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Multiplet splitting of the manganese $2p$ and $3p$ levels in MnF_2 single crystals*

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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 and shown to be in qualitative agreement with earlier x-ray $K\alpha$ emission work of Nefedov and recent Hartree-Fock calculations of Gupta and Sen. The asymmetry of the $2p_{1/2}$ and $2p_{3/2}$ levels is discussed in terms of multiplet splitting and suggested to be a good indicator of the amount of unpaired spin. The Mn $3p$ structure is also discussed and shown to obey an energy sum rule. This sum rule allows a very complicated "configuration-interaction spectrum" to be converted into a simpler "Koopmans-theorem spectrum" which can then be used to obtain a measure of the unpaired spin.

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 and coworkers,[2,3] there have been a number of studies of this effect in the metals and compounds of the first transition series[4-8] 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 theorem,[14]

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

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 MnF_2 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 $K\alpha$ x rays. The resolution of this instrument has been determined to be 0.55 eV.[23] The specimens were MnF_2 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 – 1280-eV over-all 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

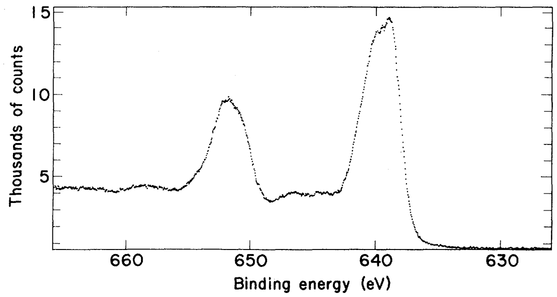

FIG. 1. Raw XPS spectrum of the $2p$ region of MnF_2, taken under electron flood-gun conditions. The binding-energy reference is the top of the valence bands of MnF_2.

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. 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. To correct for energy losses, the inelastic loss spectrum was approximated by the sum of a continuous tail with the magnitude at each point proportional to the spectra area at lower binding energy, plus a discrete loss structure constructed by folding in a response function determined from the discrete inelastic structure on the high-binding-energy side of the Mn $2p_{1/2}$ peak. This is similar to the procedure used by Fadley.[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 toward 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 Shirley[3] postulated the existence of multiplet effects in their Mn $2p$ spectra from indirect arguments based on linewidths. Later, Frost *et al.*[20] 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 ($S = \frac{3}{2}$) 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 ($S = \frac{1}{2}$) complexes by Briggs and Gibson; however, these authors did

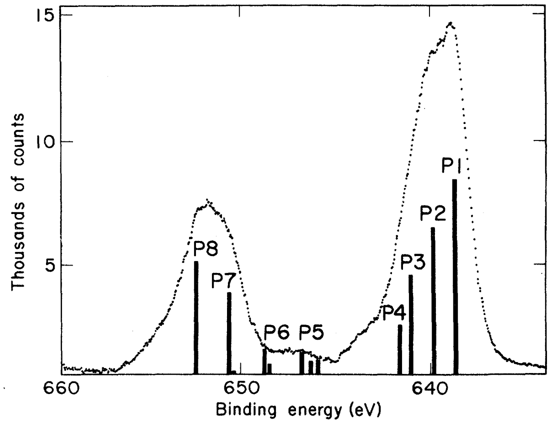

FIG. 2. Corrected Mn $2p$ spectrum (points) and spectrum calculated by GS (bars) for MnF_2. The energy scale scale of the calculated spectrum has been reduced by a factor of 0.96. The six strong peaks are labeled $P1$, $P2$, $P3$, $P4$, $P7$, and $P8$ from right for purposes of comparison with Table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

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]

[a] This work.

[b] Unpublished work of the authors.

[c] Reference 37.

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 Sen[19] (GS) have calculated the expected $2p$ XPS spectrum for MnF_2 by working out the levels of the p^5d^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 12 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 directions 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 $\alpha(\frac{3}{2}) \sim 1.7$ and $\alpha(\frac{1}{2}) \sim 0.5$, 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 spectra[29] 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 $\frac{3}{2}\xi_{2p}$, where ξ_{2p} is the spin-orbit coupling constant, given

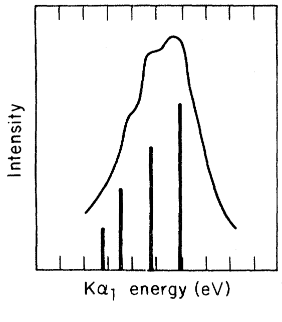

FIG. 3. $K\alpha_1$ x-ray profile of Mn in MnF_2, after Nefedov (Ref. 29). Bars indicate states calculated by Gupta and Sen. Each division on the abscissa is 1 eV.

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	...

[a] Reference 19.

[b] This work, with intensities constrained in GS values.

[c] X-ray emission spectroscopy (XES) values obtained from Ref. 29.

as the expectation value of the operator

$$(\xi)_{2p} = -\frac{e}{2m^2c^2}\,\frac{1}{r}\,\frac{\partial V}{\partial r}\,, \tag{2}$$

where $V(r)$ is the electrostatic potential. Now in the interior of an atom $\partial V/\partial r$ 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 Nefedov[29] 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, $E_B(2p_{1/2}) - E_B(2p_{3/2}) = \Delta E(2p)$, was plotted against Z for $13 \leqslant Z \leqslant 42$. Data for each element in elemental form were used. Because ΔE varies rapidly with Z, the reduced quantity

$$\Delta E_r(2p) = \frac{\Delta E(2p)_Z}{\Delta E(2p)_{\mathrm{Al}}}\left(\frac{(Z-2)}{Z}\right)^4 \tag{3}$$

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

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

and $\langle r^{-3}\rangle$ 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(RHFS) $= E(2p)/E(2p)_{\mathrm{RHFS}}$, where $E(2p)_{\mathrm{RHFS}}$ are the free-atom relativistic Hartree-Fock-Slater (RHFS) 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 $\frac{5}{2}$ and the $J = 4$ state with $S = \frac{5}{2}$ and $J(2p_{3/2}^{-1}) = \frac{3}{2}$ 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 outermost 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

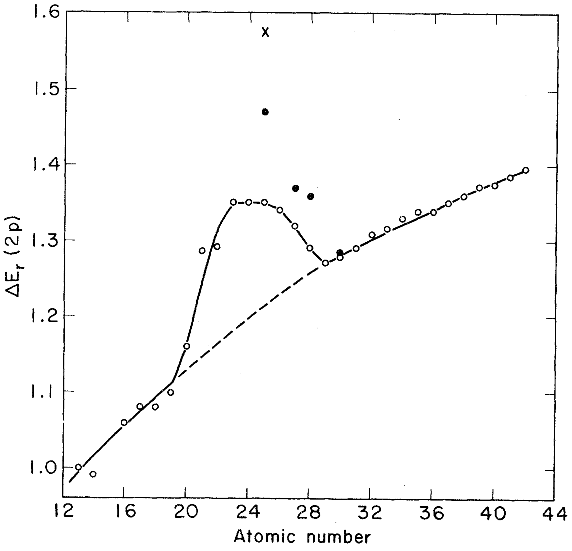

FIG. 4. Reduced $2p$ spin-orbit splitting of the elements, $\Delta E_r = [(Z-2)^3/Z^4]\,[\Delta E(2p)_Z/\Delta E(2p)_{\mathrm{Al}}]$. The filled circles denote the compounds in Table I, while the × represents separation of peak maxima in MnF_2. The open circles are for the elements in their elemental form. The results for $Z = 21$–30 were obtained by XPS and for $Z = 13$–20 and $Z = 31$–42 were obtained from x-ray work. The values are summarized in Table III. Dashed and solid curves are drawn in only to guide the eye.

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
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

[a] From J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967).

[b] Preliminary data from this laboratory.

[c] Relativistic Hartree-Fock-Slater (RHFS) values from Ref. 32.

[d] See Eq. (3). The value 0.43 eV has been used for Al.

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 analysis above 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 2*p* 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 3*s* and 3*p* 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. Mn 3*p* structure

Figure 5 shows the high-resolution XPS spectrum of the Mn 3*p* 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 Al $K\alpha_{3,4}$ satellites from the Mn 3*s* 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 $K\beta\beta'$ (3*p*-1*s*) x-ray emission spectra[33-36] have shown considerable structure. This has been given the same interpretation as the XPS results.

Fadley *et al.*[2] demonstrated the inadequacy of the Koopmans-theorem approach in explaining the 3*p* 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 3*p*-3*d* interaction than for the 2*p*-3*d* interaction analogous to the situation

TABLE IV. Summary of the observed splitting and relative intensities of the Mn 3*p* levels in MnF_2.

Mn 3*p* final state	^7P	$^5P(1)$	$^5P(2)$	$^5P(3)$	$^5P(4)$	$^5P(5)$
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		~0.28[c]	~0.21	~0.26

[a] The energies are given relative to the ^7P state.

[b] The intensities are relative to ^7P level.

[c] This is the sum of the $^5P(2)$ and $^5P(3)$ intensities.

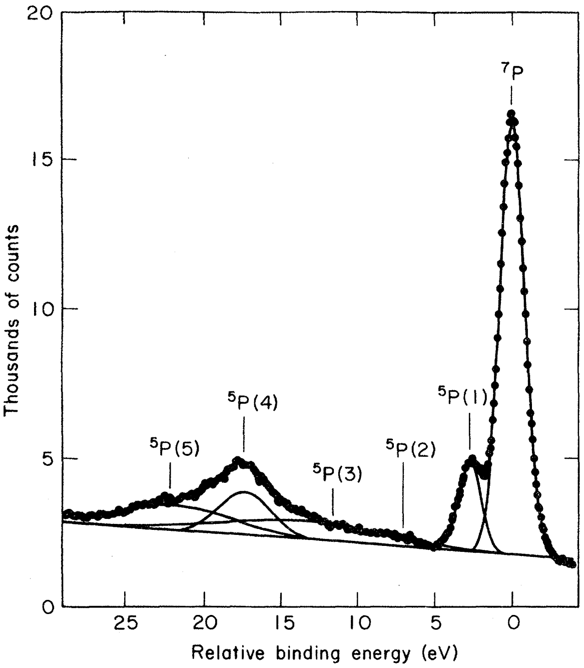

FIG. 5. Mn $3p$ XPS spectrum in MnF$_2$, together with fitted peaks. The very broad peaks probably represent several states. The binding energy of the ^7P peak is 46.76 eV relative to the top of the valence bands.

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 Wahlgren[22] 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 the 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 rearrange 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. A correlated MHT calculation on a MnF$_6^{4-}$ cluster would be useful in this respect. The simpler spectrum of MnF$_2$ makes it a better and less ambiguous test for a correlated MHT calculation than NiO.

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

$$\Delta\overline{E} = \overline{E}(^5P) - E(^7P)\ . \tag{5}$$

From these data in Fig. 5, we obtained $\Delta\overline{E} = 14.5$ eV in MnF$_2$. This should be comparable to Koopmans-theorem results, which predict only two $3p$ peaks. Values of 13.5 and 13.7 eV have been obtained with the Koopmans-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 farily 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: (i) 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; (ii) 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; (iii) 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 (iv) the XPS spectrum was shown to be in qualitative agreement with the calculation of Gupta and Sen. The XPS spectrum also agreed with earlier $K\alpha$ x-ray emission studies.

More generally, a review of x-ray $K\alpha_{12}$ 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 ($S=\frac{1}{2}$ and $S=\frac{3}{2}$, 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 $2p_{3/2}$ lines 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 (configuration interaction) spectrum," i.e., the measured spectrum, into a "Koopmans-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 Koopmans-theorem spectrum should be a good measure of the total 3d spin.

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