X-Ray Magnetic Circular Dichroism: basic concepts and theory for 4f rare earth ions and 3d metals

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I) - History and basic concepts of XAS
   - XMCD at $M_{4,5}$ edges of 4f rare earths
   - XMCD at $L_{2,3}$ edges of 3d metals

II) - Examples and perspectives

Magnetic dichroism

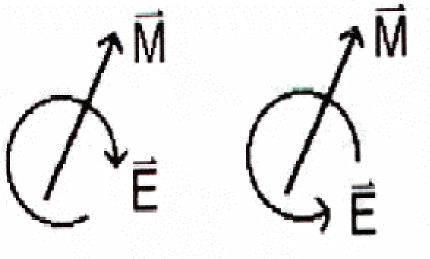
Polarization dependence of X-ray Absorption Spectra

e_q : polarisation vector q = -1 (right circularly polarized light)

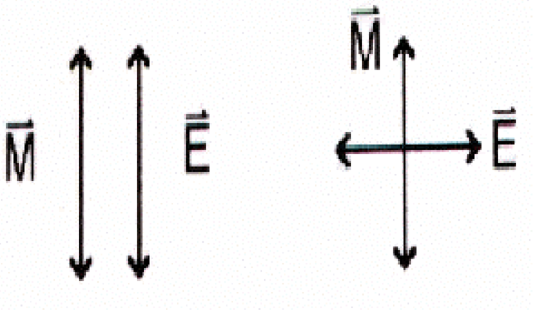
q = 0 (linearly, // to quantisation axis)

q = +1 (left circularly polarized light)

X-ray Magnetic Circular Dichroism (XMCD): difference in absorption for left and right circularly polarised light.



X-ray Linear Dichroism (XMLD): difference in absorption for linearly polarised light ⊥ and // to quantisation axis (q = ± 1 and q = 0).



X-ray Magnetic Dichroism : dependence of the x-ray absorption of a magnetic material on the polarisation of x-rays

1846 - **M. Faraday**: polarisation of visible light changes when trasmitted by a magnetic material

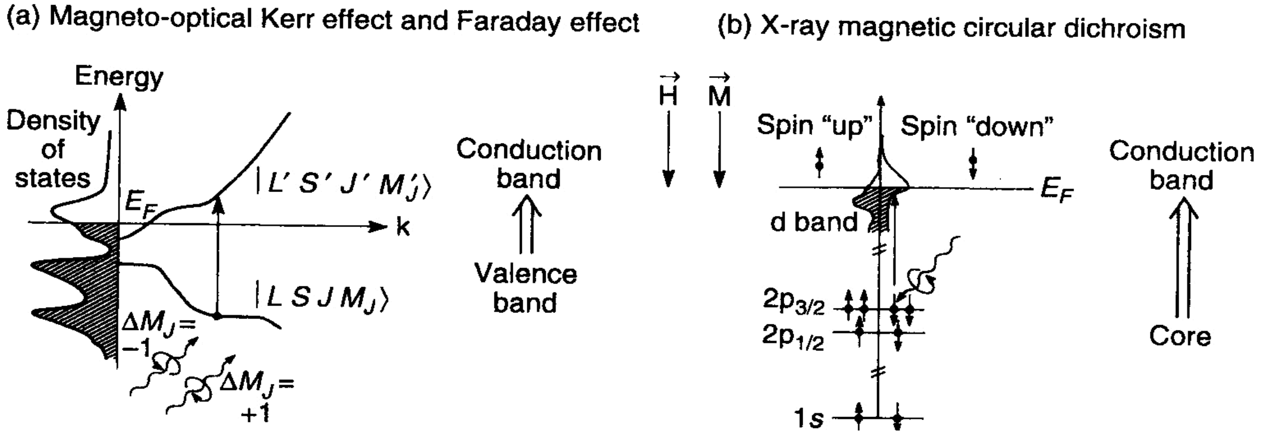
1975 - **Erskine and Stern** - first theoretical formulation of XMCD effect

excitation from a core state to a valence state for the $M_{2,3}$ *edge of Ni.*

**1985 - Thole, van de Laan, Sawatzky - ** first calculations of XMLD for rare earth materials

1986- van der Laan - first experiment of XMLD

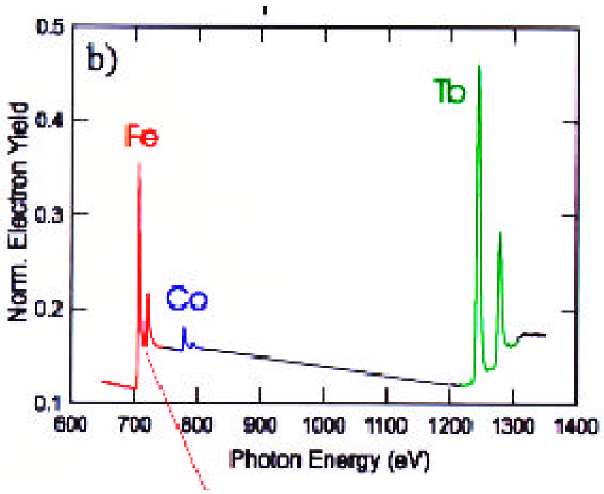
1987 - G. Schütz et al. - first experimental demonstration of the XMCD at the K-edge of Fe


(a) Magneto-optical Kerr effect and Faraday effect

(b) X-ray magnetic circular dichroism

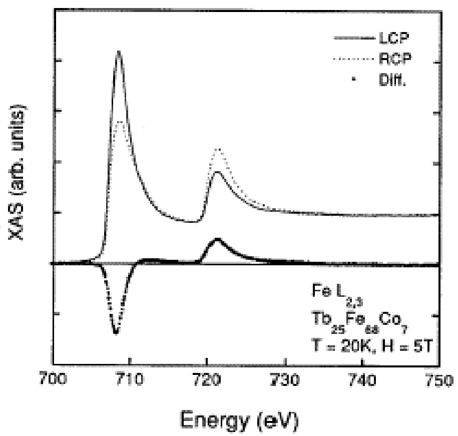
Advantages with respect to Kerr effect

- Element selectivity:
using tunable x-rays at synchrotron radiation sources one can probe the magnetisation of **specific elements** in a complex sample through one of the characteristic absorption edges.



- Orbital selectivity :
by selecting different edges of a same element we can get access to magnetic moments of **different valence electrons**

Fe : $L_{2,3}$ edges 2p → 3d ; K edge 1s → 4p



- Sum rules
allow to obtain separately orbital and spin contributions to th
from the integrated XMCD signal.

- XMCD is proportional to <M> along the propagation vector **k**. Ferromagnetic, ferrimagnetic and paramagnetic systems can be probed.

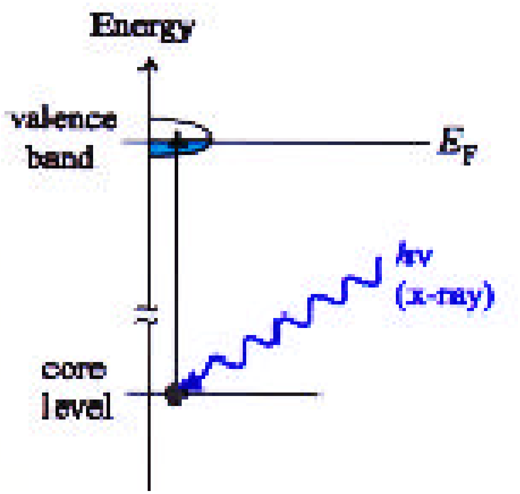
Interaction of x-rays with matter

$\mathbf{I(w) = I_0(w)\ e^{-m(w)x}}$ Lambert-Beer law

$I\ (I_0)$ = intensity after (before) the sample

x= sample thickness ;

μ= experimental absorption cross section



Fermi 's Golden Rule

$$S_{\mathbf{abs}} = \mathbf{(2}p\ \mathbf{/\ h)}\ \ |<\ F_{\mathbf{f}}\ |\mathbf{T}\ |\ F_{\mathbf{i}}\ >|^2\ r_{\mathbf{f}}\mathbf{(h}w\ \mathbf{-\ E_i}\ )$$

$|<\ F_{\mathbf{f}}\ |\mathbf{T}\ |\ F\mathbf{i}\ >|$ matrix element of the electromagnetic field operator

$|\Phi_i >$ initial *core* state; $<\Phi_f |$ final *valence* state

$\rho_f(E)$ density of valence states at E > E_{Fermi}

E_i core-level binding energy

$T = (e/mc)\ \mathbf{p}^{\chi}\mathbf{A}$ Plane wave: $\mathbf{A} = \mathbf{e_q}A_0\exp[i\ \mathbf{k}^{\chi}\mathbf{r}]$

$\mathbf{e_q}$: light polarization vector ; **k** : light propagation vector ; **r** and **p**: electron position and momentum

$$T = CS_q[\mathbf{e}_q{}^{\chi}\ \mathbf{p} + i\ (\mathbf{e}_q{}^{\chi}\ \mathbf{p})(\mathbf{k}^{\chi}\mathbf{r})]$$

dipole operator quadrupole operator

Absorption cross section

Electric dipole approximation (**k☓r << 1**)

T = C (**e**$_q$ ☓ **p**) → $_1$ ∝ (**e**$_q$ ☓ **r**)

-

Commutation relation: [r,H] = (ih/m)p

Transition probability :

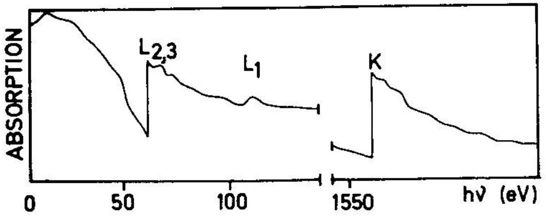
S $_{abs}$ µ |< F $_f$ | **e**$_q$ ☓ **r** | F $_i$ >|^2 r $_f$ (**h**w - **E**$_i$)

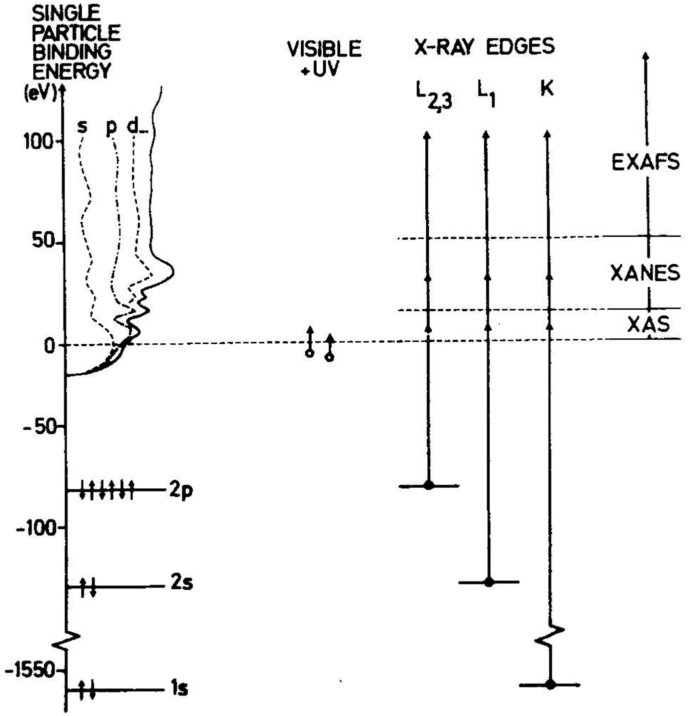
Dipolar selection rules :

D**l** = ± **1,** Ds = **0**

Absorption edges

K-edge: 1s → empty *p*-states
L_1-edge: 2s → empty *p*-states
$L_{2,3}$-edges: $2p_{1/2,\,3/2}$ → empty *d*-states
$M_{4,5}$ -edges: $3d_{\,3/2,\,5/2}$ → empty *f* -states





Spin -orbit coupling: $l \geq 1$

Spin parallel/anti-parallel to orbit:

$j = l + s,\ l - s$

p → 1/2, 3/2 d → 3/2, 5/2

Branching ratios: $-j \leq m_j \leq j$

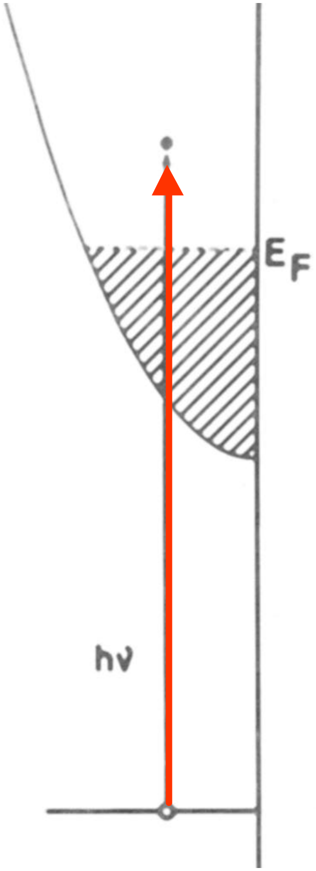
$p_{1/2} \rightarrow m_j = -1/2,\ 1/2$

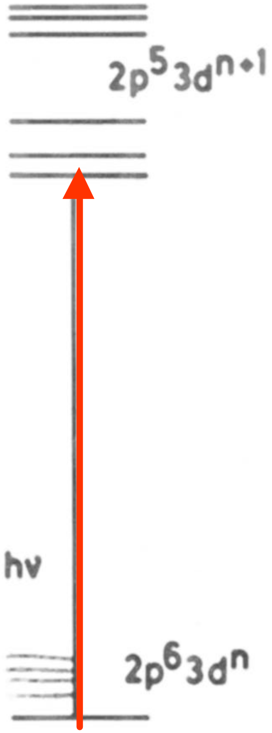
$p_{3/2} \rightarrow m_j = -3/2,\ -1/2,\ 1/2,\ 3/2$

Intensity ratio $p_{3/2} : p_{1/2} = 2 : 1$

$d_{5/2} : d_{3/2} = 3 : 2$

Single particle vs. multiplets





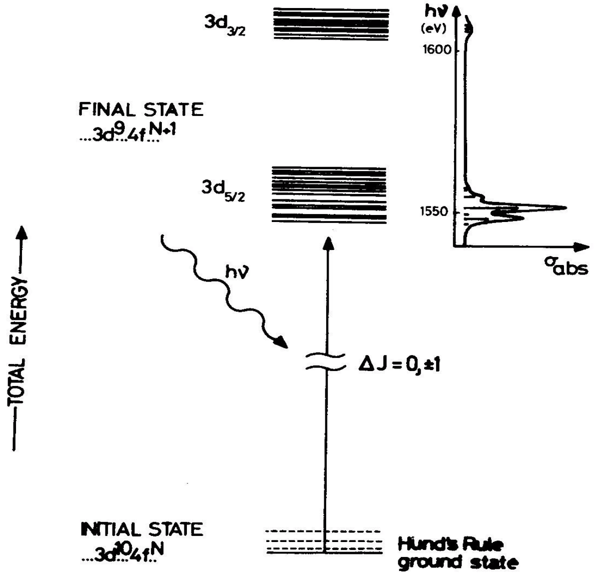
Transitions delocalised states
(interaction with neigbouring atoms >> intra-atomic interactions)
Single electron approximation
K-edges, $L_{2,3}$ edges of TM metallic systems

Transitions to localised states (intra-atomic interactions >> interaction with environment)
Multiplets - atomic approximation
$M_{4,5}$-edges of rare earths (3d → 4f transitions)
magnetic, crystal fields are weak perturbations
$L_{2,3}$ edges of TM ionic systems
crystal field environment is more important

Rare earth ions : calculation of $M_{4,5}$ (3d ® 4f) spectra

- **Atomic model** : electronic transitions take place between the ground-state and the excited state of the *complete* atom (atomic configuration) :

$3d^{10}\,4f^{N} \rightarrow 3d^{9}\,4f^{N+1}$



- calculation of the discrete energy levels of the initial and final state N-particle wavefunctions (atomic multiplets)
- the absorption spectrum consists of several lines corresponding to all the selection-rule allowed transitions from Hund's rule ground state to the excited states.

Rare earth ions : calculation of $M_{4,5}$ (3d ® 4f) spectra

$3d^{10}\,4f^{N} \rightarrow 3d^{9}\,4f^{N+1}$

Each term of the multiplet is characterised by quantum numbers L, S, J:

$$^{(2S+1)}X_J$$

L =	0	1	2	3	4	5	6
X =	S	P	D	F	G	H	I

multiplicity : (2S + 1)

S = 0 (singlet) S = 1/2 (doublet) etc ..

$|L - S| \leq J \leq L + S$

degeneracy : (2L + 1) (2S + 1)

example: term ^3P is 3x3 = 9-fold degenerate.

Calculation of atomic spectra

Fermi 's Golden Rule: $\sigma_{abs} \propto S_q \, |\langle \Phi_f | \mathbf{e}_q \cdot \mathbf{r} | \Phi_i \rangle|^2 \, \delta(h\omega - E_f + E_i)$

for a ground state |J,M> and a polarisation q

$$\sigma^{q}_{JM \rightarrow J'M'} \propto |\langle J'M' \,|\, \mathbf{e}_q \cdot \mathbf{r} \,|\, JM \rangle|^{2} \, \delta(h\omega - E_{J',M'} + E_{J,M})$$

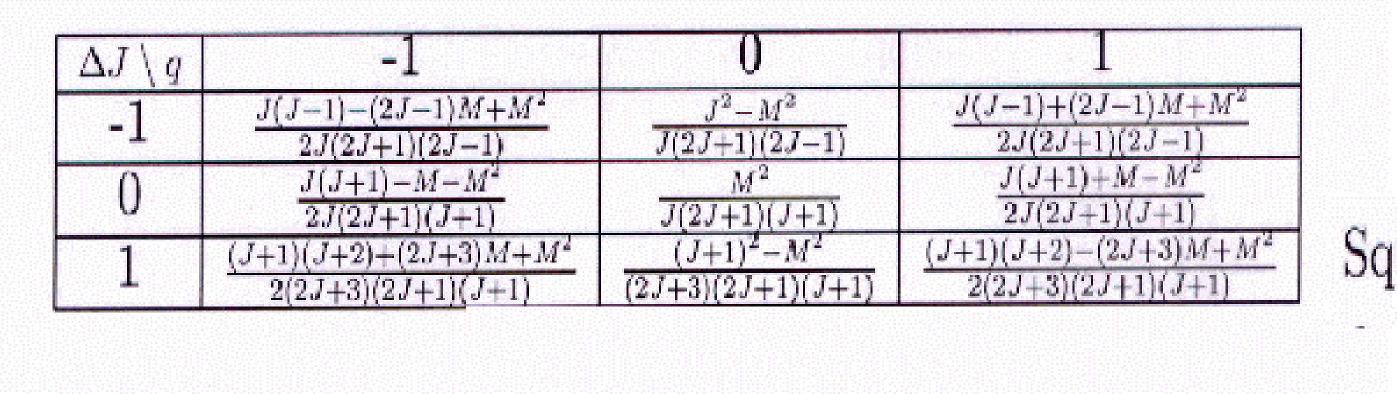
total spectrum is the sum over all the final J' states

by applying Wigner-Eckhart theorem:

$$\sigma^{q}_{JM \rightarrow J'M'} \propto < \left[(-1)^{J-M} \begin{pmatrix} J & 1 & J' \\ -M & q & M' \end{pmatrix} \right]^2 |\langle J' \| P_q \| J \rangle|^2$$

3J symbol ≠ 0 if: $\Delta J = (J' - J) = -1, 0, +1$

$\Delta M = (M' - M) = q$ q = -1 (right); q = 1 (left), q=0 (linear)



$\Delta J \setminus q$	-1	0	1
-1	$\frac{J(J-1)-(2J-1)M+M^2}{2J(2J+1)(2J-1)}$	$\frac{J^2-M^2}{J(2J+1)(2J-1)}$	$\frac{J(J-1)+(2J-1)M+M^2}{2J(2J+1)(2J-1)}$
0	$\frac{J(J+1)-M-M^2}{2J(2J+1)(J+1)}$	$\frac{M^2}{J(2J+1)(J+1)}$	$\frac{J(J+1)+M-M^2}{2J(2J+1)(J+1)}$
1	$\frac{(J+1)(J+2)+(2J+3)M+M^2}{2(2J+3)(2J+1)(J+1)}$	$\frac{(J+1)^2-M^2}{(2J+3)(2J+1)(J+1)}$	$\frac{(J+1)(J+2)-(2J+3)M+M^2}{2(2J+3)(2J+1)(J+1)}$

$$\begin{pmatrix} J & 1 & J' \\ -M & q & M' \end{pmatrix}^2$$

Squared 3J-symbols:

For a ground state |J,M> and for every ΔJ :

$$\sigma^{q=1} - \sigma^{q=-1} \propto M$$

$$\text{XMCD} \propto S_{\Delta J}\,(\sigma^{q=1} - \sigma^{q=-1}) \propto M\,[2(2J-1)\,P^{-1} + 2\,P_0 - 2(2J+3)\,P^{1}]$$

If several Mj states are occupied:

$$\text{XMCD} \propto \langle M_J \rangle$$

- XMCD is therefore proportional to the magnetic moment of the absorbing atom
- XMCD can be used as element selective probe of magnetic ordering

Case of Yb^{3+} : XAS spectrum

$Yb\ 3^+$ $3d^{10}4f^{13} \rightarrow 3d^{9}4f^{14}$

Without magnetic field:

initial state : $4f^1$ L=3 S=1/2 terms : $^2F_{5/2}$ $^2F_{7/2}$

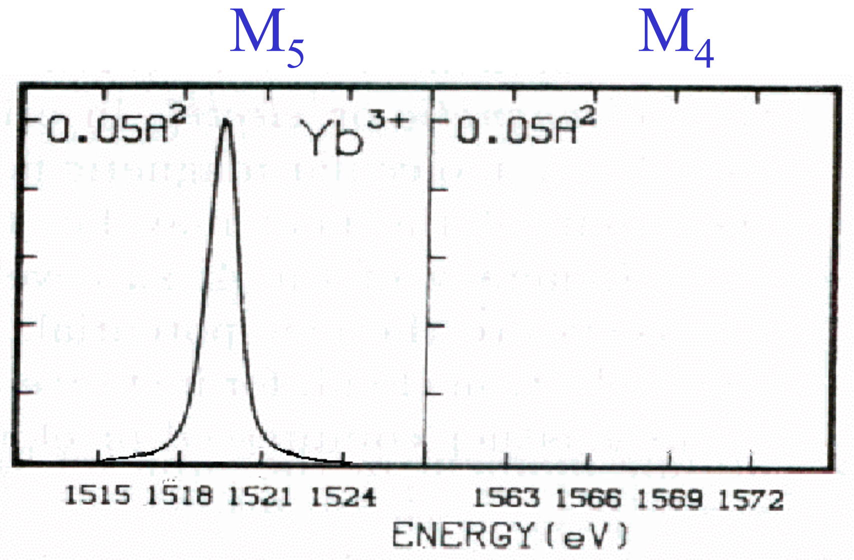
$^2F_{7/2}$ is Hund’s rule ground state (max S then max L then max J)

final state : $3d^1$ L=2 S=1/2 terms : $^2D_{3/2}$ $^2D_{5/2}$

selection rules : $\Delta J = 0; \pm 1$

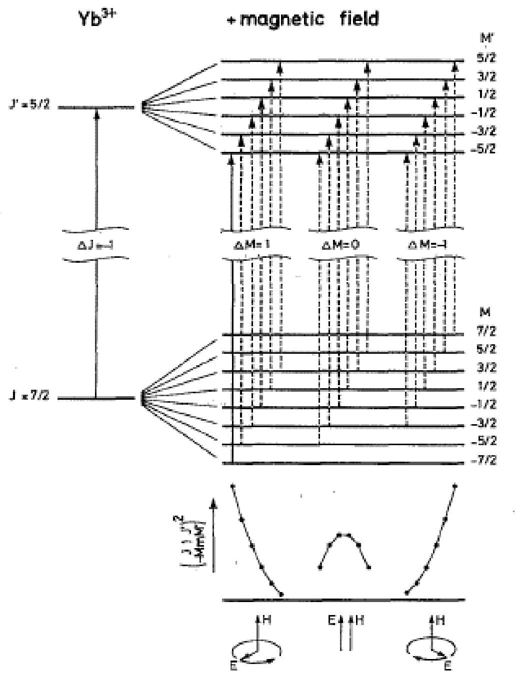
only one transition from **$^2F_{7/2}$ to $^2D_{5/2}$** with $\Delta J = -1$ (**M_5** edge)

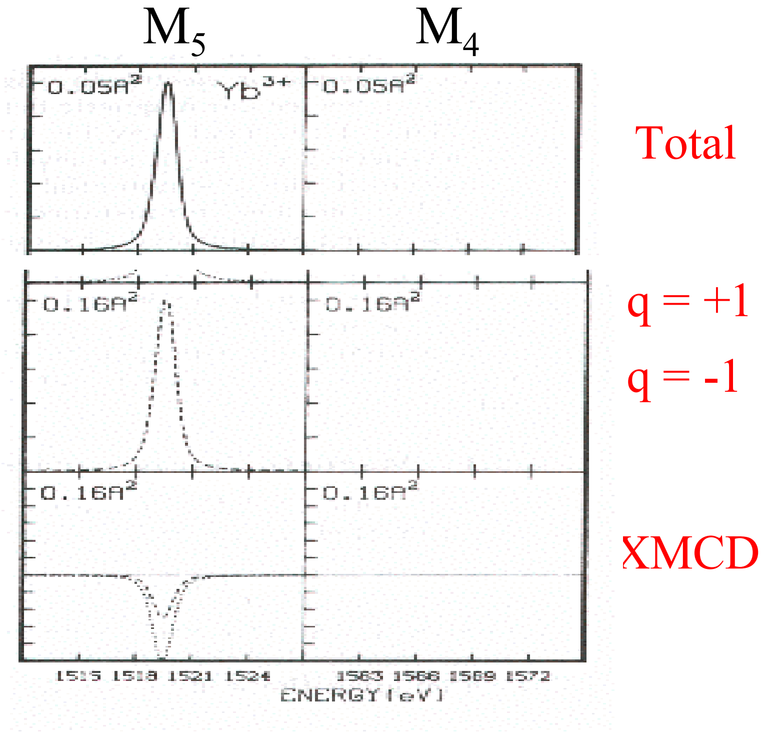
$^2F_{7/2}$ to $^2D_{3/2}$ (**M_4** edge) is **not allowed**



In spherical symmetry the GS is (2J+1) degenerate and all Mj levels are equally occupied; **<Mj>=0 and the XAS spectrum does not depend on the polarisation**

Case of Yb^{3+} : XMCD spectrum





With magnetic field - Zeeman splitting:

18 lines, 3 groups with ΔM = 0 (linear parallel) ; ΔM = ± 1 (left, right)

Energy of M$_J$ - levels: $E_{M_j} = -g_{aJ}\mu_B H M_J$

For T = 0K: only $M_j = -7/2$ level is occupied : only ΔM = + 1 line is allowed

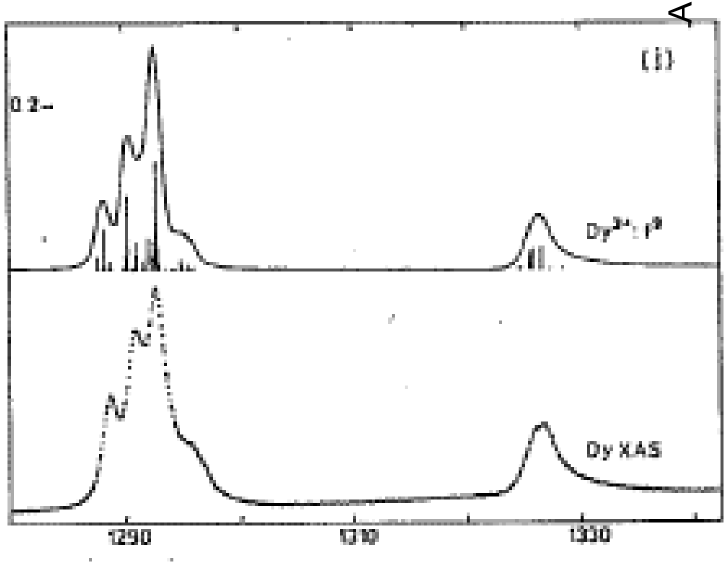
? only LEFT polarisation is absorbed: maximum XMCD signal

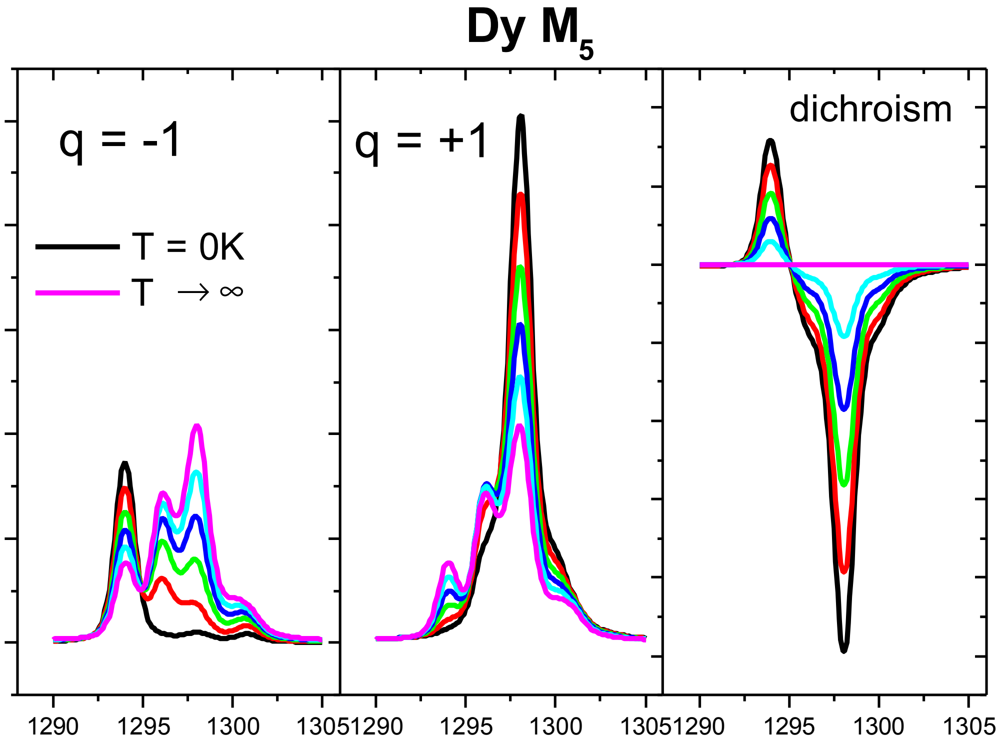
For T > 0K higher M$_J$ levels are occupied according to **Boltzmann-distribution**

XMCD is reduced, will be proportional to $\langle M_J \rangle$ and will be non zero as long as $\mathbf{kT < g_{aJ}\mu_B H}$

Case of Dy^{3+}

$4f^9$ $^6H_{15/2}$ ground state





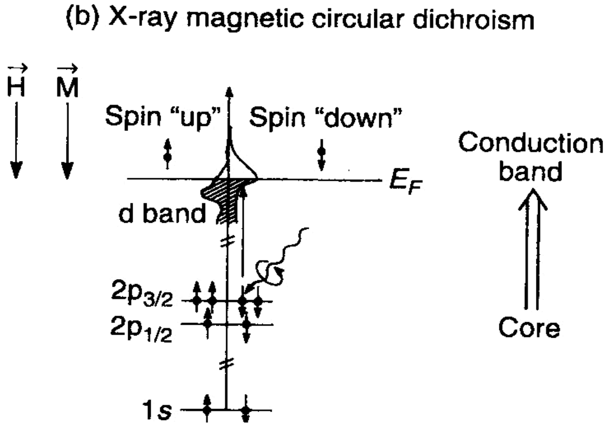
XAS spectra and XMCD vs reduced temperature

$T_R = kT / g_{aJ} \mu_B H$

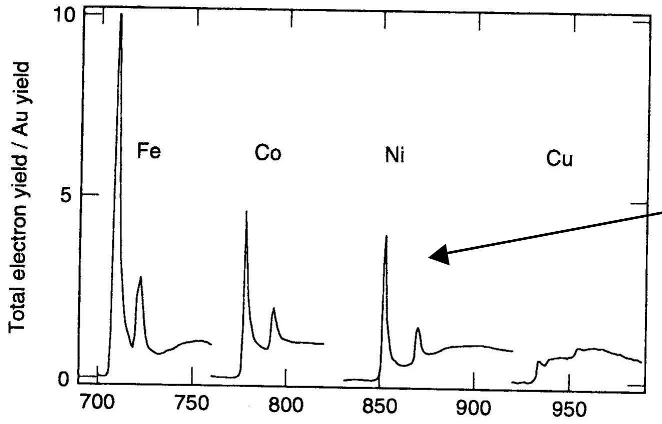
$L_{2,3}$ edge XMCD in 3d metallic transition metals

- Magnetic 3d metals: Fe ($3d^7$), Co ($3d^8$), Ni ($3d^9$)
- atomic (localized) description not valid anymore

? one-electron picture: transition of one electron from core spin-orbit split **$2p_{1/2}$, $2p_{3/2}$** level to valence **3d** band; the other electrons are ignored in the absorption process


(b) X-ray magnetic circular dichroism

Experimental $L_{2,3}$ edge spectra



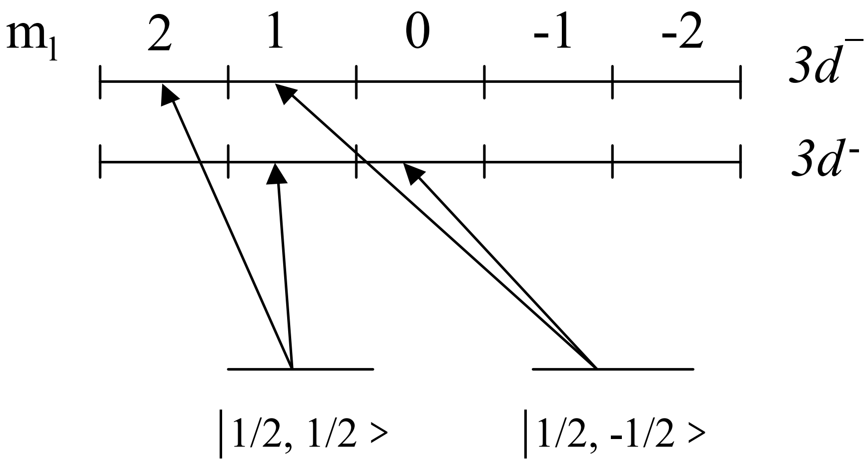
white line

here we deal with the polarisation dependence of the ' white lines '

$$s_q \ \mu \ S_q \ |< F_f \,|\, \mathbf{e_q} \,^{x}\, \mathbf{r} \,|\, F_i >|^2 \ r\ (\mathbf{h}w - \mathbf{E_i})$$

One electron picture: transitions from 2*p* to 3*d* band split by exchange in *3d*$^-$ and *3d*$^{‾}$

$$|l, m_l, s, m_s> = = a_{ml}\, Y_{1,ml}\, |s, m_s>$$



$\mid l,s,J,m_j>$	$\mid l,m_l,s,m_s>$ basis
$\mid\frac{1}{2},\frac{1}{2}\rangle$	$-\frac{1}{\sqrt{3}}Y_{10}^{\uparrow}+\frac{\sqrt{2}}{\sqrt{3}}Y_{11}^{\downarrow}$
$\mid\frac{1}{2},-\frac{1}{2}\rangle$	$-\frac{\sqrt{2}}{\sqrt{3}}Y_{1\text{-}1}^{\uparrow}+\frac{1}{\sqrt{3}}Y_{10}^{\downarrow}$

L_2 edge - left polarisation (Dm_l=+1)

R=$\grave{\text{o}}R_{nl}{}^*(r)R_{n'l'}(r)\ r^3 dr$

$$I^{\uparrow} = \sum_{i,f} |<f\,|P_1\,|i>\,|^2 = (1/3\ |<2,1\ |P_1\,|1,0>|^2 + 2/3\ |<2,0\ |P_1\,|1,-1>|^2\,)\ R^2$$

$$I^{\downarrow} = \Sigma\ |<f\,|P_1\,|i>\,|^2 = (2/3\ |<2,2\ |P_1\,|1,1>|^2 + 1/3\ |<2,1\ |P_1\,|1,0>|^2\,)\ R^2$$

It can be calculated (Bethe and Salpeter) that:

$|<2,2\ |P_1|1,1>|^2 = 2/5$
$|<2,1\ |P_1|1,0>|^2 = 1/5$
$|<2,0\ |P_1|1,-1>|^2 = 1/15$

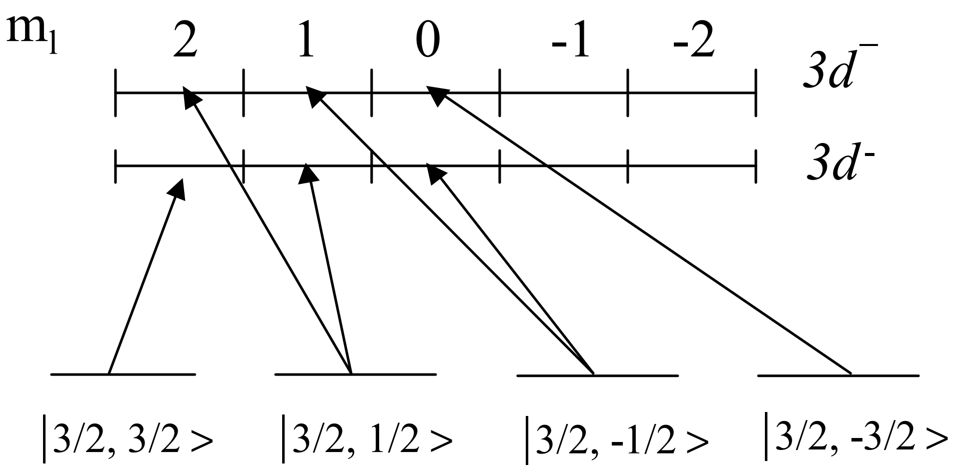
$I^{\uparrow} = 1/3(\ |<2,1\ |\mathbf{P}_1|1,0>|^2 + 2/3\ |<2,0\ |\mathbf{P}_1|1,-1>|^2\ )\ R^2 =$
$= (1/3 * 1/5 + 2/3 * 1/15)\ R^2 = 1/9\ R^2$

$I^{\downarrow} = 2/3\ |<2,2\ |\mathbf{P}_1|1,1>|^2 + 1/3\ |<2,1\ |\mathbf{P}_\mathbf{1}|1,0>|^2\ \ R^2$
$= (2/3 * 2/5 + 1/3 * 1/5)\ R^2 = 1/3\ R^2$

$I^{\uparrow} / (I^{\uparrow} + I^{\downarrow}) = 0.25$ LCP at the L_2 edge
$I^{\downarrow} / (I^{\uparrow} + I^{\downarrow}) = 0.75$

$I^{\uparrow} / (I^{\uparrow} + I^{\downarrow}) = 0.75$ RCP at the L_2 edge
$I^{\downarrow} / (I^{\uparrow} + I^{\downarrow}) = 0.25$

L_3 edge



$\vert \frac{3}{2}, \frac{3}{2} \rangle$	$Y^{\uparrow}_{11}$
$\vert \frac{3}{2}, \frac{1}{2} \rangle$	$\frac{\sqrt{2}}{\sqrt{3}} Y^{\uparrow}_{10} + \frac{1}{\sqrt{3}} Y^{\downarrow}_{11}$
$\vert \frac{3}{2}, -\frac{1}{2} \rangle$	$\frac{1}{\sqrt{3}} Y^{\uparrow}_{1\text{-}1} + \frac{\sqrt{2}}{\sqrt{3}} Y^{\downarrow}_{10}$
$\vert \frac{3}{2}, -\frac{3}{2} \rangle$	$Y^{\downarrow}_{1\text{-}1}$

Left polarisation:

$\mathbf{I}^{-} = (|\langle 2,2\, |\mathbf{P}_1|\, 1,1\rangle|^2 + 2/3\, |\langle 2,1\, |\mathbf{P}_1|\, 1,0\rangle|^2 + 1/3\, |\langle 2,0\, |\mathbf{P}_1|\, 1,-1\rangle|^2)\, R^2$

$= (2/5 + 2/3 * 1/5 + 1/3 * 1/15)\, R^2 = \mathbf{5/9\, R^2}$ $\quad \mathbf{R} = \int R_{nl}^{*}(r) R_{n'l'}(r)\, r^3 dr$

$\mathbf{I}^{\overline{\ }} = (1/3 |\langle 2,2\, |\mathbf{P}_1|\, 1,1\rangle|^2 + 2/3\, |\langle 2,1\, |\mathbf{P}_1|\, 1,0\rangle|^2 + |\langle 2,0\, |\mathbf{P}_1|\, 1,-1\rangle|^2)\, R^2$

$= (1/3 * 2/5 + 2/3 * 1/5 + 1/15) = \mathbf{1/3\, R^2}$

$I^{\uparrow} / (I^{\uparrow} + I^{\downarrow}) = 0.625$ LCP at the L_3 edge
$I^{\downarrow} / (I^{\uparrow} + I^{\downarrow}) = 0.375$

$I^{\uparrow} / (I^{\uparrow} + I^{\downarrow}) = 0.375$ RCP at the L_2 edge
$I^{\downarrow} / (I^{\uparrow} + I^{\downarrow}) = 0.625$

	I - left	I ¯ left	I - right	I ¯ right
L$_2$	1/9 R^2	1/3 R^2	1/3 R^2	1/9 R^2
L$_3$	5/9 R^2	1/3 R^2	1/3 R^2	5/9 R^2

Ni, Co metal (strong ferromagnets): only empty r ¯

L$_2$ **total** (LCP+RCP) µ (1/3 + 1/9) R^2 = **4/9R^2**
L$_3$ **total** (LCP+RCP) µ (1/3 + 5/9) R^2 = **8/9 R^2**
branching ratio L$_3$: L$_2$ = 2 : 1

L$_2$ **XMCD** (LCP-RCP) µ (1/3 - 1/9) R^2 = **2/9 R^2**
L$_3$ **XMCD** (LCP-RCP) µ (1/3 - 5/9) R^2 = **-2/9 R^2**
branching ratio XMCD DL$_3$: DL$_2$ **= 1 : -1**

In general: XMCD = (**I - left** r↑ + I ¯ left r↓) - (**I - right** r↑ + I ¯ right r↓)

= r - (**I - left - I - right**) + r↓ (I ¯ left - I ¯ right) = r↑ (**I - left - I** ¯ left) + r↓ (I ¯ left - **I - left**) =

= (r - - r¯) (**I - left - I** ¯ left) **XMCD** ¹ 0 if r↑ ¹ r↓

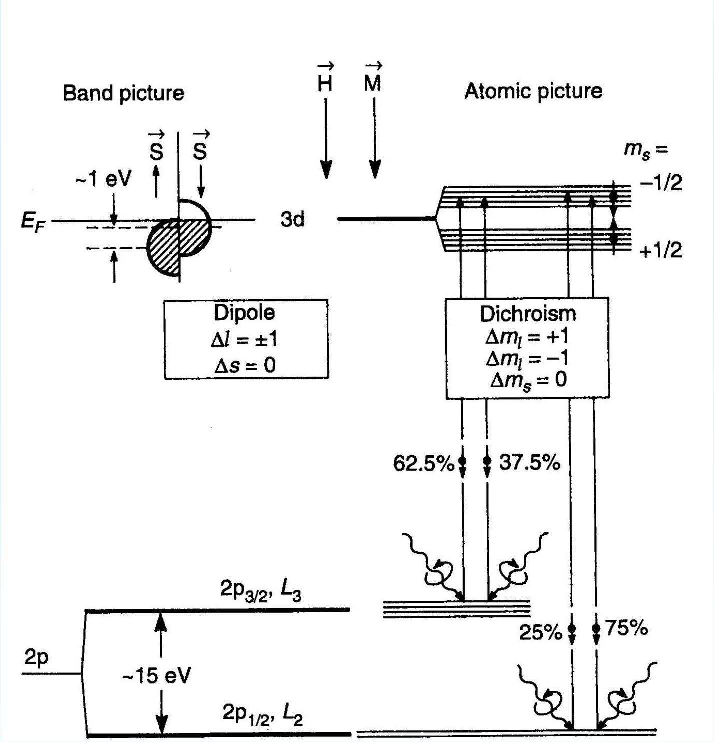
Two-step model (Wu and Stöhr)

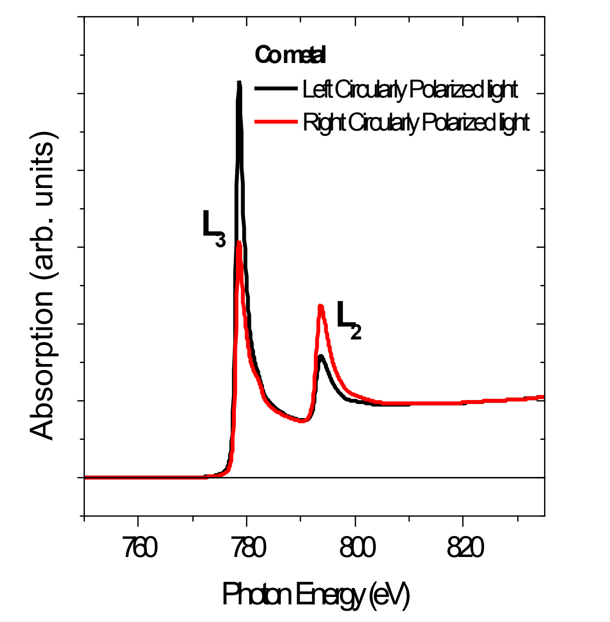
Step 1 : spin-polarised electrons emitted by the spin-orbit split 2p band

75% spin down and 25% spin up electrons at the L_2-edge with LCP light

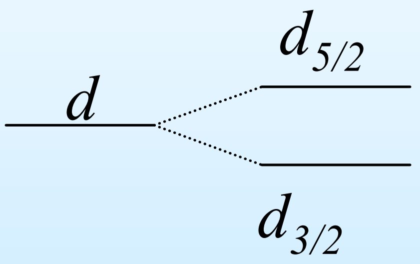
37.5% spin down and 62.5% spin up electrons at the L_3-edge with LCP light

Step 2: the exchange split *d*-band acts as spin-detector.





Spin-orbit splitting in *d*-band



$$2p_{3/2} \rightarrow 4d_{3/2,\ 5/2}$$

$$2p_{1/2} \rightarrow 4d_{3/2,\ \cancel{5/2}}$$

- Spin-orbit in the 3d states

- Intensity shift from L_2 to L_3 edge → $L_3 : L_2 \geq 2 : 1$

- for XMCD there is departure from the $\Delta L_3 : \Delta L_2 = 1 : -1$; the integrated XMCD signal is proportional to the orbital moment in the 3d band.

B.T.Thole and G.v.d.Laan, Europhys.Lett. 4, 1083 (1987)

Sum rules of XMCD

Sum rules relate dichroism and total absorption to the ground-state orbital and spin magnetic moment of the probed element and shell:

$L_{2,3}$-edges of Fe → Fe 3*d*-moments.

Orbital moment sum rule:

$$\langle L_Z \rangle = [2l(l+1)(4l+2-n)]/[l(l+1)+2 - c(c+1)] \bullet$$

$$\left[\int_{j+ + j-} dw(m^{+} - m^{-}) \,/ \int_{j+ + j-} dw(m^{+} + m^{-} + m^{0}) \right]$$

l = orbital quantum number of the valence state,
c = orbital quantum number of the core state,
n = number of electrons in the valence state

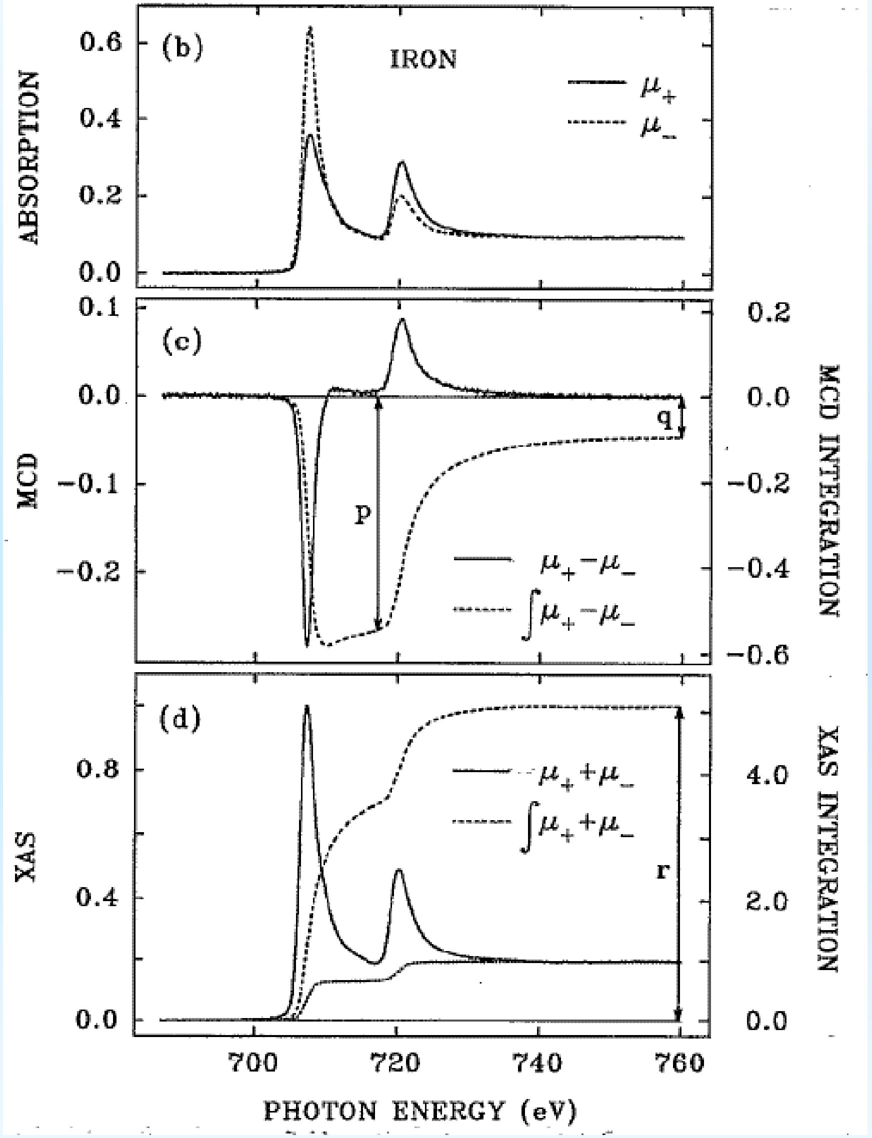
m^{+} (m^{-}) = absorption spectrum for left (right) circularly polarized light.

m^{0} = absorption spectrum for linearly polarized light, with polarization parallel quantization axis.

j^{+} (j^{-}) = (l + 1/2) resp. (l - 1/2) absorption (ex. $2p_{3/2}$, $2p_{1/2}$)

B.T.Thole *et al.*, Phys.Rev.Lett. 68, 1943 (1992)
M.Altarelli, Phys.Rev.B 47, 597 (1993)

Sum rules of XMCD



C.T.Chen *et al.*, PRL 75, 152 (1995)

For $L_{2,3}$-edges $c = 1$ ($2p$), $l = 2$ (d):

$$\langle L_Z \rangle = 2(10-n) \bullet (DL_3 + DL_2)$$

$$/ \int_{L3+L2} dw\,(m^+ + m^- + m^0)]$$

$$q = DL_3 + DL_2$$

$$r = m^+ + m^- = (2/3)(m^+ + m^- + m^0)$$

$$\langle L_Z \rangle = 4q\,(10-n) / 3r$$

Sum rules of XMCD

Spin moment sum rule

$$\langle S_Z\rangle + c_2(n)\,\langle T_z\rangle = c_1(n)\left[\int_{j+} dw\,(m^+ - m^-) - [(c+1)/c]\int_{j-} dw\,(m^+ - m^-)\right] / \left[\int_{j++j-} dw\,(m^+ + m^- + m^0)\right]$$

$c_1(n) = 3c(4l + 2 - n)/[l(l+1) - 2 - c(c+1)]$

$c_2(n) = \{l(l+1)[l(l+1)+2c(c+1)+4]-3(c-1)^2(c+2)^2\} / 6lc(l+1)(4l+2-n)$

$\langle T_Z\rangle$ = expectation value of magnetic dipole operator

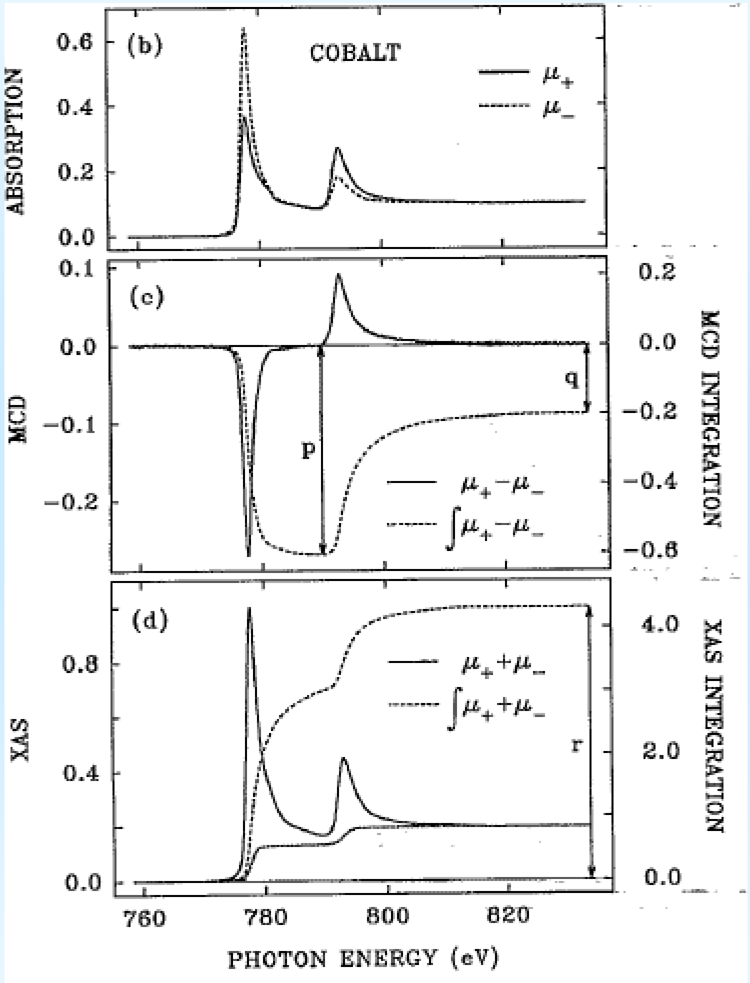
$$T = \mathbf{S} - \mathbf{r}\,(\mathbf{r} \bullet \mathbf{s}) / r^2$$

which expresses the anisotropy of the spin moment within the atom

For $L_{2,3}$-edges:

$$\langle S_Z\rangle + (7/2)\,\langle T_Z\rangle = (3/2)(10-n)[(\Delta L_3 - 2\Delta L_2)/\int_{L3+L2} dw\,(m^+ + m^- + m^0)]$$

C.T.Chen *et al.*, PRL 75, 152 (1995)



$\mathbf{\langle S_Z\rangle} + (7/2)\,\langle T_Z\rangle =$

$(3/2)(10-n)[(\Delta L3 - 2\Delta L2)/\int_{L3+L2} dw\,(m+ \;+\; m- \;+\; m\,0)]$

$= (3/2)(10-n)(p - 2\,(q-p))/(3/2)r =$

$= (3p - 2q)(10-n)/r$

The magnetic dipole operator T

An anisotropy of the spin moment (magnetic dipole) can be induced either by:

- anisotropic charge distribution (quadrupole moment)

  zero in cubic systems (isotropic charge)
  enhanced at surfaces and interfaces

- spin-orbit interaction

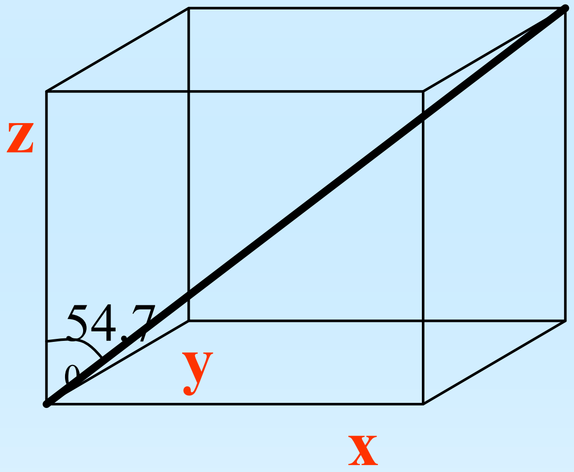
  small in 3*d* - metals
  larger in 4d and 5d metals .

Experimental determination of **<T>**

Stöhr, König [PRL 75, 3749 (1995)]

$$\langle T_x\rangle + \langle T_y\rangle + \langle T_z\rangle = 0$$

with x, y and z perpendicular to each other and z // easy magnetization axis.



Measurement along three perpendicular directions (with sa-turating field) or at « magic » angle:

$\cos 54.7\,^{0}(T_x + T_y + T_z) = 0$

allow to eliminate $\langle T_z\rangle$ and to obtain $\langle S_z\rangle$

Validity and applicability of sum rules

Determination of L_z

- main approximation $R_{2p3/2} = R_{2p1/2}$:
according to Thole *et al.* (PRL 68, 1943 (1992)) the errors in <Lz>are ~1% for transition metals

- sum rules have been obtained from atomic calculations :
according to Wu et al. (PRL 71, 3581 (1993)) who performed band structure calculations, the errors are 5-10%.

Determination of S_z

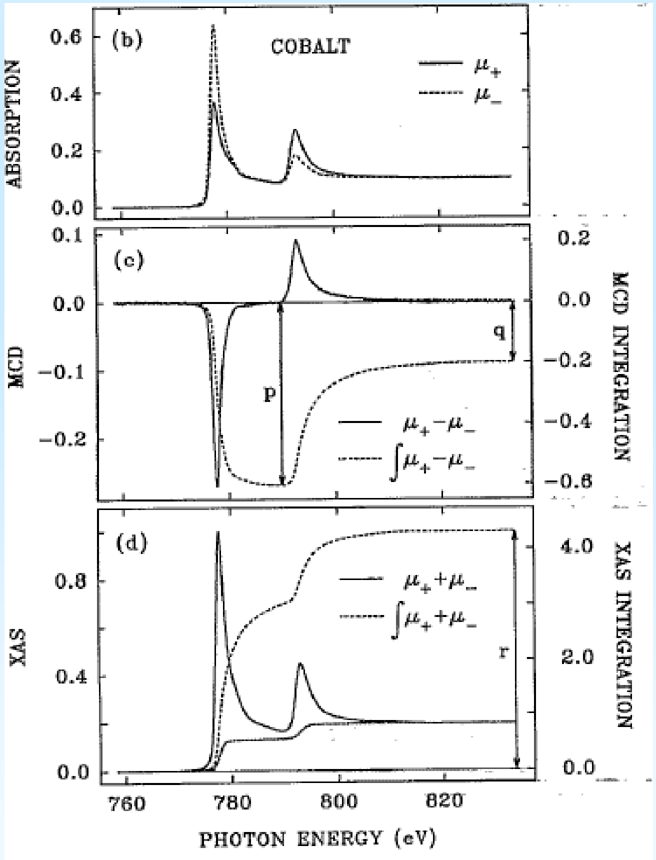
- L_2 and L_3 edge intensities need to be separated:
we suppose:
spin orbit coupling >> Coulomb interaction
not true for early transition metal

- T_z is supposed to be small: true for cubic systems but not at surfaces/interfaces

Experimental application of sum rules

Sources of errors:

- determination of the background $m^+ + m^- + m^0$
- rate of circular polarization
- number of electrons n



$$\langle L_Z \rangle = 4q\,(10-n)\,/\,3r$$

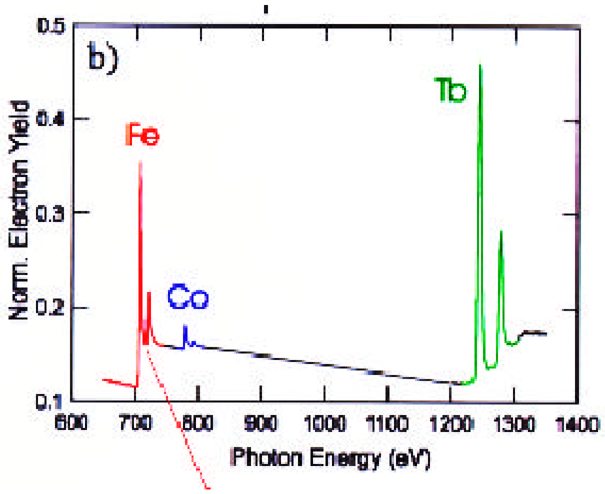
$$\langle S_z \rangle + (7/2)\langle T_Z \rangle = (3p - 2q)(10-n)/r$$

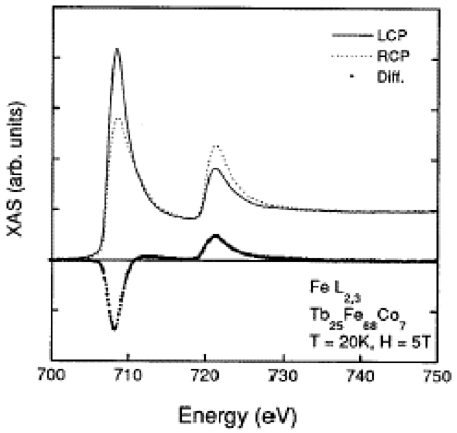
Summary:

-XMCD is an element selective probe of magnetisation

- XMCD is proportional to <M> along the propagation vector **k** of the x-ray beam

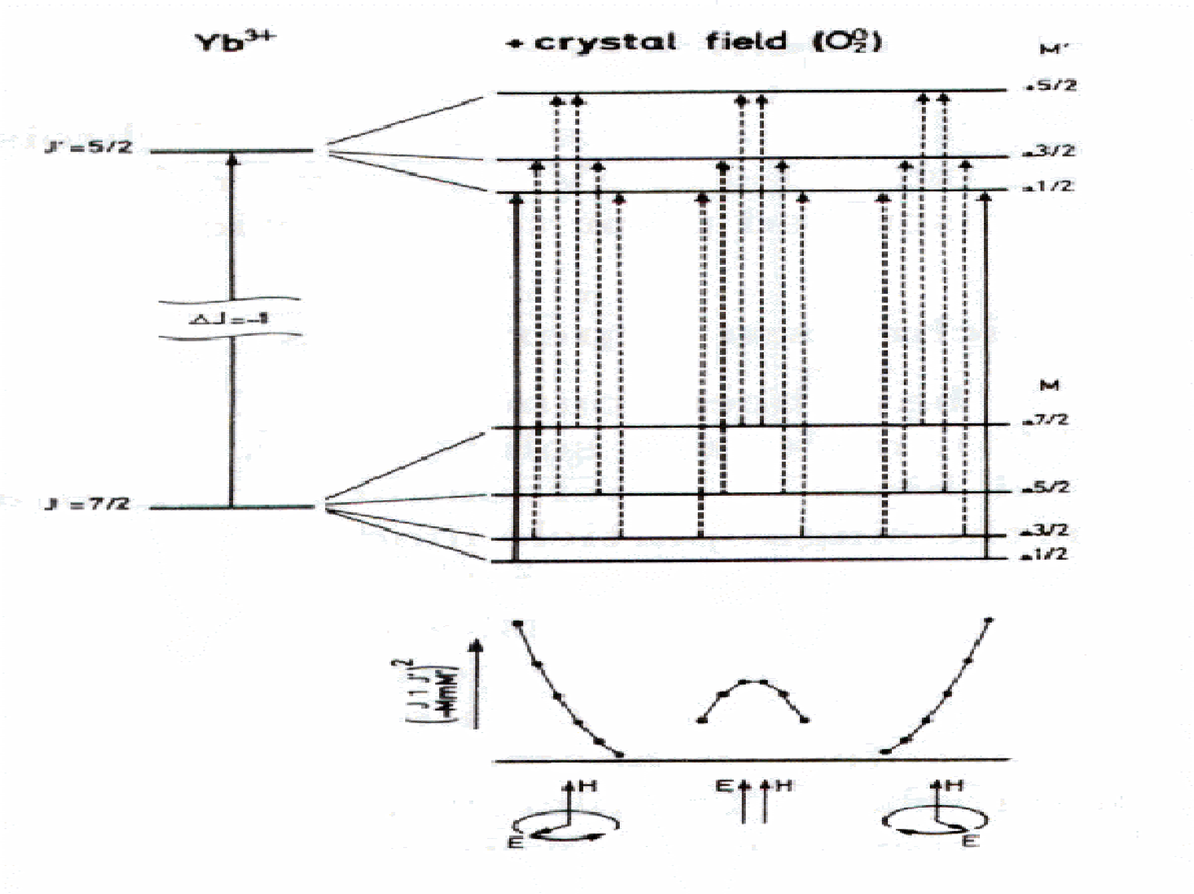
- Sum rules allow to obtain separately orbital and spin contributions to the magnetic moments from the integrated XMCD signal.





Crystal field

Axial crystal field (symmetry O_2^0)(Yb)

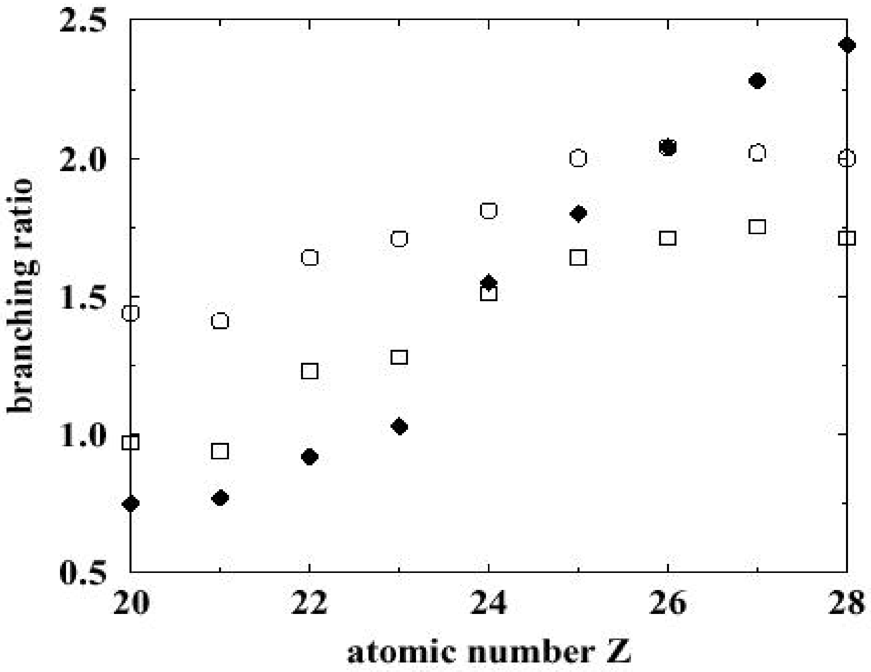


CF: no splitting of $+M_J$ and $-M_J$ → no circular dichroism

Influence of the core-hole

Shape of spectra: intensity increase at threshold

Mixing of $2p_{3/2}$ and $2p_{1/2}$ character if $2p$ spin-orbit coupling is small
→ branching ratio changed



O: calc. without with □electron- core hole interaction; ♦ experiment

J.Schwitalla and H.Ebert, Phys.Rev.Lett. 80, 4586 (1998).

Influence of the bandstructure

Valence band composed of different band states ϕ_{ik} , expanded using local spherical harmonics:

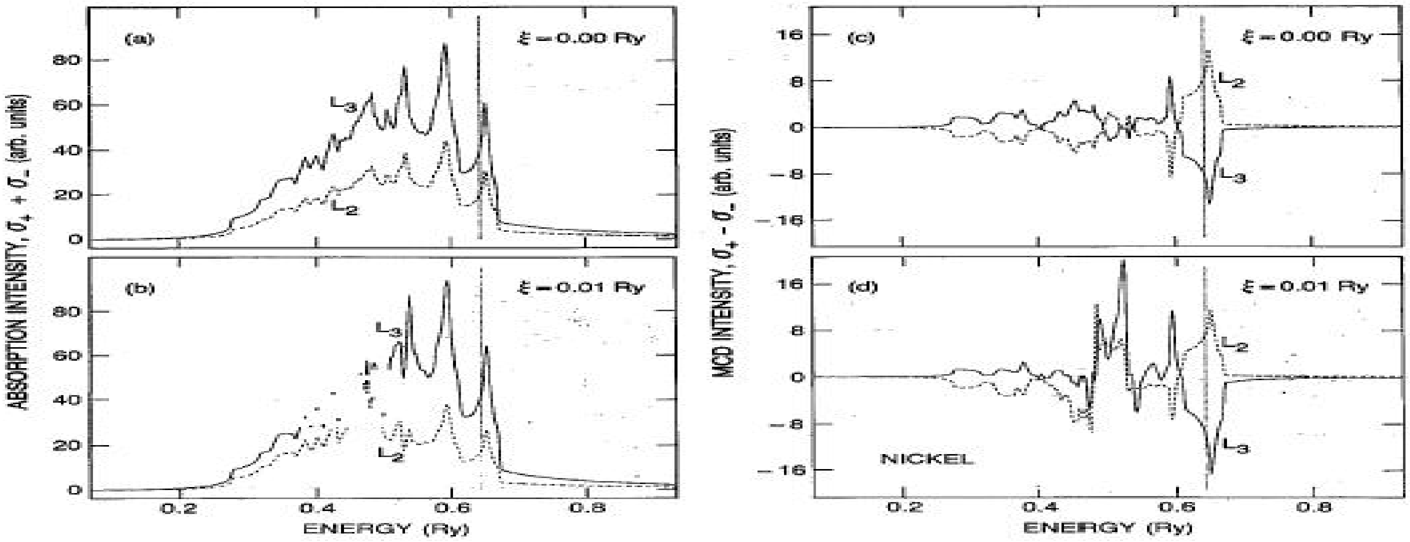
$$\phi_{ik}(r) = S\ a_{lm,ik}\ R_{nl,ik}(r) Y_{lm}^{S},$$

k = wave vector, r = position , S = spin (up or down)

Transitions from the $2p$-level to ϕ_{ik} calculated as before, replacing the factors ../√5 by $a_{lm,ik}$. Example:

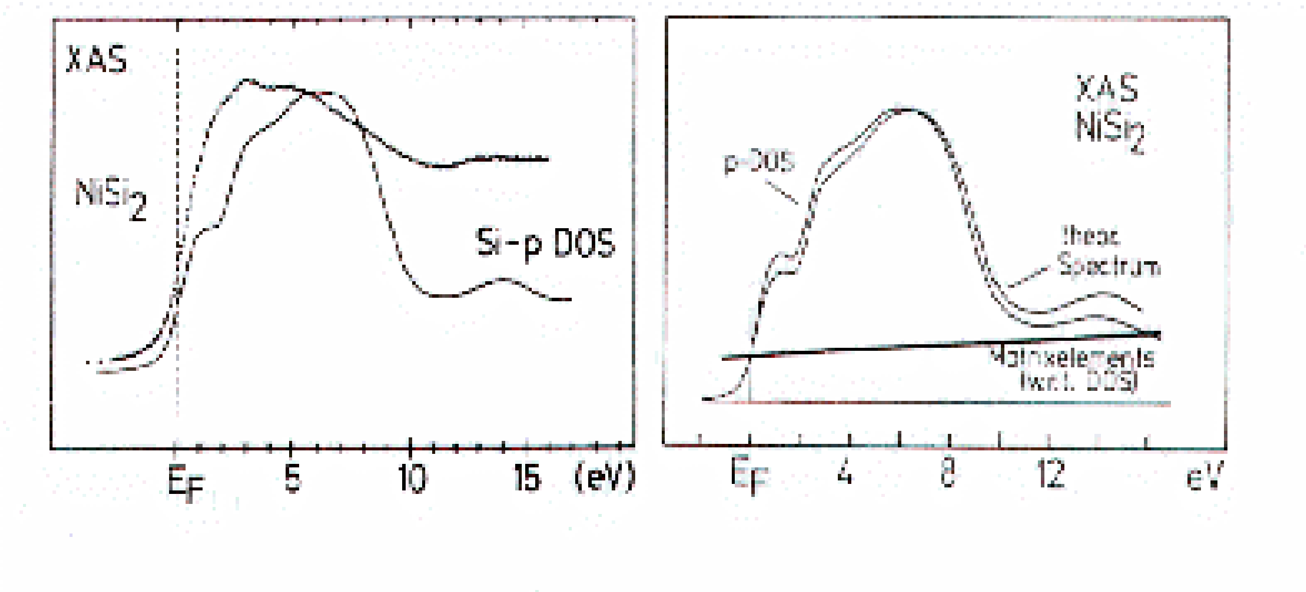
$$<\phi_{\boldsymbol{ik}}\ |\mathbf{P}_{-1}|2p_{3/2}>|^2 = \ (1/45)\{18|a_{2-2}|^2 + 6|a_{2-1}|^2 + |a_{20}|^2\}R^2.$$

Total



N.V.Smith *et al.*, Phys.Rev.B 46, 1023 (1992)

Density of states vs. XAS spectrum



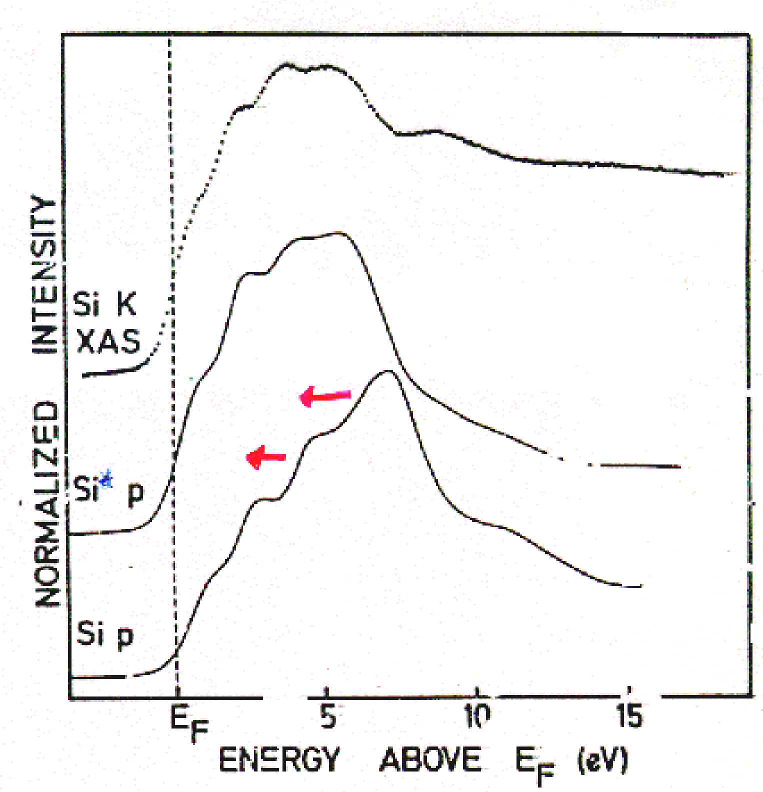
Si K-edge absorption of $NiSi_2$ compared to Si *p*-DOS.

Right: including energy dependence of matrix elements

Discrepancies:

- Influence of core hole
- Dynamics of transition

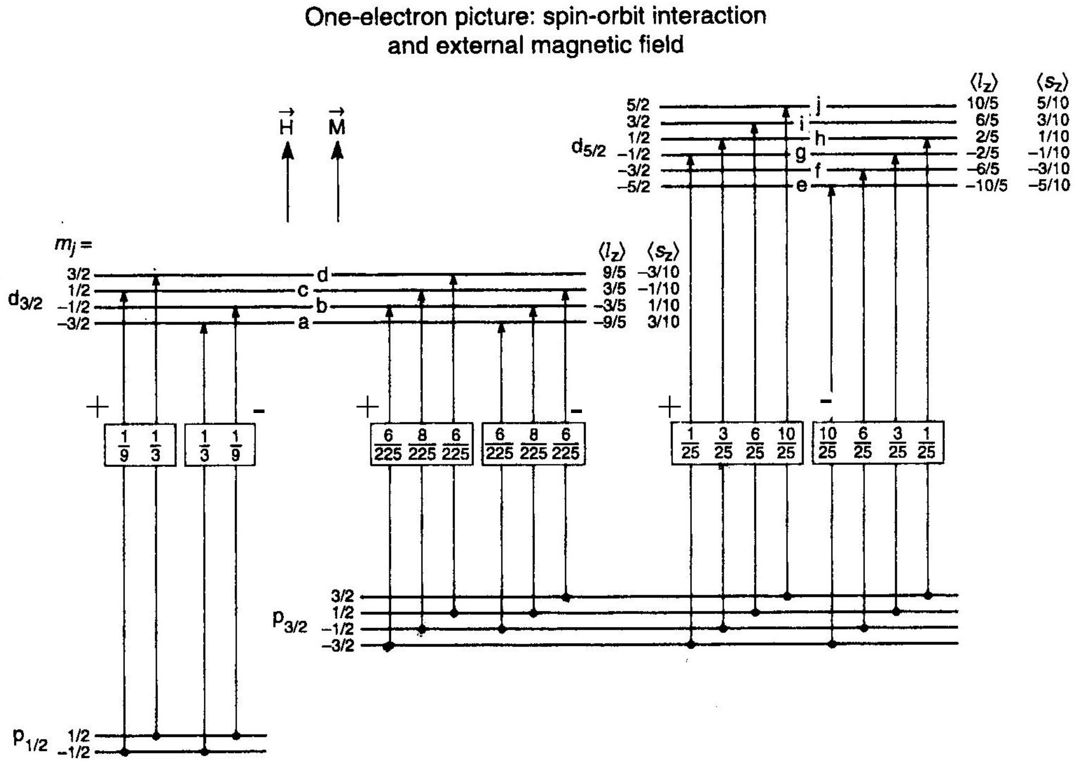
Core hole effect



- Core hole pulls down the DOS
- **Final State Rule:** Spectral shape of XAS looks like final state DOS
- **Initial State Rule:** Intensity of XAS
- is given by the initial state

Phys. Rev. B. 41, 11899 (1991)

Spin-orbit splitting in *d*-band



d$_{3/2}$

$\left\| \frac{3}{3}, \frac{3}{2} \right\rangle$	$-\frac{\sqrt{5}}{5} Y_{21}^{\uparrow} + \frac{2\sqrt{5}}{5} Y_{22}^{\downarrow}$
$\left\| \frac{3}{2}, \frac{1}{2} \right\rangle$	$-\frac{\sqrt{10}}{5} Y_{20}^{\uparrow} + \frac{\sqrt{15}}{5} Y_{21}^{\downarrow}$
$\left\| \frac{3}{2}, -\frac{1}{2} \right\rangle$	$-\frac{\sqrt{15}}{5} Y_{2-1}^{\uparrow} + \frac{\sqrt{10}}{5} Y_{20}^{\downarrow}$
$\left\| \frac{3}{2}, -\frac{3}{2} \right\rangle$	$-\frac{2\sqrt{5}}{5} Y_{2-2}^{\uparrow} + \frac{\sqrt{5}}{5} Y_{2-1}^{\downarrow}$

d$_{5/2}$

$\left\| \frac{5}{2}, \frac{5}{2} \right\rangle$	$Y_{22}^{\uparrow}$
$\left\| \frac{5}{2}, \frac{3}{2} \right\rangle$	$\frac{2\sqrt{5}}{5} Y_{21}^{\uparrow} + \frac{\sqrt{5}}{5} Y_{22}^{\downarrow}$
$\left\| \frac{5}{2}, \frac{1}{2} \right\rangle$	$\frac{\sqrt{15}}{5} Y_{20}^{\uparrow} + \frac{\sqrt{10}}{5} Y_{21}^{\downarrow}$
$\left\| \frac{5}{2}, -\frac{1}{2} \right\rangle$	$\frac{\sqrt{10}}{5} Y_{2-1}^{\uparrow} + \frac{\sqrt{15}}{5} Y_{20}^{\downarrow}$
$\left\| \frac{5}{2}, -\frac{3}{2} \right\rangle$	$\frac{\sqrt{5}}{5} Y_{2-2}^{\uparrow} + \frac{2\sqrt{5}}{5} Y_{2-1}^{\downarrow}$
$\left\| \frac{5}{2}, -\frac{5}{2} \right\rangle$	$Y_{2-2}^{\downarrow}$

The sum of transition intensities between a pair of initial and final states is the same for LCP and LCP.

XMCD is present only when the different m$_j$ states have different occupation numbers.

$d_{3/2}$-states occupancies:
a (m_j=-3/2), b (m_j=-1/2), c (m_j=1/2) and d (m_j=3/2)

$d_{5/2}$-states occupancies:
e (mj=-5/2), f (mj=-3/2), g (mj=-1/2) , h (mj=1/2) i (mj=3/2)
j (mj=5/2)

$$\Delta I_{L2} = d/3 + c/9 - b/9 - a/3 = (1/9)[3(d-a)+c-b]$$

$$\Delta I_{L3} = (2/225)[3(d-a)+c-b] + (2/25)[5(j-e)+3(i-f)+h-g].$$

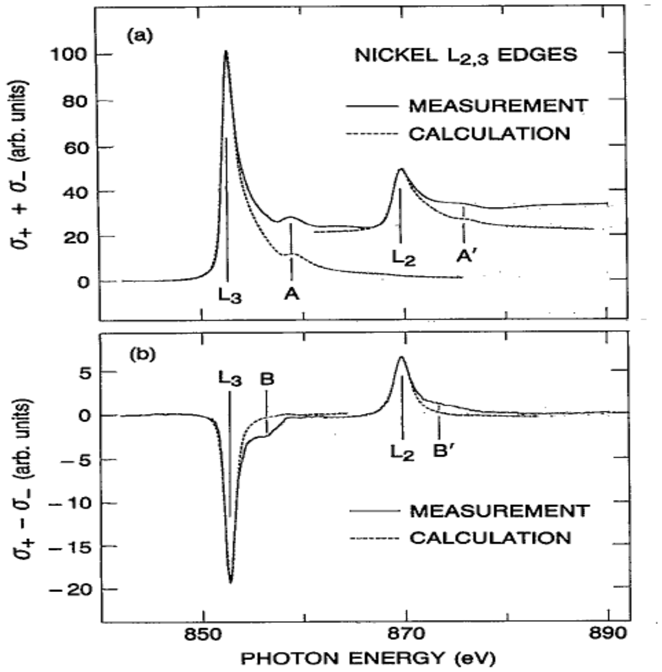
$$\langle l_z\rangle = \langle l,s,j,mj \mid l_z \mid l,s,j,mj\rangle$$
$$\langle s_z\rangle = \langle l,s,j,mj \mid s_z \mid l,s,j,mj\rangle$$

$$\langle l_z\rangle_{3/2} = -3/5\ [3(a-d)+b-c]$$
$$\langle s_z\rangle_{3/2} = 1/10\ [3(a-d)+b-c]$$
$$\langle l_z\rangle_{5/2} = -2/5\ [5(e-j)+3(f-i)+g-h]$$
$$\langle s_z\rangle_{5/2} = -1/10\ [5(e-j)+3(f-i)+g-h]$$

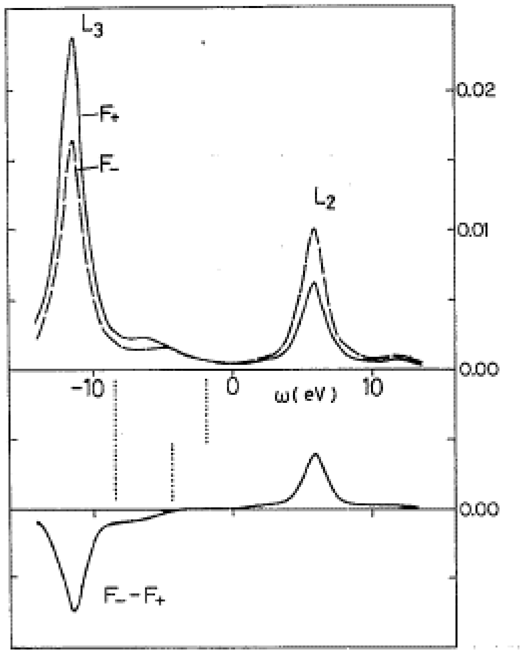
$$\langle l_z\rangle = \langle l_z\rangle_{3/2} + \langle l_z\rangle_{5/2} \quad ; \quad \langle s_z\rangle = \langle s_z\rangle_{3/2} + \langle s_z\rangle_{5/2}$$

$$\langle l_z\rangle = -5\ (\Delta L_3 + \Delta L_2) \quad ; \quad \langle s_z\rangle = -5/4\ \Delta L_3 + \Delta L_2$$

Many body effects



N.V.Smith et al., one electron model



T.Jo, G.A.Sawatzky, PRB 43, 8771 (1991), many body calculation

Anderson impurity model: ground state of Ni superposition of states with d^8, $d^9\underline{v}$ and $d^{10}\underline{v}^2$, where $\underline{v}$ denotes a hole in the *d*-band of a neighboring atom:

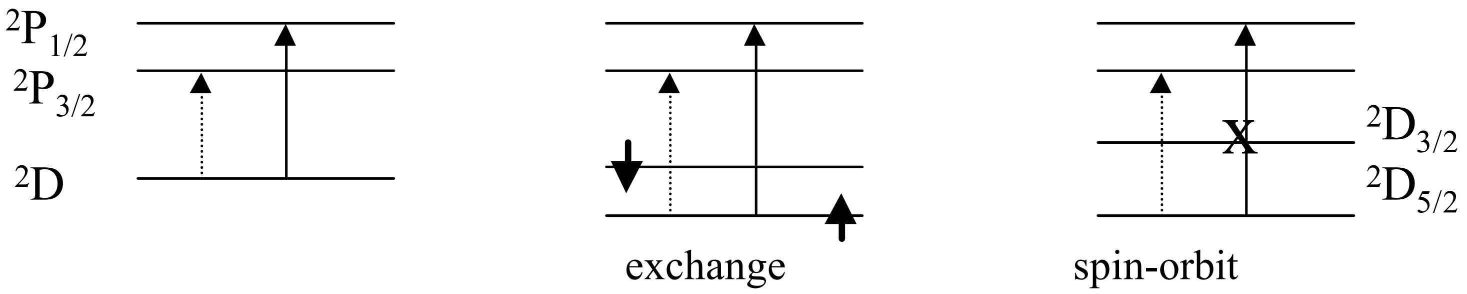
$|g\rangle = A|3d^{10}\underline{v}^2\rangle + B|3d^9\underline{v}\rangle + C|3d^8\rangle$

G.v.d.Laan, B.T.Thole, J.Phys.Condens.Matter 4, 4181 (1992): 18% d^8, 49% d^9, 33% d^{10}

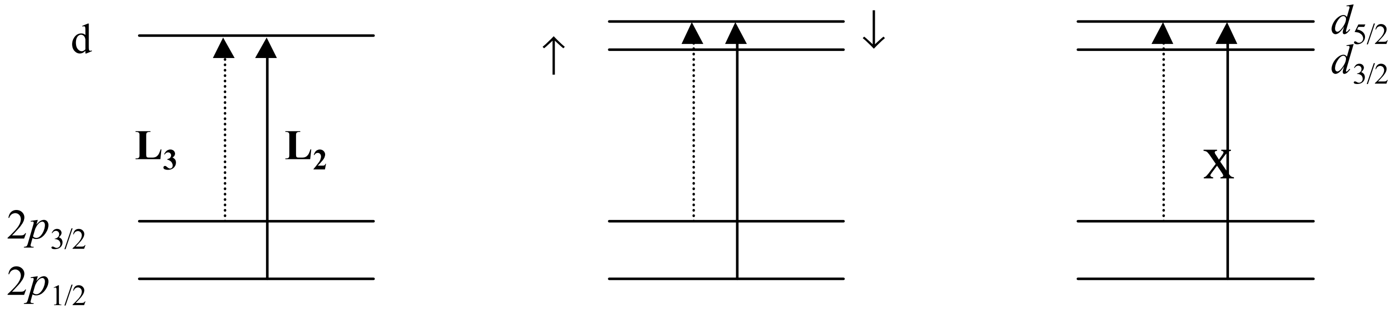
Satellite in dichroism: due to $3d^8$ character in ground-state

Configuration picture: example of Ni metal

p^6d^9 ® p^5d^{10} or d^1 ® p^1



One electron picture: p ® d transition



XMCD calculation

$$s_q\ \mu\ S_q\ |<F_f\,|\,\mathbf{e_q} \times \mathbf{r}\,|\,F_i>|^2\ r_f(\mathbf{h}w - \mathbf{E_i})$$

$\mathbf{e_q}$: x-ray polarisation unit vector
r: electron position
z: x-ray propagation direction

$r = x\mathbf{e_x} + y\mathbf{e_y} + z\mathbf{e_z}$

$\mathbf{e = 1/Ö2\,(e_x + i\,e_y)}$ **(left polarisation)**
$\mathbf{e = 1/Ö2\,(e_x - i\,e_y)}$ **(right polarisation)**

$\mathbf{P_1 = e_1} \times \mathbf{r = 1/Ö2\,(x + iy)}$ **(left)**
$\mathbf{P_{-1} = e_{-1}} \times \mathbf{r = 1/Ö2\,(x - iy)}$ **(right)**

convention for the sign of XMCD with respect to the relative orientations of photon spin and magnetisation direction**:**

$\mathbf{XMCD = I^{\uparrow\downarrow} - I^{\downarrow\downarrow} = I^{\uparrow\downarrow} - I^{\uparrow\uparrow}}$

M // - z axis
(H // -z then M and majority spin // z)

Influence of the bandstructure

Valence band composed of different band states ϕ_{ik} , expanded using local spherical harmonics:

$$\phi_{ik}(\mathrm{r}) = \mathrm{S}\ a_{lm,ik}\ \mathrm{R}_{nl,ik}(\mathrm{r})\mathrm{Y}_{\mathrm{lm}}{}^{\mathrm{S}},$$

k = wave vector, r = position , S = spin (up or down)

Transitions from the 2*p*-level to ϕ_{ik} calculated as before, replacing the factors ../√5 by $a_{lm,ik}$.
Example:

$$<\phi_{ik}\ |\mathbf{P}_{-1}|2\mathrm{p}_{3/2}>|^2 = (1/45)\{18|\mathrm{a}_{2-2}|^2 + 6|\mathrm{a}_{2-1}|^2 + |\mathrm{a}_{20}|^2\}\mathrm{R}^2.$$

Total absorption: sum over *i*, integrate over Brillouin zone.