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Dichroism in X-ray Fluorescence

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We discuss circular dichroism in the x-ray fluorescence spectra of magnetic systems in the light of a recent theory[1]. Fully relativistic local spin density functional calculations on the $L_{2,3}$ edges of ferromagnetic iron are compared with very recent experimental data, and the relationship between the dichroism spectra and the spin-resolved local density of **occupied** states is discussed.

The recent work on magnetic circular dichroism (MCD) in x-ray absorption has attracted widespread interest[2,3]. This note discusses what might be seen if one looks at the spectrum of radiation emitted from magnetic materials in x-ray fluorescence excited by circularly polarized radiation. We have in mind itinerant magnetic systems such as the 3d elemental magnets and their alloys - more localized systems may require a different treatment[4]. Our motivation is as follows. The current MCD experiments, like all absorption spectroscopies, give information on the unoccupied states, and in particular the spin-resolved unoccupied local density of states. We wanted to see if something analogous could be done for the occupied states of magnetic systems - this would obviously complement the absorption studies, and be at least as interesting in its own right since it is the occupied states which actually carry the local moments, both spin and orbital. Hence, we looked to x-ray emission processes. But the traditional way of making x-ray emission measurements involves excitation of the core hole by electron impact, followed by radiative decay of the hole. It is not easy to see how to excite emission preferentially from different spin states using electron bombardment (although it may not be impossible). In fluorescence, however, the emission is produced by photon excitation of the core hole, and the incident photons can be circularly polarized. We already know from the absorption experiments that such a process is "spin-sensitive", and, indeed MCD absorption spectra can be measured by total fluorescence yield. What happens if one measures the spectrum of emitted radiation?

The full fluorescence cross-section is, in principle, a very rich object — it is a function of the energy, direction and polarization of both incident and emitted photons. A "complete experiment" in which all of these parameters were either controlled or measured would carry a wealth of information about all the states of magnetic systems, occupied and unoccupied. It would be a demanding experiment to perform, though, since fluorescence is a weak second order process. Hence, we also wanted to find a simplified experiment which might not resolve all the photon parameters but would still be informative. In fact, we consider the case in which the incident radiation has specified energy and polarization, but the spectrum of emitted radiation is measured without resolving its polarization. Nevertheless, with the several 3rd generation synchrotron sources planned or under construction world-wide, very high brilliance insertion devices like undulators - some of them designed specifically to produce circular polarization - will certainly be available soon, and one can envisage fluorescence becoming much easier to observe in all its detail. This lends timeliness to our current study.

Our calculations are fully relativistic in all three key aspects — the core level, the valence or band states and the electron-photon interaction. In particular, the electron states are described by solving the spin-polarized Dirac equation within the local spin density approximation, with potentials taken from a self-consistent spin-polarized band structure calculation. This represents the 2p core levels of ferromagnetic iron as a pair of spin-orbit split manifolds, $2p_{3/2}$ and $2p_{1/2}$, each of which is exchange-split into 4 and 2

levels by about 0.8eV and 0.2eV respectively[5]. This description is a parameter-free prediction of the theory, and it is useful to note that it agrees quite well with recent photoemission dichroism experiments[6]. The basic formula for the fluorescence intensity is[1]

$$I^{\lambda} \propto \sum_{\Lambda\Lambda'} n_{\Lambda}(\epsilon_c + \omega_{in}) n_{\Lambda'}(\epsilon_c + \omega_{out}) |M^{\lambda}_{\Lambda_c\Lambda}|^2 . \; |M^{\lambda'}_{\Lambda_c\Lambda'}|^2 \qquad (1)$$

in which Λ represents the total electron angular momentum quantum numbers, λ =+- specifies the helicity of the photons (incoming and outgoing in an obvious notation), and the dichroic effects arise from the coupling of these quantities contained in the electron-photon matrix elements $M^{\lambda}_{\Lambda_c\Lambda}$. The other ingredients are the unoccupied and occupied local densities of states, $n^{\lambda}(\epsilon_c+\omega_{in})$ and $n^{\lambda}(\epsilon_c+\omega_{out})$ respectively (ϵ_c is the core level eigenvalue). These local densities of states are calculated using relativistic spin-polarized multiple scattering theory[7], and the matrix elements are evaluated from bound and scattering solutions of the spin-polarized Dirac equation together with the fully relativistic form of the electron-photon interaction, - eα.**A**(**r**). We define a dichroic anisotropy by

$$A = \frac{I^+ - I^-}{I^+ + I^-} \qquad (2)$$

in which, as noted above, we sum over the polarization of the emitted radiation. Thus, in eq. 2, $I^{+(-)}$ stands for the total emitted intensity excited by right (left) hand circularly polarized incident radiation.

Figure 1 shows some calculations for the case of photons incident and emitted in the same direction as the magnetization, using an incident photon energy chosen to put the excited electron about 1.5 eV above the Fermi level. The I^+ intensity is shown together with the occupied density of d-states - the two are not equal but there is a clear correspondence. Also shown is the corresponding dichroic anisotropy, compared with the difference between the spin-up and spin-down densities of d-states. There is a great deal of structure

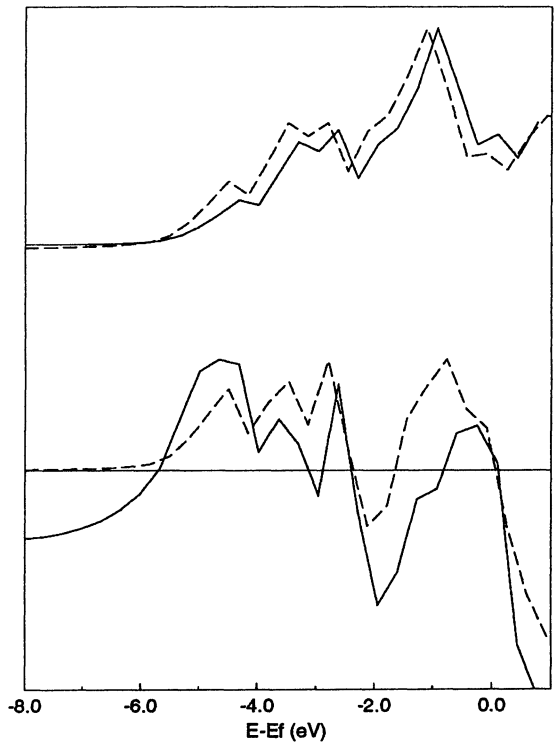

Figure 1: Calculated L_3 fluorescence spectrum (upper curves) and dichroic anisotropy (lower curves) for Fe. The dashed curves are the occupied density of states (upper curves) and energy-resolved spin-polarization, $n_{\uparrow}(E) - n_{\downarrow}(E)$ (lower curves). Units are arbitrary, and the spectra are normalized to the same maximum value.

in these unbroadened calculations, much of which will be washed out in experimental data, but there is in particular a large dip in the middle of the d-band. Again most of this structure correlates with the spin-resolved density of states. Thus, the suggestion is that this kind of fluorescence dichroism might indeed be a useful tool with which to look at the spin density of the occupied states energy by energy.

Finally, we briefly describe some very recent experimental data taken at Super-ACO, LURE. The Fe sample formed part of a horseshoe electromagnet so that the direction of magnetization could be reversed with respect to the helicity of the incident photons, whose degree of circular polarization was around 50%. The emission spectrum was measured with a Johann bent crystal spectrometer with a resolution of 0.45 eV. Figure 2 shows the L_2 and L_3 spectra together with the corresponding anisotropy spectrum. The latter is fairly noisy, but it is encouraging that dichroism can be seen at all with bending magnet radiation. The usual reversal in sign of the anisotropy between L_2 and L_3 occurs, apart from which there is little structure except for the dip in the middle of the L_3 spectrum. This is certainly as predicted in the calculations, and at this stage theory and experiment are in reasonable ac-

cord. It is, however, a little difficult to compare these

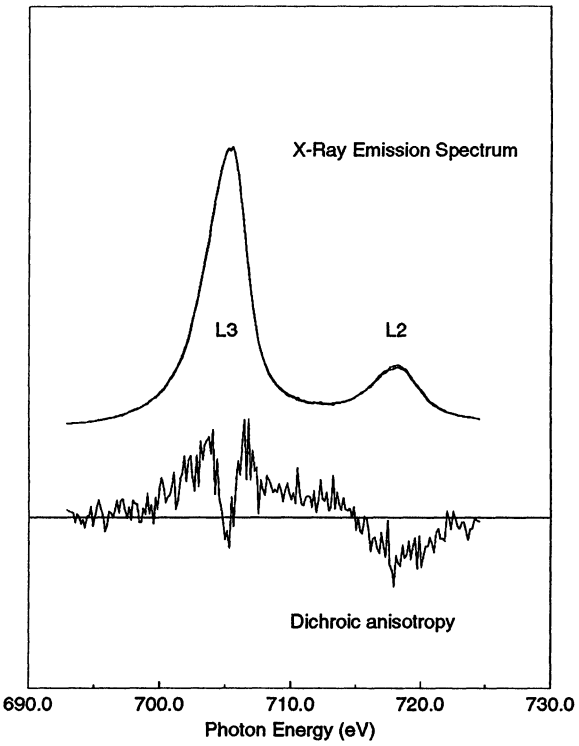

Figure 2: Experimental $L_{2,3}$ fluorescence spectra (upper curve) and dichroic anisotropy (lower curve) for Fe (see text for details). Units are arbitrary.

data directly with the calculations of figure 1. The experimental set-up is somewhat different from that modelled in the calculations, and, interestingly, the emission was excited by essentially white incident radiation, rather than the monochromatic beam assumed in figure 1. Moreover, it appears that the experimental anisotropy curve is "anomalously sharp" compared to the emission spectrum itself. The anisotropy curve looks reasonable in view of the accepted core hole lifetime broadening of 0.2 - 0.3 eV, but the emission spectrum seems to be considerably broader than that. A similar anomaly can be seen in some of the published absorption dichroism data[3]. Finally, the dip in the middle of the d-band is all but invisible in the L_2 spectrum except to the most enthusiastic eye. Hence there are some issues which remain to be resolved. Nevertheless, the data is encouraging, and we believe that dichroism in occupied state spectroscopies will prove to be a useful tool for the study of the electronic origins of magnetism.

Acknowledgments

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References

1) P.Strange, P. J. Durham and B. L. Gyorffy, Phys. Rev. Lett. **67** (1991) 3590.
2) G. Schütz, W. Wagner, W. Wilhelm, P. Kienle, R. Zeller, R. Frahm and G. Materlik, Phys. Rev. Lett. **58** (1987) 737.
3) C. T. Chen, F. Sette, Y. Ma and S. Modesti, Phys. Rev. **B42** (1990) 7262.
4) B. T. Thole, G. van der Laan and G. A. Sawatzky, Phys. Rev. Lett. **55** (1985) 2086.
5) H. Ebert, J. Phys. Condens. Matter **1** (1989) 9111.
6) L. Baumgarten, C. M. Schneider, H. Petersen, F. Schafers and J. Kirschner, Phys. Rev. Lett. **65** (1990) 492; H. Ebert, L. Baumgarten, C. M. Schneider and J. Kirschner, Phys. Rev. **B44** (1991) 4406.
7) P.Strange, H. Ebert, J. B. Staunton and B. L. Gyorffy, J. Phys. Condens. Matter **1** (1989) 2959.