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NEW MULTIPLET STRUCTURE IN PHOTOEMISSION FROM MnF_2*

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Abstract:

A high-resolution XPS investigation of the multiplet structure of manganese 2s and 3s levels in MnF_2 is reported. The Mn 3s 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 2s level is also reported and compared with calculations.

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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 3s 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, S,[3,4] 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 2s and 3s hole-state multiplet structure observed earlier. Their results provide definite predictions about additional features of these states. In this Letter 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 1s lines of carbon and oxygen (the two most common surface contaminants) were monitored *in situ* before and after the Mn 2s and 3s spectra were recorded. Very little carbon and no oxygen were detected. The peak intensity ratios relative to the Mn 3p (^7P) peak were

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

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

The simplest description of the 2s and 3s 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 2s or the 3s shell. These final states have ^7S and ^5S symmetry in each case. In the ^7S states the remaining 2s or 3s electron is coupled parallel to the d-shell spin $S = 5/2$, while in the ^5S states the two spins are antiparallel. For either the 2s or the 3s 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 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 orbitals 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 anti-parallel 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 Letter, 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

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

where $i = 1, 2 \ldots 7$, and $|\phi_j\rangle$ represents the j^{th} 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 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 eV 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 eV 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.

The 2s 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 2s 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+} ($\overline{2s}$ or $\overline{3s}$) final states is now quantitatively understood; theory and experiment show good agreement in splitting, relative intensity, and satellite structure. The complexity of the 3s spectrum precludes the quantitative validity of simplistic correlations of 3s 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 3s satellite structure should prove useful in studying interactions with ligands if this structure is sensitive to ligand properties.

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FOOTNOTES AND REFERENCES

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

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Table 1. Summary of the Mn 3s and 2s photoelectron results and comparison with theoretical predictions

	Binding Energies (eV)*				Intensity Ratios†				
Manganese 3s final state	^7S	$^5S(i)$	$^5S(2)$	$^5S(3)$	$^7S/^5S(1)$	$^5S(1)/^5S(2)$‡	$^5S(2)/^5S(3)$‡	$^5S(1)/^5S(2')$‡	$^5S(2')/^5S(2'')$‡
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‡ 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

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

†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 result of areas derived from a least squares fit to Lorentzian peak shape.

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

‡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.

FIGURE CAPTIONS

Fig. 1. The manganese 3s 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.

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

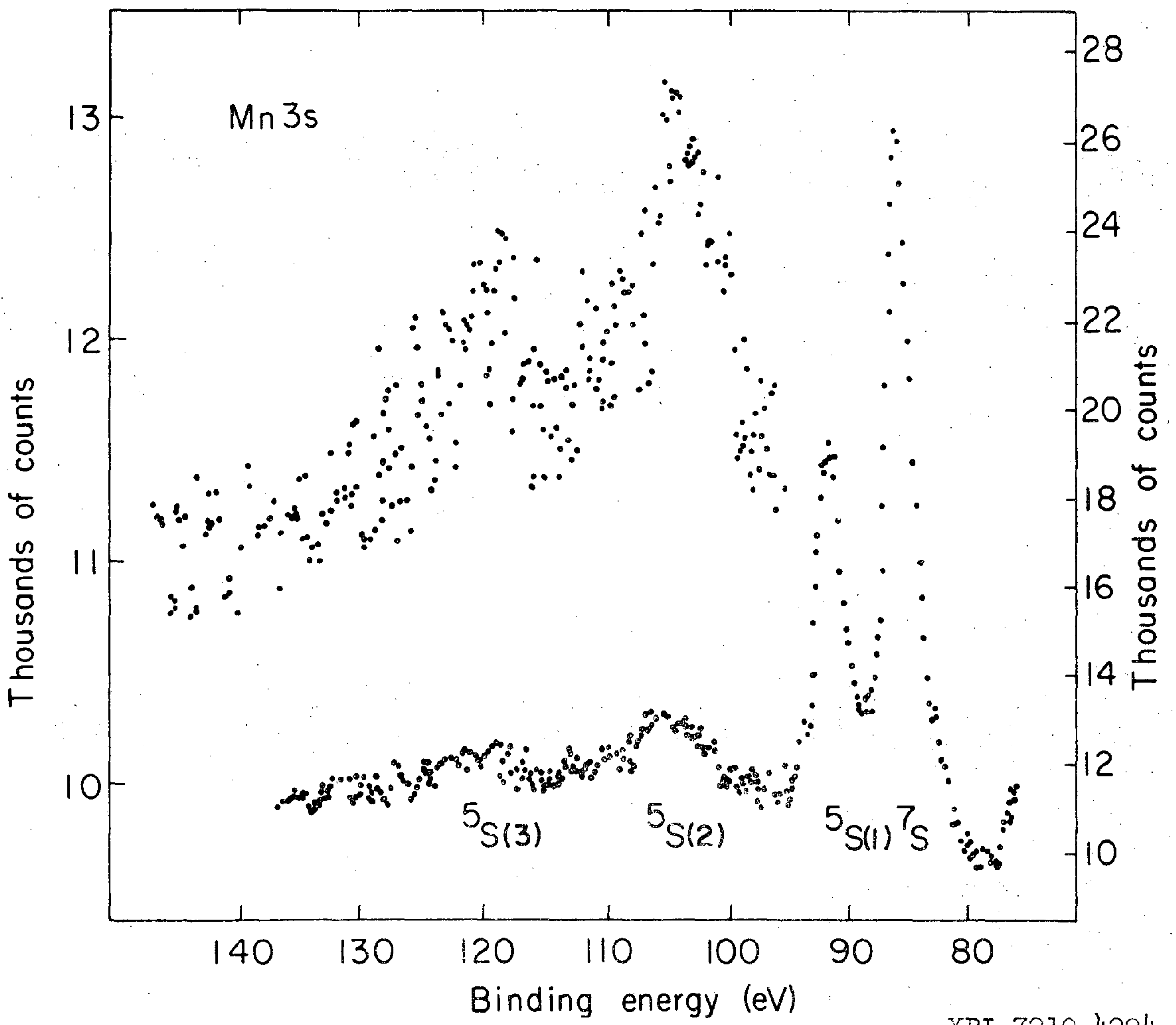

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Fig. 1

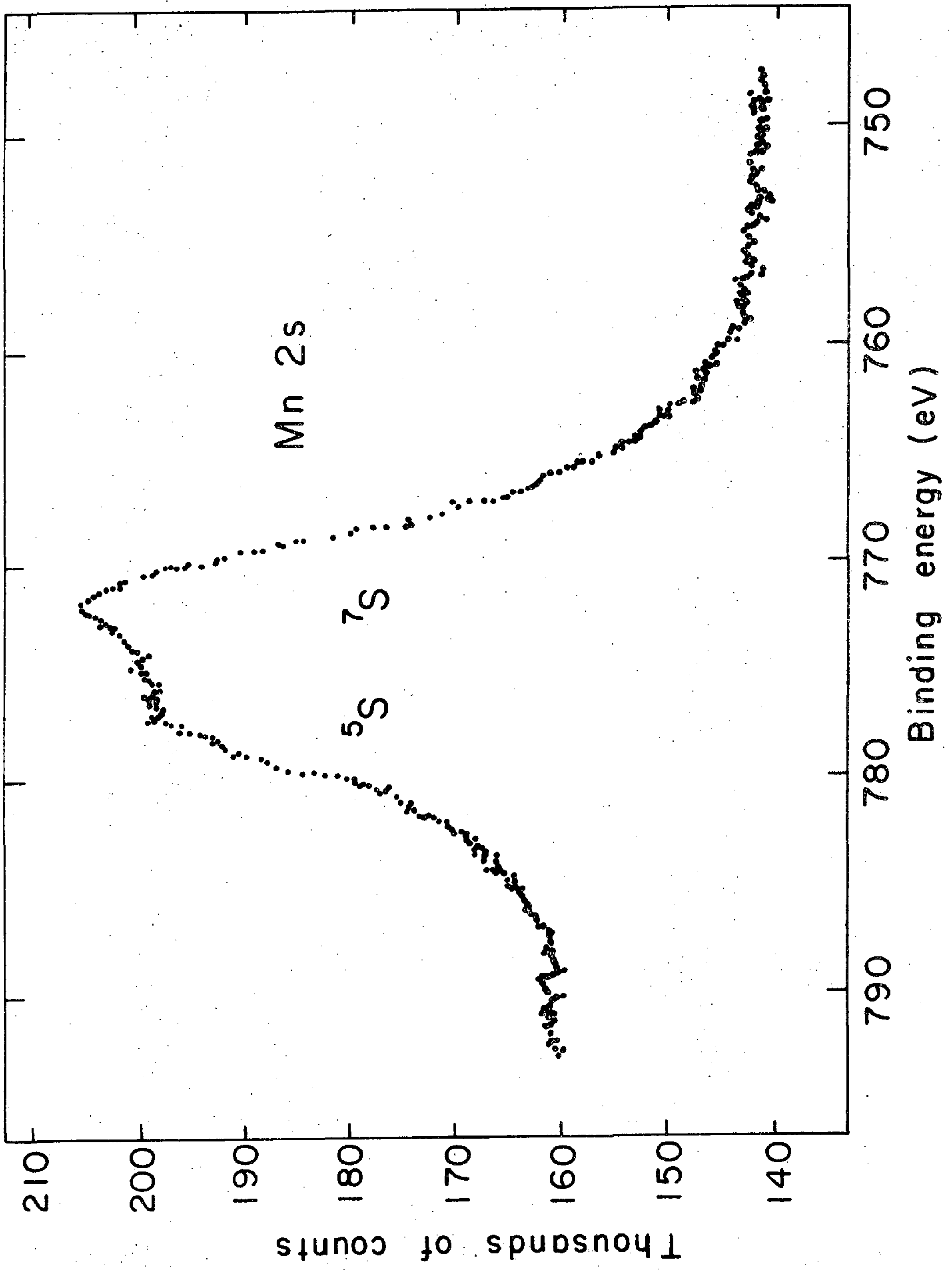

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Fig. 2

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