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Edge-absorption spectra for trigonal HgS, for both polarizations of incident light, have been measured at 300°K, 80°K, and 10°K. The measurements extend from 1 cm\(^{-1}\) to 4000 cm\(^{-1}\) in absorption coefficient, and between 2.0 eV and 2.4 eV in photon energy. Pronounced dichroism is observed, with the absorption for E \(\perp\) c exceeding that for E \(\parallel\) c. In contrast to wurtzite, the dichroism is interpreted as due to differences in transition probabilities rather than to a band-edge splitting. Structure in the low-temperature spectra indicates the presence of indirect transitions common to both polarizations, as well as a weak, higher-energy, direct transition allowed for E \(\perp\) c. A simple band model consistent with the observed spectra, providing for a non-accidental near-degeneracy between a direct and an indirect gap, is discussed.

INTRODUCTION

With one exception, the room-temperature low-pressure crystalline modification of each of the binary compounds which Zn, Cd, and Hg form with S, Se, and Te possesses either zincblende (\(T^2_d\)) or wurtzite (\(C^4_{6\nu}\)) structure. The lone exception is HgS, for which the stable form under ordinary conditions possesses a structure of \(T^4_3\) symmetry which is a diatomic analog of the trigonal elemental semiconductors, Se and Te.

Trigonal HgS (\(\alpha\)-HgS) consists of helical coils of alternating Hg
and S atoms which spiral around axes parallel to the ternary c-axis. A schematic view of the structure, sighting along the c-axis, is shown in Fig. 1. The space group is $D_3^4$ and the irreducible representations of the equivalent point group have been discussed by several authors in connection with the Tellurium lattice.\(^{1,2}\)

In this paper we report a study of electronic interband transitions in trigonal HgS by means of measurements, at several temperatures and for both polarizations of incident light, of the fundamental edge-absorption spectrum near 2 eV.

**EXPERIMENTAL**

Measurements were made on natural crystals. The optical quality of the crystals was such that the lower limit on measurable absorption coefficients (≥ 1 cm\(^{-1}\)) was set not by residual absorption but by the maximum crystal thicknesses available (∼ 1 mm). The dangers of using mechanically polished specimens were accepted warily in order to reach high absorption levels (up to $4 \times 10^3$ cm\(^{-1}\)).

An optical metal cryostat was used for the low temperature experiments, with the sample mounted freely in close contact with the cold finger in the vacuum space. The cryostat, immediately preceded by a polarizer, was located in the exit beam of a fore prism-grating spectrometer operated at a spectral slit width of about 1 meV. Spectra were recorded photoelectrically, employing phase-sensitive detection.

**RESULTS**

Trigonal HgS is optically uniaxial, so that at each temperature two spectra were obtained: for $E \parallel c$ and for $E \perp c$. The edge-absorption

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Figure 1. Crystal structure of α-HgS, viewed along the c-axis.
spectra, for three temperatures between room temperature and liquid helium temperature, are displayed in Fig. 2.

The data obtained for different samples at room temperature are quite concordant. However, at low temperatures the results obtained with thin samples exhibit a well-known surface-damage effect: the absorption drops too slowly with decreasing photon energy at the lower part of the range spanned by each sample. Despite this, the overlapping data from different samples allow the intrinsic spectra to be closely estimated, as indicated by the solid (E || c) and dashed (E ⊥ c) lines in the figure.

Absorption measurements made with unpolarized light were reported by Dovgii and Bilen'kii. Their results at 290°K and 20°K, shown as dotted lines in Fig. 2, are appreciably down-shifted in energy from ours, especially at the lower temperature, and their use of unpolarized light limits the usefulness of these data.

Fig. 2 reveals that trigonal HgS is strongly dichroic; the absorption for E || c is considerably greater than that for E ⊥ c. The two spectra exhibit distinctly different behavior with temperature, with the perpendicular edge becoming much steeper than the parallel at low temperatures.

**DISCUSSION**

We are interested in examining the edge-absorption spectra of Fig. 2 for clues to the nature of the electronic transitions connecting valence and conduction band extrema in this material.

At room temperature, where the edges are similar in shape, the rise in absorption with photon energy is somewhat slower than exponential.
Plots of $\alpha^2$ vs. $h\nu$ are sharply superlinear, with no linear portions. The latter observation may be construed as evidence against indirect transitions. However, the room-temperature spectra of Fig. 2 are very similar in shape to the absorption edges of the silver halides, (6) which correspond to indirect processes. (7)

At low temperatures the $\mathbf{E} \perp \mathbf{c}$ edge sharpens considerably and develops a weak shoulder at a $\approx 10^3$ cm$^{-1}$, located at 2.26 eV and 2.28 eV, respectively, at 80°K and 10°K. At 10°K both edges develop structure at low absorption levels.

The low-temperature edge-absorption is shown in detail in Fig. 3. Also shown, for comparison, are corresponding data for the intrinsic edges of CdTe (4) and GaP, (8) which are well-documented direct (4,9) and indirect (8,10) gap semiconductors, respectively. Three absorption thresholds are apparent in the HgS data for $\mathbf{E} \parallel \mathbf{c}$, and two for $\mathbf{E} \perp \mathbf{c}$, which are similar to the thresholds occurring at the onset of the phonon-emission components shown for the GaP indirect edge. The thresholds for $\mathbf{E} \parallel \mathbf{c}$ coincide in energy with the first two for $\mathbf{E} \perp \mathbf{c}$. The above structure is strong evidence in favor of an indirect energy gap for HgS.

Fig. 3 reveals that the low-temperature edge-absorption for $\mathbf{E} \perp \mathbf{c}$ rises at a rapid rate more akin to that for CdTe than for GaP. This may be related to the knee observed for this polarization at 2.28 eV, which is suggestive of a weak direct edge such as occurs at 0.8 eV in Ge.

Some simple band models which can serve as a basis for discussion of the above observations are illustrated in Fig. 4. For convenience, the examples discussed involve states near the zone center (Γ-point); similar selection rules apply at other points of high symmetry in the

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Figure 4, Band models: (a) wurtzite analog; (b) wurtzite-analog model; (c) a possible indirect-direct band structure in the vicinity of a symmetry point.
hexagonal Brillouin zone. Double group notation is employed for labelling the states.

In wurtzite crystals the observed dichroism is a consequence of a band-edge splitting coupled with a selection rule forbidding direct transitions across the smaller gap for one polarization. An analogous situation for space group $D_3^1$ is constructed in Fig. 4a.

A simpler mechanism giving rise to dichroism in the edge region would be a transition allowed for both but with appreciably different magnitudes for the two polarizations. This case is schematically indicated in Fig. 4b.

Figs. 4a and 4b are shown for direct processes. Analogous situations exist for indirect transitions as well.

For a splitting-induced dichroic edge, it might be expected that either absorption spectrum could be derived from the other by means of a rigid translation along the energy scale. This is the case for CdS. Such a relation does not hold for the HgS spectra of Fig. 2. Even at room temperature, where the two edges are most similar, $h\nu_{\parallel}(a) - h\nu_{\perp}(a)$ is not constant but varies between 23 meV and 60 meV over the measured range of $a$. Instead we find that at this temperature the vertical separation in Fig. 2, rather than the horizontal, is nearly constant: $\alpha_{\perp}(h\nu) \approx 4.5 \times \alpha_{\parallel}(h\nu)$. At low temperature, the absorption components shown in Fig. 3 for the two polarizations differ in magnitude rather than location. These observations strongly suggest a matrix-element mechanism (Fig. 4b), rather than a band-splitting mechanism (Fig. 4a), as responsible for the dichroism of trigonal HgS.

The following picture emerges for the energy band structure of trigonal HgS:

(a) the lowest energy gap corresponds to an indirect transition;
(b) the indirect transition probability is greater for $E \perp c$ than for $E \parallel c$;
(c) a direct gap, allowed for $E \perp c$, lies slightly higher in energy.

Fig. 4c illustrates a possible band structure consistent with the above interpretation. Hulin has pointed out that the $E(k)$ variation near a $\Gamma_6$ state is conical. Thus, if the lowest direct energy gap corresponded to a $\Gamma_4 \rightarrow \Gamma_6$ transition, the linear $k$-dependence would require an extremum to occur away from $k = 0$. The band model of Fig. 4c would give rise to indirect edges for both polarizations, followed by a direct edge for the perpendicular, but not for the parallel, polarization. An equivalent structure could occur at a symmetry point other than $\Gamma$ and the roles of valence and conduction bands shown in Fig. 4c could be reversed. This model represents an interesting possibility since it provides for a non-accidental near-degeneracy between a direct and an indirect gap.

**Summary**

Edge-absorption spectra for trigonal HgS, shown in Figs. 2 and 3, have been measured and discussed in terms of band models illustrated in Fig. 4. Unlike wurtzite, the dichroism exhibited by this material is more appropriately interpreted as due to differences in transition probabilities, rather than to a band-edge splitting. The low-temperature spectra suggest the presence of indirect transitions common to both polarizations, as well as a weak, higher-energy direct transition for $E \perp c$. A band structure of the type shown in Fig. 4c is
consistent with these observations.

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13. The $\Gamma_4$ levels shown in Fig. 4 are each degenerate with a $\Gamma_5$ level omitted for simplicity. Since the selection rules for $\Gamma_4 \rightarrow \Gamma_6$ and $\Gamma_5 \rightarrow \Gamma_6$ are identical, the arguments are not affected.
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13. The Gamma-4 levels shown in Fig. 4 are each degenerate with a Gamma-5 level omitted for simplicity. Since the selection rules for Gamma-4 to Gamma-6 and Gamma-5 to Gamma-6 are identical, the arguments are not affected.