

Electroreflectance Study of the Energy-Band Structure of CdSnP₂

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We report electroreflectance spectra for the chalcopyrite crystal CdSnP₂, the ternary analog of InP. Structure in the electroreflectance spectra is observed at 1.17, 1.25, and 1.33 eV due to direct energy gaps in CdSnP₂ corresponding to the E_0 and $E_0 + \Delta_0$ direct energy gaps in InP. From the polarization dependences of this structure, we have established an unusual ordering of the valence bands, which we explain quantitatively by a simple model for the chalcopyrite lattice. The valence bands of CdSnP₂ are regarded as equivalent to those which would occur in a strained version of its binary analog InP, could one strain InP sufficiently to achieve the lattice constants of CdSnP₂. We also observe structure at 2.56 and 2.69 eV corresponding to the E_1 and $E_1 + \Delta_1$ peaks in zinc blende. The polarization dependences of these peaks agree with observations in stressed zinc-blende crystals. Much additional structure observed in CdSnP₂ is attributed to "pseudodirect" band gaps which result from the doubling of the unit cell in the Z direction in chalcopyrite relative to zinc blende. This change in the unit cell causes the Brillouin zone of zinc blende to be imbedded into the smaller Brillouin zone of chalcopyrite. Hence at every point in the chalcopyrite Brillouin zone, new direct transitions appear. We refer to these transitions as "pseudodirect," since their strength will depend upon the degree of difference of the pseudopotentials of the two cations.

INTRODUCTION

The II-IV-V₂ semiconductors normally crystallize in the chalcopyrite structure and have physical properties similar to those of the familiar III-V zinc-blende semiconductors.¹ Although the two crystal structures are quite similar, the anisotropy of chalcopyrite crystals gives rise to many interesting properties not possible in zinc-blende crystals. The triple degeneracy of the Γ_{15} valence-band maximum in zinc blende is removed in chalcopyrite by the combined effects of the noncubic crystalline field and spin-orbit interaction. By regarding the valence bands of CdSnP₂ as equivalent to those which would occur in a strained version of its binary analog, we are able to quantitatively explain the observed valence-band splittings and the amplitudes of the polarization dependences in CdSnP₂ electroreflectance spectra.

The doubling of the unit cell in the Z direction in chalcopyrite relative to zinc blende causes the appearance of pseudodirect energy-band gaps. These pseudodirect gaps, which are direct gaps in chalcopyrite corresponding to indirect gaps in zinc blende, occur due to the mapping of the zinc-blende Brillouin zone into the smaller chalcopyrite Brillouin zone.^{2,3} Despite the potential technological importance of these pseudodirect band gaps especially for high luminescence efficiency (e. g., ZnGeP₂ may be a pseudodirect GaP), there is no prior experimental evidence for their existence in the literature.

In the present work, we report the results of an experimental study of the electroreflectance spectra of CdSnP₂, the ternary analog of InP. In addition to structure due to the direct energy gaps in CdSnP₂ corresponding to the E_0 and E_1 direct energy gaps in InP, much additional structure is observed in CdSnP₂ and is attributed to the pseudodirect band gaps mentioned above. A preliminary report of some of this work was published elsewhere.⁴ The only previous studies of the optical properties of CdSnP₂ are a report⁵ of electron-beam pumped stimulated emission near 1.01 μ at 77 °K, and photoluminescence and cathodoluminescence studies^{6,7} for 1.7 < T < 300 °K. These latter studies⁷ suggested that CdSnP₂ has a direct band gap near 1.06 μ (1.17 eV) at 300 °K.

EXPERIMENTAL TECHNIQUES

The CdSnP₂ crystals were grown from a tin solution by slow cooling from 850 °C. After solidification, the excess tin was dissolved with mercury. Undoped crystals were n type with a resistivity of about 1 Ω cm and typical dimensions were 2 × 0.5 × 5 mm. A more detailed discussion of the crystal growth is presented elsewhere.⁸ X-ray powder photographs revealed that the crystals had the chalcopyrite structure. From Laue photographs and x-ray diffraction studies we conclude that the large natural faces of the platelets were [112] planes (Fig. 1).⁹ In such a plane it is possible to polarize light with the electric vector perpendicular

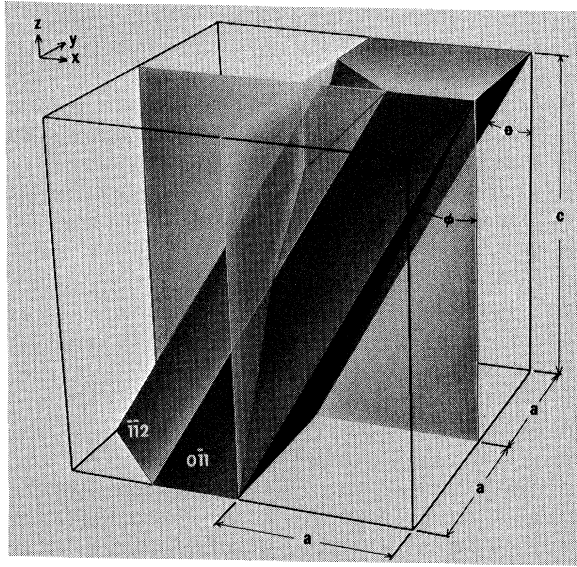


FIG. 1. Crystal habit for solution-grown single crystals of CdSnP_2 (after Ref. 9). Many crystals showed larger $\{112\}$ faces than $\{011\}$ faces. It is apparent that in such a plane one can polarize normally incident radiation with the electric vector perpendicular to the optic axis Z , but not completely parallel to it. Hence in our electroreflectance data $E \parallel Z$ is only nominal, and in fact only $\frac{2}{3}$ of the intensity lies along Z .

to the optic axis, but not completely parallel to this axis. Consequently in the electroreflectance data, $E \parallel Z$ is only nominal, and, in fact, only $\frac{2}{3}$ of the intensity lies parallel to Z .

The electroreflectance measurements were performed using the electrolyte technique developed by Cardona and co-workers.¹⁰ Natural faces were Syton¹¹ polished to remove surface layers. Alloyed tin contacts made adequate electrical contacts to the crystals.

RESULTS

A. Lowest Direct Energy Gap

In Fig. 2., we present the electroreflectance spectra of CdSnP_2 measured, respectively, for light polarized parallel and perpendicular to the optic axis. We also show in Fig. 2 for comparison the electroreflectance spectrum¹⁰ of InP , the binary analog of CdSnP_2 . The CdSnP_2 spectra show three peaks labeled A, B, and C at 1.17, 1.25, and 1.33 eV due to transitions to the conduction band from three closely spaced valence bands. These peaks are close in energy to the direct band gap of InP which is spin-orbit split into two components, E_0 at 1.34 eV and $E_0 + \Delta_0$ at 1.45 eV. We therefore conclude that the A, B, and C peaks in CdSnP_2 are derived from the $\Gamma_{15} \rightarrow \Gamma_1$ direct band gap of InP . The triple degeneracy of Γ_{15} in zinc blende is completely removed in chalcopyrite due

to the combined effects of the noncubic crystalline field and spin-orbit interaction.

The lowest-energy transition, peak A, is polarized $\vec{E} \parallel Z$, opposite to the polarization dependence observed in the tetrahedrally coordinated wurtzite semiconductors¹² CdS , CdSe , ZnS , ZnSe , and ZnO and to theoretical predictions¹³⁻¹⁶ for similar chalcopyrite semiconductors. We have previously shown⁴ that this result requires a *negative* crystal field splitting of the valence bands of CdSnP_2 . As shown in Fig. 3, in passing from zinc blende to chalcopyrite, the Γ_{15} valence band splits into a doubly degenerate Γ_5 lying *below* the nondegenerate Γ_4 . The polarization selection rules are as shown in the figure. With the inclusion of spin-orbit coupling, Γ_5 splits into Γ_7 and Γ_6 and the polarization selection rules are somewhat relaxed.¹⁷

We now show that the unusual valence-band structure of CdSnP_2 shown in Fig. 3 and the observed polarization dependences of the A, B, and C peaks in Fig. 2 can be quantitatively explained by the known properties of InP .¹⁸ Insofar as its valence-band structure is concerned, we assume that CdSnP_2 can be regarded as a strained version of its binary analog InP . Hopfield¹⁹ has given the Hamiltonian matrix describing the splitting of the triply degenerate Γ_{15} valence band of zinc blende under the simultaneous perturbations of spin-orbit coupling and a uniaxial crystalline field. Within this so-called quasicubic model, the energies of the Γ_7 levels relative to the Γ_6 level in chalcopyrite are given by¹⁹

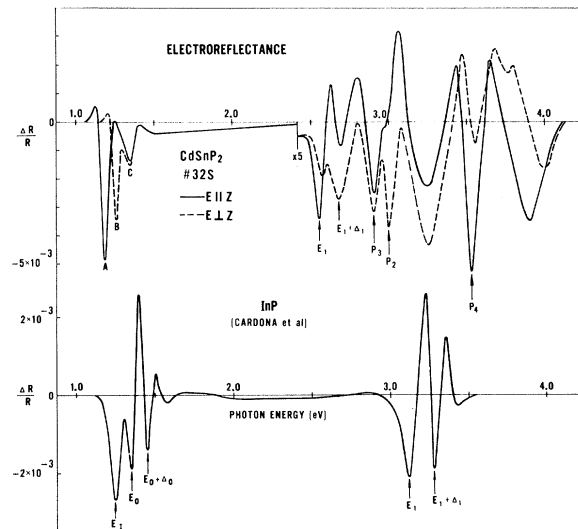


FIG. 2. Electrolyte electroreflectance spectra of CdSnP_2 for light polarized relative to the optic axis. $V_{dc} = 3.0$ V; $V_{ac} = 1.0 V_{pp}$. For comparison we also show the previously reported electroreflectance spectra of InP (Ref. 10), the binary analog of CdSnP_2 .

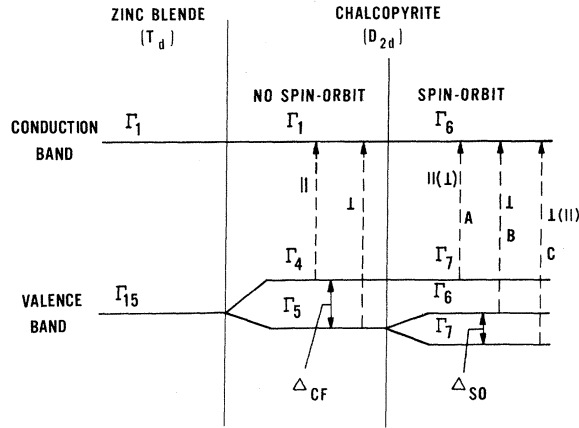


FIG. 3. Band structure and selection rules at $\vec{k} = (0, 0, 0)$ in zinc blende and chalcopyrite for light polarized relative to the optic axis. This model explains the observed polarization dependence of the A, B, and C peaks in the electroreflectance spectra of CdSnP_2 in Fig. 2. For the polarizations shown in parentheses the transitions are allowed group theoretically, but will be observed only to the extent that spin-orbit coupling mixes the unperturbed wave functions. For a finite Δ_{cf} and Δ_{so} , the valence-band splittings must be determined using Eq. (1). For example, the separation of the Γ_7 and Γ_6 levels will be equal to Δ_{so} only in the limit that $\Delta_{\text{so}} \gg \Delta_{\text{cf}}$ and will be equal to $\frac{2}{3} \Delta_{\text{so}}$ in the limit that $\Delta_{\text{so}} \ll \Delta_{\text{cf}}$.

$$E_{1,2} = +\frac{1}{2} (\Delta_{\text{so}} + \Delta_{\text{cf}}) \pm \frac{1}{2} [(\Delta_{\text{so}} + \Delta_{\text{cf}})^2 - \frac{8}{3} \Delta_{\text{so}} \Delta_{\text{cf}}]^{1/2}, \quad (1)$$

where Δ_{so} is the spin-orbit splitting parameter and Δ_{cf} is the crystal field splitting parameter (see Fig. 3). Notice that Eq. (1) is symmetrical in Δ_{so} and Δ_{cf} , and in the limit $\Delta_{\text{so}} \ll \Delta_{\text{cf}}$, $E_1 = \Delta_{\text{cf}} - \frac{1}{3} \Delta_{\text{so}}$, $E_2 = \frac{2}{3} \Delta_{\text{so}}$. For CdSnP_2 , we have from Fig. 2 that $E_1 = -0.08$ eV and $E_2 = 0.08$ eV. Using Eq. (1) we find that $\Delta_{\text{so}} = 0.10$ eV and $\Delta_{\text{cf}} = -0.10$ eV. This spin-orbit splitting is in good agreement with the spin-orbit splitting of the valence bands of InP^{10} which is 0.11 eV. We shall now estimate the crys-

TABLE I. Comparison of experimental results and theoretical predictions of the quasicubic model for the valence bands of CdSnP_2 .

	Δ_{so} (eV)	Δ_{cf} (eV)	A	I_{\parallel}/I_{\perp} B	C
Expt.	0.10	-0.10	≥ 20	$\sim 0.2^a$	$\sim 0.1^a$
Theor.	0.11	-0.12	20	0	0.3

^aExperimental intensity ratios for the B and C peaks are more reliably determined from photorelectance spectra (Ref. 4) because of the narrower line shape than from the electroreflectance spectra in Fig. 2. Nonetheless, the overlapping of oscillatory line shapes renders these values subject to error.

tal field splitting Δ_{cf} to be expected in CdSnP_2 ,

Although the atomic positions in chalcopyrite are almost identical to those in zinc blende, there are three contributions to the noncubic crystal potential: (a) The ordering of Cd and Sn relative to one another is such that the unit cell is doubled along the Z axis; this contribution will be proportional to the differences in the pseudopotentials of the two cations; (b) the anions are not located at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ (etc.) positions, but are slightly distorted; and (c) the chalcopyrite lattice of CdSnP_2 is slightly compressed along the Z axis. Theoretical estimates¹³⁻¹⁶ based on perturbation theory suggest that (a) and (b) produce a small positive crystal field splitting of the valence bands (Γ_5 above Γ_4), whereas (c) produces a negative splitting (Γ_4 above Γ_5).

It has been well established experimentally^{20,21} that uniaxial compression of a cubic material splits the valence bands and results in polarization selection rules and an ordering of the energy levels in agreement with the Γ_4 and Γ_5 levels in Fig. 3. Using the known deformation potential describing this splitting in InP^{22} and the lattice constants²³ of CdSnP_2 , we predict a crystal field splitting Δ_{cf} of -0.12 eV for CdSnP_2 . This value is close to the experimental value of -0.10 eV given earlier (Table I). It is to be expected that our model based on compression alone should slightly overestimate the negative crystal field splitting since calculations¹³⁻¹⁶ for similar chalcopyrite crystals have shown that the first two noncubic potentials listed above produce a small positive Δ_{cf} , which would tend to improve the already good agreement between theory and experiment in Table I.

It is at first surprising that the A peak in Fig. 2 is polarized $\vec{E} \parallel Z$, since we see on the right-hand side of Fig. 3 that all transitions are either polarized $\vec{E} \perp Z$ or are allowed for both polarizations. This apparent anomaly is readily explained by the quasicubic model, and is, in fact, the principal success of the theory.¹⁸ For this model, the ratio of the strengths of transitions from a given Γ_7 valence band to the Γ_6 conduction band for light polarized, respectively, parallel or perpendicular to the optic axis is given by¹⁹

$$I_{\parallel}/I_{\perp} = (2 - 3E/\Delta_{\text{so}})^2, \quad (2)$$

where E is given by Eq. (1). For the A peak, $E = -0.08$ eV, $\Delta_{\text{so}} = 0.10$ eV, and $I_{\parallel}/I_{\perp} = 20$, in good agreement with experiment (Table I).

B. Higher-Energy Gaps

The electroreflectance spectra of CdSnP_2 in the 2.5-4.0-eV region (Fig. 2) show many new transitions not observed in the electroreflectance spectrum of InP . Motivated by this abundance of structure, we now discuss a class of transitions

which we call pseudodirect transitions. They are derived from indirect transitions in zinc blende, and are allowed in chalcopyrite by virtue of the reduction of the size of the Brillouin zone^{2,3} (Fig. 4) which results from a doubling of the unit cell in the Z direction in the direct lattice of CdSnP_2 .

The lowest-order approximation to the band structure of CdSnP_2 can be obtained merely by imbedding the band structure of InP into the chalcopyrite Brillouin zone.^{2,3} The results of this procedure are shown in Fig. 5, where the dashed lines indicate the energy bands of InP ,²⁴ and the solid lines are the energy bands of CdSnP_2 in this approximation. The points X , W , as well as Γ in zinc blende all map into Γ in chalcopyrite and the point L maps into N . A detailed discussion of this mapping has been given by Chaldyshev and Pokrovskii,² and Karavaev, Poplavnoi, and Chaldyshev.³ The striking feature of Fig. 5 is the occurrence of several direct transitions in chalcopyrite corresponding to indirect transitions in zinc blende. Since the strength of these transitions will depend upon the degree of difference of the pseudopotentials of the two kinds of cations, we refer to these new transitions as "pseudodirect."

In Table II we summarize the energies and polarizations of peaks in the electroreflectance spectra of CdSnP_2 together with our assignments for this structure. The A , B , and C peaks are derived from the spin-orbit split $\Gamma_{15} \rightarrow \Gamma_1$ transition in InP and have been discussed earlier. The next two peaks which we observe at 2.56 and 2.69 eV are assigned to the same transitions that produce the E_1 and $E_1 + \Delta_1$ peaks in InP (Fig. 2). The basis for this identification is that the Δ_1 splitting in

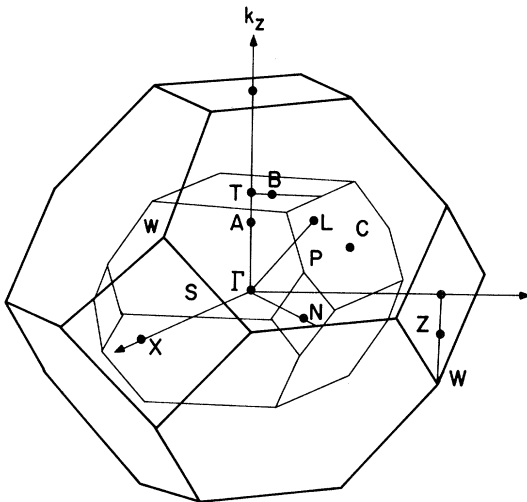


FIG. 4. Comparison of the Brillouin zones of zinc blende and chalcopyrite (after Ref. 2).

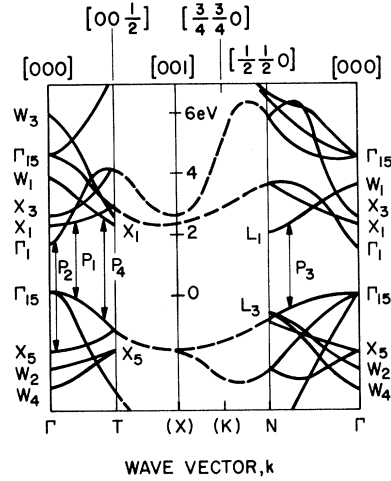


FIG. 5. Energy-band structure of CdSnP_2 (solid lines) obtained by imbedding the band structure of InP (dashed lines) from Ref. 24 into the chalcopyrite Brillouin zone. Along the lines L to W and X to W in InP we have estimated the energy bands from calculations for other crystals. P_1 - P_4 are some of the pseudodirect transitions in chalcopyrite derived from indirect transitions in zinc blende.

CdSnP_2 , 0.13 eV, is almost identical to the Δ_1 splitting in InP ,²⁵ 0.12 eV. The splitting of these peaks in CdSnP_2 should be larger than in InP , since uniaxial strain of a zinc-blende crystal²¹ increases Δ_1 to

$$\Delta_1^{\text{ch}} = [(\Delta_1)^2 + (\frac{1}{3}\Delta_{\text{cr}})^2]^{1/2}. \quad (3)$$

Using the value for Δ_{cr} from Table I we find that Δ_1^{ch} in CdSnP_2 should be 0.13 eV, as is observed. Although the L point in zinc blende maps to N in chalcopyrite,² most of the Λ direction is preserved. Consequently, if the E_1 transitions occur close enough to $\vec{k} = (0, 0, 0)$ in zinc blende, they should also appear in chalcopyrite. No estimates are available for InP , but for Ge and GaAs , it is believed²¹ that these transitions are centered $\sim 40\%$ of the distance to L from Γ and should therefore be preserved in chalcopyrite. Further evidence

TABLE II. CdSnP_2 electroreflectance structure.

Label	Energy (eV)	Polarization	Identification	Zinc-blende analog
A	1.17	\parallel	$\Gamma_7 \rightarrow \Gamma_6$	E_0
B	1.25	\perp	$\Gamma_6 \rightarrow \Gamma_6$	
C	1.33	\perp, \parallel	$\Gamma_7 \rightarrow \Gamma_6$	
E_1	2.56	\parallel, \perp	$\Lambda_3 \rightarrow \Lambda_1$	E_1
$E_1 + \Delta_1$	2.69	\perp, \parallel	$\Lambda_3 \rightarrow \Lambda_1$	$E_1 + \Delta_1$
P_3	2.90	\perp, \parallel	$N_1 \rightarrow L_1$	
P_2	3.00	\perp	$X_5 \rightarrow \Gamma_1$	
	3.26	\perp, \parallel		
P_4	3.53	\parallel, \perp	$\Delta_{3,4} \rightarrow X_1$	

supporting our identifications of the E_1 and $E_1 + \Delta_1$ transitions in CdSnP_2 is that the polarization dependence of these peaks agrees with the observations in stressed zinc-blende crystals²¹ which show that the E_1 peak is polarized predominantly $\vec{E} \parallel Z$, whereas the $E_1 + \Delta_1$ peak is polarized predominantly $\vec{E} \perp Z$, where Z is the stress direction.

The assignment of the remaining structure in Fig. 2 is more difficult simply due to the abundance of structure. Nonetheless, the strong polarization dependence of some of this structure assists us in the identification. The pseudodirect transition P_2 in Fig. 5 is expected to be strongly polarized $\vec{E} \perp Z$. Estimating the energy of X_5 in CdSnP_2 from its known value in InP , P_2 should occur near ~ 3.15 eV, although interactions between X_5 and W_4 at Γ in the valence band of CdSnP_2 will probably raise X_5 causing P_2 to lie somewhat lower than ~ 3.15 eV. We conclude that the peak at 3.0 eV in Fig. 2 is the pseudodirect transition P_2 due to $X_5 \rightarrow \Gamma_1$ transitions.

As a result of L mapping to N , the pseudodirect transition P_3 in Fig. 5 due to $N_1 \rightarrow L_1$ transitions should lie near ~ 3.0 eV and be observed for both polarizations. We therefore attribute the peak at 2.9 eV in Fig. 2 to $N_1 \rightarrow L_1$ transitions and therefore label it P_3 . The pseudodirect transition P_4 in Fig. 5 due to $(\Delta_3 + \Delta_4) \rightarrow X_1$ transitions should lie near ~ 3.5 eV and be observed principally for $\vec{E} \parallel Z$. We therefore assign the electroreflectance peak at 3.53 eV to the pseudodirect transition P_4 . A definitive assignment of the remaining structure must await a more complete energy-band calculation for chalcopyrite crystals.

CONCLUSIONS

In summary, the electroreflectance spectra of CdSnP_2 consist of two very different types of structure. The structure near the lowest direct band gap of CdSnP_2 is derived from the $\Gamma_{15} \rightarrow \Gamma_1$ direct

gap of InP , but is split by the combined effects of the noncubic crystalline field and spin-orbit interaction. We have shown that the signs and magnitudes of these splittings can be predicted from the known properties of InP , the binary analog of CdSnP_2 , taking into account only spin-orbit coupling and the uniaxial compression of the chalcopyrite lattice. We have further shown that the unusual polarization dependences of these band edge transitions as observed in the electroreflectance spectra can be quantitatively explained by the quasicubic model. We have also observed structure in the electroreflectance spectra due to states derived from the E_1 and $E_1 + \Delta_1$ direct band gaps. The splitting of these peaks and the polarization dependences are consistent with electroreflectance studies of stressed cubic semiconductors.

In addition to this electroreflectance structure due to direct band gaps in CdSnP_2 derived from direct band gaps in InP , we observe much additional structure due to pseudodirect transitions - direct transitions in chalcopyrite derived from indirect transitions in InP . These pseudodirect gaps result when many points in the zinc-blende Brillouin zone are mapped into any one point in the chalcopyrite Brillouin zone due to the doubling of the unit cell along the optic axis in chalcopyrite. We have identified the origins of much of this additional structure from the observed polarization dependences and from a knowledge of the energies of the equivalent (forbidden) transitions in InP . Some remaining structure has not been identified, and we anxiously await an energy-band calculation for chalcopyrite crystals.

ACKNOWLEDGMENTS

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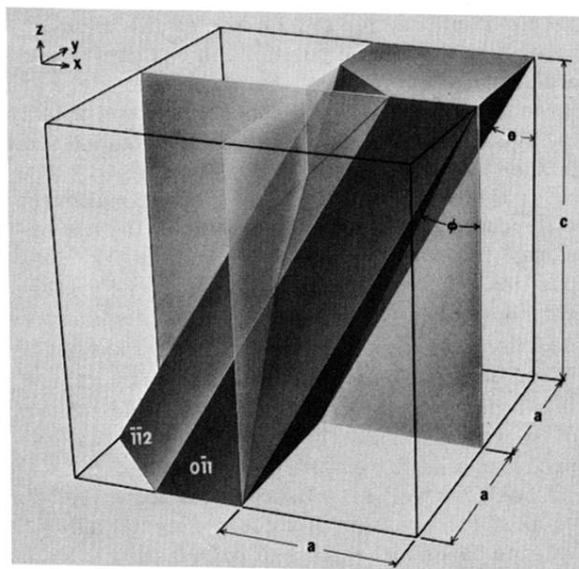


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