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
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 $\perp$ and // to quantisation axis ($q = \pm 1$ 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 transmitted 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
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 \( 2p \rightarrow 3d \); \( K \) edge \( 1s \rightarrow 4p \)

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

- XMCD is proportional to \( <M> \) along the propagation vector \( \mathbf{k} \). *Ferromagnetic, ferrimagnetic and paramagnetic* systems can be probed.
Interaction of x-rays with matter

\[ I(\omega) = I_0(\omega) e^{-\mu(\omega)x} \]

Lambert-Beer law

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

\( x= \) sample thickness ;

\( \mu= \) experimental absorption cross section

**Fermi’s Golden Rule**

\[ \sigma_{abs} = \left( \frac{2\pi}{h} \right) |< \Phi_f | T | \Phi_i >|^2 \rho_f (\hbar \omega - E_i) \]

|\( < \Phi_f | T | \Phi_i >|\) 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

\[ T = \frac{(e/mc)}{p} \cdot A \]

Plane wave: \( A = e_q A_0 \exp[i \mathbf{k} \cdot \mathbf{r}] \)

\( e_q \) : light polarization vector ; \( k \) : light propagation vector ; \( r \) and \( p \) : electron position and momentum

\[ T = C\Sigma_q [e_q \cdot p + i (e_q \cdot p)(k \cdot r)] \]

dipole operator quadrupole operator
Absorption cross section

Electric dipole approximation ($\mathbf{k} \cdot \mathbf{r} \ll 1$)

$$T = C \left( \mathbf{e}_q \cdot \mathbf{p} \right) \quad \rightarrow \quad 1 \propto (\mathbf{e}_q \cdot \mathbf{r})$$

Commutation relation: $[\mathbf{r}, H] = (\mathbf{i}h/\mathbf{m})\mathbf{p}$

Transition probability:

$$\sigma_{\text{abs}} \propto |\langle \Phi_f | \mathbf{e}_q \cdot \mathbf{r} | \Phi_i \rangle|^2 \rho_f (\hbar \omega - E_i)$$

Dipolar selection rules:

$$\Delta l = \pm 1, \Delta s = 0$$
**Absorption edges**

**K-edge:** $1s \rightarrow$ empty $p$-states  
**L$_1$-edge:** $2s \rightarrow$ empty $p$-states  
**L$_{2,3}$-edges:** $2p_{1/2, 3/2} \rightarrow$ empty $d$-states  
**M$_{4,5}$-edges:** $3d_{3/2, 5/2} \rightarrow$ empty $f$-states  

**Spin–orbit coupling:** $l \geq 1$  
Spin parallel/anti-parallel to orbit:  
$j = l + s, l - s$  
$p \rightarrow 1/2, 3/2$  
$d \rightarrow 3/2, 5/2$  

**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 neighbouring atoms >> intra-atomic interactions)

Single electron approximation
K-edges, L\textsubscript{2,3} edges of TM metallic systems

Transitions to localised states (intra-atomic interactions >> interaction with environment)

Multiplets - atomic approximation
M\textsubscript{4,5}-edges of rare earths (3d → 4f transitions) magnetic, crystal fields are weak perturbations

L\textsubscript{2,3} edges of TM ionic systems crystal field environment is more important
Rare earth ions: calculation of $M_{4,5} (3d \rightarrow 4f)$ 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.
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 $3 \times 3 = 9$-fold degenerate.
Calculation of atomic spectra

Fermi’s Golden Rule:  \[ \sigma_{abs} \propto \sum_{q} |<\Phi_f | e_q \cdot r | \Phi_i >|^2 \delta (\hbar \omega - E_f + E_i) \]

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

\[ \sigma_{qJM \rightarrow J'M'} \propto |< J'M' | e_q \cdot r | JM >|^2 \delta (\hbar \omega - E_{J',M'} + E_{J,M}) \]

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

by applying Wigner-Eckhart theorem:

\[ \sigma_{qJM \rightarrow J'M'} \propto \left\langle (-1)^{J-M} \begin{pmatrix} J \\ M \end{pmatrix} \right\rangle^2 |< J' || P_q || J >|^2 \]

3J symbol ≠ 0 if:  
\[ \Delta J = (J' - J) = -1, 0, +1 \]
\[ \Delta M = (M' - M) = q \quad q = -1 \text{ (right); } q = 1 \text{ (left), } q=0 \text{ (linear)} \]
For a ground state |J,M> and for every ΔJ:

\[ \sigma_{q=1} - \sigma_{q=-1} \propto M \]

\[ \text{XMCD} \propto \Sigma_{\Delta J} (\sigma_{q=1} - \sigma_{q=-1}) \propto M [2(2J-1) P^{-1} + 2 P_0 - 2(2J+3) P^1] \]

If several Mj states are occupied:

\[ \text{XMCD} \propto <M_j> \]

- 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 $^{3+}$ \(3d^{10}4f^{13} \rightarrow 3d^94f^{14}\)

**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 \(M_j\) levels are equally occupied; \(<M_j>=0\) and the XAS spectrum does not depend on the polarisation
With magnetic field - Zeeman splitting:
18 lines, 3 groups with $\Delta M = 0$ (linear parallel) ; $\Delta M = \pm 1$ (left, right)
Energy of $M_J$ levels: $E_{M_J} = -g_{\alpha J} \mu_B H M_J$

For $T = 0K$: only $M_J = -7/2$ level is occupied : only $\Delta M = + 1$ 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 $<M_J>$ and will be non zero as long as $kT < g_{\alpha J} \mu_B H$
Case of Dy$^{3+}$

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

XAS spectra and XMCD vs reduced temperature

$T_R = kT / g_\alpha J_B \mu_B H$

$q = -1$

$q = +1$

dichroism
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

Experimental L_{2,3} edge spectra

Here we deal with the polarisation dependence of the ‘white lines’
\[ \sigma_q \propto \sum_q |<\Phi_f| e_q \cdot r |\Phi_i>|^2 \rho \left( \hbar \omega - E_i \right) \]

One electron picture: transitions from \(2p\) to \(3d\) band split by exchange in \(3d^\uparrow\) and \(3d^\downarrow\)

\[ |l, m_l, s, m_s> = a_{ml} Y_{l,ml} |s, m_s> \]

\[ \mathbf{L}_2 \text{ edge - left polarisation (}\Delta m_l=+1\text{)} \]

\[ R = \int R_{nl}^* (r) R_{n'l'} (r) r^3 dr \]

\[ I^\uparrow = \sum \left|<f|P_1|i>|^2 = \left( \frac{1}{3} \left|<2,1|P_1|1,0>|^2 + \frac{2}{3} \left|<2,0|P_1|1,-1>|^2 \right) R^2 \right. \]

\[ I^\downarrow = \sum \left|<f|P_1|i>|^2 = \left( \frac{2}{3} \left|<2,2|P_1|1,1>|^2 + \frac{1}{3} \left|<2,1|P_1|1,0>|^2 \right) R^2 \right. \]
It can be calculated (Bethe and Salpeter) that:

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

\[
I^\uparrow = 1/3( |<2,1 | P_1 | 1,0> |^2 + 2/3 |<2,0 | P_1 | 1,-1> |^2 ) R^2 = \\
= (1/3 * 1/5 + 2/3 * 1/15) R^2 = 1/9 R^2
\]

\[
I^\downarrow = 2/3 |<2,2 | P_1 | 1,1> |^2 + 1/3 |<2,1 | P_1 | 1,0> |^2 R^2 \\
= (2/3 * 2/5 + 1/3 * 1/5) R^2 = 1/3 R^2
\]

\[
I^\uparrow / (I^\uparrow + I^\downarrow) = 0.25 \quad \text{LCP at the L}_2 \text{ edge}
\]

\[
I^\downarrow / (I^\uparrow + I^\downarrow) = 0.75
\]

\[
I^\uparrow / (I^\uparrow + I^\downarrow) = 0.75 \quad \text{RCP at the L}_2 \text{ edge}
\]

\[
I^\downarrow / (I^\uparrow + I^\downarrow) = 0.25
\]
Left polarisation:

\[
\begin{align*}
\mathbf{I}^\uparrow &= (|<2,2|\mathbf{P}_1|1,1>|^2 + 2/3 |<2,1|\mathbf{P}_1|1,0>|^2 + 1/3 |<2,0|\mathbf{P}_1|1,-1>|^2 ) \mathbf{R}^2 \\
&= (2/5 + 2/3 * 1/5 + 1/3 * 1/15) \mathbf{R}^2 = 5/9 \mathbf{R}^2 \quad \mathbf{R} = \int \mathbf{R}_{nl}^*(r)\mathbf{R}_{n'1'}(r) r^3 dr \\
\mathbf{I}^\downarrow &= (1/3|<2,2|\mathbf{P}_1|1,1>|^2 + 2/3 |<2,1|\mathbf{P}_1|1,0>|^2 + |<2,0|\mathbf{P}_1|1,-1>|^2 ) \mathbf{R}^2 \\
&= (1/3 * 2/5 + 2/3 * 1/5 + 1/15) = 1/3 \mathbf{R}^2 \quad \mathbf{I}^\uparrow / (\mathbf{I}^\uparrow + \mathbf{I}^\downarrow) = 0.625 \quad \text{LCP at the L}_3 \text{ edge} \\
\mathbf{I}^\downarrow / (\mathbf{I}^\uparrow + \mathbf{I}^\downarrow) &= 0.375 \\
\mathbf{I}^\downarrow / (\mathbf{I}^\uparrow + \mathbf{I}^\downarrow) &= 0.375 \quad \text{RCP at the L}_2 \text{ edge} \\
\mathbf{I}^\uparrow / (\mathbf{I}^\uparrow + \mathbf{I}^\downarrow) &= 0.625
\end{align*}
\]
\[ \begin{array}{cccc}
L_2 & 1/9 R^2 & 1/3 R^2 & 1/3 R^2 & 1/9 R^2 \\
L_3 & 5/9 R^2 & 1/3 R^2 & 1/3 R^2 & 5/9 R^2 \\
\end{array} \]

**Ni, Co metal (strong ferromagnets): only empty \( \rho \downarrow \)**

\[ L_2 \text{ total (LCP+RCP)} \propto (1/3 + 1/9) R^2 = 4/9 R^2 \]
\[ L_3 \text{ total (LCP+RCP)} \propto (1/3 + 5/9) R^2 = 8/9 R^2 \]
branching ratio \( L_3: L_2 = 2:1 \)

\[ L_2 \text{ XMCD (LCP-RCP)} \propto (1/3 - 1/9) R^2 = 2/9 R^2 \]
\[ L_3 \text{ XMCD (LCP-RCP)} \propto (1/3 - 5/9) R^2 = -2/9 R^2 \]
branching ratio XMCD \( \Delta L_3: \Delta L_2 = 1:-1 \)

**In general:** \( \text{XMCD} = (I_{\uparrow \text{left}} \rho \uparrow + I_{\downarrow \text{left}} \rho \downarrow) - (I_{\uparrow \text{right}} \rho \uparrow + I_{\downarrow \text{right}} \rho \downarrow) \)

\[ = \rho \uparrow (I_{\text{left}} - I_{\text{right}}) + \rho \downarrow (I_{\text{left}} - I_{\text{right}}) = \rho \uparrow (I_{\text{left}} - I_{\downarrow \text{left}}) + \rho \downarrow (I_{\downarrow \text{left}} - I_{\text{left}}) = \]

\[ = (\rho \uparrow - \rho \downarrow) (I_{\text{left}} - I_{\downarrow \text{left}}) \quad \text{XMCD} \neq 0 \text{ if } \rho \uparrow \neq \rho \downarrow \]
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

\[ d_{5/2} \quad d_{3/2} \]

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

$2p_{1/2} \to 4d_{3/2, 3/2}$

- Spin-orbit in the 3d states
- Intensity shift from $L_2$ to $L_3$ edge $\to L_3 : L_2 \geq 2 : 1$
- 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.

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 3d-moments.

**Orbital moment sum rule:**

\[ \langle L_Z \rangle = \frac{2l(l+1)(4l+2-n)}{[l(l+1)+2 - c(c+1)]} \cdot \left[ \int_{j^+ + j^-} d\omega(\mu^+ - \mu^-) / \int_{j^+ + j^-} d\omega(\mu^+ + \mu^- + \mu^0) \right] \]

- \( l \) = orbital quantum number of the valence state,
- \( c \) = orbital quantum number of the core state,
- \( n \) = number of electrons in the valence state
- \( \mu^+ (\mu^-) \) = absorption spectrum for left (right) circularly polarized light.
- \( \mu^0 \) = 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})

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

$$<L_Z> = 2(10-n) \bullet (\Delta L_3 + \Delta L_2)$$

$$/ \int_{L_3+L_2} d\omega (\mu^+ + \mu^- + \mu^0)]$$

$q = \Delta L_3 + \Delta L_2$

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

$$<L_Z> = 4q \ (10-n) / 3r$$

C.T. Chen et al., PRL 75, 152 (1995)
Spin moment sum rule

\[ <S_Z> + c_2(n) <T_Z> = c_1(n) \left[ \int_{j^+} d\omega (\mu^+ - \mu^-) - \frac{(c+1)/c}{\int_{j^+ + j^-} d\omega (\mu^+ + \mu^- + \mu^0)} \right] / \left( \int_{j^+ + j^-} d\omega (\mu^+ + \mu^- + \mu^0) \right) \]

\[ c_1(n) = \frac{3c(4l + 2 - n)}{[l(l+1) - 2 - c(c+1)]} \]
\[ c_2(n) = \frac{l(l+1)[l(l+1)+2c(c+1)+4]-3(c-1)^2(c+2)^2}{6lc(l+1)(4l+2-n)} \]

\[ <T_Z> = \text{expectation value of magnetic dipole operator} \]
\[ T = S \cdot r / r^2 \]

which expresses the anisotropy of the spin moment within the atom

For L_{2,3}-edges:

\[ <S_Z> + \frac{7}{2} <T_Z> = \frac{3}{2}(10-n)[(\Delta L_3 - 2\Delta L_2)/\int_{L_3+L_2} d\omega (\mu^+ + \mu^- + \mu^0)] \]
\[ \langle S_Z \rangle + \frac{7}{2} \langle T_Z \rangle = (3/2)(10-n)[(\Delta L_3 - 2\Delta L_2)/\int_{L_3+L_2} d\omega (\mu^+ + \mu^- + \mu^0)] \]

\[ = (3/2)(10-n)(p - 2(q-p))/(3/2)r = (3p - 2q)(10-n)/r \]
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 $\langle T \rangle$

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 saturating 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 \(<L_z>\) are \(\sim 1\%\) 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 \( \gg \) Coulomb interaction
  not true for early transition metal

- \( T_z \) is supposed to be small: true for cubic systems but not at surfaces/interfaces
Sources of errors:
- determination of the background $\mu^+ + \mu^- + \mu^0$
- rate of circular polarization
- number of electrons $n$

Experimental application of sum rules

$$<L_Z> = \frac{4q (10-n)}{3r}$$

$$<S_z> + \frac{7}{2} <T_Z> = (3p - 2q)(10-n)/r$$
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.
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 electron- core hole interaction; ♦ experiment
Influence of the bandstructure

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

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

$k = \text{wave vector}, r = \text{position}, S = \text{spin (up or down)}$

Transitions from the 2$p$-level to $\phi_{ik}$ calculated as before, replacing the factors $\sqrt[5]{5}$ by $a_{lm,ik}$. Example:

$$\langle \phi_{ik} | P_{-1} | 2p_{3/2} \rangle^2 = \frac{1}{45} \{ 18 |a_{2-2}|^2 + 6 |a_{2-1}|^2 + |a_{20}|^2 \} R^2.$$

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

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

Spin-orbit splitting in $d$-band

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:
\( a \) (\( m_j=\text{-}3/2 \)), \( b \) (\( m_j=\text{-}1/2 \)), \( c \) (\( m_j=1/2 \)) and \( d \) (\( m_j=3/2 \))

\( d_{5/2}\)-states occupancies:
\( e \) (\( m_j=\text{-}5/2 \)), \( f \) (\( m_j=\text{-}3/2 \)), \( g \) (\( m_j=\text{-}1/2 \)), \( h \) (\( m_j=1/2 \)), \( i \) (\( m_j=3/2 \)) and \( j \) (\( m_j=5/2 \))

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

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

\(<l_z> = <l,s,j,mj | l_z | l,s,j,mj> \)
\(<s_z> = <l,s,j,mj | s_z | l,s,j,mj> \)

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

\(<l_z> = <l_z>_{3/2} + <l_z>_{5/2} ; \ <s_z> = <s_z>_{3/2} + <s_z>_{5/2} \)

\(<l_z> = -5 \ (\Delta L_3 + \Delta L_2) ; \ <s_z> = -5/4 \ \Delta L_3 + \Delta L_2 \)
Many body effects

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

$$|g> = A|3d^{10}\nu^2> + B|3d^9\nu> + C|3d^8>$$


Satellite in dichroism: due to $3d^8$ character in ground-state
Configuration picture: example of Ni metal
\[p^6d^9 \rightarrow p^5d^{10} \text{ or } d^1 \rightarrow p^1\]

One electron picture: \( p \rightarrow d \) transition
XMCD calculation

\[ \sigma_q \propto \sum_q |\langle \Phi_f | e_q \cdot r | \Phi_i \rangle|^2 \rho_f (\hbar \omega - E_i) \]

\( e_q \): x-ray polarisation unit vector
\( r \): electron position
\( z \): x-ray propagation direction

\[ r = xe_x + ye_y + ze_z \]

\( e = 1/\sqrt{2} (e_x + ie_y) \) (left polarisation)
\( e = 1/\sqrt{2} (e_x - ie_y) \) (right polarisation)

\[ \mathbf{P}_1 = e_1 \cdot r = 1/\sqrt{2} (x + iy) \] (left)
\[ \mathbf{P}_{-1} = e_{-1} \cdot r = 1/\sqrt{2} (x - iy) \] (right)

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

\[ \text{XMCD} = I^{\uparrow \downarrow} - I^{\downarrow \downarrow} = I^{\uparrow \downarrow} - I^{\uparrow \uparrow} \]

\( M \parallel -z \) axis
\( H \parallel -z \) then \( M \) and majority spin \( \parallel z \)
Influence of the bandstructure

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

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

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

Transitions from the $2p$-level to $\phi_{ik}$ calculated as before, replacing the factors $../\sqrt{5}$ by $a_{lm,ik}$.

Example:

$$<\phi_{ik} | P_{-1} | 2p_{3/2}>^2 = (1/45) \{18|a_{2,-2}|^2 + 6|a_{2,-1}|^2 + |a_{2,0}|^2\} R^2.$$

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