RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 5 1 AUGUST 1993-I

Observation of magnetic circular dichroism in Fe $L_{2,3}$ x-ray-fluorescence spectra

C. F. Hague and J-M. Mariot
Laboratoire de Chimie Physique-Matière et Rayonnement, Université Pierre et Marie Curie, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

P. Strange
Physics Department, University of Keele, Keele ST5 5BG, United Kingdom

P. J. Durham
United Kingdom Science and Engineering Research Council, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom

B. L. Gyorffy
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom
(Received 27 May 1993)

We report experiments demonstrating circular dichroism in the x-ray-fluorescence spectra of magnetic systems, as predicted by a recent theory. The data, on the $L_{2,3}$ edges of ferromagnetic iron, are compared with fully relativistic local spin density functional calculations, and the relationship between the dichroic spectra and the spin-resolved local density of occupied states is discussed.

The discovery and exploration of x-ray circular dichroism in spectroscopies of magnetic systems has been one of the most interesting recent developments in the study of the electronic structure of solids.[1–6] The case which has been most fully investigated is the magnetic x-ray dichroism (MCD) at the absorption edges (K, L, and M) of Fe, Co, and Ni. There is now general agreement that this effect probes the exchange splitting in the empty part of the band structure corresponding to the final states of the absorption process. Evidently, the complementary effect of dichroism in x-ray emission would yield information about the spin polarization of the filled bands and, therefore, would be of considerable further interest. In this paper we report the first experimental observation of this phenomenon.

In nonrelativistic quantum mechanics the orbital angular momentum of cubic metals is zero by symmetry. This is so even in a spin-polarized state, and hence, on very general grounds,[7] no dichroism can be expected. In fact, the MCD observed in Fe, Co, and Ni has been interpreted,[3,8] in a fully relativistic theory, as due to spin-orbit coupling.

The prospect of observing MCD in emission is, at first sight, discouraging because simultaneous spectral resolution and polarization analysis on the weak emitted radiation is experimentally difficult. However, as predicted by Strange, Durham, and Gyorffy,[9] an interesting MCD effect can be observed even without determining the polarization of the emitted photons if the core holes are excited alternatively by right- and left-handed circularly polarized radiation. Using the same fully relativistic density functional theory as Ebert *et al.*[3,8] Strange, Durham, and Gyorffy[9] calculated the L_3 fluorescence spectra of Fe and demonstrated that the difference between the polarization-averaged spectra of emitted radiation excited by right- and left-handed circularly polarized x rays closely reflects the spin-resolved local occupied density of states. Evidently, this kind of dichroism in x-ray fluorescence closely parallels MCD in absorption, and is precisely complementary to it.

In what follows we demonstrate experimentally that the effect can be seen in an even simplier experiment. Strange, Durham, and Gyorffy[9] envisaged monochromatic incident radiation, as in x-ray-absorption experiments; here we report an observation of the effect using an effectively white beam of incident radiation.

The measurements were performed with the SUPERACO storage ring at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique. The electron current was typically 400 mA on injection with a 7–8 h lifetime at an energy of 800 MeV. The experiment was set up on a bending-magnet beamline approximately 10 m from the photon source. An adjustable slit was moved 0.375 mrad below the synchrotron plane to select a pencil of circularly polarized x rays defined by a 0.2 mrad vertical aperture. The angle between the phonon beam and the surface normal was 75°. The Fe sample (heat treated to 800 °C under hydrogen atmosphere to improve its permeability) closed the magnetic circuit of a horseshoe-shaped electromagnet. The exact degree of left-hand circular polarization for the photons exciting the fluorescence process was not determined. However, it is of the order of 50% at 17 Å (729 eV) under our operating conditions.

A Johann spectrometer fitted with an RbAP crystal bent to a 0.5 m radius was set in a vertical plane above the sample. Spectra were recorded with a proportional counter detector fitted with a 0.4 μm Formvar window providing close to 100% efficiency at these energies. The entrance slit was set to 200 μm leading to an instrumental broadening of ~450 meV. The signal-to-background ratio was ~25 at the emission peak. Scans were made in

equal spectrometer steps of 4 mÅ, corresponding to approximately 160 meV energy steps. The spectrometer is fitted with absolute encoders which ensure a high degree of reproducibility (equivalent to better than 30 meV in this energy region) so repeated scans were summed to average out effects due to beam instabilities.

To avoid possible experimental artifacts the geometrical setup was kept fixed throughout the experiments and the direction of magnetization was reversed relative to the chirality of the photon beam by reversing the current in the electromagnet. It should be noted that this is a photon-in–photon-out experiment, so stray magnetic fields have no influence on the measurements. Further, we recorded data for each direction of magnetization successively at each energy step in such a way that, on average over two spectrometer steps, there was no time lag between the measurements. The MCD signal is then straightforwardly the difference $(\sigma^+ - \sigma^-)$ between the two sets of data. Figure 1 shows the sum $(\sigma^+ + \sigma^-)$ and the difference of the $L_{2,3}$ emission bands for each direction of magnetization. Note in particular the reversal in sign of the dichroic asymmetry curve between the L_2 and L_3 edges. This is foreshadowed in the photoemission dichroism of the Fe $2p$ levels, as noted and discussed by Ebert *et al.*,[10] and is reproduced by our calculations.

Taking the Fe $2p_{3/2}$ binding energy to be 706.7 eV (Ref. 11) (and assuming the core hole to be fully screened in the x-ray-emission process) we can compare (Fig. 2) the experimental MCD signal with the theory of Strange, Durham, and Gyorffy.[9] The calculated spectrum has been broadened by convolution with a Lorentizian profile of 240 meV full width at half-maximum (FWHM) to represent the core level lifetime and a Gaussian profile of 450 meV FWHM to account for instrumental broadening. We note the satisfactory agreement. (Recall that the calculations assume perfect circular polarization and perfect ferromagnetic order in the sample, and, as indicated above, neither of these conditions is fully realized in these experiments. Hence the total fluorescence signal must contain a significant nondichroic component which will reduce the magnitude of the apparent fractional anisotropy relative to its theoretical value without, presumably, distorting the normalized MCD spectra very much.)

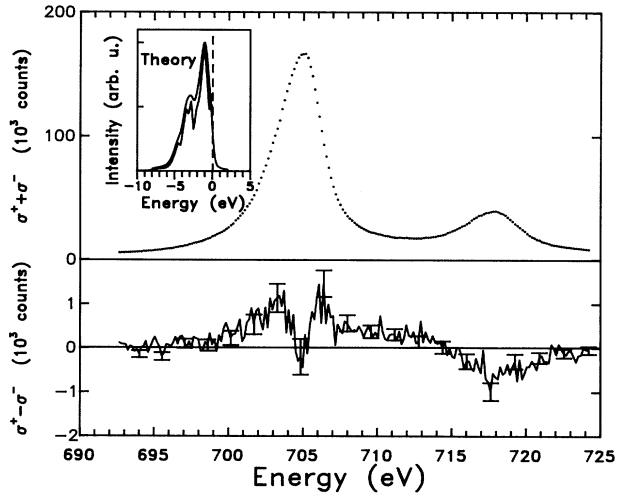

FIG. 1. The $(\sigma^+ + \sigma^-)$ fluorescence signal (upper curve) and the magnetic circular dichroism $(\sigma^+ - \sigma^-)$ signal for the Fe $L_{2,3}$ x-ray-emission bands (error bands indicating the standard deviation are shown). The inset shows the theoretical L_3 emission transition rate from Ref. 9 and the ensuing emission band obtained by folding with our experimental function.

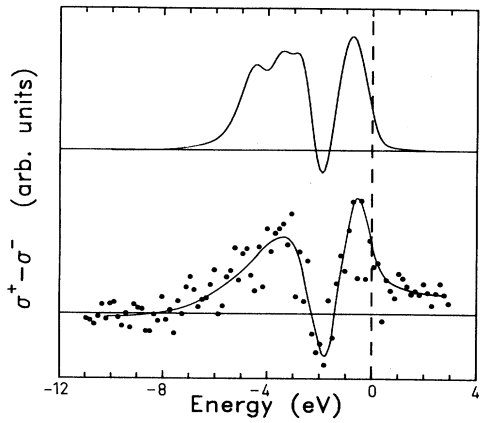

FIG. 2. The (normalized) Fe L_3 magnetic circular dichroism signal $(\sigma^+ - \sigma^-)$: the upper curve is the theoretical prediction for ω_i equals threshold energy, folded with the experimental resolution function; the experimental result is given in the lower curve (the continuous line serves as a guide for the eye).

We also note that the lack of structure in the emission spectra appears to be inconsistent with that in the MCD spectra, and indeed the same convolution procedure used in Fig. 2 gives a theoretical emission spectrum with considerably more structure than the experimental data (see inset to Fig. 1). Absorption MCD data on Fe and Ni also show a similar discrepancy, with the $L_{2,3}$ absorption white lines appearing broader and more asymmetrical than the corresponding MCD spectra.[12] This seems to indicate that a substantial part of the spectral weight in absorption and emission arises from multiple-electron effects which are not, in the main, spin sensitive and thus contribute no MCD signal. Moreover, the use of white incident radiation results in excitation of core electrons to unoccupied states of all energies from the Fermi level upwards. In processes involving excitation close to threshold, the core hole is well screened and multiple-electron excitations may be suppressed. Thus, threshold excitation may contribute an unexpectedly large part of the MCD signal, and this may bear on the agreement shown in Fig. 1.

The conclusion is that the shape of the Fe L_3 dichroic fluorescence asymmetry curve does resemble the difference between the local density of occupied spin-up and spin-down d states, as suggested by Strange, Durham, and Gyorffy.[9] If this is a general result, dichroic fluorescence is a powerful and, in the form practiced here with white incident radiation, a simple local probe of magnetic systems. Therefore we now discuss in more detail the dependence of fluorescence spectra on the energy ω_i of the incident radiation. For a given polarization,

changing ω_i amounts to changing the unoccupied state to which the core electron is excited in the absorption step. The character of the core holes produced does not vary with ω_i but only the rate at which they are formed (i.e., essentially the absorption cross section). This makes plausible our observation that while the fluorescence spectra maintain their shape for different incident energies, their absolute magnitude may vary rapidly. Indeed further calculations show that the shape of the asymmetry curve is fairly insensitive to ω_i, but that its magnitude does vary with ω_i. In the case of the $L_{2,3}$ edges of Fe, we find that the absorption dichroism varies particularly rapidly at the L_2 edge, changing sign in the unoccupied d-band region where the number of states to which the core electron can be excited is very large.

Our calculations show that fluorescence dichroism spectra at the L_2 and L_3 edges are, apart from the sign reversal, closely related, although the different matrix elements slightly modify the shapes of the asymmetry curves. However, their behavior as a function of ω_i differs markedly, following the absorption dichroism. Experimentally the L_3:L_2 emission band intensity ratio is approximately 5:1 instead of the statistical expectation of 2:1. This is mainly due to a Coster-Kronig transition which provides an extra deexcitation channel for the L_2 hole. Thus we do not expect comparison with theory to be as valid as in the L_3 region. Moreover, the standard deviation for the signal in the L_2 region is too large to draw conclusions. The MCD L_3:L_2 intensity ratio is approximately -1.5:1 instead of -1:1 predicted by simple models.[12,13] On the other hand, Ebert and Zeller[14] have shown that the L_3:L_2 absorption dichroism ratio is generally about -2:1. This is essentially a consequence of spin-orbit coupling in the d bands (related to the existence of an orbital moment), and is reflected in the variation of the fluorescence dichroism curves with ω_i. It should be noted, however, that according to Smith *et al.*[12] in the case of Fe the L_3:L_2 absorption MCD ratio is affected by many-electron interactions.

Thus, while it is not generally true that dichroic fluorescence excited by white radiation "measures" the spin-resolved local density of occupied states directly, theoretical analysis of the kind provided here should be sufficient to interpret the experimental data. Given the unique site-selective information dichroic fluorescence can provide about moment formation in, for instance, pure metals, metallic alloys, and magnetic multilayers, the need for a relatively sophisticated analysis procedure should be a small price to pay. Clearly it will be particularly interesting to study with the complementary techniques of MCD in absorption and fluorescence the transition from strong to weak ferromagnetism, as the Fermi energy enters the majority-spin d band as in Ni-Fe Invar alloys.

Finally, we note that the full fluorescence cross section for magnetic systems is, in principle, a richly informative function of the energy, direction, and polarization of both incident and emitted radiation. The future availability of undulator radiation from third-generation syncrotron sources should allow the fluorescence cross section to be probed in much greater detail than currently possible. For example, large fluxes of completely polarized monochromatic radiation may allow gains in intrinsic resolution through exploitation of the line-shape properties of the fluorescence process.[15] Moreover, angular resolution of the emitted radiation may probe the anisotropy of local moments, and, in particular, discriminate between e_g and t_{2g} components of the spin-resolved local densities of states. Such possibilities will be discussed in a subsequent paper.

We gratefully acknowledge the staff of the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique for their help in performing the exponents. C.F.H. and J-M.M. thank M. Sacchi for encouraging discussions. P.J.D. thanks C.T. Chen for helpful discussions. Laboratoire de Chimie Physique-Matière et Rayonnement is Unité de Recherche Associée au CNRS No. 176.

[1] B. T. Thole, G. van der Laan, and G. A. Sawatzky, Phys. Rev. Lett. **55**, 2086 (1985); G. van der Laan, B. T. Thole, G. A. Sawatzky, J. B. Goedkoop, J. C. Fuggle, J-M. Esteva, R. C. Karnatak, J. P. Remeika, and H. A. Dabkowska, Phys. Rev. B **34**, 6529 (1986).

[2] G. Schütz, W. Wagner, W. Wilhelm, P. Kienle, R. Zeller, R. Frahm, and G. Materlik, Phys. Rev. Lett. **58**, 737 (1987).

[3] P. Strange, H. Ebert, and B. L. Gyorffy, J. Appl. Phys. **65**, 3055 (1988).

[4] C. T. Chen, F. Sette, Y. Ma, and S. Modesti, Phys. Rev. B **42**, 7262 (1990).

[5] S. Imada and T. Jo, J. Phys. Soc. Jpn. **59**, 3358 (1990).

[6] S. P. Collins, M. J. Cooper, A. Brahmia, D. Laundy, and T. Pitkanen, J. Phys. Condens. Matter **1**, 323 (1989).

[7] D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Academic, New York, 1984).

[8] P. Strange, R. Zeller, H. Ebert, B. Drittler, and B. L. Gyorffy, *Effects of Relativity in Atoms, Molecules and the Solid State* (Plenum, New York, 1991), p. 333.

[9] P. Strange, P. J. Durham, and B. L. Gyorffy, Phys. Rev. Lett. **67**, 3590 (1991).

[10] H. Ebert, L. Baumgarten, C. M. Schneider, and J. Kirschner, Phys. Rev. B **44**, 4406 (1991).

[11] A. Lebugle, U. Axelsson, R. Nyholm, and N. Martensson, Phys. Scr. **23**, 825 (1981).

[12] N. V. Smith, C. T. Chen, F. Sette, and L. F. Mattheiss, Phys. Rev. B **46**, 1023 (1992).

[13] J. L. Erskine and E. A. Stern, Phys. Rev. B **12**, 5016 (1975).

[14] H. Ebert and R. Zeller, Physica B **161**, 191 (1990).

[15] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, Oxford, 1954).