $\text{As}_2(\text{S}_x\text{Se}_{1-x})_3$ . We have therefore used the recently discovered phenomenon of athermal laser annealing<sup>8</sup> to microcrystallize our sample at room temperature. As shown in Fig. 1, graph D, partial crystallization

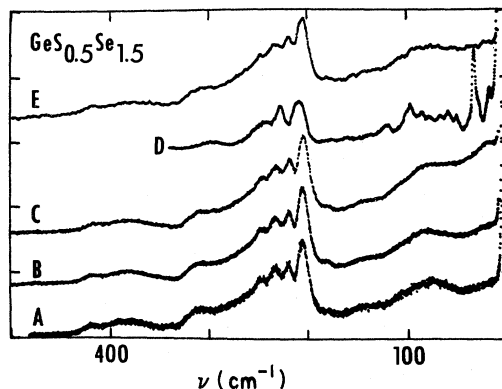


FIG. 1. Raman spectra of melt-quenched  $g\text{-GeS}_{0.5}\text{Se}_{1.5}$  at  $-196^\circ\text{C}$ . Laser excitation at  $\hbar\omega = 1.916 \text{ eV}$  with spot size fixed near  $50 \times 150 \mu\text{m}^2$  and laser power level in mW: A, 4.8; B, 48; C, 72; D, 122. Next, the sample was relaxed overnight at room temperature in the dark before recording E at 16 mW. The figure shows the various stages of athermal laser annealing in B-D, as discussed in Ref. 8 for  $g\text{-GeSe}_2$ , followed by thermal reversal in E.

shifts and broadens the  $A_1$ -like lines. Microscopic details of the athermal laser annealing of pseudobinary glasses and a comparison with a similar treatment<sup>8</sup> of  $g$ -GeSe<sub>2</sub> will be given elsewhere. The  $\nu_1(n)$   $A_1$  normal-mode glass frequencies are listed in Table I where they are compared with the corresponding frequencies of the mixed anion molecular  $\text{GeCl}_n\text{Br}_{4-n}$  species.

It is apparent from Table I that the normal mode frequencies in the solid glass  $\nu_s$  of weakly coupled Ge chalcogenide tetrahedra are consistently lower than the corresponding frequencies  $\nu_m$  of the chemically analogous Ge tetrahalide gas molecules. For qualitative purposes this pattern has been described by previous workers<sup>3,10</sup> in terms of empirical scaling factors  $\alpha_e$

$$\nu_s = \alpha_e \nu_m . \quad (1)$$

In general  $\alpha_e \leq 1$  and it varies between 0.78 and 1.05 for different normal modes of different chalcogen and analogous halogen tetrahedra. For the symmetric  $A_1$  breathing mode of  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedra compared to  $\text{GeBr}_4$

$$\alpha_e = 0.85 . \quad (2)$$

One of the reasons why  $\nu_s < \nu_m$  is that the effective nuclear charge of the chalcogens is less than that of the halogens. This factor can be calibrated quite accurately for the  $A_1$  modes because these pseudo-symmetric breathing mode frequencies depend primarily on the bond-stretching force constant  $k_r$  and are nearly independent of the weaker and less transferable bond-bending force constant  $k_\theta$ . For single bonds, differences in  $k_r$  between solid and gaseous environments are small so that the chemical scaling factor  $\alpha_c$  defined by

$$\alpha_c^2 = k_r(\text{SH}_2)/k_r(\text{ClH}) \quad (3)$$

is an accurate estimate of the frequency reduction due to the replacement of halogens by chalogens.

TABLE I. Raman frequencies ( $\text{cm}^{-1}$ ) of  $\nu_1$ -like modes of mixed-anion tetrahedra. In the gas molecules  $Y = \text{Br}$  and  $X = \text{Cl}$ . In the glass tetrahedra  $Y = \text{Se}_{1/2}$  and  $X = \text{S}_{1/2}$  (corner-sharing chalcogens). The empirical gas scaling factor is described by Eq. (2). The interacting tetrahedral (int. tetra.) model is described by Eq. (5).

Species	Gas	Scaled gas	Int. tetra.	Expt.
$\text{GeY}_4$	235	202	202	203
$\text{GeY}_3X$	258	222	221	218
$\text{GeY}_2X_2$	282	243	238	232
$\text{GeYX}_3$	310	266	241	244

The bond-stretching force constants of these hydrides are well known<sup>11</sup> and from Eq. (3) we obtain

$$\alpha_c = 0.91 . \quad (4)$$

We expect that the difference between the empirical scaling factor  $\alpha_e$  and the chemical scaling factor  $\alpha_c$  arises from intertetrahedral interactions which are present in the solid and negligible in the gas. From Fig. 1, graph A we notice that there is a Raman scattering band near  $\Omega_F = 300 \text{ cm}^{-1}$  which has previously been assigned<sup>6</sup> to tetrahedral odd-parity  $F_2$  modes. One can regard the mass defects associated with  $n \neq 0, 4$  in mixed  $AX_nY_{4-n}$  pseudotetrahedra as equivalent to dipole (odd-parity) perturbations of the valence force field, and describe their effect on the even-parity  $A_1$  modes through the phenomenological mode-mode interaction parameter  $\Gamma_{AF}$ . From second-order perturbation theory we have

$$\nu_s^2(n) = \alpha_c^2 \nu_m^2(n) + \frac{\Gamma_{AF}^4}{\alpha_c^2 \nu_m^2(n) - \Omega_F^2} . \quad (5)$$

With Eq. (5) we can use  $\nu_s(0)$  to determine  $\Gamma_{AF} = 122 \text{ cm}^{-1}$ .

We notice in Table I that

$$\nu_m(n) = \nu_m(0) + n \Delta \nu_m , \quad (6)$$

$$\nu_s(n) = \nu_s(0) + n \Delta \nu_s , \quad (7)$$

which determines the mixed tetrahedral scaling factor

$$\alpha_{mt} = \Delta \nu_s / \Delta \nu_m = 0.58 , \quad (8)$$

which is much smaller than  $\alpha_e$  or  $\alpha_c$ . The reason for this reduction is that the  $\Gamma_{AF}$  interaction produces screening of the mass defect dipole perturbations. This screening is dispersive because  $\nu_m(n)$  is close to  $\Omega_F$ . From Eq. (5) we have  $\alpha_{mt} = \alpha_c(1-g)$  with

$$g = \frac{(\alpha_e^2 - \alpha_c^2) \nu_m^2(0)}{\alpha_c^2 \nu_m^2(1.5) - \Omega_F^2} , \quad (9)$$

which yields  $\alpha_{mt} = 0.66$ , in reasonable agreement with Eq. (8). This is the first quantitative estimate of the effects of intercluster interactions on local vibrational modes in glasses.

Qualitative trends in the linewidths  $\Delta \nu_1(n)$  in glass pseudobinary alloys might be expected to be monotonic. If the structure can be qualitatively described as a continuous random network of corner-sharing tetrahedra, then interactions with similar tetrahedra (same  $n$ ) should be primarily responsible for the  $n$  dependence of  $\Delta \nu_1$ . In this case apart from a constant  $\Delta \nu_1(n)$  should decrease rapidly with increasing  $n$  approximately like  $x^n$ . On the other hand, if there is a tendency towards cluster and liquid immiscibility, then  $\Delta \nu_1(n)$  should increase with  $n$  as the cluster misfit increases in the selenium-rich predominantly  $\text{Ge}(\text{Se}_{1/2})_4$  network. Actually neither of these simple

behaviors is observed in our data.

The full widths at half maximum  $\Delta\nu_1(n)$  of the  $A_1$  peaks of the mixed tetrahedra in Fig. 1 range irregularly from 12 to 19  $\text{cm}^{-1}$ , for  $n = 0, 1, 2$ , and 3. These widths are much larger than that found in single crystals of  $\text{GeSe}_2$  [ $\Delta\nu_1(0) = 3 \text{ cm}^{-1}$ ], but they are comparable to the value found<sup>8</sup> in  $g\text{-GeSe}_2$  in similar circumstances ( $T = -196^\circ\text{C}$  and low power level) which is 17  $\text{cm}^{-1}$ . Thus the average width of the  $A_1$  mixed tetrahedral lines in the alloy glass is comparable to that of the  $A_1$  line in  $g\text{-GeSe}_2$ .

Recent experiments<sup>12-14</sup> have shown that most of the tetrahedra in  $g\text{-GeS}_2$  and  $g\text{-GeSe}_2$  are probably arranged in layer structures which closely resemble<sup>6,8</sup> fragments of the high-temperature crystalline phases of these compounds. We believe that the irregular variations in  $\Delta\nu_1$  widths in the pseudobinary alloy mixed tetrahedra arise in part from the layer geometry. For example, we can explain from the layer model why  $\Delta\nu_1(2)$  is larger than  $\Delta\nu_1(1)$ . We believe that the  $\nu_1(2)$  peak is actually composed of two peaks, corresponding to anion mixing or anion

segregation on opposite sides of layers. Similarly  $\Delta\nu_1(3)$  is probably broadened by edge-sharing constraints [as distinct from corner sharing, which characterizes  $\Delta\nu_1(1)$ ]. It will be of considerable interest to explore tetrahedral spectra in other alloys involving, e.g., Sn or Te, which have recently been studied by Mössbauer spectroscopy.<sup>13,15</sup>

In our spectra for  $\text{GeS}_x\text{Se}_{2-x}$  with  $x = 0.5$  and 0.25 we have been unable to separate the noncrystalline companion Raman line which is found at 219  $\text{cm}^{-1}$  in  $g\text{-GeSe}_2$  and which has been identified<sup>6</sup> as the signature of Se dimer "outrigger" units in layer clusters or "rafts." Experiments with smaller values of  $x$  are planned in an effort to determine what value of  $x$  is necessary for its disappearance. It is known that relatively small fractional replacements of Se by Te or Ge by Se or Sn cause the companion line or the dimer sites to disappear rapidly,<sup>2,13</sup> but it is surprising that S has a similarly large effect, because of the great similarity in the high-temperature crystals structures of  $\text{GeS}_2$  and  $\text{GeSe}_2$  and their close resemblance to the "outrigger raft."<sup>16</sup>

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