Origins of Satellites on Inner-Shell Photoelectron Spectra

A. Rosencwaig, G. K. Wertheim, and H. J. Guggenheim
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 26 May 1971)

Satellites on $2p$ photoelectron spectra of transition-metal ions are shown to arise from simultaneous outer-shell excitation. The coupling mechanism and selection rules are discussed. Energies of the $3d \rightarrow 4s$ transition have been obtained for a number of difluorides and oxides.

A systematic study of the $2p$ x-ray photoelectron spectra[1] (XPS) of the $3d$-group transition-metal compounds has shown satellites due to the simultaneous excitation of $3d$-shell electrons. The data give evidence for excitations within the $3d$ manifold as well as to higher-lying excited states. The coupling mechanism responsible for these excitations is closely related to that producing "shakeoff" with β decay, or during K-shell photoionization.

It is essential to distinguish between the two common sources of structure on photoelectron spectra[2]: (a) multiplet coupling and (b) multielectron excitation. The former is due to the coupling of the angular momentum (S and L, or J) of the original atom or ion to that of the photohole state. This effect is stronger the greater the orbital overlap between the photohole and the outer electrons. Multiplet splittings have been observed for the $3s$ electrons of the transition metals,[3] and correspond fairly well to the results of Hartree-Fock calculations. The splitting of the $2s$ electrons of the transition metals is expected to be considerably smaller.

In the independent-particle model, multielectron excitations are not produced directly by the incident photon but depend on coupling between the electrons themselves.[4] The most familiar mechanism is the dipolar coupling responsible for configuration interaction. It also depends on orbital overlap between the photohole and the outer electrons of the ion. Such configuration-interaction satellites have been seen on the $3p$ electrons of transition-metal ions[3,5] and the $3s$ electrons of alkali-metal ions.[6] In the former the interaction is with states in which the $3p$ hole is accompanied by a rearrangement within the $3d$ shell; in the latter it is with states in which the $3s$ hole is replaced by two $3p$ holes plus an electron in an outer, normally empty orbital.[7]

These effects will be greatly reduced if the original excitation is in an inner shell with smaller principal quantum number than that of the outer electrons. In that case, however, a new coupling mechanism may become important. It is based on the change in the screened central potential seen by the outer electrons when a core electron is removed.[8,9] The excess energy of the outer electrons due to the increase in the screened ionic potential may be termed "relaxation energy." In the adiabatic approximation this energy is given to the ejected photoelectron. When the adiabatic conditions are not satisfied some of the energy may be used in producing electronic excitations, particularly among the outer electrons. Discrete excitations result in discrete photoelectron satellites at greater apparent binding energy. (Note, however, that the final state due to this process may be indistinguishable from that produced by the normal configuration-interaction process.) Satellites presumably due to this mechanism and identifiable with known optical excitation energies have recently been reported in the XPS of $2p$ electrons of Cu^{2+} salts by Novakov.[10]

The selection rules[9,11] which determine the final states accessible in monopole excitation are $\Delta J = 0$ and $\Delta M_J = 0$ since there are no interactions with the outside and no radiation emitted. The relatively weak coupling to the inner-shell hole is ignored, i.e., J does not include the angular momentum of the photohole. In the central-potential approximation the additional selection rules $\Delta l = 0$, $\Delta m_l = 0$, $\Delta m_s = 0$, and $\Delta j = 0$ apply.[11]

The data[12] for the difluorides of the transition metals from Mn^{2+} to Zn^{2+}, Fig. 1, exhibit satellites and line-broadening effects which may be qualitatively interpreted in this way. The data show strong satellite structure for ions with almost-filled shells, i.e., for Cu^{2+}, Ni^{2+}, and Co^{2+}; mainly line broadening near the half-filled shell, i.e., for Mn^{2+} and Fe^{2+}; and neither effect for the filled shell in Zn^{2+}. The resolved satellites are believed to be due to $3d \rightarrow 4s$ excitation while the line broadening is due in part to excitations within the $3d$ manifold and in part to multiplet effects in the $2p$ shell.

To assess the magnitude of multiplet effects

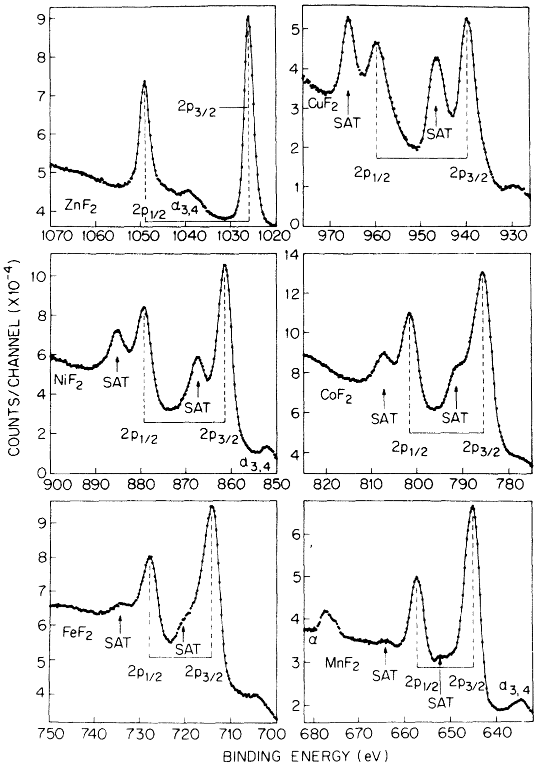

FIG. 1. X-ray photoelectron spectra of the $2p$ electrons of $3d$-group transition-metal difluorides. The data have not been corrected for charging effects which are estimated to be of the order of 4 eV. Satellites attributable to the Al $K\alpha_{3,4}$ emission are found ~ 11 eV below each line and are labeled $\alpha_{3,4}$. Satellites due to $3d \rightarrow 4s$ excitation are labeled Sat.

TABLE I. Comparison of atomic and experimental excitation energies.

Ion	n[a]	J[b]	ΔE_{4s}[c]	ΔE_{4p}[d]	Compound	ΔE_{sat}[e]
Zn^{2+}	10	0		17.5	ZnF_2	-[f]
					ZnO	-[f]
Cu^{2+}	9	5/2	7.8,9.7	-	CuF_2	6.5
					CuO	8.8
Ni^{2+}	8	4	6.8	-	NiF_2	5.9
					NiO	6.9
Co^{2+}	7	9/2	5.7,9.0	-	CoF_2	5.6
Fe^{2+}	6	4	-	-	FeF_2	$\lesssim 6$[g]
Fe^{3+}	5	5/2	-	23.5	$MgFe_2O_4$	~ 8[g]
Mn^{2+}	5	5/2	7.8,8.9	13.8	MnF_2	~ 7[g]
					MnO	-[f,g]
Mn^{3+}	4	0,1	13.8	20	$ErMnO_3$	-[g]
Cr^{3+}	3	3/2	12.8	-	Cr_2O_3	11.1
V^{3+}	2	2	12.0,12.6	-	V_2O_3	-[f,g]
V^{4+}	1	3/2	-	25.4	VO_2	-[f,g]
V^{5+}	0	0	69[h]	-	V_2O_5	-[f]
Ti^{3+}	1	3/2	-	16.0	-	-
Ti^{4+}	0	0	55[h]	-	TiO_2	-[f]
Sc^{3+}	0	0	42.2[h]	-	-	-[f]

[a] Number of d electrons.

[b] Total angular momentum of ion prior to photoionization.

[c] $3d \rightarrow 4s$ excitation energy (in eV) from Ref. 11.

[d] $3d \rightarrow 4p$ excitation energy (in eV) from Ref. 14.

[e] Satellite energy.

[f] No satellite observed.

[g] Line broadening dominates; several $3d$ excitations are allowed by the selection rules.

[h] $3p \rightarrow 4s$ excitation.

one notes that in the case of Mn^{2+} the calculations of Watson and Freeman[13] overestimate the $3s$ splitting by a factor of 2 and give a $2p$ splitting of 3.6 eV, presumably also overestimated. Multiplet effects would therefore be lost in the linewidth, and the weak satellite at ≈ 7 eV must arise from other causes. In Ni^{2+} the calculated multiplet splitting is 1.9 eV, but the satellite is found at 6 eV. The latter is comparable to the observed and calculated $3s$ splitting, again indicating that the observed satellite is not a multiplet effect. From the width of the main line one would judge that the multiplet splitting must be smaller than 2 eV. The systematics of the magnitude of the satellite separation also argues strongly against identification of the satellites with multiplet effects. The splitting is largest for Cu^{2+} with $S = \frac{1}{2}$ and *decreases* as S *increases*.

The resolved satellites must then be assigned to multielectron excitations involving the outer shell. Since the energy levels of ions with core-hole states are not available, we have used the tabulation of Moore[14] for normal ions under the assumption that differences in energy between outer-shell configurations will not change greatly when a core electron is removed, e.g., the energy required to promote a particular electron from $3d$ to $4s$ will be approximately the same. A further approximation comes from the assumption that the separations of the atomic energy levels give an adequate representation of the separations of the levels in solids. We have evidence from the study of the K^+ configuration-interaction satellites that this approximation is not unreasonable.[6] Table I lists the $3d \rightarrow 4s$ and $3d \rightarrow 4p$ excitation energies for $\Delta J = 0$ from Ref. 14, as well as the energies of the resolved satellites for the difluorides of Fig. 1 and for several transition-metal oxides. The data cover the full range of $3d$ occupation values from $3d^0$ to $3d^{10}$. The agreement between the observed satellite positions and those obtained from atomic energy levels under the $\Delta J=0$ selection rule is as good as can be expected in view of the above approximations.

The table shows significant differences in satellite position for a given ion with change in ligand. It is therefore clear that the shakeup satellites reflect the crystal and ligand fields to which the transition ion is exposed and make the normally empty conduction-band structure accessible to experiment.[10] These fields determine the positions and symmetries of the 3*d* levels and 4*s*-derived conduction-band levels, and must account for the noticeable difference in the satellite structure of Cu^{2+} in $CuSO_4$, and CuF_2. This dependence of the satellite structure on the nature of the ligands may be of considerable importance in the XPS study of transition-metal ions in both molecular complexes and other solids.

The line broadening which becomes the dominant effect as one approaches the half-filled shell is thought to arise not only from multiplet effects, but also from excitations within the 3*d* manifold. For an almost-filled shell there may be few or no $\Delta J=0$ excitations, and hence no line broadening from this mechanism. For a half-filled shell such low-energy excitations may dominate and may account for the reduced amplitude of the 4*s* excitation satellite.[15] The absence of broadening in certain compounds with partially filled 3*d* shells, namely the strong-crystal-field ferrocyanide and cobalticyanide complexes in which the metal ions are in $^1S_0$ states, is readily explained. Since these ions are diamagnetic there is no multiplet splitting. Furthermore, the energy of the lowest-lying excitation within the 3*d* band is sufficiently large, the cubic-crystal-field splitting is ≈ 4 eV, so that it will not contribute to line broadening.

In the case of ZnF_2 no shakeup satellites were detected. This may be attributed to the greater energy gap between the filled 3*d* and empty conduction-band states than in the compounds with partially filled shells. Shakeoff probabilities of a few percent,[16] like those seen in inert gas atoms,[9] might not have been detected in these experiments. The present data suggest that the large shakeup effects in transition-metal compounds are due to larger overlap of 3*d* and conduction-band wave functions than that calculated from atomic wave functions.

Finally, one naturally expects shakeup satellites on the 2*s* XPS line. These, however, are generally difficult to see because the 2*s* lines are considerably broadened (up to 5 eV) by Coster-Kronig processes. We have seen unambiguous evidence of shakeup satellites only on the 2*s* line of Cu^{2+} in CuF_2 where the satellite separation is large, and of the same size on both the 2*p* and 2*s* spectra.

We are indebted to L. R. Walker for helpful discussions, to M. Robbins for a supply of CuF_2, and to D. N. E. Buchanan for assistance with the measurements. We would like to thank T. Novakov for a preprint of Ref. 10.

---

[1] K. Siegbahn *et al.*, Nova Acta Regiae Soc. Sci. Upsal., Ser. IV 20, 1 (1967).

[2] We ignore in this discussion such essentially trivial effects as satellites due to extra lines in the emission spectrum of the x-ray source and satellites due to energy loss after the photoelectric process.

[3] C S. Fadley *et al.*, Phys. Rev. Lett. 23, 1397 (1969); C. S. Fadley and D. A. Shirley, Phys. Rev. A 2, 1109 (1970).

[4] For a many-body perturbation approach see H. Kelly and A. Ron, Phys. Rev. Lett. 26, 1359 (1971).

[5] B. Ekstig, E. Källne, E. Noreland, and R. Manne, Phys. Scr. 2, 38 (1970), trace the development of these ideas and apply them to the *Kβ* spectra of the transition metals.

[6] G. K. Wertheim and A. Rosencwaig, Phys. Rev. Lett. 26, 1179 (1971).

[7] Closely related double-electron excitation resulting from outer-shell photoionization has been reported by T. A. Carlson, Phys. Rev. 156, 142 (1967).

[8] J. S. Levinger, Phys. Rev. 90, 11 (1953).

[9] T. A. Carlson and M. O. Krause, Phys. Rev. 140, A1057 (1965); M. O. Krause and T. A. Carlson, Phys. Rev. 149, 52 (1966), and 158, 18 (1967); M. O. Krause, T. A. Carlson, and R. D. Dismukes, Phys. Rev. 170, 37 (1968).

[10] T. Novakov, Phys. Rev. B 3, 2693 (1971).

[11] H. Micklitz, Z. Phys. 215, 302 (1968).

[12] The data were taken with a Varian model IEE 15 spectrometer using an Al x-ray–tube anode. The samples were in the form of freshly crushed powder prepared from crystalline material, and were mounted with double-sided adhesive tape. The binding energies shown have not been corrected for charging effect.

[13] R. E. Watson and A. J. Freeman, Phys. Rev. 120, 1125 (1960), and 123, 2027 (1961). See also J. C. Slater, Phys. Rev. 165, 658 (1968).

[14] C. E. Moore, *Atomic Energy Levels as Derived from Analyses of Optical Spectra,* National Bureau of Standards Circular No. 467 (U. S. GPO, Washington, D. C., 1949), Vol. I.

[15] It may not be noted that *d*-shell excitation broadening will shift the centroid of the line to higher effective binding energy and give rise to pseudochemical shifts not related to valence or covalency.

[16] T. A. Carlson, C. W. Nestor, Jr., T. C. Tucker, and F. B. Malik, Phys. Rev. 169, 27 (1968).