

Circular magnetic x-ray dichroism in the heavy rare-earth metals

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The calculated circular magnetic x-ray dichroic spectra for the L_3 absorption edge of the heavy rare-earth metals is presented. For Gd and Tb, the dipolar part is evaluated directly from first-principles relativistic spin-polarized band-structure calculations, while for the others the spectra are obtained by scaling the Gd results. The quadrupolar transitions to the localized $4f$ states are evaluated separately with full atomic-multiplet calculations, and are found to be large. Implications and experimental results are discussed.

As a result of new and planned synchrotron-radiation facilities, there is an increased interest in developing and extending x-ray spectrometers and techniques. In the last few years several studies of circular magnetic x-ray dichroism (CMXD) have shown it to be a promising probe for magnetic materials,¹ and with the adoption of crossed undulators, extremely intense circularly polarized beams will be available to further stimulate research using CMXD.² The experiments measure the difference in absorption between right- and left-polarized x rays incident on a material with a net magnetic moment. The dichroic spectra near an absorption edge depends upon the local spin and orbital polarization of the final states. For example, in the L_2 and L_3 dichroic spectra for rare-earth elements, the dipole ($E1$) transitions are predominantly from the $2p_{1/2}$ and $2p_{3/2}$ core levels to the unoccupied spin-polarized states with $5d$ character. Within the single-particle model, the overall strength of the dichroic spectra depends on the size of the spin-dependent transition matrix elements and the degree of spin polarization of the conduction-band states, while the difference (from a 1:−1 ratio) between the L_2 and L_3 dichroic spectra is sensitive to the orbital moment (a manifestation of the spin-orbit coupling in a magnetic system). For local orbitals the integral over both the L_2 and L_3 dichroic spectra has been shown to be proportional to the local orbital moment.³ These characteristics of CMXD can be used to probe the element and orbital specific magnetic properties of particular states. This is an advantage when trying to sort out the magnetic interactions in structurally complicated materials such as the new rare-earth permanent magnets.

We have previously presented a detailed calculation of the CMXD for Gd metal.⁴ We found that in order to account for measured structure below the absorption edge, we had to include quadrupole ($E2$) transitions between the $2p$ and $4f$ levels. The agreement between experiment⁵ and theory was excellent. In that previous study we also gave approximate dichroic spectra for ferromagnetic Ho metal. The approximation consisted of using for Ho the scaled dipole part of the Gd spectra. The

spectra were scaled by the relative conduction electron spin polarizations. The $E2$ parts of the spectra for Ho were evaluated with full-multiplet atomic calculations. Since the crystal and conduction-band electronic structures of the heavy rare-earth metals are so similar, this scaling procedure is expected to be valid for describing the dipolar spectra for the ferromagnetic states of these metals. The quadrupole contributions, on the other hand, do change with $4f$ occupation across the series.

In our discussion here we assume that all the moments are aligned. (That is, we do not perform the angle averaging that is necessary to compare with experiment when the moments are in a spiral or other magnetic arrangement. This can be done given the angle dependence below.)

We calculate dipolar and quadrupolar circular dichroism on the basis of the expressions⁶

$$\begin{aligned}\mu_c^{E1}(k) &= \frac{6\pi N}{k} [w_{11}^{(el)} - w_{1-1}^{(el)}] \cos\theta, \\ \mu_c^{E2}(k) &= \frac{10\pi N}{k} \{ [w_{22}^{(el)} - w_{2-2}^{(el)}] \sin^2\theta \\ &\quad + [w_{21}^{(el)} - w_{2-1}^{(el)}] \cos 2\theta \} \cos\theta,\end{aligned}$$

where $\cos\theta = \hat{\mathbf{k}} \cdot \hat{\mathbf{z}}$, with $\hat{\mathbf{k}}$ and $\hat{\mathbf{z}}$ 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, $\mu_c^{EL} = \mu^{EL}(k, \hat{\mathbf{e}}^+ - \mu^{EL}(k, \hat{\mathbf{e}}^-)$, with μ^{EL} the 2^L polar absorption coefficient and $\hat{\mathbf{e}}^\pm = \pm(i/\sqrt{2})(\hat{\mathbf{e}}_1 \pm i\hat{\mathbf{e}}_2)$. Also, assuming $kr \ll 1$ and $T=0$,

$$\begin{aligned}w_{LM}^{(el)} &= 4\pi^2 e^2 \sum_{\eta} \left[\frac{L+1}{L[(2L+1)!!]^2} \right] k^{2L} \\ &\quad \times \left| \left\langle \eta \left| \sum_j r_j^L Y_{LM} \right| a \right\rangle \right|^2 \delta(\varepsilon_a - \varepsilon_{\eta} - \varepsilon).\end{aligned}$$

The nonmagnetic absorption—the white line—is given by

$$\begin{aligned}\mu_0(k) &= \mu^{E1}(k, \hat{e}^+) + \mu^{E1}(k, \hat{e}^-) \\ &= \frac{6\pi N}{k} \{ [w_{11}^{(el)} + w_{1-1}^{(el)}] \cos^2\theta + 2w_{10}^{(el)} \sin^2\theta \} .\end{aligned}$$

It is the purpose of this paper to present the $E2$ contributions and approximate $E1$ contributions for the L_3 spectra of all of the heavy rare-earth metals. Part of the motivation for this work is to explain the experimental spectra for the $(R)_2\text{Co}_{17}$ series of compounds which indicate large changes across the series.⁷ Because the $4f$ orbitals are highly localized we expect the $E2$ contributions for a particular element to remain essentially the same no matter which material the rare-earth atom is embedded in. Our results for the $E2$ part of the spectra for the different heavy rare-earth elements should thus be similar to the corresponding experimental spectra for any magnetic material containing ordered heavy rare-earth elements. We discuss the experimental studies after presenting the results of the theoretical calculations.

To test the scaling approximation for the $E1$ transitions we performed first-principles relativistic spin-polarized calculations for Tb. The calculations were made like those for Gd except that the $4f$ orbitals were treated as core states with the occupancy constrained to eight electrons. The self-consistent spin-polarized conduction bands were obtained using a linearized augmented plane-wave (LAPW) method in which the spin-orbit Hamiltonian was diagonalized using the lowest 30 spin-up and spin-down scalar relativistic bands as basis states. The calculated L_2 and L_3 CMXD spectra for Tb are shown in Fig. 1. The results include both $E1$ and $E2$ transitions, and are in good agreement with experiment,

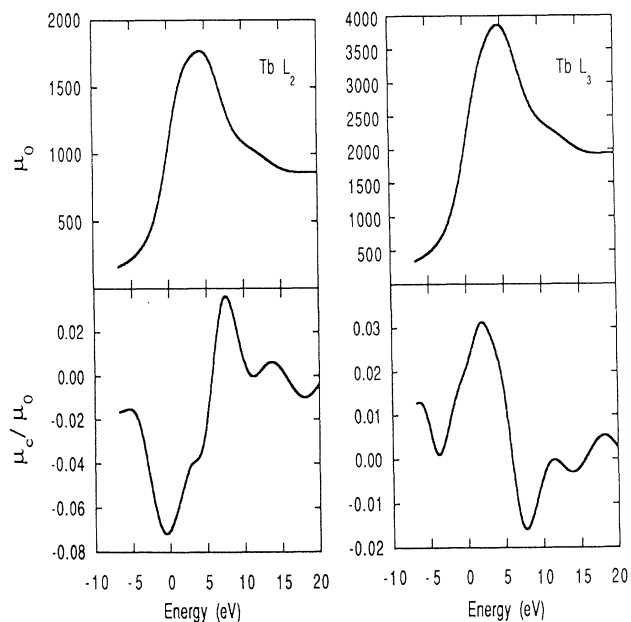


FIG. 1. The calculated L_2 and L_3 absorption spectra for Tb. The top panel shows the total absorption for unpolarized x rays, and the bottom panel shows the normalized circular dichroic spectra. Experimental data are given in Ref. 5. The units for μ_0 are cm^{-1} .

although the agreement between theory and experiment for Gd is even better. The spectra were calculated assuming that the magnetic moments were ferromagnetically aligned and that the photon wave vector was parallel to the moment. We have followed Ref. 5 in displaying the “normalized” dichroic signal in which we divide the dichroic spectra (μ_c) by the corresponding adsorption spectra (μ_0). This tends to emphasize the quadrupolar structure below the edge.

The calculation of the quadrupolar spectra was performed with Cowan’s Hartree-Fock and atomic multiplet program with relativistic corrections.⁸ Transitions from the $4f^n$ ground-state configuration to the full multiplet of the $2p^5 4f^{n+1}$ configurations were calculated. The calculated line spectra were broadened using a Lorentzian distribution corresponding to the natural line width of about 4 eV. The final theoretical spectra were further broadened with a Gaussian function corresponding to an experimental resolution of 1.0 eV. The $E2$ portion of the spectra appears below the absorption edge (defined theoretically as the energy position where $E1$ transitions to empty states begin; and defined experimentally as the inflection point in the rise of the “white-line” absorption peak). The $E2$ transitions appear lower in energy because of the stronger attractive interaction of the $4f$ states with the core hole (without the core hole, the $4f^{n+1}$ states are found about 5 eV above the Fermi energy, as determined by bremsstrahlung isochromat spectroscopy). Because the relative conduction electron-core-hole and the $4f$ -core-hole interactions cannot presently be calculated to enough precision, we have treated the position of the $E2$ peak relative to the Fermi energy ($E=0$) as an adjustable parameter. These energy shifts for the $E2$ spectra range almost linearly from -3.4 eV for Gd to -5.35 eV for Tm.

The calculated L_3 spectra for Gd is shown in Fig. 2 along with the L_3 spectra obtained using the scaling approximation dipole spectra for the other heavy rare-earth metals. We caution, however, that the dipolar spectra for the rare earths should be sensitive to the surrounding atomic environment. In fact, it is just this sensitivity which makes the development of the CMXD a possibly valuable tool for studying different magnetic materials. The first-principles Tb spectra (Fig. 1) and the scaled spectra for Tb (in Fig. 2) are very similar, which supports the validity of the scaling approach for the other elements. The overall trend of the large $E2$ contributions shown in Fig. 2 is in agreement with experiment.⁷ Before discussing the experiment, however, we would like to clear up one aspect of the rare-earth CMXD spectra which has caused confusion in the past.

For dipolar transitions a rough single-particle model has been suggested for interpreting CMXD spectra. This model relates the spectra to the spin-dependent final-state density and has been used to interpret the experimental CMXD data of Gd as indicating a large density of unoccupied spin-up states at and above the Fermi energy.⁵ This would be strange, since with more of the $5d$ spin-up states occupied [measurements of the magnetic saturation indicate a net conduction electron moment of $+0.63\mu_B$ (Ref. 9)] one naturally expects there to be more unoccu-

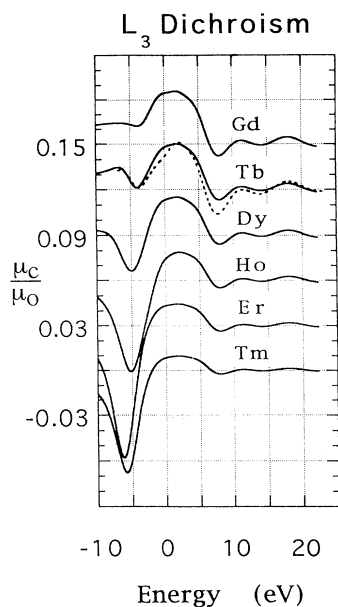


FIG. 2. The calculated normalized L_3 spectra for the heavy rare-earth metals. The Gd spectra is from first principles while the spectra for the other heavy rare earths have the dipolar part ($E > 0$) scaled from the Gd results, but with separate atomic calculations for the quadrupolar part ($E < 0$). The curves have been offset by 0.03 for clarity. Also, the first-principles Tb L_3 spectra of Fig. 1 is shown as a dashed curve for the sake of comparison.

pied spin-down states above the Fermi level. Our calculations certainly find this to be true, and furthermore show that the simple model errs because of the neglect of spin-dependent transition matrix elements. Even though there are fewer spin-up states above the Fermi level, the matrix elements for transitions to spin-up bands are larger and cause the spectra to be dominated by spin-up transitions. The reason for this significant spin dependence of the matrix elements can be found in the radial part of the wave functions for the $5d$ conduction electrons. A figure showing these functions for Gd is given in Ref. 10, where it is clear that the spin-up $5d$ radial functions are “pulled in” relative to the spin-down functions because of their stronger exchange interaction with the localized $4f$ orbitals. This “pulling in” causes the $5d$ radial functions to have a significantly larger amplitude in the region of the $2p$ radial function. Because these interactions occur deep within the rare-earth atom, they will not be affected by the atomic environment and should be essentially the same for all rare-earth compounds. However, while we expect the matrix elements to be insensitive to environment, the density of final states need not be. We also note that the difference in the spin-up and spin-down $5d$ radial functions is proportional to the net spin moment of the $4f$ states, so not only does the conduction electron magnetization (moment) decrease as the $4f$ shell fills beyond Gd, but also the difference in the spin-up and spin-down matrix elements decreases (at approximately the same rate for the elemen-

tal metals).

Our theoretical work was partially motivated by the reported measurements of the CMXD spectra for the series of $(R)_2\text{Co}_{17}$ compounds. The measured L_3 spectra exhibit the same qualitative behavior as shown in Fig. 2 for the theoretical results. That is, there is a large negative feature that appears below the absorption edge, and a positive contribution just above the edge that decreases in magnitude across the rare-earth series starting from Gd. In looking at the details of the spectra, differences with the theoretical curves can be found. In particular, the positive (dipolar) part of the spectra begins right at the Fermi energy in the theoretical results and extends to energies below the edge because of the broadening functions applied. The corresponding feature in the experimental spectra, on the other hand, appears to be shifted to slightly higher energy for some of the elements. This may be due to differences in the $5d$ density of states between the elemental metal and the corresponding Co compound. Since there is such a large core-hole lifetime broadening (4 eV), fine features of the density of states are not expected to be detectable, however, a shift of the $5d$ density of states (e.g., because the Co $3d$ bands are prominent in the vicinity of the Fermi energy) could be detectable. It will take precise measurements on a variety of compounds, and also correspondingly precise theoretical calculations for all of the material-dependent features of CMXD to be confirmed and understood.

In the above discussion, we have ascribed the structure below the edge in the CMXD spectra to quadrupolar transitions between the $2p$ core level and the partially filled $4f$ shell. Recently experiments were performed to try to confirm the quadrupolar nature of these transitions by measuring the CMXD as a function of the angle between the magnetic moment and the photon wave vector.^{11,12} Because the experiments to date have been performed using polycrystalline samples, the theoretical results need to be averaged over the appropriate random alignment of the magnetic moments of the grains. The averaging greatly reduces the expected difference between angle dependence of the dipolar and quadrupolar transitions. Experiments just reaching the degree of precision necessary to observe these differences were recently performed for the L_3 absorption edge of $\text{Er}_2\text{Fe}_{14}\text{B}$ by Lang *et al.*¹² The measured CMXD spectrum was similar to that obtained for $\text{Er}_2\text{Co}_{17}$.⁷ To within experimental uncertainty, the entire spectrum was observed to have the same angular dependence (i.e., the quadrupolar-dipolar differences were not detected). Further experiments on either grain-aligned samples, or single crystals are planned.

The use of CMXD for magnetic studies of the rare earths is a new field, and the degree to which single-particle models for the conduction states can be applied in the presence of a final-state core hole has yet to be widely explored. On the other hand, the need to treat the $4f$ states as localized and atomlike is well confirmed by measurements of the M_4 and M_5 dipolar spectra of the rare earths.¹³ Recent experimental work by Fischer *et al.* studying the systematics of the CMXD spectra for Ho in four different materials represent the kind of stud-

ies which will help establish the degree of variation encountered for different material environments.¹⁴ The interpretation of these spectra will require difficult (but nowadays feasible) calculations, and we believe a consideration of the magnetic alignment in the powdered samples is also required for quantitative analysis. There are certain to be many more investigations before CMXD can be routinely applied using the new synchrotron facilities under construction.

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- ¹G. Schütz, W. Wagner, W. Wilhelm, P. Kiemle, R. Aeller, R. Frahm, and G. Materlik, *Phys. Rev. Lett.* **58**, 737 (1987); also see T. Jo, *Synchrotron Radiat. News* **5**, 21 (1992), for a brief review.
- ²S. Yamamoto, H. Kawata, H. Kitamura, M. Ando, N. Sakai, and N. Shiotani, *Phys. Rev. Lett.* **62**, 2672 (1989).
- ³B. T. Thole, P. Carra, F. Sette, and G. van der Laan, *Phys. Rev. Lett.* **68**, 1943 (1992).
- ⁴P. Carra, B. N. Harmon, B. T. Thole, M. Altarelli, and G. A. Sawatzky, *Phys. Rev. Lett.* **66**, 2495 (1991).
- ⁵G. Schütz, M. Knülle, R. Wienke, W. Wilhelm, W. Wagner, P. Kienle, and R. Frahm, *Z. Phys. B* **73**, 67 (1988).
- ⁶P. Carra and M. Altarelli, *Phys. Rev. Lett.* **64**, 1286 (1990).
- ⁷P. Fischer, G. Schütz, and G. Wiesinger, *Solid State Commun.* **76**, 777 (1990).
- ⁸R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).
- ⁹L. W. Roeland, G. J. Cook, F. A. Muller, A. C. Moleman, R. G. Jordan, and K. R. Moewen, *J. Phys. F* **5**, L233 (1975).
- ¹⁰B. N. Harmon and A. J. Freeman, *Phys. Rev. B* **10**, 1979 (1974).
- ¹¹P. Fischer, G. Schütz, S. Stähler, and G. Wiesinger, *J. Appl. Phys.* **69**, 6144 (1991).
- ¹²J. C. Lang, S. W. Kycia, X. D. Wang, B. N. Harmon, A. I. Goldman, R. D. McCallum, D. J. Branagan, and K. D. Finkelstein, *Phys. Rev. B* **46**, 5298 (1992).
- ¹³B. T. Thole, G. van der Laan, J. C. Fuggle, G. A. Sawatzky, R. C. Karnatak, and J.-M. Esteve, *Phys. Rev. B* **32**, 5107 (1985).
- ¹⁴P. Fischer, G. Schütz, S. Scherle, M. Knülle, S. Stähler, and G. Wiesinger, *Solid State Commun.* **82**, 857 (1992).