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Photoelectron study of the valence bands of some transition-metal fluorides

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The results of a systematic photoelectron study using 40.81-eV photons of the valence bands of the transition-metal fluorides CrF_2, MnF_2, FeF_2, CoF_2, and NiF_2 are reported. Good agreement is found between the experimental values for the energy separation of the outermost levels of MnF_2, FeF_2, CoF_2, and NiF_2 and values calculated using the Born model for strongly ionic crystals. This agreement together with considerations of binding energy, relative photoionization cross sections, and F^- $2p$ bandwidths allows an unambiguous assignment of the level ordering of the valence bands in the compounds studied. The level of smallest binding energy in each compound is derived from the $3d$ bands of the transition metal. Excellent agreement is found between the present ultraviolet-photoelectron-spectroscopy work and the published x-ray photoelectron spectra of FeF_2 and NiF_2. The present work also confirms the interpretation by Wertheim *et al.* of the spectrum of FeF_2.

I. INTRODUCTION

This paper reports the results of a systematic photoelectron study of the valence bands of the transition-metal fluorides CrF_2, MnF_2, FeF_2, CoF_2, and NiF_2. An advantage of studying a number or group of very similar compounds at one time is that systematic variations of characteristics from compound to compound are readily highlighted. Such variations are considered to be a sensitive guide to the electronic structure and behavior of a group of materials and in the present work this procedure is exploited to assist in the assignment of the level ordering in the compounds studied.

In the last ten years or so the technique of photoelectron spectroscopy has developed rapidly both in the number of materials studied by this technique and the discovery and understanding of processes associated with the photoexcitation process in materials. This means that it is now possible to draw on a large and diverse range of published data to assist in the interpretation of new photoelectron spectra. In the present work our 40.81-eV UPS (ultraviolet photoelectron spectroscopy) spectra of FeF_2 and NiF_2 are compared to the XPS (x-ray photoelectron spectroscopy) spectra of Wertheim *et al.*[1] and of Hufner and Wertheim[2] taken using Mg $K\alpha$ radiation; and because of the strong dependence on photon energy of the photoionization cross sections of the atomic levels from which the valence bands are derived (see, for example, Goldman *et al.*[3]) we are able to determine unambiguously the level ordering in the valence bands of these compounds. In addition, the work of Poole *et al.*[4] on the bandwidths of alkali-metal and alkaline-earth fluorides is of assistance in the interpretation of the photoelectron spectra in the present work.

II. THEORY

The Born model of strongly ionic crystals has been highly successful in interpreting similar photoelectron studies of the alkali-metal halides[5–7] and the alkaline-earth fluorides.[4] Applying this model to the transition-metal fluorides, the theoretical binding energies $E_b^{th}(M^{++})$ and $E_b^{th}(F^-)$ of the outermost levels of the transition-metal and fluorine ions are as follows:

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

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

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

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

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

The total Madelung energy per molecule is[4] $E_M = E_M(M^{++}) + E_M(F^-)$ and may readily be computed if the Madelung constant for the particular crystal lattice is known. The Madelung constant is known[8] for MnF_2, FeF_2, CoF_2, and NiF_2 all of which have a rutile (D_{4h} space group) crystal structure but is unavailable for CrF_2 with C_{2h} symmetry. The breakdown of E_M into $E_M(M^{++})$ and $E_M(F^-)$ for the rutile crystal structure is also currently unavail-

TABLE I. Summary of the parameters and results of our Born-model calculation of the energy separation of the outermost levels of the transition-metal fluorides. Symbols are defined in the text and all values are in eV.

Sample	$E_b^{\text{fi}}(M^{++})$ $\ldots 3d^n 4s^0$ [a]	$E_b^{\text{fi}}(\text{F}^-)$ $\ldots 2p^6$	E_M	E_s^{th} [Eq. (3)]
CrF_2	30.95	3.45	...	...
MnF_2	33.69	3.45	32.66	−2.42
FeF_2	30.643	3.45	33.41	−6.22
CoF_2	33.49	3.45	33.94	−3.90
NiF_2	35.16	3.45	34.53	−2.82

[a] $n=4$ (Cr), 5 (Mn), 6 (Fe), 7 (Co), and 8 (Ni).

able; however, MX_2-type crystals share the Madelung energy approximately in the ratio 2 : 1 for the M and the X ions, respectively.[9]

In Table I we list values of E_s^{th} calculated from Eq. (3) together with values of $E_b^{\text{fi}}(\text{F}^-)$ and $E_b^{\text{fi}}(M^{++})$ from Berry and Reimann[10] and Moore[11] (third ionization potential), respectively. Relevant values of E_M are also shown in Table I.

It is interesting to note at this stage that all the values of E_s^{th} are negative. In each case this implies a crossing over of the outermost two levels; i.e., the binding energy of the transition-metal free-ion valence level, which is larger than the fluorine free-ion valence level is shifted by the crystal field so that the outermost level (of the transition-metal ion) has the smaller binding energy. This effect is shown schematically in Fig. 1.

In general, photoelectron spectroscopy measures the kinetic energies of electrons ejected by photons of known energy. Binding energies are then determined after taking account of spectrometer parameters such as the instrument constant and work function.[12] Binding energies determined by this technique essentially represent the differences in energy between initial and final states of the system. Because the binding energies include the final-state energies, then photoelectron spectra, in general, reflect a perturbed system rather than a one-electron system. The occurrence of these so-called "final-state effects" in photoelectron spectroscopy is now well established (see, for example, Ref. 13). In the present work two final-state effects are considered. The first is a relaxation (polarization) effect which arises as a result of the emission of a photoelectron from the crystal lattice, leaving a positive hole. The subsequent electronic relaxation around the hole results in a lowering of the binding energy. This is discussed further in Sec. III. Second, there may be a multiplicity of final states of different energies giving rise to a multiplicity of peaks in the photoelectron spectra. This is also discussed in Sec. III.

III. RESULTS AND DISCUSSION

The experimental details in regard to the spectrometer and sample preparation have been published in Ref. 5 and in references contained therein. Details of the photon source have been published in Ref. 14. Briefly, uv photons from a helium discharge lamp, operated under conditions to 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.

In Fig. 2 we show the photoelectron spectra of the valence bands of the transition-metal fluorides CrF_2, MnF_2, FeF_2, CoF_2, and NiF_2 taken with an instrumental resolution or full width at half maximum of 0.3 eV and the features of which are summarized in Table II. Before comparing the experimental results with the predictions of the above ionic model, as discussed in Sec. II, it is necessary to consider the possible effects of the electronic polarization on the final-state energy.

The experimental values of binding energy corrected for polarization effects, are given by

$$E_b^{\text{corr}}(M^{++}) = E_b^{\text{exp}}(M^{++}) + E_p(M^{++}), \tag{4}$$

$$E_b^{\text{corr}}(\text{F}^-) = E_b^{\text{exp}}(\text{F}^-) + E_p(\text{F}^-), \tag{5}$$

where $E_p(M^{++})$ and $E_p(\text{F}^-)$ are the corresponding polarization energies.

From Eqs. (4) and (5) the corrected experimental separation E_s^{corr} of the outermost levels of the transition-metal and fluorine ions is

$$E_s^{\text{corr}} = E_b^{\text{exp}}(M^{++}) - E_b^{\text{exp}}(\text{F}^-) + E_p(M^{++}) - E_p(\text{F}^-), \tag{6}$$

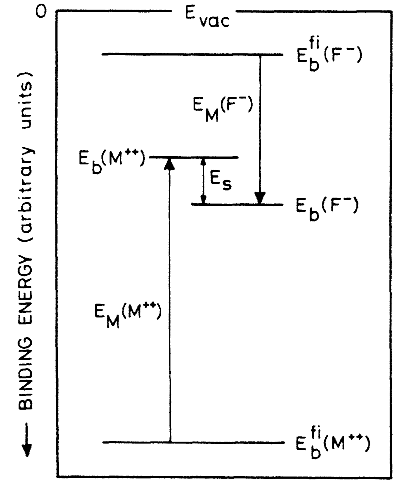

FIG. 1. Schematic diagram showing the shift in binding energies of the outermost levels of transition-metal fluorides when the free ions are placed in the crystal lattice.

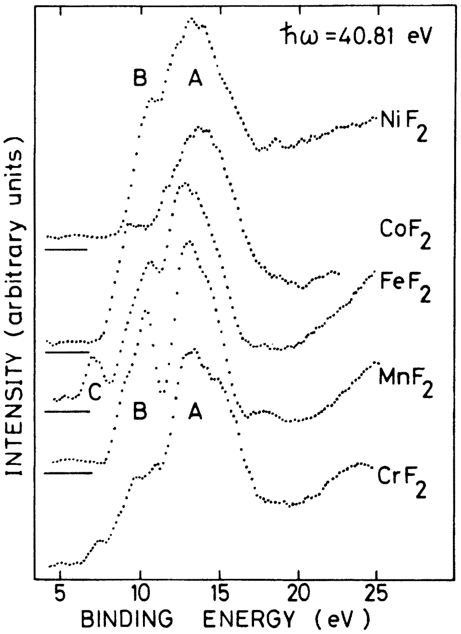

FIG. 2. Valence-band spectra of the transition-metal fluorides taken at a photon energy of 40.81 eV and an instrumental resolution (full width at half maximum) of 0.3 eV. The intensities of the spectra for the various fluorides are not related, and scattered electrons have not been subtracted from the spectra. The statistical uncertainties in the data points are of the order of the size of the dots.

which may be written

$$E_s^{\text{corr}} = E_s^{\text{exp}} + [E_p(M^{++}) - E_p(\text{F}^-)], \qquad (7)$$

where E_s^{exp} is the uncorrected experimental separation of the transition-metal and fluorine outermost levels. For the compounds studied in the present work values of $E_p(M^{++})$ and $E_p(\text{F}^-)$ are currently not available. However, similar strongly ionic solids typically have values of order 2 eV for these quantities and the difference $[E_p(M^{++}) - E_p(\text{F}^-)]$ is typically of order 0.5 eV.[4,6,7] Thus for the purposes of the present work the omission of the relaxation correction to the separation energy of the outermost levels is not expected to be serious.

As a starting point in the assignment of structure in the valence-band spectra of CrF_2, MnF_2, FeF_2, CoF_2, and NiF_2 we attribute the most intense peak (denoted peak A in each spectrum of Fig. 2) as being predominantly due to the F^- $2p$ band. In making this assignment we are guided by the following considerations.

The binding energy of peak A in each of the five spectra of Fig. 2 is remarkably similar and varies in the range 13.6–14.0 eV (see Table II). This is thought to be due to the Madelung energy E_M which varies only by 5% from MnF_2 to NiF_2 [see Table I and Eq. (2)]. Although precise theoretical values of binding energy are not available for reasons discussed above we may obtain an approximate value by taking $\frac{1}{3}E_M$ to represent $E_M(\text{F}^-)$. From Eq. (2) we then obtain $E_b^{\text{th}}(\text{F}^-) \simeq 14.5$ eV, which compares favorably to the experimental value of approximately 14 eV (Table I), although this value has not been corrected for polarization effects.

The photoionization cross sections of the atomic levels from which the valence-band levels are derived are strongly dependent on the subshell orbital quantum numbers and the photon energy. The F^- $2p$ level has a high photoionization cross section relative to other p levels and the $3d$ levels at a photon energy of 40.81 eV (see, for example, Kemeny *et al.*[15]).

Photoelectron studies of the F^- $2p$ valence-band widths of the alkaline-earth fluorides[4] and the alkali-metal fluorides[6] have shown that the total bandwidths and the full widths at half maximum are strongly dependent on the nearest-neighbor distance for the particular crystal. It seems reasonable therefore to extend this correspondence to the transition-metal fluorides as a guide to level assignment. The nearest-neighbor distances for the present compounds vary over the small range of approximately 2.1–2.0 Å for MnF_2 through NiF_2. The total bandwidths expected[4] for such values of nearest-neighbor distance are about 6.0 eV. It is apparent from the spectra of Fig. 2 that the total bandwidths of the peaks labeled as A are indeed 5 ± 1 eV.

With the assignment of the F^- $2p$ level to peak A in each spectrum we now proceed to compare the experimental separation of spectral peaks with the prediction of the ionic model as discussed above.

The values of E_s^{exp} for peaks A and B are measured (see Table II) to be 3.4, 3.4, 4.3, and 3.2 eV for CrF_2, MnF_2, CoF_2, and NiF_2, respectively. The values of $|E_s^{\text{th}}|$ are 2.4, 3.9, and 2.8 eV for

TABLE II. Summary of experimental binding energies E_b^{exp} and peak separations E_s^{exp} of the transition-metal fluoride spectral peaks. The symbols A, B, and C refer to the peaks shown in Fig. 2 and all values are in eV. The experimental uncertainties are estimated to be ±0.2 eV.

	E_b^{exp}			E_s^{exp}	
Sample	A	B	C	$A \to B$	$A \to C$
CrF_2	14.0	10.6	⋯	3.4	⋯
MnF_2	13.7	10.3	⋯	3.4	⋯
FeF_2	13.6	10.7	7.0	2.9	6.6
CoF_2	14.0	9.7	⋯	4.3	⋯
NiF_2	13.9	10.7	⋯	3.2	⋯

MnF_2, CoF_2, and NiF_2, respectively. Over all, the agreement is fairly good, and consequently we attribute the peak *B* in the spectra of MnF_2, CoF_2, and NiF_2 to be due to the 3*d* levels of Mn, Co, and Ni, respectively. It should be noted that this assignment puts the 3*d* levels at lower binding energy than the F^- 2*p* levels in each case and that this is in agreement with the negative sign for E_s^{th}; that is, that the levels have crossed over (see Fig. 1).

The value of $|E_s^{th}|$ for FeF_2 (6.2 eV) is about twice as large as the values for the other compounds listed in Table I. This is due mainly to a free-ion binding energy which is about 3 eV less than the other transition-metal ions aside from Cr^{++} (see Table I). This leads us to assign the 3*d* ground-state level of Fe^{++} to peak *C* in the spectrum of FeF_2. The value of the experimental separation between peaks *A* and *C* is 6.6 eV which compares favorably to the predicted value of 6.2 eV. It is noted that the experimental separations are all larger than the predicted values. This may be due to the omission of the relaxation correction to the experimental values as discussed above. Assignment of the peak *B* in the spectrum of FeF_2 is discussed below.

In Fig. 3 we show a comparison of our UPS valence-band spectrum of FeF_2 with the XPS spectrum of Wertheim *et al.*[1] obtained using Mg *Kα* radiation. The agreement in regard to peak positions is excellent. Peak *C* in the XPS spectrum is not fully resolved owing to the relatively poor resolution [~1.25 eV (Ref. 1)] of the XPS spectrometer. The relative peak intensities are different in the two spectra due to the strong dependence of photoionization cross sections on photon energy as discussed above. Wertheim *et al.*[1] assign peak *A* as the F^- 2*p* level by assuming a rigid energy-level separation of 21 eV between the F^- 2*s* and F^- 2*p* levels, being identical to the value for LiF. They further attribute peaks *B* and *C* to the 3*d* levels of iron and attribute the occurrence of two peaks in the spectrum to a final-state effect associated with a $3d^5$ ion in an appropriate crystal field. Thus peak *C* is attributed to the ground state of the crystal-field-split final states; whereas peak *B* is attributed to the quartet excited states. This interpretation is confirmed by our assignment as discussed above. Wertheim *et al.* estimate the relative probabilities of producing these final states as 5 : 1. Although an accurate estimate is not possible because of the substantial overlap of peaks *A* and *B* it is apparent from Fig. 3 that the relative intensity of peaks *B* and *C* is not inconsistent with this ratio.

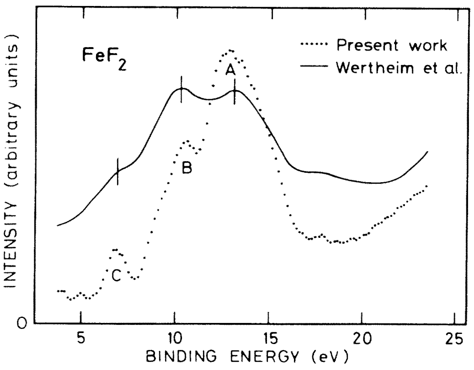

FIG. 3. Comparison of the present UPS spectrum of FeF_2 with XPS spectrum obtained by Wertheim *et al.* (Ref. 1) using a Mg *Kα* photon source.

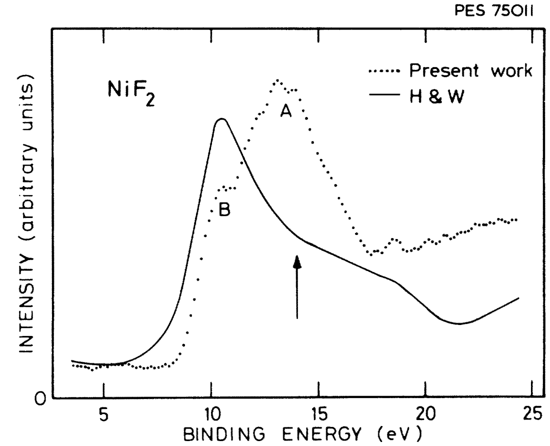

FIG. 4. Comparison of the present UPS spectrum of NiF_2 with the XPS spectrum obtained by Hüfner and Wertheim (Ref. 2) using a Mg *Kα* photon source. The arrow is referred to at the end of Sec. III.

Figure 4 shows a comparison of our UPS valence-band spectrum of NiF_2 with the XPS spectrum of Hüfner and Wertheim.[2] It is apparent from Fig. 4 that there is excellent agreement in regard to peak position. The position of the F^- 2*p* band estimated by Hüfner and Wertheim by assuming the same rigid energy-level separation of 21 eV between the F^- 2*s* and F^- 2*p* levels is shown by the arrow in Fig. 4. Peak *B* of the XPS spectrum was attributed by Hüfner and Wertheim to the Ni 3*d* band. Structure due to the F^- 2*p* band in the XPS spectrum is not as intense as in the UPS spectrum due to dominance of the Ni 3*d* band which has a much higher photoionization cross section at x-ray energies. By contrast the UPS spectrum is dominated by the F^- 2*p* band.

IV. CONCLUSIONS

Good agreement has been found between the experimental values for the energy separation of the outermost levels of the transition-metal fluorides MnF_2, FeF_2, CoF_2, and NiF_2 and values calculated using the Born model for strongly ionic crystals. This agreement together with considerations of binding energy in the Born model, relative photoionization cross sections, and F^- $2p$ bandwidths, allows an unambiguous assignment of the level ordering of valence bands in the compounds studied. In particular it is found that the level of lowest binding energy is due to the $3d$ bands of the transition metal. Comparison of the present UPS work with the published XPS spectra of FeF_2 and NiF_2 confirms this level ordering. In addition our results confirm the interpretation of Wertheim *et al.* that the peak of lowest binding energy in the spectrum of FeF_2 is the ground-state term of the $3d$ bands of Fe. Furthermore, our results support the procedure used by Wertheim *et al.* and Hüfner and Wertheim in locating the position of the F^- $2p$ band by assuming a rigid energy-band separation of the F^- $2s$ and F^- $2p$ in the compounds LiF, FeF_2, and NiF_2.

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