PHYSICAL REVIEW B VOLUME 20, NUMBER 4 15 AUGUST 1979

Electronic structure of ZnF_2, CdF_2, and HgF_2 studied by ultraviolet photoelectron spectroscopy

R. T. Poole
Department of Natural Sciences, Preston Institute of Technology, Bundoora, Victoria, Australia 3083

J. A. Nicholson, J. Liesegang, J. G. Jenkin, and R. C. G. Leckey
Department of Physics, La Trobe University, Bundoora, Victoria, Australia 3083

(Received 15 November 1977; revised manuscript received 28 November 1978)

The results of a photoelectron study using 40.81-eV photons of the outermost bands of the group-IIB-metal fluorides ZnF_2, CdF_2, and HgF_2 are reported. The relaxation-corrected experimental values for the energy separation and absolute binding energies of the outermost levels and the corresponding values given by the fully ionic crystal model are found to be in good agreement for CdF_2 and approximate agreement for HgF_2. Assignment of relaxation energies for ZnF_2, of similar magnitude to those for HgF_2, also results in approximate agreement between experimental data for this compound and the corresponding ionic-model predictions. The valence-band widths of a number of MF and MF$_2$ compounds, including rocksalt, fluorite, rutile, and tetragonal crystal types, are shown to be a function of d^{-2} (d is the bond length) and are characterized by a valence-band index that is independent of crystal type.

I. INTRODUCTION

This paper reports the results of a photoelectron study of the outermost electronic bands of the group-IIB-metal fluorides ZnF_2, CdF_2, and HgF_2. These materials are of interest as part of a wider study of the class of nominally strong ionic materials. This study has so far included the alkali-metal halides,[1,2] the alkaline-earth fluorides,[3] some transition-metal fluorides[4] all of which have been successfully interpreted in terms of a fully ionic crystal model, and a number of soft-metal fluorides which in sharp contrast to the above materials were found[5,6] to have electronic structure characteristic of covalent electronic states. The present work extends these investigations to the group-IIB-metal fluorides.

The electronic structures of CdF_2 and HgF_2 are also of interest as examples of materials which crystallize in the fluorite structure (ZnF_2 crystallizes in a rutile structure). Materials which crystallize in the fluorite structure have in the past been of considerable interest[7]; however, very little experimental data are available on the electronic structure of these materials and until very recently no energy-band calculation has been performed.[7]

II. EXPERIMENTAL

The experimental details in regard to the spectrometer parameters, energy calibration, sample preparation, and method of determining binding energies have been published in Ref. 7 and in references contained therein. Details of the photon source have been published in Ref. 9. Briefly, ultraviolet photons from a helium discharge lamp, operated under conditions which optimize the production of 40.81-eV radiation, strike a freshly evaporated target, and the photoelectrons are energy analyzed by a 90°-sector spherical electrostatic analyzer. The effects of sample charging were accounted for by recording several spectra for each sample within the first 30 s after evaporation; binding energies at time zero were determined from the spectra by an extrapolation procedure, as discussed previously.[8]

III. THEORY

In this section we consider the values of the binding energies of the outermost electronic levels of ZnF_2, CdF_2, and HgF_2 predicted by the fully ionic model of a crystal. In this model the theoretical binding energies $E_b^{\mathrm{th}}(M^{2+})$ and $E_b^{\mathrm{th}}(\mathrm{F}^-)$ of the outermost levels of the metal and fluorine ions are as follows:

$$E_b^{\mathrm{th}}(M^{2+}) = E_b^{\mathrm{fi}}(M^{2+}) - E_M(M^{2+}) , \quad (1)$$

$$E_b^{\mathrm{th}}(\mathrm{F}^-) = E_b^{\mathrm{fi}}(\mathrm{F}^-) + E_M(\mathrm{F}^-) , \quad (2)$$

where $E_b^{\mathrm{fi}}(M^{2+})$ and $E_b^{\mathrm{fi}}(\mathrm{F}^-)$ are the binding energies of the outermost levels of the free metal and free fluorine ions, respectively, with respect to the vacuum level E_{vac}; and where $E_M(M^{2+})$ and $E_M(\mathrm{F}^-)$ are the Madelung energies associated with the metal and fluorine ions, respectively.

From Eqs. (1) and (2) the predicted energy separation E_s^{th} of the outermost levels of the metal and fluorine ions is

$$E_s^{\mathrm{th}} = E_b^{\mathrm{fi}}(M^{2+}) - E_b^{\mathrm{fi}}(\mathrm{F}^-) - [E_M(M^{2+}) + E_M(\mathrm{F}^-)] . \quad (3)$$

The value of $E_b^{\text{fi}}(\text{F}^-)$ is known[10] and values for $E_b^{\text{fi}}(M^{2+})$ are given by the third ionization potential.[11]

The Madelung energy per molecule may be written

$$E_M = \tfrac{1}{2}[2e\phi(M^{2+}) + (-2e)\phi(\text{F}^-)]$$

$$\equiv E_M(M^{2+}) + E_M(\text{F}^-)\,, \qquad (4)$$

where $\phi(M^{2+})$ is the potential at a metal lattice site and $\phi(\text{F}^-)$ is the potential at a fluorine lattice site. Benson and van Zeggeren[12] have shown that a fluorite structure is obtained from the superposition of CsCl and NaCl lattices, and that $\phi(M^{2+})$ and $\phi(\text{F}^-)$ are then readily determined to be

$$\phi(M^{2+}) = A(\text{NaCl})e/2\pi\epsilon_0 a_0 - A(\text{CsCl})e/\sqrt{3}\pi\epsilon_0 a_0\,, \qquad (5)$$

$$\phi(\text{F}^-) = A(\text{CsCl})e/\sqrt{3}\pi\epsilon_0 a_0\,, \qquad (6)$$

where A(NaCl) and A(CsCl) are the well-known Madelung constants for the NaCl and CsCl crystal lattice structures, respectively, and a_0 is the lattice constant.

The corresponding expressions for the rutile structure have been derived by Gorlach and Lisitsyn[13] and are as follows:

$$\phi(M^{2+}) = -4.674\,048\,6e/4\pi\epsilon_0 C_0\,, \qquad (7)$$

$$\phi(\text{F}^-) = 2.692\,361\,3e/4\pi\epsilon_0 C_0\,, \qquad (8)$$

where C_0 is one of the unit-cell constants.

In Table I we list calculated values of $E_M(\text{F}^-)$, $E_M(M^{2+})$, E_M, $E_b^{\text{th}}(\text{F}^-)$, $E_b^{\text{th}}(M^{2+})$, and E_s^{th} for ZnF_2, CdF_2, and HgF_2. Values of lattice constants have been taken from Ref. 14.

IV. RESULTS

In Fig. 1 we show the photoelectron spectra of the outer bands of the group-IIB-metal fluorides taken with an instrumental resolution (full width at half-maximum) of 0.3 eV. Various features of the spectra of Fig. 1 are summarized in Table II. In Fig. 2 we show the method of construction used in order to extract the widths of the fluorine p-bands and the metal d-bands from the experimental spectra and it should be noted that this leads to asymmetric F^- band shapes, especially from ZnF_2. The binding energies of all bands given in Table II correspond to the centroids of the bands. Before comparing these experimental results with the prediction of the fully ionic model, as discussed above, it is necessary to consider the effects of the electronic relaxation of the final positive hole state associated with the photoelectron emission process. The experimental values of binding energy corrected for relaxation effects, $E_b^{\text{corr}}(M^{2+})$ and $E_b^{\text{corr}}(\text{F}^-)$, have been calculated from

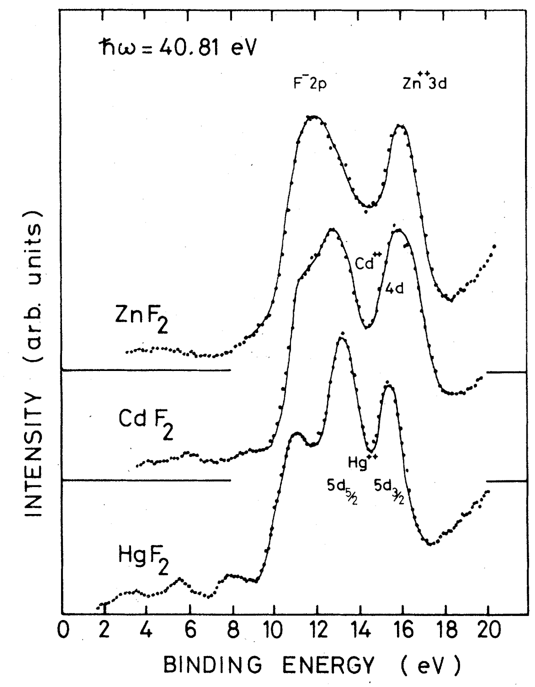

FIG. 1. Present group-IIB-metal-fluoride UPS spectra taken under the condition described in Sec. II of the text.

$$E_b^{\text{corr}}(M^{2+}) = E_b^{\text{exp}}(M^{2+}) + E_p(M^{2+})\,, \qquad (9)$$

$$E_b^{\text{corr}}(\text{F}^-) = E_b^{\text{exp}}(\text{F}^-) + E_p(\text{F}^-)\,, \qquad (10)$$

where $E_b^{\text{exp}}(M^{2+})$ and $E_b^{\text{exp}}(\text{F}^-)$ are the uncorrected experimental binding energies for the metal and fluorine levels, respectively, and $E_p(M^{2+})$ and $E_p(\text{F}^-)$ are the corresponding relaxation energies. Values of $E_p(M^{2+})$ and $E_p(\text{F}^-)$ have been calculated for the materials with the fluorite structure (i.e.,

TABLE I. Summary of fully ionic model theoretical values of binding and separation energies of the outer electronic bands of the group-IIB-metal fluorides. Symbols are defined in the text, and all energy values are in eV.

Sample	$E_b^{\text{fi}}(M^{2+})$ $nd_{5/2}$	$E_b^{\text{fi}}(\text{F}^-)$	Nearest-neighbor distance (Å)	$E_M(\text{F}^-)$	$E_M(M^{2+})$	E_M	$E_b^{\text{th}}(\text{F}^-)$	$E_b^{\text{th}}(M^{2+})$	E_s^{th}
ZnF_2	39.70	3.45	2.03	12.37	21.48	33.85	15.82	18.22	2.40
CdF_2	37.47	3.45	2.33	10.87	20.22	31.10	14.32	17.25	2.93
HgF_2	34.2	3.45	2.40	10.58	19.66	30.24	14.03	14.54	0.51

TABLE II. Summary of the present UPS experimental values of binding and separation energies of the outer electronic bands of the group-IIB-metal fluorides, together with relaxation energies and experimental values corrected for relaxation. Binding energies correspond to centroids of the relevant experimental peaks. Symbols are defined in the text and all values are in eV. The experimental uncertainties are estimated to be ±0.2 eV, except for $E_b^{exp}(F^-)$ in HgF_2.

Sample	$E_b^{exp}(F^-)$	$E_b^{exp}(M^{2+})$	E_s^{exp}	$E_p(F^-)$	$E_p(M^{2+})$	$E_b^{corr}(F^-)$	$E_b^{corr}(M^{2+})$	E_s^{corr}
ZnF_2	12.7	16.0	3.3	...	...	...	...	...
CdF_2	12.5	15.9	3.4	2.25	1.92	14.7	17.8	3.1
HgF_2	≈11	13.3	≈2.3	2.53	1.82	≈13.5	15.1	≈1.6

CdF_2 and HgF_2) using the model of Mott and Littleton (see the Appendix).

From Eqs. (9) and (10) the corrected experimental separation E_s^{corr} between the outermost levels of the group-IIB-metal and fluorine ions may be written

$$E_s^{corr} = E_b^{exp}(M^{2+}) - E_b^{exp}(F^-) + E_p(M^{2+}) - E_p(F^-), \tag{11}$$

$$= E_s^{exp} + E_p(M^{2+}) - E_p(F^-), \tag{12}$$

where E_s^{exp} is the uncorrected experimental separation. Values of $E_b^{corr}(M^{2+})$, $E_b^{corr}(F^-)$ and E_s^{corr} are also listed in Table II and have been calculated using values of $E_p(M^{2+})$ and $E_p(F^-)$ calculated in the Appendix.

We first compare the predictions of the fully ionic model with the experimental results, as discussed above, for CdF_2. More weight should be attached to the comparison of the separation of the outermost levels than the comparison of the experimental and theoretical absolute binding energies, since the inherent experimental uncertainties are much smaller in the former case. From Tables I and II we see that the experimental separation $E_s^{corr} = 3.1$ eV is in good agreement with the value $E_s^{th} = 2.93$ eV predicted by the fully ionic model, and that the absolute experimental binding energies $E_b^{corr}(M^{2+}) = 17.8$ eV and $E_b^{corr}(F^-) = 14.7$ eV are in good agreement with the predicted values $E_b^{th}(M^{2+}) = 17.25$ eV and $E_b^{th}(F^-) = 14.32$ eV.

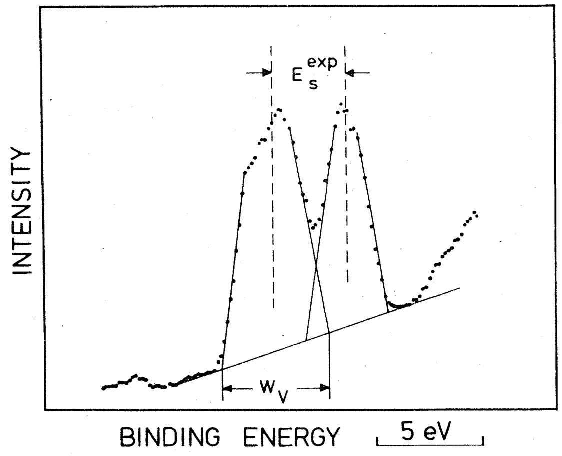

FIG. 2. Method of measuring the valence and metal d-band widths is indicated. The vertical dashed lines indicate the energy position of the centroids of the bands.

It is not possible to assign a precise value to the corrected experimental separation of ≈2 eV of the outermost levels of HgF_2 because these levels are almost totally overlapped (see Fig. 1). The value of the separation (F^- to Hg^{2+} $5d_{5/2}$) of the outermost levels predicted by the fully ionic model is $E_s^{th} = 0.51$ eV which is of the same order as the experimental observation. The absolute experimental binding energies $E_b^{corr}(M^{2+}) = 15.1$ eV and $E_b^{corr}(F^-) \approx 13.5$ eV are in approximate agreement with the predicted values of $E_b^{th}(M^{2+}) = 14.54$ eV and $E_b^{th}(F^-) = 14.03$ eV.

Relaxation energies for ZnF_2 with rutile structure are at present unavailable and consequently a detailed comparison of experimental and theoretical values is not possible at this stage. It is clear, however, that if we assign relaxation energies to the ions in ZnF_2 of similar magnitudes to those for HgF_2 then approximate agreement would exist between the experimental (relaxation corrected) energies and the corresponding values predicted by the fully ionic model.

In Fig. 3 we show the electronic energy-level diagram for the group-IIB-metal fluorides. The overall agreement between the theoretical values given by Eqs. (1) and (2) for the fully ionic crystal model and the experimental values corrected for relaxation [Eqs. (9) and (10)] is good.

V. ELECTRONIC BAND STRUCTURE

A. Spin-orbit splitting of the d bands

The initial-state electron configuration of the outermost energy band of the metal is nd^{10}, where $n = 3, 4, 5$ for Zn, Cd, and Hg, respectively. The free-ion spin-orbit splittings ΔE_{so} of the Cd^{2+} and Hg^{2+} ions[11] are $\Delta E_{so}(Cd^{2+}) = 0.71$ eV and $\Delta E_{so}(Hg^{2+}) = 1.93$ eV. In the CdF_2 spectrum (see Fig. 1) the splitting is unresolved, whereas for HgF_2 the d-

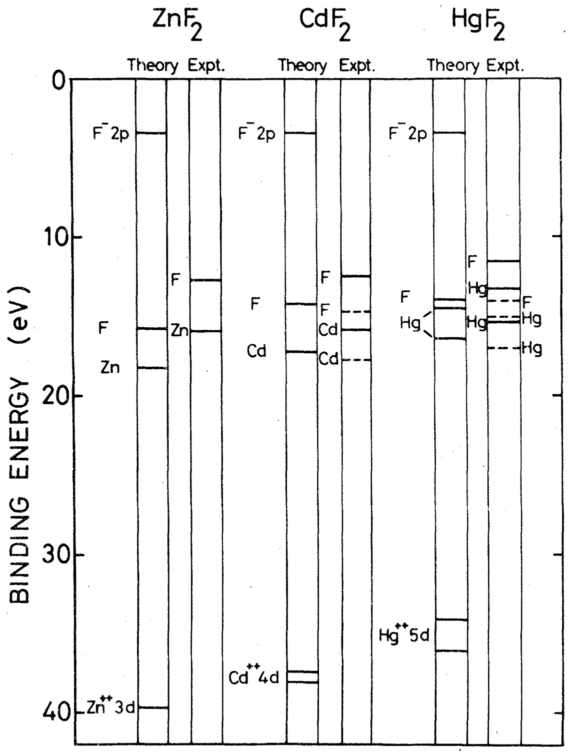

FIG. 3. Electronic energy-level diagrams for ZnF_2, CdF_2, and HgF_2. The free ion E_b^{fi} and fully ionic model theoretical E_b^{th} values are shown together with the raw experimental values E_b^{exp} (——) and the experimental values which have been corrected for relaxation effects E_b^{corr} (----).

band splitting is measured to be 2.05 eV in good agreement with the free-ion value. These observations are readily explained in terms of crystal field effects on the final-state d^9 ion and are discussed in detail elsewhere.[15] Briefly, for the d^9 final-state configuration, in the weak-field approximation, the effects of spin-orbit coupling and the crystal field are comparable perturbations on the ^2D terms and must be diagonalized together. For O_h symmetry the perturbation Hamiltonian is written

$$H=\xi\vec{L}\cdot\vec{S}+B(O_4^0+5O_4^4)\,, \tag{13}$$

where the first term is the usual spin-orbit Hamiltonian and the second term is the crystal field expressed in terms of Elliott and Stevens operators.[16] Diagonalization results in three final states (Γ_7 and two Γ_8 states in the Bethe notation). The observed splitting will clearly depend not only on the spin-orbit splitting and the crystal field, but also on the line broadening mechanisms.

B. Valence-band widths

Recently, Harrison, Ciraci, and Pantelides[17-19] have computed band characteristics of a wide range of semiconductors and insulators using a bond-orbital model and the empirical tight-binding method. Pantelides[19] has determined universal valence bands for rocksalt-type compounds and gives the following expression for the full valence-band width W_v^{rs}:

$$W_v^{rs}=7.5\ V_p\,, \tag{14}$$

where V_p is a p-bonding matrix element and is assumed to be a function of d^{-2}, where d is the bond length. The valence-band width for rocksalt compounds is written[19]

$$W_v^{rs}=\eta_v\hbar^2/md^2\,, \tag{15}$$

where η_v is a valence-band index which is taken to

TABLE III. Summary of the experimental values of valence-band widths of a number of MF and MF_2 compounds including various crystal types together with values predicted by Eqs. (15) and (19). References are shown in brackets.

Sample	Crystal structure	Full valence-band width (eV) Experiment	$\eta_v\hbar^2/md^2$	$k\chi/a_0^2$
LiF	Rocksalt	6.1[a]	6.3	6.6
NaF	Rocksalt	4.9[a]	4.7	5.0
KF	Rocksalt	3.7[a]	3.6	3.7
RbF	Rocksalt	3.1[a]	3.2	3.4
CsF	Rocksalt	2.9[a]	2.8	3.0
BeF_2	Tetragonal pseudocubic	8.9[a]	9.1	···
MgF_2	Rutile	6.3[b]	6.4	6.23[d]
CaF_2	Fluorite	4.8[b]	4.5	8.1[e]
SrF_2	Fluorite	4.4[b]	4.0	7.1[e]
BaF_2	Fluorite	3.4[b]	3.5	6.2[e]
ZnF_2	Rutile	6.2[c]	6.2	6.02[d]
CdF_2	Fluorite	4.9[c]	4.7	8.3[e]

[a] Reference 1.
[b] Reference 3.
[c] Present work.
[d] Reference 21.
[e] Reference 20.

be a function of the chemical valence Z only and is empirically given a value[19] of 3.1 and m is the free-electron mass.

Bashenov, Bagdasarov, and Timofeenko[20] have extended the work of Pantelides to fluorite-type crystals and give the following expressions for the rocksalt W_v^F valence-band widths:

$$W_v^{rs} = 7.5\ V_p = 7.5\chi/a_0^2\,, \tag{16}$$

$$W_v^F = 17.7\ V_p = 17.7\chi/a_0^2\,, \tag{17}$$

where χ is also a valence-band index.

A similar expression is given by Bashenov, Baumann, and Timofeenko[21] for the valence-band widths W_v^R of rutile-type fluorides:

$$W_v^R = 9.8\chi/a_0^2\,. \tag{18}$$

Thus in the form of Bashenov *et al.* the valence-band width of any crystal type W_v may be written

$$W_v = k\chi/a_0^2\,. \tag{19}$$

Bashenov *et al.*[20] determine the valence-band index to be $\chi = 3.57$ using the experimental values of the valence-band widths of the alkali-metal fluorides and use this value in Eqs. (17) and (18) to obtain values for W_v^F and W_v^R for some compounds as shown in Table III. It is apparent from Table III that the values for W_v^R predicted by Eq. (18) are in good agreement with the experimental values but that the values for W_v^F predicted by Eq. (17) are approximately twice the experimental values. This suggests that k might be a constant independent of the crystal type with a magnitude of approximately 8.

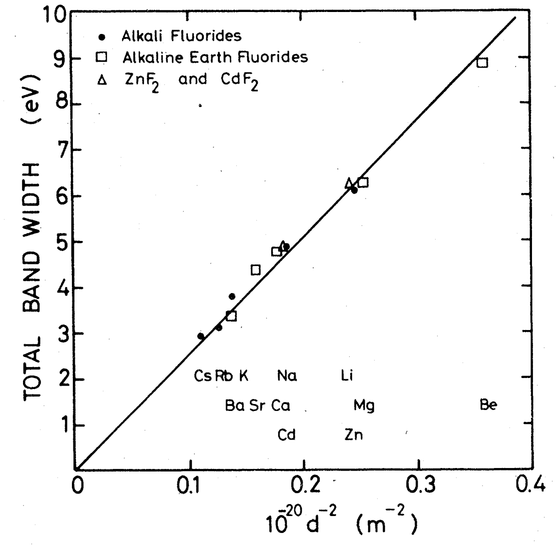

FIG. 4. Comparison between experimental values of the F^- $2p$ valence-band width and d^{-2} (where d is the bond length). The straight line is a best fit to the data for the alkali-metal and alkaline-earth fluorides.

In Fig. 4 the experimental full valence-band widths of all the fluorides listed in Table III are plotted as a function of d^{-2}. The straight line shown in Fig. 4 passes through the origin and is a best fit to the data for the alkali-metal and alkaline-earth fluorides. The gradient of this line gives a value of 3.33 for η_v which is in good agreement with the value of 3.1 given by Pantelides.[19] Values of the valence-band widths calculated using Eq. (15) and $\eta_v = 3.33$ are listed in Table III and comparison with the experimental values shows good agreement for all compounds.

Kowalczyk *et al.*[22] in analyzing the x-ray-photoelectron (XPS) spectrum of ZnF_2 found a peculiar peak shape in the Zn-$3d$–F-$2p$ region which could not be interpreted by them in terms of two simple peaks, and consequently they interpreted the valence-band spectrum in terms of crystal-field splitting in the final state.

In Fig. 5 we show a comparison of our ultraviolet-photoelectron (UPS) valence-band spectrum of ZnF_2 with the XPS spectrum of Kowalczyk *et al.*[22] On the XPS spectrum the positions of crystal-field-split final-state levels t_{2g} and e_g of the Zn $3d$ levels and the F $2p$ levels proposed by Kowalczyk *et al.*[22] are shown. This interpretation is considered to be invalid for the following reasons.

(a) The UPS spectrum of ZnF_2 in the present work (see Fig. 5) clearly shows two peaks which may readily be identified as Zn $3d$ and F $2p$ bands as may be seen from the above discussion concerning the band position and valence-band widths. This is consistent with the two-band interpretation.

(b) The relative intensities of the two peaks in both the UPS and XPS spectra are consistent with the relative subshell photoionization cross sections for Zn $3d$ and F $2p$ levels at the respective photon

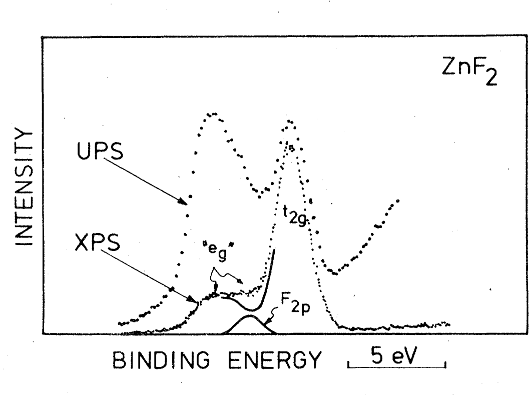

FIG. 5. Comparison of the XPS (Ref. 22) and UPS (present) spectra for ZnF_2. The spectra have been made coincident at the Zn d-band peak. Assignments of the origin of the spectral peaks are discussed in the text. The labeled assignments on the XPS spectrum are those of Kowalczyk *et al.* (Ref. 22).

energies (see Refs. 4, 23, and references contained therein). It should be particularly noted that the *change* in relative intensities of the two peaks between the x-ray and uv photon energies is consistent with the variations in relative subshell photoionization cross sections between the Zn $3d$ and F $2p$ levels with photon energy. In contrast the crystal-field description would require the relative intensities of the t_{2g} and e_g states, with common orbital character, to be approximately invariant with changes in photon energy; however, this is not observed (see Fig. 5).

(c) Various theoretical considerations favor the above simple two-band interpretation as follows.

(*i*) The valence-band structure calculation for ZnF_2 by Bashenov *et al.*[21] determines the maximum of the upper valence band to be the state Γ_5^- and its wave function to be a mixing of fluorine $2p_x$ and $2p_y$ orbitals only.

(*ii*) Since ZnF_2 and CdF_2 have a similar electronic configurations for the valence levels, we expect similarities in their electronic band structure. Recently, Albert, Jouanin, and Gout[24] have calculated the band structure of CdF_2 using the linear-combination-of-atomic-orbitals method, and they report that the higher valence band is chiefly composed of the bonding and antibonding linear combinations of the F^- p-levels and that below this band are the bands originating from the Cd^{2+} d-levels, which are rather narrow and which do not perturb significantly the upper valence bands.

(*iii*) Group theory predicts that the crystal-field splitting of the $3d^9$ final states of ZnF_2 with D_{4h} symmetry will produce four states with symmetries of a_{1g}, b_{1g}, b_{2g}, and e_g, and not simply two states (e_g and t_{2g}) as shown on the spectrum of Kowalczyk *et al.*[22]

(*iv*) A crystal-field splitting of about 4 eV would be anomalously large for a group-IIB-metal compound.

APPENDIX

Estimates for the relaxation energies used in this work have been made using the model of Mott and Littleton.[25] In this model the creation of a positive hole at a crystal lattice site during the photoelectron excitation processes polarizes the surrounding ions, and this results in a reduction of the potential and hence potential energy at the positive hole site. In the zero-order approximation of this model the relaxation energy is given by

$$E_p = \frac{e(\epsilon_\infty + 2)}{(4\pi\epsilon_0 a_0^2)^2 6\epsilon_\infty}\left(\alpha(M^{2+})\sum\frac{n(M^{2+})}{r(M^{2+})^4} + \alpha(F^-)\sum\frac{n(F^-)}{r(F^-)^4}\right), \qquad \text{(A1)}$$

where $n(M^{2+})$ is the number of M^{2+} ions of electronic polarizability $\alpha(M^{2+})$ at distance $r(M^{2+})$ from the positive hole and $n(F^-)$. $\alpha(F^-)$ and $r(F^-)$ are the corresponding quantities for the F^- ions; a_0 is the lattice constant and ϵ_∞ is the dielectric constant at optical frequencies.

The summations were carried out over 21 and 25 rings of lattice points centered on the M^{2+}-ion-hole and the F^--ion-hole lattice points, respectively, for the fluorite structure. Thus the relaxation energies for the metal ion $E_p(M^{2+})$ and the fluorine ion $E_p(F^-)$ in the fluorite crystal structure are

$$E_p(M^{2+}) = \frac{e(\epsilon_\infty + 2)}{(4\pi\epsilon_0 a_0^2)^2 6\epsilon_\infty}[68.55\,\alpha(M^{2+}) + 328.38\,\alpha(F^-)], \qquad \text{(A2)}$$

$$E_p(F^-) = \frac{e(\epsilon_\infty + 2)}{(4\pi\epsilon_0 a_0^2)^2 6\epsilon_\infty}[164.19\,\alpha(M^{2+}) + 191.76\,\alpha(F^-)]. \qquad \text{(A3)}$$

For CdF_2 values of $\alpha(Cd^{2+})$ and $\alpha(F^-)$ were taken from Tessman, Kahn, and Shockley[26]; values of a_0 and ϵ_∞ were taken from Wyckoff[14] and Bosomworth,[27] respectively.

For HgF_2 the value of $\alpha(Hg^{2+})$ was estimated by applying the Clausius-Mossotti relation

$$\alpha_e(m) = [(\epsilon_\infty - 1)/(\epsilon_\infty + 2)]3\epsilon_0 u/N \qquad \text{(A4)}$$

to $HgCl_2$ and assuming a simple additivity of polarizabilities; i.e., $\alpha_e(m) = \alpha(Hg^{2+}) + 2\alpha(Cl^-)$. Values of ϵ_∞, $\alpha(Cl^-)$, and the volume per molecule u/N were taken from Refs. 28, 26, and 14, respectively. This analysis gave $\alpha(Hg^{2+}) = 3.208 \times 10^{-40}\ \mathrm{Fm}^2$. Applying the Clausius-Mossotti relation Eq. (A4) to HgF_2 then gives the dielectric constant at optical frequencies $\epsilon_\infty = 3.296$.

---

[1] R. T. Poole, J. G. Jenkin, J. Liesegang, and R. C. G. Leckey, Phys. Rev. B 11, 5179 (1975).

[2] R. T. Poole, J. Liesegang, R. C. G. Leckey, and J. G. Jenkin, Phys. Rev. B 11, 5190 (1975).

[3] R. T. Poole, J. Szajman, R. C. G. Leckey, J. G. Jenkin, and J. Liesegang, Phys. Rev. B 12, 5672 (1975).

[4] R. T. Poole, J. D. Riley, J. G. Jenkin, J. Liesegang, and R. C. G. Leckey, Phys. Rev. B 13, 2620 (1976).

[5] R. T. Poole, J. Liesegang, R. C. G. Leckey, J. G. Jenkin, and J. B. Peel, Phys. Rev. B 13, 896 (1976).

[6] R. T. Poole, P. J. Orders, J. G. Jenkin, R. C. G. Leckey, and J. Liesegang (unpublished).

[7] *Crystals with the Fluorite Structure*, edited by W. Hayes (Clarendon, Oxford, 1974), p. 14.

[8] R. T. Poole, J. G. Jenkin, R. C. G. Leckey, and J. Liesegang, Chem. Phys. Lett. 22, 101 (1973).

[9] R. T. Poole, J. Liesegang, R. C. G. Leckey, and J. G. Jenkin, J. Electron Spectrosc. 5, 773 (1974).

[10] R. S. Berry and C. W. Reimann, J. Chem. Phys. 38, 1540 (1963).

[11] C. E. Moore, *Atomic Energy Levels*, U.S. Natl. Bur. Stand. Circ. No. 467 (U.S. GPO, Washington, D.C., 1958), Vols. 1–3.

[12] G. C. Benson and F. van Zeggeren, J. Chem. Phys. 26, 1083 (1957).

[13] V. V. Gorlach and V. M. Lisitsyn, Sov. Phys. Solid State 16, 1829 (1975).

[14] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1964), Vol. 1.

[15] R. T. Poole, J. D. Riley, D. R. Williams, J. G. Jenkin, R. C. G. Leckey, and J. Liesegang, J. Phys. C 8, 3636 (1975).

[16] R. J. Elliott and K. W. H. Stevens, Proc. R. Soc. A 219, 663 (1953).

[17] W. A. Harrison and S. Ciraci, Phys. Rev. B 10, 1516 (1974).

[18] S. T. Pantelides and W. A. Harrison, Phys. Rev. B 11, 3006 (1975).

[19] S. T. Pantelides, Phys. Rev. B 11, 5082 (1975).

[20] V. K. Bashenov, K. H. S. Bagdasarov, and V. V. Timofeenko, Phys. Status Solidi B 80, K17 (1977).

[21] V. K. Bashenov, I. Baumann, and V. V. Timofeenko, Phys. Status Solidi B 81, K55 (1977).

[22] S. P. Kowalczyk, L. Ley, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B 9, 381 (1974).

[23] R. C. G. Leckey, Phys. Rev. A 13, 1043 (1976).

[24] J. P. Albert, C. Jouanin, and C. Gout, Solid State Commun. 22, 199 (1977).

[25] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. 34, 485 (1938).

[26] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. 92, 890 (1953).

[27] D. R. Bosomworth, Phys. Rev. 157, 709 (1967).

[28] *Handbook of Chemistry and Physics*, edited by R. C. Weast (Chemical Rubber, Cleveland, Ohio, 1975), p. E-46.