Solid State Communications, Vol. 17, pp. 1567–1572, 1975. Pergamon Press. Printed in Great Britain

COORDINATION DEPENDENT VIBRATIONAL PROPERTIES OF AMORPHOUS SEMICONDUCTOR ALLOYS

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(*Received* 7 *July* 1975 *by J. Tauc*)

The i.r., Raman and depolarization spectra of the amorphous pseudo-binary alloy systems $(GeS_2)_{1-x}(As_2S_3)_x$ and $(GeSe_2)_{1-x}(As_2Se_3)_x$ are reported here. In contrast to the one-mode behavior that is anticipated on the basis of the mass ratio of the alloy atoms (Ge/As), two bond-stretching modes are observed in both the i.r. and Raman spectra. This new type of phonon behavior is interpreted in terms of differences in the local coordination via a chemical bonding model.

THERE HAVE BEEN many studies of the infrared (i.r.) and Raman spectra of the long wavelength optic modes[1] in pseudo-binary diatomic crystalline systems in which the local environment is preserved over the entire composition range. The i.r. and Raman studies of the more covalent of these systems, e.g., the III–V and II–VI semiconductors, exhibit either a one-or two-mode behavior which is primarily dependent on the relative masses of the constituent atoms. For example, the i.r. spectra of $(InAs)_{1-x}(InP)_x$ exhibits two-mode behavior where $M_P, M_{As} < M_{In}$,[2] but $(InP)_{1-x}(GaP)_x$ gives one-mode behavior for M_{In}, $M_{Ga} > M_P$.[3] The extension of these studies to amorphous solids offers a potentially broader range of optic phonon behavior because of the ability of the local environment to adjust to the covalent bonding requirements of the constituent atoms.

Previous i.r. and Raman studies of compound amorphous semiconductors have yielded spectra with relatively sharp features.[4–7] The i.r. and Raman spectra were found to be complementary and some of the Raman modes were strongly polarized. These properties could be understood in terms of the short range order via a model[8] based on valence bonding configurations. Studies of amorphous alloys have addressed two types of systems, binary alloys such as $Ge_{1-x}Y_x$, Y = S, Se, Te,[9–11] and pseudo-binary alloys such as $(As_2Se_3)_{1-x}(As_2S_3)_x$[12] and $(As_2Te_3)_{1-x}(As_2Se_3)_x$.[13] The latter studies of the pseudo-binary systems do not represent a significant departure from studies on crystalline alloys. The local order is preserved over the entire composition range and the resultant behavior in the bond-stretching modes is well correlated with the relative masses of the alloy atoms.

This report is a study of the bond-stretching modes by i.r. and Raman spectroscopy in the alloy systems: $(GeS_2)_{1-x}(As_2S_3)_x$ and $(GeSe_2)_{1-x}(As_2Se_3)_x$. New measurements of the i.r., Raman and depolarization spectra of the four end-member compounds, GeS_2,

Table 1. Model calculations and observed i.r. and Raman bond-stretching frequencies for the end-member compounds, GeS_2, $GeSe_2$, As_2S_3 *and* As_2Se_3. *Included in the table are the VFF force constants and the frequencies, symmetries and activities of the modes of the idealized structural elements,* $A'B_4$ *tetrahedra and* AB_3 *pyramids. For the Raman active modes the labels P and D indicate the polarization (Polarized or Depolarized). We have also included the frequencies of dominant features in the bond-stretching regime of the i.r. and Raman spectra*

Amorphous solid (Strucrual element)	VFF force constants (dyne/cm x 10^5)			Model Calculations			Observed frequencies (cm^{-1})	
	k_r	k_θ	$k_{rr'}$	Frequency (cm^{-1})	symmetry	activity	i.r.	R
GeS_2 (GeS_4)	1.69	0.17	0.13	ν_1, 342	A_1	$R(P)$		345 (P)
				ν_3, 367	F_2	i.r., $R(D)$	367	374 (D)
								408 (D)
$GeSe_2$ ($GeSe_4$)	1.21	0.10	0.22	ν_1, 200	A_1	$R(P)$		201 (P)
								219 (P)
				ν_3, 248	F_2	i.r., $R(D)$	254	248 (D)
								267 (D)
As_2S_3 (AsS_3)	1.39	0.32	0.16	ν_1, 345	A_1	$R(P)$		345 (P)
				ν_3, 310	E	i.r., $R(D)$	310	~310 (D)
As_2Se_3 ($AsSe_3$)	1.12	0.38	0.14	ν_1, 230	A_1	$R(P)$		239 (P)
				ν_3, 217	E	i.r., $R(D)$	217	~225 (D)

As_2S_3, etc., will also be presented. These alloy systems are of particular interest because of the differences in coordination expected at the As (3-fold) and Ge (4-fold) sites. On the basis of the masses involved in the substitution in these two systems, one-mode behavior in the i.r. and Raman spectra is anticipated. In this paper we demonstrate that this expectation is not realized.

2. EXPERIMENTAL

The glasses used in our studies were prepared by weighing high purity elemental powders into fused silica tubes. The 10 mm diameter tubes with 5–10 gm of reactants were sealed under vacuum and then heated for a period of 12 hr to about 50–100°C above the liquidus phase boundary. The reactants were held at this temperature for another 12 hr and then either air-quenched, water-quenched or quenched in a NaOH–H_2O solution. Optical samples were prepared by conventional grinding and polishing techniques. Room temperature measurements of the transmission of 6328 Å light through the GeS_2 and $(GeS_2)_{0.5}(As_2S_3)_{0.5}$ samples stationed between crossed polarizers indicated that they were of excellent optical quality with an extinction ratio that varied between 30 and 38 dB at different locations on each of the samples. The $(GeSe_2)_{1-x}(As_2Se_3)_x$ samples are opaque to 6328 Å light at room temperature; however, the strong polarization of some modes as observed in the depolarization spectra (see Fig. 2) indicates optical quality comparable to that of GeS_2.

Room temperature i.r. reflectance measurements were made at near normal incidence using a Perkin–Elmer 180 spectrophotometer operated in a double beam mode. The reflectance of the samples was normalized by comparison with the reflectance from a front surface Al mirror and is accurate to ± 0.005. The spectral resolution was approximately 2 cm^{-1}.

The Raman spectra were measured in the 90°

transmission configuration using either 6471, 6764 or 7993 Å radiation from a CRL model 52 G krypton ion laser. Since the optical band gap of the glasses studied here increases at low temperatures, all of the Raman spectra reported here were taken at near liquid He temperature (~ 9°K) in order to reduce sample heating and degradation due to absorption. Further, by defocusing the beam and using low power levels (~ 5–50 mW), photostructural changes which occur even at liquid He temperatures in some samples were avoided.

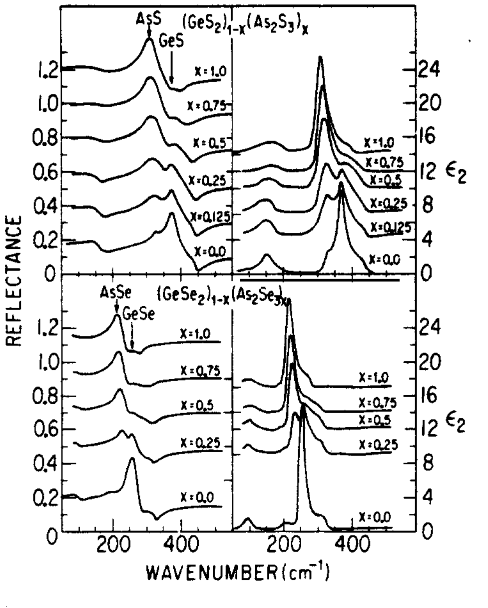

FIG. 1. Room temperature i.r. and ϵ_2 spectra of the pseudo-binary alloy systems $(GeS_2)_{1-x}(As_2S_3)_x$ and $(GeSe_2)_{1-x}(AsSe_3)_x$. The ϵ_2 spectra are obtained via a Kramers–Kronig analysis. We have used arrows to indicate the frequencies of the dominant i.r. active bond-stretching modes.

The i.r. reflectance spectra and the ϵ_2 spectra, derived via a Kramers–Kronig analysis, are shown in Fig. 1 for $(GeS_2)_{1-x}(As_3S_3)_x$ and $(GeSe_2)_{1-x}(As_2Se_3)_x$. Two mode behavior is clearly evident in the bond-stretching regime. In the $(GeS_2)_{1-x}(As_2S_3)_x$ system, the two modes are at approximately 310 and 365 cm^{-1}, whereas in the $(GeSe_2)_{1-x}(As_2Se_3)_x$ system they are at approximately 220 and 250 cm^{-1}.

Figure 2 shows the Raman HH spectra and the depolarization (HV/HH) spectra of $(GeS_2)_{0.5}(As_2S_3)_{0.5}$ and $(GeSe_2)_{0.5}(As_2Se_3)_{0.5}$ and of the four end-member compounds, GeS_2, As_2S_3, $GeSe_2$ and As_2Se_3. The Raman spectrum of $(GeS_2)_{0.5}(As_2S_3)_{0.5}$ exhibits one broad mode at 345

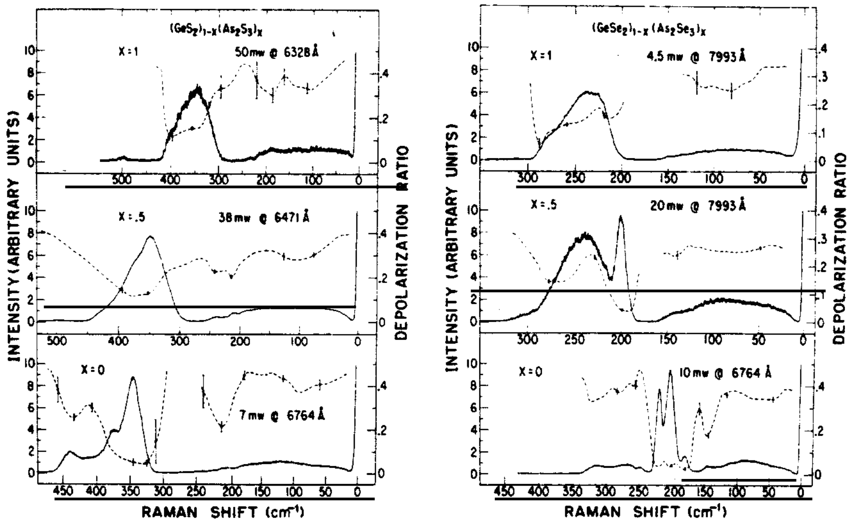

FIG. 2. Low temperature (~ 11 K) Raman and depolarization spectra of $(GeS_2)_{0.5}(As_2S_3)_{0.5}$ and $(GeSe_2)_{0.5}(As_2Se_3)_{0.5}$ and the four end member compounds, GeS_2, As_2S_3, $GeSe_2$ and As_2Se_3. The HH Raman spectra were recorded with a spectra slit width of ~ 6 cm^{-1} and are shown as solid lines. The depolarization spectra are shown as dashed lines. The As_2S_3 spectra are from reference 5. Note that the abscissae are linear in wavelength not wavenumber. The excitation wavelengths and power levels are indicated in the spectra.

cm^{-1}, whereas the spectrum of $(GeSe_2)_{0.5}(As_2Se_3)_{0.5}$ yields modes at 201 and 242 cm^{-1}. The 345 cm^{-1} GeS_2, 201 cm^{-1} and 219 cm^{-1} $GeSe_2$, and 201 cm^{-1} $(GeSe_2)_{0.5}(As_2Se_3)_{0.5}$ modes are strongly polarized as evidenced by the sharp dip in the depolarization spectra at the mode frequencies. The features in the spectra of As_2S_3 and $(GeS_2)_{0.5}(As_2S_3)_{0.5}$ at ~ 345 cm^{-1}, and in As_2Se_3 and $(GeSe_2)_{0.5}(As_2Se_3)_{0.5}$ at ~ 240 cm^{-1} are also polarized, but to a lesser degree.

3. DISCUSSION

Previous studies on the alloy systems $(As_2Se_3)_{1-x}(As_2S_3)_x$,[4] $Ge_{1-x}Se_x$[9] and $Ge_{1-x}S_x$[10] have established that bonding in these alloys follows the 8-N rule, and that there is a strong tendency to form the most heteropolar bonds at the expense of other bonding possibilities. For example in the $Ge_{1-x}S_x$ system there is a chemically ordered phase at the composition $Ge_{0.33}S_{0.67}$ in which there are only Ge–S bonds; in S-rich alloys ($x > 0.67$), there are Ge–S and S–S, but no Ge–Ge bonds, while in Ge-rich alloys there are Ge–S bonds and Ge–Ge bonds, but no S–S bonds.

We extend these bonding principles to the alloys studied here. The alloys we consider are formed along the join-lines between chemically ordered phases. Therefore in the $(GeS_2)_{1-x}(As_2S_3)_x$ system we expect Ge–S and As–S bonds, but not S–S or Ge–As bonds; in the $(GeSe_2)_{1-x}(As_2Se_3)_x$ system we anticipate a parallel situation, Ge–Se and As–Se bonds, but no Se–Se or Ge–As bonds.

The basic structural unit for the As_2S_3 and As_2Se_3 glasses is an AB_3 pyramid with the three-fold coordinated As atom at the apex.[4,5] The pyramids are interconnected by the two-fold coordinated S or Se atoms, thus maintaining the 8-N rule. Similarly the basic structural element of GeS_2 and $GeSe_2$ is an $A'B_4$ tetrahedron with the Ge at the center; the tetrahedra are interconnected by the two-fold coordinated S or Se-atoms.[6,9,10]

We apply the model of Lucovsky and Martin[8] to the alloy systems studied here. The model is based on an assumption the the characteristic i.r. and Raman frequencies of a compound amorphous solid can be understood in terms of the element of short range order. The model gives a very good description of the bond-stretching modes for which the effects of the coupling of the structural elements is small. In the bond-bending regime, < 200 cm^{-1} for $(GeS_2)_{1-x}(As_2S_3)_x$ and < 150 cm^{-1} for $(GeSe_2)_{1-x}(As_2Se_3)_x$, the model is not as reliable because the coupling between the structural elements at the bridging chalcogenide atoms cannot be treated as a perturbation. We first consider the dominant i.r. and Raman frequencies of the four end-member glasses. We analyze these in terms of the frequencies of the idealized structural elements, AsS_3 and $AsSe_3$ pyramidal units for As_2S_3 and As_2Se_3, respectively, and GeS_4 and $GeSe_4$ tetrahedral units for GeS_2 and $GeSe_2$, respectively. We do a valence force field calculation using three force constants, k_r, k_θ, and $k_{rr'}$.[14] In this calculation changes in the potential energy U are related to the changes in the equilibrium positions of the atoms, Δr and $\Delta\theta$, by

$$\Delta U = \frac{1}{2}\sum k_r(\Delta r)^2 + \frac{1}{2}\sum k_\theta(r_0\Delta\theta)^2 + \sum k_{rr'}(\Delta r\Delta r')^2. \quad (1)$$

Both pyramidal AB_3 and tetrahedral $A'B_4$ structures have four internal modes of vibration two of which are predominantly bond-stretching and two predominantly bond-bending.[14] Table 1 compares the calculated bond-stretching modes with dominant features observed in the i.r. and Raman spectra. Also included in the table are the mode symmetry, the i.r. and Raman activity, the Raman depolarization (P or D) and the force constants. Additional weaker features are clearly evident in the bond-stretching regime in both the i.r. and Raman spectra. These are not explained by the model we are employing in this analysis, and can only be accounted for by a more complete analysis which explicitly considers the coupling of the basic structural elements.[6–8]

If we apply the model to the pseudo-binary systems $(GeS_2)_{1-x}(As_2S_3)_x$ and $(GeSe_2)_{1-x}(As_2Se_3)_x$, then it is necessary to consider two structural elements for each glass, AB_3 and $A'B_4$ where A and A' are respectively As and Ge and B is either S or Se. The contribution from each component is weighted by the alloy composition. On the basis of this extension of the Lucovsky–Martin model,[8] we anticipate two strong i.r. features in the bond-stretching regime. This is just what is observed. The GeS_4 mode at ~ 365 cm^{-1} and the AsS_3 mode at ~ 310 cm^{-1} are present in the $(GeS_2)_{1-x}(As_2S_3)_x$ glasses, whereas the $GeSe_4$ mode at $\sim 250\ cm^{-1}$ and the $AsSe_3$ mode at $\sim 220\ cm^{-1}$ are present in the $(GeSe_2)_{1-x}(As_2Se_3)_x$ glasses. Their relative intensities, as evident in the ϵ_2 spectra, scale with alloy composition.

The Raman spectra of $(GeSe_2)_{0.5}(As_2Se_3)_{0.5}$ also exhibits a two-mode behavior wherein the 201 cm^{-1} $GeSe_4$ mode and 239 cm^{-1} $AsSe_3$ mode are clearly observed. Both modes are polarized as expected, with the 201 cm^{-1} mode showing the stronger polarization characteristic of the tetrahedral local order. The Raman spectra of $(GeS_2)_{0.5}(As_2S_3)_{0.5}$ exhibits only a single broad mode at 345 cm^{-1}. This is explained by an accidental degeneracy of the A_1 modes of GeS_4 and AsS_3.

The two-mode behavior in these amorphous systems can be traced to two sources, (1) differences in the Ge–S(Se) and As–S(Se) force constants, and (2) and more important, differences in the mode masses. Both of these are a result of the different local coordinations at the Ge and As sites. The main point is that on the basis of the very small mass differences between As and Ge, one would have anticipated one-mode behavior in the alloys. Clearly the two-effects cited above are large enough to override this. The fact that the dominant features of the alloys can be described in terms of an extension of the model that has been successfully applied to compounds supports the pseudo-binary character of the alloys and the chemical bonding approach to the structure of chalcogenide glasses.

4. SUMMARY

We have reported here a new type of behavior in the i.r. and Raman spectra of alloy glasses. The two-mode behavior in the systems under consideration results from a combination of two effects, differences in effective force constants, and differences in the mode masses. In diatomic crystalline alloys, two-mode behavior is primarily due to large differences in mass between the alloy atoms.[1] Two-mode behavior in crystalline solids can also result from differences in force constants, as for example in II–VI–III–V[15] quaternary alloys. However, the two-mode behavior reported here is determined primarily by differences in the local coordination at the alloy atom sites and is unique to the amorphous phase. This preliminary report is part of a more detailed investigation of the amorphous quaternary system $As_2Se_3.As_2S_3.GeSe_2.GeS_2$. The extension of this work includes additional i.r. and Raman studies, as well as a generalization of the structural model used to analyze the alloy spectra.

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