

uv Photoemission Measurements of the Upper d Levels in the IIB-VIA Compounds

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Photoemission measurements have been made of the upper d levels in ZnO, ZnSe, ZnTe, CdS, CdSe, CdTe, HgSe, and HgTe using 21.2-eV (584-Å) and 16.8-eV (740-Å) radiation. All the samples except for HgSe and HgTe were cleaved and measured in an oil-free ion-pumped vacuum system at a pressure in the 10^{-7} - 10^{-8} Torr range. The results agree extremely well with values obtained by x-ray-induced-electron-emission spectroscopy. The spectra obtained for HgSe and HgTe make it possible to positively verify the identification of certain peaks observed in photoemission spectra of the IIB-VIA compounds as being due to the upper d levels. The photoemission results reported in this study are also compared with both reflectivity and energy-loss measurements to obtain information about the optical density of states in the conduction bands of these compounds.

I. INTRODUCTION

X-ray-induced photoemission spectroscopy is being used more and more frequently as a highly precise method of measuring chemical shifts in core-level-electron binding energies and of studying the electron density-of-states distributions in solids. There are, however, several problems associated with the use of this technique in the study of insulating and semiconducting samples.

One of these problems concerns the reference level with respect to which the electron energy values are reported. In x-ray-induced electron spectroscopy this reference level is the Fermi level of the measured sample. For semiconductors, the location of the Fermi level may be anywhere within the band gap of the material, depending on the doping of the sample and the conditions, such as temperature of the sample and intensity of the incident radiation, present during the measurement. Consequently, in order to compare the results of x-ray-induced electron spectroscopy for semiconductors with other experimentally determined values and with theoretical calculations, it has been necessary to make some assumption concerning the location of the Fermi level with respect to the band structure of the measured material. In previous work on the IIB-VIA compounds, it was assumed that the Fermi level was located at the center of the band gap.

Another problem encountered in x-ray-induced photoemission spectroscopy concerns the buildup of charge on the surface of samples which are poor

conductors. Such a buildup can cause a shift of up to several eV in measured electron energy distributions and, if not accounted for, can lead to corresponding errors in the reported energy values. A procedure for determining the magnitude of this charge buildup was developed in the previously mentioned x-ray-induced-photoemission work on the IIB-VIA compounds.¹

The photoemission measurements reported in this present paper were made in order to better justify the assumption made as to the position of the Fermi level and the procedure used to correct for charge buildup. These measurements were made on several IIB-VIA compounds using 21.2- and 16.8-eV radiation. The relatively high excitation energies of 16.8 and 21.2 eV allow photoelectric interactions with the upper d levels in the IIB-VIA compounds. Since these levels were also measured in the previous work using x-ray-induced-electron spectroscopy, it was possible to work with a portion of the energy spectrum where the results of the two techniques could be compared. Since the uv measurements yield values with respect to the top of the valence band, the x-ray values should all be larger by one-half of the respective band gaps if both the assumption concerning the location of the Fermi level and the charge-buildup-correction method were valid.

Section II of this paper consists of a description of the experimental procedure and apparatus. The results of the photoemission measurements on eight of the IIB-VIA compounds are presented and discussed in Sec. III. This section also contains

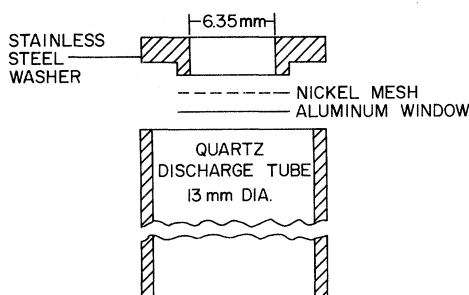


FIG. 1. Schematic drawing of the aluminum window assembly. The 1500-Å-thick aluminum window is supported by a nickel mesh and stainless-steel washer.

a discussion of the Fermi-level assumption, the procedure for correcting charge buildup, and the inferences which can be made from this data as to the high-density-of-states regions in the conduction band.

II. EXPERIMENTAL METHOD

The locations of the d levels were determined by measuring the energy distributions of photoemitted electrons. These were obtained by using the ac conductance method developed by Spicer and Berglund² and improved by Eden.³ This consists of measuring the small-signal ac conductance of a photodiode as a function of diode retarding potential. The sample serves as the emitter of the diode and a stainless-steel can in the shape of a half-cylinder and surrounding the sample serves as the collector. The ac conductance was measured by means of a phase-sensitive detector and the electron distribution curves were recorded by an x - y plotter.

The photodiode assembly was contained in an oil-free ion-pumped vacuum system separated from the light source by a thin (1500 Å) aluminum window supported on a nickel mesh. A schematic drawing of this assembly is shown in Fig. 1. This window is thin enough to allow the transmission of far uv radiation from the lamp but still free enough of pinholes to maintain a pressure of 10^{-7} to 10^{-8} Torr in the chamber when the light source is at a pressure of 1 Torr. The source itself was a rare-gas resonance lamp similar to the type previously described by Gorden *et al.*⁴ Helium was pumped through the lamp to produce the radiation at 21.2 eV and neon was used to produce the radiation at 16.8 eV. Power to maintain a discharge in the lamp was supplied by a microwave generator capable of furnishing up to 100 W at 2450 MHz. The actual maximum power used in this experiment was 40 W since the discharge tended to become unstable at higher values. An Evenson cavity was

used to obtain maximum power transfer to the lamp.

All of the samples except HgSe and HgTe were cleaved in a vacuum of 10^{-7} to 10^{-8} Torr immediately before making the measurements. Experimental difficulties made it necessary to cleave the HgSe and HgTe samples in air before insertion into the vacuum chamber. Although this procedure appeared to work well in the case of the Hg compounds, as is evidenced by the detailed spectra obtained, external cleaving was not feasible for most of the Cd and Zn compounds. In fact, for several of these compounds, considerable change occurred in peak heights in the electron distribution curve over the first hour after cleavage even for a chamber pressure as low as 10^{-7} Torr. Attainment of lower pressures and thus better surface conditions was prohibited by the construction of the Al window which could not withstand a system bakeout.

The samples used were oriented single crystals typically $6 \times 6 \times 10$ mm. Orientation was such that easy cleavage could be performed. The uv light was incident on the 6×6 -mm surface.

III. RESULTS AND DISCUSSION

The results of the uv photoemission measurements using 21.2- and 16.8-eV radiation on several of the IIB-VIA compounds are given in Table I. As a result of these measurements we were able to determine, with respect to the top of the respective valence bands, the Zn $3d$ electron energy level in ZnO, ZnSe, and ZnTe; the Cd $4d$ level in CdS, CdSe, and CdTe; and the $5d$ levels in HgSe and HgTe. Typical electron distribution curves obtained for HgTe are shown in Fig. 2. The peaks of interest in this study are those marked as Hg $5d_{\frac{3}{2}}$ and $5d_{\frac{5}{2}}$. Interpretation and analysis of this type of data has already been discussed by Spicer and co-workers.^{5,6}

A. Identification of d Levels

Any structure in an electron distribution curve (EDC) which is due to nondirect transitions from a high-density-of-states region in the valence band at an energy E_0 below the top of the valence band must satisfy the equation

$$E = h\nu - E_0,$$

where $h\nu$ is the photon energy and E is the photoelectron energy with respect to the top of the valence band. Since the energy values of the upper d levels in the compounds measured in this study should have essentially no wave-vector dependence, any peaks in the EDC produced by electrons from these levels should satisfy this equation. Consequently, a " d " peak in a 21.2-eV curve should be shifted by 4.4 eV from that in a 16.8-eV curve. This is clearly the case for the HgTe spectra

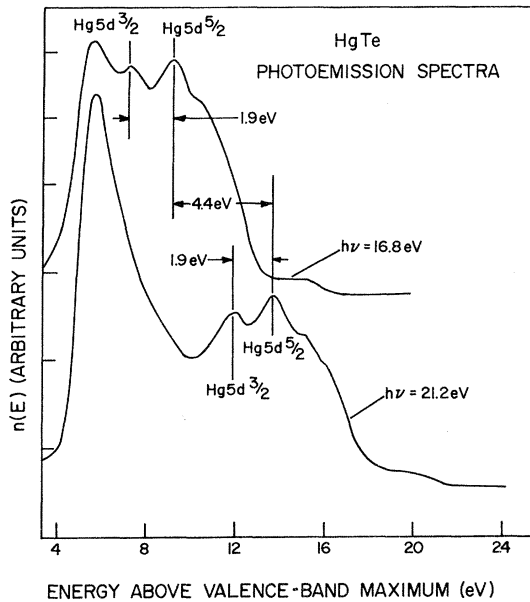


FIG. 2. Observed electron energy distributions from HgTe when $h\nu = 21.2$ and 16.8 eV.

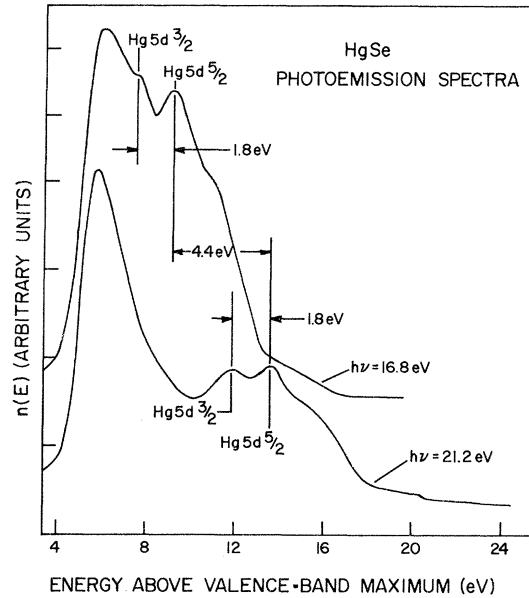


FIG. 3. Observed electron energy distributions from HgSe when $h\nu = 21.2$ and 16.8 eV.

shown in Fig. 2. This same shift is observed in the HgSe spectra shown in Fig. 3.

The spin-orbit splitting of the Hg 5*d* level can also be clearly seen in Figs. 2 and 3. This splitting is 1.9 eV in HgTe and 1.8 eV in HgSe. This splitting was also clearly seen in the x-ray photoemission spectra from these compounds. The splitting of this peak in addition to the 4.4-eV shift indicates that it is due to electrons from the Hg 5*d* level.

The spectra obtained from the Cd and Zn compounds have very similar structure to that of the Hg compounds. An example of this is seen in the

photoemission spectra of CdSe shown in Fig. 4. As a result of the structural similarity in the curves from Hg, Cd, and Zn compounds, corresponding peaks in each spectrum have been identified as arising from electrons from like bands. In this manner the *d*-band peaks in the Cd and Zn compounds were assigned. Thus the peak marked on the CdSe 21.2-eV EDC is assumed to result from transitions from the Cd 4*d* level. In this case the 4.4-eV shift is not observed since the *d* peak would be moved directly under the large conduction-band peak as a result of this shift. Furthermore since the spin-orbit splitting in CdSe is less than half

TABLE I. Comparison of uv- and x-ray-induced photoemission measurements and uv reflectivity and electron energy-loss values for the Zn 3*d*, Cd 4*d*, and Hg 5*d* electron energy levels in the indicated IIB-VIA compounds. All values are in eV and the photoemission values are given with respect to the top of the respective valence bands.

Compound	uv electron emission	X-ray electron emission	Transition energy	ΔE	<i>E</i> above CB minimum
ZnO	8.5 ± 0.4	8.6 ± 0.2			
ZnSe	8.9 ± 0.4	9.0 ± 0.2	13.7 ^a	4.8	2.0
ZnTe	9.1 ± 0.4	8.7 ± 0.4	12.4 ^a	3.3	1.9
CdS	10.0 ± 0.4	10.1 ± 0.2	14.4 ^a	4.4	1.9
CdSe	10.7 ± 0.4	10.6 ± 0.2	13.8 ^a	3.1	1.3
CdTe	10.5 ± 0.4	10.3 ± 0.5	13.6 ^a	3.1	1.5
HgSe	7.4 ± 0.4	7.6 ± 0.2	9.7 ^b	2.3	2.3
	9.2 ± 0.4	9.4 ± 0.2	11.1 ^b	1.9	1.9
HgTe	7.6 ± 0.4	7.5 ± 0.2	9.7 ^c	2.1	2.1
	9.5 ± 0.4	9.4 ± 0.2	11.3 ^c	1.8	1.8

^aElectron energy loss, R. Hengehold and F. Pedrotti (unpublished).

^buv reflectivity, W. Scouler and G. Wright, Phys. Rev. **133**, A736 (1964).

^cuv reflectivity, M. Cardona and D. Greenaway, Phys. Rev. **131**, 98 (1963).

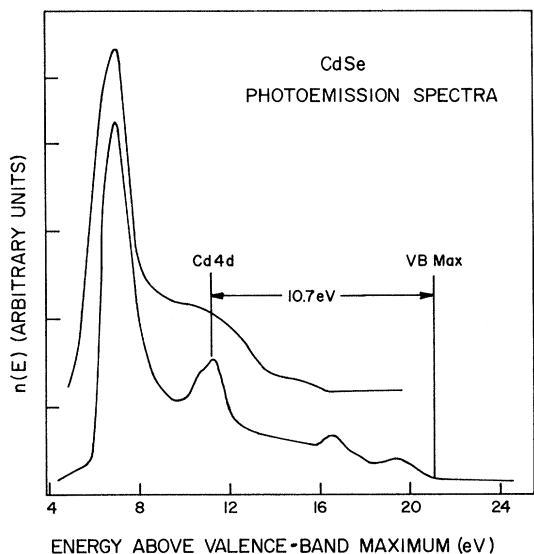


FIG. 4. Observed electron energy distributions from CdSe when $h\nu=21.2$ and 16.8 eV.

as large as it is in the Hg compounds, it was also not observed due to the resolution limit of the system. This is true of all the Cd and Zn compounds. Nevertheless, even though the spin-orbit splitting could not be observed in the Cd and Zn compounds and the 4.4-eV energy shift could be observed only in some of the compounds, the comparison of the structure in the EDC's from the Cd and Zn compounds with the Hg compounds allows identification of the d -band peak.

Qualitatively similar uv-induced-electron-emission distributions have been measured by Spicer and co-workers for four of the eight compounds which we measured, namely, ZnO,⁷ CdS,⁶ CdSe,⁶ and CdTe.⁵ These authors also assign the dominant peak in this energy region to electron emission from the Zn $3d$ and Cd $4d$ levels. Their energy values reported for these levels, 7.5 ± 0.2 eV, 9.2 ± 0.2 eV, 9.9 ± 0.2 eV, and 10.3 ± 0.2 eV, respectively, are consistently lower than our best values except for CdTe, though only slightly (0.2 eV) outside the experimental accuracies. The largest experimental uncertainty usually arises from the determination of the upper edge of the valence band which appears at the onset of the EDC and like any threshold determination is much more difficult to determine than the location of maxima. It is difficult to say whether this is the reason for the difference in results, which appears to be systematic.

A comparison of the experimentally determined values of the d -level location and the presently available theoretical estimates has been made previously by us in conjunction with the data determined by x-ray-induced photoemission¹ and for

ZnO, also by Powell *et al.*⁷

B. Comparison with X-Ray Data

As was mentioned in the Introduction, there are two problems involved with the application of x-ray-induced-electron-emission spectroscopy to semiconductors. The first of these problems is associated with the position of the Fermi level in these compounds. In previous work on IIB-VIA compounds, it was assumed that the Fermi level was located at the center of the band gap. This assumption is based upon the results of two earlier studies using x-ray-induced electron spectroscopy on semiconductors.^{8,9} In neither study did the investigators find an observable shift in the measured binding energies as a function of the doping of the samples. One possible explanation for these results is that the Fermi level near the surface of the samples is shifted to a value near its intrinsic position during the course of the x-ray measurements as a result of the very large number of electron-hole pairs produced by the x-ray radiation.

The second problem mentioned earlier concerned the buildup of charge on the surface of samples which are poor conductors. Such a buildup could cause a shift of up to several eV in measured energy distributions, which, if not accounted for, can lead to corresponding errors in the reported energy values. In the previous x-ray-induced-electron-emission work on IIB-VIA compounds,¹ a procedure was developed to determine the magnitude of this charge buildup. This procedure involved a two-step process. First, a few samples of each measured compound were prepared with a very thin layer of carbon deposited on the surface. The energies of several intense peaks in the spectra from these samples were then measured with respect to the carbon $1s$ peak which has a reported energy value of 283.8 eV for similarly prepared carbon. A second set of samples, without carbon, were then studied and all peaks in these spectra were measured with respect to the above intense lines. From the scatter in measurements on different samples of the same materials, it was estimated that this technique allowed the determination of energy levels to within ± 0.2 eV. It should be noted, however, that this technique does depend upon the assumption that the energy shift due to charge buildup is the same for both the carbon $1s$ line and the sample lines.

The measurements reported in this study allow us to test the validity of these two assumptions. This can be accomplished by comparing the results of uv-induced electron emission and x-ray-induced electron emission over the same energy range. Since the uv measurements yield values with respect to the top of the valence band, the

x-ray values should all be larger by one-half the respective band gaps if both the assumption concerning the location of the Fermi level and the charge buildup correction technique are correct.

The results of both the uv- and x-ray-induced-electron-emission measurements for the d bands are given in Table I. The values obtained from uv-induced electron emission are given with respect to the top of the valence band. The x-ray-induced-electron-emission values are those reported earlier¹ with one-half the respective band gap subtracted from each. If the above assumptions are valid, this should produce energy values with respect to the top of the valence band. As can be seen from Table I, the agreement between these values is excellent and thus these present measurements strongly support the assumptions and procedures used in the x-ray-induced-electron-emission measurements reported earlier.

C. Optical Density of States

It has been shown before^{1, 5, 6} that the results of both x-ray- and uv-induced electron spectroscopy can be used in conjunction with the results of optical reflectivity and electron energy-loss measurements to obtain information as to the optical density of states. In particular the photoemission results reported in this study have been compared with both reflectivity and energy-loss measurements to determine the high-density-of-states region in the conduction bands of the IIB-VIA compounds. Such an analysis is possible since the optical reflectivity and electron energy-loss measurements yield energy values for transitions between the d level and states in the conduction band whereas photoemission measurements yield values for the location of the d levels with respect to the top of the valence band. By taking the difference between the values yielded by these two experiments, one obtains, to within a few tenths of an eV, the locations of the maxima in the conduction-band optical density of states relative to the lower edge of the conduction band.

In Table I we have listed the transition energies between the d band and the conduction band as obtained from electron energy-loss measurements or optical reflectivity. The energy-loss values have been obtained by electron reflection from clean-cleaved single-crystal surfaces. The energy-loss values have been chosen for comparison in most cases since they are generally more precise in the energy range above the LiF cutoff (11 eV). In the case of HgSe and HgTe no energy-loss values are available and thus optical reflectivity results were used. For ZnO both energy-loss and reflectivity curves are available; however, no clear identification of the d -band transition is possible at present.

The difference between the two types of mea-

surements is also listed in Table I. This value represents the energy difference between the top of the valence band and the high-density point in the conduction band associated with the d -band transitions. As can be seen, all high-density-of-states points are 1–2 eV above the conduction-band minimum.

Optical absorption measurements have also been reported for transitions from the Zn $3p$ levels to the conduction band in ZnS, ZnSe, and ZnTe.¹⁰ In conjunction with our x-ray-induced-electron-emission data, one can perform a similar analysis and arrive at conduction-band density-of-states maxima between 0.7 and 1.9 eV above the conduction-band minima. The slight difference between the optical-density-of-states maxima of the conduction band for the transitions originating from the Zn $3d$ levels and those from the Zn $3p$ levels, while only in a few cases outside the experimental error limits, might be real and reflect the different symmetry related transition probabilities which are involved in transitions to different parts of the conduction band.

IV. CONCLUSION

The energy location of the upper d levels of the cations has been determined with respect to the respective valence-band maxima for a number of II-VI compounds by uv-induced-electron-emission spectroscopy. The results agree well with values derived from previous x-ray-induced-electron-emission measurements. Thus, two remaining uncertainties can be removed from the interpretation of x-ray-induced-electron-emission experiments, namely, the effect of charge buildup and the location of the Fermi level. Therefore, the validity of the x-ray-induced-electron-emission measurements, which cover a much larger energy range than the uv-induced-electron-emission measurements, has been confirmed as a tool for obtaining energy levels of upper and lower core states with respect to some known point in the band structure, i. e., the top of the valence band.

Consequently, the results of x-ray-induced-electron-emission studies can be used for the interpretation of electronic transition spectra (uv absorption and reflectivity or electron energy-loss spectra) in order to determine the final state of the respective transitions in relation to a singular point in the band structure. For example, a transition's terminal state, which corresponds to a maximum or maxima in the optical density of states, can be determined with respect to the minimum of the conduction band. It is also observed that the maxima of the conduction-band optical-density-of-states distributions which are determined in this manner may well depend on the origin of the transition because of symmetry-influenced

transition probabilities. In comparing such results to theoretical band-structure calculations this, however, is rather a virtue because it would allow a comparison not only with the total density of states of the conduction band but also with the relative fractions having different symmetries. The above illustrates both the complimentary nature of electron-transition measurements (between core states and the conduction band) and induced-electron-emission measurements and the

benefits which can result from a combination of these experiments.

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Phonon Conductivity of InAs

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The low-temperature thermal conductivity K of undoped n -type InAs has been measured between 5 and 300 °K, and analyzed on the basis of three different approaches, each including boundary-effect, mass-difference-scattering, and phonon-phonon processes. Various required parameters, mainly the phonon frequencies at zone boundary, have been deduced for InAs from known values of these parameters in the III-V compounds Si and Ge. Callaway's expression of K is found to give satisfactory agreement from low temperature up to temperatures slightly beyond the maximum. At low temperatures boundary and mass-difference scattering predominate. The Holland two-mode formulation explains the temperature dependence of K in the entire temperature range by emphasizing the predominant contribution of transverse phonons at low and high temperatures. The more elaborate approach, two-mode heat conduction using three-phonon relaxation times deduced from Guthrie's analysis and a quadratic relation (q, ω), suggests that at high temperatures the contribution of longitudinal phonons to K becomes comparable to that of transverse phonons. Moreover, four-phonon processes have been tentatively included in order to fit the experimental data in the higher-temperature range. It appears that no conclusion as to the relative contributions of transverse and longitudinal phonons may at present be satisfactorily established for InAs at high temperature.

INTRODUCTION

In the absence of electron-phonon scattering, three main phonon scatterings are generally taken into account in the low-temperature thermal conductivity K of pure insulators and semiconductors: boundary-effect, mass-difference-scattering, and phonon-phonon interactions. While the first two mechanisms are in satisfactory agreement with experimental results, three-phonon processes are still not well defined. Different relaxation times have been considered for the latter, depending on

the type of the processes (N or U), the polarization mode, and the temperature interval.

The Callaway expression¹ for phonon conductivity, which includes the above three mechanisms, considers an average acoustic branch in the Debye approximation. It has been shown that this expression can account for the data from low temperature up to temperatures slightly higher than the maximum in K . A refined approach to the problem has been carried out by Holland,² who distinguished between conduction by transverse and longitudinal phonons. This formulation has been successfully