Strong Magnetic Dichroism Predicted in the $M_{4,5}$ X-Ray Absorption Spectra of Magnetic Rare-Earth Materials

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A theory is presented which predicts an anomalously large magnetic dichroism in the $M_{4,5}$ x-ray absorption-edge structure of rare earths in magnetically ordered materials. Polarized synchrotron radiation can therefore be used to determine accurately the magnitude, the orientation, and the temperature and magnetic field dependence of the local rare-earth magnetic moment in a large variety of magnetically ordered materials and thin films.

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Improved resolution, synchrotron sources, and advanced theory have strongly revived interest in the edge structures of x-ray absorption spectroscopy (XAS). The multiple-component edge structure of highly correlated narrow-band systems such as transition-metal compounds[1] and rare-earth metals[2,3] and their compounds[4,5] is now well understood in terms of atomic multiplet theory and the configuration interaction involving the highly localized $3d$ or $4f$ electrons and the delocalized valence- and conduction-band states.[6] These highly correlated systems are of special interest because of their diversity of magnetic properties.

It is well known from atomic theory that the optical dipole selection rules, as in XAS, cause the observed fine structure to depend on the detailed nature of the ground state.[2] This has also been demonstrated for strongly correlated atoms in solids.[3,7,8]

In this paper we predict that the polarization dependence of the $3d \rightarrow 4f$ XAS ($M_{4,5}$) spectra of rare earths is expected to be very sensitive to the magnetic structure of the ground state and to unequal population of the M_J sublevels as found in magnetic systems. This implies that XAS can be used to determine the local magnetic moment of a rare-earth atom in a magnetically ordered material, the orientation of the local moment relative to the total magnetization direction, as well as the temperature and field dependence thereof. We derive simple equations relating these properties to the experimental temperature- and orientation-dependent spectra.

The $3d \rightarrow 4f$ XAS spectra of rare-earth metals[3] and compounds[5] have recently been shown to agree extremely well with atomic calculations of the optical transitions from a $4f^n(J)$ ground state as determined by Hund's rule to the many possible $3d^9 4f^{n+1}(J')$ final states. Optical selection rules dictate that $J'-J=0, \pm 1$ in intermediate coupling.[3] In the $3d^9 4f^{n+1}$ final configuration there are many states (hundreds) satisfying these selection rules. Upon application of a magnetic field the $(2J+1)$-fold degenerate (with of small crystal-field effects) ground state splits up into its M sublevels with energy $-g\mu_B HM$ of which only the level $M=-J$ is populated at $T=0$ K. The Boltzmann factor of the sublevels is given by $\exp(g\mu_B HM/kT)=\exp(-M/\theta)$ which defines a reduced temperature $\theta = kT/g|\mu_B|H$. Assuming that the energy spacing between the lowest J levels in the initial state is large compared to kT, we can neglect the van Vleck term,[9] which is only important for $4f^5$ and $4f^6$ ions.[10] The partition function is then given by

$$Z=\sum_{M=-J}^{J} e^{-M/\theta}=\frac{\sinh[(J+\frac{1}{2})/\theta]}{\sinh(1/2\theta)}, \tag{1}$$

and the local magnetic moment is $g\mu_B\langle M\rangle$ with $\langle M\rangle$ given by

$$\begin{aligned}\langle M\rangle &= Z^{-1}\textstyle\sum_M M e^{-M/\theta} \\ &= -(J+\tfrac{1}{2})\coth[(J+\tfrac{1}{2})/\theta]+\tfrac{1}{2}\coth(1/2\theta) \\ &= -JB_J(J/\theta),\end{aligned} \tag{2}$$

where B is the Brillouin function.

The optical dipole transitions from a state $|\alpha JM\rangle$ to a final state $|\alpha' J' M'\rangle$ are, according to the Wigner-Eckart theorem, proportional to the square of the $3j$ symbol times the reduced dipole matrix element (the latter is the line strength in the absence of a magnetic field):

$$S_{\alpha JM,\alpha' J' M'}=\begin{pmatrix} J & 1 & J' \\ M & m & -M' \end{pmatrix}^2 \times |\langle \alpha J \| C^{(1)} \| \alpha' J'\rangle|^2. \tag{3}$$

Here α labels different levels of equal J and we have $m=0$ for light polarized in the field direction (z) and $m=\pm 1$ for right- or left-circularly polarized light perpendicular to the field direction. For z-polarized light the $3j$ symbol is nonzero only for $M=M'$ and $\Delta J=0, \pm 1$. Since the magnetic splitting of the M' levels is much less in general than the experimental resolution, one will not observe this splitting but only a temperature and polarization dependence of the intensity. This is determined by the weighted average of the $3j$ symbol, which is independent of α and α':

$$\langle S^z_{\alpha J,\alpha' J'}\rangle = \langle A^z_{JJ'}\rangle \,|\langle \alpha J\|C^{(1)}\|\alpha' J'\rangle|^2,$$

where

$$\langle A^z_{JJ'}\rangle = Z^{-1}\sum_M \begin{pmatrix} J & 1 & J' \\ M & 0 & -M \end{pmatrix}^2 e^{-M/\theta}. \tag{4}$$

The squared $3j$ symbols involved[11] are linear functions of M^2. Thus we only need the weighted average of M^2,

$$\begin{aligned}\langle M^2\rangle &= Z^{-1}\textstyle\sum_M M^2 e^{-M/\theta}\\ &= J(J+1) + \langle M\rangle \coth(1/2\theta),\end{aligned} \tag{5}$$

with $\langle M\rangle$ given by Eq. (2). Substitution of $\langle M^2\rangle$ into the $3j$ symbol gives

$$\begin{aligned}\langle A^z_{JJ+1}\rangle &= \frac{(J+1)^2 - \langle M^2\rangle}{(2J+1)(J+1)(2J+3)},\\ \langle A^z_{JJ}\rangle &= \frac{\langle M^2\rangle}{(2J+1)J(J+1)},\\ \langle A^z_{JJ-1}\rangle &= \frac{J^2 - \langle M^2\rangle}{(2J+1)(2J-1)J}.\end{aligned} \tag{6}$$

Similarly for light polarized perpendicular to the magnetic field, we obtain

$$\langle A_{JJ'}\rangle = \tfrac{1}{2}(1 - \langle A^z_{JJ'}\rangle). \tag{7}$$

From the above expressions we see that, as long as we can experimentally distinguish between transitions to final states corresponding to $J+1$, $J-1$, and J, a strong polarization dependence of the spectrum can be predicted, which provides a direct measure of $\langle M^2\rangle$ as a function of temperature.

The question remaining is can we experimentally resolve the various J' components in an XAS experiment? The answer is yes for the $3d \rightarrow 4f$ transitions of the rare earths. This may be somewhat surprising at first glance because there are so many final states $3d^9 4f^{n+1}$ which cannot be resolved in the spectrum. However, the XAS spectra have been shown to be strongly structured, exhibiting all the features in almost perfect agreement with atomic theory.[3] To demonstrate that at least some of the J' structure is well resolved we show in Fig. 1(a) the experimental and in Fig. 1(b) the calculated $3d \rightarrow 4f$ spectrum of nonmagnetic ($\langle M\rangle = 0$) Dy for a ${}^6H_{15/2}$ ground state. The calculations were done with use of Cowan's[12] program. In Figs. 1(c), 1(d), and 1(e) we show the separated components $\Delta J = 1$, 0, and -1 that contribute to this spectrum, which clearly demonstrate that each component contributes in a very different manner to the total spectrum. This, together with expressions (6) and (7), shows that the spectra should be strongly polarization and temperature dependent for magnetically ordered materials. For such materials the magnetic field must be replaced by an exchange field, which is zero above the magnetic ordering temperature (T_c) in the molecular-field approximation, and therefore for $T > T_c$ the polarization dependence disappears ($\theta = \infty$).

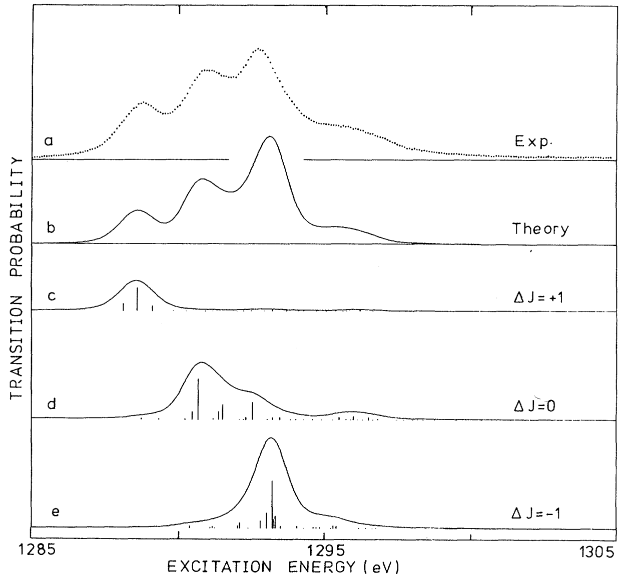

FIG. 1. (a) Experimental and (b) theoretical $M_{4,5}$ XAS spectra for Dy $4f^9({}^6H_{15/2})$ in a nonmagnetic ground state. The separated contributions with $\Delta J = 1$, 0, and -1 of this spectrum are shown in (c), (d), and (e), respectively.

To demonstrate the polarization dependence we show in Fig. 2(a) the calculated spectra for $T > T_c$ [same as Fig. 1(b)] and in Figs. 2(b) and 2(c) the spectra for $T = 0$ for a collinear magnetic system as predicted for polarization parallel and perpendicular to the internal field direction. It should be noted that the effect is not unique for Dy but, in fact, occurs in most of the rare earths.

The temperature-dependent factor for the three components ($\Delta J = \pm 1, 0$) for polarization and for $J = \frac{15}{2}$ is shown in Fig. 3 as calculated by use of Eqs. (5) and (6). Also shown are the temperature dependences of $\langle M\rangle$ and $\langle M^2\rangle$ for comparison.

We note that since the polarization dependence varies as $\langle M^2\rangle$, the temperature dependence of the local magnetic moment can be determined in antiferromagnetic, ferrimagnetic, and ferromagnetic systems. In addition, the polarization dependence can be used to determine the relative orientation of the sublattice magnetization directions in noncollinear magnetic systems such as canted or spiral magnetic structures.

In our view XAS provides an interesting possibility for studying rare-earth magnetic systems. Important

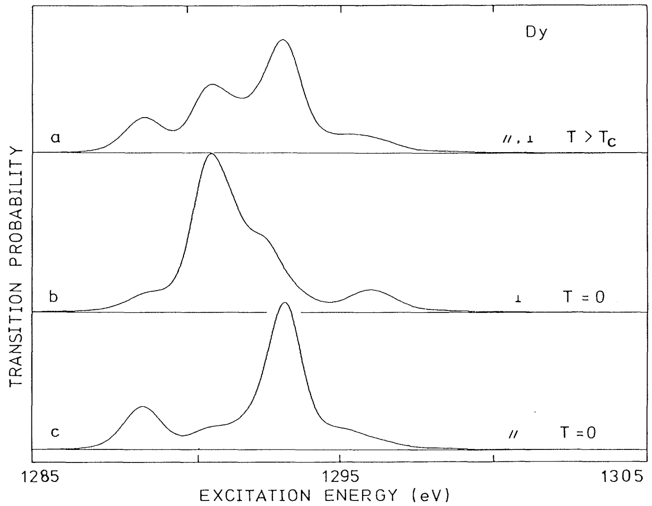

FIG. 2. The calculated XAS spectra of Dy (a) for $T > T_c$, and for $T = 0$ with polarization (b) perpendicular and (c) parallel to the internal magnetic field direction.

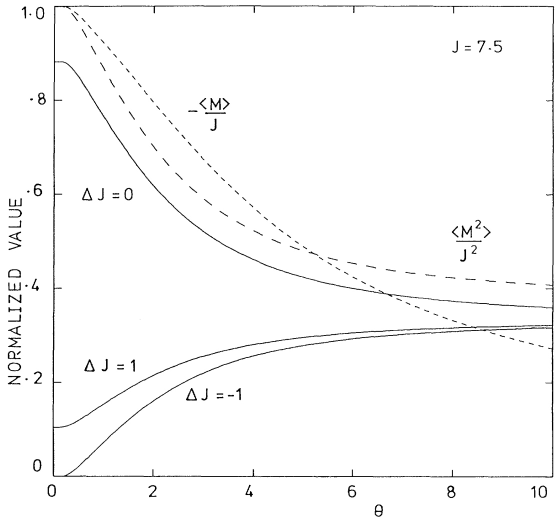

FIG. 3. The curves for $(2J+1)\langle A^z_{JJ'}\rangle$ with possible values $\Delta J = 1$, 0, and -1 (solid lines) and the curves for $-\langle M\rangle/J$ and $\langle M^2\rangle/J^2$ (dashed lines) as functions of θ, with $J = \frac{15}{2}$.

in this regard is that the energy of $3d \rightarrow 4f$ transitions is strongly element dependent so that the separate contributions of each rare earth in a mixed material can easily be determined. In the recently used highly sensitive total-electron-yield measurements[3, 5, 13] a spectrum with excellent statistics and the required energy resolution is easily obtained in a few minutes with use of polarized synchrotron radiation. Using this method one can work with thick bulk samples without significant saturation problems, since the escape depth of the secondary electrons determines the film thickness probed. Variation of the energy of detected electrons also provides the possibility of measuring the local magnetization for surface layers varying between 20 and 500 Å.

Of special interest for such studies are the rare-earth compounds like the rare-earth–iron garnets and the rare-earth intermetallic compounds as well as the pure rare-earth metals. In all of these materials the rare-earth magnetic moments are rather weakly coupled to each other or to the transition-metal moments. This causes the rare-earth moment to decrease to 50% or less of its saturation value at about 100 K, which requires low-temperature facilities for carrying out the experiments.

In a future paper we will present the calculations for all the rare earths and $3d$ transition-metal compounds. In the latter the magnetic dichroism in the $2p \rightarrow 3d$ XAS is somewhat smaller because of the quenching of the ground-state orbital magnetic moment by crystal-field effects. Nonetheless, our calculation shows that also here the effect should be observable although the theory is considerably more complicated.

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