PHYSICAL REVIEW B VOLUME 46, NUMBER 9 1 SEPTEMBER 1992-I

Circular magnetic x-ray dichroism at the erbium L_3 edge

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(Received 19 November 1991; revised manuscript received 2 March 1992)

The spin-dependent absorption of circularly polarized x rays at the L_3 edge of Er has been studied in $Er_2Fe_{14}B$. Two distinct contributions, above and below the Fermi energy, are present. While they have been ascribed to dipolar and quadrupolar transitions to the empty 5*d* and 4*f* states, respectively, we find that the angular dependence of both features was well described as dipolar. The results are compared to a theoretical spectrum for Er metal.

INTRODUCTION

The development of synchrotron radiation sources has stimulated the use of near-edge absorption as a probe of the unoccupied electron states in solids. These sources have also allowed the study of magnetic properties of matter using x rays.[1–4] One technique that has recently attracted great interest is spin-dependent absorption of circularly polarized x rays [or circular magnetic x-ray dichroism (CMXD)].[5] In CMXD, the difference, $\mu_c=\mu^+-\mu^-$, between the absorption coefficients with the magnetic moment of the absorbing atom parallel (μ^+) and antiparallel (μ^-) to the wave vector of the incoming x-ray photon is determined. Since this absorption involves transitions from well-understood core levels with well-defined angular momenta, observed structure in the spectra can yield information about the spin polarization and spin-orbit coupling of final states. Further, the information obtained is element specific since the technique requires scanning through an absorption edge.

To become a useful tool for probing electronic and magnetic structures, CMXD spectra should also be material specific. That is, the spectra for a particular magnetic ion should be sensitive to the surrounding structure so that details of that material's unique electronic and magnetic interactions can be ascertained. We are able to show that, in spite of a core-hole broadening of about 4 eV, the CMXD spectra measured for $Er_2Fe_{14}B$ is significantly different from that expected in pure metal. In addition, we have measured the change in the CMXD spectra as a function of the angle between the moment of the absorbing atom and the photon wave vector in order to distinguish the multipole character of the transitions responsible for the observed structure in the spectra.

The rare earths are set apart from other magnetic materials by their unique magnetic properties. Their highly localized partially filled 4*f* shells have negligible overlap with neighboring 4*f* shells and are responsible for large magnetic moments. Magnetic ordering in these materials arises from an exchange coupling between the 4*f* moments and the conduction electrons through which the conduction bands acquire a net magnetization.[6] This exchange is relatively well understood for elemental rare-earth metals, but exchange and spin-orbit couplings complicate the analysis in rare-earth transition-metal compounds such as in the new hard magnetic materials (e.g., $R_2Fe_{14}B$). In these materials the spin-orbit interaction is believed to play a major role in producing the large magnetic anisotropy. A CMXD study can provide key information for understanding the magnetic properties of such materials since CMXD spectra are proportional to the transition matrix elements and the local spin polarization of the final states. In addition, the CMXD spectra at the L_2 and L_3 edges differ from the ratio 1:−1 by an amount dependent upon the spin-orbit coupling in the unoccupied *d* states.[7]

Recent experiments have demonstrated that, in both the elemental rare-earth[8] and R_2Co_{17} compounds,[9] the CMXD spectra across the L_3 edge of the rare search consists of two contributions; one below the Fermi energy (E_f) and one above E_f, where E_f is defined as the inflection point in the L_3 edge absorption spectra. While the feature above E_f has unambiguously been assigned to dipolar transitions involving the 5*d* unfilled states of the *R* ion, there has not been definitive confirmation of the nature of the peak below E_f. Motivated by resonance magnetic x-ray-scattering experiments on Ho metal, which identified a feature below the edge as quadrupolar,[10] Carra and Altarelli performed calculations predicting the angular behavior of the CMXD spectra assuming that the feature below the edge was due to quadrupolar 2*p* to 4*f* transitions.[12] Quadrupolar transitions to the 4*f* states would occur for energies below E_f due to the greater 4*f* core-hole interactions.[11]

The dipole and quadrupole contributions to the absorption coefficient may be written as[12]

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

$$\mu_c^{E2}=\frac{10\pi N}{k}[(w_{22}-w_{2-2})\sin^2\theta+(w_{21}-w_{2-1})\cos2\theta]\cos\theta \qquad (2)$$

with $\mu_c=\mu_c^{E1}+\mu_c^{E2}$. Here N is the number of atoms per unit volume, k is the photon wave vector, w_{lm} are the matrix elements of the transitions, and θ is the angle between the photon wave vector and the local magnetization direction. While the dipolar term exhibits only $\cos\theta$ dependence, the quadrupolar contribution has a more complicated behavior due to the presence of the $\sin^2\theta$ and $\cos2\theta$ terms. These distinct behaviors should be detectable in experiments which measure the spectra at different θ. Measurements by Fisher, Schütz, and Stähler[13] of the angular dependence of the dichroism below E_f at the Gd and Er L_3 edges in Gd_2Co_{17} and Er_2Co_{17} found no evidence for quadrupolar transitions to the $4f$ states. For Gd with a half-filled $4f$ shell, however, the quadrupole transition matrix elements $(w_{22}-w_{2-2})=2(w_{21}-w_{2-1})$ in Eq. (2) so that no angular dependence beyond $\cos\theta$ is expected.[11] For Er, the measurement was done on the uniaxial Er_2Co_{17} compound so that the angular dependence of the quadrupole contribution is much reduced, as we describe below, after the appropriate powder averaging is performed.

EXPERIMENTAL DETAILS

The $Er_2Fe_{14}B$ sample was spun from a melt at 1300 °C with a wheel speed of 10 m/s in an argon atmosphere producing a polycrystalline ribbon. The ribbon was then micromilled producing a powder with particle sizes of $\sim 1-10$ μm. This, in turn, was distributed uniformly on Kapton tape, with several layers of tape combined to produce a film of approximately 3 absorption thicknesses (~ 10 mg/cm^2). As is true for other $R_2Fe_{14}B$ compounds, $Er_2Fe_{14}B$ is tetragonal with the $P4_{2/mnm}$ space group.[14] The material is ferromagnetic with the iron moment oriented antiparallel to the erbium moment. The Curie temperature is $T_c=550$ K with the easy magnetization direction in the basal plane. The high quench rate achieved in the melt spinning process produces a nanocrystalline material in which the crystallites are randomly oriented. This nanocrystallinity allows for an easy reversal of the spin directions within the basal plane, thus producing a net magnetization of $\sim 80\%$ of the saturation value in fields of a few kG. It must be kept in mind, however, that this is a net magnetization. Below the saturation field ($\sim$several T) there is a distribution of spins whose average moment is oriented along the field direction. This is important since, for quantitative measurements, the angle between the moments and the photon wave-vector direction must be known.

Either of two methods for measuring the CMXD spectra (μ_c) using circularly polarized x rays may be employed. The sample magnetization can be reversed for a fixed polarization of the incoming radiation or the polarization can be reversed for a fixed magnetization. In this experiment we choose the former method. The measurements were taken at the Cornell High Energy Synchrotron Source bending magnet $B2$ line making use of elliptical polarization of the synchrotron beam out of the electron orbital plane. Upstream vertical slits of 0.35 mm (13.8 m from the source) selected radiation which was 0.10–0.14 mrad below the plane, where the beam intensity dropped to $\sim 20\%$ of the peak intensity. The beam was then diffracted by a double crystal Si(220) monochromator yielding an energy resolution of ~ 1 eV. Typically, in absorption measurements the double crystal monochromator is detuned by about 50% to eliminate higher-energy harmonics in the incident beam. In our case, however, detuning is undesirable since it also degrades the degree of circular polarization in the incident beam. Therefore, in order to eliminate harmonic contamination of the incident beam, the x rays were reflected from a flat quartz mirror placed after the monochromator. The sample was placed between the poles of a 3.5-kG electromagnet and N_2 and Ar ionization chambers were used as the monitor and detector, respectively. The degree of circular polarization in the incident beam was measured to be $P_c=0.6\pm0.1$ at the Er L_3 edge. The method used for the determination of the degree of circular polarization will be described elsewhere.[15] Here we mention that it is based upon polarization-state mixing in multiple-beam diffraction processes from a single crystal of GaAs.[16]

The polarization of the field was flipped every 2 s at each step in an energy scan through the Er L_3 edge thus producing two absorption spectra. I^+ is the transmitted intensity when the magnetic moment of the sample and the photon wave vector are in the same direction and I^- is the measured transmitted intensity when the two are in opposite directions. In order to relate the absorption spectra (I^+,I^-) to the CMXD spectra μ_c, we used the same analysis as Schütz *et al.*[5] with two modifications. We have introduced a factor of $\frac{1}{2}$ to match the definition of the dichroism in Ref. 11 and a factor of (-1) to account for the fact that the moment is primarily due to the 14 iron atoms in the sample to which the erbium moment antiferromagnetically couples:

$$\frac{I^+-I^-}{I^++I^-}=\tanh(P_c\mu_c d/2)\approx\frac{P_c}{2}\frac{\mu_c}{\mu}(\mu d)_{\mathrm{eff}}\equiv\mu_c^* \ . \qquad (3)$$

Here P_c ($0\le P_c\le 1$ for left circularly polarized radiation below the orbit plane) is the degree of circular polarization of the incident beam and $(\mu d)_{\mathrm{eff}}$ represents the effective absorption length of Er in the alloy. In the analysis of the angular dependence of the dichroism, P_c is constant and the spectra are normalized for minor differences in their effective thicknesses, thus we can set this expression equal to a quantity μ_c^* which incorporates all of the constants.

Multiple scans were taken in order to increase statistical accuracy. Error bars on the data indicate the standard deviation as computed by taking each scan as an independent measurement and comparing with the mean. Data were taken with the magnetic field at 30° and 60° with respect to the beam direction. For each angle, the sample thickness was chosen so that the beam was attenuated to the same extent and that the edge jump remained the same. The data were subsequently renormalized to the edge jump of one set of data. Further, the I^+ and I^- spectra were matched at points far from the edge in order to account for any preferred sensitivity of the ionization chambers with respect to the field direction of the electromagnet.

RESULTS AND DISCUSSION

The experimental μ_c^* at 30° and 60° were obtained from data taken in 0.5-eV steps through the L_3 edge of Er. These data, divided by the respective cosines, are plotted in Fig. 1 along with theoretical curves calculated for pure hcp Er metal using the method discussed by Carra *et al.*[11] The theoretical method calculates the dipolar contributions using a self-consistent, spin-polarized, relativistic linear augmented plane-wave (LAPW) band-structure method, and uses an atomic model to evaluate the quadrupolar transitions to the highly localized $4f$ states. Actually, because of the great similarity of the band structures of all the heavy rare-earth metals, the accurate dipolar part of the theoretical Gd CMXD spectra[11] was scaled to obtain the Er spectra. The scaling depends on the exchange interaction with the net $4f$ spin moment, and includes the changes of the spin-up and spin-down matrix elements determined by atomic calculations.[17]

It is important to realize that the calculations for the theoretical curves assumed full alignment of the moments along the magnetic field direction. This is not the case,

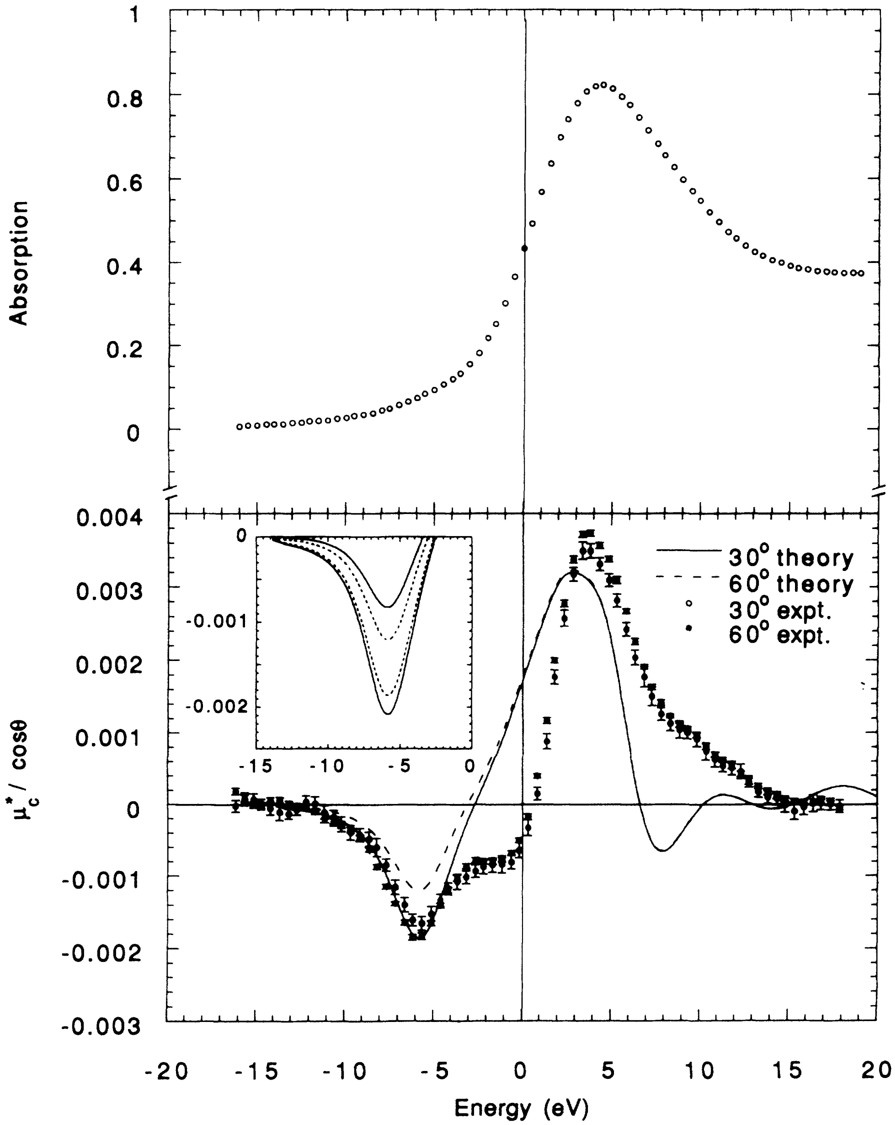

FIG. 1. Top: Absorption discontinuity at the Er L_3 edge. The background due to Fe and B has been subtracted. Bottom: CMXD spectra showing experimental data at 30° and 60° along with the theoretical curves for metallic Er as described in the text. The inset shows the affect of powder averaging on the theoretical CMXD spectra (solid line before averaging, dashed line after averaging).

however, in anisotropic materials such as $Er_2Fe_{14}B$, an easy plane ferromagnet, or Er_2Co_{17}, a uniaxial ferromagnet. Thus, in Eqs. (1) and (2) the average values of the angular terms, $\langle\cos\theta\rangle$, $\langle\sin^2\theta\cos\theta\rangle$, and $\langle\cos2\theta\cos\theta\rangle$, must be computed by integrating over a hemisphere about the magnetic field direction. To emphasize the importance of proper powder averaging, the inset of Fig. 1 shows the reduction of the difference in the angular dependence of the quadrupolar contributions (dashed lines) from that expected for full alignment of the moment (solid lines). In this integration, a random orientation of crystalline directions was assumed, appropriate to the nonocrystallinity of the material. After calculating the average angular values to obtain the theoretical curves of μ_c, they were scaled so that the 30° quadrupole peak of the experimental data and the theoretical curves matched. This is equivalent to multiplying μ_c by the factors $P_c d$ in Eq. (3) to give a theoretical μ_c^* curve.

The dichroic spectra in Fig. 1 are notable for two reasons. First, the dipolar part of the experimental spectrum is pushed to a higher energy and has a different shape than the theoretical spectrum for a pure Er metal. We note that the theoretical spectrum for the pure Gd metal is in complete agreement with experiment,[11] and scaling the theoretical dipolar part of the spectra as described above also yields good agreement with the measured spectra for a pure Tb metal. Second, there is no significant angular dependence in the experimental spectra for the features below the Fermi edge. The first observation shows there are easily measurable differences in the spectra for Er in different materials. In fact, the difference between the theoretical curves for the Er metal and the experimental curve for $Er_2Fe_{14}B$ can be qualitatively understood by referring to a recent calculation of the electronic structure of $Nd_2Fe_{14}B$.[18] This calculation showed that the Fe $3d$ states are dominant within about 2 eV of the Fermi level and that the main part of the $5d$ density of states is pushed to higher energy. This also suggests that the $5d$ contribution to the conduction electron moment is very small. The rather large positive dipolar contribution observed then arises from the spin-up matrix elements being 20–30% larger than the corresponding spin-down matrix elements. This is because the spin-up $5d$ radial functions are more contracted and larger at the position of the $2p$ orbitals (see Fig. 8 of Ref. 6). While quantitative comparison between theory and experiment for $Er_2Fe_{14}B$ is desirable, with 68 atoms per cell, the precise calculations that would be required are formidable.

The predicted angular dependence of the feature below E_f for quadrupolar transitions is not observed, and only slight differences in the data at 30° and 60° are measured. These differences, however, occur equally in the peak above and below the edge and can be accounted for by an error in the measurement of the angle between the beam and field of $\sim 2°$. If to correct for this possible error, the peaks above the edge are matched to minimize the differences in the structure, no differences outside of error bars are seen between the two experimental curves. Therefore, the feature below E_f exhibits the same angular dependence as the feature above E_f. This is indicative of dipolelike behavior which is not consistent with $E2$ transitions from $2p_{3/2}$ to $4f$ states.

The absence of the anticipated angular dependence for quadrupole transitions in our measurement for Er is unexpected in light of the reasonable match between the relative magnitudes of the peaks above and below E_f between theory and experiment, as well as the identification of a peak below E_f, in holmium, with quadrupolar transitions from x-ray-scattering measurements.[10] A mechanism (such as hybridization or phonons) which would allow dipole matrix elements to couple the $2p$ states to states with strong $4f$ character could help explain the dipole angular dependence of the peak below E_f, but the $E2$ transitions would still be expected to contribute significantly. To resolve this issue, it would be desirable to have similarly accurate measurements on simple ferromagnetic single crystals, or more detailed calculations for these complicated compounds.

ACKNOWLEDGMENTS

We would like to thank Dr. P. Carra for performing the atomic calculations of the Er quadrupolar contribution. Ames Laboratory is operated for the United States Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. Work at CHESS was supported by the National Science Foundation under Grant No. DMR-87-19764.

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