

New probe for the ground-state electronic structure of narrow-band and impurity systems

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We show that absorption core spectroscopies based on optical selection rules can provide detailed information about the local electronic structure of the ground and lower excited states of narrow-band and impurity systems involving transition-metal or rare-earth atoms.

A basic question remaining in the understanding of the electronic structure and related physical properties of transition and rare-earth metals and compounds is to what extent the one-electron bandwidths and/or hybridizations mix the various possible local electronic configurations of the atoms causing a partial or complete breakdown of an atomic description of the electronic structure. Band-structure and hybridization effects will tend to destroy the atomic picture in two ways. First of all, they cause a fluctuation in the local d - or f -electron count, resulting in a breakdown of the atomic picture, because the number of d or f electrons on an atom is no longer a constant of the motion. Secondly, they tend to mix the various possible states of d^n or f^n atomic configurations, which in atomic theory are split by Coulomb and exchange interactions as well as one-electron spin-orbit and crystal-field interactions. Both of these effects, if large enough, can destroy or strongly modify the Hund's-rule ground state expected from atomic theory. Since the Hund's-rule ground state of a d^n or f^n atom is usually magnetic, hybridization and band-structure effects can destroy the local moment. It is therefore quite important to develop experimental techniques, on a microscopic basis, which can distinguish between various possible local electronic configurations and with which one can determine the atomic Hund's-rule purity of the ground state.

Recently, electron spectroscopy techniques involving valence as well as core electrons have proven to be extremely useful in determining the local d or f count, and the degree of fluctuations therein, for the ground state.¹⁻⁶ The limited resolution as well as the complexity of the spectra have, however, hampered a more detailed description of the ground state in terms of the involvement of the various terms of each electronic configuration. In core photoemission, for example, most of the various LS terms of each final state are accessible with intensities dictated by fractional parentages. Because of the large number of possible terms and their close spacing, little can usually be said concerning the nature of the ground-state term. Another problem encountered in core-electron photoemission is that the spectra are frequently complicated by the presence of strong satellite structures corresponding to screened as well as unscreened final states.

In optical spectroscopies involving a core hole the dominant contribution to the spectrum arises instead from transitions to the screened states provided a suitable core state is selected (such as a p - d transition in transition metals or a d - f transition in rare earths), so that transitions are made directly into the screening states. In this case the observed relative intensities of transitions to the various terms of the final electronic configuration, together with the optical selection rules, make it possible to infer the nature of the ground state. The main requirement is that the resolution of the experiment (instrumental plus core lifetime) be less than 0.5–1 eV, so that the final-state multiplet structure is visible.

In this paper we demonstrate that techniques which involve core electrons and optical selection rules can be extremely useful in this context. The reason for this is simply because the dipole selection rules are very restrictive, thereby limiting the number of terms seen and allowing a characterization of the ground state. We show that spectral line shapes in x-ray absorption (XAS) and electron-energy-loss spectroscopy (EELS) are highly sensitive to the details of the ground state and carry the signature of the atomic terms involved in the ground state. To use these techniques, however, one must resort to rather complex multiplet-structure calculations involving atoms with more than one open shell. Fortunately, computer programs are now available⁷ which can handle this problem, and which also provide the oscillator strengths for the ground-configuration term of your choice.

To illustrate we present EELS data for Mn metal and Mn impurities in Ag and Cu, and compare them with calculated Mn $L_{2,3}M_{4,5}$ optical absorption spectra for various possible ground configuration terms. $AgMn$ and $CuMn$ are chosen because it is known that Mn is magnetic in these hosts with a moment close to that expected for a d^5 (${}^6S_{5/2}$) ground state.⁸ This conclusion has been supported by recent photoemission studies.⁹

Samples with a thickness of about 1000 Å have been prepared by coevaporation of Ag or Cu and Mn onto 100-Å-thick amorphous carbon films mounted on standard electron microscope grids. The evaporation rate was monitored by quartz crystals. The vacuum during evaporation was

better than 10^{-7} Torr. The nominal Mn concentration for the *AgMn* and the *CuMn* film was 5 and 3.5 at.%. By electron diffraction we verified that the samples had the fcc structure. No other phases could be detected. EELS measurements were performed using a ultrahigh-vacuum spectrometer with a primary electron energy of 170 keV, and an energy and momentum resolution chosen to be 0.6 eV and 0.2 \AA^{-1} , respectively.

The theoretical spectra were calculated using an atomic Hartree-Fock program⁷ to determine the initial- and final-state wave functions and energies using empirically scaled values for the Slater integrals F_{dd}^k and G_{dd}^k . The values used were all reduced to 80% of the free-atom Hartree-Fock values, which resulted in energy splittings close to those observed experimentally. This reduction is commonly observed in transition metals.^{9,10} Hartree-Fock values of spin-orbit parameters were used without modification. Using the above wave functions, the optical transition matrix elements were calculated for each of the final-state levels.

The Mn $L_{2,3}M_{4,5}$ EELS spectra of Mn, *AgMn*, and *CuMn* are shown in Fig. 1. Whereas the Mn-metal spectrum shows only broad lines with little structure, the *AgMn* spectrum shows well-resolved components in the ${}^2P_{1/2}$ as well as the ${}^2P_{3/2}$ regions. The theoretical spectrum calculated for an assumed $3d^5 {}^6S_{5/2}$ ground state is also shown in Fig. 1, and is seen to be nearly identical to the experimental spectrum for *AgMn*. This indicates that the ground state is that expected for a d^5 atom. The *CuMn* spectrum is similar to *AgMn*, but there are distinct differences. First, the components are somewhat broader, and second the ${}^2P_{1/2}$ region has a higher intensity. Both of these observations are consistent with a relatively stronger hybridization with the Cu *sp* conduction band of the d^6 final state as well as an increased mixing of the $d^6 ({}^5D)$ configuration in the still predominantly $d^5 ({}^6S)$ ground state.⁹

To demonstrate further the sensitivity to the details of the ground state we reproduce in Fig. 2 the calculated spectra for various possible starting configurations and multiplets. We have included only the lowest energy initial-state terms for each electronic configuration. From this we notice the surprisingly high sensitivity of the spectral line shape to the ground-state electronic configuration and term. We also no-

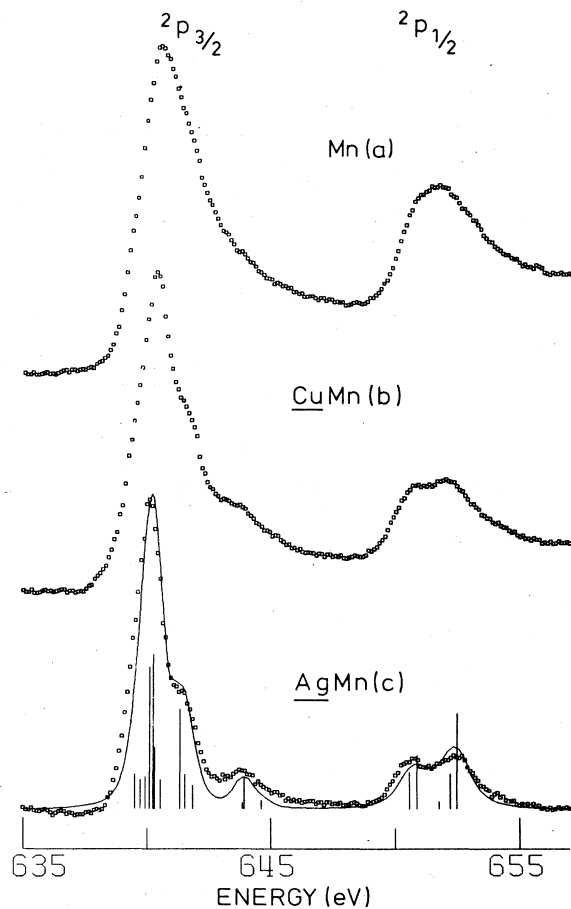


FIG. 1. The Mn $L_{2,3}M_{4,5}$ EELS spectra of (a) pure Mn metal, (b) 3.5% Mn in Cu, and (c) 5% Mn in Ag. The theoretical lines were calculated for a $d^5 ({}^6S)$ ground state as described in the text, with Slater integrals $F_{dd}^2=8.25$ eV, $F_{dd}^4=5.13$ eV, and $\zeta_d=0.04$ eV for the ground state, and $F_{dd}^2=8.92$ eV, $F_{dd}^4=5.55$ eV, $F_{pd}^2=5.06$ eV, $G_{pd}^1=3.69$ eV, $G_{pd}^3=2.09$ eV, $\zeta_p=6.99$ eV, and $\zeta_d=0.05$ eV for the $2p^5d^6$ final states. The solid curve results from a convolution of a 0.4- and 1.0-eV full width at half maximum Lorentzian for the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ regions, respectively, and a Gaussian of width 0.6 eV.

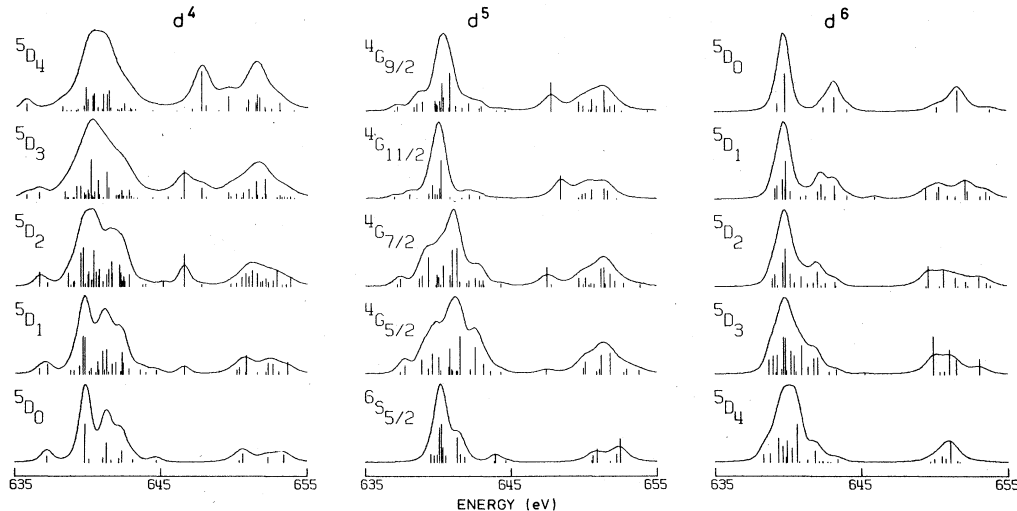


FIG. 2. Calculated EELS or XAS spectra for various possible ground-state terms. Only the lowest-energy configurations and terms for Mn are included. The parameters and convolutions are the same as in Fig. 1.

tice the high sensitivity to various states split only by spin-orbit interactions as in the d^5 (4G_J), d^4 (5D_J), and d^6 (5D_J) manifolds. Since the spin-orbit splitting of these states is only in the meV range for 3d transition metals, this demonstrates that even though the resolution of spectroscopies involving core lines is in the eV range one can distinguish possible initial states separated in energy by only a few meV. In these cases, experiments would have to be carried out at low temperature and the spectra should show considerable temperature dependence. The same sort of sensitivity is expected for distinguishing crystal-field-split states, especially if the polarization of the light source, as in XAS, or the direction of the momentum transfer, as in EELS, can be varied.

The broad lines seen in the Mn-metal spectra clearly demonstrate the limitations of these techniques. From the calculated spectra in Fig. 2 we see that the clearly identifi-

able multiplet structure will quickly be washed out if the band or hybridization width is greater than the splitting between the ground-state terms so that more than two or three terms or electronic configurations are involved in the ground state. This limits detailed interpretation of the multiplet structures to narrow-band materials and to impurity systems with strongly correlated electrons at the impurity site. This is, in itself, an area of considerable interest. Moreover, optical spectroscopy techniques involving core holes also provide a good diagnostic test for the presence of localized moments, which is unaffected by the core-hole potential, in contrast to core-level photoemission. In x-ray photoemission spectroscopy it is the multiplet splitting which is used as a diagnostic test for local moments¹¹ but the splitting, and even the observation itself of a local moment, may be partially dependent on the core-hole potential, as is clearly demonstrated for CuCl_2 .⁴

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