X-ray Magnetic Circular Dichroism (XMCD) : basic concepts and theory for rare earths and 3d metals

Stefania Pizzini – Laboratoire Louis Néel – Grenoble

- Introduction to X-ray absorption spectroscopy
- XMCD of 3d metals : one electron approximation
- Examples and perspectives

I) Introduction

XMCD measures the dependence of X-ray Absorption on the helicity of the x-ray beam by a magnetic material. It is the x-ray equivalent of Faraday or Kerr effects which occur in the visible range. I will first describe the basic concepts of x-ray absorption.
X-ray absorption spectroscopy using synchrotron radiation is a well established technique providing information on electronic, structural and magnetic properties of atoms, molecules, surfaces, liquids and solids.

We will first introduce: - the interaction of x-rays with matter; - transitions from a core state to an empty electronic state; - element selectivity; - the one electron approximation; -Fermi

$$W_{fi} = \frac{2\pi}{\hbar}\left|\left\langle \Phi_f \left| \mathrm{T} \right| \Phi_i \right\rangle\right|^2 \delta_{E_f - E_i - \hbar\omega}$$

Golden Rule : transition probability from the initial state Φ_i to the final state Φ_f :
In the dipole approximation the selection rules are $\Delta l = \pm 1$; $\Delta s = 0$. We will define K, L and M edges.

We will briefly describe some experimental aspects : - use of synchrotron radiation ; - detection in transmission and fluorescence for hard x-rays; - fluorescence or electron yield for soft x-rays; surface sensitivity.

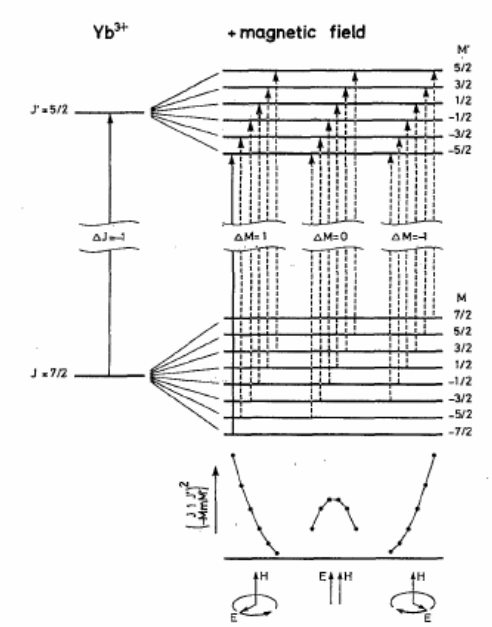
II) N-particle description of 3d → 4f transitions in rare earth ions

$M_{4,5}$ edges of rare earths have been the first test case for the XMCD theory. Edges are dominated by 3d→4f transitions which have very large absorption cross sections and are fairly independent on the local chemistry of the ion. The atomic description of 3d→4f transitions relies on the strong localisation of the 4f electrons with respect to 5d and 6s electrons. These edges are calculated for a trivalent ion that has lost the outermost $(5d6s)^3$ electrons. Electronic levels are determined by Coulomb interactions, then by spin-orbit (SO) coupling. Perturbations given by magnetic field and crystal field induce energy level separations of a few meV which can be treated as a weak perturbation with respect to Coulomb and SO interactions.

In the atomic model the electronic transition is viewed as taking place between the ground-state and the excited state of the complete atom. Description of absorption spectra involves calculation of all the energy levels of the initial and the final state N-particle wavefunctions (multiplets). Each multiplet has an atomic angular momentum quantum number J. The dipole selection rules are $\Delta J = 0, \pm 1$. The absorption spectrum is formed by the superposition of all the selection-rule allowed transitions from the ground level to the final level multiplet.

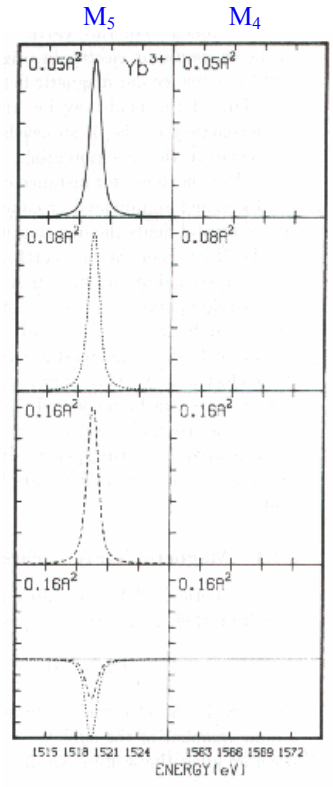
Almost perfect agreement between calculated and experimental spectra is obtained for absorption and XMCD spectra. XMCD is the difference between the $\Delta M = +1$ (left circular polarisation – LCP) and the $\Delta M=-1$ (right circular polarisation – RCP) transitions.

Magnetic circular dichroism is the absorption counterpart of Zeeman effect. The most convenient geometry for magnetic dichroism is that wherein a right or left circularly polarised x-ray beam travels along the direction of the magnetic field.



Energy diagram of the $3d^{10}4f^{13} \rightarrow 3d^{9}f^{14}$ transition of Yb^{3+} without and with magnetic field. The arrows indicate the dipole selection rule allowed transitions from J to J'. Their relative intensities are given by the dots.

Let us consider the easiest *example of a trivalent Yb ion*. In the field-free ion the spin orbit interaction leads to splitting of the initial state into $^2F_{7/2}$ and $^2F_{5/2}$ and of the final state into $^2D_{5/2}$ and $^2D_{3/2}$. The $^2F_{7/2}$ multiplet is the Hund's rule ground state.



The only allowed transition is $^2F_{7/2}$ to $^2D_{5/2}$ with $\Delta J = -1$, while the transition to $^2D_{3/2}$ which would constitute the M_4 line, is dipole forbidden. Top panel of the figure below: M_5 (left) and M_4 line (right).

When the spherical symmetry is broken by a magnetic field the $\Delta J = -1$ line is split into 18 lines divided over three groups with different ΔM : $\Delta M = 0$ for parallel linearly polarised light, $\Delta M = \pm 1$ for left and right circular polarisation (figure above).

At sufficiently high temperature all the levels remain populated and the splitting has no effect on the spectrum. However when the magnetic field splitting $g\mu H$ is large relative to thermal energy kT the upper levels are less occupied, according to Boltzman statistics, and this has an effect on the observed cross section. In the limit of 0 K only the lowest level is occupied and the transition will occur only if the light is left circularly polarised. The second panel shows the 0 K spectrum for parallel (dash) and perpendicular (dots) linear polarisation ; the third panel the difference between left (dash) and right (dots) circular polarisation ; the fourth panel gives the linear dichroism (XMLD - dash) and the circular magnetic dichroism (XMCD - dots).

More complicated absorption and XMCD spectra are obtained for the other rare earths whose outer shell has more than one f electron or hole and where more transitions are allowed; some examples will be given in the course.

REFERENCES

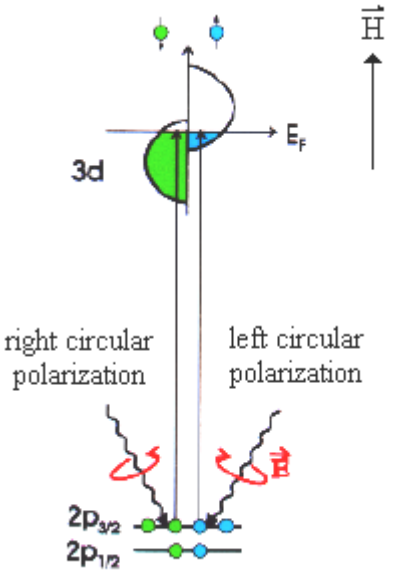
B.T. Thole, G. van der Laan and G. A. Sawatzky, Phys. Rev. Lett. 55, 2086 (1985).
B.T. Thole, G. van der Laan and P.H. Butler, Chem. Phys. Lett. 149, 295 (1988).
G. van der Laan and B.T. Thole, Phys. Rev. B 43, 13401 (1991).
G. van der Laan, B.T. Thole, G.A. Sawatzky, J.B. Goedkoop, J.C. Fuggle, J.-M. Esteva, R.C. Karnatak, J.P. Remeika and H.A. Dubkowska, Phys.Rev.B 34, 6529 (1986).
B.T.Thole, G. van der Laan, J.C.Fuggle, G.A.Sawatzky, R.C.Karnatak and J.-M.Esteva, Phys.Rev.B 32, 5107 (1985).
J.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).
M.Sacchi and J.Vogel, in *Magnetism and Synchrotron Radiation,* Lecture Notes in Physics, **Vol.565, 87**, E.Beaurepaire, F.Scheurer, G.Krill, J.P.Kappler (Eds.), Springer Verlag, 2001.

III) XMCD in 3d metal systems

Magnetic properties of transition metals are mostly due to their d electrons. We are therefore interested in exciting p core electrons i.e. to use $p \rightarrow d$ dipole transitions ($L_{2,3}$ absorption edges). Band structure effects play an important role in the shape of the absorption spectra of 3d transition metals**.** A one electron approach is generally used to treat the excitations: the electron is excited from the spin-orbit split $2p_{3/2}$ and $2p_{1/2}$ levels to empty d valence states.

The two-step model :

The two-step model proposed by Stöhr and Wu will be introduced to illustrate the origin of circular x-ray dichroism at the $L_{2,3}$ edges of 3d transition metals. Spin-orbit interaction is taken into account in the initial p-state ; the 3d band is exchange split into spin-up and spin-



down bands. In the first step, the interaction of circularly polarised x-rays with the p shell leads to the excitation of spin-polarised electrons. The core shell can therefore be viewed as an atom-specific, localised "source" of spin-polarised electrons. The spin-polarisation depends on the edge and on the polarisation of the light. It will be demonstrated that at the L_2

edge left circular polarisation (LCP) excites 25% spin up and 75% spin down electrons. Right circular polarised light does the opposite. At the L_3 edge, 62.5% (37.5%) spin up and 37.5% (62.5%) spin down electrons are excited by LCP (RCP) light. In a non magnetic material the total (spin-up plus spin-down) transition intensities are the same for LCP and RCP light; as soon as there is an unbalance in the number of available empty spin up and down states (ferro-, para- or ferrimagnetic material) the absorption of the two polarisations will be different, with a difference which is opposite at the L_2 and L_3 edges. We can then visualize a second step in which the spin-polarised electrons are analysed by a spin-resolving detector consisting of the exchange split d final state.
For a complete relativistic description of x-ray dichroism in the one-electron model, spin-orbit coupling has to be included also in the d-band. The results on the XMCD signal will be shown. Many body effects are also important and some examples will be illustrated.

The sum rules of XMCD :

Sum rules developed by Theo Thole et al. at the beginning of the 1990's allow the experimental integrated intensities of XAS and XMCD spectra to be related to the ground-state expectation values of the orbital <Lz> and spin <Sz> magnetic moments of the absorbing atom. The sum rules have been at the origin of a strong development of XMCD, which has become a reference technique for the study of magnetic properties of thin metallic films and multilayers.
These equations, their validity and applicability will be discussed in the lesson.

REFERENCES

C.T.Chen, F.Sette, Y.Ma, and S.Modesti, Phys.Rev.B 42, 7262 (1990).
N.V.Smith, C.T.Chen, F.Sette, and L.F.Mattheis, Phys.Rev.B 46, 1023 (1991).
J.Stöhr and Y.Wu, in "New Directions in Research with Third-Generation Soft X-Ray Synchrotron Radiation Sources", NATO ASI Series, Series E: Applied Sciences - Vol. 254, Eds. A.S.Schlachter and F.J.Wuilleumier, pag. 221-250 (1994)
H.A.Bethe and E.E.Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Plenum, New York, 1977).
B.T.Thole and G. van der Laan, Europhys.Lett. 4, 1083 (1987).
B.T.Thole, P.Carra, F.Sette, and G. van der Laan, Phys.Rev.Lett. 68, 1943 (1992).
J.Schwitalla and H.Ebert, Phys.Rev.Lett. 80, 4586 (1998).
G. van der Laan, Phys.Rev.B 55, 8086 (1997).
P.Carra, B.T.Thole, M.Altarelli, and X.Wang, Phys.Rev.Lett. 70, 694 (1993).
M.Altarelli, Phys.Rev.B 47, 597 (1993); T.Jo, J.Phys.Soc.Jpn. 62, 1814 (1993); F.Sette, in "New Directions in Research with Third-Generation Soft X-Ray Synchrotron Radiation Sources", NATO ASI Series, Series E: Applied Sciences - Vol. 254, Eds. A.S.Schlachter and F.J.Wuilleumier, pag. 251 (1994).

C.T.Chen, Y.U.Idzerda, H.-J.Lin, N.V.Smith, G.Meigs, E.Chaban, G.H.Ho, E.Pellegrin, and F.Sette, Phys.Rev.Lett. 75, 152 (1995).
D.Arvanitis, M.Tischer, J.Hunter-Dunn, F.May, N.Mårtensson, K.Baberschke, Spin-orbit-influenced spectroscopies of magnetic solids p.145, (Springer Verlag, Berlin, Germany 1996).
Y.Wu, J.Stöhr, B.D.Hermsmeier, M.G.Samant, and D.Weller, Phys.Rev.Lett. 69, 2307 (1992).
M.Tischer, O.Hjortstam, D.Arvanitis, J.Hunter Dunn, F.May, K.Baberschke, J.Trygg, J.M.Wills, B.Johansson, and O.Eriksson, Phys.Rev.Lett. 75, 1602 (1995).
J.Vogel and M.Sacchi, Phys.Rev.B 53, 3409 (1996).
D.Weller, J.Stöhr, R.Nakajima, A.Carl, M.G.Samant, C.Chappert, R.Mégy, P.Beauvillain, P.Veillet, and G.A.Held, Phys.Rev.Lett. 75, 3752 (1995).

H.A.Dürr and G. van der Laan, Phys.Rev.B 54, R760 (1996).
G. van der Laan, J.Phys.: Condens.Matter 10, 3239 (1998).
R.Wu and A.J.Freeman, Phys.Rev.Lett. 73, 1994 (1994).
P.Carra, H.König, B.T.Thole, and M.Altarelli, Physica B 192, 182 (1993).
J.Stöhr and H.König, Phys.Rev.Lett. 75, 3748 (1995).

G. van der Laan, Phys.Rev.Lett. 82, 640 (1999).
R.Wu, D.Wang, and A.J.Freeman, Phys.Rev.Lett. 71, 3581 (1993).
B.T.Thole and G.van der Laan, Phys.Rev.B 38, 3158 (1988).
J.Vogel and M.Sacchi, Phys.Rev.B 49, 3230 (1994).
R.Nakajima, J.Stöhr, and Y.U.Idzerda, Pys.Rev.B 59, 6421 (1999).

IV) Some examples of applications of XMCD

In the second part of the course I will give some examples of the application of XMCD to the study of element selective magnetic properties of thin films. Some of the examples are taken from the work of the group « dichroism » at the Laboratoire Louis Néel in Grenoble.
I will also talk about the recent developments of XMCD and X-PEEM, and in particular of the use of the time structure of synchrotron radiation for the use for magnetisation dynamics at sub-nanosecond timescales (see lecture of W. Kuch).

S. Pizzini, A. Fontaine et al. 'Evidence of the spin-polarisation of copper in Co/Cu and Fe/Cu multilayers', Phys Rev. Lett. 74 (1995) 1470

C. Bordel, S. Pizzini et al. 'Microscopic origin of the macroscopic magnetic properties of TbFeCoN amorphous thin films' Phys. Rev. B 56 (1997) 8149

D. Weller, J. Stohr, et al. 'Microscopic origin of magnetic anisotropy in Au/Co/Au probed with x-ray magnetic circular dichroism' Phys. Rev. Lett. 75 (1995) 3752

M. Bonfim et al. 'Element selective nanosecond magnetisation dynamics in magnetic heterostructures', Phys. Rev. Lett. 86 (2001) 3646

P. Gambardella, et al. 'Giant magnetic anisotropy of single cobalt atoms and nanoparticles' Science 300 (2003) 5622.

J.Vogel et al., "Structure and magnetism of Pd in Pd/Fe multilayers studied by XMCD at the Pd $L_{2,3}$ edges", Phys.Rev.B 55, 3663 (1997).

S.S.Dhesi et al., "Anisotropic spin-orbit coupling and magnetocrystalline anisotropy in vicinal Co films", Phys.Rev.Lett. 87, 067201 (2001).