PHYSICAL REVIEW B VOLUME 1, NUMBER 6 15 MARCH 1970

Optical Properties of Some Compound Semiconductors in the 36–150-eV Region

MANUEL CARDONA* AND RUPRECHT HAENSEL
Deutsches Elektronen-Synchrotron, Hamburg, Germany
and
II. Institut für Experimental-Physik der Universität Hamburg, Hamburg, Germany

(Received 3 November 1969)

The absorption spectra of evaporated thin films of ZnS, CdS, ZnSe, CdSe, ZnTe, CdTe, PbS, and PbTe in the 36–150-eV region are reported. The measurements were performed using the DESY electron synchrotron as a radiation source. A sharp doublet associated with transitions from the $3p$ core levels of Zn to the conduction bands ($3p \rightarrow c$) is observed for ZnS, ZnSe, and less clearly for ZnTe. The splitting of this doublet seems due to spin-orbit interaction. Other less pronounced structure (Se: $3d \rightarrow c$ in ZnSe, Cd: $4p \rightarrow c$ in CdTe) is also observed, but most spectra are dominated by broad transitions similar to the atomic $d \rightarrow f$ transitions observed in this region for Kr and Xe. The number of effective electrons whose oscillator strength has been exhausted at a given energy is obtained by integrating the absorption coefficient. In the compounds containing the heavy elements Te and Pb, all outermost d electrons of the core have exhausted their oscillator strength at 150 eV.

I. INTRODUCTION

THE intrinsic optical properties of the IIb-VIb family of semiconductors and insulators with zinc-blende and wurtzite structure have been the object of considerable study.[1–3] The measurements, usually performed on single crystals with the normal-incidence reflection technique, have been confined to the region of photon energies below 30 eV.[4–6] Transmission measurements with vacuum-deposited polycrystalline samples,[7] limited because of substrate absorption to the 1–6-eV energy region, have shown substantial agreement with reflectivity measurements on bulk single crystals.

In the 1–10-eV region, the optical properties of the IIb-VIb materials are dominated by direct interband transitions between the valence and conduction bands. The absorption coefficient has an absolute maximum in the near ultraviolet (around 6 eV) where most of the oscillator strength is concentrated. The band-structure assignment of this maximum, usually labeled E_2, has been extensively discussed in the literature.[2] Additional structure is observed at both sides of this maximum; we shall mention in particular the E_1, $E_1+\Delta_1$ peaks, split by spin-orbit interaction and located at photon energies below E_2. The line shape of these peaks is known to be strongly affected by exciton interaction.[8] Exciton effects are also responsible for the rich structure observed in the neighborhood of the fundamental edge.[1]

In the 10–30-eV region, transitions from the outermost d electrons of the cation core into the conduction band are observed.[4] These transitions are centered around 15 eV and have an approximate width of 4 eV. Fine structure in these transitions has been observed[9] for Cd but most of the reported data show a single peak. However, structure at the d peaks could have been missed in these experiments because of the inadequacy of the discrete line sources conventionally used. Such structure would be related to structure in the density of conduction states and to the spin-orbit splitting of the d-core levels: The bands formed by these levels should have negligible width other than lifetime broadening.[10] The relationship between the spectrum of the $3d \rightarrow c$ transitions of Ge,[11] a material closely related to the II-VI compounds, and the density of conduction states has been pointed our recently.[12]

The intrinsic optical properties of the lead chalcogenides (IVb-VIb compounds with rocksalt structure) have also been extensively studied. Reflectivity measurements have been performed up to 25 eV,[13] while transmission measurements on vacuum-deposited films have been confined to energies below 6 eV.[13,14] Transmission measurements are particularly attractive for these materials because of the possibility of preparing high-quality single-crystal films by epitaxial deposition on cleaved alkali-halide substrates.[14]

The results of transmission measurements on lead chalcogenides are in essential agreement with those of reflectivity measurements. They show structure presumably due to valence–to–conduction-band transitions

---

* John S. Guggenheim Memorial Foundation Fellow, on leave from Brown University, Providence, R. I.

[1] T. C. Collins, C. W. Litton, and D. C. Reynolds, Phys. Status Solidi **12**, 3 (1965).

[2] F. H. Pollak, in *II-VI Semiconducting Compounds*, edited by D. G. Thomas (W. A. Benjamin Inc., New York, 1967), p. 552; M. L. Cohen, *ibid.*, p. 462.

[3] F. Herman, R. L. Kortum, C. D. Kuglin, and J. L. Shay, in *II–VI Semiconducting Compounds*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), p. 503.

[4] M. Cardona and D. L. Greenaway, Phys. Rev. **131**, 98 (1963).

[5] M. Aven, D. T. F. Marple, and B. Segall, J. Appl. Phys. **32S**, 2261 (1961).

[6] W. J. Scouler and G. B. Wright, Phys. Rev. **133**, A736 (1964).

[7] M. Cardona and G. Harbeke, J. Appl. Phys. **34**, 813 (1963).

[8] E. O. Kane, Phys. Rev. **180**, 852 (1969).

[9] W. C. Walker and J. Osantowski, J. Phys. Chem. Solids **25**, 778 (1964).

[10] P. Eckelt, O. Madelung, and J. Treusch, Phys. Rev. Letters **18**, 656 (1967).

[11] B. Feuerbacher, M. Skibowski, R. P. Godwin, and T. Sasaki, J. Opt. Soc. Am. **58**, 1434 (1968).

[12] M. Cardona, in Proceedings of the Conference on Electronic Density of States, Gaithersburg, Maryland, 1969 (to be published).

[13] M. Cardona and D. L. Greenaway, Phys. Rev. **133**, A1685 (1964).

[14] P. R. Wessel, Phys. Rev. **153**, 836 (1967).

below 20 eV and the beginning of structure due to transitions from the outermost d electrons of Pb above 20 eV. The absorption coefficient shows a broad absolute maximum around 3 eV (E_2) with some weak structure before and after this maximum. This structure is broader and not as well defined as that observed for the zinc blende family; hence, the band-structure assignment of the observed peaks has remained somewhat uncertain. Optical-constants calculations from band structure, such as those performed recently by Buss and Parada[15] for PbTe, should contribute to the identification of the observed structure.

In this paper, we report measurements of the absorption coefficient of ZnS, CdS, ZnSe, CdSe, ZnTe, CdTe, PbS, and PbTe at room temperature in the 36–150-eV region. The measurements were performed on films vacuum-deposited on thin carbon substrates. The choice of materials was determined, in part, by the fact that they yield reasonably crystalline films when deposited on substrates at room temperature. From our experience with these films in the visible and near uv, we can state that the width of the structure observed in the 36–150-eV region (>1 eV) is not determined by crystalline imperfections in our films. The transmission technique was chosen over that of normal-incidence reflection because of the small reflectivity of our materials (<0.01) in the 36–150-eV region, which increases the error due to scattering light of long wavelengths. Most of the structure observed is rather broad and is believed related to the $d\rightarrow f$ structure observed in atomic spectra,[16] in the solid rare gases,[17] and in the alkali iodides.[18] Sharp doublet structure has been observed for the Zn compounds, especially ZnS and ZnSe. This structure is related to transitions from the outermost core levels of Zn to the conduction band and exhibits a splitting equal to that expected for these d levels (spin-orbit splitting ≈ 3 eV[19]). The absorption spectrum of ZnSe exhibits also sharp structure related to transitions originating at the outermost $3d$ levels of Se.

II. EXPERIMENTAL PROCEDURE

The absorption experiments were performed using as a radiation source the DESY electron synchrotron.[20,21] For the standard synchrotron operating conditions (final energy between 3 and 7 GeV), the photon flux on the entrance slit is 10^{12} photons/(sec eV cm^2) at 100-eV photon energy. The samples were placed in front of the entrance slit of a Rowland grazing-incidence monochromator. A gold-coated grating with 2400 lines/mm and a grazing angle of incidence of 4° 16′ was used in first order with an angle of incidence of 12° 30′; it provided an average resolution of 0.1 Å with 20-μm slits. The detector was a Bendix M 306 open magnetic electron multiplier.

The photomultiplier response in the absence of a sample had a maximum at a photon energy of about 100 eV due, in part, to the blazing of the grating and to the spectral distribution of the synchrotron radiation. As a result of the rapid decrease in the photon flux below 100 eV, the influence of higher-order radiation at a first-order setting of 50 eV is not negligible. In order to avoid this problem, we used as filters unsupported Al films about 1500 Å thick. The sharp absorption edge of this metal at 72.7 eV ensures virtually pure first-order radiation between 36 and 72 eV. Measurements at 72 eV with and without filter indicate a tolerable amount of higher-order radiation ($\lesssim 5\%$) at this and higher energies. The upper photon energy limit of our measurements was determined by the small radiation intensity available with the small grazing angle required and the beginning of the scattered light associated with the zero-order spectrum.

The samples were prepared by vacuum deposition at pressures about 10^{-6} T *in situ* and *ex situ*. The substrates were 20-μg/cm^2 carbon films supported by a 70-μm copper grid; they were kept at room temperature during evaporation. The film thickness was determined while evaporating with a quartz film-thickness monitor. After evaporation, the thickness of a film deposited on a glass substrate, placed next to the carbon substrate during evaporation, was measured by the Tolansky method: Results consistent to better than 20% with those of the quartz monitor were found. The results of the Tolansky measurements were used to evaluate the absorption coefficients, since they were thought to be more reliable than those of the quartz monitor. From the consistency of the results obtained for several samples, we believe, however, that the absorption coefficients reported for CdSe, ZnSe, CdTe, and ZnTe are affected by a scaling error of about 20% due to uncertainties in the thickness determination. This error may be as high as 30% for ZnS and CdS.

As already mentioned, measurements were performed both with samples deposited on the substrates *in situ* and with samples prepared in an external evaporator; no differences were found between samples of the same material prepared by either procedure. *In situ* preparation has the advantage of permitting the measurements of the transmissivity of the substrate immediately before deposition. This feature becomes important when the sample transmissivity is large.

III. RESULTS

Figure 1 shows the absorption spectra of CdS and ZnS at room temperature. This figure represents the

---

[15] D. Buss and N. J. Parada, Phys. Rev. (to be published).

[16] U. Fano and J. W. Cooper, Rev. Mod. Phys. **40**, 441 (1968).

[17] R. Haensel, G. Keitel, P. Schreiber, and C. Kunz, Phys. Rev. **188**, 1375 (1969).

[18] H. Fujita, C. Gähwiller, and F. C. Brown, Phys. Rev. Letters **22**, 1369 (1969).

[19] F. Herman and S. Skillman, *Atomic Energy Levels* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

[20] R. Haensel and C. Kunz, Z. Angew. Phys. **23**, 276 (1967).

[21] R. P. Godwin, in *Springer Tracts in Modern Physics*, edited by G. Höhler (Springer-Verlag, Berlin, 1969), Vol. 51, p. 1.

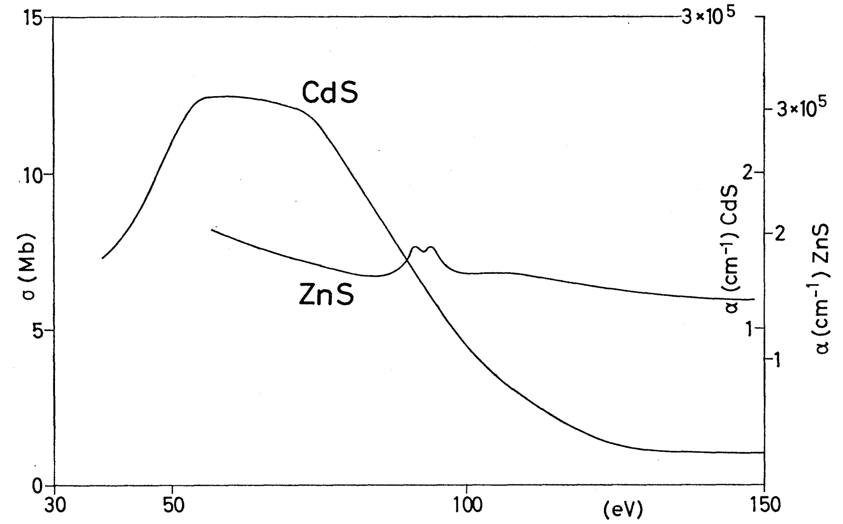

FIG. 1. Absorption spectra of ZnS and CdS at room temperature in the soft–x-ray region. In this and subsequent figures, the vertical scale on on the left represents megabarns per diatomic molecule and is common to both compounds. The vertical scales on the right represent absorption coefficients and are different for each compound.

composite results of a number of measurements with several samples of thicknesses around 1000 Å. The results are presented both in megabarns per diatomic molecule (1 Mb$=10^{-18}$-cm^2 cross section), for the purpose of comparison with atomic-absorption data, and in cm^{-1}. The cross-section scale in this and subsequent figures has been chosen common for both compounds; the absorption-coefficient scale is then different because of the difference in lattice constants. The results of this and subsequent figures were obtained from transmission measurements only, without reflection corrections. The normal incidence reflectivity of the samples was measured independently in some cases and shown to be well below 0.01 throughout our experimental region: This fact makes reflection corrections unnecessary. Transmission measurements with samples of various thicknesses also confirmed this conclusion.

The ZnS spectrum of Fig. 1 shows a relatively sharp doublet between 90 and 100 eV. The average position of these peaks, as resulting from several measurements, is given in Table I. The estimated accuracy of these peak energies is ±0.1 eV. We have also listed in Table I the energy of the $M_{\mathrm{II,III}}$ x-ray emission threshold[22] and the calculated energy (below zero) of the corresponding $3p$ levels of Zn.[19] Table I suggests that the observed doublet is related to transitions from these outermost p electrons of the Zn core into excited (conduction-band) states. The observed splitting (2.85 eV) is close to the calculated spin-orbit splitting of these p electrons (3.2 eV). The CdS spectrum shows only broad structure with a maximum around 60 eV. While the CdS films are expected to have the wurtzite structure, no essential differences between the zinc blende and wurtzite spectra should exist in our experimental region.[23]

The absorption spectra of ZnSe and CdSe are shown in Fig. 2. Like in Fig. 1, the absorption of the cadmium compound below 90 eV is stronger than that of ZnSe. This fact will be discussed quantitatively in Sec. IV. The cadmium compound shows also only broad structure with a maximum at an energy slightly higher than that of CdS. The spectrum of ZnSe shows also the doublet which we have associated with the $M_{\mathrm{II,III}}$ edge of Zn. A slightly broader peak is observed at 59 eV: Comparison with calculations of atomic levels[19] and soft–x-ray emission data[22] suggests that this peak is related to the $M_{\mathrm{IV,V}}$ edge of Se (see Table I). The spin-orbit splitting expected for this edge (∼1 eV) is too small to be resolved with the linewidth observed for this peak (∼6 eV, not resolution limited).

We show in Fig. 3 a blown-up version of the $M_{\mathrm{II,III}}$ peaks of ZnS and ZnSe. For the purpose of the discussion in Sec. IV, we include in this figure the density of conduction states calculated for ZnS by Herman *et al.*[3] As shown in this figure and in Table I, this doublet occurs in ZnSe at an energy 0.3–0.4 eV lower than in ZnS. In this regard, it is interesting to point out that

TABLE I. Position (in eV) of "sharp" peaks identified in the soft–x-ray spectra of ZnS, ZnSe, ZnTe, and CdTe. Also, corresponding emission thresholds reported by Bearden and Burr (Ref. 22) and binding energies of the assigned core levels calculated by Herman and Skillman (Ref. 19). For convenience, we use in this paper both the atomic and the x-ray level assignments for thresholds and edges, i.e., K corresponds to $1s$, L_{I} to $2s$, $L_{\mathrm{II,III}}$ to $2p$, etc.

	ZnS	ZnSe	ZnTe	CdTe	Bearden and Burr	Herman and Skillman
Zn($3p$)	90.9	90.6	89.4	···	86.6	91.6
	93.75	93.35	93	···	···	94.8
Cd($4p$)	···	···	···	65	67	74.9
	···	···	···	···	···	80.4
Se($3d$)	···	59	···	···	57	66
	···	···	···	···	···	67

---

[22] J. A. Bearden and A. F. Burr, Rev. Mod. Phys. **39**, 125 (1967).

[23] M. Cardona and G. Harbeke, Phys. Rev. **137**, A1467 (1965).

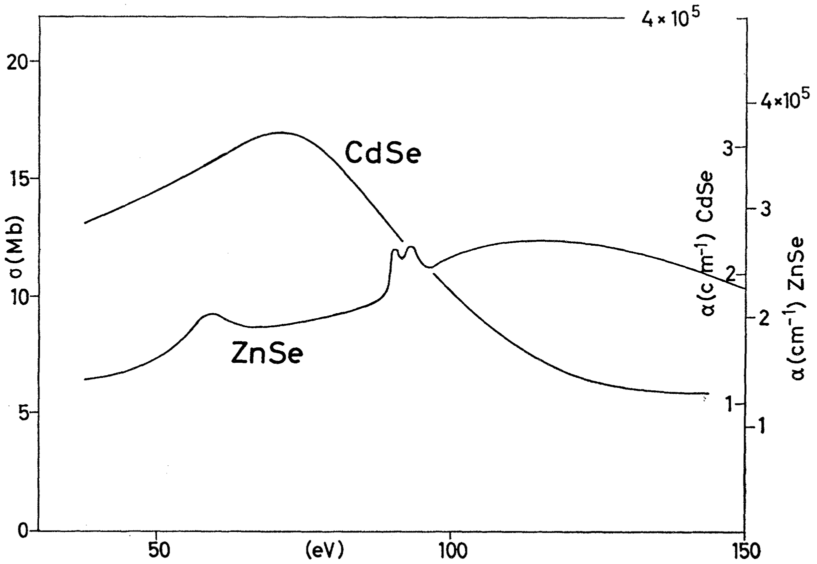

FIG. 2. Absorption spectrum of ZnSe and CdSe at room temperature in the soft-x-ray region.

the fundamental gap of ZnS is about 1.1 eV higher than that of ZnSe.

Figure 4 shows broad maxima with some superimposed structure for the absorption spectra of ZnTe and CdTe. The absorption coefficients at the maxima are considerably higher than those of Figs. 1 and 2. Some faint structure, corresponding roughly to the doublets of Fig. 3, can be seen near the maximum of the ZnSe spectrum (see Table I), but the assignment is somewhat arbitrary since more than a doublet is observed. Scattered light prevents, in view of the strong absorption background, the possibility of enhancing the observed fine structure by measuring thicker samples. The CdTe spectrum exhibits, beside some structure near the maximum, a hump at 65 eV which, according to Table I, could be related to the $N_{\rm II,III}$ edge of Cd.

Figure 5 shows the absorption spectra of PbS and PbTe. No fine structure appears in these spectra; a change in slope in the PbS spectrum at 80 eV could be related to the $O_{\rm II,III}$ threshold of Pb (see Table II). A compilation of the positions of the absolute maxima in the spectra of Figs. 1, 2, 4, and 5, together with the absorption cross sections at the maxima, is presented in Table III.

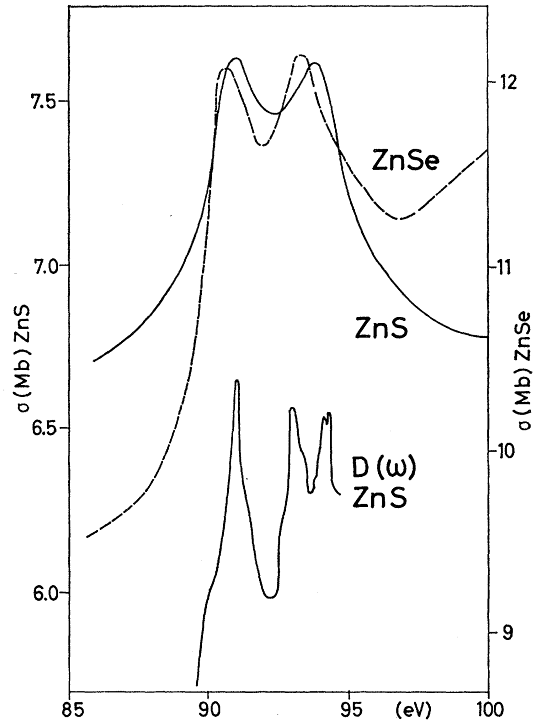

FIG. 3. Absorption doublet observed for ZnS and ZnSe in the 85–100-eV region. This doublet is associated with the $M_{\rm II,III}$ edge of Zn. Also, density of conduction states (arbitrary scale and origin of energies) calculated by Herman *et al.* (Ref. 3) for ZnS.

TABLE II. Energies (in eV) of (1) atomic core levels which may produce structure in the soft-x-ray spectra and (2) x-ray emission thresholds of the Cd, Zn, and Pb chalcogenides related to the spectral region of interest in this paper.

	d electrons			*p* electrons		
	(1)[a]	(2)[b]		(1)[a]	(2)[b]	
S	...	...	...	172	165	2*p*
	...	...		173	...	
Se	66.1	57	3*d*	166	162	3*p*
	67.0	57		172	168	
Te	54.5	40	4*d*	135	110	4*p*
	52.9	40		126	110	
Zn	17.3	8.1	3*d*	91.6	87	3*p*
	17.7	8.1		94.8	87	
Cd	18.8	9.3	4*d*	74.9	67	4*p*
	19.5	9.3		80.4	67	
Pb	32.9	19.2	5*d*	97.5	86	5*p*
	35.8	21.8		115	86	

[a] F. Herman and S. Skillman, Ref. 19.
[b] J. A. Bearden and A. F. Burr, Ref. 22.

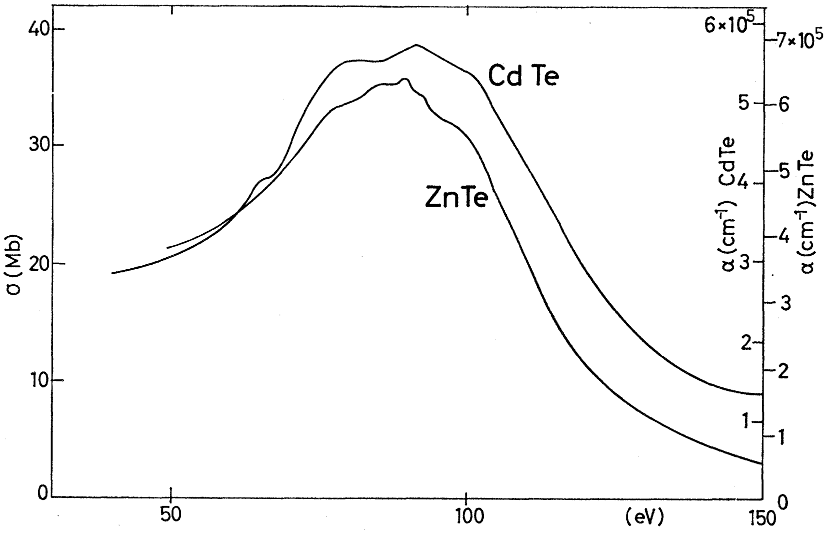

FIG. 4. Absorption spectra of ZnTe and CdTe at room temperature in the soft-x-ray region.

IV. DISCUSSION

We show in Table II the x-ray emission thresholds and the energies of the atomic core levels which could produce optical structure in our photon energy region. As already mentioned, relatively narrow structure has been observed in the Zn compounds associated with the $M_{\mathrm{II,III}}$ edge of Zn, in CdTe associated with the $N_{\mathrm{II,III}}$ edge of Cd, and in ZnSe associated with the $M_{\mathrm{IV,V}}$ edge of Se. The reason why such narrow structure does not appear for all materials measured can be associated with the existence of the broad maxima to be discussed later. The strength of the maxima (especially for the compounds of Te and Pb), and possibly broadening due to interchannel interaction,[16] prevent the appearance of such structure.

TABLE III. Effective number of electrons N_{eff} whose oscillator strength is exhausted between 30 and 150 eV, energy $E_{\max}$ (in eV), and strength ($\sigma_{\max}$) of the absolute absorption maximum in the same region for several material considered here and for gaseous Kr and Xe.

	N_{eff} (electrons per molecule)	$E_{\max}$(eV)	$\sigma_{\max}$(Mb)
ZnS	7.2	92	7.6
CdS	6.2	60	12.4
ZnSe	10.4	120	12.6
CdSe	11.5	70	16.9
ZnTe	18	89	35.5
CdTe	26.5	90	38.5
PbS	10.6	58	20
PbTe	22.5	82	34
Kr[a]	2	200	3.5
Xe[a]	10	100	29

[a] Obtained from Ref. 16.

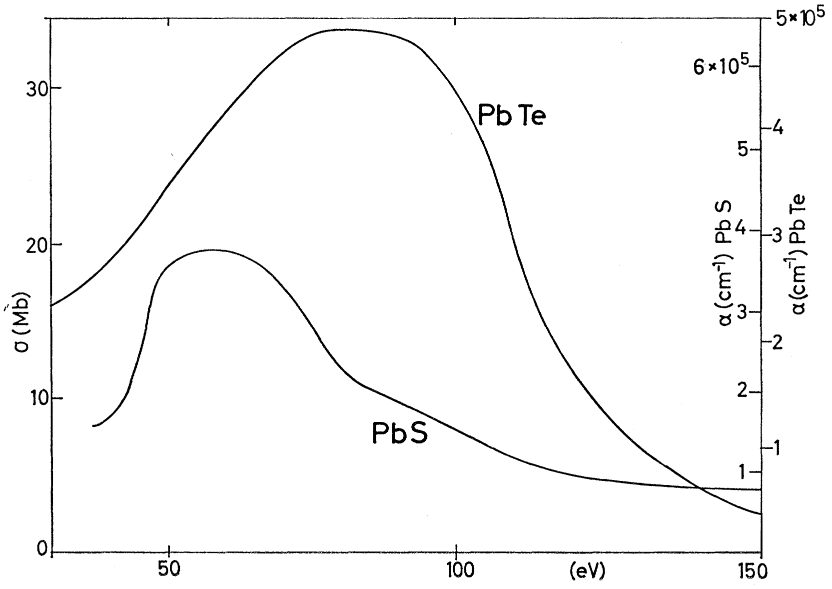

FIG. 5. Absorption spectra of PbTe and PbS at room temperature in the soft-x-ray region.

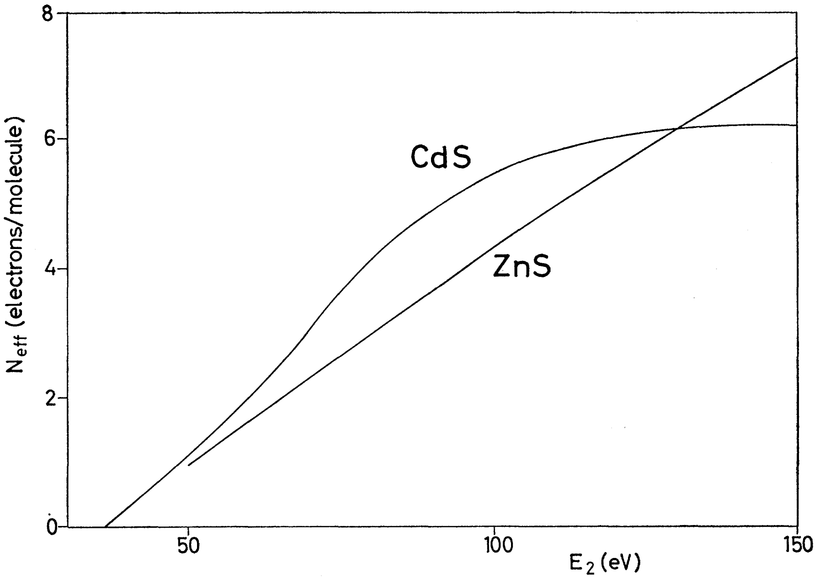

Fig.6

FIG. 6. Effective number of electrons whose oscillator strength is exhausted between 36 eV and the energy E_2, for CdS and ZnS.

We have shown in Fig. 3 the $M_{\mathrm{II,III}}$ peaks of ZnS, together with the density of conduction states calculated for this material.[3] It is possible to speculate that the first peak (lower energy) of the experimental doublet is a reflection of the first peak in the density of states, while the observed higher-energy peak is the unresolved broadened version of the second and third peaks in the density of states. The spin-orbit splitting of the *d* core levels, however, obliges us to expect the superposition of two similar density-of-states–type spectra separated by the spin-orbit energy (~3 eV). The low-energy component of this superposition should have a strength about $\frac{2}{3}$ of the high-energy component. Hence, a triplet, and not a doublet, would be expected from the density of states of Fig. 3 on the basis of the argument given above. One must, therefore, either conclude that one of the expected peaks is suppressed because of a small oscillator strength or that the observed spectra are atomiclike excitonic (Frenkel) excitations not bearing a direct relationship to the density of conduction states. We do not feel we can, at present, elucidate any further this question, which is of great interest in connection with the interpretation of fine structure also observed in this region for the alkali halides[18] and the rare-gas solids.[17]

The broad, usually dominant, components of the observed spectra bear a strong similarity to the broad spectra observed for gaseous and solid Kr and Xe[16,17] in the soft–x-ray region. Similar broad spectra have also been reported for the alkali iodides[18] and for a number of heavy elements.[24] For comparison, we have listed in Table III the energy of the broad maxima and its cross

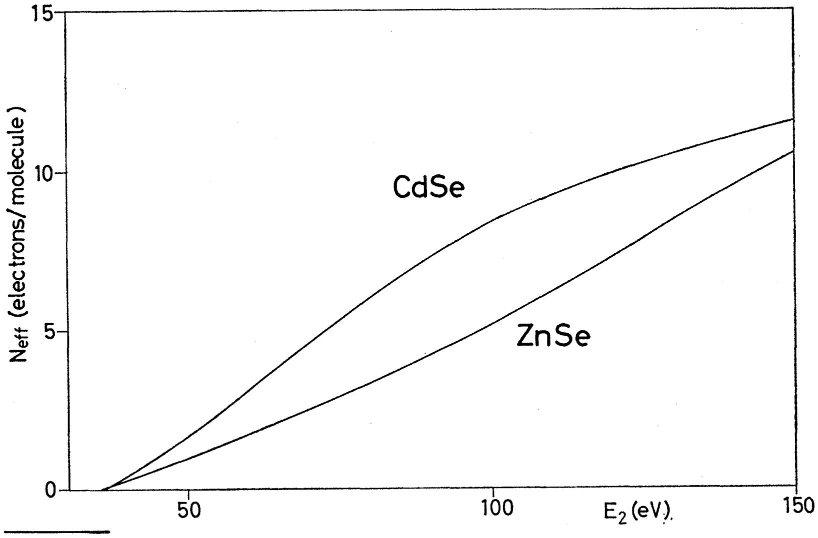

FIG. 7. Effective number of electrons whose oscillator strength is exhausted between 36 eV and the energy E_2, for CdSe and ZnSe.

---

[24] R. Haensel, C. Kunz, T. Sasaki, and B. Sonntag, Appl. Opt. **7**, 301 (1968).

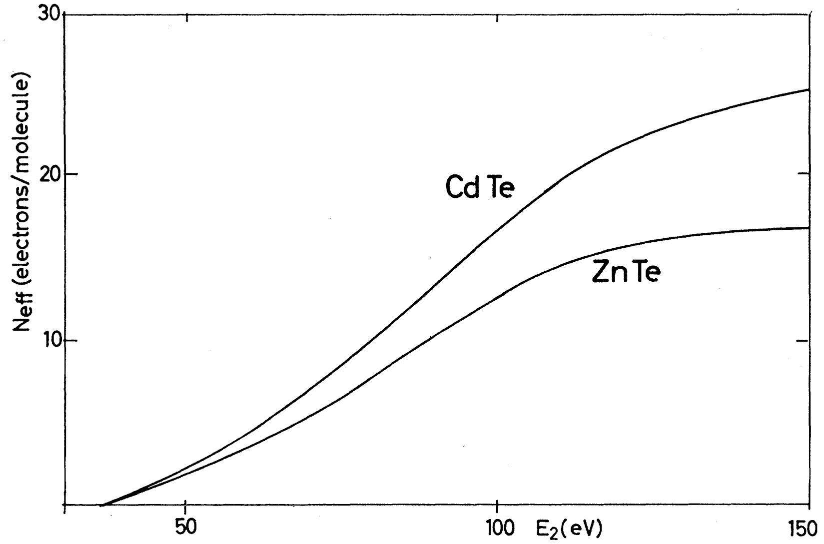

FIG. 8. Effective number of electrons whose oscillator strength is exhausted between 36 eV and the energy E_2, for CdTe and ZnTe.

section for Kr and Xe. These maxima in the atomic spectra have been attributed to $d \rightarrow f$ transitions, with the f levels above the ionization threshold (sometimes referred to as delayed d threshold).[16] These transitions are particularly strong when there are unoccupied f states belonging to the same shell as the initial filled d levels (e.g., for the fifth and lower rows of the periodic table; Cd, Te, Xe, Pb). It is clearly apparent from Table III and our figures that the observed broad maxima are particularly strong for compounds with Te and Pb, in agreement with the atomic argument given above. For reasons which we do not know, the corresponding maxima for the cadmium compounds are weaker. Recent work by Harrison *et al.*[25] on the photoionization cross section of atomic Cd shows a broad maximum at an energy similar to that of CdS (Fig. 1) and with a comparable cross section (~15 Mb at the maximum).

An examination of Tables II and III indicates that the broad maxima of all tellurides are mostly due to the $d \rightarrow f$ (same shell) transitions of Te. For PbTe, this maximum may be shifted to slightly lower energies because of the strong superposition of $d \rightarrow f$ transitions of Pb which have a maximum at 58 eV (see PbS). The thresholds of these d transitions lie all at around 30 eV and, hence, the delay of the $d \rightarrow f$ maximum is quite large. A detailed study of the threshold region (below 36 eV), to be performed at a later date, is desirable for the sake of completeness. The weaker broad spectrum of CdSe seems dominated by the $d \rightarrow f$ transitions (same shell also) of Cd (see also CdS). That of ZnSe, with a maximum at 120 eV, should be a superposition

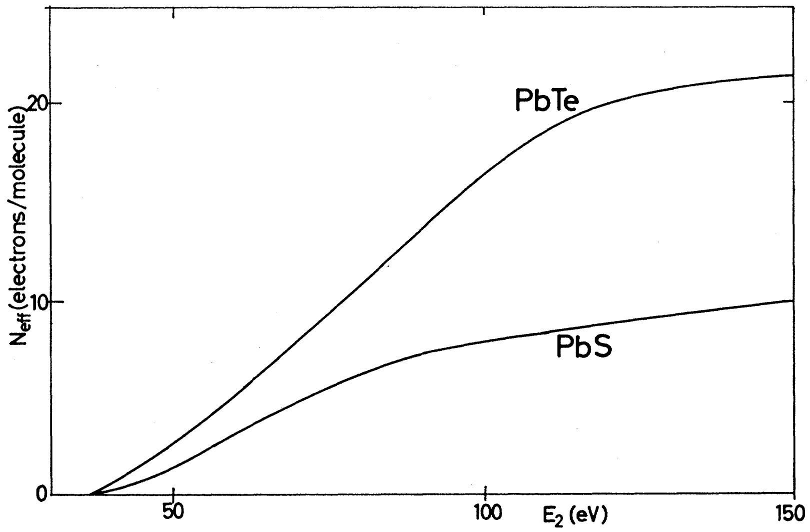

FIG. 9. Effective number of electrons whose oscillator strength is exhausted between 36 eV and the energy E_2, for PbS and PbTe.

---

[25] H. Harrison, R. I. Schoen, K. E. Schubert, and R. B. Cairns, J. Chem. Phys. (to be published).

of $d \rightarrow f$ transitions of Zn and Se plus $p \rightarrow d$ transitions of Zn: It is weaker than for the tellurides and for CdSe since all the transitions mentioned have initial and final states in different atomic shells.

For a more quantitative treatment of the broad parts of the spectra, it is convenient to calculate the effective density of states whose oscillator strength has been exhausted between energies E_1 and E_2[24,26]:

$$N_{\text{eff}}(\text{electrons/molecule}) = 2.3\times 10^{15} a^3 \int_{E_1}^{E_2} \alpha(E) n(E) dE = 9.1\times 10^{15} \int_{E_1}^{E_2} n(E)\sigma(E) dE. \quad (1)$$

In Eq. (1), a is the lattice constant and $n(E)$ is the real part of the refractive index. A calculation of the imaginary part of the refractive index $k(E)$ from the observed absorption coefficients indicates that $n(E)$ differs from 1 by no more than 10% (the maximum values of n should be similar to those of k for the observed line widths). In view of this and of the qualitative meaning of N_{eff}, we set $n(E)=1$ for the evaluation of Eq. (1) from our experimental values of $\alpha(E)$. The values of N_{eff} calculated with $E_1=37$ eV are shown in Figs. 6–9 as a function of E_2. The effective number of electrons per molecule whose oscillator strength is exhausted in our experimental region, i.e., the ordinates of Fig. 6–9 for $E=150$ eV, are tabulated under N_{eff} in Table III. It is clear from this table that N_{eff} amounts to all of the 5d electrons of Pb for PbS and these electrons plus the 4d electrons of Te for PbTe. For CdTe and ZnTe also, practically all of the outermost core d electrons are exhausted in our experimental region (slightly less for ZnTe). This number becomes smaller for the selenides, undoubtedly related to the fact that the $d \rightarrow f$ transitions of Se do not take place within the same shell. About 6 electrons/atom are exhausted for CdS in constrast to 7 electrons/atoms for ZnS. We must point out, however, that for these two materials the error in the determination of the film thickness may be as high as 30% (see Sec. II). Thus, an error of 30% in N_{eff} is possible for both ZnS and CdS.

ACKNOWLEDGMENTS

We would like to thank Peter Rabe for the construction of the equipment for *in situ* evaporation, Günter Singmann for help in the preparation of the samples and substrates, and Dr. Bernd Sonntag for a number of valuable discussions. Thanks are also due Dr. R. I. Schoen for sending us a preprint of his paper (Ref. 25) prior to publication and to the Deutsche Forschungsgemeinschaft for continuing support of this paper.

---

[26] H. R. Philipp and H. Ehrenreich, Phys. Rev. **129**, 1550 (1963).