[1] P. Lawaetz, Phys. Rev. Lett. **26**, 697 (1971).

[2] For a review, see J. C. Phillips, Rev. Mod. Phys. **42**, 317 (1970).

[3] B. F. Levine (unpublished). Some of the values of ϵ and f_i listed here differ considerably from those used in Ref. 1.

[4] R. M. Martin, Phys. Rev. B **1**, 4005 (1971).

[5] G. Lucovsky, R. M. Martin, and E. Burstein, Phys. Rev. B **4**, 1367 (1971).

[6] P. Lawaetz, Phys. Rev. B **5**, 4039 (1972).

PHYSICAL REVIEW B VOLUME 7, NUMBER 8 15 APRIL 1973

New Multiplet Structure in Photemission from MnF_2†

S. P. Kowalczyk*, L. Ley‡, R. A. Pollak, F. R. McFeely, and D. A. Shirley

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

(Received 7 December 1972)

A high-resolution x-ray-photoelectron-spectroscopy investigation of the multiplet structure of manganese 2*s* and 3*s* levels in MnF_2 is reported. The Mn 3*s* results quantitatively confirm three predictions of a recent configuration-interaction calculation concerning the magnitude of the splitting, the deviation of the observed intensity ratio from the multiplicity ratio, and new structure. The first observation of multiplet splitting of the Mn 2*s* level is also reported and compared with calculations.

Early (XPS) studies[1,2] of multiplet splitting in transition-metal ions established the effect but left some basic questions unanswered. In particular, for the 3*s* doublet in the XPS spectra of Mn^{2+} and Fe^{3+} compounds, neither the intensity ratio (2 : 1 rather than the multiplet ratio 7 : 5) nor the magnitude of the splitting was completely understood. This situation was unsatisfactory: multiplet splitting of hole states should be understood both as a problem in atomic physics and because of its application as a diagnostic tool to solid-state and chemical problems. In fact, recent studies in which multiplet splitting has been correlated with the initial-state spin[3,4] *S* or used to derive information about covalency[5,6] have emphasized the urgency of acquiring a truly quantitative understanding of the essential phenomenon.

Sasaki and Bagus[7] have recently carried out a configuration-interaction calculation on Mn^{2+} that appears to explain the 2*s* and 3*s* hole-state multiplet structure observed earlier. Their results provide definite predictions about additional features of these states. In this Note we report detailed, quantitative confirmation of those predictions in the XPS spectrum of MnF_2.

Manganous fluoride was chosen for its simplicity, its nearly complete ionicity, its large number of unpaired *d* electrons, and its extreme thermodynamic stability. Spectra were obtained from single-crystal specimens in a Hewlett–Packard 5950A ESCA spectrometer. The crystals were cleaved in an inert atmosphere and introduced directly into the spectrometer vacuum at 8×10^{-9} Torr. The 1*s* lines of carbon and oxygen (the two most common surface contaminants) were monitored *in situ* before and after the Mn 2*s* and 3*s* spectra were recorded. Very little carbon and no oxygen were detected. The peak intensity ratios relative to the Mn 3*p* (^7P) peak were

$$\text{Mn } 3p\ (^7P) : \text{O } 1s > 20 : 1,$$

$$\text{Mn } 3p\ (^7P) : \text{C } 1s = 9.3 : 1.$$

The simplest description of the 2*s* and 3*s* XPS spectra from Mn^{2+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5;\ ^6S$) is obtained by coupling each *s* hole state to the valence shell. Two final states may be reached by one-electron photoemission from either the 2*s* or the 3*s* shell. These final states have ^7S and ^5S symmetry in each case. In the ^7S states the remaining 2*s* or 3*s* electron is coupled parallel to the *d*-shell spin $S=\frac{5}{2}$, while in the ^5S states the two spins are antiparallel. For either the 2*s* or the 3*s* case the photoemission spectral line intensities should be the multiplet ratio $^7S : {}^5S = 7 : 5$ in this approximation, while the two components should be split by $(\frac{6}{5})G^2(sd)$, according to Van Vleck's theorem.[8] Here $G^2(sd)$ is the appropriate *sd* Slater-exchange integral. At this level of interpretation it would seemingly be straightforward to use the observed splitting diagnostically to deduce covalent character.

More careful consideration leads to several modifications of the above model. These have been covered in detail recently by Freeman, Bagus, and Mallow,[9] who have made calculations on MnF_6 clusters, and our discussion below leans heavily on their paper. First it should be pointed out that estimates of the ^5S-^7S splitting based on ground-state unrestricted Hartree–Fock (UHF) calculations may give fortuitously good agreement with experiment because two effects of opposite sign have been omitted. A more realistic hole-state calculation increases the splitting, both because it properly couples final-state spins and because it allows the orbital to relax properly in the hole state.[9] Electron correlation, however, tends to reduce the splitting because the ^5S state's energy is lowered more than that of the ^7S state. This is true because s and $3d$ electrons of like spin (in the ^7S state) are already relatively well correlated due to the use of antisymmetrized wave functions in HF or UHF theory to satisfy the Pauli principle. Correlation of the motion of the antiparallel s and $3d$ pairs in the ^5S states thus improves these states' energies more. Pressing this line of reasoning further, one might intuitively expect better agreement between the Hartree–Fock splittings and experiment when the one-electron hole states and the magnetic shell have different principal quantum numbers. This follows because an increase in radial separation of the s and d or s and f pairs would diminish the importance of correlation between antiparallel electrons on the multiplet splitting. Thus in rare earths the Hartree–Fock estimates of splitting should be more accurate for the $5s$ than the $4s$ shell (as observed[4]) while the $2s$ splitting would be predicted more accurately than the $3s$ splitting in the $3d$ ions (see below). Freeman *et al.*[9] have reached the same conclusion using configuration-interaction arguments.

Going beyond Hartree–Fock estimates, Sasaki and Bagus[7] made configuration-interaction calculations on the Mn^{3+} $[3s^1 3p^6(3d^5;\,^6S)]$ states. They found, for example, that ^5S states formed from the configuration $3s^2 3p^4 3d^6$ were very important. By considering a total of seven ways in which ^5S states and two ways in which ^7S states can be formed by internal correlation,[10] they were able to make three predictions that could be experimentally tested. First, the ^7S-^5S splitting was reduced to 4.7 eV (or to 7.8 eV if semi-internal correlations were also considered), in reasonable agreement with the experimental value of 6.62 eV (see Table I). Second, the intensity ratio of these two peaks is correctly predicted as 2.2:1, thereby clearing up a vexing anomaly.

The third prediction, which is tested for the first time in this Note, is that ^5S satellite peaks should appear in the spectrum. These satellites may be understood by writing the seven (or more if semi-internal correlations are considered) eigenstates of ^5S symmetry as

$$|\psi_i\rangle = C_{i1}|3s^1 3p^6 3d^5\rangle + \sum_{j=2}^{7} C_{ij}|\phi_j\rangle ,$$

where $i = 1, 2, \ldots, 7$, and $|\phi_j\rangle$ represents the jth admixed configuration. Since the intensity of a $3s$-photoemission line from the $(3s^2 3p^6 3d^5;\,^6S)$ ground state is proportional, for one-electron transition, to $|C_{ij}|^2$ (neglecting small deviations from unity of the overlap between the initial- and

TABLE I. Summary of the Mn $3s$ and $2s$ photoelectron results and comparison with theoretical predictions.

	Binding energies (eV)[a]				Intensity ratios[b]				
Manganese $3s$ final state	^7S	$^5S(1)$	$^5S(2)$	$^5S(3)$	$^7S/^5S(1)$	$^5S(1)/^5S(2)$[c]	$^5S(2)/^5S(3)$[c]	$^5S(1)/^5S(2')$[c]	$^5S(2')/^5S(2'')$[c]
Experiment	0.00	6.62 ± 0.01	20.7 ± 0.1	37.8 ± 0.7	2.3 ± 0.1	2.1 ± 0.1	2.5 ± 0.1	...	...
Theory[d] 1. Freeman, Bagus, and Mallow (MHT)[9]	0.00	14.3	...	...	1.4	...	...	...	...
2. Sasaki and Bagus (CI)[7]	0.00	4.71	22.53 23.75	43.06	...	2.87	1.58	3.58	4.00
3. Sasaki and Bagus (CI)[7]	0.00	7.83	25.19 27.58	...	2.2	4.1	...	4.48	4.47
Manganese $2s$ final state		^7S				^5S			$^7S{}^5S$
Experiment		0.00				5.85 ± 0.05			1.4 ± 0.1
Theory Freeman, Bagus, and Mallow (MHT)[9]		0.00				6.10			1.4

[a] The binding energies are given relative to the ^7S peak and are the result of analytically least squares fitting the experimental spectrum with Lorentzian line shapes. The Mn $3s$ results are the average of two runs on different single crystals.

[b] The intensity ratios for the Mn $3s$ peaks were arrived at by measuring the areas of the peaks with a planimeter. The Mn $2s$ ratios were the result of areas derived from a least-squares fit to Lorentzian peak shape.

[c] $^5S(2)$ refers to the total intensity due to two neighboring theoretical eigenstates (which could not be experimentally resolved), while $^5S(2')$ and $^5S(2'')$ refer, respectively, to the intensity due to the first and the second of the two neighboring eigenstates.

[d] Theory 1 is a multiplet hole theory—optimized orbital calculation. Theories 2 and 3 are configuration-interaction calculations. Theory 2 takes only internal correlations into account, while theory 3 also includes semi-internal correlations.

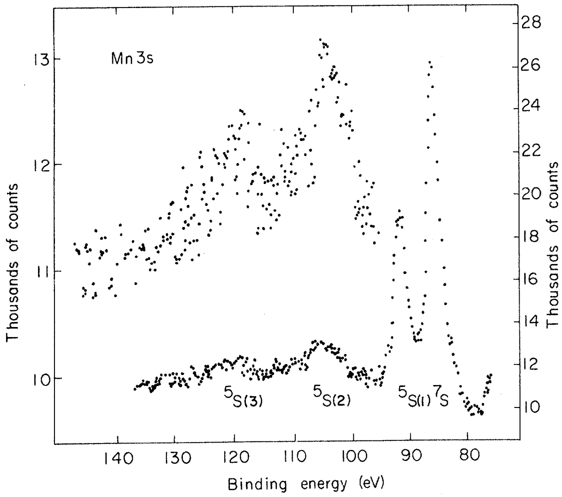

FIG. 1. Manganese 3*s* spectrum with the energy scale referenced to the Au $4f_{7/2}$ (84.00 ± 0.01 eV) peak. The right ordinate refers to the complete spectrum and the left ordinate refers to the expanded portion of the spectrum.

final-state passive electron), it follows that the intensity lost from the main ^5S line, viz., $1 - |C_{11}|^2$, must appear at eigenenergies E_i of the states $|\psi_i\rangle$. In this way Sasaki and Bagus predicted peaks at ~ 25 and ~ 43 eV relative to the ^7S peak position, with the first, more intense peak arising from two neighboring eigenstates. Our spectra (Fig. 1) confirm this prediction very nicely. We identify these satellites with the observed peaks at 20.7 and 37.8 eV below the ^7S peak. Furthermore, the ratio of the intensity of the septet peak to the sum of the intensities of the quintet peaks, 1.3 ± 0.2, compares well with the value 1.4 expected from multiplicity considerations. A detailed comparison is made in Table I. An earlier, tentative assignment of the peak at ~ 20 eV to inelastic losses[1] is not supported by the present more detailed study of line structure and satellites on MnF_2 single crystals.

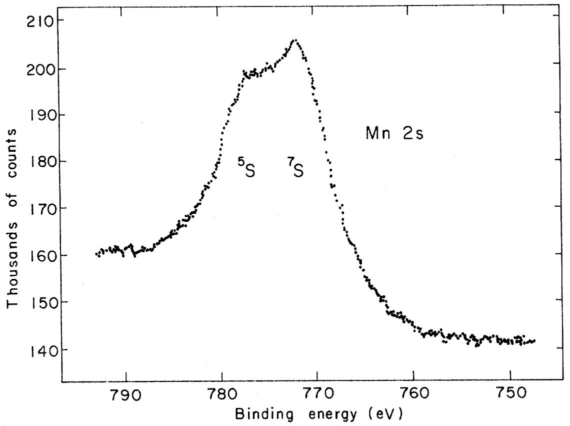

FIG. 2. Manganese 2*s* spectrum with the energy scale referenced to the Au $4f_{7/2}$ (84.00 ± 0.01 eV) peak.

The 2*s* line (Fig. 2) shows doublet structure, as expected. Both the splitting and the relative intensity are in very good agreement with the predictions of multiplet hole theory (Table I): thus the 2*s*-hole-state ^7S-^5S splitting is not strongly reduced by correlation and the ^7S:^5S ratio is very nearly the multiplicity ratio.

The hole structure for Mn^{3+}($2s^*$ or $3s^*$) final states is now quantitatively understood; theory and experiment show good agreement in splitting, relative intensity, and satellite structure. The complexity of the 3*s* spectrum precludes the quantitative validity of simplistic correlations of 3*s* splitting with total spin or covalent character (at least without further analysis), although qualitative trends of this nature have already been observed. On the other hand, the existence of observable 3*s* satellite structure should prove useful in studying interactions with ligands if this structure is sensitive to ligand properties.

One of us (L. L.) would like to thank the Max-Kade Foundation for a grant. We greatly appreciate gifts of MnF_2 single crystals from Robert Feigelson and from Herbert Rinneberg.

[†] Work performed under the auspices of the U. S. Atomic Energy Commission.

[*] In partial fulfillment of Ph.D degree.

[‡] On leave from University of Bonn, Bonn, Germany.

[1] C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and V. J. Mallow, Phys. Rev. Lett. **23**, 1397 (1969).

[2] C. S. Fadley and D. A. Shirley, Phys. Rev. A **2**, 1109 (1970).

[3] The correlation of observed 3*s* peak splitting with *S* was first made by T. Novakov in the Uppsala EUCHEM Conference, September, 1970 (unpublished).

[4] R. L. Cohen, G. K. Wertheim, A. Rosencwaig, and H. J. Guggenheim, Phys. Rev. B **5**, 1037 (1972).

[5] D. T. Clark and D. B. Adams, Chem. Phys. Lett. **10**, 121 (1971).

[6] J. C. Carver, G. K. Schweitzer, and T. A. Carlson, J. Chem. Phys. **57**, 973 (1972).

[7] F. Sasaki and P. S. Bagus, Phys. Rev. (to be published).

[8] J. W. Van Vleck, Phys. Rev. **45**, 405 (1934).

[9] A. J. Freeman, P. S. Bagus, and J. V. Mallow (unpublished).

[10] H. J. Silverstone and O. Sinanoglu, J. Chem. Phys. **44**, 1899 (1966).