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Energy bands of $AgInS_2$ in the chalcopyrite and orthorhombic structures

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The symmetries and splittings of the uppermost valence bands in orthorhombic and chalcopyrite $AgInS_2$ have been determined from electroreflectance measurements on oriented crystals using polarized radiation. The principal features of the valence-band structures in both phases are dominated by the deviations of the lattice constants from ideal wurtzite and chalcopyrite, respectively. On the other hand, the small splitting of the lowest two valence bands in orthorhombic $AgInS_2$ is attributed to the "wurtzite-like" potential. The lowest band gaps at 300 °K in the orthorhombic and chalcopyrite phases are 1.98 and 1.86 eV, respectively.

I. INTRODUCTION

$AgInS_2$ is unique among the I-III-VI_2 compounds in that it exists in two ordered phases: chalcopyrite and orthorhombic. Most II-IV-V_2 and I-III-VI_2 compounds only exist in the chalcopyrite structure, although some can also be obtained in the zinc-blende modification, which is characterized by a compositional disorder on the cation sites. The orthorhombic modification of $AgInS_2$ is pseudowurtzite, just as the chalcopyrite structure is pseudo-zinc-blende. The atomic-site positions in the former are very nearly the same as in wurtzite. However, an ordering of Ag and In atoms on the cation sublattice results in a doubling of the unit-cell dimension and reduces the symmetry, thereby permitting an internal orthorhombic distortion.

In the work reported here, we have studied the band structure of both modifications of $AgInS_2$ near the lowest direct energy gaps. The valence-band splittings observed in both crystalline modifications can be explained by crystal-field splittings alone, neglecting any spin-orbit interaction. The p-like valence bands of $AgInS_2$(ch) are split into a z and an x,y doublet by the uniaxial lattice compression, with the z valence band at higher energy. The observed splitting of 0.15 eV is consistent with uniaxial deformation potentials for II-VI compounds, and with the splittings observed in other I-III-VI_2 compounds. The valence bands of $AgInS_2$(w) are ordered x,y,z with the x valence band highest in energy. The x valence band is split away from the average of the y,z bands by 74 meV, due to a large lattice compression along the x axis. The smaller splitting of the y,z bands by 24 meV does not result from the lattice compression in the y-z plane, since it has the wrong sign.

We have verified that there are no lower-lying indirect energy gaps in either compound by the observation of efficient photoluminescence near the energy gaps in both modifications at low temperatures. To the best of our knowledge, there are no prior studies of the electronic structure of $AgInS_2$.

II. CRYSTAL GROWTH

Although $AgInS_2$ melts at $(880\pm10)^\circ C$, Hahn *et al.*[1] reported that samples annealed above 700 °C and quenched in water displayed a hexagonal structure. Samples annealed at 600 °C and similarly quenched yielded a single-phase chalcopyrite structure. Recently Roth *et al.*[2] showed that the high-temperature phase of $AgInS_2$ is orthorhombic, i.e., psuedowurtzite but with an ordering on the cation sublattice. They reported that the phase transition temperature was $(620\pm10)^\circ C$.

We have found that stoichiometric samples of $AgInS_2$, slow cooled from above the melting point to room temperature, are mostly single-phase chalcopyrite with lattice constants $a=5.88$ Å and $c=11.20$ Å, in agreement with the results of Roth *et al.*[2] For the ideal chalcopyrite structure, the correspondence between the chalcopyrite lattice constants a_{ch} and c_{ch} and the zinc-blende lattice constant a_{zb} is: $a_{ch}\rightarrow a_{zb}$, $c_{ch}\rightarrow 2a_{zb}$. Quenching from slightly below the melting point yields a few well-developed platelets having the orthorhombic structure with lattice constants $a=7.00$ Å, $b=8.28$ Å, and $c=6.70$ Å, also in agreement with the results of Roth *et al.*[2] These pseudowurtzite platelets are oriented with the wurtzite c axis normal to the major faces. Laue photographs of such platelets are not easily distinguished from those of (112) oriented chalcopyrite $AgInS_2$, so great care must be taken for proper identification and orientation of these crystals. For the ideal structures, the correspondence between the orthorhombic lattice constants (a,b,c) and wurtzite lattice constants (a_w,c_w) are $a\rightarrow\sqrt{3}\,a_w$, $b\rightarrow 2a_w$, and $c\rightarrow c_w$. For ideal wurtzite $c_w=(2\sqrt{2}/\sqrt{3})a_w$. The x, y, and z coordinate system is oriented parallel to the a, b, and *c* crystallographic axes, respectively.

Bulk crystals of orthorhombic $AgInS_2$ were grown by slow-cooling of stoichiometric melts containing small amounts of Li. Since $LiInS_2$ normally crystallizes only in the orthorhombic phase,[3] the addition of small quantities of Li to $AgInS_2$ stabilizes the orthorhombic modification of $AgInS_2$. The lattice constants of one such crystal were $a = 6.954$ Å, $b = 8.264$ Å, $c = 6.683$ Å. When interpolated between the orthorhombic lattice constants of $AgInS_2$ and $LiInS_2$, these values indicate that our alloy had the composition $(Ag_{0.94}Li_{0.06})InS_2$. Quantitative chemical analysis for Li yielded concentrations consistent with this composition.

As previously reported,[4] bulk crystals can be rendered sufficiently *n*-type conducting for electroreflectance measurements by suitable anneals. Similar anneals of the thin orthorhombic platelets were not attempted.

III. EXPERIMENTAL RESULTS

A. $AgInS_2$(ch)

The room-temperature electrolyte electroreflectance spectra of $AgInS_2$(ch) are shown in Fig. 1 for light polarized respectively parallel and perpendicular to the projection of the optic axis in the plane of the sample. The orientation was close to (112). The two structures observed at 1.87 and 2.02 eV are attributed to transitions from the *z* and *x,y* valence bands to the conduction band. As has been reported for other sulfides[5] the spin-orbit splitting of the *x,y* doublet is unobservable in electroreflectance spectra.

The electroreflectance spectrum of this sample at 77 °K is shown in Fig. 2. For these measurements an MIS package was prepared consisting of a Syton-polished semiconductor (S), a thin (~200 Å) insulating $CuGaS_2$ evaporated film (I), and a semi-transparent Ni electrode (M). The structure near the lowest direct band gap has shifted to higher energy relative to the room-temperature data in Fig. 1, and the separation of the structures has increased slightly to 0.165 eV from the room-temperature value of 0.15 eV.

The polarization properties of the spectra in Figs. 1 and 2 suggest that these features result from a crystal-field splitting Δ_{cf} of the triply degenerate *p*-like levels by the uniaxial crystalline field. The sense of this splitting is such that the energy gap due to transitions from the *z* valence band to the conduction band is at lower energy than the energy gap due to transitions from the *x,y* valence band. In other I-III-VI_2 compounds[5] it has been found that the sign and magnitude of Δ_{cf} is determined principally by the built-in compressive lattice distortion, $c < 2a$. The room-temperature splitting of 0.15 eV for $AgInS_2$(ch) is plotted in Fig. 3 at the appropriate value of $(2-c/a)$. It is apparent that Δ_{cf} is proportional to the compressional lattice distortion in these compounds,[5] especially for those containing Ag. Furthermore, the sign and magnitude of the deformation potential $b \simeq -1$ is close to typical values observed in II-VI crystals under externally applied uniaxial stress.[6] The slight decrease in Δ_{cf} for $AgInS_2$ between 77 and 300 °K suggests that $2-c/a$ may be decreasing in this temperature range, but this cannot be confirmed until the lattice constants have been measured at low temperatures.

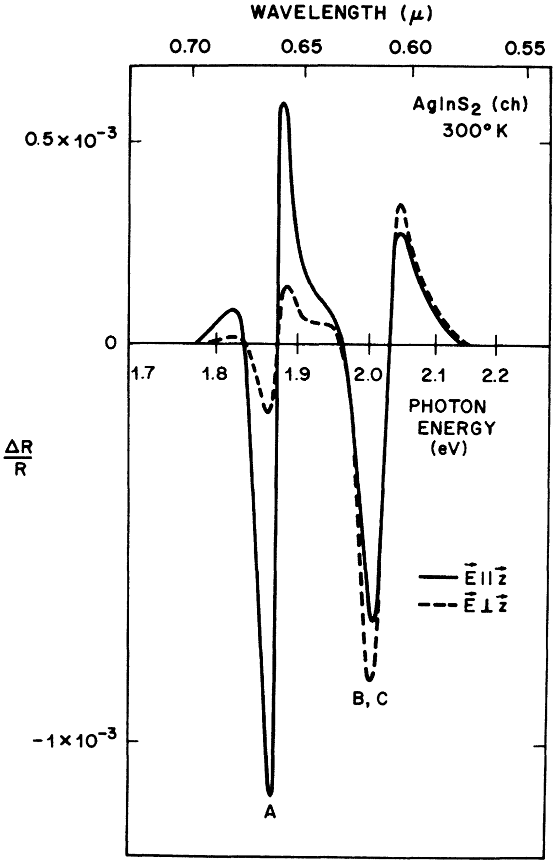

FIG. 1. Electrolyte electroreflectance spectra of chalcopyrite $AgInS_2$ for light polarized respectively parallel and perpendicular to the projection of the optic axis in the plane that was approximately (112).

The electroreflectance structures in Fig. 2 probably result from exciton transitions at this low temperature rather than strictly band-to-band transitions. Assuming an exciton binding energy (0.02 eV) equal to that of CdSe[7] (the II-VI compound with approximately the same band gap), we estimate the 77 °K band gaps, shown in parentheses in Table I. The lowest band gap of $AgInS_2$(ch) therefore decreases by, at most, 40 meV between 77 and 300 °K, whereas that of the binary analog CdS

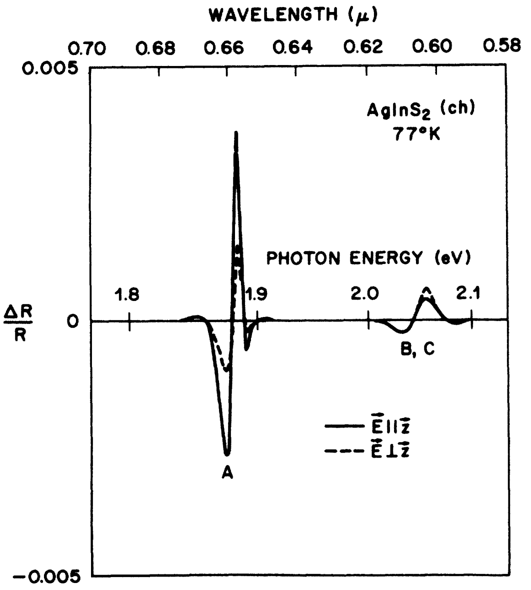

FIG. 2. Low-temperature electroreflectance of the sample in Fig. 1 using a metal-insulator-semiconductor package.

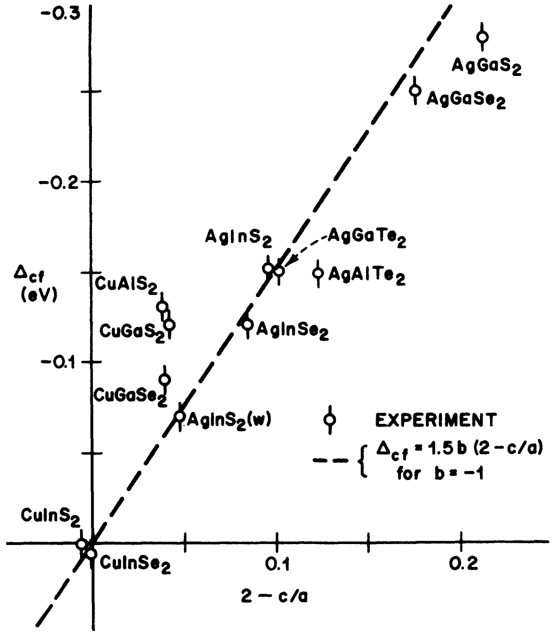

FIG. 3. Plot of the crystal-field splittings (Δ_{cf}) of many I-III-VI_2 compounds as a function of their respective compression lattice distortions.

decreases by 130 meV in the same temperature range.[7] A similar anomalously small temperature dependence was reported for $AgInSe_2$,[8] and is as yet unexplained.

B. $AgInS_2$(w)

The orthorhombic platelets of $AgInS_2$ show pronounced exciton reflection anomalies at 2 °K as shown in Fig. 4. The platelets are oriented with the "wurtzite" c axis normal to the major face, so only the polarizations $\vec{E} \parallel \vec{x}$ and $\vec{E} \parallel \vec{y}$ are available. There would be no polarization dependence to this spectrum for a truly "wurtzite" crystal structure, even for nonideal lattice constants. The energy separation of the x and y bands therefore results from an orthorhombic distortion away from nonideal wurtzite. Reflectivity anomalies are also observed at 77 °K. Within experimental error (± 3 meV), the exciton energies are the same as found at 2 °K. The exciton anomalies in Fig. 4 were strongest for the polarizations indicated. They were also observed in the opposite polarizations with strengths that were sample dependent but always at least five times weaker.

The separation of 69 meV between the x and y structures in Fig. 4 results from the large distortion of the lattice constants of $AgInS_2$(w) in the x-y plane. The lattice constants of Roth *et al.*[2] imply a 2.4% compression in this plane. It can be seen in Fig. 3 that the observed Δ_{cf} of 69 meV correlates nicely with the equivalent $2\text{-}c/a$ for this lattice distortion. Of course it is not legitimate, strictly speaking, to compare this x-y splitting with the (001) deformation potential for zinc-blende and chalcopyrite crystals, but the essential idea is correct. Using the measured deformation potentials[6] of wurtzite CdS for externally applied uniaxial stress normal to c, one predicts $\Delta_{cf} \sim 74$ meV for $AgInS_2$(ch), remarkably close to the observed value of 69 meV.

The photoluminescence spectrum of an orthorhombic platelet is shown in Fig. 5. The shoulder near 2.024 eV results from the lowest energy exciton (cf., Fig. 4). The other lines apparently

TABLE I. Valence-band parameters of $AgInS_2$ (in eV).

	T(°K)	E_{g1}	E_{g2}	E_{g3}	E_{x1}	E_{x2}	E_{x3}	Δ_1	Δ_2
$AgInS_2$(ch)	300	1.87	2.02	2.02	···	···	···	0.15	(< 0.01)
	77	(1.90)	(2.06)	(2.06)	1.880	2.045	2.045	0.165	(< 0.01)
$AgInS_2$(w)	2	(2.05)	(2.12)	···	2.024	2.093	···	0.069	···
$AgInS_2$: Li(w)	300	2.081	2.144	2.168	···	···	···	0.063	0.0024

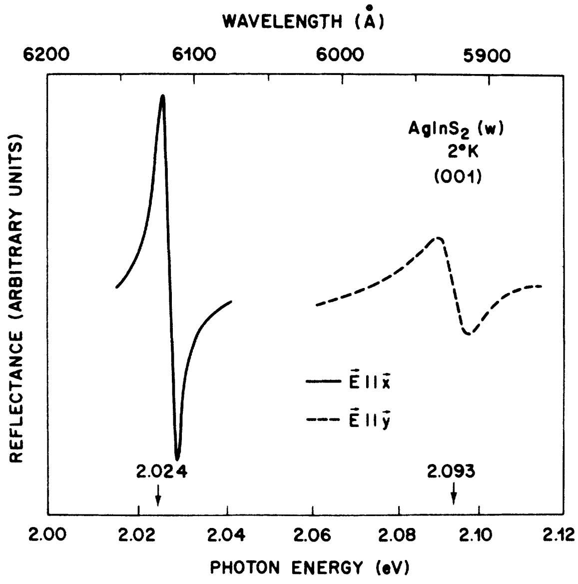

FIG. 4. Exciton reflectance spectra for light polarized along x and y, respectively, in a platelet of orthorhombic $AgInS_2$. The "pseudowurtzite" platelet was oriented such that the wurtzite c axis was normal to the major face. There would be no polarization dependence to this spectrum for a truly "wurtzite" structure, even for nonideal lattice constants.

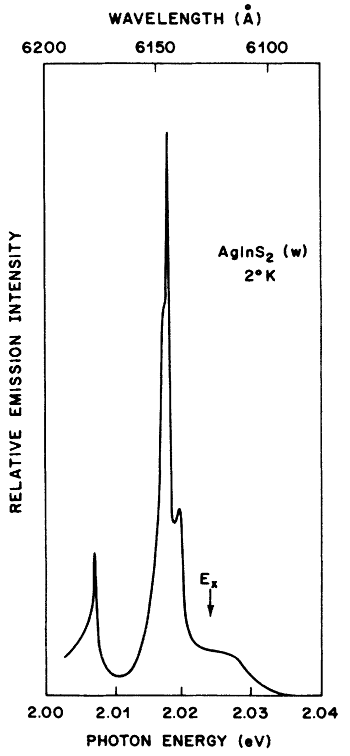

FIG. 5. Photoluminescence spectrum of orthorhombic $AgInS_2$ at 2 °K.

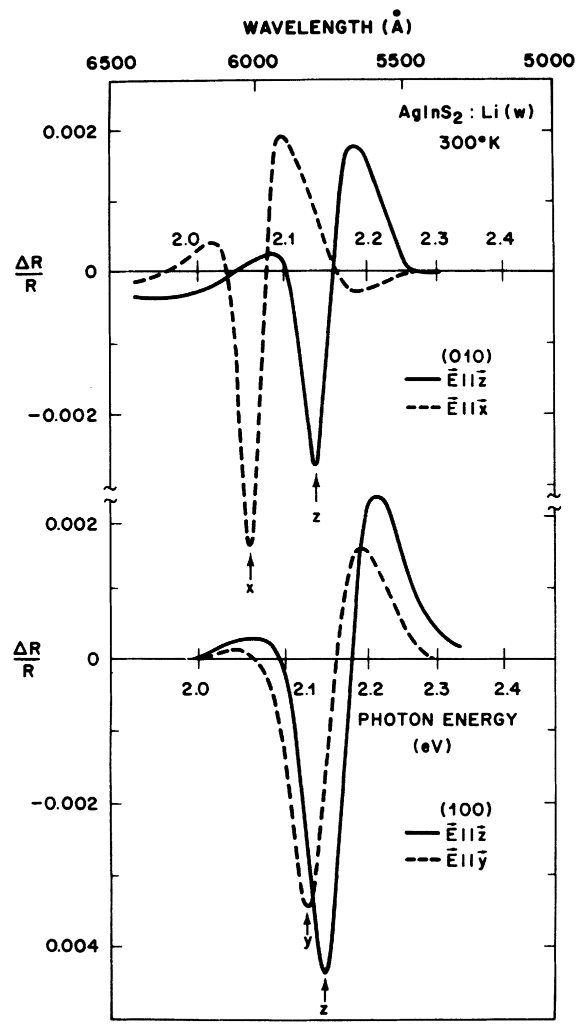

FIG. 6. Electrolyte electroreflectance spectra of orthorhombic $AgInS_2$ containing ~6-at. % Li.

result from excitons weakly bound to impurities and defects. Sharp-line photoluminescence was not observed from chalcopyrite crystals, although several bands were observed $\gtrsim 0.05$ eV below the exciton energy deduced from the electroreflectance measurements (Fig. 2). These photoluminescence experiments imply that $AgInS_2$(w) has no lower-lying indirect gaps, and that any indirect gap in $AgInS_2$(ch) is at most 0.05 eV below the direct gap.

C. $AgInS_2$: Li(w)

The large differences in the spectra for $AgInS_2$ (w) in Fig. 4 prompted us to grow bulk crystals in order to study the optical properties in the three inequivalent directions. As explained in Sec. II, the addition of small quantities of Li stabilizes the orthorhombic structure of $AgInS_2$. This addition of Li to noble metal I-III-VI_2 compounds, i.e.,

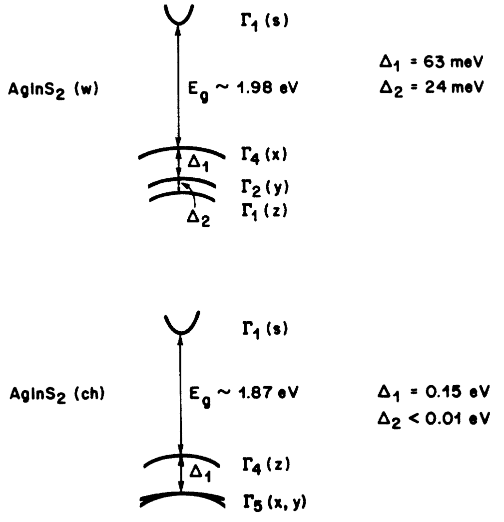

FIG. 7. Energy band structures of orthorhombic (w) and chalcopyrite (ch) $AgInS_2$ as deduced from the electroreflectance measurements at room temperature.

$(Ag_{1-x}Li_x)InS_2$, shifts the direct energy gap to higher energies due to the $\gtrsim 3.6$-eV band gap of $LiInS_2$.[9,10]

The electrolyte electroreflectance spectra of two crystalline slabs containing, respectively, the x, z and y,z axes are shown in Fig. 6. As mentioned in connection with Fig. 4, the x valence band is split off from the y,z bands by a large compressive distortion of the lattice constants away from ideal wurtzite. The smaller splitting of the y,z valence bands by 24 meV does not result from the lattice distortion in the y-z plane alone. The c/b ratio is small relative to that for the ideal-wurtzite structure due to a built-in compression along the c axis. Such an externally applied distortion in CdS[6,11] moves the z valence band to higher energy relative to the y valence band, whereas just the opposite ordering is observed in Fig. 6. Consequently, we attribute the small splitting of the y,z structures in Fig. 6 to a "wurtzite-like" potential resulting from the displacement of the second-nearest neighbors by 60° relative to their location in the zincblende structure. "Wurtzite-like" splittings of a similar magnitude are observed in II-VI crystals[7] having nearly ideal-wurtzite lattice constants.

IV. CONCLUSIONS

The band structures near the lowest direct energy gap of the orthorhombic and chalcopyrite phases of $AgInS_2$ are summarized in Fig. 7 and Table I. The room-temperature values of Δ_1 and Δ_2 for $AgInS_2$(w) are assumed equal to those measured in $AgInS_2$: Li owing to the very low (~ 6 at.%) Li concentration. However, since the energy gap of $LiInS_2$ is ~3.6 eV,[10] the lowest direct energy gap in $AgInS_2$: Li(w) is ~0.10-eV high owing to the presence of Li. The energy gap for $AgInS_2$(w) in Fig. 7 has been corrected for this shift.

The crystal-field splitting of the valence bands in $AgInS_2$(ch) has the sign and magnitude expected as a consequence of the large compressive distortion of the chalcopyrite lattice constants ($c < 2a$). Similarly, the x valence band in $AgInS_2$(w) is split off from the y,z bands by the large distortion of the a lattice constant away from ideal wurtzite. On the other hand, the splitting of the y and z bands (Δ_2) in $AgInS_2$(w) does not result from lattice compression, since it has the wrong sign relative to experimental deformation potentials in II-VI wurtzite crystals. The lowest band gaps at 300 °K in the orthorhombic (1.96 eV) and chalcopyrite (1.86 eV) phases are remarkably close in view of the greatly dissimilar structures.

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