Dichroism in the X-Ray Absorption Spectra of Magnetically Ordered Systems

Paolo Carra^(a)

Department of Physics, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

Massimo Altarelli

European Synchrotron Radiation Facility, Boîte Postale 220, F-38043 Grenoble CEDEX, France

(Received 10 October 1989)

A general formulation of linear and circular dichroism in the absorption of x rays in magnetically ordered systems is presented. The processes which induce sensitivity to magnetic properties are discussed. We demonstrate that the usually neglected electric quadrupole transitions can be as important as the dipole terms for the interpretation of magnetic dichroism experiments on transition metals and rare earths.

PACS numbers: 78.70.Dm, 75.10.Lp, 75.50.Bb, 78.20.Ls

Magnetic dichroism phenomena make the near-edge, inner-shell absorption of polarized x rays a promising technique for investigating the magnetism of transitionmetal, rare-earth, and actinide systems.

Linear dichroism was observed in Tb₃Fe₅O₁₂, near the $M_{4,5}$ edges,^{1,2} in the energy range $\hbar \omega = 1.2 - 1.3$ keV. In this case, the dipole-allowed electric transitions (*E* 1) are to highly localized 4f states, which could be well described by atomic theory. Circular dichroism was detected near the *K* edges of 3d metals, and the *L* edges of 4f ferromagnets and of 5d impurities in Fe or Ni hosts,³⁻⁶ in the range $\hbar \omega = 7 - 14$ keV. In these systems, the *E* 1 transitions are to more delocalized bandlike states.

In this Letter we show that, in the case of circular dichroism, the quadrupole terms (E2), which involve the localized 4f states of the rare earths (or, to a lesser extent, the 3d states of transition metals), can give effects which are comparable in magnitude to those of the E1transitions. To demonstrate this we provide a unified theoretical framework which includes both classes of experiments and clarifies the relationship between the information they provide. A strong magnetizationsensitive quadrupolar absorption may explain (at least to some extent) the disagreement between band theory and experiment.⁴ It should be noticed that *multipolarity* and other features of circular dichroism are closely related to those recently established for resonant x-ray scattering in magnetic systems,⁷⁻¹⁰ given that absorption is determined by the imaginary part of the forward scattering amplitude.

To leading order, magnetization-sensitive absorption is determined by the coupling

$$H_{\text{int}} = -\sum_{j} \frac{e}{mc} \mathbf{p}_{j} \cdot \mathbf{A}(\mathbf{r}_{j}, t) , \qquad (1)$$

where *m* and **p** denote, respectively, electron mass and momentum. The resulting effects are large compared to genuine magnetic processes, not included in H_{int} , which are depressed by the factor $\hbar \omega/mc^2$.¹¹

Given a magnetic ion, the absorption coefficient, for an electric 2^L pole transition, is proportional to^{7,12}

$$W_{EL} = 4\pi\lambda \sum_{M=-L}^{L} |\hat{\mathbf{e}} \cdot \mathbf{Y}_{LM}^{(el)}(\hat{\mathbf{k}})|^2 w_{LM}^{(el)}(k) , \qquad (2)$$

where $\hat{\mathbf{k}}$ and $\hat{\mathbf{e}}$ stand for, respectively, the unit vector in the direction of the photon momentum and the unit polarization. Also,

$$w_{LM}^{(el)}(k) = \frac{8\pi^2}{\lambda} \sum_{\eta} \frac{L+1}{L} k^{2L} \times |\langle \eta | Q_{LM}^{(el)} | \alpha \rangle|^2 \delta(\epsilon_{\eta} - \epsilon_{\alpha} - \epsilon); \quad (3)$$

the labels α, η denote the ground and excited electronic states. The quantity $Q_{LM}^{(el)}$ represents the electric multipole operator, given by

$$Q_{LM}^{(el)} = -\frac{e}{(2L+1)!!} \sum_{j} r_{j}^{L} Y_{LM}(\hat{\mathbf{r}}_{j}) \,.$$

We have assumed $kr \ll 1$ and set T=0.

Dipolar and quadrupolar contributions to the absorption coefficient are calculated in terms of the expansion¹³

$$\hat{\mathbf{e}} \cdot \mathbf{Y}_{LM}^{(\mathbf{e}\mathbf{l})}(\hat{\mathbf{k}}) = \left(\frac{4\pi(2L+1)}{3(L+1)}\right)^{1/2} \sum_{\mu} C(1,L-1,L;\mu,M-\mu) Y_{1,\mu}(\hat{\mathbf{e}}) Y_{L-1,M-\mu}(\hat{\mathbf{k}})$$

We obtain

$$W_{E1} = \frac{3}{4} \lambda \{ w_{11}^{(e1)} + w_{1-1}^{(e1)} - i(\hat{e}^* \times \hat{e}) \cdot \hat{z}(w_{11}^{(e1)} - w_{1-1}^{(e1)}) + |\hat{e} \cdot \hat{z}|^2 (2w_{10}^{(e1)} - w_{11}^{(e1)} - w_{1-1}^{(e1)}) \}$$
(4)

© 1990 The American Physical Society

$$W_{E2} = \frac{5}{4} \chi \{ w_{22}^{(el)} + w_{2-2}^{(el)} + i(\hat{\mathbf{e}}^* \times \hat{\mathbf{e}}) \cdot \hat{\mathbf{z}} [w_{22}^{(el)} - w_{2-2}^{(el)}] - [|\hat{\mathbf{e}} \cdot \hat{\mathbf{z}}|^2 + (\hat{\mathbf{k}} \cdot \hat{\mathbf{z}})^2] [(w_{22}^{(el)} + w_{2-2}^{(el)}) - (w_{21}^{(el)} + w_{2-1}^{(el)})] - i[(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}})^2 (\hat{\mathbf{e}}^* \times \hat{\mathbf{e}}) \cdot \hat{\mathbf{z}}] [(w_{22}^{(el)} - w_{2-2}^{(el)}) - (w_{21}^{(el)} - w_{2-1}^{(el)})] - 2(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}) \mathrm{Im}[(\hat{\mathbf{e}}^* \cdot \hat{\mathbf{z}}) (\hat{\mathbf{k}} \times \hat{\mathbf{e}}) \cdot \hat{\mathbf{z}}] (w_{21}^{(el)} - w_{2-1}^{(el)}) + (\hat{\mathbf{k}} \cdot \hat{\mathbf{z}})^2 [\hat{\mathbf{e}} \cdot \hat{\mathbf{z}}]^2 [2w_{20}^{(el)} - 4(w_{21}^{(el)} + w_{2-1}^{(el)}) - (w_{22}^{(el)} + w_{2-2}^{(el)})] \}.$$
(5)

In these expressions \hat{z} denotes the (local) quantization axis of the magnetic ion.

Magnetization-sensitive absorption, in the configurations so far experimentally investigated, is best examined by dividing the terms appearing in expressions (4) and (5) into two classes (orders refer to \hat{z}).

(i) Terms of even order.— They determine the absorption of linearly polarized x rays, a process which, in the cases considered in Refs. 1, 2, and 14, is controlled by E1 transitions. In a magnetic system, where the various transition lines (labeled by $\Delta J = J_i - J_f$, J = L + S) can be separated experimentally, at low temperature, magnetic dichroism is observed: The different ΔJ^z series show unequal strength, resulting in different absorption coefficients for different polarizations. For linear polarization parallel and perpendicular, respectively, to the low

cal magnetization, we have

$$W_{E1}(\hat{\mathbf{e}} \| \hat{\mathbf{z}}) = \frac{3}{2} \chi w_{10}^{(e1)}, \quad W_{E1}(\hat{\mathbf{e}} \perp \hat{\mathbf{z}}) = \frac{3}{4} \chi (w_{11}^{(e1)} + w_{1-1}^{(e1)}).$$
(6)

[Compare with expression (6) in Ref. 14.] Thole and co-workers^{1,14} have discussed the information contained in this kind of absorption spectroscopy of the local moment in magnetically ordered rare earths.

(ii) Terms of odd order.—These contributions describe magnetic dichroism of circularly polarized x rays. Defining circular polarization vectors as $\hat{\mathbf{e}}^{(\pm)} = \mp (i/\sqrt{2})(\hat{\mathbf{e}}_1 \pm i\hat{\mathbf{e}}_2)$, we obtain

$$\Delta W_{E1} = W_{E1}(\hat{e}^{(+)}) - W_{E1}(\hat{e}^{(-)})$$

= $\frac{3}{2} \chi(\hat{e}_1 \times \hat{e}_2) \cdot \hat{z}(w_{11}^{(e1)} - w_{1-1}^{(e1)})$ (7)

and

$$\Delta W_{E2} = W_{E2}(\hat{e}^{(+)}) - W_{E2}(\hat{e}^{(-)}) = -\frac{5}{2} \chi((\hat{e}_1 \times \hat{e}_2) \cdot \hat{z} \{ [1 - (\hat{k} \cdot \hat{z})^2] (w_{22}^{(e_1)} - w_{2-2}^{(e_1)}) + (\hat{k} \cdot \hat{z})^2 (w_{21}^{(e_1)} - w_{2-1}^{(e_1)}) \} - (\hat{k} \cdot \hat{z}) [(\hat{e}_1 \cdot \hat{z}) (\hat{k} \times \hat{e}_2) \cdot \hat{z} - (\hat{e}_2 \cdot \hat{z}) (\hat{k} \times \hat{e}_1) \cdot \hat{z}] (w_{21}^{(e_1)} - w_{2-1}^{(e_1)}) \}.$$
(8)

Circular dichroism is ascribed to the spin-orbit interaction and to the exchange splitting of the conduction bands.¹⁵ In this case, x-ray absorption probes spin-polarization effects in the empty states, near the Fermi energy, of ferromagnetic (or ferrimagnetic) systems.

In the ferromagnetic rare earths, circular dichroism was observed near the $L_{2,3}$ edges,⁴ involving the transitions $2p \rightarrow 5d$ (E1) and $2p \rightarrow 4f$ (E2). Larger dichroism is expected at the $M_{4,5}$ edges, involving E1 transitions to the strongly polarized 4f final states.¹⁶ Similar considerations apply to the elements of the actinide series.

Since circular dichroism depends on the spin polarization of the final states (as suggested by the antisymmetric combinations $w_{LM}^{(el)} - w_{L-M}^{(el)}$), dipole and quadrupole contributions may become comparable, given that the moment carried by the 4f electrons is much larger than that of the 5d, and could compensate the weaker strength (typically¹⁷ a few percent) of quadrupole transitions. Consider an excited state with a finite width, i.e., let $\delta \rightarrow 2/\pi\Gamma(x^2+1)$ in expression (3); here

$$x = (\epsilon_{\eta} - \epsilon_{a} - \epsilon)/(\Gamma/2)$$

Also, assume an exchange splitting Δ ($\ll\Gamma$) of the outer levels, as described by $x \pm x \pm \Delta/\Gamma$. Then, with the definition $w_{LM}^{(el)} = v_{LM}^{(el)} 2/\Gamma(x \pm 1)$, we obtain

$$w_{LM}^{(el)} - w_{L-M}^{(el)} = \frac{2/\Gamma}{x^2 + 1} \left[(v_{LM}^{(el)} - v_{L-M}^{(el)}) - \frac{\Delta}{\Gamma} \frac{2x}{x^2 + 1} (v_{LM}^{(el)} + v_{L-M}^{(el)}) \right],$$
(9)

displaying the dependence of circular dichroism on the spin polarization (first term) and exchange splitting of the empty states. Expression (9) is readily identified with the imaginary part of the corresponding contributions in the amplitude for x-ray resonant exchange scattering (XRES). Given that XRES is, in general, a multipolar process,⁷⁻¹⁰ circular dichroism is expected to exhibit multipolarity as well. An example is provided by the L_3 spectra of Gd and Tb⁴ where, on the basis of the preceding considerations, the structure below the edge has to be associated with quadrupolar transitions. Numerical calculations,¹⁸ performed in the atomic limit

with use of Cowan's program¹⁹ (Hartree-Fock theory with relativistic corrections), fully support this picture; a complete account will be given elsewhere.

On the other hand, the dipole terms of Eq. (7) are sufficient to provide a basis for the interpretation of the $L_{2,3}$ -edge spectra of 5d impurities ^{5,6,20} in 3d hosts.

An interesting experimental possibility to test the importance of the quadrupole terms is to measure the dependence of the dichroic signal on the angle θ between the photon wave vector **k** and the magnetization direction **z** (which is equal to zero in the Faraday **k**||**z**

configuration). From Eqs. (7) and (8), we obtain

$$\Delta W_{E1} = \frac{3}{2} \chi (w_{11}^{(e1)} - w_{1-1}^{(e1)}) \cos\theta,$$

$$\Delta W_{E2} = -\frac{5}{2} \chi \{ (w_{22}^{(e1)} - w_{2-1}^{(e1)}) \sin^2\theta + (w_{21}^{(e1)} - w_{2-1}^{(e1)}) \cos2\theta \} \cos\theta,$$
(10)

showing that dipolar and quadrupolar terms have different angular dependences. Measurements at different angles allow their separate determination, at any given frequency. In particular, any deviation from pure $\cos\theta$ dependence is a signature of quadrupole contributions.

In addition, we observe that for the elements of the 3d series, where circular dichroism was observed from the K edge,³ the effect is weaker in the absence of spin-orbit splitting of the core level; in this case, relativistic terms,¹¹ coupling the photons directly to the electron spins, might result in magnetic absorption processes of the same magnitude. This applies to *s* levels, in general.

We are grateful to F. de Bergevin and G. A. Sawatzky for stimulating discussions. This work was supported in part by the Natural Sciences and Engineering Research Council of Canada and the Research Board of the University of Manitoba.

¹B. T. Thole, G. van der Laan, and G. A. Sawatzky, Phys. Rev. Lett. **55**, 2086 (1985).

²G. van der Laan, B. T. Thole, G. A. Sawatzky, J. B. Goedkoop, J. C. Fuggle, J. M. Esteva, R. Karnatak, J. P. Remeika, and H. A. Dabkowska, Phys. Rev. B 34, 6529 (1986).

³G. Schütz, W. Wagner, W. Wilhelm, P. Kienle, R. Zeller, R. Frahm, and G. Materlik, Phys. Rev. Lett. **58**, 737 (1987); S. P. Collins, M. J. Cooper, A. Brahmia, D. Laundy, and T. Pitkanen, J. Phys. Condens. Matter **1**, 323 (1989). ⁴G. Schütz, M. Knülle, R. Wienke, W. Wilhelm, W.

Wagner, P. Kienle, and R. Frahm, Z. Phys. B 73, 67 (1988). ⁵G. Schütz and R. Wienke (to be published).

⁶G. Schütz, R. Wienke, W. Wilhelm, W. Wagner, P. Kienle, R. Zeller, and R. Frahm, Z. Phys. B **75**, 495 (1989).

⁷J. P. Hannon, G. T. Trammel, M. Blume, and D. Gibbs, Phys. Rev. Lett. **61**, 1245 (1988); **62**, 2644(E) (1989).

⁸D. Gibbs, D. R. Harshman, E. D. Isaacs, D. B. McWhan, D. Mills, and C. Vettier, Phys. Rev. Lett. **61**, 1241 (1988).

⁹P. Carra, M. Altarelli, and F. de Bergevin, Phys. Rev. B **40**, 7324 (1989).

¹⁰In the rare earths, as predicted in Ref. 7 and confirmed experimentally in Ref. 8, the (virtual) E1 and E2 transitions, respectively, to the weakly polarized 5d band and to the strongly polarized 4f shells give magnetization-sensitive contributions to the coherent scattering amplitude of comparable strength; see also Ref. 9.

¹¹These processes are described by the interaction

$$H_{\text{int}}^{(\text{spin})} = -(e\hbar/2mc)\sum_{j}\sigma_{j} \cdot [\nabla \times \mathbf{A}(\mathbf{r},t)]_{\mathbf{r}} - \mathbf{r}_{j}$$

¹²A detailed discussion of the vector spherical formalism is given in A. I. Akhiezer and V. B. Berestetsky, *Quantum Electrodynamics* (Consultants Bureau, New York, 1957); see also J. P. Hannon and G. T. Trammel, Phys. Rev. **186**, 306 (1969).

¹³M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

¹⁴J. B. Goedkoop, B. T. Thole, G. van der Laan, G. A. Sawatzky, F. M. F. de Groot, and J. C. Fuggle, Phys. Rev. B **37**, 2086 (1988).

¹⁵See, e.g., J. L. Erskine and E. A. Stern, Phys. Rev. B 12, 5016 (1975), and references therein.

¹⁶However, it should be pointed out that the $M_{4,5}$ edges fall in a difficult spectral region for the monochromatization of circularly polarized x rays.

¹⁷J. E. Müller and J. W. Wilkins, Phys. Rev. B 29, 4331 (1984).

¹⁸P. Carra, B. T. Thole, M. Altarelli, and G. A. Sawatzky (unpublished).

¹⁹R. D. Cowan, *The Theory of Atomic Spectra* (Univ. of California Press, Berkeley, 1981).

²⁰H. Ebert, B. Drittler, R. Zeller, and G. Schütz, Solid State Commun. **69**, 485 (1989)

^(a)Present address: European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble CEDEX, France.