

## Microscopic origin of the companion $A_1$ Raman line in glassy $\text{Ge}(\text{S},\text{Se})_2$

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A solution to the long-standing problem of the companion  $A_1$  Raman line [symmetric breathing mode of  $\text{Ge}(\text{S},\text{Se})_4$  tetrahedra] in  $\text{Ge}(\text{S},\text{Se})_2$  glasses is proposed based on the observation of a similar doublet in the crystal. The proposed model assumes that  $g\text{-Ge}(\text{S},\text{Se})_2$  consists of units with a layered structure, in sharp contradistinction to  $g\text{-SiO}_2$ , which consists of a random, fully three-dimensional network.

The basic building block in crystalline  $\text{Ge}(\text{S},\text{Se})_2$  is a  $\text{Ge}(\text{S},\text{Se})_4$  tetrahedron, which also explains<sup>1</sup> the radial distribution function  $P(r)$  of glassy  $\text{Ge}(\text{S},\text{Se})_2$ . A large number of strong, narrow Raman lines are observed in the crystal and the glass.<sup>2-6</sup> In  $\text{Ge}(\text{S},\text{Se})_2$  glasses four strong Raman and infrared-active lines, corresponding to the four normal modes of vibration (symmetries  $A_1$ ,  $E$ ,  $F_2$ ,  $F_2$ ) have been observed which are comparable<sup>4</sup> in frequency and polarization to the tetrahedral modes of  $\text{Ge}(\text{Cl},\text{Br})_4$  molecules. The existence of local tetrahedral modes in the glass can be explained<sup>7</sup> from the fact that the corner-sharing bond angle at the chalcogen is  $100^\circ$ , very close to  $90^\circ$ , where the tetrahedra are effectively decoupled.

The special interest in this problem arises from the observation, which has puzzled many workers,<sup>2-6</sup> that the  $A_1$  (symmetric tetrahedral breathing) Raman mode seems to be split in the glass. A variety of explanations have been tentatively put forward<sup>2-6</sup> for the "extra" Raman line, which is strongly differentiated from the normal  $A_1$  line by its anomalous dependence on composition.<sup>2,3</sup> (In  $g\text{-Ge}_x\text{Se}_{1-x}$  alloys the intensity of the normal line at  $198\text{ cm}^{-1}$  varies with  $x$ , while the anomalous line at  $213\text{ cm}^{-1}$  varies with  $x^5$  for  $0 \leq x \leq 0.33$ .)

In this short paper we present new diagnostic Raman-scattering data on crystalline  $\text{GeSe}_2$  which show that two similar lines are present in the high-temperature (layer) form<sup>8</sup> of  $\text{GeSe}_2$  crystals, but with a much smaller splitting than is found in the glass. We suggest assignments of the split lines in the crystal and in the glass which are consistent with their small separations and structural shifts with environment. The model assumes that  $g\text{-GeSe}_2$ , in sharp contradistinction to  $g\text{-SiO}_2$  does not consist of a random (i.e., fully three-dimensional) network.<sup>9</sup> Instead the covalent network in  $g\text{-Ge}(\text{S},\text{Se})_2$  is made up of stacked chalcogenide-covered wafers, with an average diam-

eter and stacking thickness of order  $10\text{--}20\text{ \AA}$ .

Elemental Ge (99.999%) and Se (99.999%) in a 1:2 mole ratio were sealed in a quartz tube and thoroughly mixed in a rocking furnace at  $800^\circ\text{C}$  before being quenched in water. The glassy product  $\text{GeSe}_2$  was ground, resealed in another quartz ampoule, and placed in a horizontal growth furnace. The temperature gradient on cooling was  $5^\circ/\text{hr}$ . The materials crystallizing first were high-quality crystals but the gradual buildup of impurities or concentration gradients in the liquid phase resulted in the formation of lower quality crystals as growth continued. The final boule consisted of stacks of single-crystal layered  $\text{GeSe}_2$  up to 3 cm in length along the growth direction. Only the highest quality portion, consisting of apparently defect-free transparent yellow crystals, was taken for the Raman study. In preparing the glass we found it necessary to keep the sample weight ( $<2.5\text{ g}$ ) and reactive tube dimensions ( $<4\text{ cm}^3$ ) small in order to obtain reproducible results on quenching. In all cases a few percent of the sample of as yet undetermined composition condensed from the gas phase. This material was excluded in taking samples for measurement. The tubes were heated to  $900^\circ\text{C}$  for a period of 4 h. Experiments carried out with a holding time of 16 h did not show any change in the differential thermal analysis (DTA) which was carried out on all samples. The tubes were mechanically agitated while at  $900^\circ\text{C}$  to affect mixing. A container of water was positioned at the mouth of the furnace and the tubes were quenched directly into the water bath from  $900^\circ\text{C}$ .

The micaceous sample was mounted in the back-scattering configuration such that the light beam from a Spectra Physics Model 164 krypton-ion laser entered the sample at an angle of  $70^\circ$  to the normal to the flat lamellar surface. The electric vector was in the plane of incidence ( $H$ ) and the scattered light at  $90^\circ$  to the incident beam was collected and analyzed with an Instruments S. A.

Model HG-2S Raman spectrophotometer. Raman signals were recorded unanalyzed ( $HU$ ), or polarization analyzed ( $HH$ ) and ( $HV$ ) in the normal way.

Spectra of the glassy form of  $\text{GeSe}_2$  were obtained with somewhat more difficulty because of the tendency for the samples to smolder and even melt when exposed to a low-power (50 mW) focused  $\text{Kr}^+$  laser beam (6471 Å). The sample characterized by a typical conchoidally fractured surface, was held in a quartz tube fitted with quartz windows positioned at  $90^\circ$  to each other, one to pass the incident laser beam and the other to pass the Raman-scattered light. The whole system was purged with argon during the experiment so that oxidation of the sample would be minimal and scattering due to air at low frequencies would not contribute to the observed spectrum.

Spectra are shown in Fig. 1 and can be compared with those reported earlier.<sup>4</sup> The insert shows the

two strong Raman bands near  $210\text{ cm}^{-1}$  of crystalline  $\text{GeSe}_2$  ( $\nu = 210.3\text{ cm}^{-1}$ ,  $\nu_{1/2}$  [full width at half maximum (FWHM)] =  $3.0 \pm 0.2\text{ cm}^{-1}$ ,  $\rho = I_{HV}/I_{HH} = 0.11 \pm 0.02$ ;  $\nu' = 215.4 \pm 0.5\text{ cm}^{-1}$ ,  $\nu_{1/2}$  (FWHM) =  $3.2 \pm 0.4\text{ cm}^{-1}$ ,  $\rho = 0.12 \pm 0.03$ ). The linewidths are considerably narrower than the corresponding Raman bands of the glassy form. Peak positions and their relative intensities are listed in Table I.

When the corner-sharing bond angle is  $100^\circ$ , tetrahedra pack very poorly and are deformed (internal tetrahedral cation-centered bond angles range from  $100^\circ$  to  $120^\circ$ ). Thus the two crystalline forms<sup>8</sup> of  $\text{Ge}(\text{Se}, \text{Se})_2$  are each unique. The low-temperature form consists entirely of corner-sharing tetrahedra, but there are 24 tetrahedra unit cell, wrapped around an elliptical bubble.<sup>10</sup> The high-temperature form<sup>8</sup> consists of two offset central layers of Ge atoms covered above and below by chalcogen atoms. The Ge tetrahedra form two parallel linear chains cross-linked by rings.

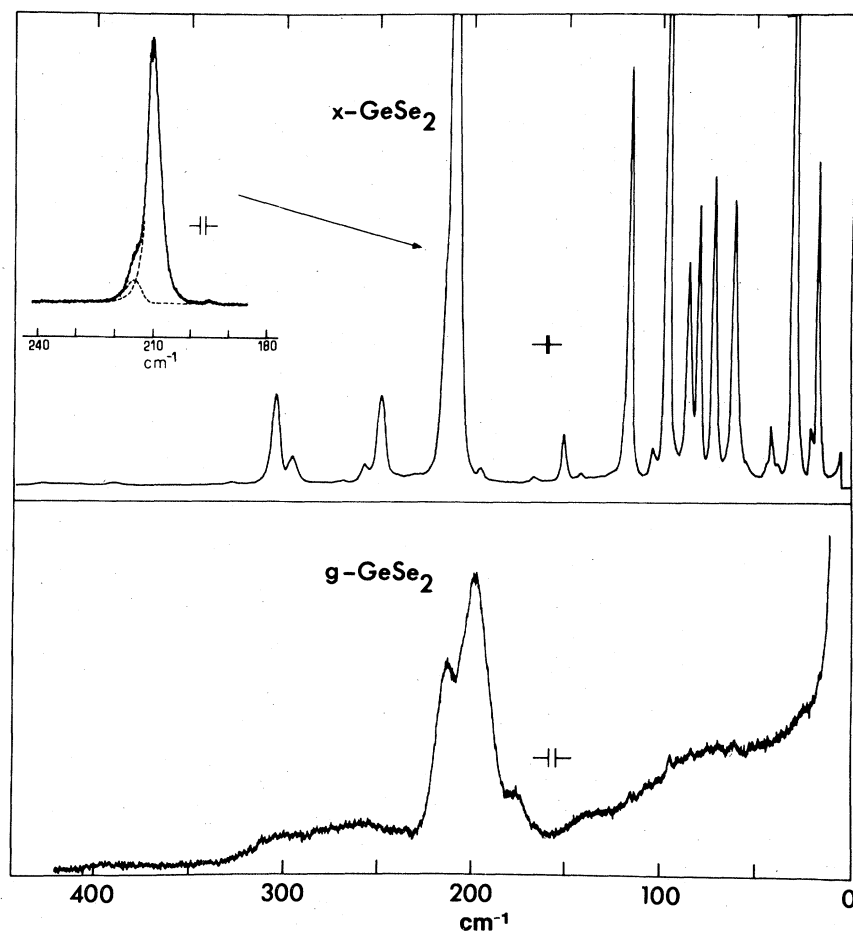


FIG. 1. Raman spectrum of crystalline  $\text{GeSe}_2$  (top). Laser power (6471 Å) 100 mW, scan rate  $10\text{ cm}^{-1}/\text{min}$ , spectral slit width  $1.6\text{ cm}^{-1}$ , sensitivity 3000 Hz (FS) time constant 1 sec. Polarization ( $HH$ ). Vibrational temperature of  $415 \pm 25\text{ K}$  from anti-Stokes to Stokes ratio for 11 Raman bands. Raman spectrum of glassy  $\text{GeSe}_2$  (bottom). Laser power (6471 Å) 50 mW, spectral slit width  $4\text{ cm}^{-1}$ . All other experimental variables are the same as above.

TABLE I. Strong Raman-active lines in GeSe<sub>2</sub>.

Crystal <sup>a</sup>		Glass		
$\omega$ (cm <sup>-1</sup> )	Intensity (arb. units)	$\omega$ (cm <sup>-1</sup> )	<i>I</i> (arb. units)	Comment
17.5	69	17 <sup>b</sup>		Interlayer <i>a</i>
29.7	>100	29	10	Interlayer <i>b</i>
61.0	60			
71.9	66			
80.0	60	82	35	Tetra <i>E</i>
85.1	48			
97.0	>100			Tetra <i>F</i> <sub>2</sub>
116.5	89	135	15	...
...	...	175	32	Ge <sub>2</sub> (Se <sub>1/2</sub> ) <sub>6</sub>
210.3	>100	198	142	Tetra <i>A</i> <sub>1</sub>
215.3	10	212	100	Companion
249.9	19	257	18	Tetra <i>F</i> <sub>2</sub> + Ge <sub>2</sub> (Se <sub>1/2</sub> ) <sub>6</sub>
306.3	20	304	14	Tetra <i>F</i> <sub>2</sub>

<sup>a</sup> Weak lines have been omitted from the table.

<sup>b</sup> See Ref. 3 and text.

The chain tetrahedra share corners, but the cross-linking tetrahedra share one edge.

Several new features have been identified in the spectrum shown in Fig. 1. We have resolved for the first time the *A*<sub>1</sub> modes localized on the edge-sharing tetrahedra (at 215 cm<sup>-1</sup>) in the lateral rings, which are split off from similar modes of the corner-sharing chain tetrahedra (at 210 cm<sup>-1</sup>) by only 5 cm<sup>-1</sup>. The splitting in the glass of the *A*<sub>1</sub> mode and its companion is 14 cm<sup>-1</sup>. We therefore conclude that the companion mode is not a tetrahedral breathing mode, but like the tetrahedral mode it probably does involve predominantly chalcogen displacements. A striking feature of the crystalline spectrum is the large number of strong lines at frequencies as low as 17 and 30 cm<sup>-1</sup>.

The number of such lines as well as their low frequencies suggest that they are associated with the vibrations of tetrahedral units in large rings, such as the 6- and 16-membered rings which are found in the layered crystalline structure.

A surprising feature of the low-frequency modes is that, although broadened, they are apparently preserved in the glass, as indicated in Table I and Fig. 1. This suggests a cluster model of the glass in which the 6- and 16-membered rings of the crystal are still present. The smallest such cluster is shown in Fig. 2. Two parallel chains (of indefinite length, indicated by the dashed bond lines) are cross-linked by edge-sharing tetrahedra, as in the layered crystal. The chalcogens on the outer edges of the chains are treated as surface atoms which have dimerized (indicated by double lines; actually for the given molecular geometry the dimer bonds will have the length of normal Se-Se single bonds if the tetrahedral angles

are distorted in one of several ways by <10°). The local "edge modes" associated with dimerized chalcogens can be assigned to the "anomalous" companion line at 213 cm<sup>-1</sup>. Note the equivalence of these edge modes, which makes possible the narrow width of the companion line (comparable

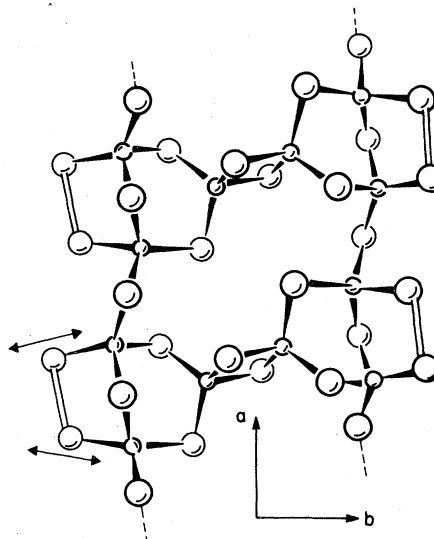


FIG. 2. The large clusters which are the dominant structural elements of glassy GeSe<sub>2</sub> are supposed to be made of stacked layer units of the kind shown here. The chalcogen atoms on the edges of the units have dimerized, while the chalcogen atoms at the ends of the chains reconstruct in some other manner, e.g., in a Se-rich environment they may polymerize with Se chains. Note the edge-sharing tetrahedra which stabilize the double-chain structure. The companion Raman line is associated with coupled motion of the dimerized chalcogens, as indicated by the double arrows.

to the normal  $A_1$  line). More complex quasicrystalline models, involving, e.g., partial dislocations, would be expected to generate either broad or multiple companion lines.

The most natural interpretation of the 17- and 30- $\text{cm}^{-1}$  lines is that they correspond to interlayer optic modes polarized along the  $a$  and  $b$  axes of Fig. 2. Because adjacent layers are offset along the  $b$  axis (in order to achieve denser packing of the corrugated layers) we assign the 17- (30-) $\text{cm}^{-1}$  to the optic  $a$ - ( $b$ -) polarized interlayer modes. The 30- $\text{cm}^{-1}$  line corresponds well to the lowest glass band observed in our room-temperature data, while the 17- $\text{cm}^{-1}$  line agrees well with the low-frequency shoulder<sup>3</sup> at 10 K.

In the glass at low temperatures there is a plateau in the scattering spectra between  $\omega_a = 17 \text{ cm}^{-1}$  and  $\omega_b = 29 \text{ cm}^{-1}$ . Suppose the planar, approximately square clusters are stacked together but that each cluster is rotated in the ( $a, b$ ) plane relative to adjacent clusters by an angle  $\phi$  which is distributed almost randomly. For  $\phi = 0$  the optic  $a$ - ( $b$ -) polarized modes are narrow and have their crystalline values, but for  $\phi = \pi/2$ , there is only one interlayer optic mode at  $\omega_c^2 = (\omega_a^2 + \omega_b^2)/2$ . The spectral distribution for random  $\phi$  (variable polymerization with the disordered environment) will approximate the observed plateau.<sup>3</sup>

It has been suggested by Nemanich and Solin<sup>3</sup> that the anomalous 213- $\text{cm}^{-1}$  line in the glass is associated with the symmetric breathing mode of a "necklace" or ring of  $\text{Ge}_p\text{Se}_p$  atoms with  $p = 6$ . In this geometrical model topological problems arise from the necessity of embedding a high density of such rings in a space-filling covalent network, and justifying the choice  $p = 6$ . In the light of the crystalline data presented here, our model appears more plausible. [Of course, both models trivially explain the  $x^5$  concentration dependence of the intensity of the companion line, because both involve more than five  $\text{Ge}(\text{Se}_{1/2})_4$  building blocks in their basic structural units.]

An anomalous first sharp diffraction peak has been observed in glassy and liquid  $\text{GeSe}_2$  and  $\text{As}_2\text{Se}_3$  by many workers,<sup>11</sup> and similar peaks have been seen<sup>12</sup> in amorphous B, P, As, and Sb. In  $\text{GeSe}_2$  this peak has been geometrically explained<sup>13</sup> as a diameter of the "necklace," but its value also fits very well the interlayer spacing in crystals of the above materials. Moreover, the persistence of the peak in the liquid apparently requires stable units (such as the chalcogenide-covered layers in Fig. 2) in contrast to more loosely constrained ring structures.

The reader will note that our glass data give evidence of the presence of  $\text{Ge}_2(\text{Se}_{1/2})_6$  ethanelike clusters,<sup>14</sup> although our glasses nominally have

the  $\text{GeSe}_2$  composition. It may be that with ultrafast quenching these clusters, which contain excess Ge, compensate the stoichiometry of the Se-rich large clusters illustrated in Fig. 2. With slower quenching other workers have found evidence for excess Se, for example.<sup>6</sup> In any case the composition at which Se and  $\text{Ge}_2(\text{Se}_{1/2})_6$  Raman or infrared lines are absent need not, in our model, correspond to  $\text{GeSe}_2$  to better than a few percent.

The molecular structure shown in Fig. 2 can be described as an "outrigger raft." We advise strongly against the use of the phrase "microcrystallite" in describing clusters composed of stacked rafts because (1) the anomalous first sharp diffraction peak associated with interlayer spacing<sup>11</sup> persists to temperatures higher than  $1.5T_m$ ; (2) a similar peak is seen in  $\text{As}_2\text{Se}_3$  but it has been shown<sup>13</sup> to be derived from the spacing of spheroidal  $\text{As}_4\text{S}_4$  clusters; and (3) the implication of long-range order conceals the unique reasons for the formation and stability of large clusters in chalcogenide alloys. Casual use of this phrase obscures the topological origin of the glass-forming tendencies of these materials.<sup>15</sup>

In conclusion, we have presented Raman-scattering data which show a companion Raman line in  $\text{GeSe}_2$  crystals similar to that found in the glass, but with a quite different structural origin. We have proposed a model for  $\text{Ge}(\text{S}, \text{Se})_2$  glasses which suggests that the medium-range order of the network structure is basically layered rather than three dimensional, as in  $\text{SiO}_2$ . Using the hypothesis of glassy layers we can explain the origin of the companion of the  $A_1$  Raman line (tetrahedral breathing mode.) Our model is compatible with other recent data, but may be more conclusive because of the richness of detail in the crystalline spectrum and its close correspondence to the glass spectrum even at very low frequencies. We wish to emphasize that we believe that our model is the only specific molecular structure which is capable of yielding two sharp Raman lines at the proper frequencies (which scale almost identically with chalcogenide mass) and which can be satisfactorily polymerized with the extensive covalent network of the glass. The present model has been extended to  $g$ - $\text{As}_2\text{Se}_3$  to yield orpimental rafts.<sup>16</sup>

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