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Partial density of valence states of amorphous and crystalline $AgInTe_2$ and $CuInS_2$

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Measurements of the energy-distribution curves of photoemitted electrons were made for amorphous and crystalline samples of $AgInTe_2$ and $CuInS_2$. The energies of the exciting photons were 21.2 eV (He I), 40.8 and 48.4 eV (He II), 16.8 eV (Ne I), 26.9 eV (Ne II), and 1486.6 eV (Al $K\alpha$). The crystalline and amorphous samples were in the form of thin sputtered films, although, to demonstrate consistency, some measurements were also performed on bulk samples with Al $K\alpha$ radiation. It is shown that the obtained photoelectron-distribution curves represent the heavy *d* admixture present in the valence bands. They can be decomposed into approximate partial *p* and *d* densities of valence states by using atomic cross sections for the corresponding partial excitation probabilities. These results are compared with information available on *p*-*d* mixing based on the spin-orbit splitting of the band-edge excitons. The binding energies of the outermost core levels of the constituent atoms and their core shifts are presented. The energy of the valence plasmons is found to be 13.3 eV for $AgInTe_2$ and 16.6 eV for $CuInS_2$. These plasma frequencies contain a negligible contribution of the *d* electrons.

I. INTRODUCTION

The semiconducting I-III-VI_2 chalcopyrite compounds are ternary analogs of the II-VI zinc-blende compounds. However, due to the presence of the noble-metal *d* levels in the valence-band region, one does not expect a simple relationship to exist between the valence bands of the I-III-VI_2 and those of the II-VI compounds. It is therefore of considerable interest to determine experimentally approximate partial *p* and *d* densities of valence states for the I-III-VI_2 compounds in order to study the effect of *p*-*d* hybridization, and also to relate the structure in the partial densities of valence states thus determined to band-structure calculations. Due to *p*-*d* hybridization the direct energy gap as determined by electroreflectance measurements is found to be up to 1.6 eV smaller in the I-III-VI_2 compounds than in the analogous II-VI compounds.[1-5] The spin-orbit splittings of the uppermost valence-band states of the I-III-VI_2 compounds, as measured by electroreflectance, are also found to be smaller than those in the binary analogs.[1,2] This fact directly reflects the *d* admixture of the corresponding valence states: The *d* electrons, split by the crystal field, yield a negative contribution to the spin-orbit splitting at the center of the Brillouin zone.

In the case of the ternary copper compounds the partial *d*-like character at the top of the valence band has been estimated from the spin-orbit splitting of the band-edge exciton to be between 35 and 45%.[2] The properties of the ternary chalcopyrite compounds have been reviewed recently by Shay and Wernick.[1]

In the present work partial *p* and *d* densities of valence states of I-III-VI_2 compounds have been determined from photoelectron energy-distribution curves (recorded for a wide range of photon energies; $h\nu = 16.8$, 21.2, 26.9, 40.8, 48.4, and 1486.6 eV) by exploiting the strong dependence upon photon energy of the cross sections of atomic levels having different angular momentum.[6-9] This method, which is justified provided there is no interference between *p* and *d* cross sections (see Appendix), has been used recently to obtain partial *p* and *d* densities of states for the Ag and Cu halides.[10,11]

II. EXPERIMENTAL

The measurements were performed with a Vacuum Generators ESCA III system, which includes a He capillary discharge lamp. By varying the He pressure in the lamp, we are able to perform measurements with either the He I (21.2 eV) or the He II (40.8 and 48.8 eV) lines. A similar procedure yields the Ne I (16.8 eV) and Ne II (26.9 eV) lines. The instrumental resolution for uv work was always better than or equal to 0.3 eV. Measurements were also performed with nonmonochromatized Al $K\alpha$ x rays (1486.6 eV, resolution 1.2 eV). These measurements were particularly useful to establish the absence of oxygen and carbon contaminants. The thin-film samples were prepared *in situ*, in an ultrapure argon atmosphere, by sputtering from the polycrystalline ternary compounds onto an aluminum substrate held at room temperature. The amorphous nature of the $AgInTe_2$ sample so prepared was confirmed by x-ray diffraction and Raman scattering.[12] A comparison of the broad x-ray diffraction lines of the amorphous film with that of the crystalline material also indicates tetrahedral coordination in the amorphous sample. The $AgInTe_2$ sample was crystallized by annealing in vacuum at 200 °C for 3 h. X-ray diffraction measurements performed on this sample as well as on the unannealed $\mathrm{CuInS_2}$ sample prepared on a substrate held at room temperature show them to be polycrystalline. Because of the similarity in the scattering form factors of Ag and In, it is not possible to decide whether the crystallized $\mathrm{AgInTe_2}$ films have the ordered chalcopyrite structure or a zinc-blende structure with Ag and In occupying random cation positions. In spite of the more different form factors of Cu and In we did not see any characteristic chalcopyrite lines in in the diffraction patterns of the crystalline $\mathrm{CuInS_2}$ films. Because of the method of preparation they are likely to be in the random zinc-blende structure. Raman measurements being performed at present should clarify this point. We point out here that we also performed photoemission experiments on bulk chalcopyrite $\mathrm{AgInTe_2}$ with Al $K\alpha$ radiation and obtained the same photoelectron distribution curves as for the crystalline films. General experience with photoelectron spectroscopy in disordered systems[13,14] indicates that the possible random nature of our samples should, at most, produce a slight smearing of the features in the photoelectron-distribution curves. Because of surface contamination (these samples could not be cleaved *in situ*) the bulk polycrystalline samples were useless for uv work.

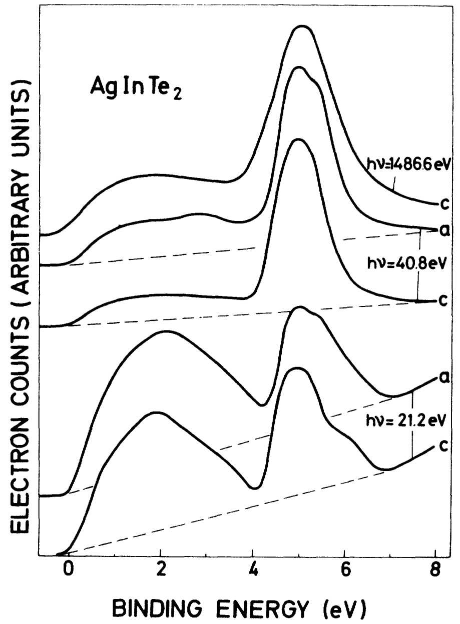

FIG. 1. Photoelectron energy distribution curves, $\tilde{N}(E, h\nu)$, obtained at room temperature for amorphous (a) and crystalline (c) films of $\mathrm{AgInTe_2}$ at photon energies 21.2, 40.8, and 1486.6 eV.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the experimental photoelectron-distribution curves obtained from films of amorphous and crystalline $\mathrm{AgInTe_2}$ and crystalline $\mathrm{CuInS_2}$ at $h\nu = 21.2$, 40.8, and 1486.6 eV. The zero of binding energy in Figs. 1 and 2 was taken to be the top of the valence band and was found to ±0.1 eV by extrapolating the steepest rise in the valence band onset to the background level. The estimated contribution of secondary electrons is indicated by the dashed lines.

The structure in the 40.8- and 1486.6-eV curves of Fig. 1 represents essentially the density of d states; at these energies the excitation probability for p-valence electrons is small compared to that for d electrons.[6-9] At 21.2 eV, on the contrary, p and d excitation probabilities are nearly equal[6-9] and features of the p density of states (a prominent peak at 2 eV, a shoulder at 6 eV) appear. It is thus clear that most of the d density of states in $\mathrm{AgInTe_2}$ is concentrated in a nearly corelike 1.2-eV-wide region centered at 5 eV below the top of the valence band. The p electrons form wider bands centered around 2 eV below the top of the valence band.

This situation is reversed for $\mathrm{CuInS_2}$ in Fig. 2. In this case, the d partial density of valence states peaks around 2.4 eV, while the characteristic p peak now appears at about 3.6 and 7 eV. Both structures have rather large non-core-like widths.

In order to derive from the curves of Figs. 1 and 2 the partial p and d densities of valence states we make the following assumptions: The photoelectron-energy-distribution curves $\tilde{N}(E, h\nu)$ are expressed in a tight-binding approximation as[10]

$$\tilde{N}(E, h\nu) = AL(h\nu - E)T(h\nu - E)\left(\sum_i \rho_i(E)\frac{\sigma_i(h\nu)}{n_i} + S_e\right), \tag{1}$$

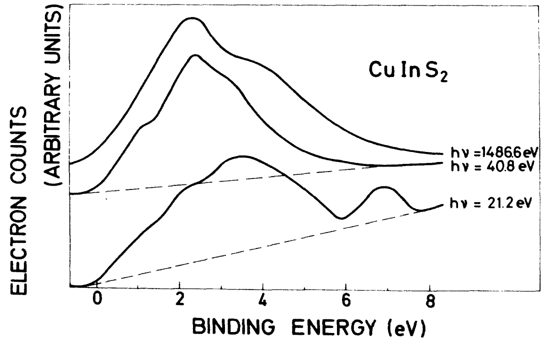

FIG. 2. Photoelectron energy distribution curves obtained for crystalline films of $\mathrm{CuInS_2}$. Same conditions as Fig. 1.

where S_e is the contribution of the inelastically scattered electrons, A is a normalization constant, E is the binding energy of the electrons, ρ_i is the partial density of states, and σ_i/n_i is the photoionization cross section per electron of orbital quantum number i. The transmission factor of the analyzer $T(h\nu - E)$ is inversely proportional to the electron kinetic energy $h\nu - E$.[15] The same holds for the escape depth $L(h\nu - E)$ in the considered range.[16] Equation (1) does not contain interference terms between the p and d orbitals situated at different positions in the unit cell. However, it can be shown (Appendix) that at points of high symmetry in the Brillouin zone this interference term vanishes and is small over the whole Brillouin zone. The s levels in these compounds and the In $4d$ levels are more tightly bound than the p and d levels and thus do not significantly mix into the valence band. After correction of the experimental curves for the transmission factor of the analyzer, the escape depth of the electrons, and the inelastically scattered electrons, Eq. (1) can be written

$$N(E, h\nu) \simeq A[\tfrac{1}{6}\rho_p(E)\sigma_p(h\nu) + \tfrac{1}{10}\rho_d(E)\sigma_d(h\nu)] . \qquad (2)$$

The p-like components of the valence band originate from the p valence levels of the chalcogen atom. Therefore we use for σ_p the corresponding experimental partial cross sections of the isoelectronic rare gas nearest in the periodic table to the chalcogen of interest[8,9] since data for the chalcogens are not available. The rare-gas approximation has been successfully used for the σ_p of the halogens.[10] Measurements of σ_p for the chalcogens are in progress. We use for σ_d the corresponding experimental cross section of metallic Ag and Cu.[6,7] They are nearly constant in the region of our uv measurements and represent essentially the cross section for a filled d shell. The cross sections used are listed in Table I.

To obtain the partial densities of valence states the following procedure was employed. Integration of Eq. (2) (i.e., substitution of the number of electrons per atom) yields

$$\int_{\mathrm{VB}} N(E, h\nu)\, dE = A[2\sigma_p(h\nu) + \sigma_d(h\nu)] . \qquad (3)$$

TABLE I. Experimental cross sections σ_{tot} for Cu (Ref. 6) and σ_p for Ar and Xe (Ref. 9).

Element	σ (21.2 eV) (Mb)	σ (40.8 eV) (Mb)
Cu	10.4	7.96
Ag	26.4	25.5
Ar	36.4	2.4
Xe	33.3	1.1

Using the corrected photoemission data measured at 21.2 and 40.8 eV A was obtained from the areas below these curves and the experimental values of σ_d[6] and σ_p.[9] Inserting A and the experimental values for σ_d and σ_p into Eq. (2), the partial densities of valence states (DOVS) $\rho_p(E)$ and $\rho_d(E)$ are obtained (see Figs. 3 and 4). The shape of the partial p density of states of the ternary compounds is surprisingly similar to the density of valence states of their III-V and II-VI analogs.[14,17] This analogy is particularly striking for $AgInTe_2$. In the crystalline phase, structure labeled in Fig. 4 in accordance with the notation used for the II-VI and III-V compounds ($I_1 - I_5$) appears in the upper portion of the p density of valence states. These structures correlate fairly well with those found for CdTe and InSb, the analogous binary compounds.[14,17] We note that the $I_1 - I_5$ structures are washed out in the amorphous modification, an effect which also occurs in the III-V and II-VI compounds.[13,14] The upper portions of the valence bands of $AgInTe_2$ (0–4 eV) contain a higher proportion of d states in the amorphous than in the crystalline material. This fact is probably due to disorder-induced mixing. The corelike peak centered at 5 eV shows a splitting Δ_d which correlates well with the spin-orbit splitting of atomic Ag (0.65 eV).[18] Similar splitting has been obtained recently for dilute Ag in disordered Cu-Ag systems.[19] The splitting Δ_d is not seen for the crystalline sample of Fig. 4. Peak II in Fig. 3 ($CuInS_2$) occurs at higher binding energies than for the II-VI analogs.[17] This fact may be due to the strong p-d repulsion and mixing in this compound. The partial d density

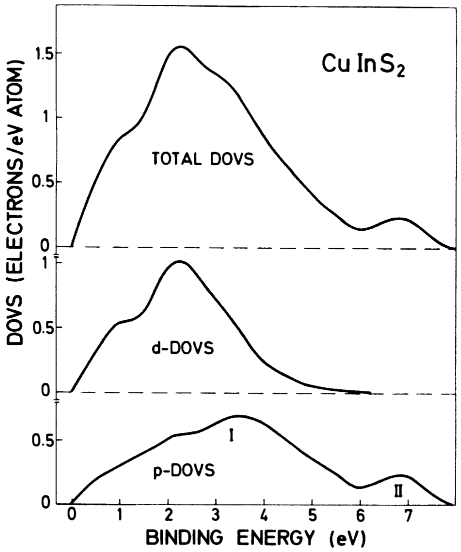

FIG. 3. Partial and total densities of valence states (DOVS) for $CuInS_2$ obtained from the data of Fig. 2.

of states (Figs. 3 and 4) exhibits a very close resemblance to the d-type valence band of the zinc-blende phase of the Cu halides and AgI.[10] This is a consequence of the approximately similar tetrahedral environment of the Ag and Cu atoms.

The d admixtures at the top of the valence band can be estimated from our results. Several other authors[2,4] have determined the fractional d-like character of the uppermost valence bands from a quantitative analysis of the spin-orbit splittings of the band-edge excitons in the crystalline compounds. This analysis yields the admixture only at the upper edge (Γ) of the valence band. In Table I the results of the spin-orbit splitting analysis are compared with the d admixture obtained here from the slopes of the upper edge of the valence bands.

The p-d hybridization for the Ag compound is seen from Table II to be smaller than that for the Cu compound, as would be expected from the binding energies of the d levels in the elements.[20] The average d admixture from the slopes of the partial density of valence states is about 20% larger than the value found at Γ from the spin-orbit splitting. This deviation is not surprising in view of the fact that a finite energy difference must be used to define the slopes.

We have also measured the binding energies of most of the core levels in the ternary compounds with respect to the top of the valence band. The $4d$ levels of In are obtained very accurately with uv radiation ($4d_{5/2} = 17.4 \pm 0.1$ eV, $4d_{3/2} = 18.2 \pm 0.1$ eV for $CuInS_2$; $4d_{5/2} = 17.0 \pm 0.1$ eV, $4d_{3/2} = 17.83 \pm 0.1$ eV for $AgInTe_2$). The spin-orbit splitting of these levels (0.80 and 0.83 eV) is nearly the same as found for InAs, InSb, and InP.[14] It is, however, 0.10 eV smaller than found for metallic In, a result common to many semiconductors.[14] To compare chemical shifts between the ternary compounds and their elemental constituents we now refer all binding energies to the vacuum level. For the compounds under study we find 5.5 ± 0.3 eV for the photoelectric threshold. Using photoelectric-threshold and binding-energy data for the elements from Refs. 10 and 14 we get the following result. The In $4d$ core levels are shifted by -1.7 eV in $CuInS_2$ and -1.3 eV in $AgInTe_2$ with respect to metallic In. In the same compounds we find core-level shifts of -0.4 eV for Cu and -0.3 eV for Ag. The core levels of Te are moved up by $+0.3$ eV in $AgInTe_2$.[17] The core binding energies of the core levels of In in $CuInS_2$ are, with respect to the vacuum level, equal to those of InP.[14] Hence, the charge of the In ion can be expected to be about the same in both compounds. Likewise, because of similarities in the shifts (within experimental error), the charge of In in $AgInTe_2$ should be nearly the same as that in InSb.[14] The noble metals in the ternary compounds have chemical shifts around -0.4 eV, considerably smaller than in the tetrahedral noble-metal halides (-1 eV).[10] We thus infer that the changes in the ionicity of the noble metals in the chalcopyrites are smaller than those in the zinc-blende-type nobel-metal halides. At the present time, these statements must be regarded as qualitative because of the uncertainties in the determination of the vacuum levels (± 0.3 eV).

As a by-product of the core-level measurements and their plasmon satellites, we found the plasma energy of the valence electrons to be 13.3 ± 1 eV for $AgInTe_2$ and 16.6 ± 1 eV for $CuInS_2$. These plasma energies correspond to an average of 4.1 and 4.0 valence electrons per atom, the same electron densities as found for other tetrahedral semi-

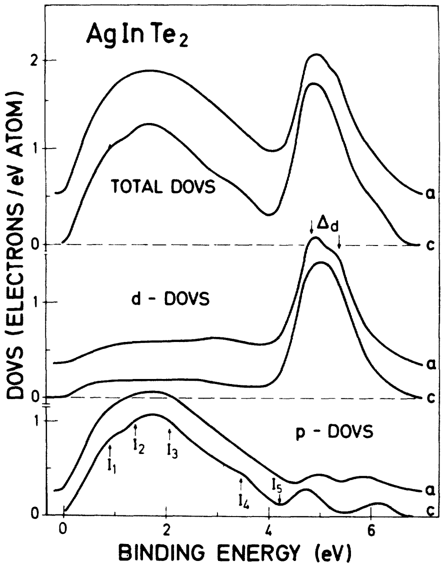

FIG. 4. Partial and total densities of states (DOVS) for amorphous (a) and crystalline (c) $AgInTe_2$ obtained from the data of Fig. 1.

TABLE II. Admixture of d states at the top valence bands of Cu and Ag ternary semiconductors.

	From spin-orbit[a] splitting	This work
$AgInTe_2$ amorphous	...	(17–27)%
$AgInTe_2$ crystalline	17[b]	(23–27)%
$CuInS_2$ crystalline	45%	(55–59)%

[a] See Ref. 2.

[b] d admixture for $AgInSe_2$ from Ref. 4.

conductors without d electrons.[21] Thus we conclude that the contribution of the d electrons to the plasma frequencies is negligible. A similar result has been reached for the copper and silver halides.[10]

We found the calibrated Fermi energy of the spectrometer to lie 1.0 eV above the top of the valence band of both materials. In view of the fact that the gap of $AgInTe_2$ is 1.04 eV,[22] and that of $CuInS_2$ 1.53 eV,[5] we conclude that the surface Fermi level is close to the bottom of the conduction band.

The bulk conduction type of our thin samples was not determined, but is expected to be n on the basis of Refs. 3 and 4. Thus the Fermi level near the surface may agree with that of the bulk.

Recently Luciano and Vesely[23,24] have reported x-ray photoemission from the valence bands of $AgGaS_2$ and $CuAlS_2$. Their resolution is poor (~1 eV) because of the use of unmonochromatized x rays. Our results are consistent with this work.

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APPENDIX

We want to show that the interference term occuring in the square modulus of the transition matrix element ($|\langle f|\nabla|i\rangle|^2$) taken between the initial state (the p-d hybrid wave function) and the final state (the plane wave) is expected to be small. In a tight-binding approximation the p-d hybrid wave function can be written as

$$\chi_k(\vec{r}) = \sum_R [a\chi_p(\vec{r}-\vec{R}) + b\chi_d(\vec{r}-\vec{R}-\vec{\tau})]e^{i\vec{k}\cdot\vec{R}}, \tag{A1}$$

where the coefficient a can be chosen to be real and b is complex with phase α, the wave functions χ_p and χ_d are real, and τ is a basis vector in the unit cell.

The final states are plane waves of the form $e^{i\vec{k}\cdot\vec{r}}$. The matrix element taken between the final state and the hybridized valence state is then proportional to

$$\begin{aligned}\int \sum_R [a\chi_p(\vec{r}-\vec{R}) + b\chi_d(\vec{r}-\vec{R}-\vec{\tau})]e^{i(\vec{k}'\cdot\vec{r}-\vec{k}\cdot\vec{R})}d\vec{r} &= N\left(\int_{\text{unit cell}} [a\chi_p(\vec{r}) + b\chi_d(\vec{r}-\vec{\tau})]e^{i\vec{k}'\cdot\vec{r}}\,d\vec{r}\right)\delta(\vec{k}-\vec{k}'-\vec{G}')\\ &= N\left(a\int_{\text{unit cell}} \chi_p(\vec{r})e^{i\vec{k}'\cdot\vec{r}}\,d\vec{r}\right.\\ &\quad \left.+ be^{i\vec{k}'\cdot\vec{\tau}}\int_{\text{unit cell}} \chi_d(\vec{r})e^{i\vec{k}'\cdot\vec{r}}\,d\vec{r}\right)\delta(\vec{k}-\vec{k}'-\vec{G}'),\end{aligned} \tag{A2}$$

where $\vec{G}'$ is an arbitrary reciprocal-lattice vector. Since $\chi_p(\chi_d)$ is an odd (even) function, the Fourier integrals of Eq. (A2) are real (for χ_d) and pure imaginary (for χ_p). Thus the matrix element of Eq. (A2) can be abbreviated

$$(iA + e^{i\vec{k}'\cdot\vec{\tau}}B)\delta(\vec{k}-\vec{k}'-\vec{G}') \quad \text{with } A \text{ real and B complex}. \tag{A3}$$

From Eq. (A3) we find that the square modulus of the factor multiplying the δ function is

$$A^2 + |B|^2 + 2A|B|\sin(\vec{k}'\cdot\vec{\tau}+\alpha). \tag{A4}$$

In polycrystalline material the interference term in Eq. (A4) has to be averaged for all possible orientations of $\vec{\tau}$. The result of this procedure is

$$A^2 + |B|^2 + 2A|B|\,\frac{\sin k'\tau}{k'\tau}\,\sin\alpha. \tag{A5}$$

In the energy range considered the interference term of Eq. (A5) contributes less than 20% to the transition probability. Moreover, this interference is zero at points in the Brillouin zone where b is real and thus $\alpha = 0$. This is the case at Γ and at symmetry points with $\vec{k} = \frac{1}{2}\vec{G}'(L, X)$, where $\vec{G}$ is a reciprocal-lattice vector. The wave function for $\vec{k} = \frac{1}{2}\vec{G}$ and $\vec{k} = -\frac{1}{2}\vec{G}$ must be the same; hence

$$\chi^*_{\vec{k}=\vec{G}/2}(\vec{r}) = \chi_{\vec{k}=\vec{G}/2}(\vec{r}) = \chi_{\vec{k}=-\vec{G}/2}(\vec{r}).$$

This equation holds provided the spin-orbit splitting is neglected, so that the potential is real and $\chi^*_{\vec{k}}$ degenerate with $\chi_{\vec{k}}$:

$$\begin{aligned}&\sum_R [a\chi_p(\vec{r}-\vec{R}) + b^*\chi_d(\vec{r}-\vec{\tau}-\vec{R})]e^{-i\vec{k}\cdot\vec{R}}\\ &\quad = \sum_R [a\chi_p(\vec{r}-\vec{R}) + b\chi_d(\vec{r}-\vec{\tau}-\vec{R})]e^{i\vec{k}\cdot\vec{R}}.\end{aligned} \tag{A6}$$

For $\vec{k} = \frac{1}{2}\vec{G}$, $e^{-i\vec{k}\cdot\vec{R}} = e^{i\vec{k}\cdot\vec{R}} = \pm 1$ and therefore $b = b^*$ is a real quantity, which implies $\alpha = 0$. Since the interference term of Eq. (A5) amounts at most to 20% of the total cross section and vanishes at a large number of high-symmetry points in the Brillouin zone, its total contribution is found to be very small.

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