Temperature Dependence of Local Order in the Layer-Type Liquid Semiconductors As_2Se_3 and $Tl_2Se{\cdot}As_2Te_3$

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Far-infrared vibrational modes in vitreous As_2Se_3 and $Tl_2Se{\cdot}As_2Te_3$ have been observed above the glass transition temperatures (T_g) and are an indication of the preservation of local order in the liquid phase. In As_2Se_3 these modes exist above the melting point of the crystalline material. At a well-defined temperature $T_s = 480°K$ ($> T_g$) the vibrational modes disappear in $Tl_2Se{\cdot}As_2Te_3$. Similar behavior is predicted for all layer-type semiconducting glasses, and T_s is proposed as a characteristic temperature for an abrupt change of local order in these materials.

The non-oxide amorphous semiconductors can be divided into three loosely defined structural categories: (1) materials which are primarily tetrahedrally bonded such as amorphous Ge and Si; (2) materials which consist primarily of one-dimensional intertwining chains such as S, Se, Te, and Se-Te alloys; and (3) materials which consist primarily of two-dimensional layers "bonded" together at random points such as As_2S_3 and As_2Se_3.[1] Probably some of the "switch-glass" compositions fall into the third structural category.

Tetrahedrally bonded amorphous semiconductors crystallize well below their melting temperatures, but both chain-type and layer-type vitreous semiconductors can, in principle, be studied continuously through their glass transition temperatures T_g well into the liquid phase without devitrification. Substantial evidence for the preservation of local order in chain-type vitreous semiconductors above T_g has been provided by neutron diffraction,[2] x-ray diffraction,[3-5] viscosity,[6,7] and magnetic susceptibility[8] studies. Magnetic susceptibility[9] and viscosity[10,11] measurements on the layer-type vitreous semiconductor As_2Se_3 in the liquid phase indicate that the local covalent bonding is essentially unchanged. There is no sharp break in the electrical conductivity of either As_2Se_3[12,13] or $Tl_2Se{\cdot}As_2Te_3$[14] in going through T_g, which is consistent with no essential change in the local order. Only small changes in the short-range order are inferred from magnetic susceptibility studies of the crystal-liquid transition in As_2Se_3.[9]

This Letter reports far-infrared vibrational absorption measurements in vitreous As_2Se_3 and $Tl_2Se{\cdot}As_2Te_3$ from 4.2°K to temperatures well into the liquid phase. These measurements yield the first direct and detailed evidence for the preservation of local order in layer-type vitreous semiconductors well above the glass transition temperatures. In addition, there is a well-defined temperature above which the vibrational modes disappear abruptly in liquid $Tl_2Se{\cdot}As_2Te_3$. This leads to the hypothesis that in the layer-type semiconducting glasses there exists a characteristic temperature T_s above which the local order changes abruptly.

Recent room-temperature transmission and reflection measurements[15,16] from 10 to 600 cm^{-1} indicate strong Gaussian absorption peaks at 102, 156, and 237 cm^{-1} in As_2Se_3 and at 80, 189, and 246 cm^{-1} in $Tl_2Se{\cdot}As_2Te_3$. These peaks are essentially independent of temperature from 4.2 to 300°K. A simple statistical model assuming a Gaussian distribution of Lorentzian oscillators is found to be consistent with both the experimental data and the random nature of a disordered structure.[15]

The transmission measurements from room temperature to 675°K reported in this Letter were performed by sealing the glass samples in high-temperature cells employing silicon windows. Thermocouples (0.001-in. Chromel-Alumel) were imbedded in the glass samples, and temperatures were maintained constant to within ± 3°K. Corrections were made at all temperatures for the experimentally determined silicon absorption and reflection. Increased silicon absorption with increasing temperature cut down the extremes of glass absorption that could be accurately measured at the highest temperatures.[17] For all high-temperature samples, agreement was checked at room temperature with measurements obtained on free-standing samples both before and after the temperature cycling. Sample thickness ranged from 25 to 75 μm in As_2Se_3 and from 25 to 50 μm in $Tl_2Se{\cdot}As_2Te_3$. Transmission measurements were made on a Perkin-Elmer 301 grating monochromator and on an interferometric spectrome-

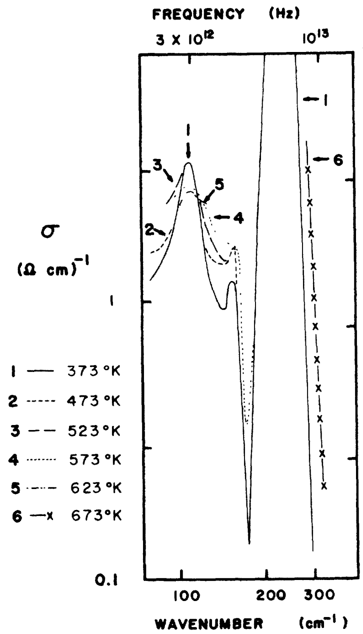

FIG. 1. Temperature dependence of the vibrational conductivity σ (index of refraction times absorption coefficient) versus frequency on a log-log scale in vitreous As_2Se_3. The data at 623°K extend only from 90 to 110 cm^{-1}, the data at 673°K extend only from 290 to 305 cm^{-1}. At all other temperatures the data extend from approximately 40 to 300 cm^{-1}. From 4.2 to 373°K the vibrational peaks are essentially independent of temperature. The glass transition temperature T_g for As_2Se_3 is 460°K.

ter as described elsewhere.[15,16] In calculating the curves of the conductivity σ of Figs. 1 and 2 the index of refraction was assumed to be temperature independent and equal to the room-temperature values determined in previous investigations.[15,16] Changes in the conductivity spectra of these two figures represent changes in the imaginary part of the index k with temperature. Reflection losses at the silicon-glass interfaces were taken into account assuming room-temperature indices of refraction.

The three absorption peaks in vitreous As_2Se_3 fall near three groups of peaks observed in the crystalline material. Below T_g this information is not surprising if one considers the conclusions of infrared and Raman studies of layered crystalline semiconductors, namely, that the layer symmetry dominates over the total symmetry of the crystal as far as the vibrational modes are concerned.[18,19] Of the three peaks at 102, 156, and 237 cm^{-1} in vitreous As_2Se_3, only the peak at 237 cm^{-1} has been conclusively identified from infrared and Raman studies of crystalline As_2Se_3.[19]

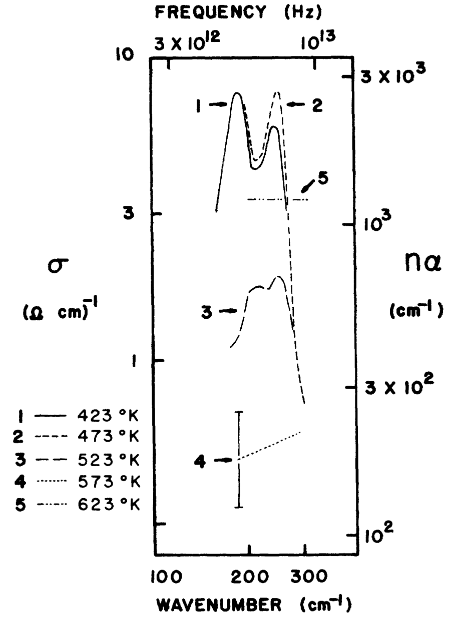

FIG. 2. Temperature dependence of the vibrational conductivity (index of refraction times absorption coefficient) versus frequency on a log-log scale in vitreous $Tl_2Se \cdot As_2Te_3$. From 4.2 to 423°K the two vibrational peaks are essentially independent of temperature. T_g is 359°K for this glass.

This peak is attributed to an in-plane rigid sublattice vibration in which the arsenic and selenium sublattices undergo oppositely directed rigid translations. Presumably the lower-frequency peaks also result from some kind of rigid sublattice motion.

Figure 1 shows the data for As_2Se_3. The strong peak at 237 cm^{-1} is essentially independent of temperature up to the highest temperatures measured although there is some indication of broadening of the Gaussian line at 673°K. Most significant, however, is the fact that this vibrational absorption peak still exists not only above T_g (460°K) but also above the melting point for crystalline As_2Se_3 (633°K). The peaks at 102 and 156 cm^{-1} also persist well into the liquid phase with the peak at 102 cm^{-1} gradually becoming more Lorentzian in character as the temperature is increased.[20] This trend toward a Lorentzian line shape could reflect the increased influence of anharmonic terms in the potential with increasing temperature.

The structural model which the data of Fig. 1 suggest is that the weak forces between layers in the glass are breaking up at the glass transition temperature leading to the precipitous drop in the viscosity around T_g. But the layers themselves remain intact as evidenced by the relatively unchanged vibrational absorption of Fig. 1. Even above the melting point of crystalline As_2Se_3, the layers remain essentially intact.

The question may reasonably be asked, "At what point do the layers begin to break up?" In the hope of answering this question a glass of the same general structure as As_2Se_3 but with a lower softening point was studied, namely, vitreous $Tl_2Se \cdot As_2Te_3$ where $T_g = 359°K$.[21] The two vibrational absorption peaks at 189 and 246 cm^{-1} correspond to the peak at 237 cm^{-1} in As_2Se_3, and they probably represent arsenic-selenium rigid sublattice vibrations. Figure 2 indicates that these two peaks are essentially temperature independent up to 473°K at which temperature they diminish precipitously and become unobservable above 573°K. The line shapes of the two peaks remain essentially unchanged until their sudden disappearance. Above 573°K the conductivity increases again, but a broad absorption which is independent of frequency is observed in contrast to the sharp peaks present at the lower temperatures. This absorption above 573°K is exponentially dependent on temperature. It is associated with the thermally activated absorption observed in this glass[14,16] from 3 to 15 μm at temperatures below T_g and is discussed in a separate publication.

The data for Fig. 2 support the structural model proposed above for the behavior of layer-type vitreous semiconductors above T_g with the addition of one significant feature. There is a characteristic temperature at which these layers in the liquid disintegrate as indicated for $Tl_2Se \cdot As_2Te_3$ in Fig. 3. This temperature T_s is $480 \pm 10°K$ for $Tl_2Se \cdot As_2Te_3$ as obtained from the maximum heights of the peaks at 189 and 246 cm^{-1} versus temperature. Since the widths of the two lines are temperature independent, Fig. 3 is essentially a plot of the intensities.

A comparison of the present results with the general behavior of the viscosity η with temperature in layer-type semiconducting glasses is illustrative. In the region of T_g (T_g is defined as that temperature for which $\eta = 10^{13}$ P) the slope of $\log\eta$ vs T is large and negative for all layer-type chalcogenide glasses. This sharp fall in the viscosity is attributed to a breakup of the bonds between layers with increasing temperature. The interlayer forces are inherently weak so that the viscosity changes dramatically in this region. There is a break in the typical viscosity curve of a layer-type chalcogenide glass somewhere between 10^3 and 10^4 P which occurs at about 625°K for As_2Se_3.[11] Above this temperature the viscosity drops more slowly with temperature. This slower drop is attributed to the breakup of the layers themselves. Since the covalent intralayer bonds are stronger than the bonds between layers, the viscosity drops more slowly in this region.

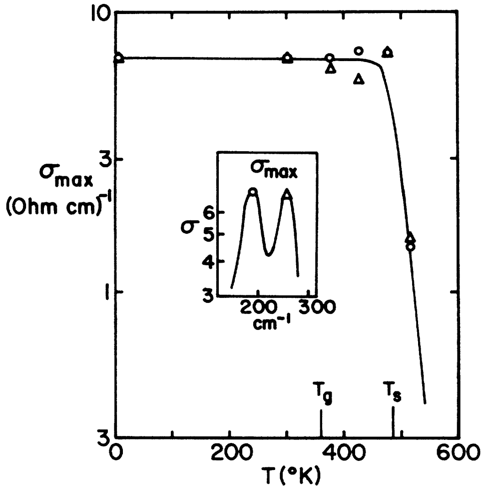

FIG. 3. Peak conductivity of the Gaussian vibrational lines at 189 (circles) and 246 cm^{-1} (squares) versus temperature in vitreous $Tl_2Se \cdot As_2Te_3$. T_g is the glass transition temperature; T_s is a characteristic temperature for an abrupt change in local order as described in the text. The insert indicates the features represented by the circles and squares (see also Fig. 2).

Although complete viscosity data for $Tl_2Se \cdot As_2Te_3$ are not available, the region of sharp fall in the viscosity can be accurately positioned by the value of $T_g = 359°K$[21] where by definition the viscosity is 10^{13} P. If the slope of $\log\eta$ near T_g is assumed to be identical with that for As_2Se_3, and if the break in the viscosity curve is assumed to fall at 1000 P, then the onset of the slower drop in viscosity due to the breakup of the layers would occur in the vicinity of 450–500°K. This is consistent with the observed value of $T_s = 480°K$ since this is the temperature at which the vibrational modes of the layers vanish. On the basis of the break in the viscosity curve for As_2Se_3, the predicted value of T_s for this glass is $725 \pm 50°K$. Experiments are in progress to evaluate T_s for As_2Se_3 and other chalcogenide glasses.

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[1] In As_2Se_3, the points at which the layers are "bonded" together are As atoms in octahedral coordination, i.e., three Se atoms from each layer. X-ray radial-distribution analyses of As_2Se_3 place the percentage of

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Electron Coupling to Bound Phonon Pairs*

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A number of anomalous peaks in the photoconductivity of n-type InSb in strong magnetic fields have recently been reported. We explain these anomalies in terms of electron-hole hybridization with a single LO phonon together with coupling to bound phonon pairs. The hybridization process introduces extra peaks in the photoconductivity spectrum in the vicinity of the LO phonon as well as the bound-state energies in agreement with experiment.

In recent photoconductivity experiments on n-type InSb in the presence of a magnetic field, Kaplan and Wallis[1] observed several anomalous peaks whose positions and widths exhibit a peculiar field dependence. For a wide range of magnetic field strengths the photoconductivity spectra exhibit sharp peaks due to cyclotron resonance absorption by free electrons and electrons bound to impurity atoms.[1] In the present paper we shall be concerned only with absorption due to the bound electrons. The energies of the peaks corresponding to impurity-bound electron transitions are plotted as a function of magnetic field in Fig. 1. The peak energies labeled LO, LO + (001), LO + (0$\bar{1}$0), and LO + (0$\bar{2}$0) have been attributed by Kaplan and Wallis[1] to transitions involving various impurity energy eigenstates. However, the two branches labeled LO + Δ and LO − Δ seem to be completely anomalous in terms of previous theories. The aim of the present study is to explain the latter peculiar branches by considering the influence of bound phonon-pair states on the electronic transitions involved in photoconductivity.

The manner in which phonons can modify the photoconductivity is shown diagrammatically in