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Spin-polarized photoemission from shallow core levels in localized materials

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We present spin-resolved photoemission measurements from the $5p$ core levels of Gd and Tb metal. In contrast to the $3d$ transition-metal $3p$ spectra, the rare-earth $5p$ spin-resolved spectra show a detailed fine structure that cannot be explained within a one-electron model. The spin-orbit, Coulomb, and exchange interactions have to be treated on an equal footing. For the case of Gd, a remarkable agreement is obtained between experiment and theory when the spin polarization of the $5p$ emission is analyzed on the basis of atomic-multiplet calculations in intermediate coupling. For Tb, however, small discrepancies remain that cannot be analyzed in the absence of a more detailed magnetic characterization. The results emphasize strongly the potential of spin analysis in core-level studies. [S0163-1829(97)51642-0]

In ferromagnetic materials the exchange field induced by the polarized outer-shell electrons splits the core-level excitation spectra into a set of magnetic sublevels. The exchange interaction and its coupling to the Coulomb and spin-orbit interaction give rise to orbital and spin-polarization effects in core-level photoemission spectra. These effects, which can be analyzed within a common framework, are increasingly exploited to probe experimentally the magnetic structure on an atomic scale. The analysis is, however, complicated in all those cases where spin-orbit, Coulomb, and exchange interactions have to be treated on an equal footing. This is the situation encountered in shallow core levels, such as the $3p$ core levels of the transition metals (TM) and the $5p$ levels in rare-earth (RE) materials.

Spin-polarized photoemission, linear and circular-magnetic dichroism in photoemission have been reported by several groups for the $3p$ levels of ferromagnetic iron, cobalt, and nickel.[1] The analysis of these TM core-level spectra has been largely based on a single-particle picture. The basic idea is that the exchange interaction between the core hole and the outer magnetic shell can be simply mimicked by an external *exchange field* as a result of the largely itinerant character of the $3d$ electrons.[2] In these cases it has been pointed out that for the $3p$ spectra, even a quantitative explanation can be obtained on the bases of simple one-particle models in which the spin-orbit and the exchange interaction are properly introduced.[3] However, the large number of free parameters used in these fittings seriously weakens the validity of the conclusions.

Here we propose a detailed analysis of the spin polarization of $5p$ core levels of the two RE materials with a simple ferromagnetic configuration: Gd and Tb. The data show for both metals a detailed fine structure, with more than ten distinct spin-polarized peaks. Although the gross features of the spectra can be qualitatively understood in terms of simple atomic models, a many-body calculation, based on intermediate coupling in the atomic limit is necessary in order to account for all the structures present in the spin-resolved spectra. Furthermore, the only parameter used to fit the data is a small rescaling of the Slater integrals to account for solid-state effects. The excellent agreement found between theory and experiments emphasizes the potential of spin detection for core levels.

The atomic character of the RE $5p$ levels has been recently a matter of discussion. Although the weakly bound $4f$ levels have traditionally been considered as highly localized, band-structure calculations using the local spin-density functional approximation (LSD) indicated an influence of the deeper $5p$ core levels on the bonding. Theoretical calculations[4] found a 7% difference in the calculated lattice constant between treating the Gd $5p$ levels as frozen core levels or taking them as relaxed band states. Experimentally the participation of the $5p$ levels in the bonding was studied with angular-dependent photoemission.[5] From the large variation in the spin-orbit branching ratio as a function of the emission angle, the existence of a strong bandlike behavior has been concluded. However, the spin-integrated photoemission spectra of the $5p$ levels for Gd and Tb have been recently remeasured[6] and compared with the *atomic*-multiplet structure calculated in intermediate coupling. A good agreement between the spectra and the calculations has been found.

Our measurements were performed on the TGM5 undulator-wiggler beamline at BESSY. Gd(0001) and Tb(0001) single crystals were prepared by epitaxial growth (about 100 monolayers) on W(110) surfaces. The samples were magnetized by applying a magnetic pulse along the [1200] axis, and measured in remanence at 80 K. Monochro-

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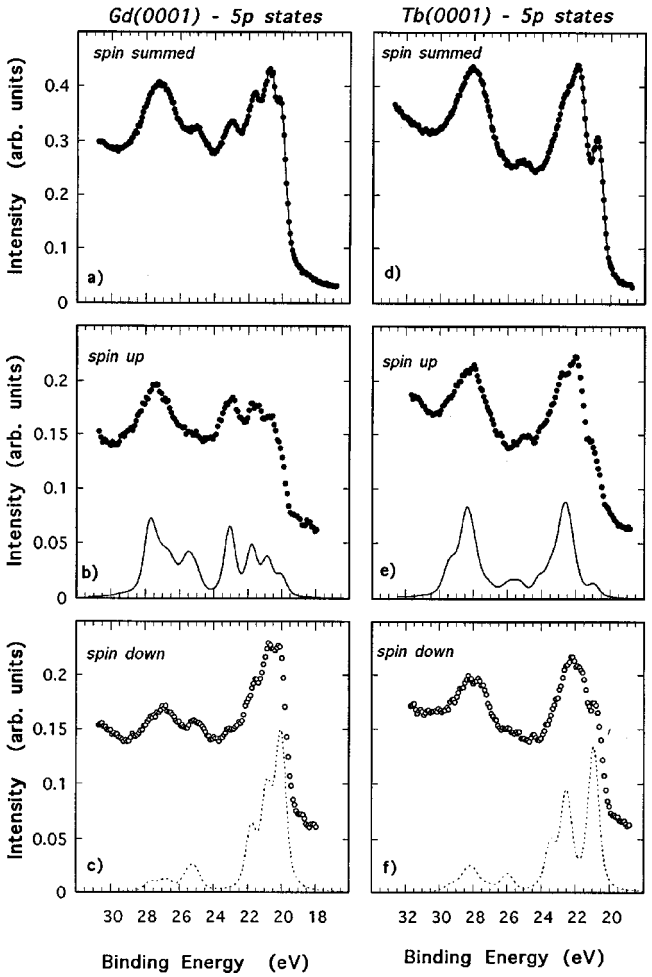

FIG. 1. Gd and Tb 5p photoemission spectra measured in normal incidence and normal emission conditions at 55 eV photon energy. Top row (a), (d): spin-summed spectra; middle row (b), (e) spin-up spectra; bottom row (c), (f): spin-down spectra. The spin-resolved spectra are compared with the calculated ones (drawn curve) in intermediate coupling with polarization vector perpendicular to the magnetic moment.

matic synchrotron radiation with a photon energy of 55 eV was shone onto the crystals at normal incidence through a small opening in the electron analyzer. The polarization vector of the light was along the [1000] direction. Energy distribution curves were measured at normal emission with an energy resolution of 300 meV. The spin polarization of the emitted electrons was measured by high-energy Mott scattering. Spin-up (down) electrons are here defined as those electrons with spin moment parallel (antiparallel) to the magnetization direction of the sample. The easy axis of magnetization in bulk crystals is [1200] for Gd and [00$\underline{1}$0] for Tb. Thus in Tb there could be an angle of 30° between the magnetization direction and the easy axis, although the easy axis in thin films might be different from the one in the bulk. There are, furthermore, some experimental indications that the surface moment may be in some cases partially tilted out of the surface plane.[7] Incomplete alignment of the remnant magnetization along the [1200] axis would reduce the spin-dependent effects in our spin-resolved measurements. Figure 1 shows the photoemission spectra for Gd (left column) and Tb (right column) 5p levels. For both elements the data display a remarkable degree of complexity with a well-resolved fine structure clearly visible.

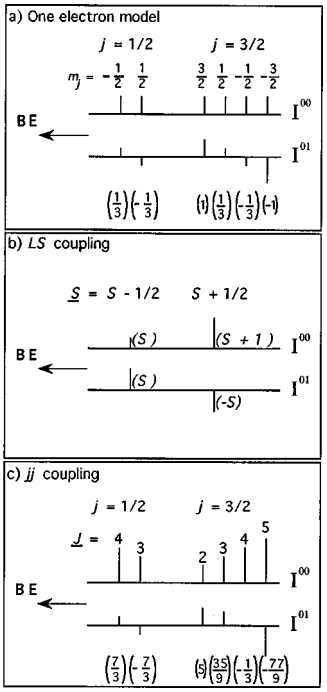

FIG. 2. Isotropic spectrum I^{00} and spin spectrum I^{01}, for a p core-level of Gd^{3+} in the case of (a) the one-electron model, (b) LS coupling, and (c) jj coupling. The numbers in brackets give the relative signals. In case (c) these have been normalized to the intensities of the isotropic signals, which are equal to $2\underline{J}+1$.

To understand the influence of the core-hole interactions on the spin polarization we will first discuss various coupling schemes of the moments involved (Fig. 2). The initial state configuration f^n has orbital, spin, and total angular momentum quantum numbers L, S, and J, respectively. The quantum numbers of the photoionized configuration $5p^5 4f^n$ are indicated with $\underline{L}$, $\underline{S}$, and $\underline{J}$, and those of the core hole with l, s, and j. The ground state of Gd is $f^7(^8S_{7/2})$ and that of Tb is $f^8(^7F_6)$.

First we will discuss the one-electron picture with an *exchange field* acting on the core level. The core-hole spin-orbit interaction splits the photoelectron spectrum into a $j=\frac{3}{2}$ and a $j=\frac{1}{2}$ structure with an intensity ratio of 2:1, where the $j=\frac{3}{2}$ has the lowest binding energy. When we apply a small exchange interaction, which couples the core-hole spin to the average magnetization of the valence electrons, both levels split into $2j+1$ sublevels m_j with equal energy spacing [Fig. 2(a), I^{00}]. The sign of the exchange field is reversed for more and less than half-filled $4f$ shells. When the ground state of the rare-earth ion is $J_z=-J$, the value of S_z is positive for $n<6$, zero for $n=6$, and negative for $n\geq 7$.[8] Consequently, the core-hole state with spin parallel to the exchange field has a lower energy than antiparallel for $n<6$, but a higher energy for $n\geq 7$. Thus when $n\geq 7$ the spin parallel character increases and, therefore, the binding energy also increases with the m_j value in the sublevels of the $j=l+s=\frac{3}{2}$ level, but both are decreasing with the m_j value in the sublevels of the $j=l-s=\frac{1}{2}$ level. The transition probability of each core-hole sublevel is easily derived from the wave function, e.g., for the sublevel with highest binding energy, $j=\frac{1}{2}$; $m_j=-\frac{1}{2}$, and we have $\Psi=\sqrt{(1/3)}(0)^- - \sqrt{(2/3)}(-1)^+$, so that the spin-up minus spin-down intensity I^{01} is $\frac{1}{3}$ [see Fig. 2(a), I^{01}].[9]

In the case of localized materials, it is more appropriate to analyze the spectra in terms of the atomic-multiplet structure generated by the coupling between the core hole and the localized outer $4f$ shell, maintained into a single configuration (i.e., $^8S_{7/2}$ for Gd). In the limit of LS coupling (exchange interaction dominant over the $5p$ spin orbit), the $5p_j4f^n$ final state is split into $\underline{LS}$ levels with $|\underline{L}-L|\leqslant l$ and $|\underline{S}-S|=\frac{1}{2}$. The high-spin $S+\frac{1}{2}$ and low-spin $S-\frac{1}{2}$ final states have an intensity ratio $S+1:S$ [Fig. 2(b), I^{00}]. The spin-down spectrum contains only high-spin states times a factor of $(2S+1)/(2S+2)$. The spin-up spectrum contains high-spin states with a factor of $1/(2S+2)$ and low-spin states with a factor of 1.[10] Thus the spin spectrum I^{01} (spin up minus spin down) provides a way to obtain the spin multiplicity of the final states [Fig. 2(b)].

In jj coupling (spin-orbit interaction dominant with respect to the exchange) each j level splits into $\underline{J}$ levels with $|\underline{J}-J|\leqslant j$. For example, in Gd^{3+} $4f^7(^8S_{7/2})$ the $5p_{3/2}$ final state splits into $\underline{J}=2$, 3, 4, and 5, whereas the $5p_{1/2}$ level splits into $\underline{J}=3$ and 4. The I^{01} spectrum can be obtained using angular momentum coupling techniques.[9] For the Gd case, the results are reported in Fig. 2(c).

In the $j=\frac{3}{2}$ level the spin parallel character increases with the $\underline{J}$ value and when $n<6$ ($n\geqslant 7$) the binding energy increases (decreases). In the $j=\frac{1}{2}$ level the spin parallel character decreases with the $\underline{J}$ value and when $n<6$ ($n\geqslant 7$) the binding energy decreases (increases) [Fig. 2(c), I^{01}]. Thus the spin spectra have an opposite sign for more and less than half-filled shells. This is in agreement with the fact that for $n<6$ ($n\geqslant 7$) the core-hole state with spin parallel to the exchange field has a lower (higher) energy than antiparallel.

A comparison of the data with these simple atomic predictions indicate that the jj coupling is the more appropriate. For example, an inspection of the spin-summed spectrum of Fig. 1(a) shows that a partition of the lines in one quartet and one doublet (jj coupling) seems more correct than in two sets of triplets (LS coupling).[6] Furthermore, in the spin-resolved spectra, the dispersive behavior of the spin polarization described above, negative at the low-energy side and positive at the high-energy side, is clearly visible in each spin-orbit split structure.

However, when the spin-orbit and electrostatic interactions are of comparable size (as is the case in the $5p$ spectra), j is no longer a good quantum number. In this case it is more correct to use the intermediate coupling scheme where all the possible states of the $4f^n$ configuration with the $5p$ hole are included (i.e., for Gd the only constraint is an occupancy of seven electrons for the $4f$ shell). The calculations have been performed starting from the ground-state configurations of the rare-earth atoms $4f^n$. The $5d$ shell has been neglected because its interaction with the $5p$ and $4f$ shells is small. The $5p$ photoemission of RE f^n with magnetic ground state $M_J=-J$ were calculated in intermediate coupling using the programs of Cowan.[11] The Hartree-Fock values of electrostatic, exchange, and spin-orbit parameters used in these calculations are the same as given in Refs. 6 and 12. The calculated line spectra were convoluted with a Lorentzian line shape of $\Gamma=0.2$ eV and a Gaussian of $\sigma=0.22$ eV.

The calculated spin-resolved spectra for the εd continuum are compared to the experimental data in Fig. 1 (drawn curves are spin up; dashed curves are spin down). Clearly in both cases of Gd and Tb the agreement is fairly good and all the experimental features are well reproduced in the calculations. Indeed the agreement is excellent for Gd. With Tb, however, there remains small discrepancies, possibly indicating a more complex spin structure than the simple ferromagnetic configuration at the surface and at this temperature. Generally it is believed that a major complication is that the details of the multiplet structure disappear due to the broadening of the photoemission spectrum. As our data show, much of this broadening is not intrinsically due to core-hole decay but to the averaging over the spin directions. It is a usual procedure to simulate the effects of intra-atomic correlation by reducing the Hartree-Fock values for the Slater integrals. In the calculations reported in Ref. 6, the Hartree-Fock values for the Coulomb and exchange parameters have been reduced to 80%. We found that a scaling of 95% for the Gd $5p$ spectrum gives a better agreement. For the Tb $5p$ spectrum, however, the scaling makes less difference.

The apparent differences between experiment and theory in the spin-up and spin-down spectra are primarily due to the incomplete magnetization along the direction of the spin detection. It is therefore better to discuss the spin polarization in terms of the spin spectrum I^{01}. The structure of the spin spectrum also depends on the polarization direction of the light and the emission angle of the photoelectron. Although the magnetic linear dichroism is strong for emission into the ϵs continuum state, it is ten times weaker for the ϵd photoemission, which is the dominant channel at the photon energy used in this experiment.[8] This can be seen in Fig. 3, where in the top row the calculations are displayed with the light polarization perpendicular to the magnetization direction, while in the middle row the polarization is turned parallel to the magnetization. Clearly, the differences are only minor ones. In this case the spin spectrum has the advantage over the separate spin-up and spin-down spectra in that only the magnitude but not its structure depends on the magnetization direction.

The two extreme coupling schemes analyzed above (LS and jj) help us to understand the intermediate coupling case. Indeed, the general appearance of the spin spectrum is the same in every coupling scheme, depending only on whether the core-hole spin is coupled parallel or antiparallel to the exchange field, i.e., the spin spectrum measures the alignment of the core-hole spin with the induced valence states.[10] In the case of the jj coupling, this coupling varies within each spin-orbit split peak. Obviously, in the intermediate case (going from the jj towards the LS), one expects a net transfer of high-spin character to the $5p_{3/2}4f^n$ level (more negative spin signal), and consequently low-spin character to the $5p_{1/2}4f^n$ structure (more positive spin signal). Indeed this is exactly what is seen in the bottom panels of Fig. 3, where the calculated spin spectra ($\mathbf{E}\perp\mathbf{M}$) are compared with the experimental ones. Since the absolute intensity of the $5p_{1/2}4f^n$ structure is much smaller, the spin transfer results in an almost completely positive peak. Notice that for Gd where the statistics are considerably better than for Tb, the

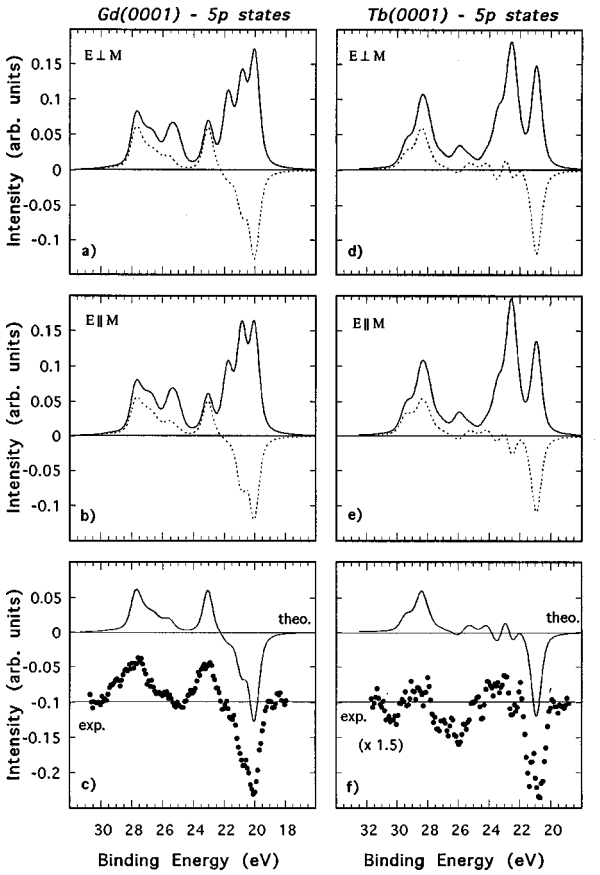

FIG. 3. Calculated spin-summed photoemission spectra (I^{00}; drawn line) for Gd and Tb $5p$ in intermediate coupling with polarization vector and magnetic moment perpendicular [(a), (d), top row] and parallel [(b), (e), middle row]. The calculated spin spectra (I^{01}; dashed curves) for both cases are also shown. In the bottom row (c), (f) the comparisons between the experimental and calculated spin spectra are presented.

calculation reproduces with remarkable accuracy even the finer details of the experimental results.

Finally it is worth noticing that the data also show that the intrinsic linewidth considerably increases with binding energy. For example, a fit of the Gd data indicates that the intrinsic linewidth increases by approximately a factor of 5 from the low binding energy to the high binding energy peak, i.e., the low-spin states are broader than the high-spin states. In the Gd $5p$ photoemission this can be easily understood when we consider the main decay channel: $4f^7 \rightarrow 5p4f^7\varepsilon \rightarrow 4f^5\varepsilon\varepsilon'$. From the Hund's rule ground state with $S=\frac{7}{2}$, intermediate states with $S=3$ and $S=4$ can be reached. However, only the states with $S=3$ can decay to f^5 ($S \leqslant \frac{5}{2}$). Therefore, the $S=4$ intermediate states will have a longer lifetime and will consequently be narrower. This will be most prominent in LS coupling. Since the Auger decay is due to Coulumb interaction, there is no Auger matrix element between different LS eigenstates, giving strict selection rules for the Auger decay process. As a result we have a strong LS-term dependence of the lifetime. However, spin-orbit coupling will mix the LS states, resulting in a more gradual change with binding energy. The leading $J=5$ level will give the most narrow peak, since this J value is not present in the ^7P states so that it cannot interact with low-spin states.

In conclusion, we have shown the importance and validity of core-level spectroscopy for localized materials, such as RE. The spin spectra reveal more structure than the isotropic spectrum and give an indication for the expectation value of the spin magnetic moment. The broadening in the spin-summed spectra is not intrinsically due to core-hole decay but to the averaging over the spin directions. When the anisotropy is small, as in the case presented here, we can take the spectrum equal to the spin spectrum measured with isotropic light. To couple the magnetization with the spin of the photoelectron requires a $5p$-$4f$ exchange interaction. However, both the $5p$ spin-orbit interaction and $5p$-$4f$ electrostatic interactions have a strong influence on the spectrum.

Thus spin-polarized core-level spectroscopy is a powerful method to obtain information about the ground-state electronic structure. The excellent agreement between experiment and calculation makes it possible to draw firm conclusions for localized materials with more complicated magnetic structures.

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