EXPERIMENTAL STUDIES OF ENERGY
BAND STRUCTURE OF CHALCOPYRITE CRYSTALS

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Résumé. — Dans cet article, nous passons en revue les études expérimentales de la structure de bandes de cristaux des types II-IV-V₂ et I-III-VI₁. Les sujets présentant un intérêt pour des études ultérieures sont discutés.

Abstract. — In this paper we review experimental studies of the energy band structure of II-IV-V₂ and I-III-VI₁ crystals. Topics of interest for further study are discussed.

1. Introduction. — Ternary chalcopyrite II-IV-V₂ and I-III-VI₁ semiconductors are the closest electronic and structural analogs of the zincblende III-V and II-VI semiconductors respectively. Experimental studies of the energy band structure of these ternary compounds prior to 1972 have been reviewed elsewhere [1-5]. In this work we review experimental studies since 1972 and discuss topics of interest for further study. In Section 2 a new interpretation of the electroreflectance spectrum of the pseudodirect crystal ZnSiP₂ is presented, and experiments to substantiate the interpretation are proposed. In Section 3 we describe recent X-ray photoemission studies of the valence bands of I-III-VI₁ compounds which have confirmed in detail the importance of noble-metal d-levels in the valence bands. The need for energy band calculations including these d-levels is emphasized.

2. II-IV-V₂ compounds. — There are two qualitatively different types of energy band structures of II-IV-V₂ compounds. They correspond to ternary compounds analogous to direct-band-gap and indirect-band-gap III-V compounds respectively. The band structure of ZnGeAs₂, the analog of the direct-band-gap compound GaAs, is shown in figure 1. The band structure of ZnGeP₂, the analog of the indirect-band-gap compound GaP, is shown in figure 2. The theoretical energy levels (indicated by circles in figures 1 and 2) were calculated by the pseudopotential method without spin-orbit coupling at the high symmetry points Γ, T, N and P of the chalcopyrite Brillouin zone [6]. The lines between calculated energy levels were drawn taking into account the compatibility relations and following the energy band structures of ZnGeAs₂ and ZnGeP₂ obtained by imbedding the energy bands of their closest zincblende analogs (GaAs and GaP) into the chalcopyrite Brillouin zone.

The uppermost valence bands are similar in both types of band structure and are derived from the Γ₁₅ valence band maximum in III-V zincblende crystals.

Due to the reduced symmetry of the chalcopyrite structure, the triple degeneracy of Γ₁₅ is lifted and the nondegenerate Γ₄ lies above the doubly degenerate Γ₅. This crystal field splitting Aᵥ between Γ₄ and Γ₅ has been measured for several compounds and is plotted in figure 3 as a function of the uniaxial lattice compression 2 - c/a, where c and a are the lattice constants. It is apparent that the crystal field splitting of the uppermost valence bands is a linear function of 2 - c/a. Theoretical calculations [6] predict such a trend, but quantitative agreement is not obtained. Unfortunately a recent calculation [7] of the band structure of ZnGeP₂ obtains the wrong sign of the crystal field splitting. The lowest conduction band Γ₁ in ZnGeAs₂ (Fig. 1) is derived from the Γ₁ conduction band in GaAs. The
higher energy $\Gamma_3$ and $\Gamma_2$ conduction bands are derived from the $X_1$ and $X_3$ conduction bands in GaAs and are mapped into the $\Gamma$ point due to the smaller Brillouin zone of the chalcopyrite structure. The opposite ordering of the conduction bands is observed in ZnGeP$_2$ (Fig. 2). Optical transitions between levels at the same point in the chalcopyrite Brillouin zone but derived from indirect transitions in the II-VI analog have been termed pseudodirect [8] since their strengths will depend upon the differences in the cation pseudopotentials. Typically, pseudodirect transitions are about an order of magnitude weaker than direct transitions.

Direct optical transitions from $\Gamma_4$ and $\Gamma_5$ to the $\Gamma_1$ conduction band are allowed only for $E \parallel z$ and $E \perp z$ respectively, where $z$ is the optic axis. Although these selection rules are relaxed somewhat when the double degeneracy of $\Gamma_5$ is lifted by spin-orbit interaction, the observed polarization properties of the three transitions labelled A, B and C are quantitatively explained by a single, quasicubic model [5].

The electroreflectance spectrum [8] of the pseudodirect crystal ZnSiP$_2$ is shown in figure 4. The lowest energy direct transitions near 3.0 eV in figure 4 cannot be due to $\Gamma_{15} \rightarrow \Gamma_4$ transitions since the observed polarization dependences are opposite to those observed in other ternary crystals. We suggest instead that the structure observed near 3.0 eV results from the $\Gamma_{15} \rightarrow \Gamma_1$ transition in zincblende crystals. The origin of the structure near 3.0 eV is not certain, but it may be derived from $\Gamma_{15} \rightarrow \Gamma_1$ transitions in zincblende crystals. The strength of the 3 eV structure renders an interpretation based upon pseudodirect transitions unlikely. Our suggested ordering for the conduction band levels (i.e. $\Gamma_{15}$ below $\Gamma_1$) conflicts with an energy band calculation [6] which predicts

$$(\Gamma_{15} \rightarrow \Gamma_4) \approx 3.2 \text{ eV} \quad \text{and} \quad (\Gamma_{13} \rightarrow \Gamma_1) \approx 4.2 \text{ eV}.$$  

A recent calculation [9] using a generalization of the dielectric theory of Phillips and Van Vechten [10] predicts a larger value for the fundamental band gap $(\Gamma_{15} \rightarrow \Gamma_1) = 3.9 \text{ eV}$. A definitive determination of
which structure in ZnSiP₂ results from \( \Gamma_{\text{4}} \rightarrow \Gamma_{\text{1}} \) transitions is possible by a study of these peaks in the electroreflectance spectra of Zn(Si,Ge_{1-x})P₂ or ZnSiP₂, since the band gaps in ZnGeP₂ and ZnSiAs₂ are well established [5]. The interpretation of the electroreflectance spectrum of ZnSiP₂ could also be established by a full-zone calculation of the optical properties as has been done for binary compounds by many workers.

3. I-III-VI₂ compounds. — In an earlier review [3] it was shown that the uppermost valence bands of a I-III-VI₂ compound are profoundly influenced by the proximity of noble metal d-levels in the valence band. The consequence of this interaction are easily described with the simple sketch shown in figure 5. The fivefold degenerate d-levels split into a threefold \( \Gamma_{\text{15}} \) and a twofold \( \Gamma_{\text{12}} \) in a tetrahedral field; p-levels transform as \( \Gamma_{\text{1}} \). Allowing for spin splits the p-like \( \Gamma_{\text{18}} \) into a doublet \( \Gamma_{\text{6}} \) above a singlet \( \Gamma_{\text{7}} \), whereas the d-like \( \Gamma_{\text{15}} \) splits into a doublet \( \Gamma_{\text{8}} \) below a singlet \( \Gamma_{\text{7}} \). These results follow simply from a diagonalization of the I.s matrices [11]. Interaction between the \( \Gamma_{\text{15}} \) levels in figure 5 will have two effects. The uppermost \( \Gamma_{\text{15}} \) will be raised to higher energy, i.e., the band gap will be reduced, and the spin-orbit splitting of the uppermost valence bands will be reduced, because the negative spin-orbit parameter (\( \Gamma_{\text{8}} \) splitting) of the d-levels partially cancels the positive spin-orbit parameter of p-levels. A quantitative estimate of the p-d hybridization can therefore be determined from the measured spin-orbit splitting of the uppermost valence bands.

In figure 6 is plotted for each I-III-VI₂ compound, the reduction of the energy gap relative to its binary analog, and the fractional d-like character of the uppermost valence bands. The noticeable correlation between these quantities is taken as proof for the validity of p-d hybridization in I-III-VI₂ compounds.

Recent X-ray photoemission studies [12, 13] (XPS) have substantiated the essential validity of this concept. Figure 7 shows the XPS valence band spectra of CuInS₂, CuGaS₂, CuAlS₂ and AgGaS₂ obtained with MgKα, (1.253.6 eV) excitation. The spectra in figure 7 show a striking contrast between the Cu-compounds and the Ag-compounds in that each Cu-compound has the major peak in the low-binding-energy region of the spectrum and the Ag-compound in the high-binding-energy region. Since d-states generally offer intense peaks in an XPS spectrum, the major peaks in figure 7 may be attributed to the states which consist mainly of noble metal d-wave-functions. These quantitative results agree with the data in figure 6 which show the uppermost valence bands in Cu-compounds to be considerably more d-like than those in Ag compounds. Moreover the energies of the d-peaks for the Cu-compounds in figure 7 agree with values deduced from optical transitions attributed to transitions originating on the d-levels themselves [14, 15]. The larger binding energy of d-levels in AgGaS₂ (Fig. 7) agrees with the absence of any observed optical transitions from d-levels in this compound.

Since the optical and X-ray experiments substantiate the importance of noble-metal d-levels in I-III-VI₂ compounds, a theoretical calculation including d-levels would be of considerable interest. The only existing calculation for I-III-VI₂ compounds [16] ignores d-levels and as a result fails to explain most of the experimental observations in these compounds [14]. A theoretical calculation [17] of nonlinear optical suscep-
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CuInS$_2$ is shown in figure 8a and consists of two structures separated by 19 meV. Since this spectrum is independent of the polarization of the incident light, the 19 meV splitting results from spin-orbit interaction. An earlier exciton-oscillator fit to the reflectivity of CuInS$_2$ required that the oscillator strength of the higher energy transition be twice that of the lower energy transition [20]. Consequently, it was concluded that the doubly degenerate valence band B, C lay below the nondegenerate band A. As shown in figure 8b, the addition of slight amounts of Ga to CuInS$_2$ shifts the spectrum to higher energies, lifts the degeneracy of the B, C transitions, and produces an observable polarization dependence in the WMR spectrum. From the splittings of the three structures in figure 8b, we derive spin-orbit and crystal field parameters of $-22$ meV and $-11$ meV respectively.

The crystal-field parameters of several alloys are plotted as a function of composition in figure 9a [21]. It is apparent that the crystal-field splitting is nearly linear in $x$ varying from zero in CuInS$_2$ to $-130$ meV in CuGaS$_2$. The vanishing of $\Delta_{ct}$ in CuInS$_2$ is of interest since the built-in lattice distortion (Fig. 9b) should lead to an observable $\Delta_{ct}$. In earlier studies of chalcopyrite crystals (see Fig. 3) for which $2 - c/a$ was large and positive, $\Delta_{ct}$ was negative and approximately proportional to $2 - c/a$. Since CuInS$_2$ has a negative $2 - c/a$, yet $\Delta_{ct} \approx 0$, the expected $\Delta_{ct}$ due to this elongation must be cancelled by a negative $\Delta_{ct} \approx -35$ meV due to the internal distortion (the deviation from perfect-tetrahedral bonding) and the restructuring of the Brillouin zone as a consequence of

Fig. 7. — X-ray photoelectron spectra of the valence bands in CuInS$_2$, CuGaS$_2$, CuAlS$_2$ and AgGaS$_2$ (after ref. [13]).

Fig. 8. — Wavelength-modulated reflectance spectra at 2K of (a) CuInS$_2$ and (b) CuGa$_{0.1}$In$_{0.9}$S$_2$ (after ref. [18] and [19]).

Fig. 9. — Compositional dependence of (a) the crystal-field parameter $\Delta_{ct}$, and (b) the built-in lattice distortion $2 - c/a$, in the system CuGa$_{1-x}$In$_x$S$_2$ (after ref. [18] and [19]).
the two different cations. This phenomenon has yet to be observed in any other ternary crystal.

4. Conclusion. — In conclusion we emphasize the need for sophisticated energy band calculations and full-zone calculations of the optical properties of chalcopyrite compounds. In Section 2 we discussed the pseudodirect compound ZnSiP₂, whose anomalous band structure could be definitively interpreted by such calculations. Higher energy transitions in figure 4 and many other crystals [1, 4, 5] await such calculations for definitive interpretation.

The importance of noble metal d-hands in I-III-VI₂ compounds is clear from electroreflectance and X-ray photoemission experiments. Band structure calculations incorporating these d-levels are needed. The assignment of certain electroreflectance structures to transitions from the d-levels themselves could readily be verified by full-zone calculations of the optical properties of I-III-IV₂ compounds.

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References


[21] Compositions were determined from the measured lattice constants using Vegard's law which has been shown to be valid in this system by Yamamoto, N. and Miyachi, T., Japan J. Appl. Phys. 11 (1972) 383.