Magnetic Circular Dichroism in Core-Level Photoemission of Localized Magnetic Systems

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Circular dichroism in photoemission can be described by an atomic approach and a comparison is made with an itinerant-electron model. The latter cannot describe the multiplet effects arising from the many-particle Coulomb and exchange interactions. The atomic model predicts a strong dichroic effect in localized transition-metal, rare-earth, and actinide compounds; for Cu p core-hole emission an asymmetry ratio of 45% is calculated. In contrast to x-ray absorption, the angular-dependent part of the electrostatic interaction between the core hole and localized valence holes is essential for circular dichroism.

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The recently discovered x-ray magneto-optical effects, such as magnetic dichroism,[1] Kerr effect and Faraday rotation,[2] and x-ray resonance exchange scattering,[3] can be described in a uniform formulation.[4] Baumgarten *et al.*[5] have observed magnetic x-ray dichroism (MXD) in core-level photoemission (XPS) of ferromagnetic iron using circularly polarized radiation. This phenomenon differs from the aforementioned effects because it is observed in the emission of electrons from core levels into free-electron states, rather than in the cross section for x-ray scattering. The authors gave a qualitative description in the itinerant-electron limit valid for metals.[5] However, in many transition-metal and rare-earth compounds the magnetic moments are localized. Here, we will give a detailed atomic model for such systems with many-particle local interactions. We show that there are important differences between the itinerant and the atomic models. Further, we discuss the differences between dichroism in XPS and x-ray-absorption spectroscopy (XAS).

Local spin-density-functional theory, such as the spin-polarized relativistic Korringa-Kohn-Rostoker Green's-function method, which has been used to calculate MXD in XAS,[6] can also be applied to calculate MXD in photoemission. The exchange interaction between core levels and valence bands, causing a splitting of the core one-electron levels into m_j sublevels, is then responsible for the circular dichroism.[7] Each sublevel gives a single peak with a polarization-dependent intensity.

In the atomic counterpart of this effect, the ground state is the lowest level of a d^n (or f^n) configuration which is polarized by a (super)exchange interaction with neighboring moments. In $2p$ photoemission the exchange interaction between the core hole and d^n valence electrons results in multiplet splitting in the p^5d^n final states. The individual transitions to these final states from the polarized ground state are dependent on the polarization of the light. This can be seen by considering a *polarized* ground state $3d^n(\alpha)$. Let us assume that a transition is made to a final state, which contains an antisymmetrized product of $3d^n(\alpha)$ and a *polarized* core hole, say $2p(\beta)$. When there is no interaction between the $3d$ and $2p$ levels this final state is degenerate with other states which contain $3d^n(\alpha)$ with all other $2p$ functions, and the $2p$ hole is called nonoriented. When there is interaction, the $3d^n(\alpha)$ is combined with only $2p(\beta)$. In order to create such a polarized hole the absorbed photon must be polarized. There are two ways to propagate the polarization of the spin of the ground state to the orbital of the excited core electron. In the first way, the p-d Coulomb and exchange interactions couple the d^n spin to the spin of the core hole and then the $2p$ spin-orbit interaction couples this spin to the core electron orbital, e.g., parallel, antiparallel, or in a more complex way, depending on the final state. In the second way the spin-orbit interaction couples the spins of the d electrons to their orbits and these are coupled by Coulomb and exchange interactions to the orbit of the core hole. The latter effect does not occur in single-particle theory because p-d orbital-orbital interactions are absent.

Although the physics of the transition in two models is the same, the single-particle model cannot describe the multiplet effects arising from the many-particle Coulomb and exchange interactions in the p^5d^n final states.

The general theory of photoemission in localized transition-metal compounds can be extended towards the itinerant limit by treating the ground state as a mixture of several configurations with n electrons, such as d^n and $d^{n-1}k$, which are mixed by d-k interaction, where d denotes a localized state and k a band-type state.[8] Because of the interaction with the core hole the final-state energies of the corresponding p^5d^n and $p^5d^{n-1}k$ configurations are no longer similar, so that they mix less strongly. Each final-state configuration gives a characteristic multiplet structure due to the electrostatic interactions. This allows us to separate and identify the different configurations in the XPS spectrum.[9] This configuration interaction in the initial and final states can be taken into account using a cluster[10] or impurity model,[11] but this introduces several parameters which are not important for the mechanism of MXD. Therefore, it is more instructive to discuss an idealized transition which takes only spin-orbit, magnetic, and core-hole interactions into account. If we take the d-k interactions equal to zero, the p core-hole photoemission spectrum of a $3d^9$ compound is given by the transition $3d^9 \rightarrow p^5 3d^9 + e^-$. The results can be compared to the photoemission satellite peaks of divalent Cu compounds, of which the isotropic spectrum has been well studied.[9]

The photoemission has been calculated using Cowan's atomic multiplet program and here we adopt his notation.[12] The calculated line spectra have been convoluted with a Lorentzian of a width corresponding to the expected intrinsic lifetime.[13] Apart from a reduction of the free-ion Slater integrals to 80% to account for intra-atomic relaxation effects, the calculation contains no free parameters. At high photon energies the emission is given by transitions $3d^n \rightarrow p^5 3d^n \varepsilon d$, where εd is a level of d symmetry with zero spin-orbit, Coulomb, and exchange interactions. In a spherically symmetric potential the spin-orbit interaction splits the initial-state LS terms into levels LSJ with total angular momentum J. These levels are $(2J+1)$-fold degenerate with sublevels labeled by $M_J = -J, -J+1, \ldots, J$. The interatomic exchange interaction is treated as a magnetic field acting on the spin S only. This exchange field lifts the degeneracy, making the energy of the M_J sublevels equal to $-g\mu_B H M_J$, where only the sublevel with $M_J = -J$ is populated at $T=0$ K. The magnetic sublevels in the final state cannot be resolved, in contrast to the Zeeman effect. Without spin-orbit interaction the initial-state LS term is split into spin levels $M_S = -S, \ldots, S$. In the case of crystal-field symmetry the initial state $\Gamma S \Gamma_J$ (where Γ and Γ_J are the orbital and total symmetry, respectively) is split into a number of sublevels equal to the dimension of Γ_J.

The $2p$ ($3p$) spectra of Cu d^9 in spherical symmetry are shown in parts (a) and (b) of Fig. 1 (Fig. 2) with and without $3d$ spin-orbit interaction, respectively. Part (c) is for octahedral symmetry with spin-orbit interaction. The isotropic, left-circularly, and right-circularly polarized spectra are indicated by I_i, I_L, and I_R, respectively. The isotropic spectra are in agreement with earlier calculations.[9-11] The circular dichroism I_c is given by $I_L - I_R$. The asymmetry ratio I_c/I is defined as $(I_L - I_R)/(I_L + I_R)$, which gives a more pronounced dichroic effect at lower intensity. As seen in Figs. 1 and 2, I_c/I is nonvanishing throughout a region of at least 40 eV. Since the $2p$ spin-orbit interaction is larger than the $2p$-$3d$ interaction, the spectrum can be divided into a $2p_{3/2}$ and a $2p_{1/2}$ structure. Roughly, I_c/I shows an antisymmetrical shape for both of these edges but with opposite signs. Near the edges there is a fine structure, which depends strongly on the symmetry of the ground state. In the $3p$ spectrum, the three distinguishable structures can be assigned to ${}^3F + {}^1D$, ${}^3P + {}^3D$, and ${}^1P + {}^1F$, in order of increasing energy. This LS assignment is appropriate because the Coulomb and exchange interactions are much larger than the spin-orbit interactions. It is clear that I_c/I has the same order of magnitude in the $2p$ and in the $3p$ spectrum, attaining values of 45% when there is spin-orbit splitting in the ground state. Thus, the circular dichroism is not reduced by the decreased core-hole spin-orbit splitting, because ap-

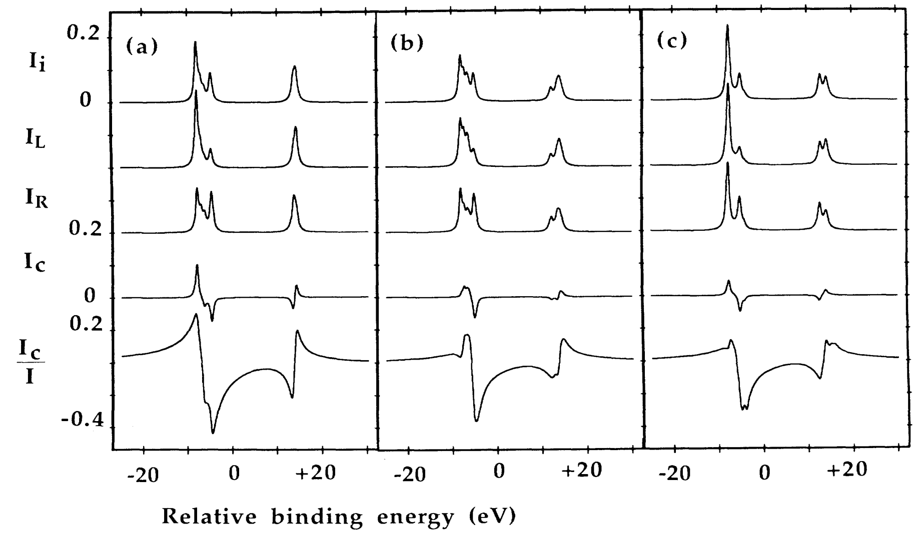

FIG. 1. The calculated Cu $2p$ photoemission with a magnetic exchange field in the direction of the light propagation vector. (a) $3d^9$ ground state in spherical symmetry with $3d$ spin-orbit splitting, (b) without $3d$ spin-orbit splitting, and (c) in octahedral symmetry with $10Dq = 1.5$ eV. Spectra: I_i, isotropic; I_L, left-circularly polarized; I_R, right-circularly polarized; $I_C = I_L - I_R$, circular dichroism; and $I_c/I = (I_L - I_R)/(I_L + I_R)$, asymmetry ratio. The free-ion Slater integrals and spin-orbit parameters are $F^2(2p,3d) = 8.782$, $G^1(2p,3d) = 6.699$, $G^3(2p,3d) = 3.813$, $\zeta_{2p} = 13.496$, and $\zeta_{3d} = 0.135$ (0.102) eV for the final (initial) state. Convoluted with a Lorentzian of $\Gamma = 0.4$ (0.5) eV for the $2p_{3/2\,(1/2)}$.

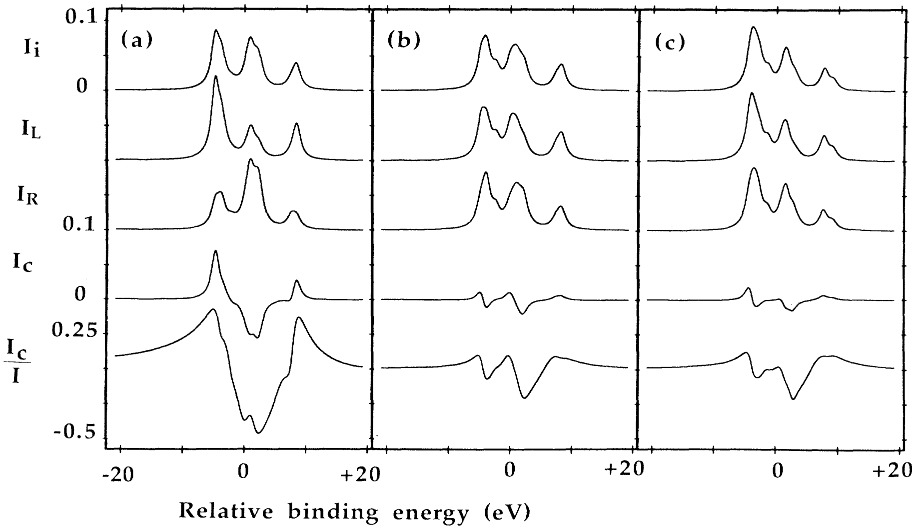

FIG. 2. The calculated Cu $3p$ photoemission with a magnetic exchange field in the direction of the light propagation vector. Parts as in Fig. 1. The free-ion Slater integrals and spin-orbit parameters are $F^2(3p,3d) = 14.950$, $G^1(2p,3d) = 18.458$, $G^3(2p,3d) = 11.250$, $\zeta_{2p} = 1.6562$, and $\zeta_{3d} = 0.113$ (0.102) eV for the final (initial) state. Convoluted with a Lorentzian of $\Gamma = 0.8$ eV.

parently the second way of coupling the valence spin to the core orbital is sufficiently large. Accordingly, the circular dichroism is larger in the presence of $3d$ spin-orbit splitting and reduces when octahedral symmetry mixes the spin-orbit-split levels, partially quenching the spin-orbit interaction.

The overall shape of Fig. 1(a) resembles the experimental Fe spectrum.[5] This shows the expected behavior of the first type of coupling of the valence spin to the core orbit. In the $p_{3/2}$ peak the orbit is parallel to the spin and in the $p_{1/2}$ peak it is antiparallel, giving an opposite dependence of the intensity on the light polarization. The measured asymmetry ratio of ~2% is much smaller than the predicted atomic value, which apart from instrumental broadening and incomplete polarization of the x rays may be due to the large d-k mixing in the metal.[8] When the angular-dependent part of the electrostatic interaction couples the core hole with the $3d$ valence electrons, the energy distribution of the final-state levels becomes polarization dependent. This core-hole interaction increases when the wave function of the $3d$ valence electrons becomes more localized; thus the dichroism will be more pronounced in materials with localized valence electrons.

It is interesting to make a comparison between XPS and XAS. The different coupling in the final state causes a strong difference in spectral behavior. X-ray absorption can be considered as a special case of photoemission, in which the core electron is directly excited to the valence shell, instead of to the continuum. When the d^n ground state is polarized, the holes accessible to the excited core electron are also polarized due to the Pauli principle. Thus, even in the absence of core-hole interactions, circular dichroism in XAS can be observed in the total intensity as well as in the branching ratio, as has been shown for the transition Cu $d^9 \rightarrow 2p^5 3d^{10}$.[14] In the XPS final state $p^5 3d^n \varepsilon d$, there is no coupling between the electron state εd and the remaining state $np^5 3d^n$. For spherical shells the L and R spectrum have equal total intensity and the $2p$ branching ratio is statistical. Only with core-hole interaction is there circular dichroism. The photon spin acts on the orbital momentum of the core electron, which has to be coupled by electrostatic and spin-orbit interaction to the spin of the valence electrons.

Circular dichroism in photoemission is complementary to other magnetic techniques. Compared to magneto-optical effects in optical and x-ray-absorption spectroscopy, it probes the magnetic moment of only those electrons which have electrostatic interaction with the core hole. Contrary to neutron diffraction, paramagnetic resonance, susceptibility measurements, and Mössbauer spectroscopy, it provides information about the *local* magnetic structure. The well-defined wave function of the core hole offers a different approach than in optical spectroscopy, because it gives element and site selectivity. The magnetic dichroism can be analyzed using an atomic calculation including crystal field, hybridization (mixing), and configuration interaction. Although, we have only given a simple example, the analysis can generally be applied to transition-metal, rare-earth, and actinide compounds with localized valence electrons with their large variety of magnetic structures.

In conclusion, MXD in XPS has a large potential as a magnetic tool, especially in dilute materials, overlayers, interfaces, and thin films, where spin-resolved photoemission is limited by low intensity. It is sensitive to the localization, spin-orbit splitting, and symmetry in the ground state. Interesting research applications may be found in systems where the localized character of the valence electrons changes by dimensionality effects due to reduced coordination of the magnetic atoms, e.g., surface magnetic moments are enhanced over the bulk values due to narrowing of the $3d$-band width; or by substrate effects due to interaction between the differing materials. Also the character of the magnetic moments in metal-semiconductor interfaces differs from that in the bulk due to in-plane localization of magnetization.

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