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p-d Hybridization of the Valence Bands of I-III-VI$_2$ Compounds

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The valence bands of I-III-VI$_2$ compounds result from a hybridization of the noble-metal d levels with p levels on the other atoms. This results in large downshifts in the energy gaps relative to the binary analogs, and the absence of spin-orbit splitting in the uppermost valance bands of several sulfides. We estimate that the uppermost valence bands are ~40% d-like in the Cu compounds and ~20% d-like in Ag compounds.

There has been a great deal of interest lately in the I-III-VI$_2$ chalcopyrite compounds as potential candidates for optical parametric oscillators[1] and visible-light emitters.[2] However, there has been little experimental work[3] and no theoretical work concerning the nature of the electronic energy-band structure of these crystals. This paper represents the first attempt to elucidate the electronic energy-band structure of the I-III-VI$_2$ Ag and Cu sulfides and selenides.

As the ternary analogs of II-VI compounds, it might be expected that I-III-VI$_2$ compounds such as CuGaS$_2$ would have energy-band structures similar to their binary analogs (e.g., ZnS). This expectation is based to some extent on a similar analogy which is known to exist between II-IV-V$_2$ and III-V compounds.[4,5] Contrary to this expectation we find that the uppermost valence bands in these compounds are essentially different from those of the II-VI compounds. In other pseudocubic systems (e.g., II-VI wurtzite, II-IV-V$_2$ chalcopyrite), the triple degeneracy of the p-like Γ_{15} level in cubic zinc-blende compounds is completely lifted under the simultaneous effects of the noncubic crystalline field and spin-orbit interaction. However, in each of the five sulfides which we have investigated, only two valence bands have been observed. In addition we find that the energy gap in each of the eight compounds investigated is downshifted relative to the energy gap in its binary analog by amounts ranging from ~0.5 to ~1.6 eV. For comparison, the energy gaps of several II-IV-V$_2$ compounds[4] lie within ±0.3 eV of the energy gaps in their respective binary analogs.

In Fig. 1, we show the electroreflectance spectra of CuInS$_2$, CuGaS$_2$, and CuAlS$_2$ near their lowest direct energy gaps. A striking feature of the data is that the energy gaps are considerably downshifted in energy relative to the binary analogs. For example the energy gap in CuGaS$_2$ (2.40 eV) is ~1.4 eV below the energy gap in ZnS. The energy gaps and downshifts for several I-III-VI$_2$ compounds which we have investigated are summarized in Table I. The second striking feature of the data in Fig. 1 is that there is evidence for only two closely spaced energy gaps. Low-temperature studies of exciton reflectivity and photoreflectance have failed to locate a third valence band in any of these sulfides. In contrast to the results for the sulfides, three transitions are observed in the electroreflectance spectra of CuGaSe$_2$ (A, B, and C in Fig. 2) and in all of the selenides investigated (Table I). These results lead us to conclude that the uppermost valence bands in all of these compounds are derived from the p-like Γ_{15} level in cubic crystals but with a significant admixture of noble-metal d states.

A quasicubic model[4,5] which accounts for the uniaxial distortion of the chalcopyrite structure has quantitatively explained the structure of the uppermost valence bands in II-IV-V$_2$ compounds. An attempt to use this quasicubic model to interpret the present results for I-III-VI$_2$ compounds has met with mixed success. In Table I, we compare the theoretical values for the crystal field (Δ_{cf}) and spin-orbit (Δ_{so}) parameters predicted by the quasicubic model with experimental values derived from our electroreflectance data. The experimental values for Δ_{cf} in the Cu compounds (except CuInS$_2$)

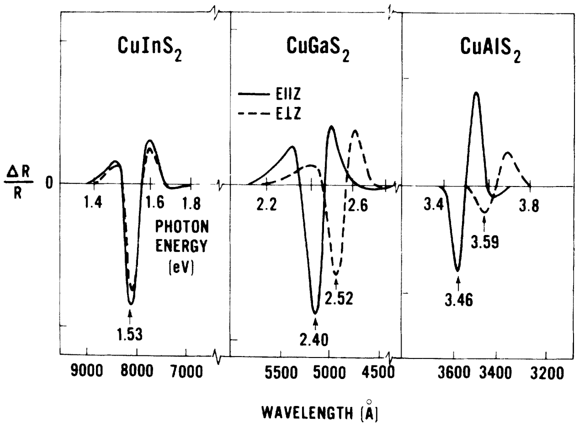

FIG. 1. Room-temperature electrolyte electroreflectance spectra for CuInS$_2$, CuGaS$_2$, and CuAlS$_2$. One unit on the ordinate corresponds to $\Delta R/R$ values of 2×10^{-2}, 10^{-2}, and 5×10^{-4}, respectively.

TABLE I. I-III-VI_2 valence-band parameters (in eV).

	Energy gap	Down shift[a]	$-\Delta_{cf}$ Quasicubic model[b]	$-\Delta_{cf}$ Expt.	Δ_{so} Quasicubic model	Δ_{so} Expt.[c]	Estimated % d-like
$CuInS_2$	1.53	1.58	−0.005		0.07	−0.02	45
$CuGaS_2$	2.40	1.37	0.05	0.12	0.07		
$CuAlS_2$	3.46		0.04	0.13	0.07		
$CuGaSe_2$	1.68	1.00	0.05	0.09	0.43	0.23	36
$AgInS_2$	1.87	0.68	0.09	0.15	0.07		
$AgInSe_2$	1.24	0.48	0.11	0.13	0.42	0.30	17
$AgGaS_2$	2.73[d]	0.52	0.23	0.28	0.07		
$AgGaSe_2$	1.82[d]	0.51	0.23	0.25	0.42	0.31	16

[a] Relative to energy gap in II-VI binary analog.

[b] Using $b = -0.71$ for sulphides and $b = -0.88$ for selenides [P. Lawaetz, Phys. Rev. B 5, 4039 (1972)].

[c] No entry implies $|\Delta_{30}| < 0.02$ eV due to experimental linewidths.

[d] 77 °K values; all others 300 °K.

are considerably larger than expected, whereas the agreement for the Ag compounds is satisfactory. The experimental values for Δ_{so} are considerably smaller than expected and in fact were not observed in the sulfides (except $CuInS_2$).

We attribute this breakdown of the quasicubic model to a hybridization of Cu and Ag d levels with the p levels on the other atoms. The hybridization reduces the experimental values for Δ_{so} below the values observed in the binary analogs since the negative Δ_{so} characteristic of d levels[6–8] tends to cancel the positive Δ_{so} of p levels. We have attempted to obtain a estimate of the hybridization in the I-III-VI_2 compounds using[8]

$$\Delta_{so}^{expt} = \alpha\Delta_p + (1-\alpha)\Delta_d,$$

where α is the fractional admixture of p levels and $(1-\alpha)$ is the fractional admixture of d levels in the uppermost valence bands. For Δ_p we have used quasicubic values for Δ_{so} (Table I), and for Δ_d we have used −0.13 eV for Cu compounds and −0.28 eV for Ag compounds.[9] The hybridizations determined in this way are included in Table I. The uppermost valence levels are ~40% d-like in $CuGaSe_2$ and $CuInS_2$, and ~20% d-like in $AgGaSe_2$ and $AgInSe_2$. This trend is consistent with previous studies of the Cu and Ag halides in which p-d hybridization is greater in Cu than in Ag compounds.[6–8] If the hybridizations determined above apply to the other Cu and Ag compounds, the expected spin-orbit splittings would be reduced to values less than the linewidths of the experimental spectra in all the sulfides except $CuInS_2$. Hence, the absence of spin-orbit splitting in all of the sulfides but $CuInS_2$ may result from a coincidental

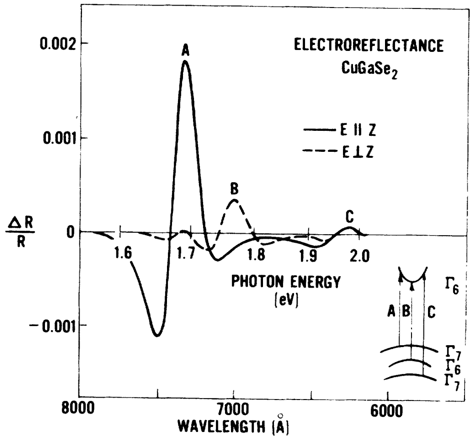

FIG. 2. Room-temperature electrolyte electroreflectance spectra for $CuGaSe_2$.

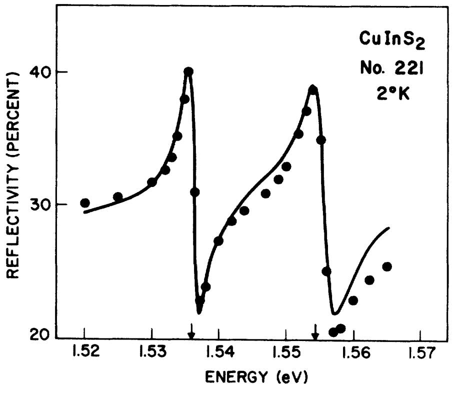

FIG. 3. Simple damped oscillator fit (dots) to the exciton reflectivity (solid line) of $CuInS_2$. Using an expression for the dielectric constant given by J. J. Hopfield and D. G. Thomas [Phys. Rev. 132, 563 (1963)] we obtain the parameters $E_1 = 1.536$ eV, $E_2 = 1.5545$ eV, $\epsilon_0 = 11$, $4\pi\alpha_1 = 0.01$, $4\pi\alpha_2 = 0.02$, $\Gamma_1 = 1.3$ meV, $\Gamma_2 = 3.0$ meV. The parameters Γ and α are, respectively, the damping constant and oscillator strength appropriate to the oscillator at energy E.

cancellation of the p-like and d-like spin-orbit splittings. It is also possible that some unknown mechanism is clamping the spin-orbit splitting to nearly zero in the sulfides, in which case the hybridizations estimated above for selenides would not apply to the sulfides. In either case, the general trends manifest in Table I suggest that the uppermost valence bands in all of these crystals are basically derived from the Γ_{15} valence band of zinc-blende crystals hybridized with noble metal d levels.

The absence of any polarization dependence to the low-temperature reflectivity of $CuInS_2$ (Fig. 3) indicates that the splitting is spin-orbit in nature. For virtually all crystals in which the valence bands are p-like, spin-orbit interaction splits the valence bands such that the lowest-energy transition is doubly degenerate followed by a nondegenerate transition at slightly higher energy. For $CuInS_2$ just the opposite is observed. The simple damped oscillator fit to the data shown in Fig. 3 yields an oscillator strength for the higher-energy transition which is twice as strong as that for the lower-energy transition. This result indicates a negative spin-orbit splitting such as previously observed in only two compounds, CuCl[6] and ZnO.[10]

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[9] M. Cardona, in *Solid State Physics, Supplement* 11, edited by F. Seitz. and D. Turnbull (Academic, New York, 1969), p. 67. We have increased the atomic values by a factor of 1.4 to allow for renormalization of the wave function in the solid.

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ERRATUM

Electron Energy Levels in $LaSn_3$. II. Relativistic Corrections Using Perturbation Theory, D. M. Gray and L. V. Meisel [Phys. Rev. B 5, 1308 (1972)]. (1) The correct title is "Electron Energy Levels in $LaSn_3$. II. Relativistic Corrections Using Perturbation Theory." (2) In Eqs. (B13), (B28), (B41), (B47), (B48), (B49), and (B65),

$$“X_{lb}\frac{\vec{\rho}}{\rho},”$$

etc., should read “$X_{lb}(\vec{\rho}/\rho)$,” etc.