Electronic Core Levels of Zinc Chalcogenides

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X-ray-induced photoemission studies were used to determine the energy levels of core electrons in ZnO, ZnS, ZnSe, and ZnTe. The investigated energy range extends from the Fermi level to about 1200 eV below the valence band. The observed Auger transitions in these compounds are in good agreement with the measured energy levels. Some of the uncertainties in using this technique for the study of electron energy levels in semiconducting or insulating crystals were investigated and are discussed. The measured energy levels are compared with published experimental data for the respective pure elements. Comparison is also made with energy values predicted by several different types of theoretical calculations. Significant conclusions are: (i) The location of the Zn $3d$ level in the zinc chalcogenides has been unambiguously determined and (ii) the discrepancy between our measured values and the theoretically determined energy values is angular momentum dependent.

INTRODUCTION

The energy levels of electrons in the inner, closed shells of atoms are primarily determined by the positive charge of the nucleus, the total number of electrons surrounding the nucleus, and the distribution of these electrons in the various allowed orbitals. The mutual interaction between electrons plays an additional role which in terms of the one-electron formalisms is dealt with under the terminology "exchange" and "correlation."

When free atoms condense to form solids, especially crystalline solids, the outer electronic shells spread into bands because of the interactions among the outer-shell electrons of the many atoms. Ionic bonding can result if atoms of different valence make up the solid and if the electrons in the bands rearrange so that charge is transferred between the atoms. The effect on core states in such a case is a shift in energy corresponding to the redistribution of charge. Even without ionic bonding, however, the core states of an atom will be shifted to some degree during the transition into the solid phase by the so-called "solid-state effects." These are due to the overlap of atomic potentials and to the symmetry of the crystal.

Several theoretical approaches of varying degrees of complexity have been used to calculate the electron energy levels in free atoms and in crystalline solids. Many data have been published on the energy levels of electrons in samples of the elements in pure form. The purpose of the present work is to present our experimentally determined values for the electronic core levels of the partially ionic zinc chalcogenide crystals and to compare these data with the above-mentioned experimental data and theoretical calculations.

X-ray absorption or emission techniques have conventionally been used to measure the electronic core levels in solids. More recently, outer core states of selected materials have been investigated to a depth of about 150 eV by measuring the reflection and absorption of synchrotron-produced ultraviolet (uv) radiation,

and also by measuring the energy loss of monochromatic beams of electrons. All these methods measure energy differences by inducing transitions between electronic levels or by exciting collective modes (e.g., plasmons). The peaks in the uv spectra and in electron-loss measurements correspond to electronic transitions from upper valence-band states to upper conduction-band states, and from lower valence-band states or upper core states to the lower edge of the conduction band and to excitations of plasmons. Considerable effort and ingenuity have to be devoted to the proper identification of features in these spectra.

Another method for the investigation of a comparable energy region which is based on the photoelectric effect, extended to the x-ray region, has been developed mainly by Siegbahn and his co-workers at Uppsala during the past ten years. It has been used by these investigators with considerable success to measure the electron energy levels of many of the elements and to measure the core states of a few selected compounds. Siegbahn has also elaborated convincingly in a recent summary[1] on the practical advantage of this method with respect to x-ray absorption and emission measurements. The principal peaks in the spectra gained by this method represent the sequence of the "optical" density of electronic states below the Fermi level. In comparison with the above-mentioned group of experiments the interpretation is much less ambiguous. For example, structure due to the excitation of plasmons, which is observable in uv absorption and reflection spectra, and which is dominant in electron-loss spectra, will only occur as relatively small satellite peaks to the principal peaks in a photoemission spectrum.

For our investigations we used the x-ray-induced photoemission technique which is relatively new, and little information is available about its application to the measurement of electron energy levels in semiconducting or insulating crystals. Consequently, we will go into some detail when discussing a few of the uncertainties concerning its use for making measurements of this type.
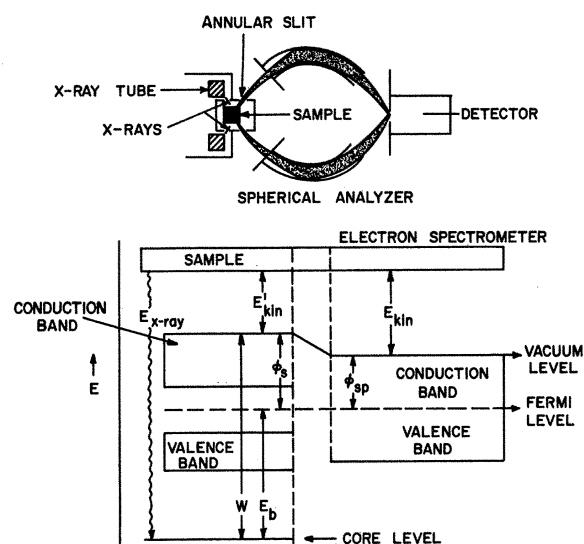
FIG. 1. Top section shows a schematic of the instrument. X rays generated by an annular Al anode strike the sample, which is usually in the shape of a cylinder. The kinetic energy of emitted electrons is analyzed in a spherical electrostatic analyzer. The bottom section shows the energy-level diagrams of the spectrometer (metal) and the sample (semiconductor).

EXPERIMENTAL METHOD

Our measurements were made with a Varian Associates IEE spectrometer equipped with an aluminum x-ray anode and a spherical electrostatic electron spectrometer. Most of the measurements reported in the next section were made with an electron analyzer potential of 100 V which yielded an effective resolution of 2.7 eV full width at half-maximum for the carbon $1s$ peak. Peak positions should be considered accurate to ± 0.2 eV (not including systematic errors).

The principles of operation are as follows: AlK$\alpha_{1,2}$ x rays from the aluminum x-ray anode with an energy of 1486.6 eV and a half-width of 1.0 eV interact photoelectrically with electrons in the sample. If the binding energy W of the electron is less than the energy of the x ray and if all inelastic interactions of the electron after it is excited can be neglected, then the electron is emitted from the sample with a kinetic energy E_{kin}', given by

$$E_{kin}' = E_{x\,ray} - W. \qquad (1)$$

Siegbahn demonstrated that indeed a substantial number of electrons are emitted without such inelastic interactions and that the observed kinetic-energy spectra can therefore be associated with the electronic energy levels.[2]

Every principal peak in the emission spectrum which corresponds to electron emission from a core level without inelastic scattering is usually accompanied by a tail region, which in our case was far less intense and much broader than the principal peak, and which corre-

sponds to electrons that left the solid with lower kinetic energy. The electrons in this tail region originate from the same core level but undergo inelastic interactions of one type or another before leaving the sample. One therefore expects to find structure in the tail region that is similar to that observed in electron-loss measurements because of the correspondence of the monochromatic electrons created by the interaction of x rays with electrons in the same core level and the monochromatic electrons used as the primary beam in electron-loss measurements. The energy losses due to the excitation of plasmons should be detectable as satellite peaks in these tail regions. We will only be concerned with the principal peaks in the following discussion.

Figure 1 shows a schematic of the method applied to a semiconductor or insulator. E_{kin}' is the kinetic energy of the emitted electron with respect to the vacuum level of the sample. The kinetic energy E_{kin} actually measured by the electron spectrometer, however, is measured with respect to the vacuum level of the spectrometer material. If the sample and spectrometer are in good electrical contact, and if the system is in equilibrium, then the Fermi levels of the sample and spectrometer material will coincide. If the work function ϕ_{sp} of the spectrometer material is known, the binding energy of the electron E_b with respect to the Fermi level of the sample can be determined by using the following equation:

$$E_b = E_{x\,ray} - E_{kin}' - \phi_s = E_{x\,ray} - E_{kin} - \phi_{sp}, \qquad (2)$$

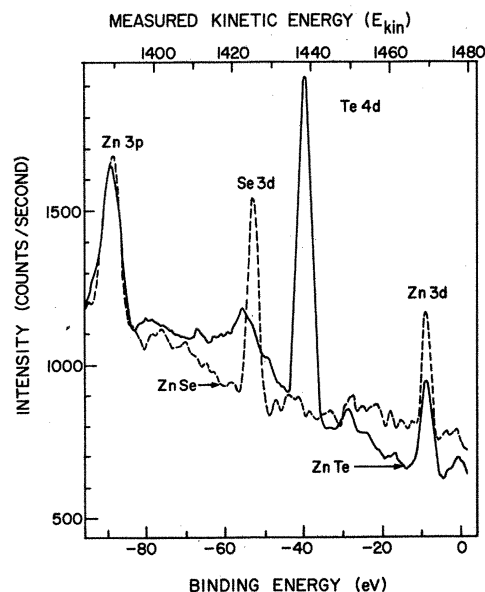where ϕ_s is the work function of the sample. The work

FIG. 2. Electron emission spectrum of ZnSe and ZnTe. The upper scale denotes measured kinetic energy of the electrons, E_{kin}; lower scale denotes the electron binding energy with reference to the Fermi level of the respective compounds, E_b.

function of the spectrometer can be obtained by calibration with respect to a known electron binding energy. We used the carbon $1s$ level at 283.8 eV for this purpose.[3]

For insulators there exists the justifiable questions whether the necessary alignment of the Fermi level has taken place and whether an equilibrium condition is maintained in the sample-spectrometer system during the process of the measurement. One could expect an x-ray-induced Fermi-level shift and also a charge buildup on the sample surface due to the emission of electrons and the poor conductivity of the sample. In order to investigate these questions, we repeated measurements on ZnSe and the carbon $1s$ level under various conditions.

Normal sample preparation consisted of taking a single crystal and crushing it into pieces of about 0.25-mm^3 volume just before putting it into the sample chamber. A sample of this type was measured with maximum x-ray intensity (70-mA current) and with less than half the maximum intensity (30-mA current). No shifts were detectable in the measured E_{kin} values for the ZnSe core levels or the C $1s$ calibration level. Some carbon black was deposited on part of another sample of the same type just before insertion into the sample chamber. This time the measured E_{kin} values for the ZnSe core levels all shifted to higher values by an amount less than 1 eV. However, the E_{kin} value for

FIG. 4. Electron emission spectrum of ZnO. The upper scale shows E_{kin}; the lower scale shows the electron binding energy E_b. Additional peaks were identified as the result of Auger transitions and labeled correspondingly.

the C $1s$ level also shifted by the same amount so that the calculated binding energies agreed with the previous results.

For comparison, we also performed a series of measurements on two large single crystals of ZnSe about 3 mm thick and with faces about 8×5 mm. Fine copper wires were used to attach the crystals to the sample holder in such a manner that good electrical contact was made between the sample holder (spectrometer) and those surfaces of the crystals that were exposed to the x rays. This time the measured E_{kin} values for all levels increased by 2.5 eV, but again the calculated binding energies agreed with the previous results. The point is that the value obtained for ϕ_{sp} by using Eq. (2) and a reference energy level that can be measured at the same time as the sample is not the true spectrometer work function. It includes the shift in E_{kin} due to charge buildup on the surface of the sample. The measurements on the sample consisting of two crystals with contacts on their surface indicated the least amount of charge buildup. The signal-to-noise ratio for this sample, however, was much poorer than for the crushed samples because of the reduced surface area exposed to x rays. The results of the measurements using different x-ray intensities indicate that the charge buildup, for the particular sample measured, must have reached an equilibrium at some value of the x-ray intensity corresponding to a current of less than 30 mA.

For a useful comparison with energy-band calculations, a further problem exists, that of locating the Fermi level with respect to some known point in the band structure. This is necessary because all of the binding energies we determine are with respect to the Fermi level.

In the following, we have assumed that the Fermi level lies halfway between the top of the valence band and the bottom of the conduction band. Any deviation of the actual case from this assumption will result in a constant shift of all the levels for any particular sample.

FIG. 3. Electron emission spectrum of the zinc chalcogenides in a spectral region that corresponds to electronic states between the Fermi level ($E_b = 0$ eV) and 16 eV below it. The peaks correspond to the Zn $3d$ levels in the respective compounds. The line indicates the position of the Zn $3d$ level in Zn metal. The vertical scale for each compound has been arbitrarily shifted in order to clarify the figure.

TABLE I. Electronic core levels of Zn in metallic zinc and in Zn compounds. Energy values are in eV. The experimental values are determined with reference to the Fermi level of each sample. The theoretical values for the compounds refer to the center of the respective band gaps, those for the zinc atom to its ionization potential. Values in parentheses are from unresolved doublets. In each Expt.-Theor. column, for each line, the theoretical values are below the experimental values.

Element Zn Expt.[a] Theor.[c]	Δ	Level	ZnO Expt.[b]	ZnS Expt.[b] Theor.[d]	Δ	ZnSe Expt.[b] Theor.[d]	Δ	ZnTe Expt.[b] Theor.[d]	Δ
9 / 17.4	8.5	Zn $3d$	9.3	9.5 / 16.1	6.6	9.4 / 14.1	4.7	9.1 / 14.0	4.9
(87) / 91.8	(5.8)	Zn $3p\,\frac{3}{2}$	87.8	88.1 / 89.6	(0.5)	87.7 / 87.6	(−1.7)	87.7 / 87.4	(−1.3)
(87) / 94.9	(5.8)	Zn $3p\,\frac{1}{2}$	90.7	91.1 / 89.6	(0.5)	90.4 / 87.6	(−1.7)	90.6 / 87.4	(−1.3)
137 / 138.9		Zn $3s$	138.6	139.1 / 132.2	−6.9	138.0 / 130.2	−7.8	138.8 / 130.0	−8.8
1021 / 1033.5	12.5	Zn $2p\,\frac{3}{2}$	1020.2	1020.8 / 1027.0	(−1.5)	1020.6 / 1024.9	(−3.4)	1020.4 / 1024.7	(−3.3)
1044 / 1057.4	13.4	Zn $2p\,\frac{1}{2}$	1043.3	1043.8 / 1027.0	(−1.5)	1043.6 / 1024.9	(−3.4)	1043.4 / 1024.7	(−3.3)
1194 / 1191.4	−2.6	Zn $2s$	1194.2	1194.8 / 1157.2	−37.6	1194.4 / 1155.1	−39.3	1194.1 / 1155.8	−38.3

[a] From electron emission data on Zn metal in Ref. 1, p. 225.
[b] Present work on Zn compounds.
[c] Self-consistent atomic potential calculations, Ref. 10.

[d] Self-consistent OPW calculations for Zn compounds, Ref. 8, calculated band gaps for 0°K: ZnS, 3.8 eV; ZnSe, 2.8 eV; ZnTe, 2.4 eV.

TABLE II. Experimental Auger electron energies (eV) for Zn in the zinc chalcogenides. Values calculated in the right section are based on Zn core levels in Zn compounds, in the left column on such in metallic Zn. In each Expt.-Calc. column, for each line, the calculated values are below the experimental values.

Element Zn Calc.	Transition	ZnO Expt. Calc.	ZnS Expt. Calc.	ZnSe Expt. Calc.	ZnTe Expt. Calc.
1017	$L_{II}M_{IV,V}M_{IV,V}$	1012.6 / 1016.0	1014.1 / 1016.3	1014.6 / 1016.2	1015.2 / 1016.3
994	$L_{III}M_{IV,V}M_{IV,V}$	990.1 / 992.9	991.1 / 992.3	989.6 / 992.2	991.8 / 992.3
939	$L_{II}M_{II,III}M_{IV,V}$	932.3 / 936.0	935.6 / 936.2	935.9 / 936.5	935.6 / 936.2
916	$L_{III}M_{II,III}M_{IV,V}$	910.6 / 912.9	912.6 / 913.2	911.6 / 913.5	...

Such a shift should certainly be no larger than one-half the energy gap. This would result in higher values for the n-type materials ZnO, ZnS, and ZnSe (maximum shift of 1.6, 1.8, and 1.1 eV, respectively) and a shift to lower values for the p-type sample of ZnTe (maximum shift 0.8 eV). All samples were of relatively high resistivity. Wurtzite-type ZnO was grown from the vapor phase in the form of platelets. ZnS and ZnSe were melt grown under pressure and were cubic in structure. The ZnS samples had many microscopic stacking faults resulting in a number of polytypes. This should have a negligible effect on the core states, however, since the band gap only differs by 0.07 eV between wurtzite and zinc-blende ZnS.[4] The ZnTe crystals were also grown from a melt and were of perfect cubic structure.

To conclude this section, we point out that the *energy differences* between the measured electronic levels of the compounds we are reporting on are determined to within ±0.4 eV even though there are uncertainties in the actual location of the Fermi level.

EXPERIMENTAL RESULTS

In order to demonstrate the experimental results and to allow judgments on signal-to-noise ratios, three examples of the measurements are presented.

Figure 2 shows the electron spectrum $(1486 > E_{\text{kin}} > 1386 \text{ eV})$, which corresponds to the electronic energy levels between the Fermi level and a depth of 100 eV, for ZnTe (solid line) and for ZnSe (dashed line). The dominant peaks are easily identified with the corresponding atomic core levels as indicated. Many of the smaller peaks are systematic and reproducible but not yet well enough understood to comment on. The electronic states of the valence bands, composed of the Se $4p$ and $4s$ states in ZnSe and of Te $5p$ and $5s$ states in ZnTe, are not contributing much to the spectrum, as an inspection of the first 10 to 15 eV shows. This is because their density of states here is relatively small and their coupling to the kilovolt x rays is relatively weak.

In Fig. 3, the least-bound peak Zn $3d$ is compared among the four investigated zinc compounds. The vertical line indicates the position of the Zn $3d$ level in pure zinc as determined by Nordling[5] if the Fermi levels for the element and compounds are equated. For all compounds, the Zn $3d$ level has shifted toward higher binding energies, which is symptomatic of an additional positive charge on the zinc atom in the compound, and which was to be expected due to the ionic character of the bonding.

Figure 4 illustrates a similar point for the $1s$ state of oxygen in ZnO. The shift toward a lower binding energy is indicative of the extra negative charge on oxygen in ZnO. The other peaks shown here are due to electrons emitted by the Auger process. Their half-width is clearly wider because the inherent width of another core level contributes to them. Many such peaks could be identified and they are summarized later in Table II.

The experimental values in the right part of Table I are a summary of our measurements of the zinc levels in ZnO, ZnS, ZnSe, and ZnTe, analogous to the detail of the Zn $3d$ level illustrated in Fig. 3. The zero of the energy scale is at the Fermi level of each sample.

Nordling's experimental values for zinc metal are listed in the left part of the table for comparison. His values are given with respect to the Fermi level in zinc metal. To the extent that a comparison based on scales with reference to the Fermi level is justifiable, ZnO, ZnS, ZnSe, and ZnTe show the effect of tighter binding for the $3d$, $3p$, $3s$, and $2s$ levels. The results for the $2p$ level cannot be explained similarly. We also observe the splitting of the two Zn $3p$ levels, $\frac{1}{2}$ and $\frac{3}{2}$, which Nordling had not resolved for zinc metal.

Recently the zinc $3p$ levels of ZnS, ZnSe, and ZnTe have been observed in optical absorption measurements by Cardona and Haensel[6] using synchrotron radiation. They ascribe the observed peaks to transitions from the Zn $3p$ levels to the conduction band. In order to compare these values with our measurements which are referred to the Fermi level, approximately at center of gap, we subtracted one-half of the respective energy gap from Cardona's absorption values. His energies for the Zn $3p$ levels are then: 89.0 and 91.85 eV for ZnS, 89.2 and 91.95 eV for ZnSe, and 88.4 and 91.8 for ZnTe. Even so, all his values appear to be on the order of 0.7–1.6 eV higher than our measurements, which partially might be understood if one assumes that the transitions at the absorption peak will correspond to transitions to some point in the conduction band which is considerably above the bottom of the band. Where such a point lies, however, can only be checked by a detailed consideration of the density-of-states distribution in the conduction band and the respective transition probabilities. The splitting between the Zn $3p$ levels, however, which Cardona determined for ZnS, ZnSe, and ZnTe (2.85, 2.75, and 3.6 eV, respectively), agrees well with our values (3.0, 2.7, and 2.9 eV, respectively) except for ZnTe.

The results of our Auger electron measurements are listed in Table II. They are included not only for completeness, but also to emphasize the self-consistency of our results. The experimentally determined values are compared with the values calculated according to the equation

$$E_{LXY} = E_L(\text{Zn}) - E_X(\text{Zn}) - E_Y(\text{Ga}). \quad (3)$$

The column on the left shows the energies calculated by using Eq. (3) and Nordling's binding-energy data for the pure elements Zn and Ga. The columns on the right list the values calculated by using our binding-energy data from Table I where possible along with Nordling's data for Ga. The agreement thus obtained is better, as is to be expected since the shift of the Zn levels due to ionic bonding in the crystals was taken properly into account.

TABLE III. Electronic core levels of O, S, Se, and Te in elemental form (left column) and in the Zn compounds, ZnO, ZnS, ZnSe, and ZnTe. Energy values are in eV and the experimental values are determined with reference to the Fermi level of each sample. The theoretical values for the compounds refer to the center of the respective band gaps, and those for the free atoms refer to their ionization levels. Values in parentheses are from unresolved doublets. In each Expt.-Theor. column, for each line, the theoretical values are below the experimental values.

Element Expt.[a] Theor.[c]	Δ	Level	Compound Expt.[b] Theor.[d]	Δ	Element Expt.[a] Theor.[c]	Δ	Level	Compound Expt.[b] Theor.[d]	Δ
532.0 537.5	5.5	O 1s	529.7		(110) 125.8	(18.9)	Te 4p $\frac{3}{2}$	(109.4) (118.0)	(8.6)
164.1 172.1	8.0	S 2p $\frac{3}{2}$	(160.0) (169.8)	(9.9)	(110) 135.0	(18.9)	Te 4p $\frac{1}{2}$	(109.4) (118.0)	(8.6)
165.3 173.5	8.2	S 2p $\frac{1}{2}$	(160.0) (169.9)	(9.9)	168 178.2	10.2	Te 4s	167.8 158.5	−9.3
229.2 226.6	−2.6	S 2s	225.1 222.6	−2.5	572 601.0	29	Te 3d $\frac{5}{2}$	570.3 (592.9)	(18.0)
57 66.7	9.7	Se 3d	53.3 62.1	8.8	582 612.1	30.1	Te 3d $\frac{3}{2}$	581.7 (592.9)	(18.0)
162 166.4	4.4	Se 3p $\frac{3}{2}$	159.5 (160.5)	(−0.8)	819 833.2	14.2	Te 3p $\frac{3}{2}$	817.9 (809.6)	(−25.2)
168 172.3	4.3	Se 3p $\frac{1}{2}$	165.1 (160.5)	(−0.8)	870 880.8	10.8	Te 3p $\frac{1}{2}$	868.7 (809.6)	(−25.2)
232 228.5	−3.5	Se 3s	228.3 215.1	−13.2	1006 1006.6	0.6	Te 3s	1004.4 925.3	−79.1
40 53.8	13.8	Te 4d	39.6 48.5	8.9					

[a] From electron emission data on Zn metal in Ref. 1, p. 225.
[b] Present work on Zn compounds.
[c] Self-consistent atomic potential calculations, Ref. 10.

[d] Self-consistent OPW calculations for Zn compounds, Ref. 8, calculated band gaps for 0°K: ZnS, 3.8 eV; ZnSe, 2.8 eV; ZnTe, 2.4 eV.

Table III presents a summary of the electronic core levels of oxygen, sulfur, selenium, and tellurium. Our experimental values are listed on the right-hand side and were determined by measuring the respective zinc compounds. The experimental values shown on the left-hand side were determined by Siegbahn's group (a table of electron binding energies with references is given in Ref. 1) by measuring the respective pure elements. The expected shift toward lower binding energies in the compounds is readily observed. Cardona and Haensel[6] have determined the Se 3d level from absorption measurements. Adjusted to our reference level, they find that it should lie at 57.6 eV below the Fermi level compared with our value of 53.3 eV. This discrepancy could only be explained if the absorption data represent transitions from the Se 3d level to levels that are about 4.3 eV above the bottom of the conduction band.

DISCUSSION

The main purpose of this investigation was to determine experimental values for the electronic core levels of the partially ionic zinc chalcogenide crystals. Furthermore, it should be worthwhile to compare our results to theoretical calculations. Exact calculations pertaining to our measurements have not been carried out because of their enormous complexity. The value which corresponds to the electron emission measurements is in principle obtainable for isolated atoms. It should correspond to the difference of the total energies of the neutral atom and that ion from which the appropriate core electron has been removed. Such calculations according to the Hartree-Fock method have been carried out for noble-gas atoms and showed a good agreement to electron emission data.[7] In these calculations the relaxation of the atom into an ion is properly taken into account.

TABLE IV. Zinc $3d$ level in eV with reference to the center of the energy gap (or Fermi level for electron emission).
Band-gap energies used for adjustment: ZnO 3.4 eV; ZnS, 3.8 eV; ZnSe, 2.8 eV; and ZnTe, 2.4 eV.

Compound	El. Em.	Experiment Refl.	Abs. and EEL	Theory SC-OPW	ER-OPW	KKR
ZnO	9.3	5.4(10.8)[a] 9.9[c]	11.8[c]			6.3[b]
ZnS	9.5	8.9[d] 9.0[f]	8.7[d] 9.8[g]	16.1[e]	6.9[e]	9.0[b] 8.6[h]
ZnSe	9.4	9.1[f]	10.4[g]	14.1[e]	7.7[e]	8.9[h]
ZnTe	9.1	9.4[i] 9.4[j]	10.1[i] 10.0[g]	14.0[e]		10.7[h]

[a] Reference 14.
[b] Reference 15.
[c] R. L. Hengehold, R. J. Almassy, and F. L. Pedrotti, Phys. Rev. B **1**, 4784 (1970).
[d] M. Cardona and Harbeke, Phys. Rev. **137**, A1467 (1965).
[e] Reference 8, value for ZnTe (private communication).
[f] M. Balkanski and Y. Petroff, in *Proceedings of the Seventh International*

Conference on the Physics of Semiconductors, Paris, 1964 (Dunod, Paris, 1964), p. 245.
[g] Reference 16.
[h] J. Treusch, P. Eckelt, and O. Madelung, in Ref. 4, p. 588.
[i] Reference 17.
[j] M. Cardona and Greenaway, Phys. Rev. **131**, 98 (1963).

None of the present-day calculations for solids has advanced far enough to include relaxation. Furthermore, it is still questionable how to best treat the problems of electron correlation and exchange. In a particular calculation it is also questionable as to what degree either or both are included and what magnitude the correction due to relaxation might have. Nevertheless—and with these reservations in mind—we would like to compare our results with the results of some band-structure calculations.

Calculations according to a nonrelativistic self-consistent orthogonalized-plane-wave (OPW) method with Slater's exchange approximation have been carried out for cubic ZnS, ZnSe, and ZnTe by Stukel et al.[8] Their results with the zero of the energy scale adjusted to the center of the energy gap are listed below the experimental values for the compounds in Tables I and III. The respective differences between the calculations and the experimental values are listed under Δ. Values in parentheses are results of unresolved doublets; differences in such cases were taken using the weighted averages of the split components.

An initial inspection of these differences might suggest that the outer core levels are computed to be more tightly bound than the experimental values indicate, whereas this relation reverses for the inner core levels. This is only true as a general trend, however. Closer inspection, especially of the Te data, reveals that another correlation exists, as Euwema[9] has pointed out. The calculated binding energy is always too large for the d states, not as large or even somewhat smaller than the experimental values for

the p states, and always too small for the s states. These two tendencies may well characterize the differences between the experimental and theoretical core levels for these compounds.

It is interesting to note that the correlation of Δ with the angular momentum of the orbital states has obviously nothing to do with the ionicity of the compound as Table I shows, and because the same correlation exists when comparing experimental and theoretical results for the pure elements in the left-hand columns of Tables I and III. Under the experimental values for the elements we have listed theoretical values according to nonrelativistic self-consistent calculations with Slater electron exchange and a spin-orbit coupling correction by Herman and Skillman.[10] This theoretical treatment for free atoms is analogous to the method subsequently employed by Stukel et al. for the band calculations. The energy reference for the values by Herman and Skillman is the ionization level of the respective atoms, and exact correspondence to the values published by Siegbahn's group (Se, Te, and Zn were measured while in the solid phase of the element) can only be made if one includes the solid-state effects and subtracts the work functions of the elements (4.73 eV for Se,[11] 4.76 eV for Te,[12] and 4.31 eV for Zn[13]) from the theoretical values. Nevertheless, the mismatch of the calculated values within each element is greatest for d states, less for p states, and least or of opposite sign for s states.

All this leads to the conclusion that the origin of the observed deviations might be suspected in (a) the Slater exchange approximation, which at present does not include terms which could lead to an angular-

momentum-dependent exchange, or (b) the lack of relaxation corrections, which should turn out to be most important for d electrons, less so for p electrons, and least so for s electrons, or (c) some combination of both.

There have been empirical refinements (ER-OPW) made to the self-consistent OPW method (SC-OPW) for the purpose of achieving a better agreement with the observed band gaps. These corrections have also simultaneously led to a better agreement of the least-bound core states with the corresponding experimental values (cf. Table IV). The possibility cannot be excluded, however, that such a better agreement is fortuitous.

Of all the core levels, the Zn $3d$ level exerts the strongest influence on the band structure of the zinc chalcogenides. We therefore compare in detail, in Table IV, our results with all available experimental and theoretical results for this level. We have subtracted one-half of the band gap from the original absorption and reflection data. Our data are with respect to the Fermi level and we assume that the Fermi level is at the center of the band gap.

Comparison of our data with the reflection peaks shows good agreement and, therefore, indicates that the Fermi level is indeed very close to the center of the gap. Our interpretation of the reflection data, however, does not always agree with that of the authors. An inspection of the data by Park et al.[14] for ZnO shows that they observed a peak at 10.8 eV which would agree much better with our measurements than the peak at 5.4 eV, which they correlate with the Zn $3d$ level. Their motive for assigning the 5.4-eV peak to transitions between the Zn $3d$ level and the conduction band was the good agreement that this gave with the Korringa-Kohn-Rostoker (KKR) theorectical value calculated by Rössler.[15] We think, however, that this particular value is out of line with the other KKR calculations which have shown the best agreement of all theoretical approaches with the Zn $3d$ experimental data. Rössler had also predicted that the width of the Zn $3d$ level in ZnO is wider than

in the other zinc compounds. This is, as Fig. 3 shows, not in accordance with our observations.

Electron energy-loss experiments (EEL) offer yet another possibility for investigating the energy spectrum in the region of the Zn $3d$ level. Tomoda and Mannami[16] have recently reported such measurements for ZnS, ZnSe, and ZnTe. They observe absorptions at 9.8, 10.4, and 10.0 eV for ZnS, ZnSe, and ZnTe, respectively (adjusted by subtraction of half the band-gap energy). They assign these energies to the excitation of plasma modes. We tend to disagree on this point because of the relatively good agreement of these values with the reflectivity data and our data for the Zn $3d$ level, and since the peaks which we observe cannot be plasmon peaks due to the nature of our experiment. Gilbert, Hengehold, and Pedrotti[17] performed similar measurements on ZnTe and obtained a peak at 10.1 eV which they attribute to interband transitions.

In conclusion, we have determined the energies of the electronic core levels in ZnO, ZnS, ZnSe, and ZnTe. Observed Auger transitions agree well with these core levels. In comparison to theoretical calculations, we find that the least-bound core level Zn $3d$ is, in general, best represented by KKR-type calculations and also well represented by the ER-OPW calculations. We further show that deviations from experiment of all core levels calculated according to the SC-OPW method depend on the angular momentum of the core level in question. Also, there is a need for a rescaling term which should expand the outer core levels to lower binding energies and compresses the innermost core levels to higher binding energies.

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