

X-ray photoelectron spectroscopic studies of the electronic structure of transition-metal difluorides*

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(Received 21 June 1976)

The valence-electron densities of states of the 3*d* transition-metal difluorides MnF₂, FeF₂, CoF₂, NiF₂, and ZnF₂ were obtained by means of high-resolution x-ray photoemission spectroscopy (XPS). Except for NiF₂, single-crystal samples were cleaved and studied in ultrahigh vacuum. With the aid of previous XPS results from alkali fluorides, the partial 3*d* densities of states were derived, using the constancy of the F 2*s*-F 2*p* energy separation and relative intensity ratio. The results are in very good agreement with recent multiconfigurational Hartree-Fock calculations by Viinikka and Bagus on cluster hole states, both for valence bands and for correlation-state satellite peaks.

I. INTRODUCTION

Transition-metal compounds are of great scientific and technological interest, because they possess a wide range of interesting magnetic and electrical properties. In this paper we report a high-resolution x-ray-photoemission-spectroscopy (XPS) investigation of several 3*d* transition-metal difluorides MnF₂, FeF₂, CoF₂, NiF₂, and ZnF₂.

The 3*d*-metal compounds have spatially localized 3*d* bands near the Fermi level. It is the *d* electrons that give rise to the interesting and wide range of properties which characterize these compounds.¹⁻⁴ Because the orbitals in 3*d* bands do not have a very large spatial extent beyond the ionic cores, they are not broadened very much by nearest-neighbor overlap. Thus the *d* bands are narrow and atomiclike. Photoemission studies of the 3*d* bands are of particular interest theoretically because the usual band-structure methods that work well for other solids⁵ fail to deal with the highly localized (correlated) nature of the 3*d* electrons.^{6,7} However, simple atomic models have not been completely successful in explaining the properties of these materials, either.

We selected the 3*d*-metal difluorides for study because they are the most ionic, and among the simplest, of 3*d*-metal compounds. They are also the most stable, an important factor experimentally. Their electronic structures may provide fiducial marks in understanding the 3*d* bands in more complicated, more covalent compounds. These results also serve as a stringent test of electronic structure calculations. In particular, for cluster molecular-orbital models (i.e., models wherein the central metal atom and its nearest ligands are explicitly considered), which have been suggested as being appropriate for these compounds. If these models are successful for the

(very ionic) fluorides, they should also be applicable to other 3*d*-metal systems.

Experimental procedures for this study are described in Sec. II. Results for each compound are given and discussed separately in Sec. III. Finally, conclusions are drawn in Sec. IV. Comparisons with previous photoelectron spectroscopic work on the valence-band region of 3*d* transition-metal compounds⁸⁻¹⁴ are made where relevant.

II. EXPERIMENTAL

The high-resolution XPS measurements were performed on a modified Hewlett-Packard HP 5950A electron spectrometer.^{15,16} This spectrometer employs monochromatized Al *K* α x rays ($h\nu = 1486.6$ eV) as the photon source.¹⁷ The resolution of the spectrometer is 0.55 eV.¹⁸ The system has been modified for ultrahigh-vacuum studies.^{15,16}

All the specimens used in these studies were single crystals¹⁹ of the rutile (*D*_{4h}) structure. The samples were cleaved *in situ* under ultrahigh-vacuum conditions²⁰ ($5 \times 10^{-10} \leq P \leq 5 \times 10^{-9}$ Torr) in the sample preparation chamber of the spectrometer¹⁶ and immediately transported into the analyzer chamber without breaking the ultrahigh vacuum. Before and after measurement of the valence band spectra, *in situ* analyses for carbon and oxygen contamination were performed, yielding, in most cases, undetectable amounts of these contaminants.

It is well known that photoelectron studies of nonconducting solids is plagued with the problem of sample charging. Even though we were not interested in obtaining *absolute* binding energies, nonetheless, charging presented some problems due to *inhomogeneous* line broadening. To minimize this source of resolution degradation, the

TABLE I. Characteristic features (in eV) of the transition-metal difluorides (relative to top of the valence band).

	1 ^a	2	3	4	5	6	7
MnF ₂	2.2(3) ^b	3.2(3)	4.6(3)	6.6(3)	9.6(4)
FeF ₂	2.0(2)	2.8(3)	5.1(2)	6.5(2)	8.0(3)	11.0(4)	14.0
CoF ₂	2.5(3)	5.1(3)	7.2(3)	10.4(4)	11.2(3)	13.7(4)	...
NiF ₂	4.0(3)	6.8(3)	8.4(3)	10.0(3)	11.5(3)	14.5(3)	...

^a Column headings are numbers of spectral "features" in Figs. 1, 4, 6, and 8.

^b Error in last place is given in parentheses.

samples were bathed with low-energy electrons from an electron flood gun.^{21,22} The flood gun settings were determined empirically by plotting the F 1s full width at half-maximum versus the flood gun voltage and current settings. Use of the flood gun resulted in narrowing the observed line-widths ~ 25%.

III. RESULTS AND DISCUSSION

We will discuss each of the transition metal difluorides separately below. Table I summarizes the characteristic valence-band energies of these compounds relative to the top of the valence band.

A. MnF₂

Manganous difluoride has proven to be a very useful compound in earlier detailed studies of Mn core-level spectra which led to an experimental understanding of multiplet splitting and electron correlation in photoelectron spectra of transition-metal compounds.²³ MnF₂ is the simplest transition-metal fluoride except for the d^0 case. It has a half-filled $3d$ shell with a $t_{2g}^3 e_g^2$ configuration. The valence region of MnF₂ (Fig. 1) exhibits two broad peaks. One extends from 0 to ~5 eV and is centered at ~3.3 eV relative to the top of the valence band, while the other is centered at about 6.6 eV and extends from ~5 to ~10 eV. With the aid of the alkali-fluoride spectra,²⁴ we can safely

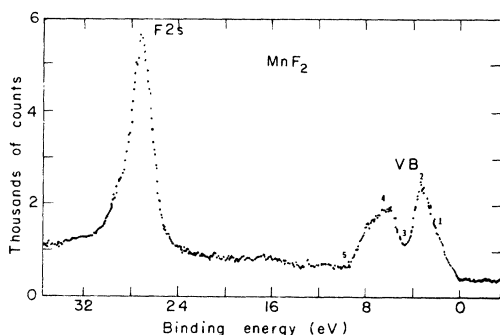


FIG. 1. MnF₂: XPS F 2s valence-band (VB) spectrum.

and unambiguously assign the 6.6-eV peak to the F $2p$ band. This follows because both the F $2s$ to F $2p$ separation and the intensity ratio are essentially constant in the various alkali fluorides. In this analysis, they matched the separation in MnF₂ of the F $2s$ peak to the 6.6-eV peak and the relative intensity of the F $2s$ to the 6.6-eV peak.²⁵ This deduced ordering of fluorine $2p$ and metal $3d$ agrees also with the ordering proposed by Poole *et al.* on the basis of the Born-model analysis.¹⁴ Figure 2 shows the MnF₂ spectrum after the F $2p$ contribution has been subtracted from the valence region. This was accomplished by (i) normalizing the intensity of F $2s$ peaks in MnF₂ to that in LiF, (ii) aligning the F $2s$ peak in LiF with the F $2s$ peak in MnF₂, and (iii) taking the difference between the two spectra. The results should yield the density of $3d$ states plus some contribution from multielectron satellites and differences in the inelastic losses in the two compounds.

Recent ultraviolet-photoemission-spectroscopy (UPS) studies¹⁴ (Fig. 3) at 40.8-eV photon energy yield results similar to Fig. 1 for the valence region. In the UPS spectrum the 6.6-eV peak, which we have assigned to F $2p$ region, is more intense than the 3.3-eV peak, which has been assigned to

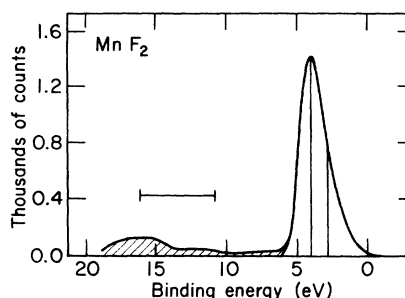


FIG. 2. MnF₂: Partial d -band density of states, obtained as discussed in text. The solid vertical bars represent calculated d states from MCHF calculations of Ref. 27. Hatched area represents mostly shake-up intensity. The horizontal bar represents the region of predicted shape-up from Ref. 27.

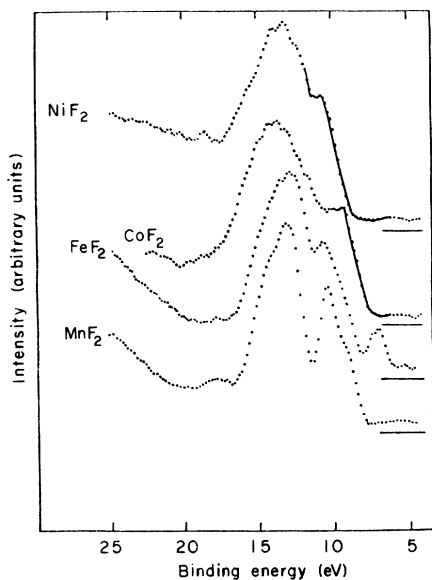


FIG. 3. UPS spectra obtained at $h\nu = 40.8$ eV (after Ref. 14).

the d states. In our XPS spectrum the relative intensities of these two peaks are reversed. This confirms our interpretation, because the F $2p$ cross section at 40.8 eV is expected to be favored over the Mn $3d$ cross section when compared to these cross sections at 1486.6 eV.

Photoionization of a $3d$ electron in MnF_2 results in either a 5E_g or a ${}^5T_{1g}$ final state with a relative intensity ${}^5T_{1g}/{}^5E_g = 1.5$. We derived a value of 1.0(1) eV for the $E_g - T_{1g}$ splitting by fitting our data with this ratio. Multiple scattering $X\alpha$ (MSX α) calculations of Larsson and Connolly²⁶ on MnF_6^{4-} cluster gave 1.36 eV for the splitting. Recently, Viinikka and Bagus²⁷ have performed calculations on transition-metal fluoride clusters using a multiconfigurational Hartree-Fock (MCHF) treatment. This *ab initio* treatment yields a 1.1-eV separation between the 5E_g and ${}^5T_{1g}$ final states of MnF_6^{4-} , in better agreement with experiment. In the spectral region to higher binding energy from the Mn $3d$ and F $2p$ peaks is some intensity which is not accounted for by either the p or d bands. This intensity is probably due to correlation ("shake-up") states, which are well known in core-level spectra of transition-metal compounds.²⁸⁻³³ Correlation states derived from ligand-to-metal charge transfer are predicted in this region by the MCHF calculations (see Fig. 2).²⁷ Both calculations^{26,27} predict the p band to be too narrow. The $2p$ bandwidth is ~ 5.6 eV, with a fullwidth at half-maximum of ~ 3.3 eV. The MCHF calculation gives ~ 3.0 eV for the width, while the MSX α calculation predicts a width of 1.5 eV. The MCHF calculation

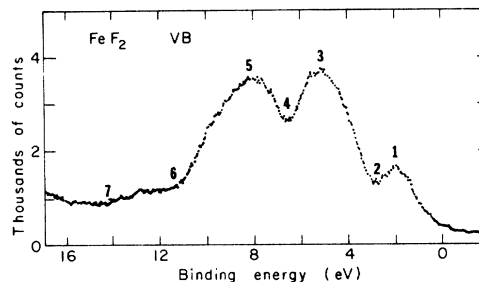


FIG. 4. FeF_2 : XPS valence-band spectrum.

places the p bands at ~ 4.9 eV below the E_g final state, while the MSX α calculation positions these states at ~ 3.8 eV. The experimental value is ~ 4.4 eV.

B. FeF_2

The valence-band spectrum of FeF_2 (Fig. 4) is very similar to MnF_2 except for a new well-resolved feature at the top of the valence band. We can use the procedure applied to MnF_2 above to obtain the $3d$ partial density of states. This results in the partial $3d$ density of state spectrum of Fig. 5. Thus the region from 0 to ~ 7 eV is due to the d states and the region from ~ 7 to ~ 11.0 eV is due to the F $2p$ states. This partitioning into p and d regions is further supported by the results of Poole *et al.*¹⁴ on the basis of cross-section differences between their 40.8-eV spectrum and our 1486.6-eV results. The new feature at 2.0 eV is due to final-state multiplets. Photoemission from $\text{Mn}^{2+}(3d^5)$, with a half-filled d shell, can only lead to quintet final states. In $\text{Fe}^{2+}(3d^6)$, the one extra d electron is antiparallel to the other majority-spin d electrons. Thus both quartet and sextet final states are now possible. The peak centered at 5.1 eV represents the manifold of quartet states, and the peak at 2.0 eV with about $\frac{1}{5}$ the intensity (0.23) of the quartet states is the 6A_1 final state.

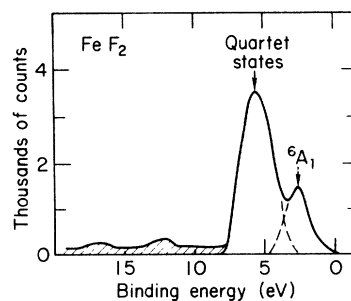


FIG. 5. FeF_2 : Partial d -band density of states, resolved as described in text.

A similar conclusion was drawn by Wertheim *et al.*³⁴ from a spectrum in which the 6A_1 state was just resolved. This points up the very localized nature of the $3d$ bands. In the rare-earth metals the $4f$ electrons of the trivalent ion cores are well known to be very localized, and they give similar spectra in their compounds, such as trifluorides.³⁵ We have an analogous case in going from Gd metal with a half-filled $4f$ shell to Tb with one electron beyond a half-filled $4f$ shell. Photoemission from the Gd $4f$ states can only yield 7F states, while for Tb, photoionization of the $4f$ electrons produces a manifold of sextet states from the majority spin states plus an 8S state (minority spin state) with $\frac{1}{7}$ the intensity of the sextet state. In FeF_2 as in MnF_2 there are also correlation states in the higher binding-energy region of the valence band. Unfortunately, there are as yet no theoretical results available for FeF_2 .

C. CoF_2

The valence-band density of states (VB DOS) of CoF_2 (Fig. 6) is not as simple as those of MnF_2 or FeF_2 . However, our success in using the LiF data to decouple the F $2p$ contribution from the $3d$ states in the simpler cases of MnF_2 and FeF_2 gives us confidence to apply this technique to CoF_2 . The results are shown in Fig. 7. Also shown in Fig. 7 as lines are the most intense final states predicted by the MCHF calculation of Viinikka and Bagus.²⁷ The agreement is remarkably good. The hatched area represents correlation-state structure, which is much more intense than in FeF_2 or MnF_2 . However, Co core levels of CoF_2 also exhibit intense correlation-state satellites, while in MnF_2 and FeF_2 the metal core levels have much weaker satellites.²⁹ The MCHF calculation predicts correlation states in this region, as indicated in Fig.

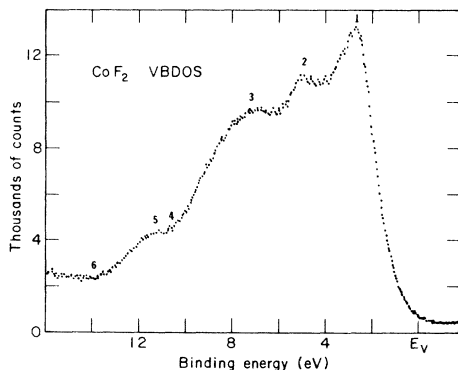


FIG. 6. CoF_2 : XPS valence-band spectrum.

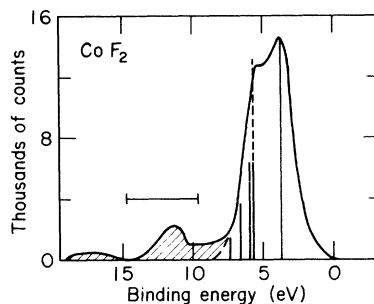


FIG. 7. CoF_2 : Partial d -band density of states. See caption for Fig. 2 (the dashed vertical line indicates the sum of the adjacent lines).

7. Again, the UPS¹⁴ results are in good agreement and show the expected cross-section modulation. The p band falls about 4.7 eV below the most intense feature in the d bands. The MCHF calculation predicts this peak to fall at 7.0 eV, far too low.

D. NiF_2

The XPS VB DOS of NiF_2 , like CoF_2 , is not very simple as there is a large degree of overlapping of the metal $3d$ bands with F $2p$ bands. Also the NiF_2 spectrum may not be as well resolved as the above difluorides because the sample was not a single crystal. We do get good agreement (Fig. 8) with the (polycrystalline) XPS spectrum of Wertheim *et al.*³⁴ Poole and co-workers¹⁴ have done UPS measurements at $h\nu = 40.8$ eV on NiF_2 . Figure 9 shows the result of subtracting out the F $2p$ contribution. Again very reasonable agreement with MCHF calculation for the $3d$ states is observed. Intense correlation structure is also observed in agreement with the Ni core-level spectra in NiF_2 .²⁹ The p levels are observed to be ~ 5.2 eV below the ${}^4T_{1g}$ state, which compares with ~ 6.1 and ~ 3.8 eV predicted by the MCHF and MSX α calculations, respectively. As in the case of MnF_2 , both calculations predict the p bands to be too narrow. The

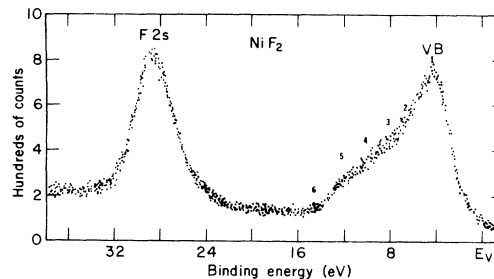


FIG. 8. NiF_2 : XPS F $2s$ VB spectrum.

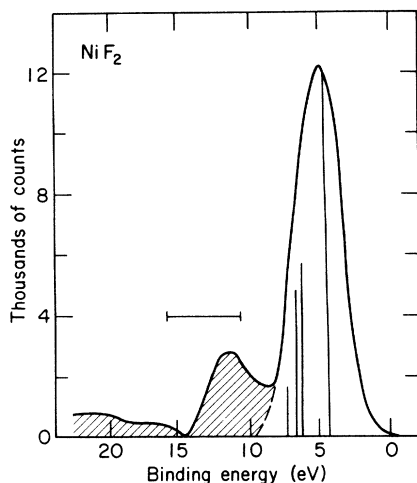


FIG. 9. NiF_2 : Partial d -band density of states. See caption for Fig. 2.

$\text{MSX}\alpha$ calculation yields a bandwidth of 1.8 eV, while the MCHF calculation is somewhat better with a bandwidth of ~ 3.0 eV. As in the case of MnF_2 , the $\text{MSX}\alpha$ calculation tends to suggest about a 1-eV splitting in the p bands, which is not observed.

E. ZnF_2

ZnF_2 was discussed earlier and we will just summarize our conclusions here.³⁶ The F $2p$ contribution to the valence region was estimated by the above procedure of using the LiF spectrum. After subtraction, considerable spectral intensity remained between the intense Zn $3d$ feature and the top of the valence band. This was attributed to crystal-field split $3d$ levels. The interpretation is supported by the fact that if only the most intense feature is assigned to the Zn $3d$ band, then (i) the intensity ratio of Zn($2p_{3/2}$) to Zn($3d$) is too high compared to zinc metal, and (ii) the Zn($2p_{3/2}$)

to Zn($3d$) energy separation would be low by 1 eV compared to the metal. It is clear that the Zn $3d$ levels are crystal-field split; however, the exact nature of this splitting is not yet known.³⁶

IV. CONCLUSIONS

For these difluorides, to a good approximation the metal d bands and the F $2p$ band are decoupled, as is well known. In cases where we have MCHF calculations (MnF_2 , CoF_2 , and NiF_2), these calculations appear to give very good agreement with our derived partial d densities of states. In these calculations the $3d$ electrons are allowed to rearrange among themselves, all the electrons are explicitly treated, and final-state effects are treated. Both the MCHF calculation and the $\text{MSX}\alpha$ calculation in general do not do very well for the F $2p$ bands. They tend especially to be too narrow. The MCHF results are much better than the $\text{MSX}\alpha$. The MCHF calculation also does well in predicting the energy of the correlation states. It would be particularly useful to obtain spectra over a wide range of photon energies in the cases where there is large overlap between the d and p bands (CoF_2 and NiF_2). Such data would give a good test of the usefulness of the technique used above to obtain partial densities of states. Also angle resolved photoemission measurements would be important in further clarifying the exact nature of the partial density of d states.³⁷

ACKNOWLEDGMENTS

We would like to thank Dr. R. S. Feigelson, Dr. H. Rinneberg, and Dr. J. Hartman for the gifts of several single crystals. Many useful discussions with Dr. P. S. Bagus, Dr. E.-K. Viinikka, Professor L. M. Falicov, Dr. B. Koiller, and Dr. B. H. Brandow are gratefully acknowledged. We are also grateful to Dr. R. C. G. Leckey for communication of the UPS results (Ref. 14) on the difluorides prior to publication.

*This report was done with support from the U. S. ERDA.

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