XAS/XMCD Sum Rules

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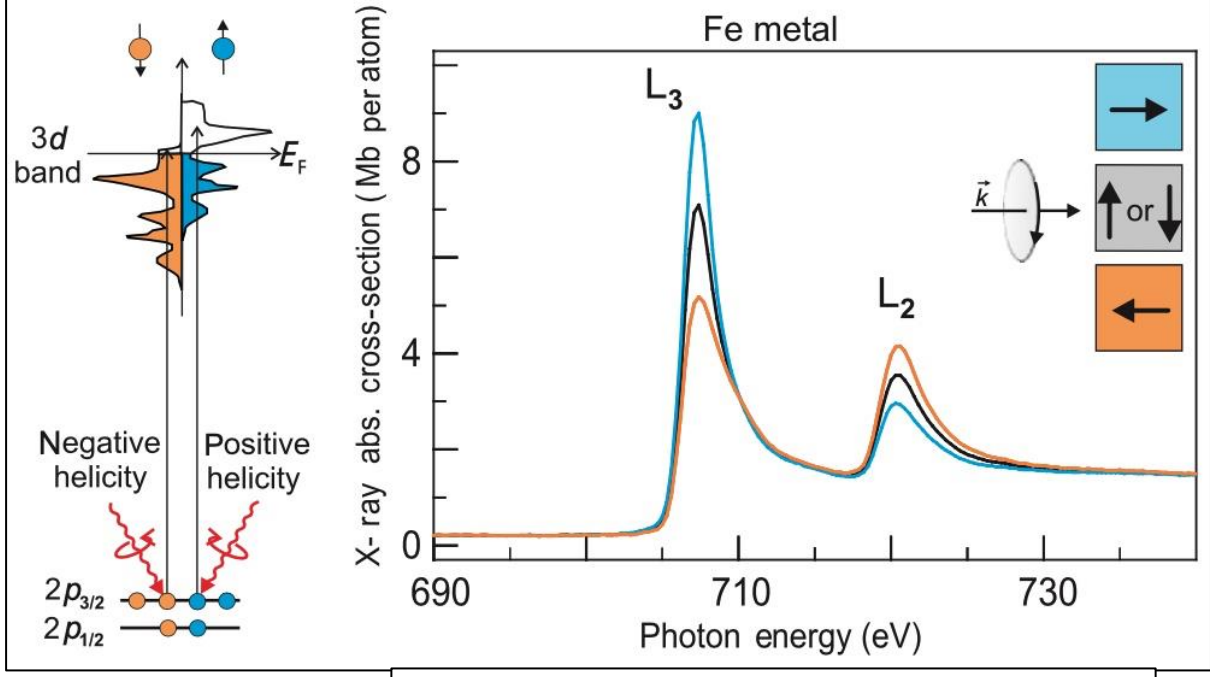
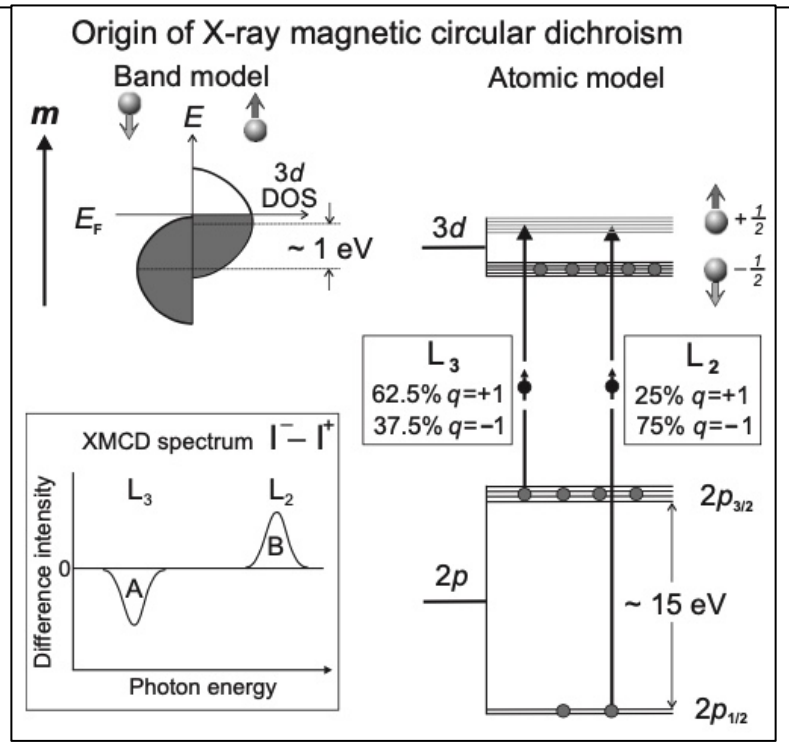
Source: *Magnetism: From Fundamentals to Nanoscale Dynamics* by Stöhr & Siegmann

XAS of d-orbitals in Ni, Co

- Partially filled d-orbitals; look for $L_{2,3}$ transitions
  - $2p_{1/2} \Rightarrow 3d : L_2$
  - $2p_{3/2} \Rightarrow 3d : L_3$
- Band model: net moment due to difference between majority/minority electrons
- Energy difference due to spin-orbit splitting in p-orbitals
  - "Orbital quenching" in d-orbitals suppresses orbital moment





QM Description of Absorption

- Photon polarization $\vec{\epsilon}$ interact with charge to low order in dipole approximation

- $\vec{p} \cdot \vec{\epsilon}\, e^{i\vec{k}\cdot\vec{r}} \sim \vec{p} \cdot \vec{\epsilon}\left(1 + i\vec{k} \cdot \vec{r}\right) \sim \vec{p} \cdot \vec{\epsilon}$
  - $\vec{k} \cdot \vec{r}$ constant over atomic distances

The polarization dependent *X-ray absorption resonance intensity* in the *dipole approximation* is given by

$$I_{\text{res}} = \mathcal{A}\, |\langle b|\, \boldsymbol{\epsilon} \cdot \boldsymbol{r} |a\rangle|^2 \,. \tag{9.60}$$

The proportionality factor, given by

$$\mathcal{A} = 4\pi^2 \frac{e^2}{4\pi\epsilon_0 \hbar c}\, \hbar\omega \tag{9.61}$$

contains the dimensionless *fine structure constant* α_{f}

$$\alpha_{\text{f}} = \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137.04}. \tag{9.62}$$

The intensity I_{res} has the dimension [length$^2\times$ energy] and is usually expressed in units of [Mb eV], where $1\,\text{Mb} = 10^{-22}\,\text{m}^2$.

$$\langle b|\, P^q_\alpha\, |a\rangle = \underbrace{\delta(m'_s, m_s)}_{\text{spin}}\, \underbrace{\langle R_{n',l}(r)|r|R_{n,c}(r)\rangle}_{\text{radial}}\, \underbrace{\sum_{m_c, m_l, p} e^q_{\alpha,p}\, \langle l, m_l|\, C^{(1)}_p\, |c, m_c\rangle,}_{\text{angular}} \tag{9.80}$$

The *X-ray absorption resonance intensity* for different X-ray propagation directions α and polarization states q can be written as

$$I_{\text{res}} = \mathcal{A}\, |\langle b|\, P^q_\alpha |a\rangle|^2, \tag{9.75}$$

where $\mathcal{A}$ is given by (9.61) and the polarization dependent dipole operators P^q_α with $\alpha = x, y,$ or z and $q = +1, 0,$ or -1 are listed in Table A.4.

$$P^0_z = r\, C^{(1)}_0 = r\, \cos\theta = z, \tag{9.71}$$

$$P^{\pm}_z = r\, C^{(1)}_{\pm 1} = \mp r \frac{1}{\sqrt{2}}\, \sin\theta\, \mathrm{e}^{\pm \mathrm{i}\phi} = \mp \frac{1}{\sqrt{2}}\, (x \pm \mathrm{i}y). \tag{9.72}$$

QM Description of Absorption

- Polarized photon (linear, RCP, LCP) sets interaction Hamiltonian between initial, final states
- Determination of non-zero matrix elements sets spin, radian, angular selection rules for absorption
  - Most complex part is angular component

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$$P_z^0 = r\,C_0^{(1)} = r\,\cos\theta = z, \tag{9.71}$$

$$P_z^{\pm} = r\,C_{\pm1}^{(1)} = \mp r\frac{1}{\sqrt{2}}\,\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\phi} = \mp\frac{1}{\sqrt{2}}\,(x \pm \mathrm{i}y). \tag{9.72}$$

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Short QM II Refresher

Racah's spherical tensor operators are defined as [181],

$$C_m^{(l)} = \sqrt{\frac{4\pi}{2l+1}}\, Y_{l,m}(\theta,\phi)\ , \qquad \left(C_m^{(l)}\right)^* = (-1)^m C_{-m}^{(l)}\ . \qquad (9.70)$$

- Spherical Harmonics : $Y_{\ell,m}(\theta,\phi) = \langle\theta,\phi|\ell,m\rangle$
- Orthonormality rules : $\iint Y^*_{\ell',m'}\, Y_{\ell,m}\, d\Omega = \delta_{\ell\ell'}\delta_{mm'}$
- $\left|\ell,s,j,m_j\right\rangle = \sum C\ |\ell,s,m_\ell,m_s\rangle$ (Clebsch-Gordon Coefficients)
- Gaunt coefficients : $c^k(l'm';lm) = \sqrt{\frac{4\pi}{2k+1}} \iint Y^*_{\ell',m'}\, Y_{\ell,m} Y_{k,m'-m}\, d\Omega$

Example of Transition Matrix Elements

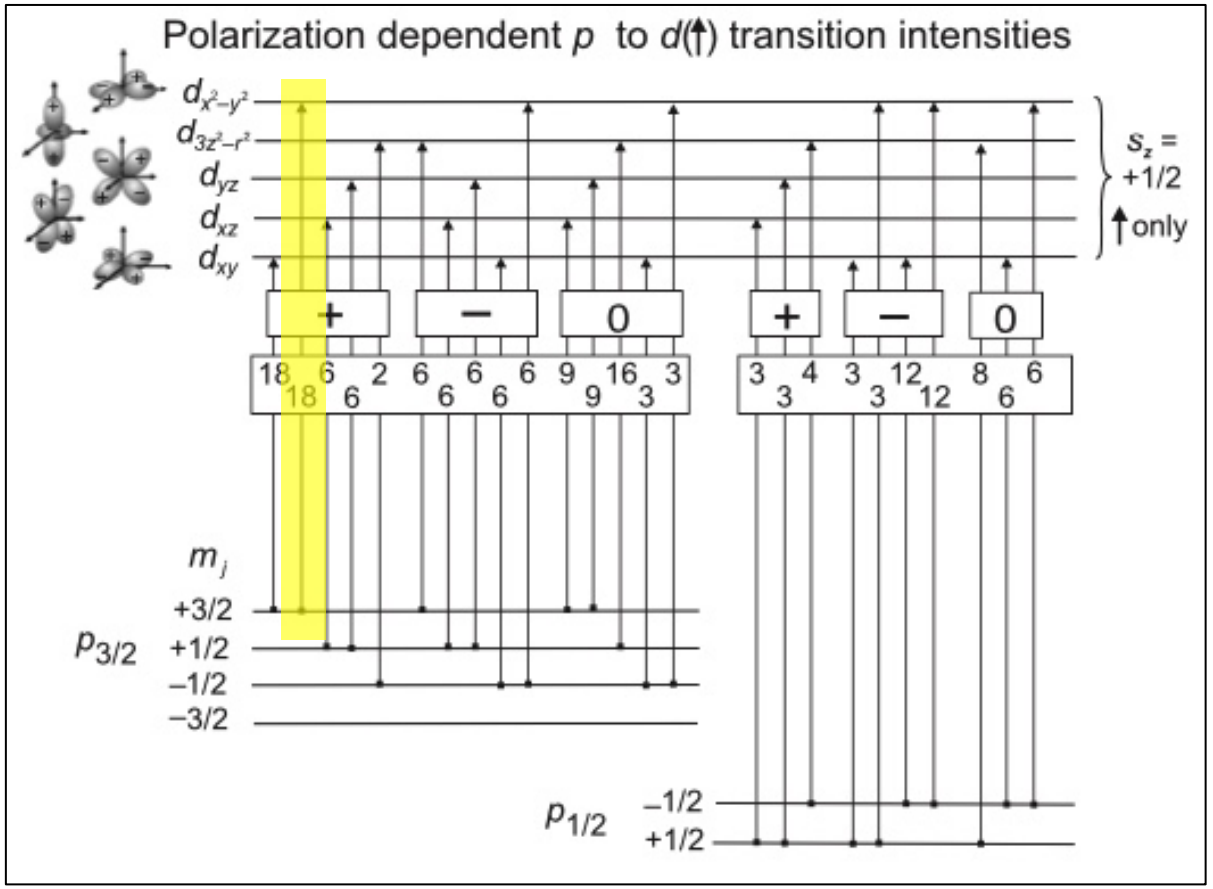
$$|d_{x^2-y^2}\rangle = \frac{1}{\sqrt{2}}(Y_{2,-2} + Y_{2,2})$$

$$|p_{3/2}, +\tfrac{3}{2}\rangle = Y_{1,1}$$

$$\left\langle d_{x^2-y^2}\middle|C^{(1)}_{+1}\middle|p_{3/2}, +\tfrac{3}{2}\right\rangle$$

$$= \frac{1}{\sqrt{2}}\left\{\langle 2,-2|C^{(1)}_{+1}|1,1\rangle + \langle 2,2|C^{(1)}_{+1}|1,1\rangle\right\}$$

$$= \frac{1}{\sqrt{2}}\sqrt{\frac{4\cdot 3}{2\cdot 3\cdot 5}} = \frac{1}{\sqrt{5}}$$



Squares of matrix element, multiplied by 90

Rule 1 : Total Intensity

- Orientation averaged / polarization averaged intensity gives number of states at Fermi Energy (N_{holes})

$$\langle I \rangle = \frac{1}{3}\left(I_x^q + I_y^q + I_z^q\right) = \frac{1}{3}\left(I_\alpha^{-1} + I_\alpha^0 + I_\alpha^{+1}\right) \ . \qquad (9.87)$$

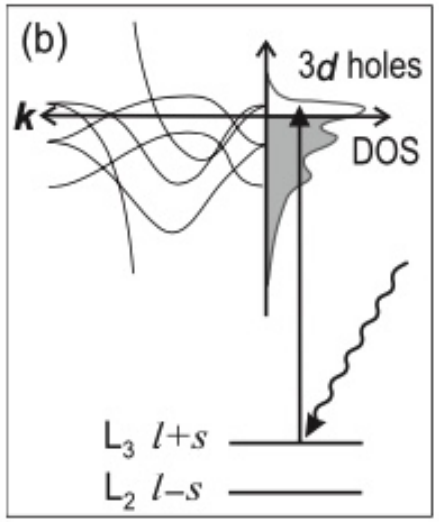
The *orientation averaged "white line" intensity* of a core to valence $nc \rightarrow n'L$ transition with $c = L - 1$ is directly related to the total number of valence holes N_h in the *electronic ground state* according to

$$\langle I \rangle = C\, N_h \ . \qquad (9.90)$$

where

$$C = \mathcal{A}\mathcal{R}^2 \frac{L}{3(2L+1)} \ , \qquad (9.91)$$

$\mathcal{A} = 4\pi^2\hbar\omega/137$ and $\mathcal{R}$ is the radial $nc \rightarrow n'L$ matrix element.



$$\Delta I_{L_3} = \mathcal{A}\mathcal{R}^2 \sum_{n,m_j} |\langle d_n, \chi^+ | C_{-1}^{(1)} | p_{3/2}, m_j \rangle|^2 - |\langle d_n, \chi^+ | C_{+1}^{(1)} | p_{3/2}, m_j \rangle|^2$$
$$= -\frac{2}{9}\mathcal{A}\mathcal{R}^2 \ , \qquad (9.96)$$

and

$$\Delta I_{L_2} = \mathcal{A}\mathcal{R}^2 \sum_{n,m_j} |\langle d_n, \chi^+ | C_{-1}^{(1)} | p_{1/2}, m_j \rangle|^2 - |\langle d_n, \chi^+ | C_{+1}^{(1)} | p_{1/2}, m_j \rangle|^2$$
$$= +\frac{2}{9}\mathcal{A}\mathcal{R}^2 \ . \qquad (9.97)$$

Rules 2 & 3 : Spin/Orbital Sum Rules

- In principle come from previous transition rules

- Additional derivation of spin (P. Carra, *et al,* PRL 1993) and orbital (Thole *et al,* PRL 1992) rules detailed elsewhere

The *spin sum rule* links the angle averaged dichroism intensities with the size of the spin moment per atom according to

$$\langle -A + 2B \rangle = \frac{C}{\mu_B} m_s \qquad (9.105)$$

where the constant C is the same as in the charge sum rule.

The *orbital moment sum rule* links the angle averaged dichroism intensities with the size of the average orbital moment per atom according to

$$-\langle A + B \rangle = \frac{3C}{2\mu_B} m_o \qquad (9.106)$$

The constant C is the same as in the charge and spin sum rules.

Summary

- XAS, XMCD spectra detail states at Fermi level
- Integrated XMCD peaks determine magnetic moments from spin, OAM