Core-Electron Splittings and Hyperfine Fields in Transition-Metal Compounds

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$2s$ and $3s$ core-electron exchange splittings have been measured for a number of transition-metal compounds. It is found that the $2s$ splittings agree roughly with values from Hartree–Fock calculations, whereas measured $3s$ splittings are smaller by about a factor of 2. This discrepancy is tentatively linked to correlations connected with the hole produced by the photoelectric process. A comparison of exchange splittings with hyperfine fields in spin-only compounds suggests a close relationship between these two properties.

I. INTRODUCTION

The exchange interactions between core s electrons and those in incomplete shells, e.g., $3d$ or $4f$ electrons, give rise to two well-known effects: (i) the Fermi contact interaction between nuclear and electronic spin,[1] and (ii) the exchange or multiplet splitting of the s electrons themselves.[2,3] The former is obtained from NMR, EPR, or Mössbauer-effect measurements; the latter from x-ray photoemission spectroscopy (XPS). The former measures the integral effect of all the s shells, whereas the latter is a measure of the exchange integrals of the individual s shells with the spin of the unfilled shell. It might therefore be possible to study the individual contributions to the Fermi contact field through XPS data.

Hartree–Fock calculations are successful in reproducing the core-polarization hyperfine fields,[4] though large cancellations occur between the con-

tributions from the different shells; e.g., -700 kOe is calculated for Mn^{2+}, as against -650 kOe measured in MnF_2 and -690 kOe extrapolated to zero covalency in Mn^{2+} compounds.[5,6] The application of these calculations to core-electron splittings is less direct because of two additional effects. In XPS the final state has a hole in the s shell, thus differing from the ground state in which the hyperfine field is measured. The *correlation* energy between the hole and the electrons may alter the results of the calculations performed in the Hartree–Fock scheme. In addition there is the question of the *relaxation* of the electronic shells which accompanies photoelectron emission.

A comparison of hyperfine data, core-electron splittings, and Hartree–Fock calculations can in principle give indications of the importance of relaxation and correlation effects in the XPS data. In addition, the trends in the hyperfine fields and core-electron splittings with ionicity may indicate the relative importance of $3d$ and $4s$ covalency.

Ions of the $3d$ series are especially well suited for a study of these effects because only $2s$ and $3s$ polarizations contribute to the hyperfine field[4] (the $1s$ contribution is known to be very small[4]) and because large changes in hyperfine fields with covalency have been observed.[5]

II. EXPERIMENTAL RESULTS

XPS spectra were obtained with a Varian IEE 15 spectrometer using $MgK\alpha$ radiation. The data relevant to the following discussion are given in Table I. The $2s$ splittings for MnF_2, MnO, and FeF_2 are reported here for the first time. They were obtained from data such as those shown in Fig. 1. The solid lines are least-squares fits obtained with a Lorentzian line shape and a sloping background, and include the $\alpha_{3,4}$ satellites. Figure 2 shows the $3s$ lines of Ni, Co, and Fe metals. The metals were cleaned by argon-ion sputtering. Other materials were in the form of freshly crushed crystalline powder. The MnO was prepared as a thin film on Mn metal to avoid the for-

TABLE I. Core-electron splittings and core-polarization hyperfine fields for various $3d$ transition-metal ions.

Compound	$\Delta E(2s)$ (eV)	$\Delta E(3s)$ (eV)	$-H_{hf}$ (kOe)
K_2NaFeF_6		$7.0(1)$[a]	620[a]
$\gamma-Fe_2O_3$		$6.5(1)$[a]	515[a]
$FeCl_3$		$5.3(1)$[b]	468[c]
Fe metal		$3.5(2)$[a]	337[d]
MnF_2	$5.9(2)$[a]	$6.5(1)$[a,b,e]	650[f]
MnO	$5.6(2)$[a]	$6.1(1)$[a]	580[g]
MnS		$5.4(1)$[a,b]	560[h]
FeF_2	$4.3(2)$[a]	$5.9(1)$[a,b]	$\cdots$
Co metal		$2.1(4)$[a]	220[d]
CoF_2		$5.1(1)$[a,b]	$\cdots$
Ni metal		$1.8(3)$[a]	75[d]
NiF_2		$3.1(1)$[a]	260[i,j]

[a]This work.
[b]Reference 3.
[c]Reference 7.
[d]Reference 8.
[e]Reference 2.
[f]Reference 9.
[g]Reference 10.
[h]Reference 11.
[i]Reference 12.
[j]After correction for orbital contributions.

mation of higher oxides. The γ-Fe_2O_3 was carefully checked for other impurities which were found to be present in many other iron compounds.

III. DISCUSSION

We begin our analysis by comparing the core-electron splittings with those calculated in the Hartree–Fock approximation. The necessary information has been compiled in Table II. It has been noted before[2,3] that the measured 3s splittings are smaller by about a factor of 2 than those calculated. However, if the calculated 3s splittings are scaled by the ratio of the 2s-3d to 3s-3d exchange integrals obtained from the same type of calculation, the resulting 2s splittings agree roughly with
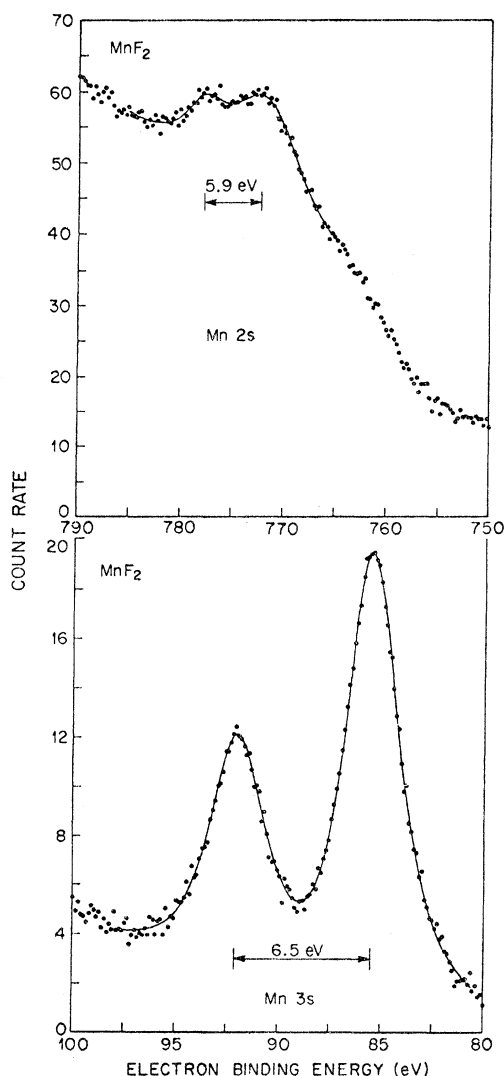

FIG. 1. 2s and 3s core-electron splitting for MnF_2. The solid line is a least-squares fit utilizing a sloping background and two lines of adjustable shape with their $K\alpha_{3,4}$ satellites.
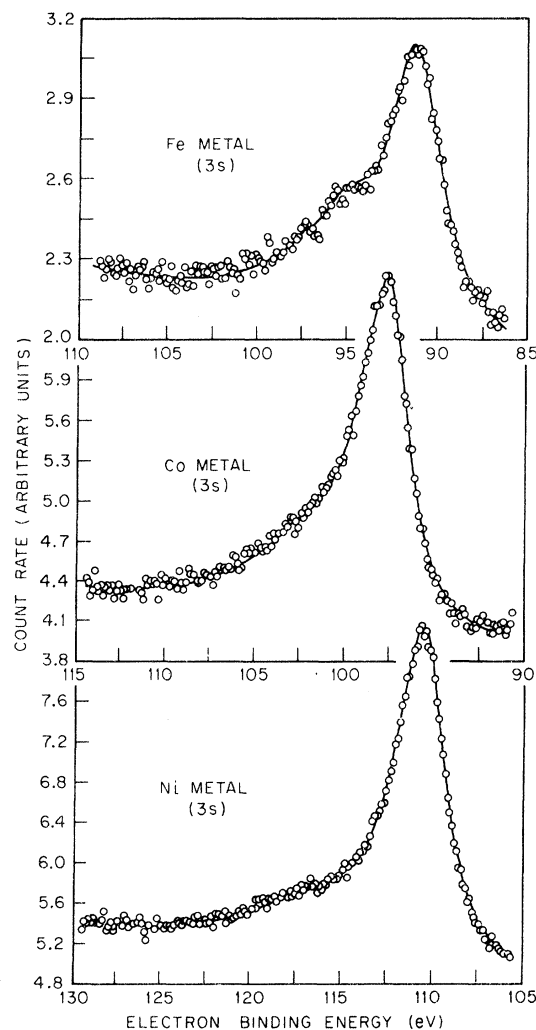

FIG. 2. 3s core-electron splitting for Fe, Co, and Ni metal. The solid line is a least-squares fit utilizing a sloping background, a plasmon line, and two lines of equal width and adjustable shape with their $K\alpha_{3,4}$ satellites.

the experimental results. The same is true for the rare earths, where the measured 4s splittings are too small by about a factor of 2, while the 5s splittings are in agreement with experiment.[13,14] Since it is the deeper-lying 2s state in the case of the 3d series and the shallower 5s state in the case of the 4f series which agree, while the 3s and 4s disagree, with the calculation, the data suggest that correlation effects may be responsible for the disagreement when photoemission comes from the incomplete shell. Correlation effects are likely to be strongest for electrons with the same principal quantum number. Relaxation effects should scale with energy and are therefore less likely to be the cause of the discrepancy.

A comparison of 3s splittings and hyperfine fields as an implicit function of covalency is made in Fig.
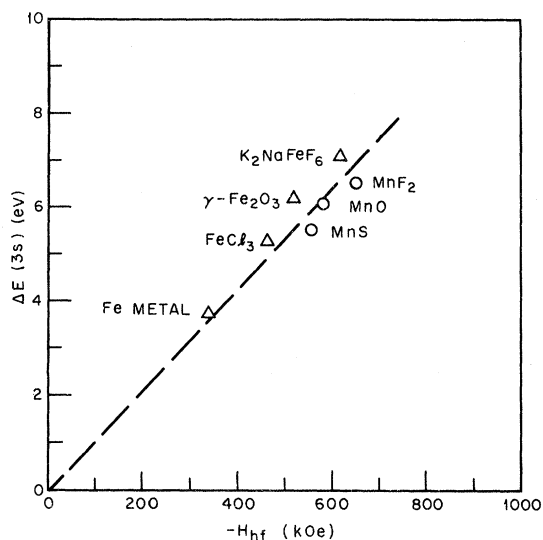
FIG. 3. $3s$ core-electron splitting for various Mn^{2+} and Fe^{3+} (spin only) compounds vs hyperfine fields. The $3s$ splitting of $FeCl_3$ is taken from Ref. 3.

3. The decrease in hyperfine field with increasing covalency[15] can be ascribed to the combined effects of d-electron delocalization and population of the $4s$ orbitals of the metal ion.[5] These $4s$ electrons give a positive core-polarization field.[4] The $4s$ population can also alter the $2s$ and $3s$ core-electron splittings by increasing the shielding of the $3d$ wave functions. This increases their radial distribution and decreases the overlap with inner s electrons. An order-of-magnitude estimate for this effect can be obtained in the following way. The $3s$-$3d$ exchange integral, which is proportional to the $3s$ core-electron splitting, decreases by 10% in going from Mn^{2+} to neutral Mn.[4] On the other hand, the hyperfine field decreases by ~ 70 kOe in going from MnF_2 to MnO. Assuming that the core-polarization hyperfine field of the $4s^2$ configuration in Mn is 700 kOe,[4] the $4s$ population can increase at most ~ 10% between MnF_2 and MnO. Assuming that all the hyperfine-field change comes from a $4s$ population of the metal orbitals, the corresponding decrease of the $3s$ splitting between MnF_2 and MnO due to $4s$ shielding is then certainly less than 0.1 eV. The major contribution to the reduction in $3s$ splitting with increasing covalency must therefore be due to d-electron delocalization. This conclusion is consistent with the fact that the

TABLE II. Experimental and theoretical results for $3d$ core-electron exchange in MnF_2 and FeF_2. The theoretical $2s$ splittings have been obtained by multiplying the available splittings by the ratio of the exchange integrals G^2 calculated for the atomic configurations (Ref. 4).

	Experiment		Theory			
	$\Delta E(2s)$ (eV)	$\Delta E(3s)$ (eV)	$\Delta E(2s)$ (eV)	$\Delta E(3s)^a$ (eV)	$G^2(3d, 2s)^b$ (Mn^0, Fe^0)	$G^2(3d, 3s)^b$ (Mn^0, Fe^0)
MnF_2	5.9	6.5	4.7	14.2	0.265	0.802
FeF_2	4.3	5.9	4.3	12.4	0.293	0.844

[a] See Ref. 3.   [b] See Ref. 4.

$2s$ splitting, though having a larger uncertainty, decreases by the same percentage as the $3s$ splitting on going from MnF_2 to MnO.

The fact that the data for metallic Fe fall on the line in Fig. 3 can also be interpreted from a consistent point of view. The $3s$ splitting in an ion is proportional to the magnetic moment of that ion. Since the hyperfine fields in K_2NaFeF_6 and Fe metal scale roughly with their magnetic moments, a proportionality between hyperfine field and exchange splitting results. Much less information is available on Ni, but within the uncertainties the data on Ni metal and NiF_2 would also fall close to a straight line through the origin.

IV. SUMMARY

$2s$ core-electron splittings for MnF_2, MnO, and FeF_2 have been obtained. They agree with theoretical predictions, whereas the $3s$ splittings in the same compounds are only one-half as large as those calculated. A comparison with $4s$ splittings in the rare earths, which are also about one-half of those estimated by the Hartree–Fock calculations, suggests correlation effects as the cause of the discrepancy. A linear relationship is found between $3s$ core-electron splittings and core-polarization hyperfine fields as a function of covalency. This is interpreted in terms of a substantial d-electron delocalization as a consequence of increasing covalency.

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Inelastic-Electron-Tunneling Spectroscopy of Metal-Insulator-Metal Junctions*

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The inelastic tunneling of electrons in a metal-insulator-metal junction has been shown to be a spectroscopic method for studying the vibrational modes of the whole system. In the present paper we consider the possibility of deducing precise information from this spectroscopy. The low-voltage part of the spectrum (i.e., the d^2I/dV^2-vs-V characteristic) gives information about the phonons of the electrodes. The phonon density, which is deduced for a Mg electrode, is critically compared with the density deduced from neutron scattering. The range of this phonon probe is then studied by tunneling into multilayer electrodes. The 40–90-meV range of the characteristic of a Mg-Pb junction exhibits a specific structure due to the lattice vibrations of the insulator. This structure is compared with the infrared spectrum and the phonon density of states of MgO, as well as with a theoretical calculation of the tunneling current in the transfer-Hamiltonian formalism. From the fit obtained, it is deduced that the 30-Å-thick insulator, grown on Mg, is an oxide, in contrast with the insulator grown on Al, which was previously deduced to be a hydroxide. At higher energies (100–500 meV), the vibrational spectrum of molecules contained in the insulator region is observed. The identification of the lines is shown to be accurate and it gives precise information on these molecules, especially about their chemical binding with the insulator. This last point could be important in the future for studying the problem of adsorption on solid surfaces.

I. INTRODUCTION

A new field in the study of tunneling in metal-insulator-metal (MIM) junctions was devised in 1966 by Jaklevic and Lambe.[1,2] They observed structures in the d^2I/dV^2 characteristics which were related to vibrational excitations of molecular impurities contained in the insulator. Since that date a considerable amount of work has been devoted to the subject. It has been found that the phenomenon is more general than was at first thought, because vibrational modes of the metallic electrodes[3,4] and of the insulating barrier itself[5-7] have also been observed.

The physical origin of these structures is mainly due to the inelastic tunneling of electrons.[8] An electron can cross the potential barrier of the insulator by (elastic) tunneling with conservation of its energy. But this barrier potential may contain dynamic terms, such as those due to the vibrational modes of the insulator. Then an electron also has the possibility of going from one electrode to the other, exciting one mode of vibration, and losing the corresponding energy $\hbar\omega_0$. Clearly, this can happen only when the applied voltage is greater than $V_0 = \hbar\omega_0/e$. This gives the threshold for the new process to occur. Above this applied voltage the total probability of crossing the barrier, for an electron at the Fermi level, is the sum of the elastic and inelastic probabilities, and the conductance is increased (see Fig. 1).

Actually, the inelastic tunneling of electrons involves the vibrational spectroscopy of the whole MIM system. In the present paper we report new results on the topic, mainly on structures in which the identification can be carried out with more precision. We also try to give answers to various questions which have been raised on the subject.

We have studied particularly Mg-MgO-Pb junctions because, in that structure, the completeness