Magnetic X-Ray Dichroism in Gadolinium Metal

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We present a calculation of magnetic x-ray dichroism at the $L_{2,3}$ edges of Gd metal, which takes into account dipolar transitions to the spin-polarized conduction bands, as well as quadrupole transitions to the highly localized $4f$ states. The striking agreement with the data demonstrates the validity of the single-particle approximation in the whole range of energies, above the Fermi level, probed by the experiments. The quadrupolar dichroism is important in determining the pre-edge structure of the measured spectra. Results for the $L_{2,3}$ edges of Ho are also briefly discussed.

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The properties of synchrotron radiation sources have stimulated experiments investigating the polarization dependence of near-edge x-ray absorption and scattering.[1-3] A particularly notable example is the recent measurement of the magnetic circular x-ray dichroism at the L_2 and L_3 edges of Gd and Tb metals.[4] These experiments detect the difference in absorption between right- and left-circularly polarized light, incident on a material with a net magnetic moment. Since the absorption involves transitions from well understood core levels, any structure in the observed spectra gives information about the final states. In particular, these measurements are sensitive to the net spin polarization of the final states and to spin-orbit interactions; for the L_2 and L_3 absorption in Gd (or Tb) the final states of interest are the unoccupied conduction bands, which are predominantly of $5d$ character. It is through their exchange coupling with the incomplete $4f$ shell that these bands acquire a net magnetization. In turn, the spatial extent of the $5d$ orbitals results in overlap with neighboring atoms and an indirect coupling among the highly localized $4f$ moments. While these interactions are relatively well understood among elemental rare-earth metals, the interplay of exchange and spin-orbit couplings can be more complicated in magnetic rare-earth–transition-metal compounds, and are particularly dramatic in some of the new hard magnetic materials.

In the analysis of the x-ray dichroism experiments on Gd a very simple model was used to compare the experimental results with a spin-polarized band calculation. The obvious disagreement was noted,[4] and attributed to possible many-body effects, caused by a modification of the $5d$ spin density through interactions with the core hole. It is important to establish if the spectra obtained using this relatively new experimental probe must be analyzed with models including the core hole, or if the one-electron model for the empty ground-state conduction bands is adequate. The latter is certainly easier to

evaluate and to interpret, and its validity for these experiments would help confirm the utility of x-ray dichroism measurements as a valuable new tool for studying the ground-state properties of magnetic solids.

In this Letter we show that excellent agreement with experiment can indeed be obtained by considering dipole transitions to the spin-polarized conduction bands, as well as quadrupole transitions to the localized, atomic-like $4f$ states. The conduction bands are treated within the single-particle model, while the $4f$ states are treated with an atomic model which takes into account the multiplet structure. The atomic model for the $4f$ states is known to be essential for calculating the dipolar M_4 and M_5 spectra of the rare earths.[5]

For the $L_{2,3}$ dichroic spectra we were led to consider both dipole ($E1$) and quadrupole ($E2$) transitions for two reasons. First, numerical estimates that we performed in the atomic limit suggested that the two contributions could be comparable. Second, in the experimental dichroic spectra there appears to be some structure below the "white line" edge. As pointed out in Ref. 6, this pre-edge structure is similar, in nature, to the one observed in x-ray resonant exchange scattering (XRES) for Ho,[7] and ascribed to quadrupolar effects. (The "edge" corresponds to the onset of $E1$ transitions to the broad region of unoccupied band states; $E2$ transitions can appear below the edge because of the strong attraction, in the final state, between the localized $4f$ electrons and the $2p$ core hole.) Absorption is controlled by the imaginary part of the forward-scattering amplitude; hence there is a sharing of features between XRES and circular dichroism.

In XRES, the quadrupolar contribution to the cross section is readily identified: Given a helimagnet (e.g., Ho), $E1$ and $E2$ (virtual) transitions result in different magnetic satellites, as predicted[7] and observed.[3] In circular dichroism, the association of pre-edge structures with $E2$ transitions is still an open issue which could be

clarified by experiments designed to detect the different angular dependence expected for $E1$ and $E2$ transitions.[6] In fact, part of the motivation for the present work was to make accurate theoretical estimates to aid in the identification of any quadrupole features of the spectrum below the edge.

We calculate dipolar and quadrupolar circular dichroism on the basis of the expressions[6,8]

$$\mu_c^{E1}(k) = \frac{6\pi N}{k}[w_{11}^{(el)} - w_{1-1}^{(el)}]\cos\theta, \qquad (1)$$

$$\mu_c^{E2}(k) = \frac{10\pi N}{k}\{[w_{22}^{(el)} - w_{2-2}^{(el)}]\sin^2\theta$$

$$+ [w_{21}^{(el)} - w_{2-1}^{(el)}]\cos2\theta\}\cos\theta, \qquad (2)$$

where $\cos\theta = \hat{k}\cdot\hat{z}$, with $\hat{k}$ and $\hat{z}$ the unit vectors in the direction, respectively, of the photon momentum and local magnetization; N represents the number of atoms per unit volume. By definition, $\mu_c^{EL} = \mu^{EL}(k,\hat{e}^+) - \mu^{EL}(k, \hat{e}^-)$, with μ^{EL} the 2^L polar absorption coefficient and $\hat{e}^\pm = \mp(i/\sqrt{2})(\hat{e}_1 \pm i\hat{e}_2)$. Also, assuming $kr \ll 1$ and $T=0$,

$$w_{LM}^{(el)} = 4\pi^2 e^2 \sum_\eta \left[\frac{L+1}{L[(2L+1)!!]^2}\right]k^{2L}$$

$$\times \left|\left\langle\eta\left|\sum_j r_j^L Y_{LM}\right|\alpha\right\rangle\right|^2 \delta(\varepsilon_\alpha - \varepsilon_\eta - \varepsilon). \qquad (3)$$

Nonmagnetic absorption—the white line—is given by

$$\mu_0(k) = \mu^{E1}(k,\hat{e}^+) + \mu^{E1}(k,\hat{e}^-)$$

$$= \frac{6\pi N}{k}\{[w_{11}^{(el)} + w_{1-1}^{(el)}]\cos^2\theta + 2w_{10}^{(el)}\sin^2\theta\}.$$

The self-consistent, spin-polarized band-structure calculations were performed using the linear augmented-plane-wave method. The scalar-relativistic Dirac equation was solved for the lowest 30 bands of each spin, and then the lowest 60 states were used to diagonalize the spin-orbit Hamiltonian at each k point.[9] Four separate energy windows were used to extend the energy range for accurate wave functions to about 2 Ry above the Fermi energy. The calculated energy bands agree well with those reported earlier for Gd.[10-13] The relativistic Bloch functions were then used to evaluate the $E1$ matrix elements with the $2p$ core states. Since the short core-hole lifetime results in a broadening of about 4 eV, the fine structure of the band density of states is greatly smeared out, and therefore in performing the k-space summation we only needed to include 24 tetrahedrons in the irreducible $\frac{1}{24}$th of the Brillouin zone. The calculation was performed for the magnetic moment along the c axis of the crystal and the matrix elements for right- and left-circular polarization were evaluated with the photon propagation wave vector along the magnetic-field direction. For comparison with experiment we followed Materlik, Müller, and Wilkins[14] by adding the core-hole

lifetime (about 4 eV) and including an energy-dependent final-state lifetime.

The calculation of the atomic quadrupolar spectra was performed with Cowan's atomic Hartree-Fock program with relativistic corrections.[15] Transitions from the lowest level of the $4f^7$ configuration of Gd^{3+} to the full multiplet of the $2p^54f^8$ configuration were calculated. The calculated dichroic spectra for both the L_2 and L_3 transitions were found to be essentially Lorentzian peaks (no structure). This is because the Coulomb and exchange interactions give rise to a multiplet structure that is narrower than the natural linewidth of about 4 eV. The final theoretical spectrum ($E1$ and $E2$) was broadened with a Gaussian function corresponding to the quoted experimental resolution of 1.5 eV.

The results of the calculations for the x-ray-absorption and dichroic spectra are shown in Fig. 1, as a function of the photoelectron energy, for the L_2 and L_3 edges of Gd. These spectra should be compared with the corresponding experimental data[4] depicted in Fig. 2. The peak intensities of the calculated white lines are within a few percent of the experimentally determined values; for the dichroism the theoretical amplitude is ~40% larger than the experimental value. However, the experimental normalization has a large uncertainty arising from beam polarization and magnetization corrections. The agreement in shape of the two curves is significant and nearly
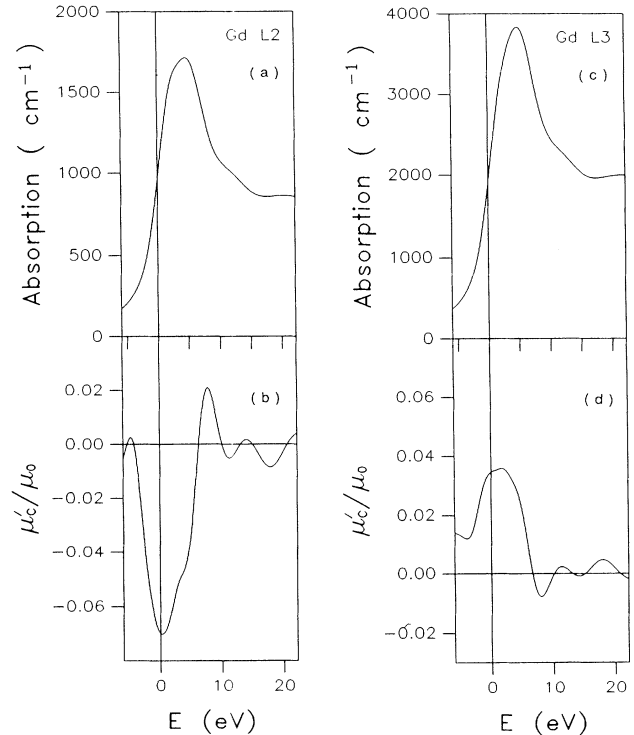

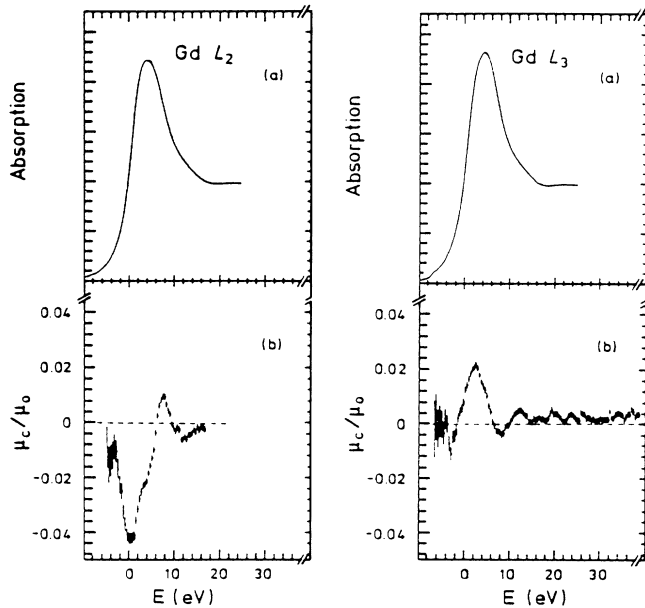FIG. 1. Calculated "white line" μ_0 and circular dichroism μ_c'/μ_0 at the $L_{2,3}$ edges of Gd metal (see text).

FIG. 2. Experimental data (after Ref. 4). Upper panels: total (nonmagnetic) absorption—the "white line." Bottom panels: circular dichroism.

FIG. 3. Calculated circular dichroism at the $L_{2,3}$ edges of Ho. The dichroic signal is shown for $\theta = 0°$ (solid line), 30° (dashed line), and 60° (dotted line).

perfect. In Gd, a large $5d$ orbital radius makes the atomic $2p$-$5d$ Coulomb integral (Slater's F^0) rather small: 13.5 eV;[16] in the solid, screening brings it down to 2 eV (or less), a value smaller than the $5d$ bandwidth. As a consequence, no core excitonic state is formed. One could compare this to F^0 for $2p$-$4f$: 40 eV for the free atom and 8–10 eV in the solid, the latter certainly much larger than the $4f$ bandwidth, and in fact large enough to pull the $2p^5 4f^8$ state below the Fermi level by 3–4 eV. (Without the core hole, the $4f^8$ state is found at about 5 eV above ε_F, as determined by bremsstrahlung isochromat spectroscopy.[17]) The fine tuning of the position of the $E2$ peak relative to $E = 0$ (the Fermi energy) is treated as an adjustable parameter. These spectra were calculated at $\theta = 30°$,[18] correcting for $\cos\theta$ in (1) and (2) ($\mu_c^{\prime EL} = \mu_c^{EL}/\cos\theta$), to match the experimental conditions. In the figures we have followed Ref. 4 in displaying a "normalized" dichroic signal: $\mu_c^{\prime}/\mu_0 = (\mu_c^{\prime E1} + \mu_c^{\prime E2})/\mu_0$. This tends to emphasize the structure below the edge, which is due to quadrupolar transitions in our calculated curves.

In general, the quadrupolar nature of the dichroism below the edge can be identified experimentally from the difference between the angular dependences of $E1$ and $E2$ transitions [see Eqs. (1) and (2)]. The case $w_{22} - w_{2-2} = 2(w_{21} - w_{2-1})$ represents an exception, as the expressions for $E1$ and $E2$ are then both proportional to $\cos\theta$. In Gd (and in general for the $^8S_{7/2}$ ground-state configuration) the ratio of the two quadrupolar contributions happens to be $\cong 2$; consequently, the angular dependences of the $E1$ and $E2$ transitions are nearly
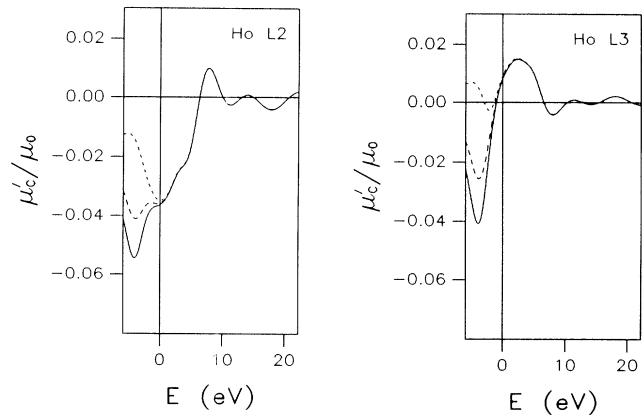
identical. It is not so, however, for other rare earths; in particular, for Ho the angular dependence below and above the edge is strongly different and thus, in principle, detectable. The Ho dichroic spectra, evaluated at the $L_{2,3}$ edges for $\theta = 0°$, 30°, and 60°, are shown in Fig. 3.

The calculations for Ho, which assume a ferromagnetic alignment of the rare-earth ions as in the intermetallic compounds R_2Co_{17} recently probed by Fischer, Schütz, and Weisinger,[19] were performed as follows: The dipolar part of the spectra was obtained by scaling the corresponding Gd dipolar spectra by the ratio of the measured conduction-band polarization for the pure metals.[20] As this scaling argument does not apply to the quadrupolar transitions, a full-multiplet atomic calculation was performed for the $E2$ contributions.

In summary, the agreement found between our theoretical curves and the experimental results is excellent, demonstrating the validity of the one-particle approximation for describing the contribution of d-like final states to the $L_{2,3}$-edge x-ray circular dichroism in rare-earth systems. The energy dependence of the $E1$ spectra reflects the spin-polarization of unoccupied $5d$ levels in the ground state. Similar considerations apply to the $E2$ spectra with the difference that, in this case, the core-hole potential "pulls" the quadrupolar peak ($4f$ levels) below the edge. The spin-orbit coupling within the $5d$ bands of Gd is not so important for determining the dichroic spectra; it does contribute structure at the 10%–15% level.

Very recently, Namikawa and co-workers have reported the observation of XRES, with linear polarization, at the $L_{2,3}$ edges of ferromagnetic Gd metal.[21] This experiment, which detects the interference between Thomson scattering and the magnetic component of anomalous scattering,[22] represents the diffractive counterpart of circular dichroism. The observed line shapes are in good agreement with the calculation described in this Letter.

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