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Publication Date

1974-08-01

Submitted to Physical Review B

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Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

LBL-2976

c.d.

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MULTIPLY SPLITTING OF THE MANGANESE 2p AND 3p LEVELS IN MnF_2 SINGLE CRYSTALS*

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ABSTRACT

High-resolution x-ray photoemission spectra of the Mn 2p and Mn 3p levels in MnF_2 single crystals are reported. Both the Mn 2p and Mn 3p spectra show structure which we attribute to multiplet splitting. The Mn 2p spectrum is compared with earlier x-ray K α emission work of Nefedov and recent Hartree-Fock calculations of Gupta and Sen. The Mn 3p structure is also discussed and shown to obey an energy sum rule.

I. INTRODUCTION

Multiplet splitting of core-level peaks in x-ray photoemission (XPS) spectra is of interest both as a probe of the interactions between electrons in atoms, molecules, and solids, and as a diagnostic tool for acquiring information about unpaired spin in chemical systems. Since the first reports of multiplet splitting in paramagnetic gases by Hedman *et al.*¹ and in solids by Fadley *et al.*,^{2,3} there have been a number of studies of this effect in the metals and compounds of the first transition series⁴⁻⁸ and the lanthanide series.⁹⁻¹² These studies have been confined primarily to the core s levels because of the simplicity of their spectra.

Multiplet splitting is expected to be observed in an XPS spectrum if the specimen possesses unpaired electrons in its outer valence shells. The splitting arises when upon ejection of a core electron, the resulting partially filled core shell can couple with the open valence shell to form several multiplets of different energy.¹³ The simplest spectrum is expected for a core s level. This should result in two peaks with an energy separation given by Van Vleck's theorem¹⁴

$$\Delta E_{ns} = \frac{2S+1}{2\ell+1} G^{\ell}(ns, n'\ell) \quad (1)$$

where S is the initial-state spin formed by coupling n'ℓ electrons, G^{ℓ} is the appropriate atomic exchange integral, and the principal quantum numbers n and n' may or may not be equal. The relative intensities expected from this simple picture is given by the multiplicity ratio (S+1)/S. This level of interpretation neglects electron correlation and is only approximately correct.

Recently a more careful consideration^{15,16} of the multiplet splitting of core s levels in transition metal ions has shown that intra-shell electron correlation can drastically alter the spectra of ns levels when $n = n'$. The understanding of multiplet splitting of ns peaks now appears to be on firm quantitative ground.^{17,18} Only recently have the 2p levels in transition metal compounds been given a comprehensive theoretical treatment.¹⁹ The few reports of experimental evidence for splittings in these levels have been largely indirect.^{3,20,21} The XPS spectra of 3p levels of the transition metal compounds exhibit very complex spectra for which the Hartree-Fock one-electron model gives a poor description.^{2,16,22} As a step toward understanding the multiplet structure in XPS spectra of non-s levels, we have studied the multiplet splitting of the Mn 2p and 3p levels obtained in high resolution XPS measurements of MnF₂ single crystals. The experimental procedure is outlined in Sec. II. The results are presented and discussed in Sec. III. Conclusions are given in Sec. IV.

II. EXPERIMENTAL

High-resolution XPS measurements were performed with a Hewlett-Packard 5950A electron spectrometer employing monochromatized Al K α x-rays. The resolution of this instrument has been determined to be 0.55 eV.²³ The specimens were MnF₂ single crystals, cleaved in the spectrometer vacuum of $< 5 \times 10^{-9}$ torr. No oxygen or carbon could be detected in scans of the O 1s and C 1s regions. No lines of other contaminants were observed in a 0 to 1280 eV overall scan.

It is well known that under typical XPS measuring conditions,

insulating and semiconducting samples become charged and the resulting peaks are shifted and broadened. Since in this study we are interested in peak splittings, and not absolute peak positions, the shifting of peaks does not hinder us but the peak broadening can be very deleterious. In fact, in the earlier XPS experiments on MnF_2 ,^{3,17} charging effects broadened the spectra to such an extent that no direct evidence of multiplet splitting could be obtained. To minimize charging, the specimen crystals were flooded with low energy electrons.^{24,25} This resulted in greatly improved resolution and allowed an accurate determination of Mn 2p line shape. The flood-gun settings were determined by empirically optimizing the electron emission and energy for best resolution as determined by the full-width at half-maximum (FWHM) of the F 1s line. The best settings for this experiment were determined to be 0.5 ma emission and 0.5 eV electron energy.

III. RESULTS AND DISCUSSION

A. The Mn 2p Structure

Figure 1 shows the raw Mn 2p spectrum of MnF_2 . To facilitate analysis of multiplet structure, we have subtracted the inelastic background and characteristic energy loss structure by means of a suitable response function.²⁶ The resulting corrected spectrum is shown in Fig. 2.

The most striking feature of Fig. 2 is that the Mn $2p_{3/2}$ peak is asymmetric toward higher binding energy and the Mn $2p_{1/2}$ peak is asymmetric to lower binding energy. This agrees qualitatively with early x-ray emission data on the 3d metals and their compounds, in which the $K\alpha_1$ ($2p_{3/2}$ -1s) emission line has an asymmetry index α of greater than 1.0 and the $K\alpha_2$ ($2p_{1/2}$ -1s) emission line has α close to but less than 1.0.²⁷⁻³⁰ Here α is defined as

the ratio of the half-width at half-maximum on the high binding-energy side, W_H , to the half-width at half-maximum on the low binding energy side, W_L . The spectrum of Fig. 2 yields $\alpha(2p_{1/2}) = 0.8$ and $\alpha(2p_{3/2}) = 1.6$ in good agreement with the x-ray emission work. It was proposed by the x-ray workers that the asymmetry of the $K\alpha$ lines arose from multiplet splitting. In the first XPS work on MnF_2 , Fadley and Shirley³ postulated the existence of multiplet effects in their Mn 2p spectra from indirect arguments based on line widths. Later, Frost et al²⁰ studied the 2p levels of cobalt ion complexes. These workers observed that the separation of the peak maxima between the Co $2p_{1/2}$ and Co $2p_{3/2}$ levels was systematically larger by 1 eV in the high spin ($S = 3/2$) complexes than in the low spin ($S = 0$) complexes. This was interpreted as indirect evidence of multiplet splitting, in which the degeneracy of J is broken by the exchange interaction with the states of higher J shifting to lower binding energy for the $2p_{3/2}$ and to higher binding energy for the $2p_{1/2}$, thus yielding an apparent increase in the spin-orbit splitting. For MnF_2 , we found the splitting of the $2p_{3/2} - 2p_{1/2}$ peak maxima to be 13.0 (1) eV and the mean peak separation to be 12.1 (1) eV, versus 11.18 (25) for both in Mn metal.³¹ It has already been shown that there is less uncompensated spin in the metal than in MnF_2 ,⁷ so the interpretation of increased splitting being due to multiplet effects is in the same direction as in Co. Similar results have been obtained for the oxides of Ni and Co in comparison to the metals; however, diamagnetic ZnF_2 has the same splitting (within experimental error) as Zn metal. These data, which provide further support for the multiplet interpretation, are summarized in Table I. So far the only report of direct observation of

splitting has been for the Co $2p_{3/2}$ level in Co ($S = 1/2$) complexes by Briggs and Gibson; however, these authors did not observe any splitting in the Co $2p_{1/2}$ level.²¹

Besides the asymmetry of the peaks and the enhanced $2p_{1/2} - 2p_{3/2}$ splitting, two other features of Fig. 2 should be noted. First, a rather substantial area remains between the two main peaks after background correction. If our correction procedure is right, this area must represent structure. A similar correction procedure for ZnF_2 gave no intensity in this region, reinforcing the interpretation that the additional intensity in the MnF_2 spectrum is intrinsic. Secondly, the tops of the $2p_{1/2}$ and $2p_{3/2}$ peaks show signs of possible structure.

Recently Gupta and Sen¹⁹ (GS) have calculated the expected $2p$ XPS spectrum for MnF_2 by working out the levels of the $p^5 d^5$ system, employing Hartree-Fock results on the Mn^{+2} ground states. The calculations were done on three levels of sophistication. At level one, they considered only the effect of electrostatic interaction. At the second level, the spin-orbit interaction was introduced. Crystal field effects were included at the last level. For the $2p$ levels, we will compare our results with GS level-two results (their Fig. 1), since the spin-orbit interaction is comparable to the electrostatic interaction and crystal field effects did not significantly alter their results. The solid bars in Fig. 2 show the positions and intensities of the twelve eigenstates found by GS. Their energy scale was reduced by 4% to match the experimental spectrum. Adjustments of this magnitude are not surprising, because GS did not do a relaxed hole-state calculation. Figure 2 shows the GS calculation to be compatible with our XPS spectrum in considerable detail. The two peaks are asymmetric in direction that

agree with the GS results. In fact, when the latter were broadened with Lorentzian functions of appropriate intensities the resulting simulated spectrum showed asymmetries of $\alpha(3/2) \sim 1.7$ and $\alpha(1/2) \sim 0.5$ in fair agreement with the experimental values of 1.6 and 0.8, respectively, mentioned above. The $2p_{3/2} : 2p_{1/2}$ peak intensity ratio is greater than 2:1 because the six lowest-intensity lines correspond to states formed mostly from the $p_{1/2}$ level. The residual structure in the experimental spectrum just to the right of the $p_{1/2}$ peak is attributable to these states. The failure of these states to appear as sharper structure (as their intensities would require) probably indicates that these states are in fact distributed further by electron correlation effects not considered in the GS calculation. Both main peaks also show small residual tails on their left (high binding energy) sides. This tailing is chronic in our XPS spectra. We are uncertain of its origin, but we do not attribute it to the kind of multiplet splitting under discussion. On the basis of the comparison shown in Fig. 2, we conclude that the GS calculation explains the essential features of the $2p_{1/2} - 2p_{3/2}$ XPS spectrum of MnF_2 .

Figure 3 shows the $K\alpha_1$ x-ray emission spectrum of MnF_2 , after Nefedov.²⁹ This spectrum is to be compared to the $2p_{3/2}$ part of Fig. 2. The spectra are qualitatively very similar with the x-ray spectrum appearing to show more resolved structure. Both spectra have a FWHM of 3.7 eV. The components in Nefedov's spectrum are about 1.0 eV apart. A least-squares fit of our XPS $2p_{3/2}$ spectrum with four Gaussian functions restrained to have the relative intensities given by the GS results are separated by a similar amount. The agreement with the GS calculation is not quite so good. The

results of the two experiments and the GS calculation are summarized in Table II. The agreement is fair for the $2p_{3/2}$ peak and not quite so good for the $2p_{1/2}$ peak.

It seems useful at this point to comment on the extent to which the anomalous $2p_{1/2} - 2p_{3/2}$ results for MnF_2 should be generally observable in transition metals and their salts. In doing so we must first acknowledge the pioneering work of Nefedov on the manifestation of this effect in x-ray spectra²⁹ and the recent discussion by Frost *et al.* on its influence in XPS spectra.²⁰ Our comments are largely based on theirs.

The $2p_{1/2}$ and $2p_{3/2}$ peaks are separated by $3/2 \xi_{2p}$, where ξ_{2p} is the spin-orbit coupling constant, given as the expectation value of the operator

$$(\xi)_p = - \frac{e}{2m} \frac{1}{c^2} \frac{1}{r} \frac{\partial V}{\partial r} \quad (2)$$

where $V(r)$ is the electrostatic potential. Now in the interior of an atom $\frac{\partial V}{\partial r}$ is affected very little by changes in the valence shell, and the observed anomalies in $\Delta E(2p)$ in the transition elements are much too large to be attributed to any real variation in ξ_{2p} . That such anomalies do exist was demonstrated by Nefedov²⁹ in his Fig. 1. We have made a similar plot (Fig. 4) using new x-ray data and XPS data from this Laboratory. The object of this plot is to display any anomaly that may exist in $\Delta E(2p)$. To this end, the x-ray difference energy, $E(K\alpha_1) - E(K\alpha_2) = \Delta E(2p)$ or the XPS binding-energy difference $E_B(p_{1/2}) - E_B(p_{3/2}) = \Delta E(2p)$ was plotted against Z for $13 \leq Z \leq 42$. Data for each element in elemental form were used. Because ΔE varies rapidly with Z , the reduced quantity

$$\Delta E_r(2p) = \frac{\Delta E(2p)_Z}{\Delta E(2p)_{Al}} \left[\frac{(Z-2)}{H} \right]^4, \quad (3)$$

was actually plotted. This form was suggested by the fact that in a Coulomb field $V(r) = Ze/r$ the operator ξ takes the form

$$\xi = \frac{Ze^2}{2m^2c^2} r^{-3}, \quad (4)$$

and (r^{-3}) is proportional to Z^3 . We used $(Z-2)^4$ rather than Z^4 to account for shielding of the 2p electrons by the 1s shell. Data and references are given in Table III. Also listed are $E_r(\text{HFS}) = E(2p)/E(2p)_{\text{HFS}}$, where $E(2p)_{\text{HFS}}$ are the free-atom Hartree-Fock-Slater orbital energy differences calculated by Lu et al.³² Finally, points representing the compounds in Table I are included in Fig. 4.

The anomalous behavior of $\Delta E(2p)$ for the transition series metals is very obvious from Fig. 4. The anomaly is even larger for compounds. Nefedov explained this effect in terms of exchange coupling between the unpaired 3d spin S and the $2p_{3/2}$ and $2p_{1/2}$ holes, with the highest-spin state in each case being pushed to the extremes of the multiplet pattern. That this is the essence of the GS calculation is apparent from Fig. 2, in which the intensities of the eigenstates are nearly proportional to their multiplicities. The extreme eigenstates are thus the $J = 3$ state with the total angular momentum of the $2p_{1/2}^{-1}$ state coupled parallel to the $3d^5$ spin of $5/2$ and the $J = 4$ state with $S = 5/2$ and $J(2p_{3/2}^{-1}) = 3/2$ parallel. The additional configurations considered by GS have the effect of introducing additional eigenstates between the two main peaks. These will have interacted

and pushed the outer-most states further apart. It would appear that this is a rather general phenomenon for cases in which there is unpaired spin in the 3d shell. Transition metals cannot be discussed in terms of simple configurations such as $3d^5$, $6s$, but they are known to possess localized 3d spins, at least in the series Cr-Ni, and the enhancement of $\Delta E(2p)$ apparent in Fig. 4 is qualitatively understandable.

A cursory search for a similar anomaly in $\Delta E(3p)$ from x-ray data on the 4d transition metals failed to show any effect. From a practical point of view, the 2p transition metal photoemission lines are often the most intense features in the spectra of transition metal compounds; thus they would be the first choice to use in diagnostic work. However, with the presently available resolution in XPS the structure is at best barely resolvable, and the value of these lines as a "spin fingerprint" is limited. There are, however, two features from our above analysis which allow these lines to be used as a "spin probe." These are the line asymmetry and the $2p_{1/2} - 2p_{3/2}$ peak maximum separation, which should scale with spin. The 2p lines also have some disadvantages. First the peaks are usually superimposed on a high and often rapidly varying background. Second, this area of the spectrum is often complicated by Auger lines. The 3s and 3p spectra, while of much lower intensity, are usually on a low and flat background. These spectra however have the problem of being complicated by electron correlation effects which are largely absent in spectra of $N = 2$ lines. These correlation effects are discussed in Sec. III-B.

B. The Mn 3p Structure

Figure 5 shows the high resolution XPS spectrum of the Mn 3p region of MnF_2 . The features of this spectrum are summarized in Table IV. The spectrum is qualitatively the same as the earlier work of Fadley *et al.*^{2,3}, but the features are better resolved. The satellite structure is also less ambiguous, because the present study employed monochromatized x-rays, and the spectrum is free of $\text{AlK}\alpha_{3,4}$ satellites from the Mn 3s peaks and bremsstrahlung background. Improved vacuum conditions (5×10^{-9} vs. 10^{-6} torr) plus *in situ* cleavage of the specimen crystal add further confidence that the structure in this region is intrinsic to MnF_2 .

We note also that $\text{K}_{\beta\beta}$, (3p-1s) x-ray emission spectra³³⁻³⁶ have shown considerable structure. This has been given the same interpretation as the XPS results.

Fadley *et al.*² demonstrated the inadequacy of the Koopman's theorem approach in explaining the 3p multiplet structure. Multiplet-hole theory (MHT) gave some improvement but the agreement was still somewhat less than satisfactory. Their theoretical results have been duplicated and confirmed by Gupta and Sen.¹⁹ It was suggested by Fadley *et al.*² that part of the discrepancy between the experimental results and theory might be due to spin-orbit and crystal-field effects. These two effects were studied by GS and found to have a negligible effect.

The next step would appear to be the inclusion of electron-correlation effects. Correlation should be more important for the 3p-3d interaction than for the 2p-3d interaction analogous to the situation that obtains in the 3s and 2s levels.¹⁷ Electron correlation effects are crucial in understanding

the Mn 3s spectrum in MnF_2 .^{15,17} Inclusion of correlation effects leads to more 3s peaks than the Hartree-Fock one-electron model and affects the distribution of intensity among the peaks. These predictions have been confirmed by experiments.¹⁷ Intra-shell correlations are thus usually important in XPS multiplet spectra, while inter-shell correlations are not. Thus correlation must be considered in the Mn 3p spectrum even though the 2p spectrum could be explained without taking correlation into account.

Correlation can be introduced into a Hartree-Fock multiplet-hole calculation by including configuration interaction.¹⁵ This approach, which worked very well in explaining the anomalies in the Mn 3s spectrum, does not appear to work for 3p spectra.²² Bagus and Wahlgren²² have performed a Hartree-Fock calculation with configuration interaction to predict the Ni 3p spectrum in a NiO_6^{10-} molecular cluster. This calculation gave satisfactory agreement with XPS results of Ref. 37, although a detailed comparison with experiment was not possible because of the rather complicated nature of the spectra. The new peaks in the cluster calculation were attributed to the symmetry of the cluster being lower than in the free ion, enabling the nickel d electrons to re-arrange themselves in more ways than possible in the free ion. These results suggest that perhaps the XPS results of MnF_2 can be explained in similar terms. The simpler spectrum of MnF_2 makes it a good test for a correlated MHT calculation.

While a detailed comparison with theory is not yet possible, the good resolution in the 3p spectrum in Fig. 5 allows to perform a sum-rule test that has not been feasible before. The weighted average of the energy of the satellites, $\bar{E}(^5\text{P})$ can be used to define an average $^5\text{p} - ^7\text{p}$ energy separation $\Delta\bar{E}$, given by

$$\Delta\bar{E} = \bar{E}({}^5P) - E({}^7P) \quad (5)$$

From this data in Fig. 5, we obtained $\Delta\bar{E} = 14.5$ eV in MnF_2 . This should be comparable to Koopman's theorem results which predict only two 3p peaks. Values of 13.5 and 13.7 eV have been obtained with the Koopman's theorem description.^{2,3} Also the intensity ratio of the area of the 7P peak to the sum of the areas of 5P peaks was 1.1 or fairly close to the multiplicity ratio of 1.4. This good agreement provides further support to the multiplet-hole theory of the 3p spectrum even though we do not as yet have a theory that can predict the positions, or even the number, of final-state 5P peaks.

IV. SUMMARY

High-resolution XPS spectra were obtained for the Mn 2p levels in MnF_2 . Structure attributable to multiplet splitting was observed. The evidence for multiplet splitting is fourfold: 1) The asymmetry of the $2p_{3/2}$ peak is greater than unity and the asymmetry of the $2p_{1/2}$ peak is less than unity; 2) The separation of the peak maxima of the $2p_{1/2}$ from $2p_{3/2}$ lines is significantly larger in MnF_2 than in pure Mn metal; 3) After the subtraction of inelastic background and characteristic energy loss structure, there remained significant intensity in the region between the main $2p_{1/2}$ and $2p_{3/2}$ peaks; and 4) The XPS spectrum was shown to be in qualitative agreement with the calculation of Gupta and Sen. The XPS spectrum also agreed with earlier K α x-ray emission studies.

More generally, a review of x-ray K α_{12} spectra and XPS data showed an anomalously large $2p_{1/2} - 2p_{3/2}$ splitting in the transition elements Sc through Ni, as noted earlier in the x-ray literature. Since the $2p_{1/2}^{-1}$ and $2p_{3/2}^{-1}$ states are expected to couple to an unpaired spin S in the 3d shell

in such a way as to place the maximum J states ($S = 1/2$ and $S = 3/2$, respectively) at extreme energies, it is likely that the anomalous values of $\Delta E(2p)$ arise through multiplet coupling of 2p and 3d electrons.

The Mn 3p spectrum of MnF_2 was measured with improved resolution. Effects of electron correlation and crystal symmetry were concluded to be extremely important. It was suggested that a calculation on a MnF_6^{4-} cluster would be a good test of the correlated MHT theory. There is still a need for high resolution XPS work on transition metal compounds, to test and encourage theoretical work in this area. These results indicate that a qualitative understanding of the 2p and 3p spectra of transition metal ions is possible within the framework of existing theoretical models.

Besides attempting to understand these spectra as a problem in atomic physics, we can try to use these spectra as a probe of unpaired spin density in transition metal compounds. While the presently available XPS resolution does not yet allow the intense 2p lines in transition metals to be used as a definitive spin "fingerprint," these lines can still be used to probe spin density in two ways. The asymmetry of the $2p_{1/2}$ and $2p_{3/2}$ line should scale with spin, as should the separation of the $2p_{1/2}$ and $2p_{3/2}$ maxima. The 3p spectra were also shown to have possible diagnostic value by converting the "CI spectrum" into a "Koopman's theorem spectrum." It would be very valuable if this approach could be systematically applied to a series of transition metal salts, because the separation of the high- and low-spin centroids in the Koopman's theorem spectrum should be a good measure of the total 3d spin.

ACKNOWLEDGMENTS

We would like to thank Drs. P. S. Bagus, U. I. Wahlgren, R. P. Gupta, and S. K. Sen for making their results available to us prior to publication. We would also like to thank Dr. Judy Hartman for a gift of several MnF_2 single crystals. SPK would like to acknowledge several fruitful conversations with Dr. P. S. Bagus.

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*Work performed under the auspices of the U. S. Atomic Energy Commission.

† IBM Fellow.

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Table I. Separation of $2p_{1/2}$ and $2p_{3/2}$ peaks in XPS spectra of some transition metal ions and metals (in eV)

Compound	$\Delta E(2p)$
Mn (MnF_2)	12.07(10) ^a (Centroid separation)
	13.0(1) ^a (maxima separation)
Mn (Metal)	11.18(25) ^b
Co (CoO)	15.8(1) ^c
Co (Metal)	15.35(20) ^b
Ni (NiO)	18.16(20) ^c
Ni (Metal)	17.25(10) ^b
Zn (ZnF_2)	23.22(20) ^b
Zn (Metal)	23.15(5) ^b

^aThis work.

^bUnpublished work of the authors.

^cRef. 37

Table II. Energy Separations of Components of the 2p Spectrum of Mn in MnF_2
(in eV).

Group	Level	E(GS) ^a	E(XPS) ^b	E(XES) ^c
$2p_{3/2}$	P1	(0)	(0)	(0)
$2p_{3/2}$	P2	1.3	1.2	1.2
$2p_{3/2}$	P3	2.5	2.1	2.1
$2p_{3/2}$	P4	3.1	3.2	3.1
$2p_{1/2}$	P5	7.9	7.8	---
$2p_{1/2}$	P6	10.4	10.8	---
$2p_{1/2}$	P7	12.4	11.8	---
$2p_{1/2}$	P8	14.2	13.1	---

^aRef. 19.

^bThis work, with intensities constrained in GS values.

^cRef. 29

Table III. Values of $\Delta E(2p)$ for $13 \leq Z \leq 42$ (in eV).

Z	$E(K\alpha_1) - E(K\alpha_2)^a$	ΔE_{XPS}^b	$E_r(RHFS)^c$	E_r^d
13	0.43		0.90	(1.00)
14	0.60		0.85	0.99
15	~ 1		---	---
16	1.20		0.85	1.06
17	1.61		0.89	1.08
18	2.07		0.93	1.08
19	2.7		0.90	1.10
20	3.59		0.93	1.16
21	4.5	4.92	1.04	1.32
22	5.98	6.13	1.00	1.29
23	7.56	7.82	1.04	1.35
24	9.21	9.31	1.03	1.35
25	11.10	11.18	1.03	1.35
26	13.00	13.10	1.01	1.34
27	15.02	15.33	0.99	1.32
28	17.26	17.25	0.95	1.29
29	19.95	19.8	0.94	1.27
30	23.12	23.13	0.94	1.28
31	26.92		0.95	1.29
32	31.10		0.95	1.31
33	35.73			1.32
34	41.0			1.33

continued

Table III. continued

Group	$E(K\alpha_1) - E(K\alpha_2)^a$	ΔE_{XPS}^b	$E_r(RHFS)^c$	E_r^d
35	46.6			1.34
36	52.5			1.34
37	59.5			1.35
38	67.1			1.36
39	75.5			1.37
40	84.2			1.37
41	94.1			1.39
42	105.0			1.40
$MnF_2(\bar{E})$	12.1			1.47
$MnF_2(Max)$	13.0			1.58
CoO	15.8			1.37
NiO	18.16			1.36
ZnF_2	23.22			1.28

^aFrom J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967).

^bPreliminary data from this Laboratory.

^cRef. 32.

^dSee Eq. (3). The value 0.43 eV has been used for Al.

Table IV. Summary of the Observed Splitting and Relative Intensities of the

Mn3p Levels in MnF_2

Mn3p final state	^7P	$^5\text{P}(1)$	$^5\text{P}(2)$	$^5\text{P}(3)$	$^5\text{P}(4)$	$^5\text{P}(5)$
Energy (eV) ^a	0.0	2.75(5)	7.6(5)	12.75(30)	17.5(2)	21.8(1)
Relative Intensity ^b	1.0	0.19		$\sim 0.28^c$	~ 0.21	~ 0.26

^aThe energies are given relative to the ^7P state.

^bThe intensities are relative to ^7P level.

^cThis is the sum of the $^5\text{P}(2)$ and $^5\text{P}(3)$ intensities.

FIGURE CAPTIONS

Fig. 1. Raw XPS spectrum of the 2p region of MnF_2 , taken under electron flood-gun conditions. The binding energy reference is the top of the valance bands of MnF_2 .

Fig. 2. Corrected Mn 2p spectrum (points) and spectrum calculated by GS (bars) for MnF_2 . The energy scale of the calculated spectrum has been reduced by a factor of 0.96. The six strong peaks are labelled P1, P2, P3, P4, P7, and P8 from right for purposes of comparison with Table II. The triplet and doublet of small peaks between P4 and P7 are considered as two groups, labelled P5 and P6, respectively. Reference level is the top of the valence bands, as in Fig. 1.

Fig. 3. The $\text{K}\alpha_1$ x-ray profile of Mn in MnF_2 , after Nefedov (Ref. 29). Bars indicate states calculated by Gupta and Sen. Each division on the abscissa is 1 eV.

Fig. 4. Reduced 2p spin-orbit splitting of the elements, $\Delta E_r = [(Z-2)^4/Z^4] \Delta E_r(\text{Al})$. The filled circles denote the compounds in Table I, while the X represents separation of peak maxima in MnF_2 . Dashed and solid curves are drawn in only to guide the eye.

Fig. 5. Mn 3p XPS spectrum in MnF_2 , together with fitted peaks. The very broad peaks probably represent several states. The binding energy of the ^7P peak is 46.76 eV relative to the top of the valence bands.

XBL 748-4057

Fig. 1

XBL 748-4056

Fig. 2

XBL 748-4058

Fig. 3

XBL 748-4055

Fig. 4

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Fig. 5

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