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NEGATIVE CRYSTAL-FIELD SPLITTING OF THE VALENCE BANDS IN $CdSnP_2$

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The polarization selection rules governing the band-edge electroreflectance and photoreflectance spectra of $CdSnP_2$ are opposite to those observed in wurtzite II-VI semiconductors and to theoretical predictions for similar chalcopyrite semiconductors. This result is explained by a new valence-band model with the essential feature that the sign of the crystal-field splitting is opposite to that observed in wurtzite II-VI semiconductors.

The II-IV-V_2 compounds are ternary semiconductors which normally crystallize in the chalcopyrite structure. They have physical properties similar to the familiar diamond, zinc blende, and wurtzite semiconductors by virtue of their tetrahedral coordination.[1,2] It is reasonable, therefore, to expect that the optical and electronic properties of the chalcopyrite crystals can be predicted by extrapolating from the well-understood binary semiconductors. Although this assumption has been invoked often in the interpretation of various experiments,[1-4] it has never been placed on a sound experimental basis.

It was the original purpose of this work to establish the viability of this assumption by measuring the electroreflectance and photoreflectance spectra of $CdSnP_2$, and interpreting these spectra in terms of a slightly perturbed zinc blende band structure. Instead, we have found that the polarization dependences of the electronic transitions from the valence-band maxima to the lowest conduction-band minimum are opposite to those which have been predicted theoretically[3,4] for similar chalcopyrite crystals. The polarization dependences which we observe in $CdSnP_2$ are opposite to those observed in wurtzite II-VI semiconductors. To explain our results we propose for $CdSnP_2$ an ordering of the valence bands in which the chalcopyrite perturbation produces a negative crystal-field splitting of the valence-band maxima. The triply degenerate Γ_{15} in zinc blende is split in $CdSnP_2$ such that the nondegenerate level Γ_4 lies above the doubly degenerate Γ_5, just opposite to the ordering observed in II-VI wurtzite semiconductors.[5] The doubly degenerate state Γ_5 is then split by spin-orbit coupling. We conclude that the chalcopyrite crystal potential has significant effects on the electronic structure.

In Fig. 1 we present the electrolyte electroreflectance[6] spectra near the fundamental edge of solution-grown[7-9] $CdSnP_2$ measured, respective-

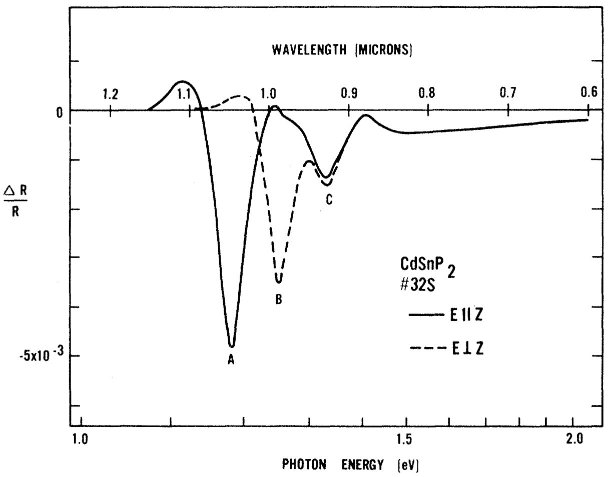

FIG. 1. Room-temperature electroreflectance spectra for light polarized relative to the optic axis. $V_{dc} = 3.0$ V; $V_{ac} = 1.0$ V peak to peak.

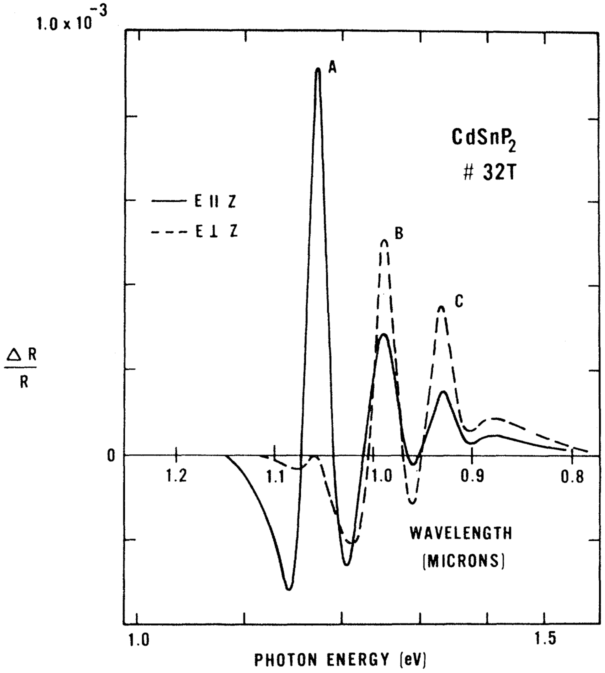

FIG. 2. Room-temperature photoreflectance spectra for light polarized relative to the optic axis.

ly, for light polarized parallel and perpendicular to the optic axis. In Fig. 2, we present the photoreflectance spectra measured using a He-Ne laser to modulate the reflectance. As is usually the case[10] the photoreflectance spectra are sharper, though weaker, than the electroreflectance spectra, and of opposite sign. For both experiments the surfaces were prepared by Syton[11] polishing a natural face to remove surface damage. The natural faces were {112} planes as was established by Laue x-ray photographs which showed the expected pseudothreefold symmetry. In this plane, it is possible to polarize entirely $E \perp Z$, but not $E \parallel Z$. Consequently in Figs. 1 and 2, $E \parallel Z$ is only nominal and, in fact, only $\frac{2}{3}$ of the intensity lies parallel to Z. The platelets were too thin to be prepared in any other orientation.

The spectra of Figs. 1 and 2 show three major peaks 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 reasonably close to the band gap of InP (1.34 eV),[6] the binary analog of $CdSnP_2$. However the lowest-energy transition (peak A) is polarized $E \parallel Z$, opposite to the polarization dependence observed in the wurtzite semiconductors[12] CdS, CdSe, ZnS, ZnSe, and ZnO and to theoretical predictions[3,4] for similar chalcopyrite semiconductors. The orientation of the $CdSnP_2$ crystals was readily determined by inspection of their habit of growth.[1,13] Nonetheless, the location of the optic axis was confirmed by measuring the angles of x-ray diffraction with a precision of a few minutes of arc.

Although the data in Figs. 1 and 2 clearly show that peak A is polarized $E \parallel Z$, the polarization dependences of the peaks B and C are less clear. Superficially it would appear that the B peak is extinguished for $E \parallel Z$ in electroreflectance (Fig. 1) but not in photoreflectance (Fig. 2). We believe that this apparent discrepancy is due to a cancellation of the B peak and a higher-energy oscillation of the A peak in electroreflectance for $E \parallel Z$. Notice that in the photoreflectance (Fig. 2), the narrower line shapes cause this higher-energy oscillation of the A peak to fall midway between the A and B peaks, and therefore the B peak is observed for $E \parallel Z$. A similar explanation probably explains the discrepancy between Figs. 1 and 2 regarding the C peak. The polarization dependencies of the B and C peaks are further complicated by the experimental restriction that $E \parallel Z$ is only nominal.

To explain the polarization dependences observed in Figs. 1 and 2, we propose the valence-band model shown in Fig. 3. In passing from zinc blende to chalcopyrite, the reduction in symmetry causes the Γ_{15} valence band to split into a doubly degenerate Γ_5, lying below the nondegenerate Γ_4. The polarization selection rules for optical transitions are as shown in the figure. The occurrence of this negative crystal-field splitting probably results from an interaction be-

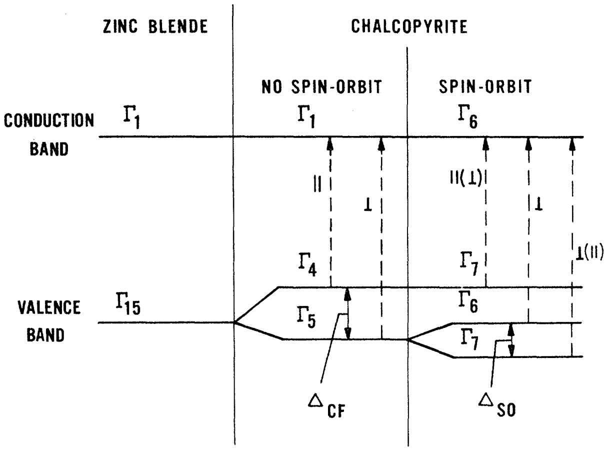

FIG. 3. Band structure and selection rules at $k = (000)$ in zinc blende and chalcopyrite for light polarized relative to the optic axis. This model is proposed to explain the observed polarization dependence of the electroreflectance and photoreflectance data. For the polarizations shown in parentheses the transitions are allowed group theoretically, but will be observed only to the extent that spin-orbit coupling mixes the unperturbed wave functions.

tween the Γ_5 and Γ_4 bands and new states which occur at Γ in the chalcopyrite structure due to the smaller Brillouin zone.[14] With the inclusion of spin-orbit coupling, Γ_5 splits into Γ_7 and Γ_6, and the polarization selection rules are somewhat relaxed. However, the transitions for the polarizations shown in parentheses are allowed only to the extent that the perturbation mixes the unperturbed wave functions. Hence in the limit of weak spin-orbit coupling, the Γ_5 degeneracy is split, but the polarization dependences are not appreciably altered. Transitions from the uppermost valence band will be polarized predominantly $E \parallel Z$, as we observe experimentally, even though transitions are also allowed for $E \perp Z$. Of course, this argument regarding the parentage of the states prior to the inclusion of spin-orbit coupling is exact only in the limit that the spin-orbit splitting is much less than the crystal-field splitting. Nonetheless, detailed calculations[15] using Hopfield's quasicubic model[16] show that transitions from the uppermost valence band are weak for $E \perp Z$ even though the crystal-field and spin-orbit splittings are comparable in $CdSnP_2$. We suggest that transitions from the Γ_7 states in $CdSnP_2$ retain the polarization of their parentage to a larger extent than in wurtzite II-VI semiconductors as the spin-orbit interaction is turned on, because the negative crystal-field splitting in $CdSnP_2$ prevents the Γ_7 levels from approaching or crossing each other.

In constructing the valence-band model shown in Fig. 3, we have tacitly assumed that the direct transitions observed in Figs. 1 and 2 occur at $k = (000)$ and represent the lowest energy direct band gap. This assumption is consistent with with the band structure of InP, the binary analog of $CdSnP_2$, which has a direct band gap at $k = (000)$ at 1.34 eV. Further supporting evidence is obtained from unpublished transmission data (unpolarized) which show a very abrupt absorption edge between 1.10 and 1.06 μm. Lastly, the model in Fig. 3 leads to several predictions which can be checked independently: (1) The low-temperature luminescence should be polarized $E \parallel Z$; (2) the absorption edge should lie at shorter wavelengths for $E \perp Z$ than for $E \parallel Z$; and (3) the conduction-band effective mass should display a measurable anisotropy, since the splitting of the A and B peaks is ~7% of the band gap. Preliminary photoluminescence experiments, to be reported in detail elsewhere, show that the band edge "exciton" emission is strongly polarized $E \parallel Z$ at 1.7°K.

In conclusion, the polarization dependences of electroreflectance and photoreflectance spectra of $CdSnP_2$ are opposite to those observed in wurtzite II-VI semiconductors and to theoretical predictions for similar chalcopyrite semiconductors. To explain these observations we propose a valence-band model with the essential feature that the sign of the crystal-field splitting is opposite to that observed in wurtzite II-VI semiconductors. The occurrence of this negative crystal-field splitting probably results from an interaction between the valence-band maxima and new states which occur at Γ in the chalcopyrite structure due to the smaller Brillouin zone.

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EXCITONIC EFFECTS ON THE E_1 AND $E_1+\Delta_1$ TRANSITIONS IN InAs

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The metamorphism of critical points due to Coulomb interaction, predicted by the theory of Toyozawa, has been determined experimentally through a careful examination of the temperature dependence of the line shapes of the E_1 and $E_1+\Delta_1$ structure of InAs. Besides, it has been possible to determine the shift coefficient $\partial\omega_g/\partial T=-5.5\times10^{-4}$ eV/°K and the broadening parameter $\partial\Gamma/\partial T=+0.9\times10^{-4}$ eV/°K of the E_1 structure.

The E_1 and $E_1+\Delta_1$ spin-orbit–split doublet, that appears in most zinc-blende semiconductors in the 2-3 eV region, has been quite conclusively identified as due to optical transitions associated with M_1 critical points (c.p.) located in the $\{111\}$ directions of the Brillouin zone.[1,2] On the other hand, several authors[3-5] have observed that electroreflectance, thermoreflectance, and wavelength-modulated reflectance spectra in the E_1 region cannot be simply explained in the framework of the one-electron theory with lifetime broadening correction, and have suggested that Coulomb interaction should be responsible for the observed discrepancies.

In a series of papers, Toyozawa et al.[6] have tried to take into account the effects of the excitonic interaction on the optical spectra of solids by replacing the attractive Coulomb potential with a finite-range potential. On the basis of this model, they have predicted the mixing of M_j and M_{j+1} line shapes as a consequence of the attractive interaction between holes and electrons.

Through a careful examination of the thermoreflectance line shape at different temperatures of the E_1 and $E_1+\Delta_1$ structure of InAs, we have been able to determine the energies ω_g and the broadening parameters Γ of both c.p., as well as their derivatives as a function of temperature. Besides, the analysis of these data yields full evidence for the metamorphism of the Van Hove singularities (M_1, M_2 mixture) according to the predictions of Toyozawa.

The thermoreflectance spectra of etched crystals of InAs (n type, with $N_D-N_A\simeq10^{16}/\text{cm}^3$) were taken with the usual technique of phase-sensitive detection, at ten temperatures ranging from 74 to 397°K, and for photon energies between 1.8 and 4.0 eV. All the spectra were measured at near normal incidence using light from a 500-mm Bausch & Lomb monochromator with a bandwidth of 12 Å. The thermal modulation was obtained by sending current square waves at 7 Hz through the sample and never exceeded 1°K in amplitude, as determined by the modulated infrared emission of the sample. All spectra of $\Delta R/R$ were processed by Kramers-Kronig transformations in order to obtain $\Delta\epsilon_r$ and $\Delta\epsilon_i$ separately.[4]

The values of n and k used in our computation were taken from the room-temperature data of