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PHOTOEMISSION OVERVIEWS OF VALENCE BAND DENSITIES-OF-STATES FOR Ge, GaAs, GaP, InSb, ZnSe AND CdTe USING SYNCHROTRON RADIATION (*)

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Abstract. — We present photoemission overviews of major valence band features for the valence bands of several common group IV, III-V and II-VI semiconductors, which were obtained using synchrotron radiation in the 20-90 eV range from the 2.5 GeV storage ring at the Cambridge Electron Accelerator. Comparisons of our photoemission data with empirical pseudopotential method (EPM) calculations fit to optical data show systematic and significant differences which typically increase with increasing ionicity. InSb is described in some detail, including measurements of core level binding energies, spin-orbit splittings and Auger processes. Several precautions when interpreting valence band photoemission measurements in the 20 to 90 eV photon energy range are discussed (e. g. Auger processes, surface preparation, small matrix elements).

1. Introduction. — We describe photoemission measurements for several common group IV, III-V and II-VI semiconductors which have been obtained in the 20-90 eV photon energy range using synchrotron radiation. From these measurements we have obtained overviews of the valence bands' optical density of states and have determined several valence band edges or critical points for each semiconductor with a typical precision of about 0.2 to 0.3 eV with respect to the upper valence band edge E_v [1], [2].

The current understanding of the electronic structure of semiconductors away from the gap has been obtained primarily by interpreting optical (including modulation) measurements via model band calculations [3], [4] such as the empirical pseudopotential method [3] (EPM). This procedure, which determines differences in band energies but usually not absolute band energies is a sensitive probe of the upper valence bands and lowest conduction bands. Previously, ultraviolet photoemission measurements for $h\nu \leq 11.6$ eV (LiF window cutoff) have proved useful for deter-

mining certain valence band features within ~ 4 eV of the valence band edge [5].

Our measurements provide additional band information, including the lower valence bands [5] which, combined with optical data, should provide a guide for refining and testing local and non-local empirical pseudo-potential models as well as effective one-electron potentials in « first-principles » calculations such as OPW or APW calculations. Our data at high photon energies ($h\nu \gtrsim 30$ -50 eV) are quite similar to recent X-ray photoemission data ($h\nu \simeq 1\,500$ eV), which are also proving to be very useful in determining valence band features [6]. This close similarity is seen even though the bulk penetration depth, e. g. electron escape depth, is considerably shorter in the 20-90 eV range than at 1 500 eV.

We use InSb as an example to discuss the trend from the UV photo-emission regime (roughly $h\nu \lesssim 20$ eV) where both energy and momentum conservation are important to the « X-ray limit » ($h\nu \gtrsim 30$ -50 eV) where only energy conservation is important, i. e. where photoemission spectra reflect single-particle density of states features. Various precautions when interpreting photoemission data in the 20-90 eV range are offered...

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The use of intense synchrotron radiation has permitted us to obtain high resolution (~ 0.1 - 0.4 eV) in the 10-100 eV range. For example, for InSb we have determined In and Sb 4d core level binding energies

$$\begin{aligned} (\text{In} : d_{5/2} &= 17.40 \pm 0.05 \text{ eV} , \\ \text{Sb} : d_{5/2} &= 32.52 \pm 0.05 \text{ eV}) , \end{aligned}$$

spin-orbit splittings

$$\begin{aligned} (\text{In} : \Delta &= 0.85 \pm 0.03 \text{ eV} , \\ \text{Sb} : \Delta &= 1.25 \pm 0.03 \text{ eV}) \end{aligned}$$

and line widths

$$\begin{aligned} (\text{In} : 2\Gamma &= 0.48 \pm 0.03 \text{ eV} , \\ \text{Sb} : 2\Gamma &= 0.62 \pm 0.05 \text{ eV}) . \end{aligned}$$

Various trends can be seen in our valence band overviews. For example, we observe that the upper three valence bands narrow with increasing ionicity, i. e. on going from group IV (Ge) to group III-V (GaAs, GaP, InSb) to group II-VI (ZnSe, CdTe) semiconductors. Also, as theoretically expected [3], the lowest (first) valence band is seen to split off from the upper three valence bands for the heteropolar semiconductors (e. g. GaAs, etc.). EPM calculations fit to optical data consistently obtain widths for the upper three valence bands which are narrower than we observe, and in the case of the II-VI semiconductors (ZnSe, CdTe), these differences become quite large. For example, in GaAs the upper three valence bands ($E_v - X_3$) are 6.9 eV wide (experiment) while the EPM [8] yields 6.4 eV while in ZnSe the corresponding widths are 5.3 eV (experiment) and 3.8 eV (EPM) [8]. Typically, OPW calculations show somewhat better agreement with our data for the lower valence bands than EPM calculations fit to optical data [9], [12]. Recently, various workers have modified EPM calculations via the inclusion of non local potentials and obtain much better agreement with experiment [13], [15].

2. Experimental. — A schematic diagram of the experimental system at the 2.5 GeV Cambridge Electron Accelerator is shown in figure 1. An ellipsoidal focusing mirror with a 0.6° grazing angle captures 10 mrad of horizontal beam spread and focuses an image of the source point ($\sim 1 \times 2$ mm) in the storage ring into the user room about 20 meters from the source [16]. This mirror can be adjusted remotely and passes all wavelengths λ greater than $\lambda_c \simeq 3.5$ Å, i. e. $h\nu_c \simeq 3.5$ keV. Radiation shielding permits occupancy of the user room during all phases of storage ring operation. With the storage ring operating at 2.5 GeV and 30 mA of d. c. beam current, the flux of focused radiation is about 10^{14} - 10^{15} photons/eV.s in the 10-100 eV range.

FIG. 1. — Schematic diagram of photoemission system using synchrotron radiation at the CEA 2.5 GeV storage ring (not to scale). The storage ring is ~ 80 m diameter and the experimental system is ~ 20 m from the source.

A planar beam splitter mirror with a 2.5 mm diameter hole is used to split the beam for simultaneous operation of an X-ray microscope [16] and our photoemission system. This mirror has a 9° grazing angle and acts as a low pass filter, i. e. passes only radiation with $h\nu \lesssim 200$ - 300 eV, so as to avoid X-ray damage to the Au-coated replica gratings in the monochromators.

Ultra-high-vacuum (UHV) monochromators

$$(p \lesssim 1 \times 10^{-9} \text{ torr})$$

have been constructed so as not to degrade the vacuum of the sample chamber ($p \lesssim 3 \times 10^{-10}$ torr). Two monochromators with fixed exit slits have been built, a 1-m Seya-Namioka type (slits S_1 and grating G_1 in figure 1) useable in the 12,000-180 Å range and a 2-m grazing incidence type (slits S_2 and grating G_2) useable in the 250-100 Å range. In order to both maximize efficiency over a wide spectral range and to minimize unwanted higher order diffraction effects, the Seya-type monochromator has two gratings blazed at ~ 1200 Å and 300 Å, respectively which can be interchanged *in situ*. This arrangement, together with a LiF filter for wavelengths $\lambda > 1060$ Å, has proved satisfactory for most measurements. Adjustable slits permit the band width $\Delta\lambda$ to be varied from $\Delta\lambda = 32$ Å to 1 Å in the range 12,000-180 Å.

The 2-m grazing incidence monochromator consists of a fixed exit slit S_2 , fixed-position 2400 groove/mm spherical grating blazed at ~ 120 Å and a moveable entrance slit which consists of a 0.15 mm wide planar mirror (Au coated) which translates and rotates along the Rowland circle in the path of the photon beam. The band width $\Delta\lambda$ can be varied from about 0.3 Å to 4 Å throughout the 100 Å to 250 Å range.

The monochromatic beams of both monochromators pass through the focal point of the three-stage cylindrical mirror electron analyzer. Samples can be positioned for use with either monochromator by a simple rotation. The cylindrical mirror analyzer consists of a retard/accelerate stage constructed from two concentric hemispherical grids centered about the sample, followed by a two-stage electrostatic deflection, 2" i. d. cylindrical mirror analyzer with a Bendix spiraltron electron multiplier [17]. The passband width ΔE (typically 0.1 to 0.4 eV) is determined by selecting the pass energy $E_p = \Delta E \cdot R$ with a resolution $R \approx 125$. This analyzer has spatial focusing which permits easy alignment to both monochromators, and operates quite well down to zero kinetic energy by pre-accelerating the emitted electrons using the inner hemispherical grid.

Single crystal semiconductors of 2 mm $\times$ 2 mm cross section were cleaved (with some faceting) and measured *in situ* at about 3×10^{-10} torr, with a (111) surface for Ge and (110) surfaces for the heteropolar semiconductors. Lightly-doped samples (except for ZnSe) were used to avoid complications due to short bandbending depths.

3. Data and discussion. — **3.1 InSb.** — We shall first describe InSb as a prototype, illustrating various features which can be determined as well as pointing out various precautions which should be observed in interpreting photoemission data.

A photoemission energy distribution (PED) for $h\nu = 70$ eV is shown in figure 2 for InSb and gives an overview of both the valence bands and the 4d core levels. In addition to primary emission from the valence bands and 4d core levels, we observe several characteristic energy loss peaks (CEL) which accompany the core level lines as well as two broad Auger

FIG. 2. — Photoemission energy distribution for InSb with $h\nu = 70$ eV. Photon and electron energy band widths of $\Delta h\nu \approx \Delta E^* \approx 0.38$ eV were used for the valence bands and $\Delta h\nu \approx \Delta E^* \approx 0.2$ eV for the core levels. The core level counting rates were $\sim 50,000$ elec/s (for $\Delta h\nu \approx \Delta E^* \approx 0.4$ eV; 30 mA beam).

peaks which remain stationary in kinetic energy near $E^* \approx 8$ eV and 25 eV. These Auger peaks result from $N_{4.5}$ VV transitions of the In 4d and Sb 4d core levels, respectively.

Considering first the valence bands, several PED's are shown in figure 3. These PED's were selected because they show various valence band features and also illustrate effects due to Auger emission and transition probabilities. Valence band energies are measured relative to the valence band edge $E_v = 0$. The valence band edge E_v was determined by measuring the Fermi level E_F of a gold film evaporated *in situ*; E_v for lightly-doped InSb was determined via a PED for $h\nu = 8$ eV to lie ~ 0.25 eV below E_F [18].

FIG. 3. — InSb valence band energy distributions for $h\nu = 20, 30, 40$ and 70 eV. Experimental valence band critical points are marked above the 70 eV curve. A theoretical density of states curve [10], [22] (empirical pseudopotential method) is also shown with critical points marked along the lower axis. The counting rates varied monotonically from $\sim 4 \times 10^4$ elec/s at $h\nu = 20$ eV ($\Delta h\nu \approx \Delta E \approx 0.2$ eV) to 2×10^3 elec/s at $h\nu = 70$ eV ($\Delta h\nu \approx \Delta E \approx 0.4$ eV) with a beam current of ≈ 30 mA.

The PED for $h\nu = 20$ eV shows the width of the valence p-bands (bands 3 and 4), i. e

$$E_v - \Sigma_{1\min} = 3.65 \text{ eV},$$

as well as additional structures due to primary photoelectron emission (features $P_1 - P_4$ and X_3) and to Auger electron emission (A_1, A_2). While feature P_1 corresponds to the L_3 edge seen at higher $h\nu$'s, features

TABLE I

Positions of energy band features measured relative to the valence band edge (eV).
Theoretical EPM values are given in parenthesis (see ref. [22])

	$\overline{L_3}$	$\overline{\Sigma_{1\min}}$	$\overline{L_1}$	$\overline{L_2}$	$\overline{\Gamma_1}$
Ge	1.1 (1.1)	4.5 (3.8)	7.7 (6.9)	10.6 (9.9)	12.6 (12.0)
	$\overline{L_3}$	$\overline{\Sigma_{1\min}}$	$\overline{X_3}$	$\overline{X_1}$	$\overline{\Gamma_1}$
GaAs	0.8 (0.9)	4.1 (3.2)	6.9 ^(a) (6.4)	10.0 (9.7)	12.9 (12.0)
GaP	0.8 (0.9)	4.1 (3.8)	6.9 (5.8)	9.7 (11.5)	11.8 (13.0)
InSb	1.05 (0.6)	3.65 (2.1)	6.5 (5.4)	9.0 (7.6)	11.2 (8.9)
ZnSe	0.7 (0.45)	3.4 (2.7)	5.3 (3.8)	—	— (14.2)
CdTe	0.7 (0.4)	2.8 (2.0)	4.7 (2.9)	8.8 (12.5)	— (12.9)

^(a) See footnote 25.

$P_2 - P_4$ vary with photon energy for $h\nu \lesssim 20$ eV. This behavior is characteristic of momentum conservation in the excitation process at lower energies [2]. The weak but well-defined feature X_3 corresponds to the bottom of band 2 (this critical point is best seen at $h\nu \simeq 15$ eV).

Interestingly, no emission from the lowest valence band (band 1) centered near -10 eV is seen for $h\nu \lesssim 25$ eV. Emission from this lowest Sb-derived band is seen for $h\nu = 30$ eV and increases relative to p-bands 3 and 4 with increasing $h\nu$ (e. g. see PED for $h\nu = 70$ eV). We have observed a similar behavior for several semiconductors (e. g. GaAs and GaP). This serves as a warning that a PED at a fixed energy such as 21 eV in general will not reflect all valence bands, i. e. bands can be « missing ». Also for $h\nu = 20$ eV, Auger emission due to In 4d-holes overlaps valence band emission and results in intense emission for initial energies $E_i \lesssim -5$ eV, with Auger structure observed at -7.5 and -8.5 eV (A_1, A_2). Thus, care must be used in interpreting observed features when Auger emission is possible. Such Auger emission does not interfere with valence band emission for $h\nu = 30$ eV, as is seen in figure 3.

The PED for $h\nu = 30$ eV reflects many valence band density of states features, including the Ledge L_3 of band 4, features L_2 and X_3 of band 2 and features X_1, L_1 and Γ_1 of band 1. However, the minimum of band 3 ($\Sigma_{1\min}$) is not clearly seen for $h\nu = 30$ eV (or for $h\nu = 40$ eV). Comparing PED's for $h\nu = 40$ eV and 30 eV, at $h\nu = 40$ eV, emission from bands 1 and 2 has become more intense relative to that from bands 3 and 4. However at 40 eV, increased emission for initial energies $E_i \lesssim -10$ eV is also observed due to Auger emission from the Sb 4d-holes.

At higher energies, e. g. at $h\nu = 70$ eV, the « X-ray limit » (or continuum limit) is reached and valence band density-of-states features are reflected in the PED. Valence band features (i. e. critical points) observed for this PED as well as other PED's are indicated by the vertical dashes. These energy levels are summarized in table I and were determined by

comparison with suitably-broadened theoretical single-particle density of states due to Alvarez, *et al.* [19], for which the corresponding critical points are known [2]. The disagreement between our experimental values and the EPM values [19] is not unexpected in that the latter bands were fit only to dielectric constant data, involving mainly valence band 4. As seen in figure 3 the EPM bands are too narrow, and have a much smaller separation ($X_3 - X_1$) between the first and second valence bands than is observed. Unadjusted OPW calculations [9], [20] (see Table I) give a better fit to these lower valence bands. It should be interesting to see how well such calculations can fit both optical data and our valence band data.

Considering now the 4d core levels of InSb, the high resolution spectrum in figure 2 clearly shows the spin-orbit splittings and level widths of the In 4d and Sb 4d levels. These binding energies (measured relative to the Fermi level E_F which is at the conduction band minimum E_c), splittings, and level widths are summarized in table II. For comparison, we have measured the 4d levels in metallic In (Table II). Comparing InSb and In metal, a chemical shift of 0.70 eV is observed [20] for the In 4d level. Also, our measured In 4d level width (FWHM 2Γ) is greater for InSb ($2\Gamma = 0.48 \pm 0.03$ eV) than for In metal ($2\Gamma = 0.37 \pm 0.03$ eV).

In our photoemission studies of semiconductors

TABLE II

InSb core levels (E_F reference).
The Fermi level E_F is ≈ 0.25 eV
above the valence band edge E_v .

Level	Energy (eV)	Width 2Γ (eV)
In 4d _{5/2}	17.40 ± 0.05	0.48 ± 0.03
4d _{3/2}	18.25	($\Delta_{s0} = 0.85$)
Sb 4d _{5/2}	31.52	0.62 ± 0.05
4d _{3/2}	32.77	($\Delta_{s0} = 1.25$)
In metal 4d _{5/2}	16.70	0.37 ± 0.03
4d _{3/2}	17.58	($\Delta_{s0} = 0.88$)

in the 10-100 eV range, we have observed that surface preparation, both structural preparation and surface cleanliness, is very important, especially for the more covalent materials Si, Ge, GaAs, etc. We have observed greater surface sensitivity for $20 \text{ eV} \lesssim h\nu \lesssim 40 \text{ eV}$ than for $h\nu \lesssim 15 \text{ eV}$ or $h\nu \gtrsim 50 \text{ eV}$. This is consistent with the shortest electron escape depth occurring at about twice the plasma energy $\hbar\omega_p \sim 15 \text{ eV}$, as is given by free electron gas calculations.

We next consider photoemission data for Ge, GaAs, GaP, ZnSe and CdTe and give brief descriptions of various valence band features. Photoemission energy distributions (PED's) have been selected at sufficiently high energies to give overviews of main valence band features. Experimental valence band «photoemission densities of states» (PDS's) and previously reported theoretical band densities of states determined via the empirical pseudopotential method are also presented. The PDS's are derived from the experimental PED's by subtracting a smooth background of inelastically scattered secondary electrons [2]. As discussed for InSb, principal features in these «high energy» PED's at photon energies which avoid interference from Auger emission are expected to correspond to structure in the valence band density of states.

3.2 GERMANIUM. — A photoemission energy distribution curve for Ge is shown in figure 4a and the corresponding photoemission density of states (PDS) together with an EPM density of states $N(E)$ is shown in figure 4b [22]. The EPM curve is broadened by a Lorentzian of full-width 2Γ varying linearly with energy from 0.2 eV at the valence band edge E_v to

0.75 eV at $E_v - 12 \text{ eV}$ in order to roughly simulate intrinsic lifetime broadening and experimental broadening [24].

Our experimental valence band edges and critical points for Ge are summarized in table I together with corresponding EPM values. All values are measured relative to the valence band edge E_v . Experimental band edges and other critical points were determined by comparing with corresponding features in the «lifetimes-broadened» EPM calculations for which the corresponding critical points are known [22] (lower arrows in figure 4b). Considering that the EPM results were not fit to the lower valence bands, the overall shape of the EPM valence band density of states for Ge is in good agreement with our PDS, and the disagreement in position of the lower bands is not surprising. The enhanced edge just below E_v in our PDS is believed to be due to intrinsic surface states [19]. The presence of these surface states might also slightly affect our assignment of the L_3 edge (1.1 eV). Experimentally, the most accurately determined features are the low energy features of the second and third valence bands (L_1 and $\Sigma_{1\min}$) and EPM calculations (as well as OPW calculations) predict band widths which are generally too narrow by $\sim 0.5 \text{ eV}$, or more. Recently, an EPM calculation which includes a non local d-phase shift has been reported [13] which fits our experimental edges very well.

3.3 GALLIUM ARSENIDE. — A photoemission energy distribution curve is shown in figure 5a together with the corresponding PDS and an EPM density of states $N(E)$ in figure 5b. Our experimental valence

FIG. 4. — (a) Photoemission energy distribution for Ge. (b) «Photoemission density of states» (PDS) and EPM density of states $N(E)$. Experimental critical points (upper set) and theoretical critical points (lower set) are marked. See reference [22].

FIG. 5. — (a) Photoemission energy distribution for GaAs. (b) «Photoemission density of states» (PDS) and EPM density of states $N(E)$ [23].

band edges (critical points) are shown in figure 5b (upper arrows) and are summarized in table I. For GaAs (as for the other semiconductors) the assignments for $\Sigma_{1\min}$, X_3 , etc., were checked and made more precise by reference to PED's for other photon energies. Such lower energy PED's show the $\Sigma_{1\min}$ and X_3 edges with better resolution but do not directly reflect other density of states features (due to momentum conservation) and cannot give an overview of the entire valence band. The valence band edges Γ_1 and X_1 for band 1 were determined from a PED for $h\nu = 70$ eV which better shows this lowest valence band.

The EPM density of states fit to optical data [8] gives a good overview of the upper three valence bands. However, the EPM band edges X_3 and $\Sigma_{1\min}$ of the second and third bands are too high by 0.5 eV and 0.9 eV respectively [25]. Interestingly, the EPM model shown in figure 5b, which represents a refinement [8] of an earlier model [7] in that optical modulation data were also fit, shows poorer agreement with our data in the position of certain band edges such as $\Sigma_{1\min}$ than the earlier calculation.

3.4 GALLIUM PHOSPHIDE. — Photoemission energy distributions (PED's) for photon energies of $h\nu = 20$ eV and 78 eV are shown in figure 6a. Our resulting PDS is shown in figure 6b together with an EPM density of states $N(E)$ [22]. Experimental critical points L_3 , $\Sigma_{1\min}$, X_3 , X_1 and Γ_1 are shown by the upper arrows in figure 6b and are summarized in table I. As seen in figure 6a, the PED for $h\nu = 20$ eV more clearly shows the band edge critical points

FIG. 6. — (a) Photoemission energy distributions for GaP. (b) « Photoemission density of states » (PDS) and EPM density of states $N(E)$ [8].

$\Sigma_{1\min}$ and X_3 , while the PED for $h\nu = 78$ eV gives a much better overview of all 4 valence bands.

Comparing our experimental PDS's for GaP and GaAs with the corresponding EPM densities of states, the width of the upper two valence bands ($\Sigma_{1\min}$) shows better agreement for GaP than for GaAs. This is probably due to the fact that, in contrast with GaAs, GaP is an indirect-gap III-V semiconductor, and both the indirect gap X_1 (conduction band), $E_v(\Gamma_{15})$ and the $X_1 - X_5$ band separations have been determined from the optical data. This determines the $E_v - X_5$ separation, which is proportional to the width $\Sigma_{1\min}$ of the upper two valence bands.

3.5 ZINC SELENIDE. — Photoemission energy distributions for $h\nu = 20$ eV and 30 eV are shown in figure 7a. Our resulting PDS is shown in figure 7b together with an EPM density of states [22] $N(E)$. Comparing the PED's for $h\nu = 20$ and 30 eV in figure 7a, a large change in the spectral shape of the emission from the upper three valence bands is observed. The Zn 3d bands centered at 8.9 eV below E_v are also shown for the 30 eV PED. For photon energies $h\nu \leq 40$ eV, we do not see emission from the lowest valence band (Se-derived).

FIG. 7. — (a) Photoemission energy distributions for ZnSe. (b) « Photoemission density of states » (PDS) and EPM density of states $N(E)$ [8].

Our experimental critical points for the upper three valence bands are summarized in table I. The band edges ($X_3 = 5.3 \pm 0.3$ eV and $\Sigma_{1\min} = 3.4 \pm 0.3$ eV) of the second and third valence bands, respectively, obtained from our data are seen to be much deeper than the corresponding EPM values [8].

3.6 CADMIUM TELLURIDE. — A photoemission

energy distribution for $h\nu = 24$ eV is shown in figure 8a and the corresponding PDS is shown in figure 8b, together with an EPM density of states [22]. Experimental valence band features are again summarized in table I.

FIG. 8. — (a) Photoemission energy distribution for CdTe. (b) « Photoemission density of states » (PDS) and EPM density of states $N(E)$ [12].

As with ZnSe, the widths of the second and third valence bands (e. g. $X_3 = 4.7 \pm 0.2$ eV and $\Sigma_{1\min} = 2.8 \pm 0.2$ eV) are seen to be much broader than the EPM results ($X_3 = 2.9$ eV and $\Sigma_{1\min} = 1.9$ eV). Also the gap between the first and second bands ($X_3 - X_1 = 4.1$ eV) is much smaller than the EPM results ($X_3 - X_1 = 9$ eV). This spectroscopically determined band gap has recently been shown to be a good measure of the ionicity parameter C of the Phillips-Van Vechten theory [26].

The large discrepancy in $X_3 - X_1$ in the EPM appears to be due to the sensitivity of the lowest band to the pseudopotential coefficients and the previous lack of experimental data for the lower bands; however, recent EPM calculations indicate that a non local pseudopotential is required to describe the lower bands [14], [15].

In figure 8a we also observe the spin-orbit split Cd 4d levels, at -10.0 eV ($D_{5/2}$) and -10.6 eV ($D_{3/2}$), respectively, which overlap the first valence band (mostly Te 5s level) that has an edge X_1 at 8.8 ± 0.3 eV. The bottom of the valence bands Γ_1 is roughly estimated as 10.8 ± 0.6 eV; this estimate is based on the position of the X_1 edge and typical broadening of such deep bands (a lower bound of $\Gamma_1 < 11.5$ eV is obtained by inspection of the PED). Comparison with OPW calculations shows

that unadjusted OPW calculations [11] give a more accurate picture of the lower valence bands than the EPM fit to optical data [12].

4. Summary. — We have presented overviews of the valence band structure for several common group IV, III-V and II-VI semiconductors. While overall shapes (but not amplitudes) of our photoemission densities of states are in qualitative agreement with EPM and OPW densities of states, we generally find significant differences in band edges and critical points for the lowest three valence bands. Ge, GaAs and ZnSe share the same row in the periodic table and show a systematic narrowing of valence bands 2, 3 and 4 as one goes from Ge to more ionic ZnSe. This trend is also seen in the EPM results as well as in OPW calculations [4]. However, the EPM bands are always narrower than experiment, with the discrepancy becoming significantly larger for II-VI ZnSe and CdTe. While it is beyond the scope of this paper to compare all available band calculations (OPW, etc.) with various one-electron potentials, we note that unadjusted OPW calculations [9], [11], [20] generally give a better description of the lower valence bands than do EPM calculations fit only to optical data.

Experimental valence band data such as presented in table I, used together with optical data, should provide a valuable guide to future band calculations e. g., in ascertaining the adequacy of various effective one-electron potentials in first-principles band calculations (OPW, APW) and in inquiring whether local pseudopotentials can fit semiconductor energy bands over a wide energy range or whether non-local corrections are required.

Photoemission overviews of valence band structure such as we have presented are in a preliminary stage and future work is expected to furnish additional valence band information as well as data for new materials. Recently, good overviews of valence band structure for semiconductors have been obtained via X-ray photoemission measurements [6]. Once overviews of valence band structure for semiconductors are established, then calculations of lower energy PED's ($h\nu \lesssim 25$ eV), which show structure in the joint density of states, should become more useful and hopefully will yield much additional information about both valence and conduction bands. Such photoemission measurements and interpretations for semiconductors have yielded much information in the past [5], [27], mainly for $h\nu \lesssim 11.6$ eV and for the upper valence bands, and are expected to yield additional information at higher energies which have become available with the use of synchrotron radiation sources.

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