Confirmation of Quadrupolar Transitions in Circular Magnetic X-Ray Dichroism at the Dysprosium L_{III} Edge

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The angular dependence of the circular magnetic x-ray dichroism at the Dy L_{III} edge of the alloy $Dy_{0.4}Tb_{0.6}$ has been studied at $T = 80$ K to ascertain the multipolar nature of the features in the dichroic spectra below the absorption edge. Angular behavior, consistent with quadrupolar transitions, is observed in the feature below the edge. We discuss the reasons for numerous recent failures to observe such an effect.

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Circular magnetic x-ray dichroism (CMXD), defined as the difference $\mu_c = \mu^+ - \mu^-$ between the absorption of left and right circularly polarized x rays by a magnetized sample, has recently attracted great interest as a probe of the magnetic properties of a variety of condensed matter systems [1–4]. A particularly important development in the field has been the derivation of sum rules for the dichroic signal, which make it possible to separately determine the orbital $\langle L_z \rangle$ [5] and spin $\langle S_z \rangle$ [6] contributions to the magnetic moment for individual orbitals and constituent elements. Independent measurements of the spin and orbital angular momenta are highly desirable for comparison with theoretical models because they provide information about the spin-orbit interaction, which governs the size of the orbital moment in itinerant ferromagnets and is also responsible for magnetocrystalline anisotropy and magneto-optical phenomena (e.g., the Kerr and Faraday effects). The sum rules have been applied to obtain values for transition metal $3d$ [3] and rare-earth $4f$ [4] moments, which are the predominant magnetic electrons in these systems. For rare-earth materials, it is also desirable to obtain information on the more extended $5d$ states that mediate the magnetic ordering through the RKKY interaction. The application of the sum rules to obtain information about these states, however, has been hampered by the lack of a complete understanding of the features present in the CMXD spectra at the $L_{II,III}$ edges of rare-earth compounds.

While features above the absorption edge in these spectra have unambiguously been assigned to dipolar transitions involving the unfilled $5d$ band, the origin of prominent peaks below the edge is still uncertain. Carra *et al.* [6] pointed out that a similar preedge structure ascribed to quadrupolar $2p$ to $4f$ transitions had been observed in x-ray resonance exchange scattering experiments on Ho metal [7,8]. Therefore, they suggested that the preedge features in the CMXD spectra could also arise from quadrupole transitions to the $4f$ states pulled below the $2p$ to $5d$ absorption edge due to the strong attraction between the localized $4f$ electrons and the $2p$ core hole [9,10]. Identification of possible quadrupolar features in the dichroic spectra is essential in correctly applying the sum rules because they call for the separation of the spectra according to the multipolarity of the transitions involved (i.e., dipolar and quadrupolar transitions obey distinct sum rules) [11].

The determination of the multipolar nature of the features in the dichroic spectra is possible through the measurement of the different angular dependence predicted for features associated with dipolar and quadrupolar transitions given, respectively, by the expressions [9]

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

$$\mu_c^{E2} = \frac{10\pi N}{k}[(w_{22} - w_{2-2})\sin^2\theta + (w_{21} - w_{2-1})\cos 2\theta]\cos\theta\,, \tag{2}$$

where $\mu_c = \mu_c^{E1} + \mu_c^{E2}$. Here N is the number of atoms per unit volume, w_{lm} are the matrix elements of the transitions, and θ is the angle between the photon wave vector $\mathbf{k}$ and the local magnetization direction. We note that Eq. (2) can be rewritten in tensor form, separating the angular dependence into two parts: one that has a first order Legendre polynomial $P_1(\cos\theta)$ or dipolelike dependence and a second that has a third order $P_3(\cos\theta)$ dependence. In this Letter, we offer the first experimental evidence for nondipolar angular dependence, conclusively demonstrating the $E2$ nature of the preedge structure in rare-earth $L_{II,III}$ edge CMXD spectra.

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A number of previous attempts were made to observe the angular dependence given by Eqs. (1) and (2) in Er_2Co_{17} [12], $Er_2Fe_{14}B$ [13], $Ho_3Fe_5O_{12}$ [14,15], $REFe_2$ [16], and $Gd_{0.8}Ho_{0.2}$ [17], yet none demonstrated any angular behavior inconsistent with pure dipolar transitions. The lack of any signature of quadrupolar transitions in the preedge structure was puzzling in light of the excellent agreement between theoretical models including quadrupole transitions and experimental CMXD spectra in other respects, such as the absolute magnitude, relative intensities of structures below and above the edge, and the observed trends in the heavy rare-earth series [18]. A possible explanation for this discrepancy between theory and experiment was suggested by König *et al.* [19] who noted that experimental measurements of the angular dependence had been performed on polycrystalline samples at room temperature. These authors pointed out that grain misalignment and thermal fluctuations tend to cancel the $P_3(\cos\theta)$ terms responsible for the deviation of the $E2$ contributions from dipolelike angular dependence. Previously, it had been assumed that a distribution in the direction of the moments could be accounted for by replacing the angular terms in Eqs. (1) and (2) with average values resulting in a reduced, but still observable, quadrupolar angular dependence. The failure of these experiments was then understood as an indication of the purely dipolar character of the dichroic spectra [17]. In this Letter, we show that this is not the case. Our measurements of the low energy portion of the dichroic spectrum clearly exhibit the expected quadrupolar angular dependence. The difficulty with observing this dependence in previous experiments is traced to the coefficient that determines the quadrupolar feature's departure from dipolelike angular dependence. This coefficient of $P_3(\cos\theta)$ decreases rapidly with increasing magnetic disorder. Therefore, in order to observe any angular dependence beyond that associated with dipolar transitions ($\cos\theta$) and thus unambiguously to determine the multipolarity of the transitions, an almost complete alignment of the magnetic moments is required ($M' \sim 90\%$). In this experiment, we achieve this high degree of magnetic alignment by using a cooled ($T = 80$ K) textured sample, allowing the predicted quadrupolar angular behavior in the preedge CMXD spectra to be detected.

The magnetic ordering in the $Dy_{0.4}Tb_{0.6}$ alloy is similar to that of both Tb and Dy metals; below $T_N = 210$ K, the alloy has a spiral magnetic structure, while below $T_c = 165$ K, the moments lock into a ferromagnetic structure with the easy magnetization direction in the basal plane. The starting materials were arc-melted in an argon atmosphere and subsequently cold rolled to produce thin foils. The cold rolling helped in the attainment of a high magnetization since it produced a texture in the sample such that the basal plane (containing the easy axis of magnetization) was oriented coincident with the plane of the foil. Magnetometer measurements at $T = 80$ K indicated that, for the field employed in the experiment, the sample was magnetized to 87 ± 3% of the $T = 0$ K saturation value.

The CMXD measurements were performed at the Cornell High-Energy Synchrotron Source bending magnet D line. A Si (2, 2, 0) monochromator provided an energy resolution of 3 eV near the Dy L_{III} edge, and a flat quartz mirror was used to eliminate harmonics. The natural linear polarization of the synchrotron beam in the particle orbital plane was transformed to circular polarization by a transmission-type diamond (2, 2, 0) quarter wave plate in the Laue geometry [20–22]. This wave plate provides an ideal circularly polarized x-ray source for low temperature CMXD measurements because it eliminates the need for magnetic field reversal and combines rapid helicity reversal (~10 Hz) with a high degree of polarization, $P_c = 0.75 \pm 0.5$. Magnetization reversal at low temperatures poses experimental difficulties since an electromagnet must be mounted outside the cryostat, limiting the size of the applied field, and a superconducting magnet cannot provide the rapid field reversal (~1 Hz) necessary to prevent systematic errors in the data. The elimination of these errors is crucial, because the expected differences in the angular behavior are only ~0.1% of the x-ray absorption spectrum.

The dichroic spectra were taken by reversing the sense of the circular polarization at each step in energy. Multiple data sets were taken and combined with a total accumulation time of approximately 10–15 h. The sample was magnetized by placing it between soft iron pole pieces attached to a NdFeB permanent magnet. This arrangement provided a large 1–2 T field because the sample effectively closed the gap on the pole pieces. The magnet and sample were mounted inside a rotatable nitrogen cryostat allowing for temperature control from 80 to 300 K. The cryostat and magnet limited the lower angle that the beam made with the magnetic field to 35°. For comparison 65° was chosen in order to maximize the expected nondipolar angular dependence yet maintain a sufficient statistical accuracy in the dichroic signal. Data sets were obtained for parallel and antiparallel orientations of the magnetic field in order to eliminate any nonmagnetic effects. The data were normalized by scaling to the edge jump of one data set and by dividing P_c and $\cos\theta$, where θ is the angle between the beam and magnetic field directions.

Dichroic spectra taken at $T = 80$ K at the Dy L_{III} edge with $\theta = 35°$ and $65° \pm 2°$ are shown in Fig. 1. A clear difference in the angular behavior of the preedge feature is observed. This can be seen in more detail in Fig. 2, in which we have also overlaid theoretical spectra of the expected angular dependence. The dipolar part of the CMXD spectra was calculated for Gd metal using a relativistic spin-polarized band structure code, then scaled by the appropriate $5d$ spin polarization for $Dy_{0.4}Tb_{0.6}$

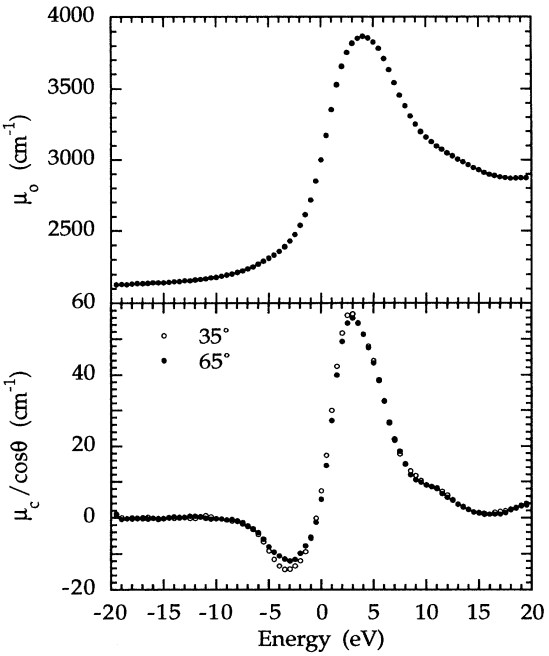

FIG. 1. Dy L_{III} absorption edge (top) and CMXD spectra showing data at 35° and 65° (bottom).

alloy [18], and the quadrupolar part was calculated using Cowan's atomic Hartree-Fock program with relativistic corrections [23] and with broadening to account for the core hole lifetime and experimental resolution. In order to directly compare the relative magnitude of the theoretical and experimental angular dependence, the quadrupolar contribution has been scaled to match the magnitude 35° data. We note that the small departure on the low energy side of the dipolar feature shown in Fig. 1 from pure $\cos\theta$ dependence is consistent with theory and is due to the broadening of the quadrupolar feature at higher angles, slightly lowering the 65° spectra. The departure of the experimental data from pure $\cos\theta$ dependence in the lower feature is clearly not as great as that predicted by theory. The theoretical spectra, however, are calculated assuming complete magnetic alignment. As we demonstrate below, the quadrupolar angular dependence is diminished by the incomplete magnetic alignment ($M' \approx 87°$) of our sample.

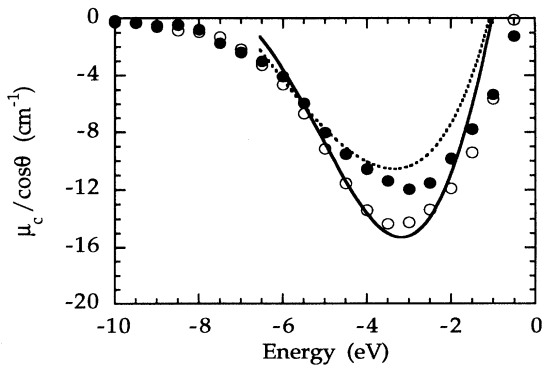

FIG. 2. Preedge structure in the CMXD spectra along with theoretical spectra for quadrupolar transitions.

We consider the sum rule derived by Carra *et al.* [11] for quadrupolar transitions given by

$$\int \mu_c^{E2}(\omega)\, d\omega = P_1(\cos\theta)\langle \hat{P}_z\rangle + P_3(\cos\theta)\langle \hat{P}_{zzz}\rangle, \quad (3)$$

where $\hat{P}_z$ is a combination of dipolar operators, $\hat{P}_{zzz}$ is a combination of octupolar operators, and the $P_1(\cos\theta)$'s are Legendre polynomials. This equation describes the same angular behavior as Eq. (2) and is similar to the result obtained by Brouder [24]. This expression demonstrates that the quadrupolar dichroic signal is made up of two parts, a "dipolar" part that scales as $\cos\theta$, just as for dipole transitions, and an "octupolar" part that exhibits the additional angular dependence ($\frac{1}{2}[5\cos^2\theta - 3]$). The expected departure from dipolar angular behavior is determined by the relative weight of $\langle \hat{P}_z\rangle$ and $\langle \hat{P}_{zzz}\rangle$, which is affected by the degree of magnetic order in the sample. To illustrate this, we consider an isotropic rare-earth ion with total angular momentum J in an effective external magnetic field B_{eff} [25]. The zero temperature ground state of this ion will be $|J, -J\rangle$, where J is the total angular momentum. As the temperature rises, subsequent $|J, M\rangle$ levels with $M = -J + 1, \ldots, J$ will become populated. The thermal average of these operators is obtained using the Boltzmann distribution for the population of the individual $|J, M\rangle$ levels of the multiplet

$$\langle \hat{P}\rangle = \frac{\sum_M \langle J, M|\hat{P}|J, M\rangle \exp(-\beta\gamma M B_{\text{eff}})}{\sum_M \exp(-\beta\gamma M B_{\text{eff}})}, \quad (4)$$

where γB_{eff} is the Zeeman splitting energy and $\beta = (k_B T)^{-1}$. In Fig. 3, we plot the coefficients $\langle \hat{P}_z\rangle$ and $\langle \hat{P}_{zzz}\rangle$ as a function of temperature, showing how the octupolar coefficient drops off much more rapidly with increasing magnetic disorder than the dipolar coefficient. Because the dipolar coefficient is proportional to $\langle\cos\theta\rangle$, it scales with the magnetization of the sample. Thus, we have also plotted the approximate position of the magnetization attained in previous measurements of the angular dependence on Fig. 3. Although not all these measurements were performed on Dy, a semiquantitative comparison is possible due to the nearly identical nature of Fig. 3 for all the heavy rare-earth elements. For the highest previous magnetization of $M' \approx 70\%$, in $Gd_{0.8}Ho_{0.2}$ [17], the octupolar coefficient is down to $\sim$15% of the saturation value. Thus, considering the relative weight of the coefficients, the angular dependence will be only $\sim$20% of the saturation value given in Ref. [10], placing it near the limit of observability. Furthermore, the value of M' given for this experiment was a bulk measurement dominated by the Gd moment.

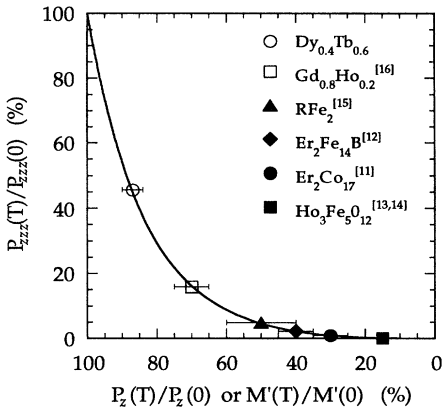

FIG. 3. Dipolar and octupolar coefficients in Eq. (3) as a function of temperature. The magnetization values of previous measurements of the angular dependence are indicated.

It is suspected that the Ho sublattice magnetization was considerably lower, further reducing the expected angular dependence. In this experiment, on the other hand, the Dy sublattice magnetization of $M' \approx (87 \pm 3)\%$ produces an angular dependence that is $\sim(50 \pm 10)\%$ of the saturation value. Thus the size of the angular dependence observed for the experimental spectra in Fig. 2 is consistent with the predicted behavior for quadrupolar transitions.

In conclusion, we report the first experimental observation of a nondipolar angular dependence in the preedge structure of a rare-earth L edge CMXD spectra. We demonstrate that the observed deviation from $\cos\theta$ is consistent with the theory of quadrupolar CMXD calculated in an atomic framework. The failure of previous measurements is attributed to the relatively incomplete magnetization of the samples, which diminished the relative weight of the $\langle \hat{P}_{zzz} \rangle$ coefficient, resulting in a greatly reduced quadrupolar angular dependence. The identification of the preedge feature as arising from quadrupolar transitions opens the possibility of deconvoluting the CMXD spectra at rare-earth $L_{II,III}$ edges to obtain information on both the $4f$ and $5d$ spin and orbital moments [11].

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