Prediction of New Multiplet Structure in Photoemission Experiments

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(Received 10 January 1973)

Correlation effects are included in a detailed theoretical study of the multiplet structure observed by x-ray photoelectron spectroscopy. This correlated multiplet hole theory resolves the difficulties of earlier multiplet hole theory studies: It correctly determines the magnitude of the observed 2*s* and 3*s* (doublet) splittings and their intensity ratios, and predicts the existence of new structure for the 3*s* binding energy splittings—structure which does not exist in one-electron theory and which has now been confirmed by Kowalczyk *et al.*

Photoelectron spectroscopy (PS) has become an important tool for studying the electronic and magnetic properties of solids in both the ultraviolet[1] (UPS) and x-ray[2] (XPS) energy regions. As with the application of any new technique, new observations[1,3,4] have revealed serious flaws in our theoretical understanding.[5] We present here the results of a detailed theoretical study of the multiplet structure of the core-electron binding-energy splittings observed by XPS in transition-metal ions such as Mn^{2+} and Fe^{3+} in insulating compounds. We show that correlation effects are of prime importance for understanding the magnitude of the splittings and their intensity ratios. We predict new structure for the 3*s* multiplet structure, which does not exist in any rigorous one-electron theory. In addition, we correctly determine the magnitudes of the[6] 2*s* and[4] 3*s* (doublet) splittings in the XPS spectra of these ions, thus eliminating the factor of 2 discrepancy between multiplet hole theory[7] (MHT) and experiment, and obtain the correct intensity ratio of the 3*s* splittings (2:1 rather than the MHT ratio of 7:5). The recent confirmation by Kowalczyk *et al.*[8] of the predicted structure demonstrates a unique success of theory and indicates the possible importance of correlation effects on other photoelectron-spectroscopy studies of solids.[1-3,5]

XPS multiplet splittings, first observed in the *K*-shell peaks of the paramagnetic molecules NO and O_2,[9] have now been observed in a series of transition-metal[4,6,10] and rare-earth metal[11] compounds. To understand the origin of these splittings, consider the case of the free Mn^{2+} ion whose ^6S ground state has the configuration $[(\text{core})\, 3s^2 3p^6 3d^5]^6S$. If a 3*s* electron (or equivalently a 2*s* electron) is removed, two states of the Mn^{3+} ion may be formed which are eigenfunctions of L^2 and S^2: $[(\text{core})\, 3s^1(^2S)3p^6 3d^5(^6S)]^7S$ and $[(\text{core})\, 3s^1(^2S)3p^6 3d^5(^6S)]^5S$. These two states differ in the angular-momentum coupling of the $3d^5(^6S)$ shell. For the ^7S state, the 3*s* electron can be thought of as having its spin parallel to those of the five (parallel) 3*d* electrons; for the ^5S state, the 3*s* spin may be thought of as antiparallel to the 3*d* spins. In terms of the Slater F^k (Coulomb) and G^k (exchange) integrals, the energy difference between these two states is $\frac{6}{5}G^2(3s, 3d)$. Now if the reorganization (relaxation) effects are small, the multiplet splitting may be obtained by evaluating the G^2 integral using the Hartreee-Fock (HF) 3*s* and 3*d* orbitals for Mn^{2+} [frozen-orbital (FO) approximation]. However, using the one-electron model, the 3*s* multiplet splitting is most appropriately obtained by subtracting the HF total energies for the $Mn^{3+}(^7S)$ and $Mn^{3+}(^5S)$ multiplets [optimized-orbital (OPT) approach]; results are given in Table I along with the experimental splittings.[4,8] The FO and OPT ^7S-^5S splittings are quite close to each other, indicating that reorganization effects are small. However, both calculated splittings are more than a factor of 2

TABLE I. Calculated and observed splittings for Mn as described in the text.

		3s splitting (eV)	2s splitting (eV)[a]
Observed	MnF_2	6.5[b]	5.85 ± 0.05[c]
	MnO	5.7[b]	...
$s\alpha/s\beta$	SUHF-FO	11.27[d]	3.67[d]
	SUHF-OPT	12.14	...
MHT	FO	13.31[d]	4.43[d]
	OPT	14.32[d]	6.10[d]
CI	Internal	4.71	...
	Semi-internal	8.2	...

[a] The 2s splitting in FeF_2 observed in Ref. 6 is 4.8 eV.

[b] Ref. 4.

[c] Refs. 6, 8.

[d] Ref. 7.

larger than the observed splittings in MnF_2 and MnO crystals.

A crude (but physically simple and commonly used) model is to consider the electron ejected by the incident photon to be either a $3s\alpha$ (spin-up) or $3s\beta$ (spin-down) electron. Two final states of Mn^{3+} are formed: $[(\text{core})\, 3s\alpha 3p^6 3d^5\alpha]$ and $[(\text{core})\, 3s\beta 3p^6 3d^5\alpha]$. These states differ in energy because of the different exchange interaction between $3s\alpha$-$3d\alpha$ and $3s\beta$-$3d\alpha$, i.e., the same mechanism which is responsible for the core-polarization contribution to the magnetic hyperfine interaction. The spin-unrestricted Hartree-Fock (SUHF) orbitals obtained for the Mn^{2+} ion (FO approximation) can be used to calculated the energy difference between the two states. As with the more correct MHT methods, one can compute the SUHF orbitals and total energies separately for the $3s\alpha$ and $3s\beta$ hole states (OPT approximation), and this method accounts for relaxation as well as spin polarization. The SUHF splittings (Table I) are smaller than the MHT values. Similarly, MHT (and SUHF) calculations may be done for the 2s splittings (Table I). Comparing these theoretical predictions (Table I) with experiment we see that, unlike the 3s case, there is very good agreement for the MHT-OPT value.

Another experimental consequence of the theory is the ^7S:^5S ratio of the intensities. If we assume the sudden approximation[12] and (as found) small differences (2%) in the overlap integrals between ground and final states, MHT predicts that this intensity should be the multiplet ratio 7:5 (whereas the SUHF schemes yield the ratio 1:1) for both the 3s and 2s cases. This is in excellent agreement[4,8] with the observed intensity ratio for the 2s lines (1.4 ± 0.1), but in marked disagreement with the 3s intensity ratio (2.0 ± 0.1).

While covalency and overlap effects may account for some of these discrepancies between theory (for the free ion) and experiment (on the solid), the selective and large disagreements cited above indicate the failure of one-electron theory.

To determine the effects of electron correlation, we have used the configuration interaction (CI) method; calculations were carried out on two levels. The first set of configurations is formed by distributing the M-shell electrons among the 3s, 3p, and 3d orbitals in all ways consistent with the angular momentum of the multiplet. In the absence of the electron repulsion terms, $1/r_{ij}$, these "internal" configurations[13] would be degenerate. Further, the Slater F^k and G^k integrals involved in the off-diagonal matrix elements are large, and substantial mixing of the internal configurations can occur. Table II lists these internal configurations with the HF configuration listed first. Triple or quadruple orbital replacement configurations have not been listed in Table II. These have zero off-diagonal matrix elements with the HF configuration. Since these configurations do not contribute to the second-order perturbation energy in the (reasonably) valid one-electron model, we ignore them here. This will slightly bias the results: The lowest root of the CI expansions is treated more accurately than higher roots. The form of the internal CI wave function is

$$\Psi_i = \sum_{K=1}^{N} C_{iK}\Phi_K,$$

TABLE II. Internal configurations and results of MCHF calculation for Mn^{3+}.

Multiplet	Excitation	Configuration	C_i
^7S		1. $3s^1(^2S)3p^6(^1S)3d^5(^6S)$	0.996
	$3p^2 \rightarrow 3d^2$	2. $3s^1(^2S)3p^4(^3P)3d^7(^4P)$	-0.087
^5S		1. $3s^1(^2S)3p^6(^1S)3d^5(^6S)$	0.794
	$3p^2 \rightarrow 3s3d$	2. $3s^2(^1S)3p^4(^3P)3d^6(^3P_1)$[a]	0.232
		3. $3s^2(^1S)3p^4(^3P)3d^6(^3P_2)$[a]	-0.106
		4. $3s^2(^1S)3p^4(^1D)3d^6(^5D)$	-0.550
	$3p^2 \rightarrow 3d^2$	5. $[3s^1(^2S)3p^4(^3P)](^4P)3d^7(^4P)$	0.011
		6. $[3s^1(^2S)3p^4(^3P)](^2P)3d^7(^4P)$	-0.020
		7. $[3s^1(^2S)3p^4(^3P)](^4P)3d^7(^2P)$	0.020

[a] This notation distinguishes the two linearly independent ^3P multiplets.

where i labels the root of the secular equation and K sums over the Table II configurations. The wave functions Ψ_i are determined by the multiconfiguration Hartree-Fock (MCHF) method[14] which yields the optimum orbitals *and* the optimum mixing coefficients. The orbitals for each of the two ^7S or seven ^5S roots of the CI problem are determined separately for the appropriate root.

Some results of the MCHF calculations (Table II) show that the ^7S multiplet is essentially unchanged by the CI, and that for ^5S the $3p^2 \rightarrow 3s3d$ excitations mix very strongly. The internal CI $3s$ splitting is 4.71 eV (reduced by 10 eV from the MHT-OPT value) and is now in reasonable agreement with experiment. The key correlation effect results from the near degeneracy of the HF and $3p^2 \rightarrow 3s3d$ excitations and the large off-diagonal matrix element connecting this configuration to the HF configuration. Since the $3s$ shell lies lower in energy than the $3p$, and the $3d$ higher, much less energy is required for the $3p^2 \rightarrow 3s3d$ than for the $3p^2 \rightarrow 3d^2$ excitations (~ 10 eV for $3p^2 \rightarrow 3s3d$ as opposed to ~ 100 eV for $3p^2 \rightarrow 3d^2$). However, because of spin and orbital angular momentum coupling, ^7S multiplets cannot be formed for this excitation. Thus this correlation effect *lowers* the ^5S energy and substantially reduces the ^7S-^5S $3s$ splitting. The energy of the lowest root of the $Mn^{2+}(^6S)$ and $Mn^{3+}(^7S)$ multiplets is lowered by only 0.7–0.8 eV from the HF energy. However, the lowest $Mn^{3+}(^5S)$ root is 10.3 eV lower than the corresponding HF energy!

Note that the second through fourth roots for ^5S have large values of C_1, the coefficient of the HF configuration (Table I). Since the intensity of the XPS peaks are proportional[12] to C_1^2, this leads us to predict that XPS peaks corresponding to these roots should be (and now have been[8]) observed. These added roots and the loss of intensity in C_1 for the lowest root ($C_1 = 0.795$) arise from the mixing of configurations 1 to 4 of Table II. The intensity ratio of the ^7S to ^5S lowest roots is approximately given as $7 \times (1.00)^2 / 5 \times (0.79)^2 = 2.2$ and is now in excellent agreement with experiment.[8]

Internal configurations are not the only ones which contribute to the correlation of different multiplets.[13] Thus, we have carried out more extended CI calculations including "semi-internal" configurations[13]; these involve excitations of one electron out of the $n = 1$, 2, or 3 shells (86 configurations for the ^7S multiplet and 221 for the ^5S). The splitting is raised to 8.2 eV. The dominant terms remain the internal configurations; the sum of the squares of the weights of the "semi-internal" configurations is 0.064 for ^5S and 0.077 for ^7S. Thus, the key correlation effect in the "semi-internal" CI remains the $3p^2 \rightarrow 3s3d$ excitation even though quantitative improvements are made in the wave functions. The remaining difference with experiment can be reasonably ascribed to additional CI[13] and covalency effects.[4,7]

The very good agreement for the Mn^{2+} $2s$ splittings (Table I) between the best MHT result (MHT-OPT) and experiment in MnF_2 shows the importance of relaxation effects and indicates that correlation is much less important for the $2s$ than the $3s$ peaks. Larger relaxation effects are expected for the $2s$ than for the $3s$ hole states from Slater's well-known rules for the larger change in the effective charge of the M-shell electrons when a $2s$ rather than a $3s$ electron is removed. This may be understood by noting that from the HF $2s$-hole configuration ($2s^1 2p^6 3s^2 3p^6 3d^5$), the appropriate definition of internal excitations redistributes the seven L-shell electrons among the $2s$ and $2p$ shells and the thirteen M-shell electrons among the $3s$, $3p$, and $3d$. This case differs from the $3s$-hole case in that all double-excitation internal distributions can give rise to both ^7S and ^5S states and are not likely to be nearly degenerate with the HF configuration. Thus we do not have preferential correlation for the ^5S state from the $3p^2 \rightarrow 3s3d$ excitation. The intensity ratio ^7S:^5S should be the MHT value, 1.4, which also agrees with experiment (1.4 ± 0.1).

We have been able to obtain a striking and detailed agreement between CMHT and experiment for the various hole states observed for Mn^{2+} ions in solids. Clearly, correlation effects will be preferentially important when the hole is created in the shell having the same principal quantum number as the open valence shell. Thus, we may use CMHT to explain the observations in the rare-earth compounds[11] which show that while the $5s$ splittings agree with simple FO-MHT calculations,[15] the observed $4s$ splittings are reduced by about a factor of 2 with respect to the MHT predictions.

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*Work supported by the U. S. Air Force Office of Scientific Research, by the U. S. Atomic Energy Commission, and by the National Science Foundation.

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Thickness Dependence of Hopping Transport in Amorphous-Ge Films*

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(Received 7 December 1972)

The conductivity of gas-free thin films of amorphous germanium was measured as a function of temperature and film thickness. Existing theories of hopping conduction have been modified to apply to very thin films. The results are consistent with experiment, indicating that hopping conduction near the Fermi energy is the mechanism responsible for the conductivity below room temperature. The radius a of the localized wave functions and the density of states N_F at the Fermi energy found are $a = 10$ Å and $N_\mathrm{F} = 1.5 \times 10^{18}$ eV^{-1} cm^{-3}.

Various attempts have been made to explain the transport properties of amorphous germanium in terms of hopping conduction. In particular, the transport below room temperature seems to obey the ubiquitous $T^{-1/4}$ law derived by Mott.[1] Extensive criticism[2-6] has been voiced of the hopping interpretation of the observed $T^{-1/4}$ law for the amorphous group-IV films. The evidence here is that the hopping interpretation is correct.

We present here an extension of the theory to two dimensions[7] and experimental data for a-Ge films of varying thickness,[8] which show that hop-