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Final-State Structure in Photoemission from Transition-Metal Compounds

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It is suggested that the valence-band structure observed in x-ray photoemission from certain insulating $3d^n$ compounds can be identified with the crystal-field states of the $3d^{n-1}$ final state.

Although it is customary to discuss x-ray photoemission (XPS) data of core levels in terms of an initial-state binding energy of the photoelectron, it is generally recognized that detailed interpretation rests on an analysis of the energy of the final hole state. This becomes compelling when one considers the multiplet splitting or core levels in transition-metal compounds,[1,2] which are readily understood only in terms of the coupling of the core hole to the outer incomplete shell, e.g., d or f. It is also well illustrated by other electron correlation[3] and shakeup effects[4] which involve multielectron transitions.

The interpretation of valence-band XPS spectra appears to be less clearcut. In the case of the noble metals it has been possible to take XPS data as a direct representation of the density of occupied states.[5,6] Comparisons with one-electron band-structure calculations lend support to this interpretation and indicate that distortions in the data arise only through the transition probability which changes the relative intensity of electrons originating from s- and d-like bands. On the other hand, valence-band XPS spectra of rare-earth salts showed structure in the $4f$ bands which could only be interpreted in terms of the final hole state.[7] In brief, peaks in the $4f^n$ bands of rare earths with a more than half-filled $4f$ shell could be attributed to ground and excited state levels of the $4f^{n-1}$ configuration. These peaks were absent in the spectra of the rare earths with seven or fewer $4f$ electrons. The fact that the $4f$ electrons lie well below the Fermi energy and are therefore quite atomiclike, with little crystal-field splitting, makes this interpretation plausible. One step towards bandlike behavior is represented by ionic transition-metal compounds such as the transition-metal fluorides or oxides. The d bands in these compounds lie much closer to the Fermi energy and show much larger crystal-field splitting than do the $4f$ electrons in the rare earths. The exact nature of the d bands is still a subject of some controversy which photoemission could in principle resolve. But before this object can be achieved, the question of the extent to which the valence bands exhibit final-state structure must be resolved.[8]

In this note we consider the interpretation of x-ray photoemission data from the valence bands of a number of insulating transition-metal compounds. Most samples were in the form of freshly crushed powder, but in the case of $NiCl_2$ and

NiF_2, we used thin films grown on a metallic substrate. Data were taken with a Varian IEE-15 spectrometer using Mg $K\alpha$ radiation. The instrumental resolution was ~1.25 eV as measured by the full width at half-height of the Au $4f$ lines. No attempt was made to determine the charging correction for the data shown since this is not required for the discussion of structure within the valence region.

The approach is quite similar to that used for the rare earths, but the crystal-field interaction must be taken into account. The simplest example is that of the d^6 configuration, typified by the insulating, transparent compound FeF_2 with ${}^5T_2$ ground state. We assume that the photoemission spectrum is determined by the final state, which is that of a $3d^5$ ion in a suitable crystal field.[9] The ground state of that configuration, ${}^6A_1$, is well separated from the quartet excited states making this a particularly favorable case. The value of the cubic crystal field, Dq (see Ref. 9), which should be used for a trivalent iron atom in the FeF_2 lattice is, of course, not known, but it can be assumed to be between that for FeF_2 and FeF_3. This puts the ${}^4T$ states about 3 eV above the sextet state.[9] In order to estimate the relative probabilities of producing these final states, we take a greatly simplified point of view. The free $3d^6$ ion has a half-filled spin-up (α) shell, plus one spin-down (β) electron. Photoionization of one of the five α electrons produces a quartet state, while photoionization of the β electron produces the sextet state, with 5:1 intensity ratio. In terms of the crystal-field description of the ${}^5T_2$ state $(t_{2g(\alpha)}{}^3t_{2g(\beta)}e_{g(\alpha)}{}^2)$, one obtains the same intensity ratio, suggesting that even in a weak crystal field where neither description is adequate, a similar ratio will be found.

The data for FeF_2, shown in Fig. 1, are compatible with the above final-state descriptions. The F $2p$ derived valence band is readily identified by comparison with the spectrum of a simple fluoride, e.g., MgF_2 or LiF. The $3d$ contribution then clearly shows the structure anticipated in the discussion above. This indicates that a localized description is appropriate for the final state of photoemission from a transition-metal compound like FeF_2. The limited resolution provided by the use of Mg $K\alpha$ radiation for the excitation prevents us from assigning widths to the observed states. Before the implications of this result on the description of the d band of insulating transition-metal compounds are considered two further examples will be discussed.

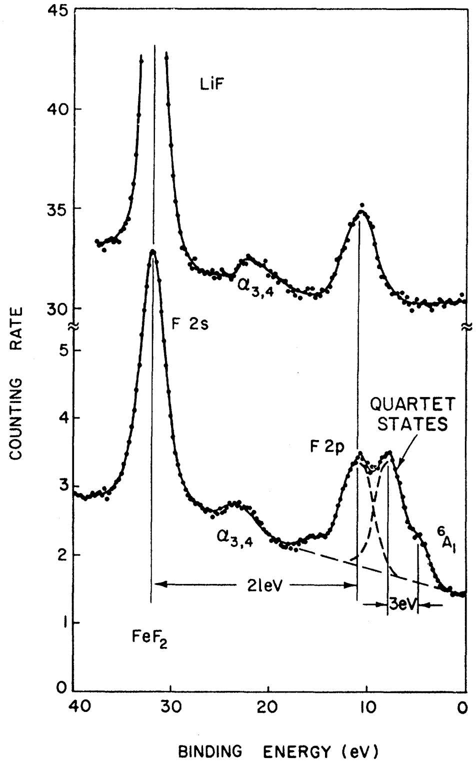

FIG. 1. The XPS valence-band spectrum of FeF_2 compared with that of LiF. The latter spectrum has been shifted so as to bring the F $2s$ lines into coincidence. States are labeled in terms of the final states.

The general analysis predicts that weak-crystal-field compounds with not more than 5 d electrons will generally have little resolved final-state structure. In Fig. 2 we examine Cr_2O_3, $3d^3$, with a ${}^4A_2$ ground state. Photoemission should almost exclusively populate the ${}^3T_1$ state of Cr^{4+}, i.e., we expect a single, narrow $3d$ component in the valence-band photoemission spectrum. Comparison with the spectrum of $K_2Cr_2O_7$, in which the chromium has no d electrons, identifies the O $2p$ band. The remaining narrow line represents the Cr $3d$ electrons. The absence of structure is in accord with the above discussion.

Data on Ni compounds do not allow as simple an interpretation as in the two cases above. The difference is thought to arise in the following way. With increasing Z the d levels move toward greater binding energies and thus come closer to the energy of the anion p bands. On the one hand this implies increasing localization of the d wave functions, but on the other it means greater hybridization.

Figure 3 shows the XPS valence-band spectrum of NiF_2. It is remarkably similar to that of NiO.[10] The position of the anion $2p$ band taken from

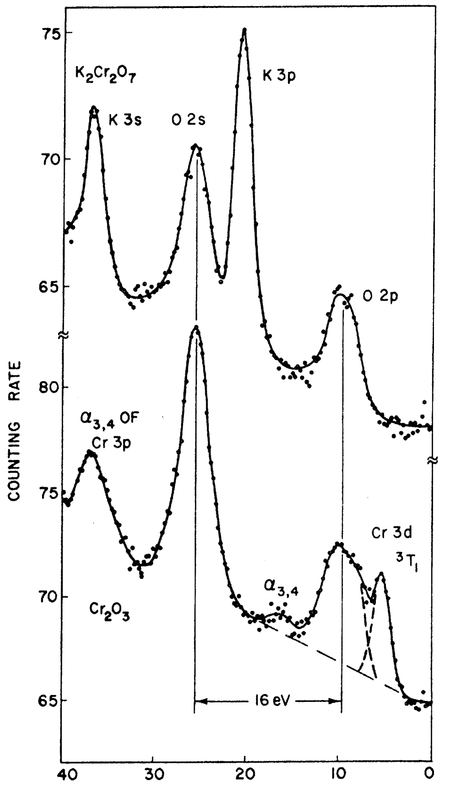

FIG. 2. The valence-band structure of Cr_2O_3 compared with that of $K_2Cr_2O_7$. The O 2*s* lines have been brought into coincidence.

FeF_2 does not correspond to any obvious structure in the valence band. The final-state assignment applied to the *d* bands shows that photoionization of the $3d^8$, $^3A_2$ state of divalent nickel leads to the $^4T_1$, ^2E, and ^2T states of the $3d^7$ configuration. In this case the final state is very sensitive to the value of Dq/B. The high-spin to low-spin transition occurs at $Dq/B \sim 2.2$, only slightly higher than the value appropriate for trivalent nickel. We therefore expect that ^2E will lie slightly above $^4T_1$, and $^2T \sim 2.3$ eV above $^4T_1$. The $^4T_2$ state should not be appreciably populated by photoemission. Intensities, estimated as above, are in the ratio of 3:2:3 for $^4T_1$, ^2E, and ^2T. Comparison with the data in Fig. 3 shows that the ^2T separation is smaller than predicted by the crystal-field approach. It may be surmised that because of stronger hybridization the states are more bandlike than for FeF_2 and that the state produced by photoemission differs from that obtained for Ni^{3+} in a stable environment.

Data for $NiCl_2$ indicate that the crystal field is smaller than in NiO of NiF_2, causing greater separation between $4T_1$ and ^2E.

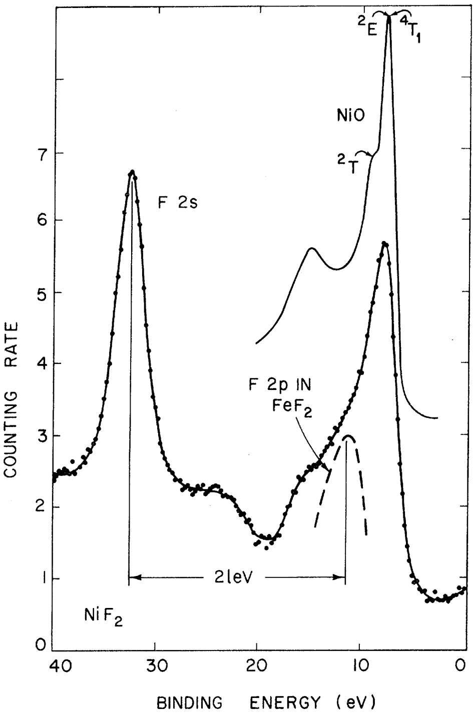

FIG. 3. The XPS valence band spectra of NiF_2 and NiO. The location of the center of the F 2*p* band in FeF_2 is indicated. The identification of the final states in terms of crystal-field levels is shown.

The most important observation regarding the Ni compounds, including $NiCl_2$, is that the anion *p*-band structure in no case agrees with that obtained from similar compounds without *d* electrons. Whether this is because of a strong *p*-*d* hybridization or the occurrence of multielectron satellite transitions in the *d*-electron compounds cannot be determined from the spectra alone, but other evidence points to the former interpretation. In the case of NiO a multielectron satellite in the Ni $2p_{3/2}$-core-electron spectrum suggested a multielectron process for the origin of the peak in the valence-band spectrum here labeled ^2T. In the case of $NiCl_2$, however, the Ni $2p_{3/2}$ spectrum does not have such a low-energy satellite. It therefore becomes likely that the interpretation here given for NiF_2 and $NiCl_2$ also applies to NiO. In the latter case it has, moreover, already been shown that a molecular-orbital treatment,[11] based on a NiO_6^{10-} cluster, which includes the crystal field, gives good agreement with all features in the XPS data between 0 and 25 eV. The levels resulting from the molecular-orbital treatment cannot, of course, be brought into one-to-one correspondence with the crystal-field states.

The above discussion of the Ni^{2+} compounds clearly indicates the inadequacy of a pure crystal-field description when there is significant hybridization. In those cases where a final-state crystal-field description is adequate, an initial-state description must fail. Even if one were to include the excited states of the $3d^n$ ion there is no simple correspondence between those of the $3d^{n-1}$ final state and those of the initial state. This is particularly clear in the case of a more than half-filled shell. (In compounds with metallic d-band conductivity many-electron effects may add another dimension of complexity.)[12]

We should ask whether it is currently possible to distinguish between localized and bandlike d electrons by XPS. With the resolution currently available (0.5 eV) it is difficult to distinguish between a bandwidth obtained in a one-electron band-structure calculation and the effects of final-state structure for localized d electrons. In cases where a localized description satisfactorily accounts for the observed structure, one may wish to assume that a localized description applies to the final state. It is not self-evident, however, that it must also apply to the unperturbed band.

Finally we should point out that these effects are not specific to XPS but should also manifest themselves in x-ray emission and photoabsorption experiments which have the same final state.

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Charge Fluctuations in Europium in Metallic $EuCu_2Si_2$

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Recoilless-absorption measurements of the 21.6-keV γ ray of Eu^{151} in $EuCu_2Si_2$ reveal an absorption line which has a strongly temperature-dependent isomer shift. The lines fall at neither the Eu^{3+} nor the Eu^{2+} valence positions, but in between. The results are interpreted in terms of fast fluctuations ($\tau < 3.5\times10^{-11}$ sec) of an electron between the localized $4f$ level and the conduction band. The difference in energy between the Eu^{2+} and the Eu^{3+} states in $EuCu_2Si_2$ is found to be about 0.07 eV.

We report here recoilless-absorption studies of the 21.6-keV γ ray of Eu^{151} in $EuCu_2Si_2$, which exhibit a strongly temperature-dependent isomer shift in a region corresponding neither to divalent nor to trivalent Eu ions. The results are interpreted in terms of fast fluctuations ($\tau < 3.5\times10^{-11}$ sec) of an electron between the localized $4f$ level and the conduction band, leading to a fluctuating charge (and spin) density at the Eu nuclei.

Europium ions are usually found to be either