

has not yet been satisfactorily explained.

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Electronic Structure of Crystalline and Amorphous As_2S_3 and As_2Se_3

R. Zallen, R. E. Drews, R. L. Emerald, and M. L. Slade

Xerox Research Laboratories, Rochester, New York 14603

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The optical properties of crystalline and amorphous As_2S_3 and As_2Se_3 have been investigated from 1 to 14 eV. A simple rigid-band relationship connects the band structures of the two crystals, and the lowest-energy features observed near the interband thresholds are assigned to direct transitions. The effect of disorder on the electronic spectra, aside from the disappearance of critical-point structure, is remarkably slight; the principal density-of-states thresholds are preserved, essentially unshifted, in the glasses.

In this Letter we report an experimental investigation of the effect of disorder on the electronic structure of As_2S_3 and As_2Se_3 , by studies of the visible and ultraviolet optical properties of the crystals and glasses from 1 to 14 eV. Few solids have been studied in both crystalline and amorphous forms. Among the simplest solids stable as bulk melt-quenched glasses are the arsenic chalcogenides; considerable infrared-visible work has been reported for these amorphous semiconductors.¹⁻⁴ In marked contrast to the situation for Ge and Si, for which the crystals are well understood while little is securely known about the amorphous forms, very little is known about the crystals of As_2S_3 and As_2Se_3 .

As_2S_3 and As_2Se_3 crystallize isomorphically as low-symmetry (monoclinic) *layer* crystals,⁵ molecular crystals in which the molecular unit is infinitely extended in two dimensions. Recent far-infrared and Raman studies of these crystals have shown that it is the *diperiodic* symmetry of the individual layer (not the usual triperiodic crystal symmetry) which dominates their lattice spectra⁶; we show here that this holds for the

electronic spectra. The diperiodic layer symmetry is orthorhombic,⁶ so that there are three principal directions of polarization; our crystal spectra are for the two polarizations in the plane of the layer, $E\parallel c$ and $E\parallel a$.

While the atomic arrangements in the glasses are, of course, much less well established, x-ray studies are quite consistent with the same short-range order as found in the crystals,⁷ that is, each As surrounded by three nearest-neighbor S's or Se's, and each S or Se surrounded by two nearest-neighbor As's. Furthermore, comparison of the infrared¹ and Raman⁸ spectra of the glasses with those of the crystals⁵ provides evidence that the molecular sheets of the crystals substantially retain their integrity in the amorphous forms. The spectral results reported in this Letter support this view of the glass structure.

Reflectivity measurements at 1-6 eV and at 5-14 eV were obtained with a prism spectrometer and an evacuated grating spectrometer, respectively. Transmission measurements at 1-3 eV were obtained with a foreprism-grating double

monochromator. A sensitive ($\Delta R \leq 0.001$) ratio reflectometer was used in the reflectivity studies, and experiments at low temperatures were performed with a cold-finger arrangement in a helium cryostat.

Overall views of the electronic spectra of crystalline As_2S_3 and As_2Se_3 , in the fundamental absorption regime, are provided by the room-temperature interband reflectivities presented in Figs. 1(a) and 1(b). These data were obtained on cleaved natural crystals of As_2S_3 and on as-grown vapor-deposited crystals of As_2Se_3 .⁶ The pronounced polarization dependence of these spectra reflects the dominance of the molecular (i.e., layer) symmetry for these crystals: The a and c axes, which are observed to be the principal axes in the visible,⁹ are symmetry axes for the isolated layer but are nonspecial directions in the crystal symmetry.⁶

The unmistakable similarity of the two pairs of polarization-dependent spectra demonstrates the

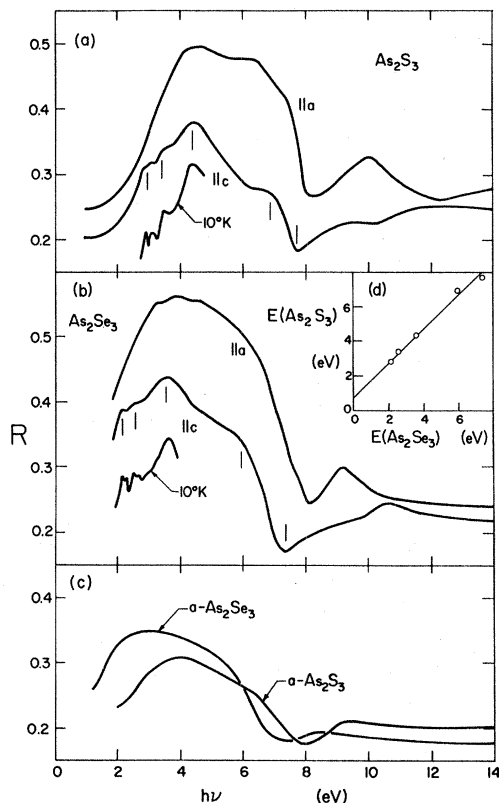


FIG. 1. (a), (b) Interband reflectivity spectra of crystalline As_2S_3 and As_2Se_3 . The 10°K spectra shown for $E||c$ are downshifted in reflectivity by 0.10, for clarity. (c) Reflectivity spectra of the amorphous forms. (d) Plot of interband energies of crystalline As_2S_3 versus energies of crystalline As_2Se_3 .

close isomorphism of these crystals: Throughout the uv the reflectivity for $E||a$ is higher, and exhibits less pronounced structure, than that for $E||c$; very similar structural features occur for corresponding polarizations, such as the four peaks and shoulders (2-7 eV) and the sharp minimum (7-8 eV) indicated on each $E||c$ spectrum. The corners in the 2- to 7-eV region are characteristic of critical-point singularities in the joint density of states for direct interband transitions. This structure sharpens dramatically at low temperatures; spectra for $E||c$ at 10°K are included in Fig. 1. Along with the development of additional fine structure, as some room-temperature peaks become well-resolved doublets, cooling to this temperature is accompanied by a general increase in transition energies of ~ 0.1 eV.

The fundamental electronic reflectivity spectra of the amorphous forms are shown in Fig. 1(c). These data were obtained with evaporated films; similar results were observed for the bulk glasses. The 2- to 7-eV structure, which was displayed by the crystals as a result of singularities associated with symmetry points in the Brillouin zone, is now gone in the absence of long-range order and is replaced by a broad featureless band of the same overall shape. For the glasses, no structure appears in this region even at liquid-helium temperature, in sharp contrast to the crystals.

However, there is spectral feature which survives the transition to the disordered state: The trough near 8 eV persists, though broadened, in the absence of long-range order. Kramers-Kronig analyses of the room-temperature reflectivities of Fig. 1 reveal that the 8-eV minima correspond to the threshold of a new contribution to $\epsilon_2(h\nu)$ (imaginary part of the dielectric constant), i.e., to the inception of a new absorption process. The insensitivity of this density-of-states structure to order-disorder indicates that it is associated with the onset of electronic transitions out of a low-lying valence band. The tightly bound electrons of such a deep band would be expected to be relatively indifferent to the presence or absence of long-range order.

The Kramers-Kronig analyses of the crystal spectra also show that the low-energy reflectivity peaks correspond to edges (steps) in ϵ_2 , and that ϵ_2 peaks at about 4 eV with ϵ_2^{max} for $E||a$ being about twice as large as for $E||c$ [$\epsilon_2^{\text{max}}(||a) \approx 20$ for As_2S_3 , ≈ 30 for As_2Se_3]. While the overall absorption in the uv is higher for $E||a$, the first edge in ϵ_2 occurs for $E||c$. This is confirmed, as

shown below, by the directly observed dichroism at the interband threshold in the visible region.

A clear illustration of the intimate similarity between the two sets of crystalline spectra of Fig. 1 is provided by the data displayed in insert (d). Here the photon energies of prominent features in the sulfide spectrum are plotted against the energies of the corresponding features in the selenide spectrum. Despite the naiveté of this idea, the results are quite well described by a straight line of slope unity. The implication of this is the existence of an approximate rigid-band relationship connecting the electronic structures of the two crystals, i.e., we conclude that the sulfide band structure can be roughly derived from the selenide band structure by rigidly separating valence and conduction bands by an additional 0.7 eV [the vertical-axis intercept in Fig. 1(d)].

We now focus down on the vicinities of the electronic thresholds. The fundamental absorption edges of the four solids are shown in Fig. 2. By means of transmission measurements on a variety of samples, the edge has been followed over four decades in absorption coefficient α for crystalline As_2S_3 , and over three decades in α for crystalline As_2Se_3 and both glasses. At room temperature both crystals exhibit smooth edge-absorption spectra without manifest structure. Despite the roughly exponential dependence on $h\nu$

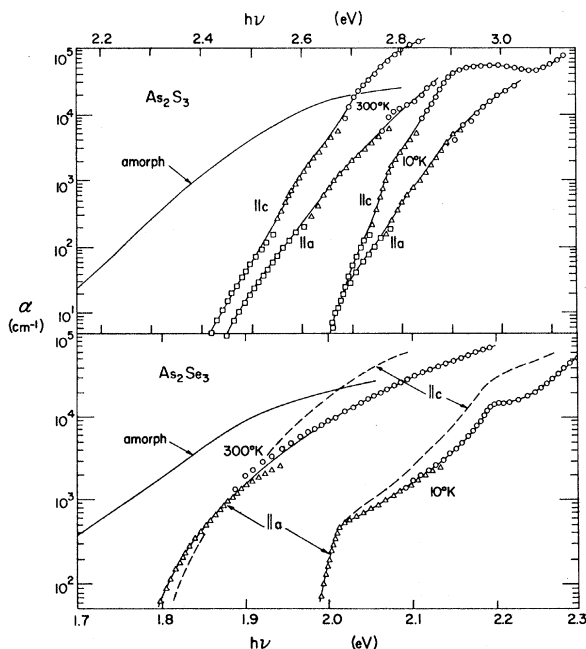


FIG. 2. Edge-absorption spectra of crystalline and amorphous As_2S_3 and As_2Se_3 .

over appreciable ranges of α , the clearcut structure which develops at low temperatures precludes interjection of Urbach-law behavior.¹⁰ At 10°K, two separate components of the As_2Se_3 edge stand exposed at 2.01 and 2.19 eV. The stronger edge ($\epsilon_2 \approx 1$ at 2.2 eV for $E \parallel c$) corresponds in position to the first peak seen in reflectivity [the 10°K spectrum of Fig. 1(b)]; the low-energy edge was too weak ($\epsilon_2 \approx 0.01$ at 2.0 eV) to be discernible in reflectivity. For crystalline As_2S_3 at 10°K, a strong ($\epsilon_2 \approx 1$) edge is observed at 2.90 eV for $E \parallel c$, coinciding with the first low-temperature reflectivity peak of Fig. 1(a). Unlike As_2Se_3 , for As_2S_3 the strong edge seen for $E \parallel c$ is not apparent also for $E \parallel a$, for which α is an order of magnitude lower at 2.9 eV. The dichroism in these crystals is not simply interpretable in terms of band-edge splittings (as is possible, e.g., for wurtzite CdS, for which the polarized absorption edges can be brought into coincidence by a shift in photon energy), but depends in more detail on polarization-dependent differences in transition-matrix elements.

Our optical experiments point to these crystals as direct-gap semiconductors. All of the edge-absorption features discussed above are definitely attributable to direct transitions by virtue of the *shape* and the *strength* of the structure in $\alpha(h\nu)$. An absorption threshold associated with a direct gap occurs as a steep edge ending in a sharp knee (sudden *decrease* in slope), sometimes with an excitonic peak, at an absorption level of the order of 10^3 - 10^5 cm^{-1} , whereas an indirect threshold appears as a sudden *increase* in slope of $\alpha(h\nu)$, and occurs at very low absorption, 0.1-10 cm^{-1} . Thus the low-temperature thresholds at 2.0 and 2.2 eV in As_2Se_3 , and at 2.9 eV in As_2S_3 , are unambiguously earmarked as direct-gap thresholds, in contradiction to earlier assignments^{3,4,9} as indirect transitions. Our measurements extend down to 5 cm^{-1} for As_2S_3 , 50 cm^{-1} for As_2Se_3 ; it would be valuable to extend these results to lower α 's in order to put to rest the question of possible lower-energy indirect transitions. It is significant, however, that the sharpness of the crystalline absorption edges at the lowest α 's of Fig. 2 are typical of the steep absorption tails produced by phonon-assisted direct transitions below a direct threshold, rather than the much more gradual increase in α with $h\nu$ observed above an indirect threshold.

The data shown in Fig. 2 for the room-temperature absorption edges of the amorphous forms were obtained with both evaporated films and

bulk samples, and are concordant with results reported by other workers.^{1,2,4} The edge-absorption spectra of the two glasses are broad and featureless, and while they shift towards the blue on cooling to low temperatures (like the crystal edges), they undergo no appreciable change in shape. In the absence of spectral markers, the determination of characteristic energies from the bland edge-absorption spectra of the glasses is not so straightforward as for the crystals. It has been observed that such edges can be reasonably well described by an exponential $\alpha(h\nu)$ followed by a quadratic [$\alpha \sim (h\nu - h\nu_0)^2$] behavior at high α 's.^{2,11} The values of $h\nu_0$ (which is a quantity commonly associated with an "optical gap" for the glass) derived from Fig. 2 are 2.34 and 1.73 eV for α -As₂S₃ and α -As₂Se₃, respectively. These photon energies correspond to α 's of about $5 \times 10^2 \text{ cm}^{-1}$, and are seen to be 0.1-0.3 eV lower than $h\nu(\alpha)$ for the corresponding crystals at 300°K. While this might be viewed as a measure of a disorder-induced shift of the optical band gap, this prescription focuses on the tail of the edge, at an absorption 2-3 orders of magnitude weaker than the characteristic of the fundamental band. A more appropriate criterion is one attentive of α 's representative of the first strong direct transitions in the crystals. From this viewpoint, the electronic thresholds of the crystals and glasses are virtually identical, and the crystal-to-glass shift in the tail region becomes interpretable merely as the smearing out of the edge for the latter.

Our results thus show that the effect of disorder on the electronic structure of these materials is remarkably slight. Aside from the loss of structure specific to symmetry points in the zone, and a broadening of a few tenths of an eV, the spectra of the amorphous solids are extremely close to those of the crystals. These data are

concordant with the molecular nature of these solids, lending credence to the view (provided by the vibrational spectra) that the amorphous forms are composed of weakly interacting polymer networks similar to the molecular layers of the crystals.

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