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MULTIPLET SPLITTING OF CORE ELECTRON BINDING ENERGIES IN TRANSITION METAL IONS*

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ABSTRACT

Core electron binding energy splittings were measured in manganese and iron compounds. X-ray photoelectron spectra indicate splittings of ∿6 eV for the 3s levels in MnF_2, MnO, and FeF_3, and less pronounced effects on the 3s levels in MnO_2 and Fe metal. These splittings are considerably reduced from free ion predictions but agree well with calculations for Mn in a cluster environment. The 3p multiplet splittings are shown to behave in a quantitatively different fashion.

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In any atomic system with unpaired valence electrons, the exchange interaction affects core electrons with spin-up and spin-down differently. This interaction is responsible for the well-known core polarization contributions to magnetic hyperfine structure.[1] The binding energies of core electrons will also be affected. For example, unrestricted Hartree-Fock (UHF) calculations predict large splittings in the core electron energy eigenvalues of transition metal ions[2] (∿12 eV for the 3s level of atomic iron), and it has been pointed out that these splittings should be reflected in measured binding energies.[3] Using x-ray photoelectron spectroscopy (XPS) such splittings were sought in core-level peaks from iron and cobalt metal, but with negative results.[3]

Recently, splittings of ∿1 eV have been observed in the 1s-derived photoelectron peaks of the paramagnetic molecules O_2 and NO.[4] We report here the first observation of large effects in the 3s-like levels of Mn and Fe in various magnetic solids. The splittings are ∿6 eV and considerably reduced from free ion predictions,[2] in agreement with recent UHF molecular orbital calculations for the MnF_6 cluster.[5] Certain extra peaks in the 3p region provide evidence for large splittings of the 3p levels in these solids. In contrast with the 3s splittings, which may be interpreted from either an exchange polarization or multiplet structure view-point, the 3p splittings do not correspond to any picture based solely on exchange polarization in the UHF model.[6]

The experimental procedure has been described previously.[3,7] Samples were bombarded with x-rays of ∿1 keV energy (primarily $MgK\alpha_{1,2}$, 1253.6 eV). The ejected electrons were analyzed for kinetic energy in a magnetic spectrometer. The kinetic energy distributions so obtained contain photoelectron peaks corresponding to excitation from all the accessible core and valence electronic levels in the sample. If a photoelectron peak involves only the ejection of one electron from the parent system, the observed kinetic energy (E_{kin}) is directly related to the difference in energy between the initial state of the system and the final state after photoemission by

$$h\nu = E_f - E_i + E_{kin} + \text{work function and charging corrections} \qquad (1)$$

where E_i is the total energy of the initial state, E_f is the total energy of the final state with a hole in some subshell. The quantity $E_f - E_i$ is the binding energy of the electron removed from the subshell, relative to a final state corresponding to E_f. The work function and charging corrections will be constant for a given sample[7] and so can be disregarded in the measurement of splittings. If the ejection of an electron from a subshell can result in several final states of the system, a corresponding number of photoelectron peaks will be observed; thus the energy splittings of these final states are in principle

directly measurable.

Measurements were made on Mn levels in MnF_2, MnO, and MnO_2, and on Fe levels in FeF_3, Fe metal, and $K_4Fe(CN)_6$. Figure 1 shows the spectra obtained from these materials in the region corresponding to ejection of 3s and 3p electrons from the transition metal atoms. Also noted are significant peaks in these spectra resulting from the weaker $K\alpha_3$ and $K\alpha_4$ x-rays. All samples were studied at room temperature at a pressure of approximately 10^{-5} Torr with the exception of iron metal, which was heated in a hydrogen atmosphere to clean its surface.[3]

Table I summarizes our experimental results and for convenience of interpretation presents the free ion electron configurations. Concentrating on the 3s regions of Fig. 1 we see that the $3d^5$ compounds exhibit two peaks, denoted 3s(1) and 3s(2). MnO_2 shows a somewhat weaker 3s(2) peak at smaller separation and $K_4Fe(CN)_6$ shows essentially no 3s(2) peak. Iron metal exhibits a distinct shoulder (not observed in earlier work due to poor statistics[3]) which persists with no appreciable change from 810°C (40°C above the Curie point) to 565°C. The separations, relative intensities, and widths of these peaks as derived by least-squares fits of standard peak shapes are presented in Table I. Also noted in Fig. 1 and Table I are those cases where known properties and the observation of broadening of certain photoelectron peaks seem to indicate slight chemical reaction within the thin ($\sim 10^{-6}$ cm) surface layer that produces photoelectrons in the full energy, inelastic peaks. Both the observation of the 3s(2) peak for cases where d electrons are known to couple to a high spin ground state (MnF_2, MnO, FeF_3, and ferromagnetic Fe) and the reduction of the separation and intensity of this peak relative to 3s(1) for a case in which the number of unpaired 3d electrons is smaller (MnO_2) or the transition metal ion exists in a diamagnetic ground state ($K_4Fe(CN)_6$) are fully consistent with the two peaks 3s(1) and 3s(2) representing two final states of the Mn(Fe)

ion split primarily by the exchange interaction. Also consistent with this interpretation is an analogous spectrum from Cu metal (d electron configuration $3d^{10}$), which shows a narrow, single 3s line as observed in $K_4Fe(CN)_6$.

We note at this point several other possible sources of the extra peak 3s(2), all of which can be ruled out: (1) Auger electron peaks can be distinguished by a constant kinetic energy regardless of exciting x-ray energy. (2) A surface contaminant or incompletely hidden portion of the sample mount could give rise to unexpected photoelectron peaks, but these should be present on all samples at the same kinetic energy and probably with varying intensity relative to Mn(Fe) peaks. The 3s(2) peak does not behave in this fashion. (3) If surface chemical reaction produces two different types of metal atoms, shifts of the 3s binding energies due to changes in valence electron screening could give rise to two photoelectron peaks.[7] However, in this case, both 3s and 3p peaks should show the same structure[7] and this is not observed. (We note a small effect of this kind on the 3p(1) peak of FeF_3.) (4) Quantized energy losses suffered by photoelectrons in leaving the solid can give rise to peaks on the low kinetic energy side of an elastic photoelectron peak,[8] but the loss mechanisms for 3s and 3p photoelectrons should be essentially identical due to their proximity in kinetic energy. No peak with relative intensity and separation corresponding to the 3s(2) peak is seen near the 3p(1) peaks of MnF_2 and MnO. Also, most quantized losses would contribute some inherent line width to the secondary peaks,[8] but Table I indicates that the 3s(2) peaks are essentially equal in width to the 3s(1) peaks for MnF_2 and MnO. (5) A photoemission process resulting in simultaneous excitation of both a photoelectron and some quantized mode of excitation could give rise to such a peak.[9,10] However, the specificity of appearance of the intense doublet near 3s and not 3p, and the relative widths of the 3s(2) peaks for

MnF_2 and MnO make this explanation seem unlikely.

Let us consider the origin of these photoelectron spectra, using the free Mn^{2+} ion as an illustrative example. The initial state is $3d^5\ ^6S$ and the ejection of a 3s or 3p electron gives rise to final states which we denote as $Mn^{3+}[3s]$ and $Mn^{3+}[3p]$ respectively. In first approximation, the binding energies of ejected electrons are given by their one-electron energy eigenvalues, ε_i, calculated for the ground state configuration of Mn^{2+}. Since a detailed allowance for exchange predicts that for any shell $\varepsilon_i^\alpha \neq \varepsilon_i^\beta$, where α, β denote spin directions, two peaks are predicted for the photoemission of both the 3s and 3p levels. The simplest estimate of this effect treats the exchange interaction as a perturbation which splits the restricted Hartree-Fock (RHF) 3s and 3p one-electron eigenvalues, and yields the values given in Table II. Spin unrestricted Hartree-Fock (SUHF) calculations represent a higher-order estimate, but the energy splittings are not appreciably altered (see Table II).

This use of Koopman's theorem to equate binding energies to ε_i is known to have severe shortcomings. The correct definition of electron binding energy is given as the difference between computed total energies for initial and final states [cf. Eq. (1)]. The possible final states are ^7S and ^5S for $Mn^{3+}[3s]$ and ^7P and ^5P for $Mn^{3+}[3p]$. But unlike the other final states just given, the ^5P state can be formed in three different ways from parent d^5 terms of ^6S, ^4P, and ^4D. This multiplicity predicts 4 final states for $Mn^{3+}[3p]$ instead of 2 final states as in the SUHF scheme and rules out the simple connection of 3p photoemission splittings (or splittings of any non-s electron) to ground state one-electron energies. We have calculated the total energies of these final states using two "multiplet hole theory" (MHT) methods: diagonalization of the appropriate energy matrix assuming Coulomb and exchange integrals to be given by RHF single determinant values for the initial state (a frozen orbital approximation), and more accurate multi-configuration Hartree-Fock calculations[11]

on the final hole states (an optimized orbital calculation). The results are presented in Table II. The agreement between frozen orbital and optimized orbital estimates is very good, with slightly larger splittings for the optimized orbitals. The agreement between the MHT and SUHF results for the final state $Mn^{3+}[3s]$ is good, particularly in view of the known errors associated with the use of Koopman's theorem. These results confirm the essential equivalence between the MHT and exchange polarization views for the splittings of s electron levels. No such equivalence exists for non-s electron levels. Similar results were also obtained from calculations on the initial and final states of $Fe^{3+}(3d^5)$, $Mn^{4+}(3d^3)$, and neutral $Mn(3d^5 4s^2)$.

The results of Table II are borne out qualitatively by our 3s spectra from MnF_2, MnO, and FeF_3. The 3s region shows a doublet whose weaker component lies at lower kinetic energy, in qualitative agreement with a calculated ratio of 7:5 for $^7S:^5S$ relative intensities based on one-electron transitions in photoemission. The observed separation of approximately 6 eV is only about half the value predicted by the free ion calculations. While electron-electron correlation will act to reduce the theoretical splittings,[3] a larger effect is expected from covalency in chemical bonding.

Recently, a full spin and orbital unrestricted HF (UHF) calculation was done for the $(MnF_6)^{4-}$ cluster by Ellis and Freeman.[5] Their predicted splittings of energy eigenvalues, listed in Table II, show a substantial decrease from the free ion values and rather remarkable agreement with the measured splittings in MnF_2. The reduced splitting (5.7 eV) in MnO is consistent with the well-known effects of covalency in that oxygen coordination is more covalent than fluorine coordination. On the other hand the larger splitting observed for FeF_3 over MnF_2 is consistent with our free ion calculations which give a greater exchange splitting for Fe^{3+} than for Mn^{2+}. The measured ratio of separations for MnF_2

and MnO_2 (1.41:1.00) is larger than the computed free ion ratio for Mn^{2+} and Mn^{4+} (1.22:1.00), as expected from covalent bonding effects.

The observed 3s(1):3s(2) intensity ratio of ∿2.0:1.0 for MnF_2 and MnO does not agree with the ^7S:^5S ratio of 1.4:1.0 obtained from a free-atom calculation based on one-electron transitions. The 1.5:1.0 ratio for FeF_3 does agree but the apparent surface reaction indicates that this agreement is probably fortuitous. There are several reasons for a discrepancy between such simple estimates and experiment: (1) If the initial and final states are described in terms of SUHF wave functions, the dipole matrix elements between 3sα and 3sβ and their corresponding P-wave continuum states may be different. (2) Overlap integrals between initial and final state orbitals of passive electrons may be different for different final states. (3) Multi-electron transitions may be significant enough to alter observed intensity ratios from one-electron predictions. (4) Bonding effects will distort initial and final states from a free-atom description, as has been found in UHF cluster calculations.[5] (5) A small fraction of the photoelectron producing atoms may exist as surface states of different electron configuration.

Let us turn now to the 3p regions of the spectra in Fig. 1, where several extra peaks are observed. The peaks 3p(2) and 3p(3) of $K_4Fe(CN)_6$ appear to be associated with two electron transitions of potassium, and are not observed in similar spectra from $Na_4Fe(CN)_6$ and $(NH_4)_4Fe(CN)_6$. The extra peaks for MnF_2, MnO_2, and FeF_3 may be related to multiplet splittings, however. There is at least qualitative agreement with predictions from MHT in that peaks resulting from p electron ejection are spread out in intensity over a broad region. We note in this connection that the intensity of each ^5P state will be proportional to the square of the mixing coefficient of the $d^5\ ^6S$ parent term; the values obtained from our MHT calculations are: $^5P_1$,0.66; $^5P_2$,0.01; and $^5P_3$,0.32. Spectra for MnF_2 in fact show two weaker components (3p(2) and 3p(3)) in

addition to 3p(1). One of these is close to the main peak (∿2 eV) and the other much further away (∿17 eV) (cf. Table II). However, peak 3p(3) is probably enhanced in intensity by a broad inelastic peak analogous to that labeled I. In general, covalent bonding effects will reduce the overall splittings and, together with spin-orbit interactions, they will also modify the peak structure from that predicted by our MHT calculations. Thus, while it appears that peaks due to multiplet splittings may be present in the 3p regions of our spectra, further experimental and theoretical study will be necessary to assign the observed peaks to specific final hole states.

As stated earlier, four peaks are predicted for the 3p hole states by MHT whereas exchange polarization predicts only two. Actually, UHF theory also predicts four peaks (but in two pairs of closely spaced peaks) if one relaxes the orbital (m_ℓ) restriction along with the spin (m_s) restriction in the HF calculation for the hole state. Such calculations have been carried out for the 3p hole state of Mn^{2+}. While 4 peaks are predicted using the resulting ε_{3p}'s, their energy separations are not much larger than the exchange polarization values, i.e., ∿14 eV, and so fall far short of reproducing either the MHT predictions or experiment. Apparently the requirement that the final state be one of good (non-zero) angular momentum is one the UHF calculation cannot satisfy.

FOOTNOTES AND REFERENCES

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FIGURE CAPTIONS

Fig. 1. Photoelectron spectra in the region corresponding to ejection of 3s and 3p electrons from Mn and Fe in various solids. MgKα radiation was used for excitation.

Table I. Transition metal ion electron configurations for the solids indicated in Fig. 1, together with experimental separations, ratios, and widths of 3s photoelectron peaks.

Atom	Compound	Electron Configuration	3s(1)-3s(2) Separation (eV)	3s(1):3s(2) Intensity Ratio	3s(1) FWHM (eV)	3s(2) FWHM (eV)
Mn	MnF_2	$3d^5\ ^6S$	6.5	2.0:1.0	3.2	3.2
	MnO	$3d^5\ ^6S$	5.7	1.9:1.0	3.6	3.5
	MnO_2[a]	$3d^3\ ^4F$	4.6	2.3:1.0	3.9[b]	3.9[b]
Fe	FeF_3[c]	$3d^5\ ^6S$	7.0	1.5:1.0	4.5[b]	4.5[b]
	Fe	$(3d^6 4s^2)$	4.4	2.6:1.0	3.5	4.0

(continued)

Table I (continued)

Atom	Compound	Electron Configuration	3s(1)-3s(2) Separation (eV)	3s(1):3s(2) Intensity Ratio	3s(1) FWHM (eV)	3s(2) FWHM (eV)
Fe	$K_4Fe(CN)_6$	$(3d^6)$	---	>10:1	3.5	---

[a]Probably slightly reduced; often a non-stoichiometric compound.

[b]FWHM for 3s(1) and 3s(2) constrained to be equal.

[c]Probably slightly reduced (see Fig. 1).

Table II. Theoretical predictions of core electron binding energy splittings (eV).

	Final state:	$Mn^{3+}[3s]$			$Mn^{3+}[3p]$		
	Description:	3sα hole	3sβ hole		3pα hole		3pβ hole
(1)	RHF + exchange perturbation (Mn^{2+})	11.1	0		13.5		0
(2)	SUHF (Mn^{2+})	11.3	0		13.7		0
(3)	UHF, $(MnF_6)^{4-}$ cluster	6.8	0		8.1		0
	Description:	^5S	^7S	$^5P_1$	$^5P_2$	$^5P_3$	^7P
(4)	MHT, Frozen orbital[a]	13.3	0	22.4	8.5	3.6	0
(5)	MHT, Optimized orbital[b]	14.3	0	23.8	9.4	4.0	0

[a]Orbitals obtained from an RHF calculation on Mn^{2+} $3d^5$ ^6S.

[b]Values based on multiconfiguration Hartree-Fock calculations for $Mn^{3+}[3s]$ and $Mn^{3+}[3p]$.

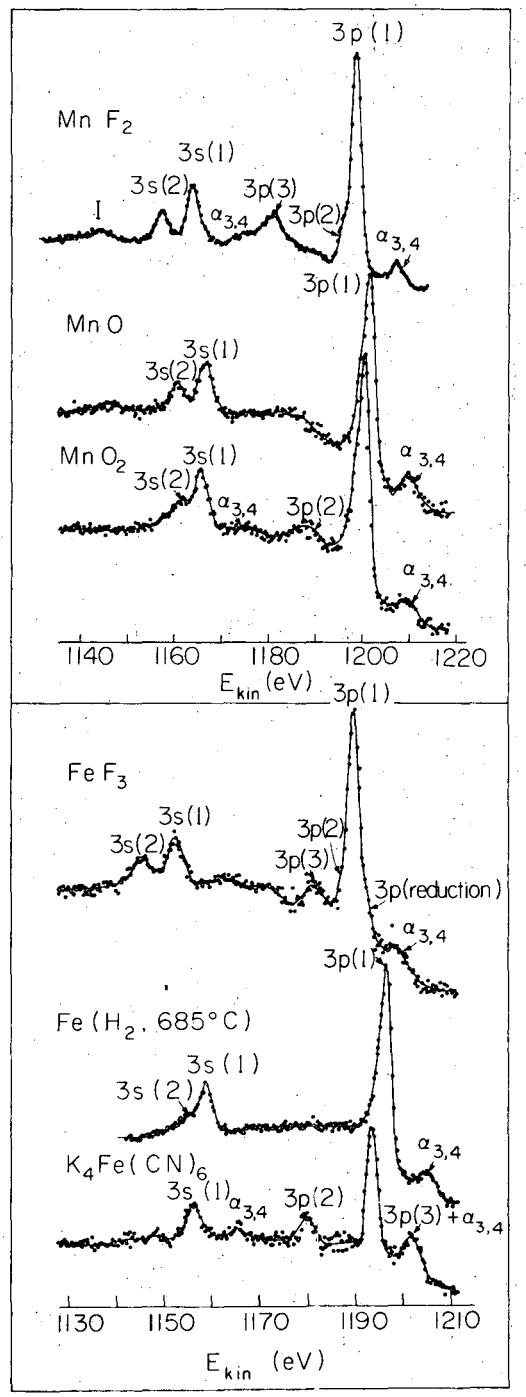
3p(1)
Mn F2
3s(1)
3s(2)
3p(3)
I
α3,4
3p(2)
α3,4
3p(1)
Mn O
3s(1)
3s(2)
Mn O2
3s(1)
3s(2)
α3,4
3p(2)
α3,4
α3,4
1140
1160
1180
1200
1220
Ekin (eV)
3p(1)
Fe F3
3s(1)
3s(2)
3p(2)
3p(3)
3p(reduction)
α3,4
3p(1)
Fe (H2, 685°C)
3s (1)
3s (2)
α3,4
K4Fe(CN)6
3s (1)
α3,4
3p(2)
3p(3) + α3,4
1130
1150
1170
1190
1210
Ekin (eV)
XBL698-3635

Fig. 1.

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