X-ray magnetic circular dichroism and linear dichroism

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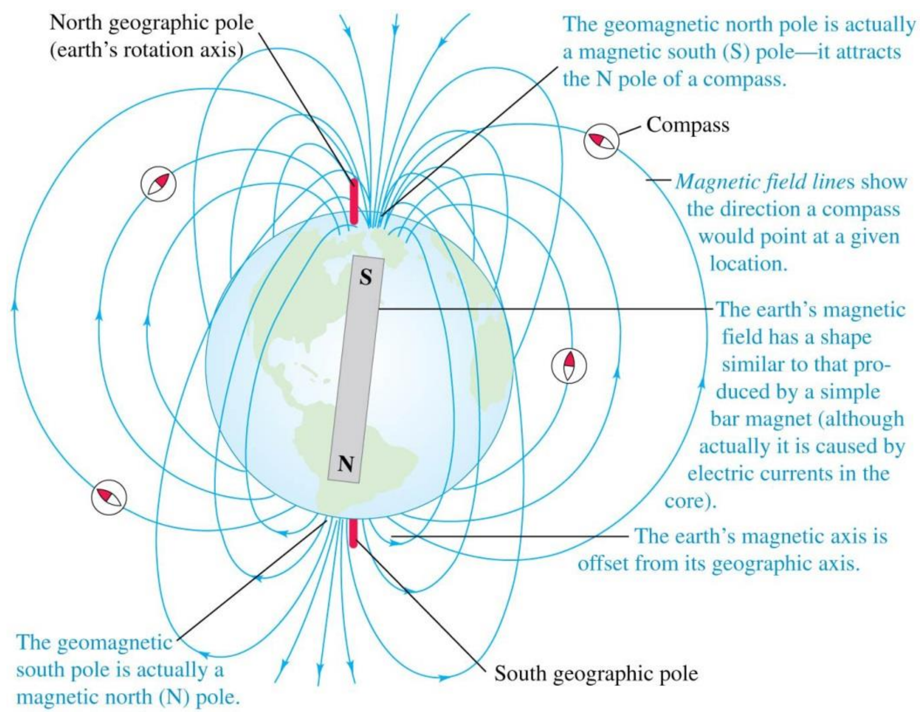
A compass needle aligning itself with the earth's magnetism is an example of magnetic interaction.

Compass was invented in China ~ 2200 years ago, and first used in navigation ~1000 years ago.

Wikipedia



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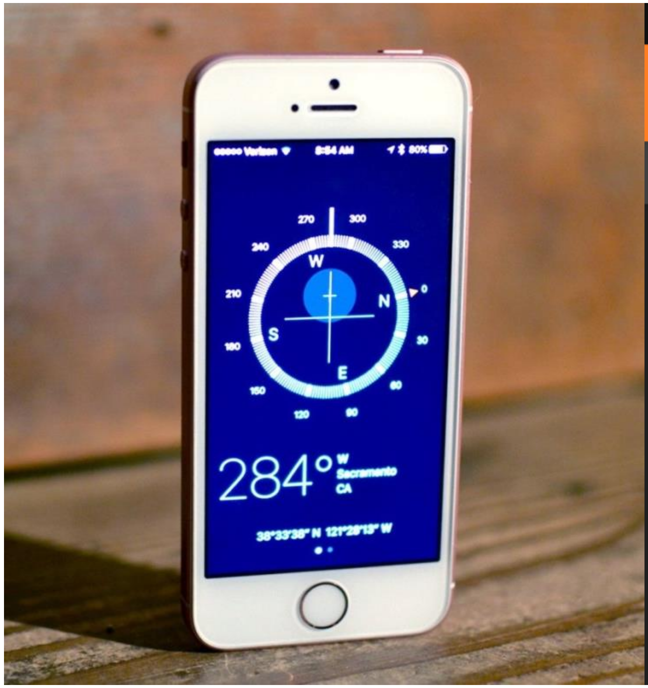
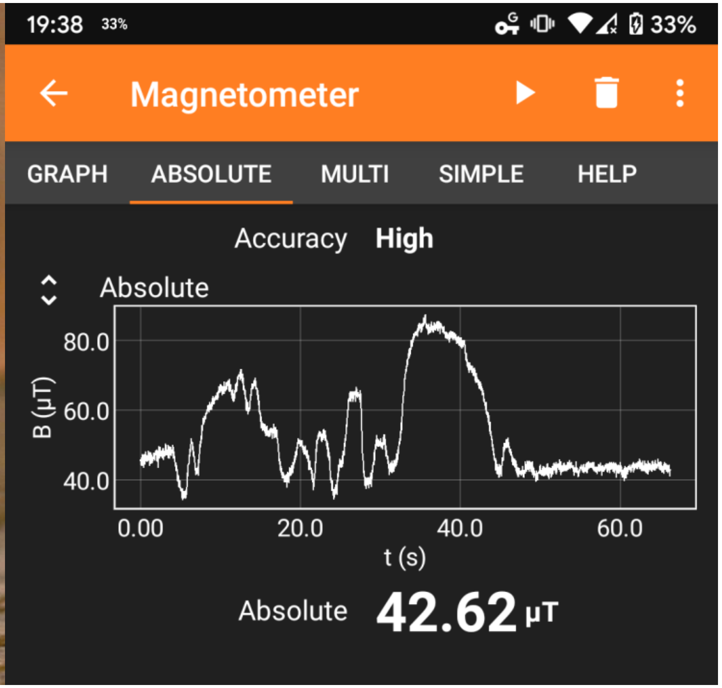
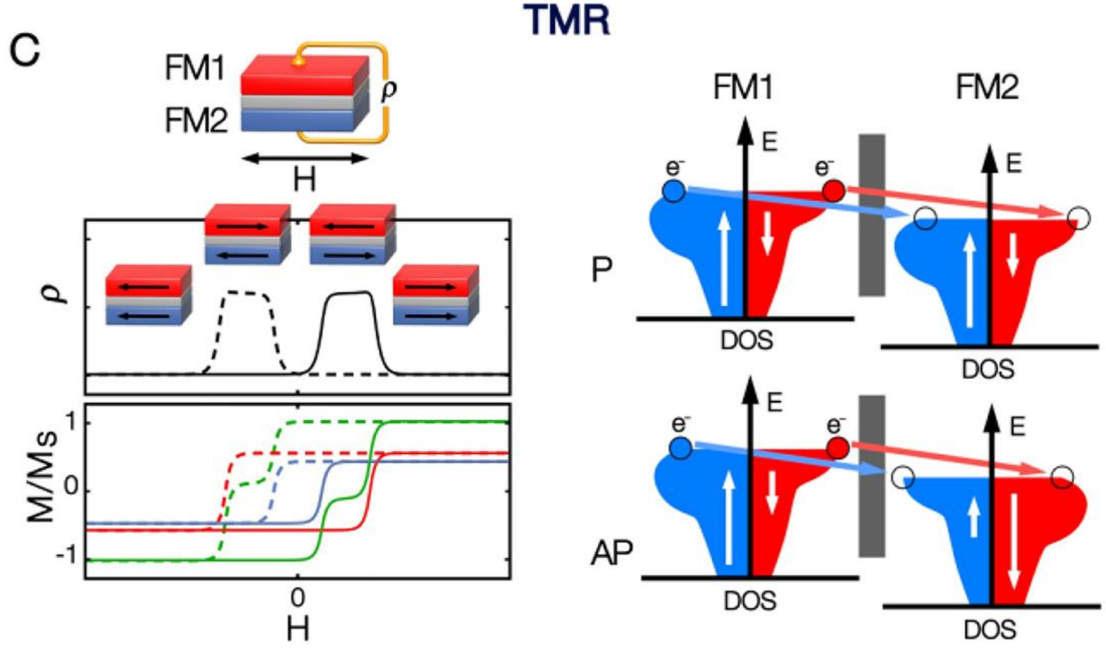
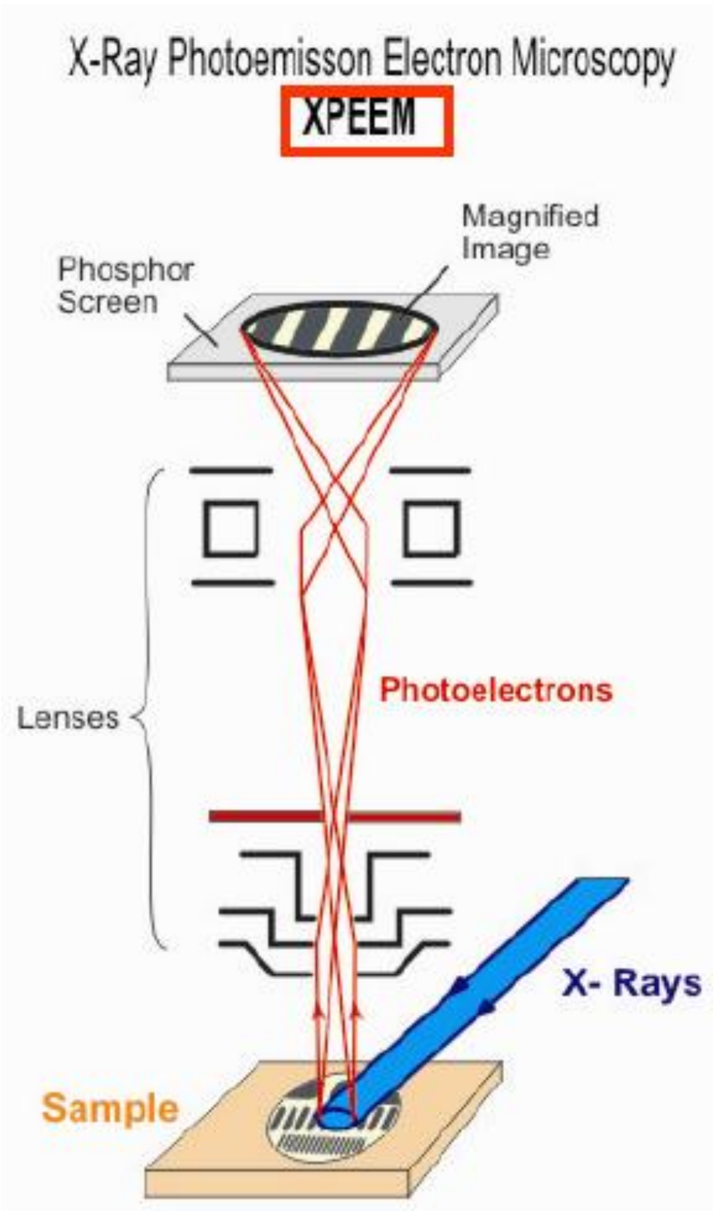


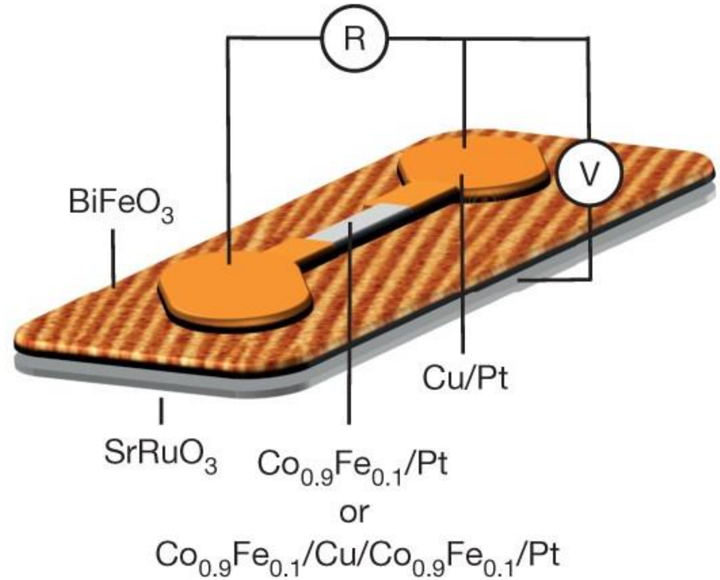


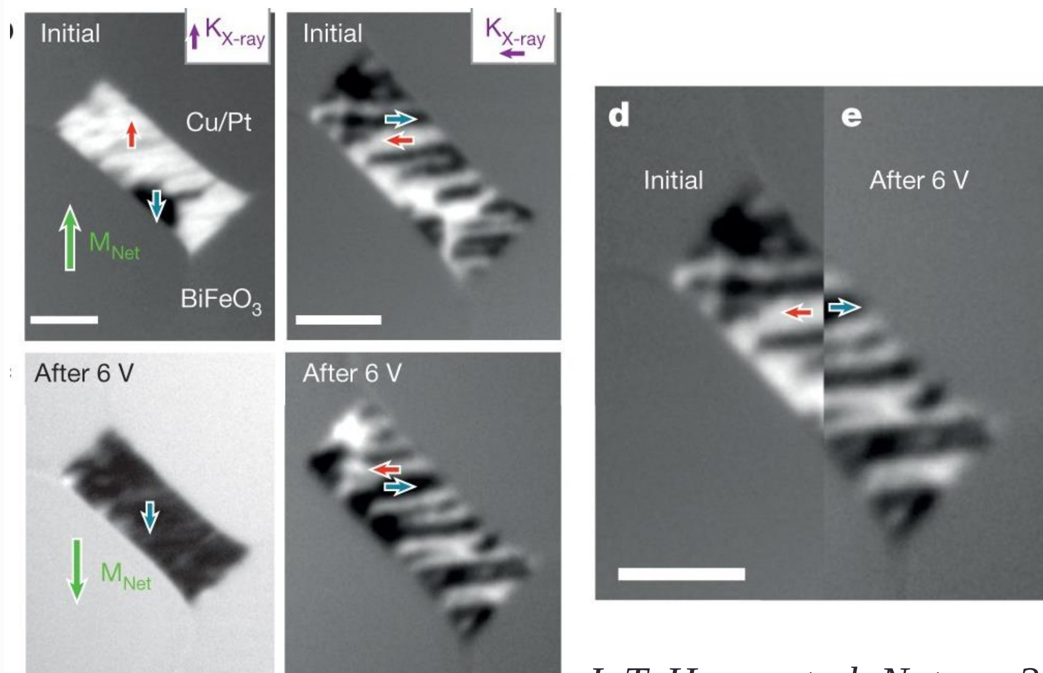
Technology Advancement

TMR









J. T. Heron et al. Nature, 2014

What does it take to explore advanced magnetic materials and phenomena ?

General requirements:	*Technique requirements:*
see the invisible	nanoscale spatial resolution
separate spin and orbital contributions	sensitive to s-o coupling
study thin films and interfaces	large cross section for "signal"
look below the surface	depth sensitivity
distinguish components	elemental (chemical) specificity
resolve dynamic motions	time resolution < 1 nanosecond

Where is magnetism coming from microscopically?

State of electron in atom

State of electron in atom is defined by a set of quantum numbers: $(n,\ l,\ m_l, m_s)$

n - principal quantum number

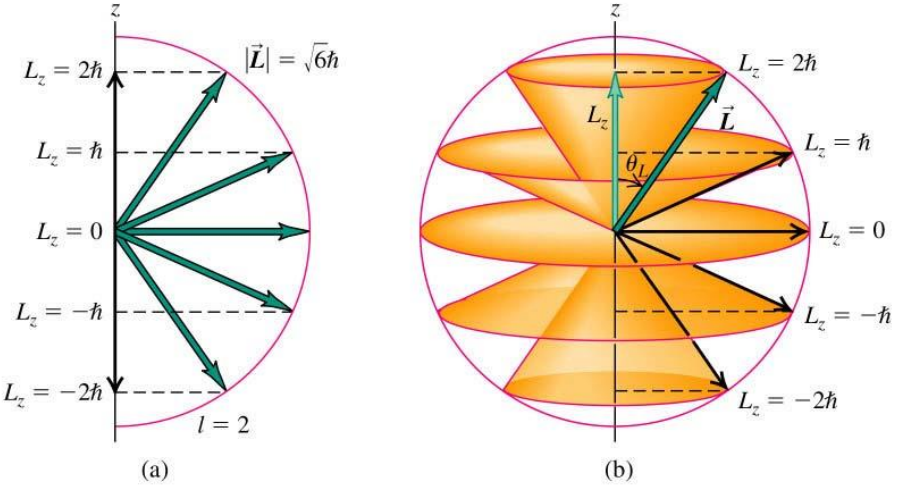
$L = \sqrt{l(l+1)}\ \hbar$; l - orbital q.n. ; $l = 0,\ 1,\ 2,\ \ldots\ (n-1)$

$L_z = m_l \hbar$; m_l - magnetic q.n. $|m_l| \le l$

$S = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\ \hbar$; $S_z = m_s \hbar$; $m_s = \pm\frac{1}{2}$; m_s - spin q.n.

$$\langle m^z_{\text{tot}} \rangle = -\frac{\mu_{\text{B}}}{\hbar}\ (2\langle s_z \rangle + \langle l_z \rangle)$$

So far we have been talking about wavefunction or state for one electron. *What happen if we have multiple electrons?*



Pauli Exclusion Principle (1925)

No two electrons in an atom can be in the same quantum state; i.e. they cannot have the same set of values for the quantum numbers n, l, m_l and m_s

TABLE 41.2 Quantum States of Electrons in the First Four Shells

n	l	m_l	Spectroscopic Notation	Number of States		Shell
1	0	0	1s	2		K
2	0	0	2s	2	8	L
2	1	−1, 0, 1	2p	6		
3	0	0	3s	2	18	M
3	1	−1, 0, 1	3p	6		
3	2	−2, −1, 0, 1, 2	3d	10		
4	0	0	4s	2	32	N
4	1	−1, 0, 1	4p	6		
4	2	−2, −1, 0, 1, 2	4d	10		
4	3	−3, −2, −1, 0, 1, 2, 3	4f	14		

$2n^2$ electrons

Completely filled orbits are very stable !

Many-Electron Atoms

Similar to hydrogen atom, but with more complicated potential due to the screening effect of other electrons (multi-body problem)

State of electron in atom is defined by a set of quantum numbers: (n, l, m_l, m_s)

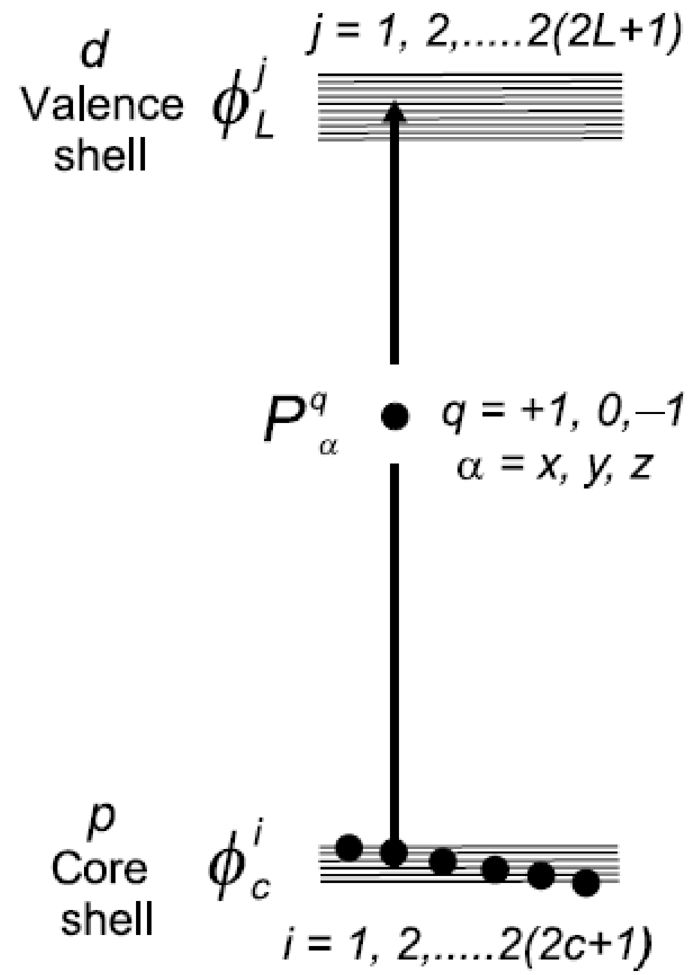
$$E_n \propto -\frac{1}{(4\pi\varepsilon_0)^2}\frac{mZ_{eff}^2 e^4}{2n^2\hbar^2}$$

$$n \geq 1 \quad 0 \leq l \leq n-1 \quad |m_l| \leq l \quad m_s = \pm\frac{1}{2}$$

(allowed values of quantum numbers)

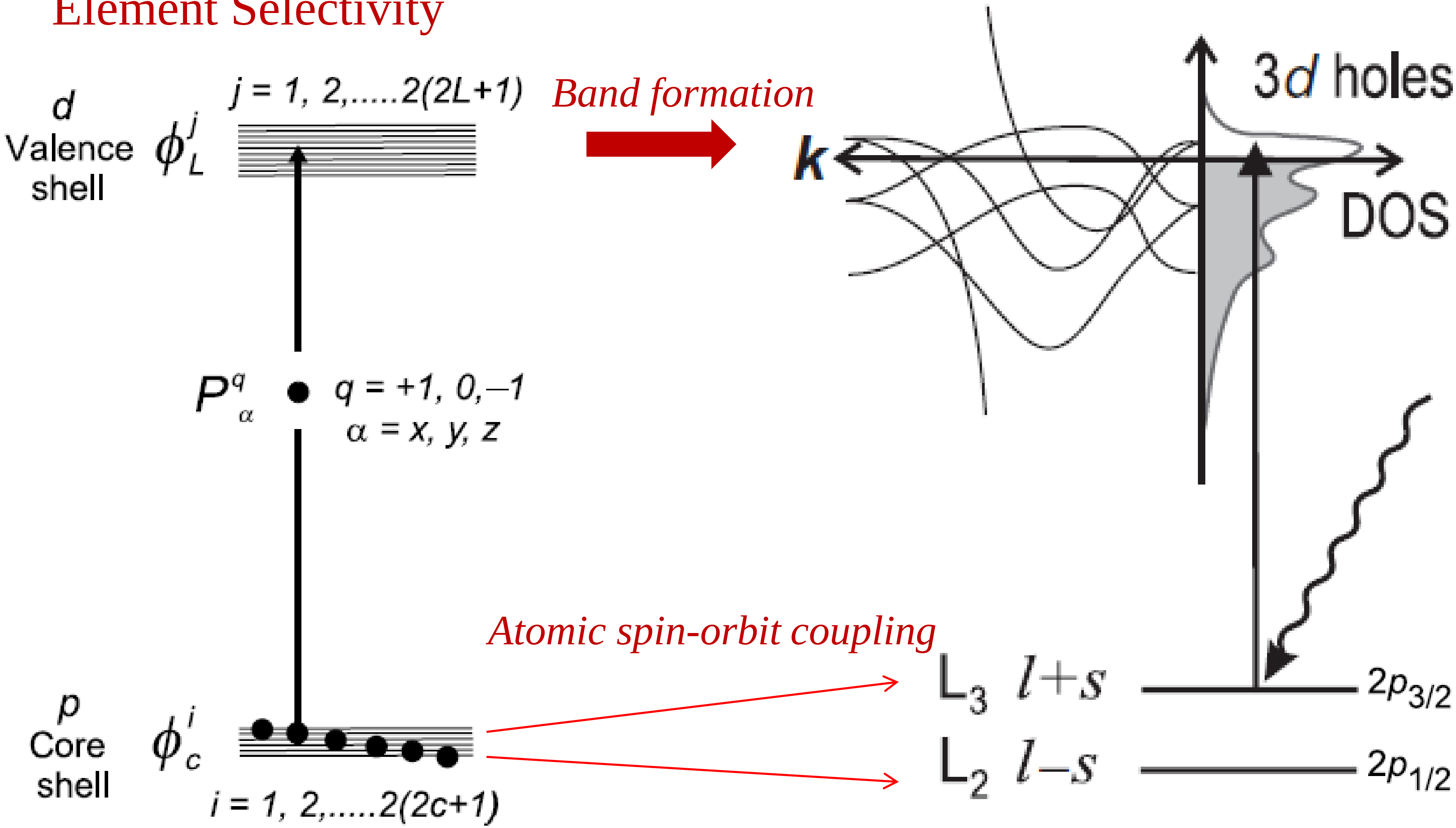
TABLE 41.3 Ground-State Electron Configurations

Element	Symbol	Atomic Number (Z)	Electron Configuration
Hydrogen	H	1	$1s$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2 2s$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p$
Carbon	C	6	$1s^2 2s^2 2p^2$
Nitrogen	N	7	$1s^2 2s^2 2p^3$
Oxygen	O	8	$1s^2 2s^2 2p^4$
Fluorine	F	9	$1s^2 2s^2 2p^5$
Neon	Ne	10	$1s^2 2s^2 2p^6$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	Al	13	$1s^2 2s^2 2p^6 3s^2 3p$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d$
Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s 3d^5$
Manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
Nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s 3d^{10}$
Zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$



How to probe partially a filled shell of an element?

Element Selectivity



- *Each element may have multiple core levels.*
- *The core level may split due to spin-orbit coupling*

X-ray absorption cross-section is given by

$$\sigma^{\mathrm{abs}} = 4\pi^2 \frac{e^2}{4\pi\epsilon_0 \hbar c} \hbar\omega \underbrace{|\langle b|\boldsymbol{\epsilon}\cdot\boldsymbol{r}|a\rangle|^2}_{\text{Transition Probability}} \overbrace{\delta[\hbar\omega - (E_b - E_a)]}^{\text{Energy Conservation}} \underbrace{\rho(E_b)}_{\text{Density of States}}$$

Energy Conservation

Transition Probability

Density of States

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

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

Integrate over the empty states in $\rho(E_b)$

Obviously, it depends on the electric field direction.

Electron position: $\mathbf{r} = x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z$

Electric field unit vectors of linearly polarized light:

$$\boldsymbol{\epsilon}_x^0 = \boldsymbol{\epsilon}_x = \boldsymbol{e}_x \qquad \boldsymbol{\epsilon}_y^0 = \boldsymbol{\epsilon}_y = \boldsymbol{e}_y \qquad \boldsymbol{\epsilon}_z^0 = \boldsymbol{\epsilon}_z = \boldsymbol{e}_z$$

Electric field unit vectors of circularly polarized light:

$$\boldsymbol{\epsilon}_z^{\pm} = \mp \frac{1}{\sqrt{2}} (\boldsymbol{\epsilon}_x \pm \mathrm{i}\, \boldsymbol{\epsilon}_y) \qquad \boldsymbol{\epsilon}_z^0 = \boldsymbol{\epsilon}_z = \boldsymbol{e}_z$$

(Photon angular momentum equal to1.)

Dipolar operator: $P_\alpha^q = \boldsymbol{\epsilon} \cdot \mathbf{r} = \boldsymbol{\epsilon}_\alpha^q \cdot \mathbf{r}$

For example:

$$P_z^{\pm} = \boldsymbol{\epsilon}_z^{\pm} \cdot \mathbf{r} = \mp \frac{1}{\sqrt{2}} (x \pm \mathrm{i} y) = r \sqrt{\frac{4\pi}{3}}\, Y_{1,\pm 1},$$

$$P_z^0 = \boldsymbol{\epsilon}_z \cdot \mathbf{r} = \qquad z \qquad = r \sqrt{\frac{4\pi}{3}}\, Y_{1,0}.$$

Racah's spherical tensor operators are defined as

$$C_m^{(l)} = \sqrt{\frac{4\pi}{2l+1}}\; Y_{l,m}(\theta,\phi) \quad \xrightarrow{\textit{for photon}} \quad C_p^{(1)}$$

Transition Probability: *It depends on spin, orbital, and the x-ray polarization!*

$$\langle b|\, P_\alpha^q \,|a\rangle = \underbrace{\delta(m_s', m_s)}_{\text{spin}}\; \underbrace{\langle R_{n',l}(r)|r|R_{n,c}(r)\rangle}_{\text{radial}}\; \underbrace{\sum_{m_c,m_l,p} e_{\alpha,p}^q\,\langle l, m_l|\, C_p^{(1)}\,|c, m_c\rangle}_{\text{angular}},$$

For example:

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

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

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The *dipole selection rules* for transitions between states of the form $|n, l, m_l, s, m_s\rangle$ are:

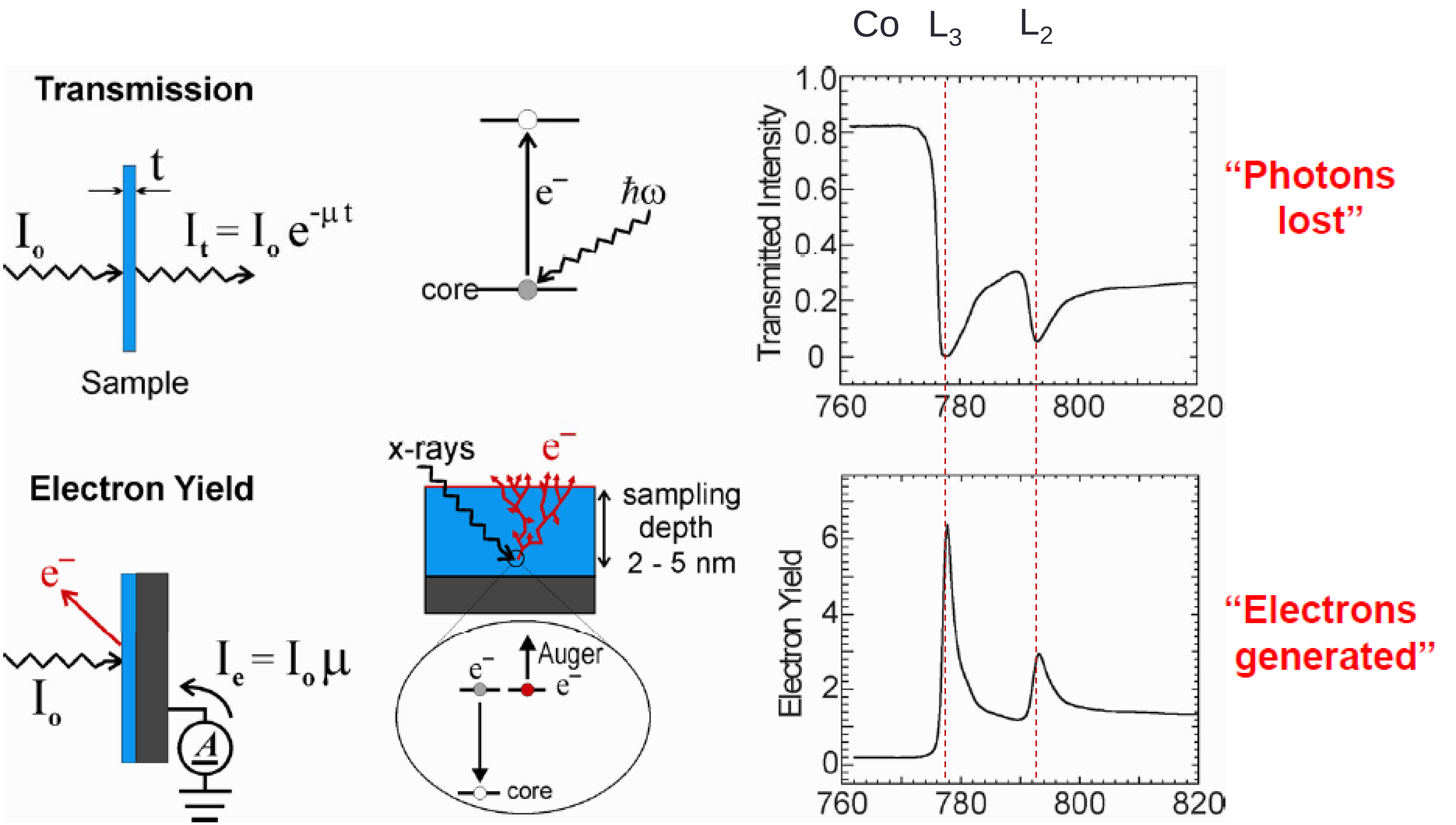
$\Delta l = l' - l = \pm 1,$

$\Delta m_l = m_l' - m_l = q = 0, \pm 1,$

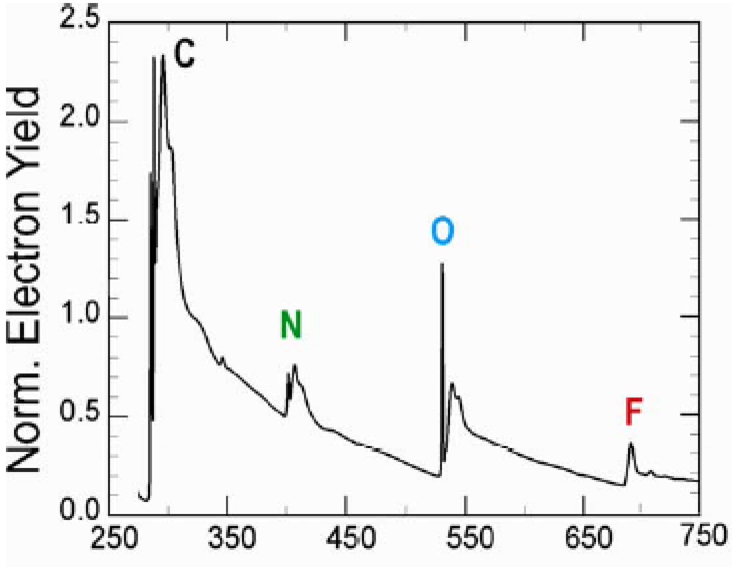
$\Delta s = s' - s = 0,$

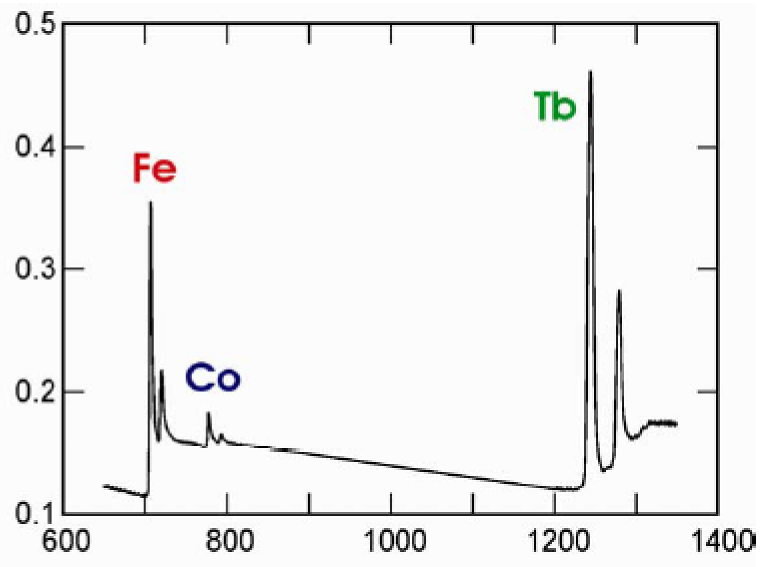
$\Delta m_s = m_s' - m_s = 0.$

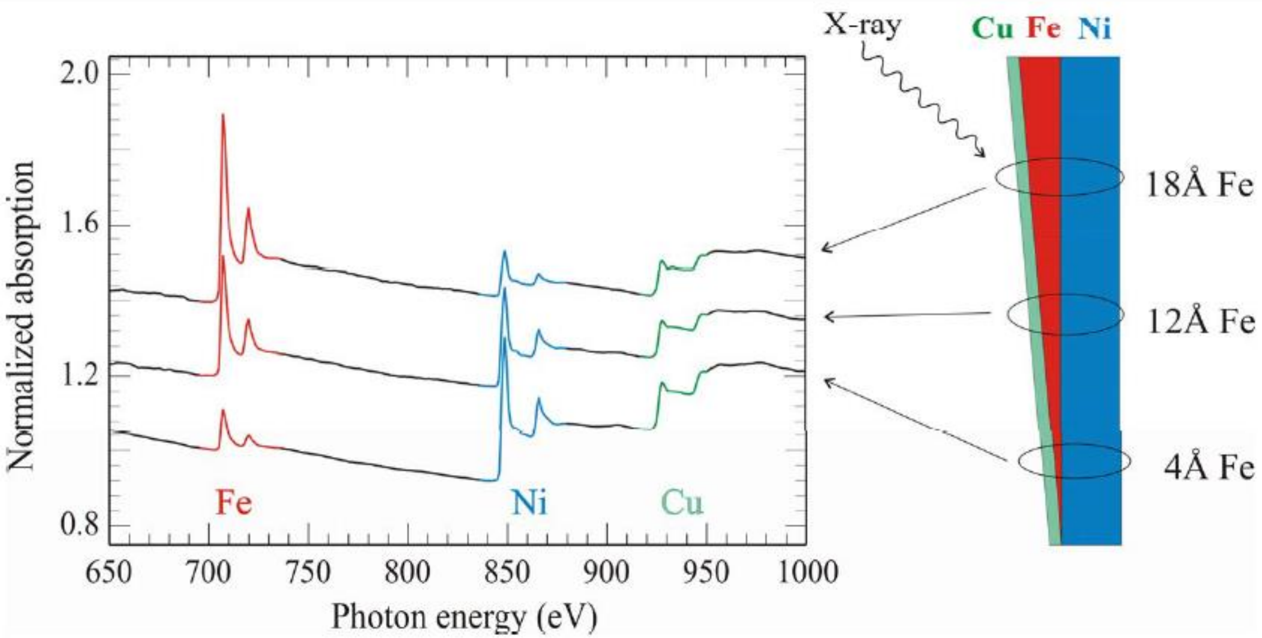
Orientation-Averaged Intensity



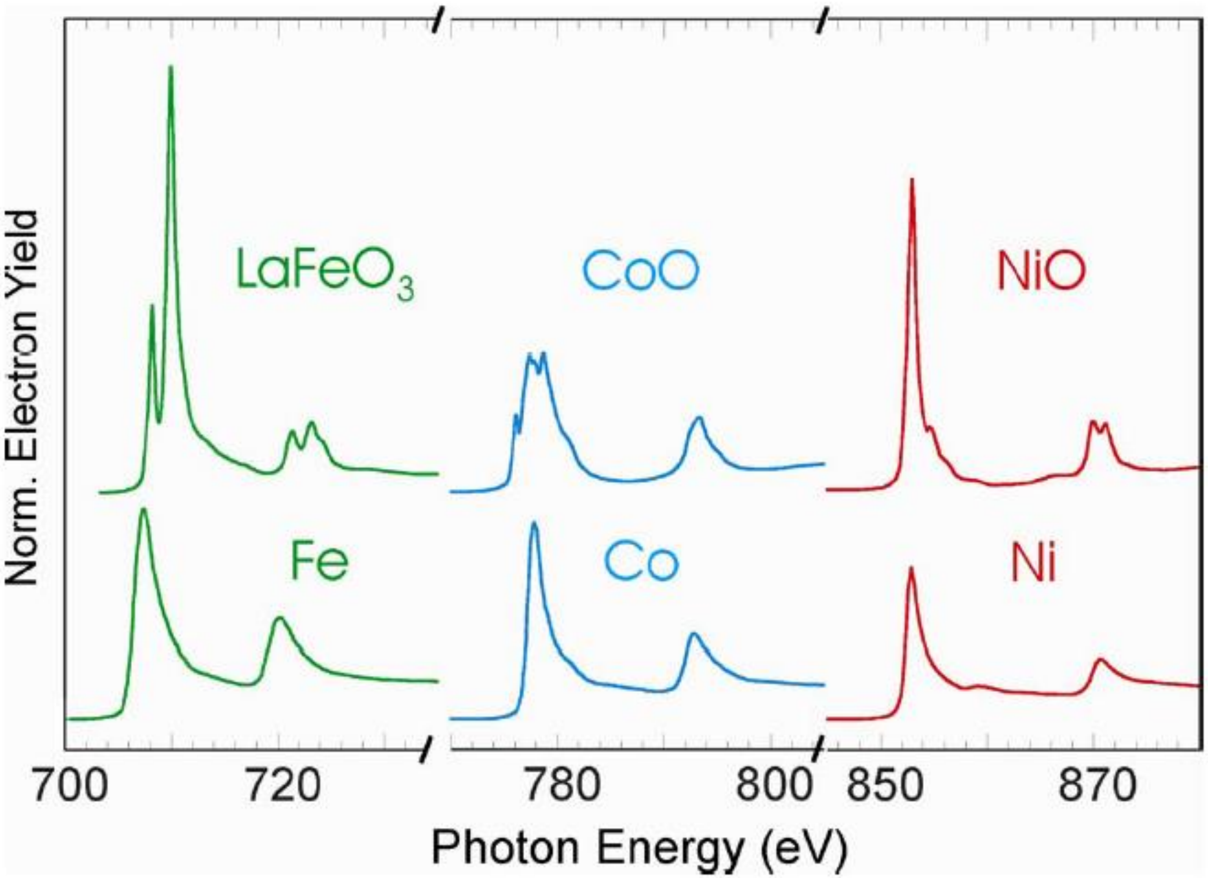
Tunable x-rays offer elemental specificity

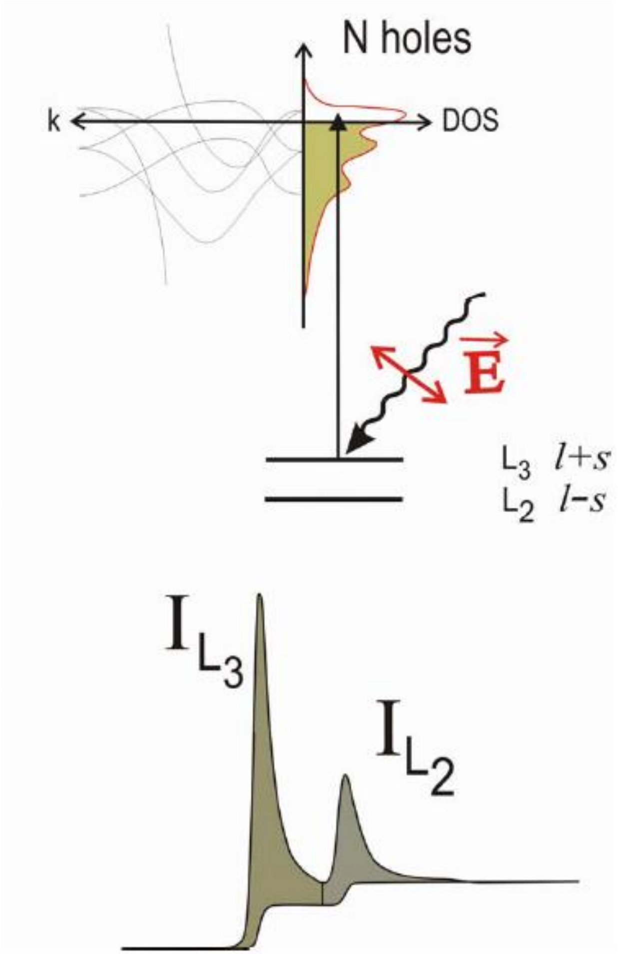






Rich “multiplet structure” reveals local bonding

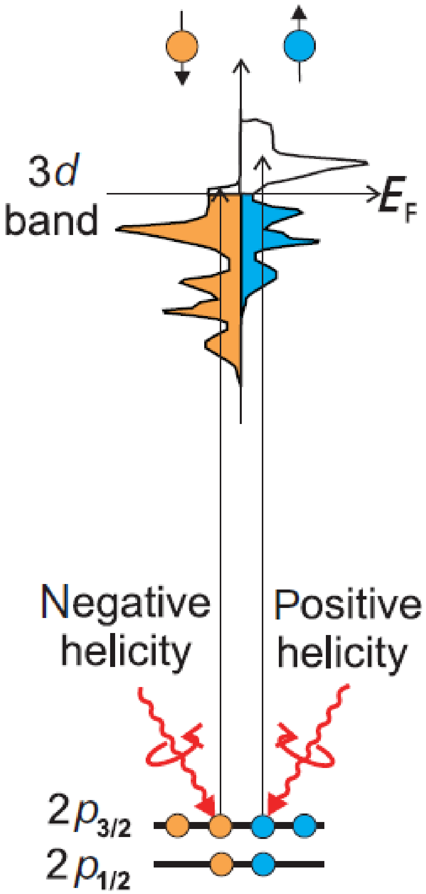




The charge sum rule: $\langle I \rangle = C\, N_{\mathrm{h}}$

$$N_h = \langle I_{L_3} + I_{L_2} \rangle / C$$

X-ray Magnetic Circular Dichroism



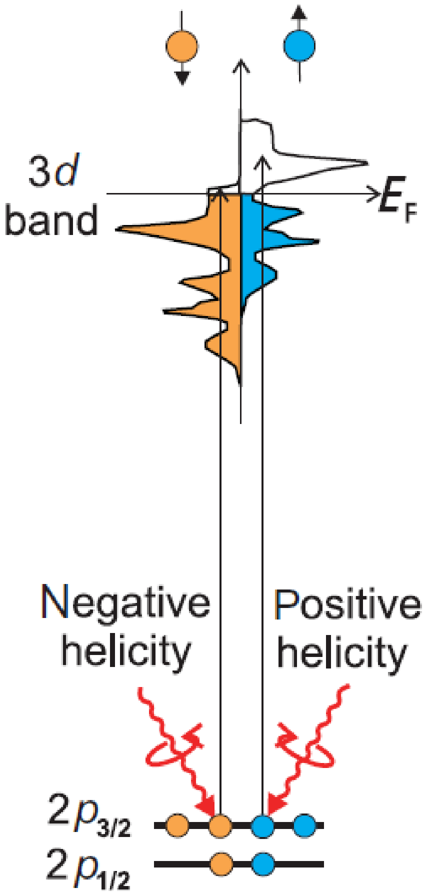
Ferromagnetic ↑ ↑ ↑ ↑ ↑ ↑ ↑	Below T_C, spins are aligned parallel in magnetic domains
Antiferromagnetic ↑ ↓ ↑ ↓ ↑ ↓ ↑	Below T_N, spins are aligned antiparallel in magnetic domains
Ferrimagnetic ↑ ↓ ↑ ↓ ↑ ↓ ↑	Below T_C, spins are aligned antiparallel but do not cancel
Paramagnetic ↑ ↓ ↑ ↑ ↓ ↑ ↓	Spins are randomly oriented (any of the others above T_C or T_N)

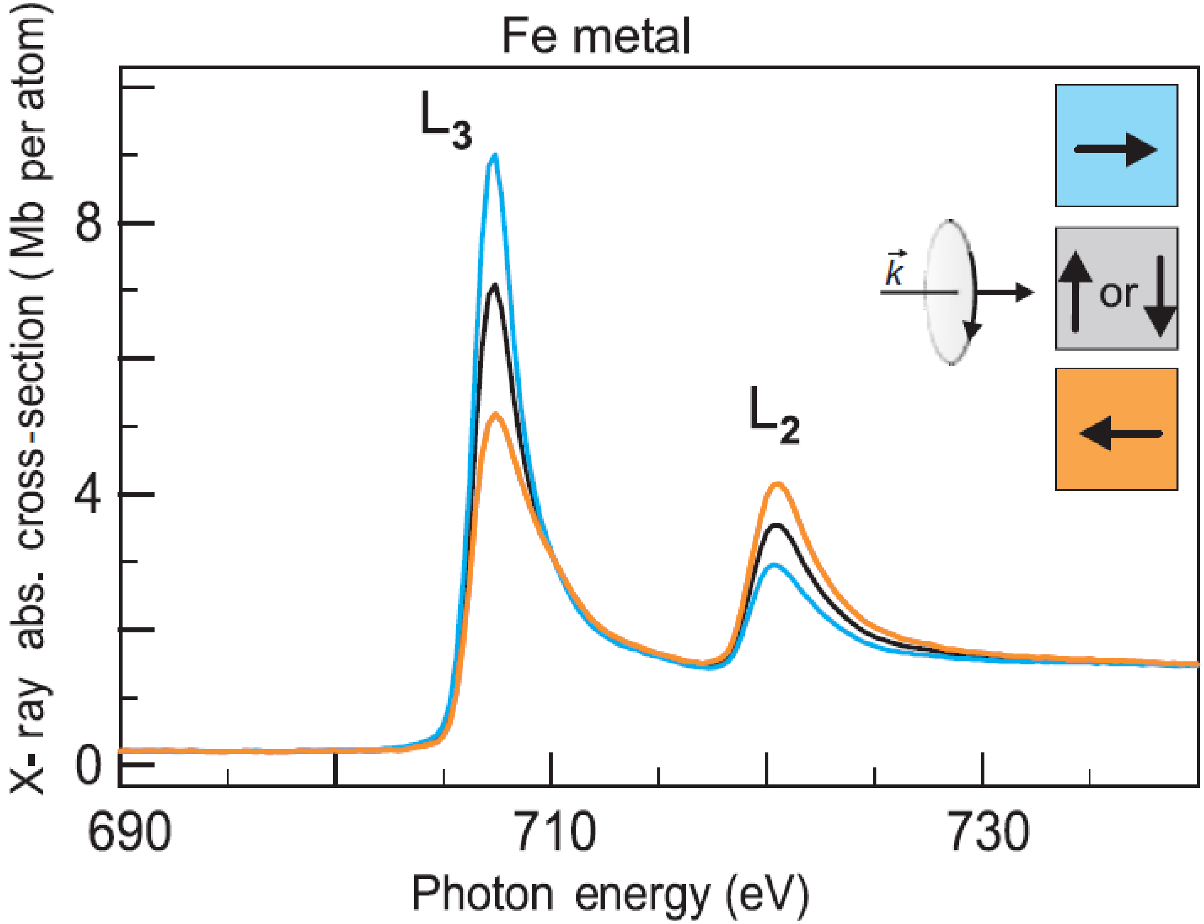
$$\Delta I_{\mathrm{L}_3} = \mathcal{A}\mathcal{R}^2 \sum_{n,m_j} |\langle d_n, \chi^+ | C^{(1)}_{-1} | p_{3/2}, m_j \rangle|^2 - |\langle d_n, \chi^+ | C^{(1)}_{+1} | p_{3/2}, m_j \rangle|^2$$

$$\epsilon_z^{\pm} = \mp \frac{1}{\sqrt{2}} (\epsilon_x \pm \mathrm{i}\, \epsilon_y)$$

$$\Delta I_{\mathrm{L}_2} = \mathcal{A}\mathcal{R}^2 \sum_{n,m_j} |\langle d_n, \chi^+ | C^{(1)}_{-1} | p_{1/2}, m_j \rangle|^2 - |\langle d_n, \chi^+ | C^{(1)}_{+1} | p_{1/2}, m_j \rangle|^2$$

X-ray Magnetic Circular Dichroism

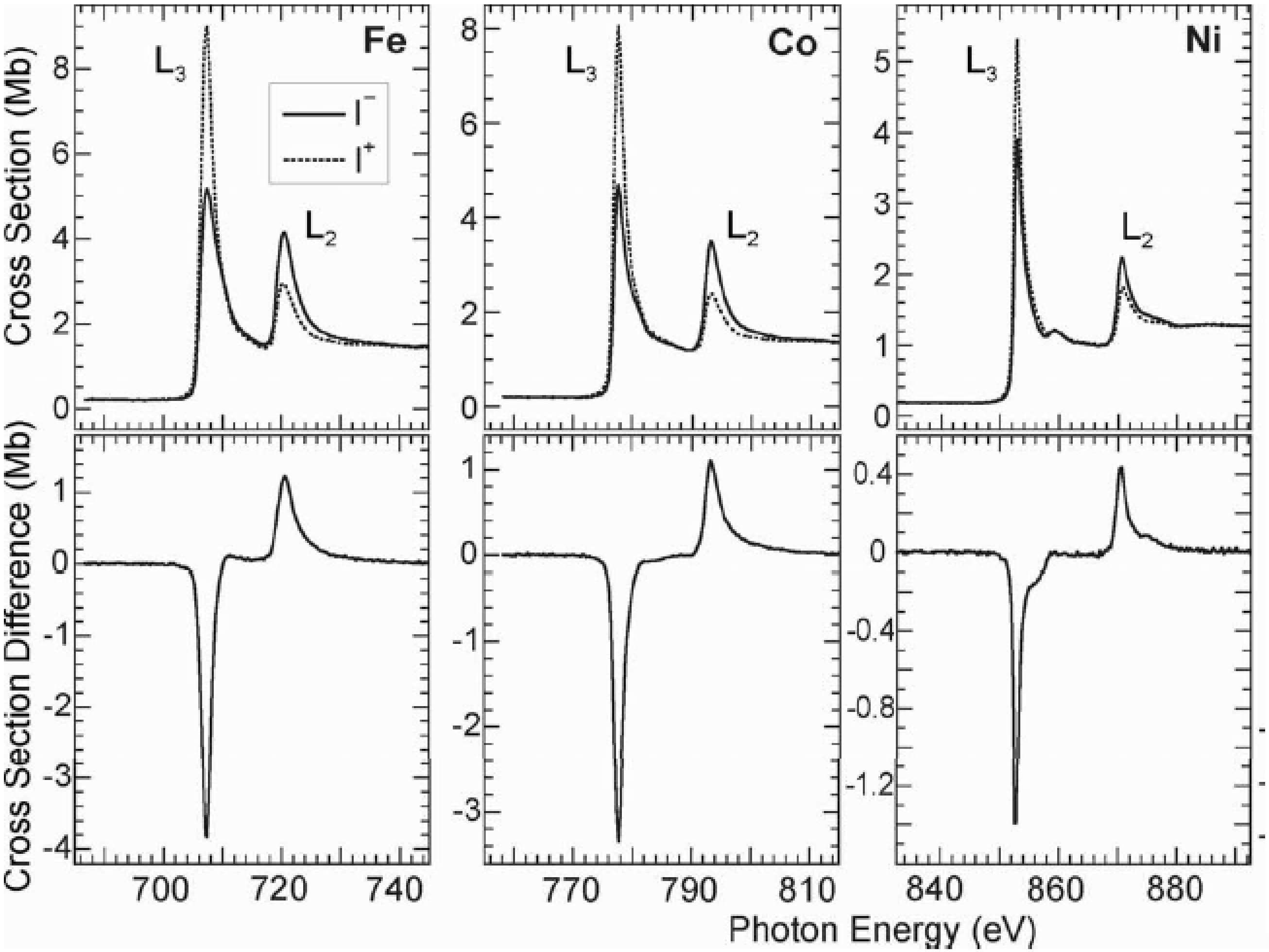




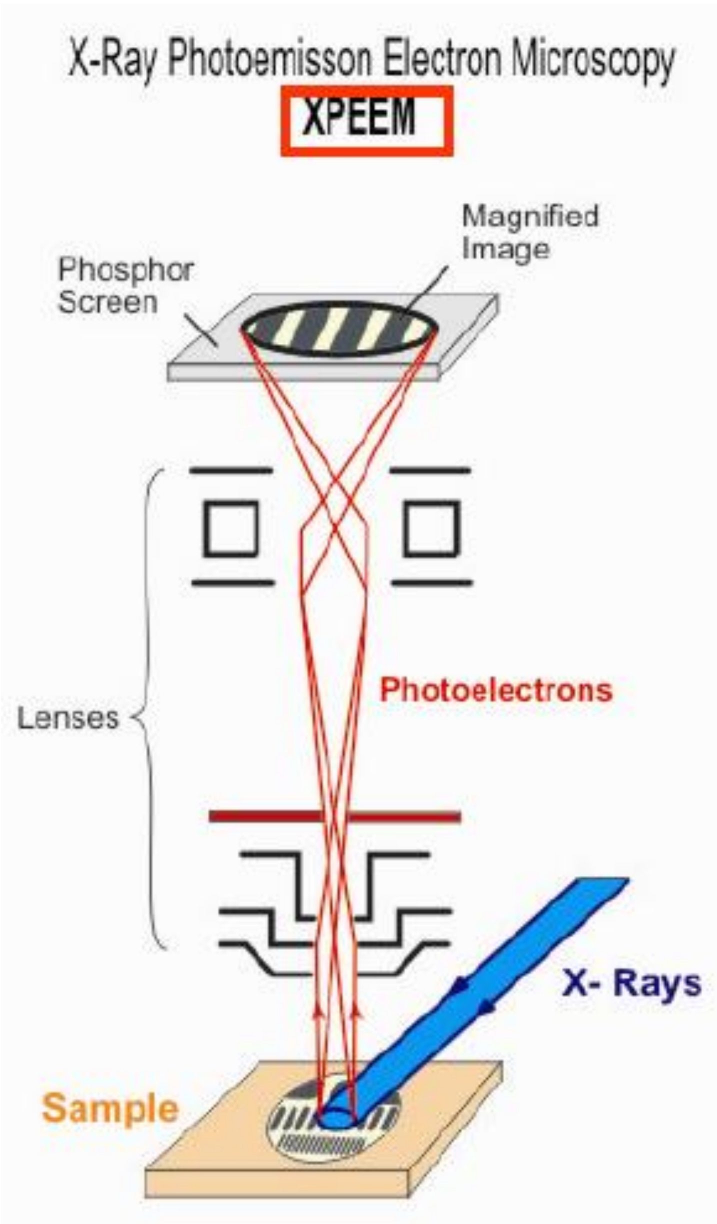
$$\epsilon_z^{\pm} = \mp \frac{1}{\sqrt{2}} (\epsilon_x \pm \mathrm{i}\, \epsilon_y)$$

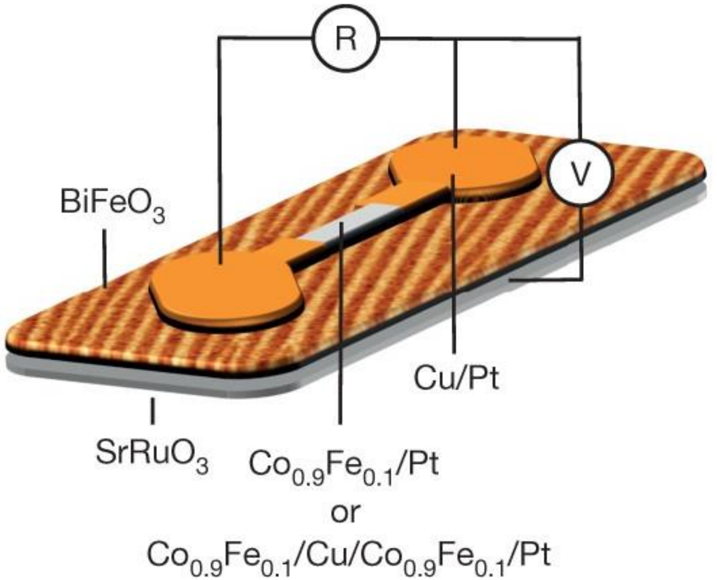
- *The intensity depends on x-ray polarization.*
- *This dependence is opposite between L_3 and L_2.*

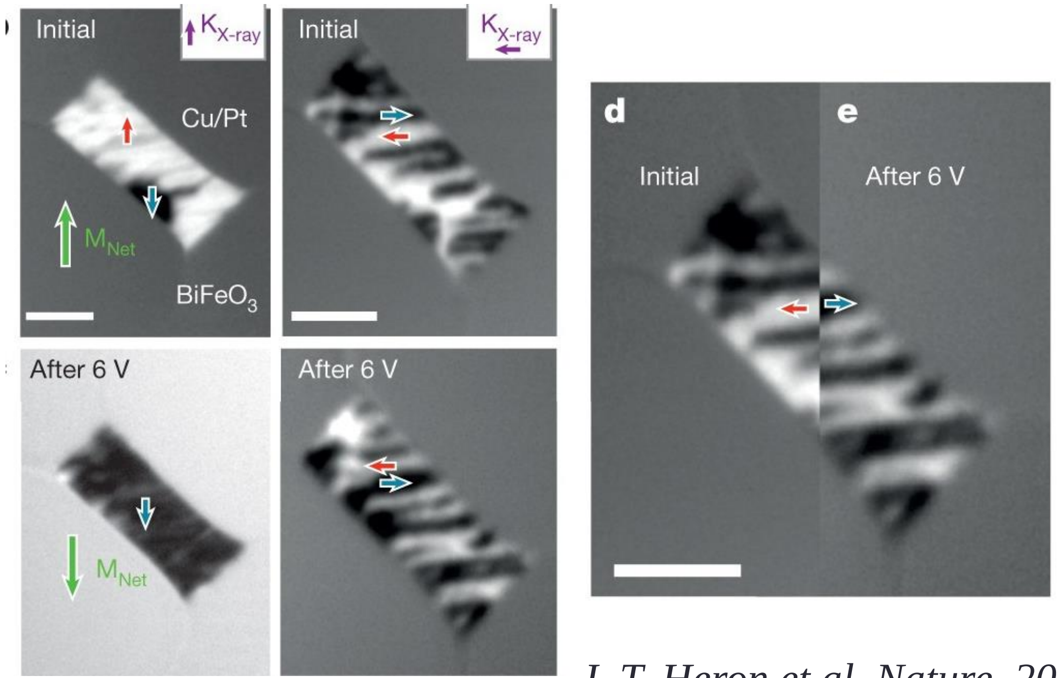
XMCD spectra of the pure ferromagnetic 3d metals



Defining the difference: $\Delta I = I^{\uparrow\downarrow} - I^{\uparrow\uparrow} = I^- - I^+$



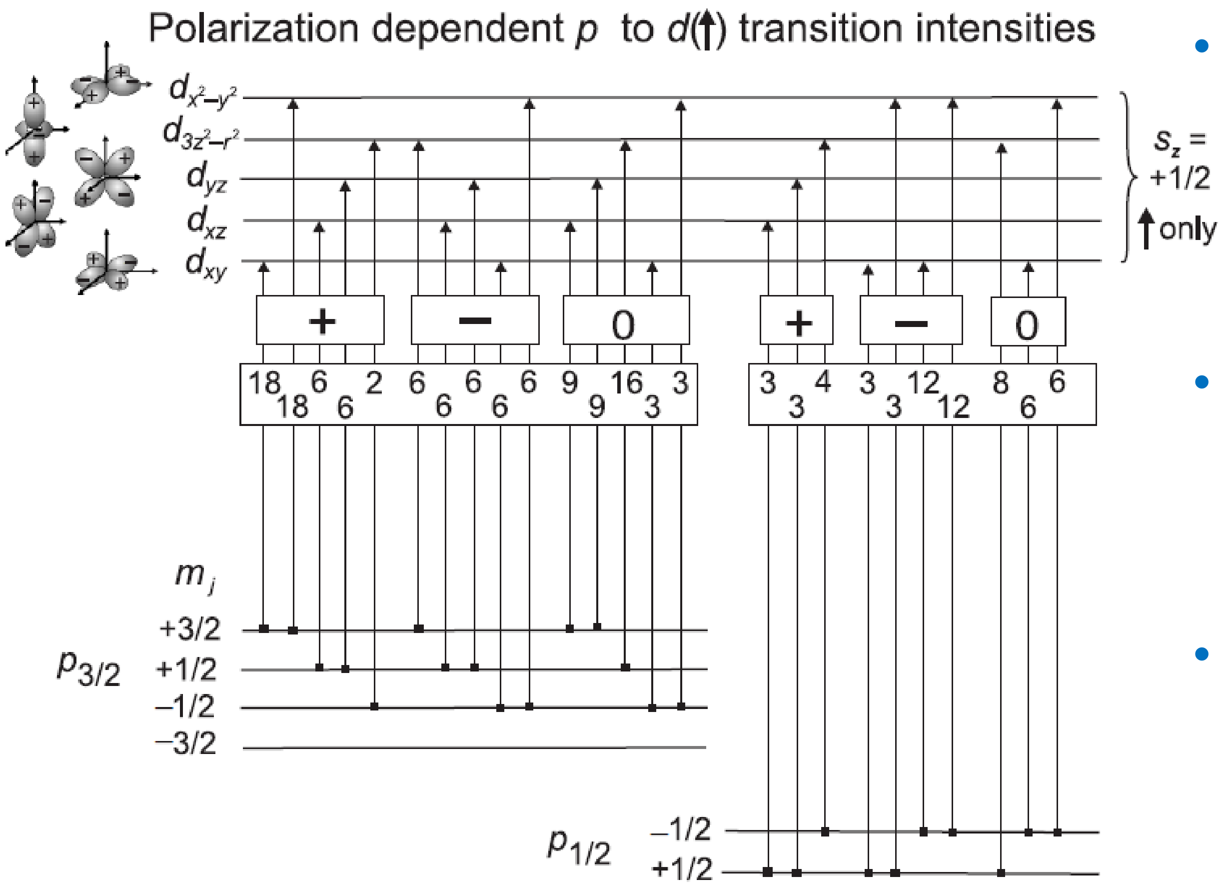




J. T. Heron et al. Nature, 2014

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

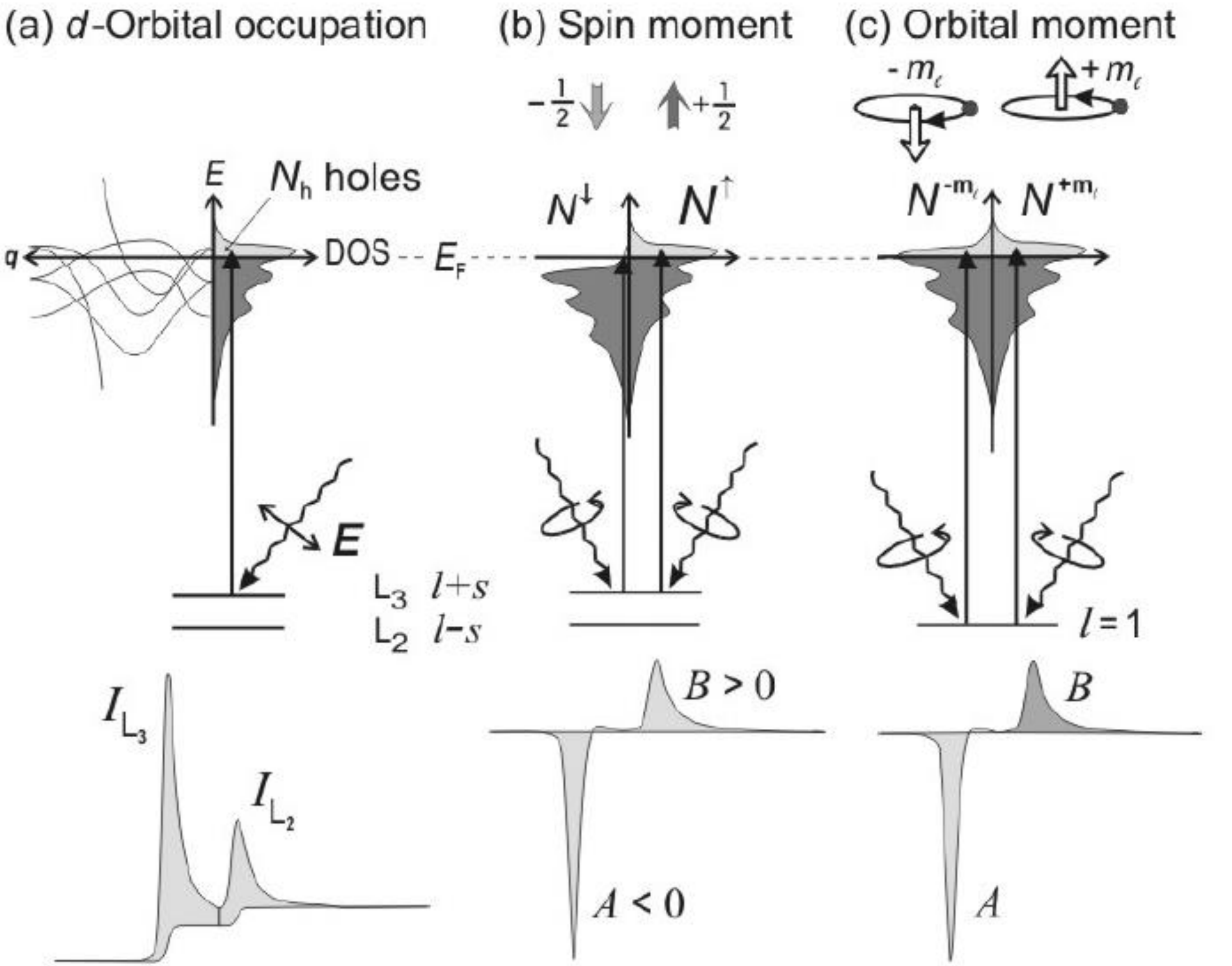
$$\Delta I_{L_2} = \mathcal{A}\mathcal{R}^2 \sum_{n,m_j} |\langle d_n, \chi^+ | C^{(1)}_{-1} | p_{1/2}, m_j \rangle|^2 - |\langle d_n, \chi^+ | C^{(1)}_{+1} | p_{1/2}, m_j \rangle|^2$$



- *The same core state can transit to all d-states but through different polarization and with different probabilities.*
- *The same d-state can be reached by all polarizations but from different core states.*
- *The opposite polarizations are favored between L_3 and L_2.*

Fundamentally, XMCD requires SOC in the core level or the valence state or both.

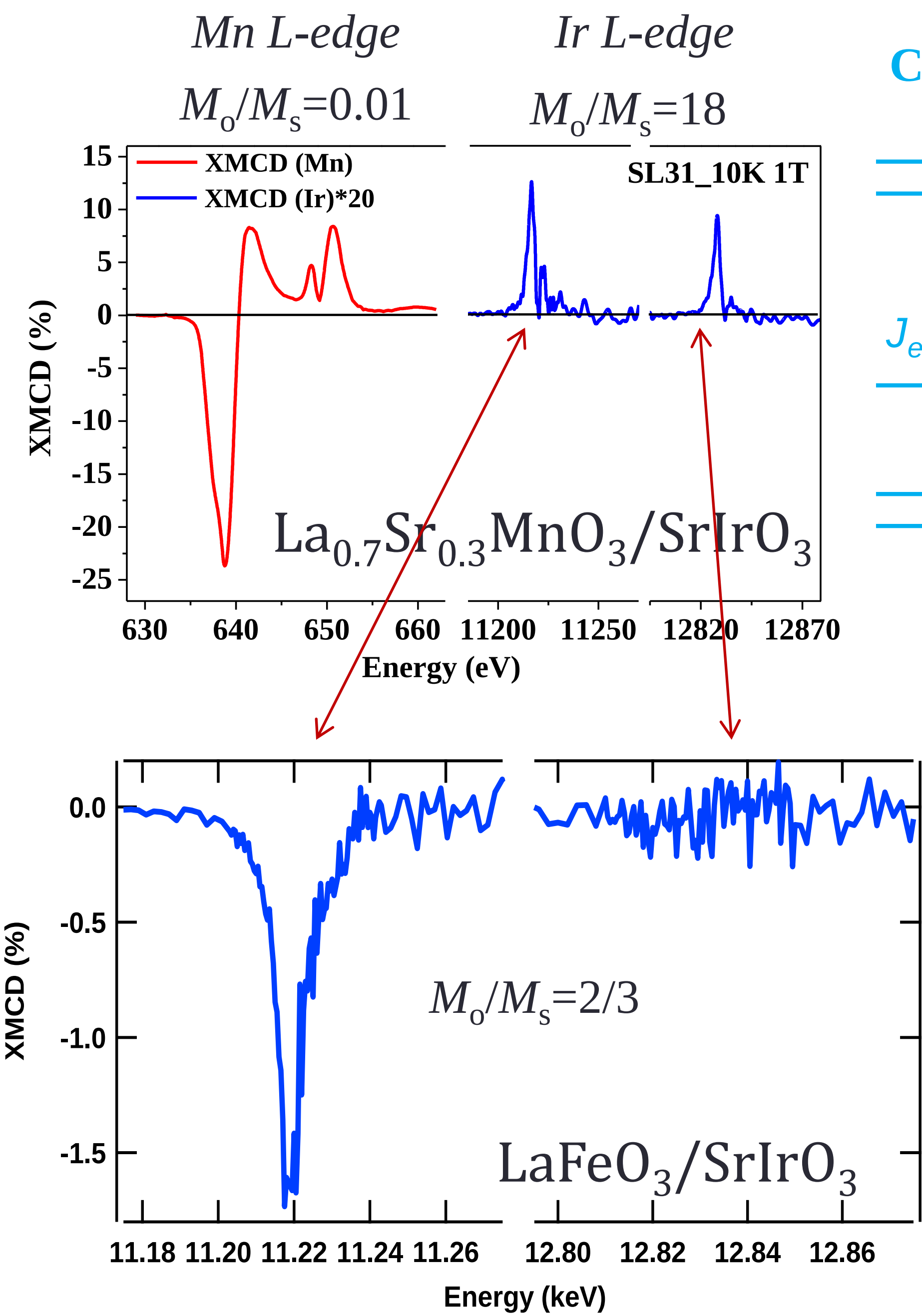
The sum rules

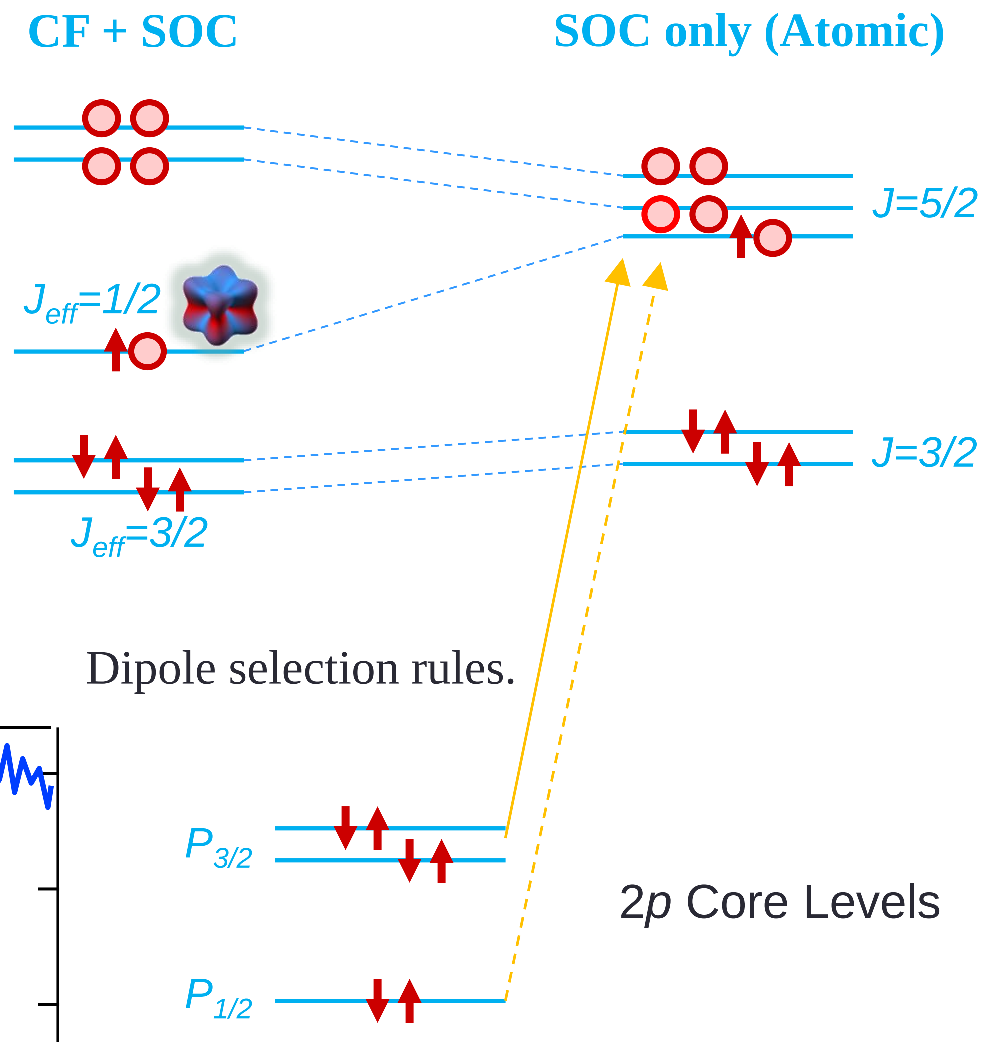


$N_h = \langle I_{L_3} + I_{L_2} \rangle / C$

$m_s = \mu_B \langle -A + 2B \rangle / C$

$m_o = -2\mu_B \langle A + B \rangle / 3C$





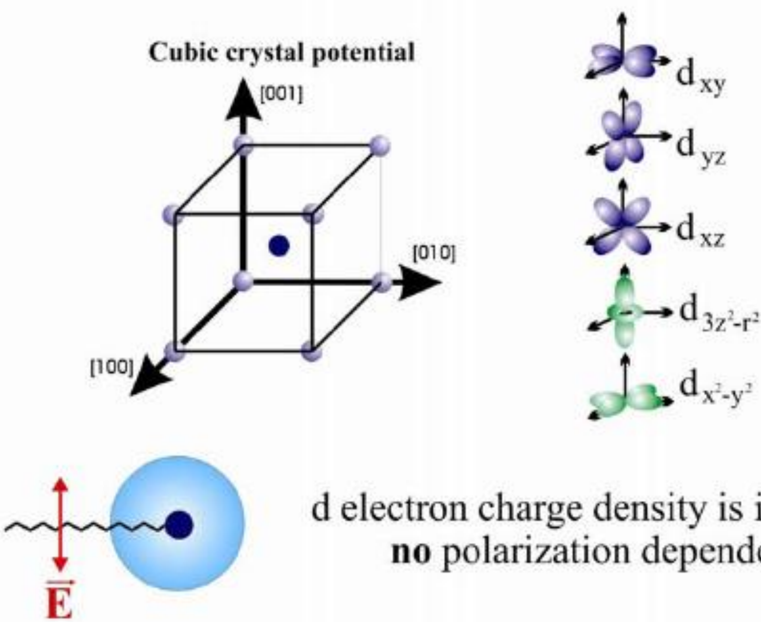
$m_s = \mu_B \langle -A + 2B \rangle / C$

$m_o = -2\mu_B \langle A + B \rangle / 3C$

D. Yi et al. PNAS, 2016

Polarization, Charge and Spin: X-Ray Magnetic **Linear** Dichroism

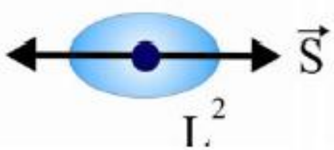
Non-magnetic state



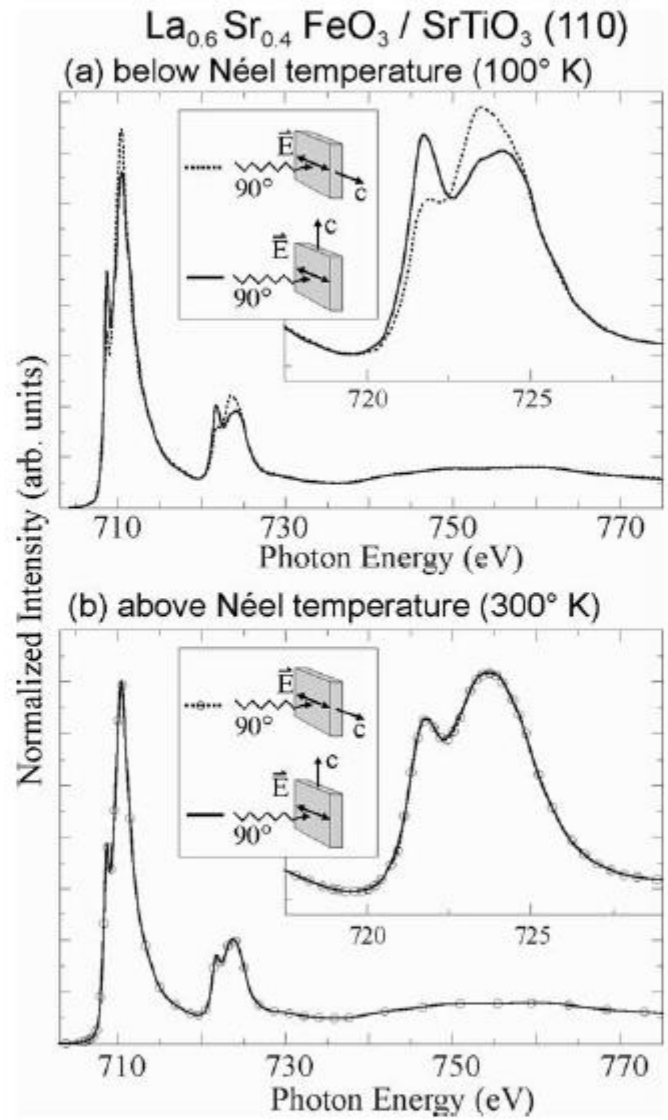
d electron charge density is isotropic
no polarization dependence

$$\epsilon_x^0 = \epsilon_x = e_x \qquad \epsilon_y^0 = \epsilon_y = e_y \qquad \epsilon_z^0 = \epsilon_z = e_z$$

Magnetic state - preferred spin axis

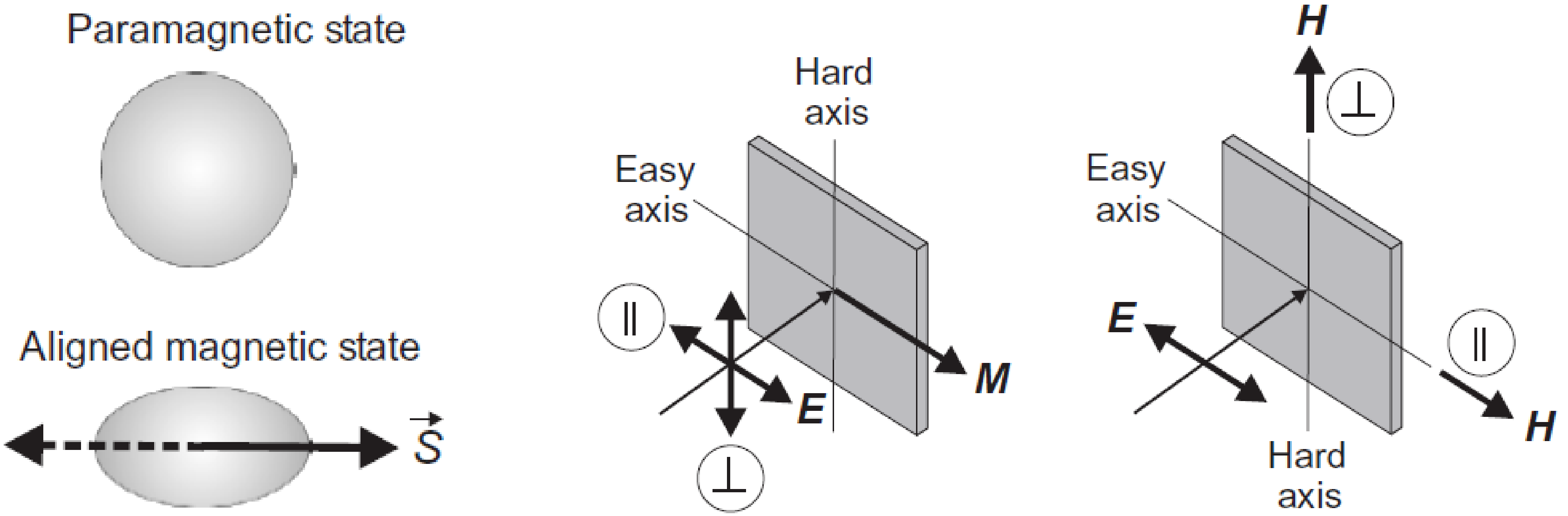


spin-orbit coupling distorts charge
creates polarization dependence



Lüning et al. Phys. Rev. B 67, 214433 (2003)

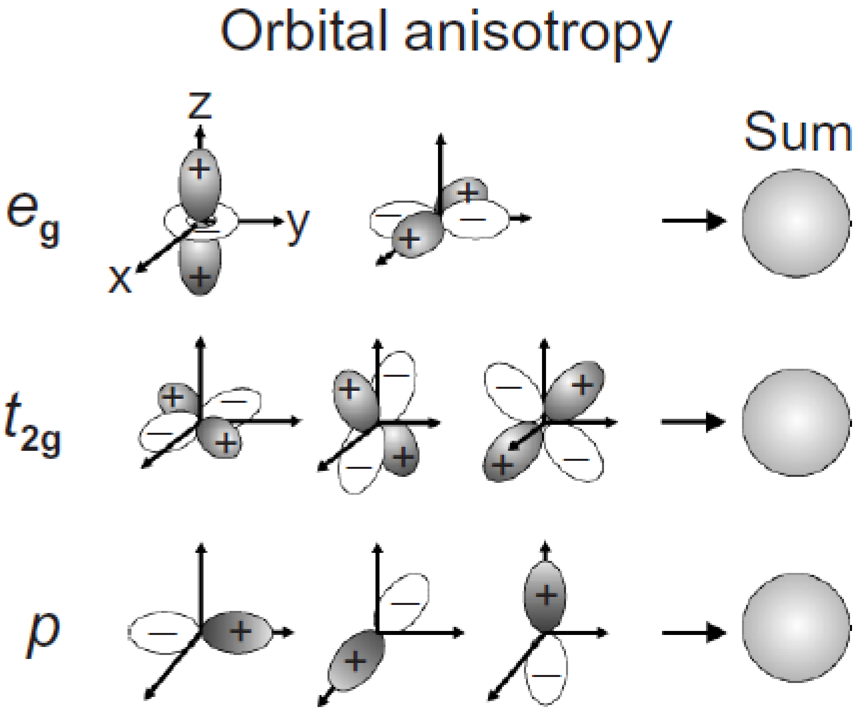
Unequal populations occur when the moments pick a specific axis.

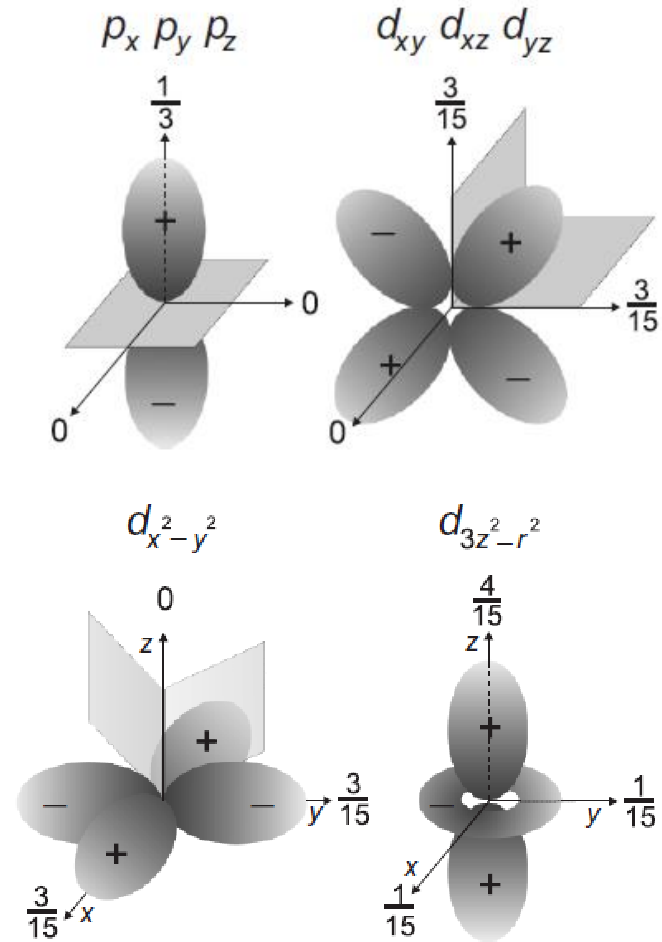


The *XMLD effect* arises from a nonspherical distortion of the atomic charge by the spin–orbit interaction when the *atomic spins* are axially aligned by the exchange interaction.

$$\Delta I_{\mathrm{XMLD}} = I^{\parallel} - I^{\perp}$$

$$= \mathcal{A}\mathcal{R}^2 \sum_{n,j,m_j} \left| \langle d_n, \chi^+ | C_0^{(1)} | p_j, m_j \rangle \right|^2 - \frac{1}{2} \left| \langle d_n, \chi^+ | C_{-1}^{(1)} - C_{+1}^{(1)} | p_j, m_j \rangle \right|^2$$



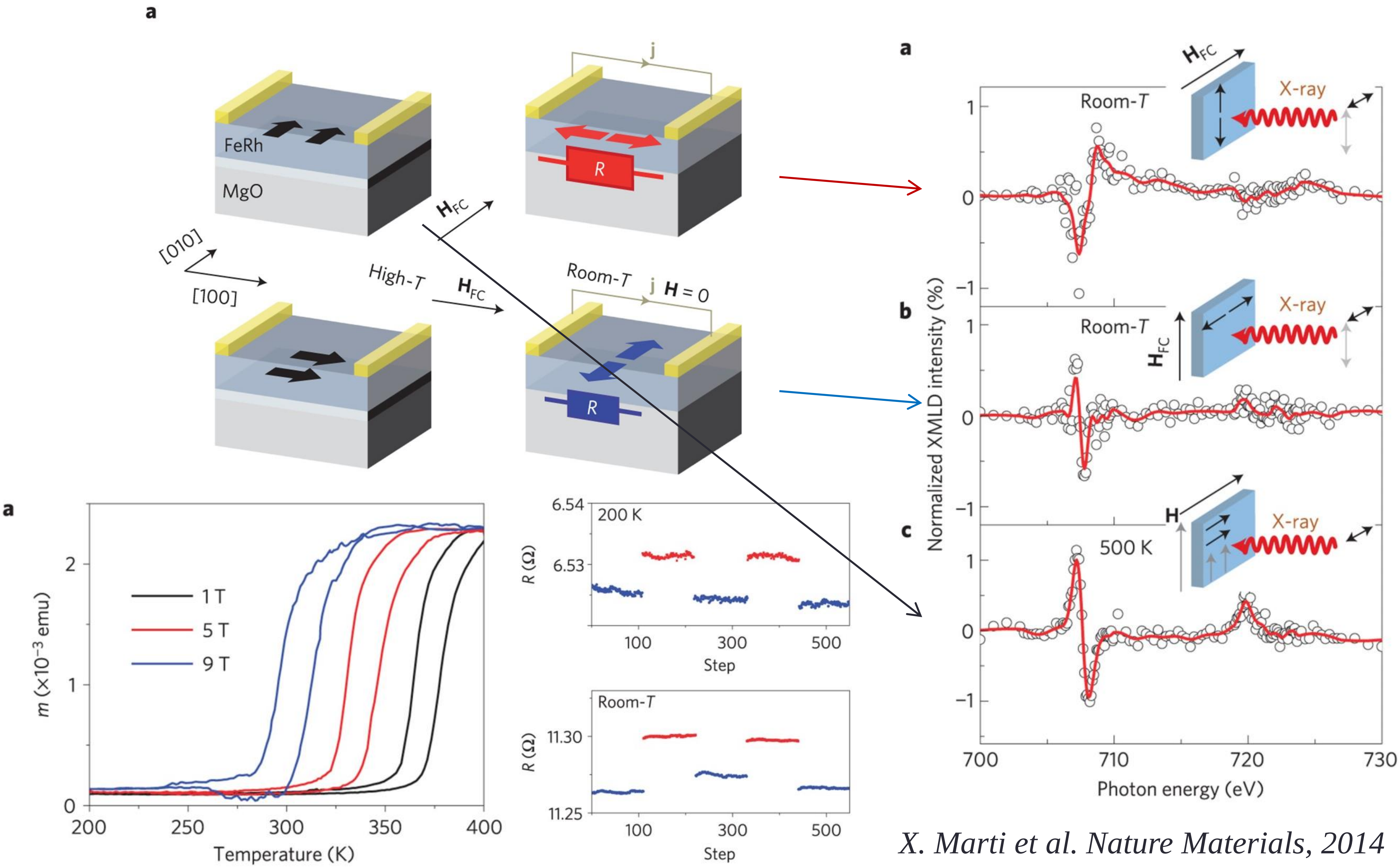


$$I_z^0 = \mathcal{A}\mathcal{R}^2 \left|\langle b|C_0^{(1)}|a\rangle\right|^2$$

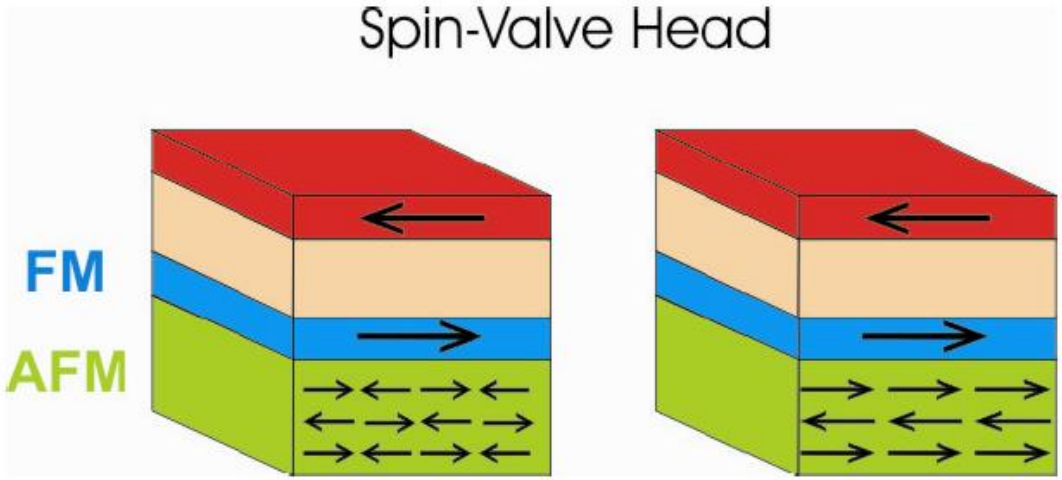
$$I_x^0 = I_y^0 = \frac{1}{2}\mathcal{A}\mathcal{R}^2\left[\left|\langle b|C_{-1}^{(1)}|a\rangle\right|^2 + \left|\langle b|C_1^{(1)}|a\rangle\right|^2\right]$$

- *Orbitals have anisotropic shapes.*
- *The transition probability of a particular orbital depends on whether the polarization is along its principle axis.*
- *For equally populated orbitals,* $I_\alpha^q = I_{\alpha'}^q = I_\alpha^{q'}$

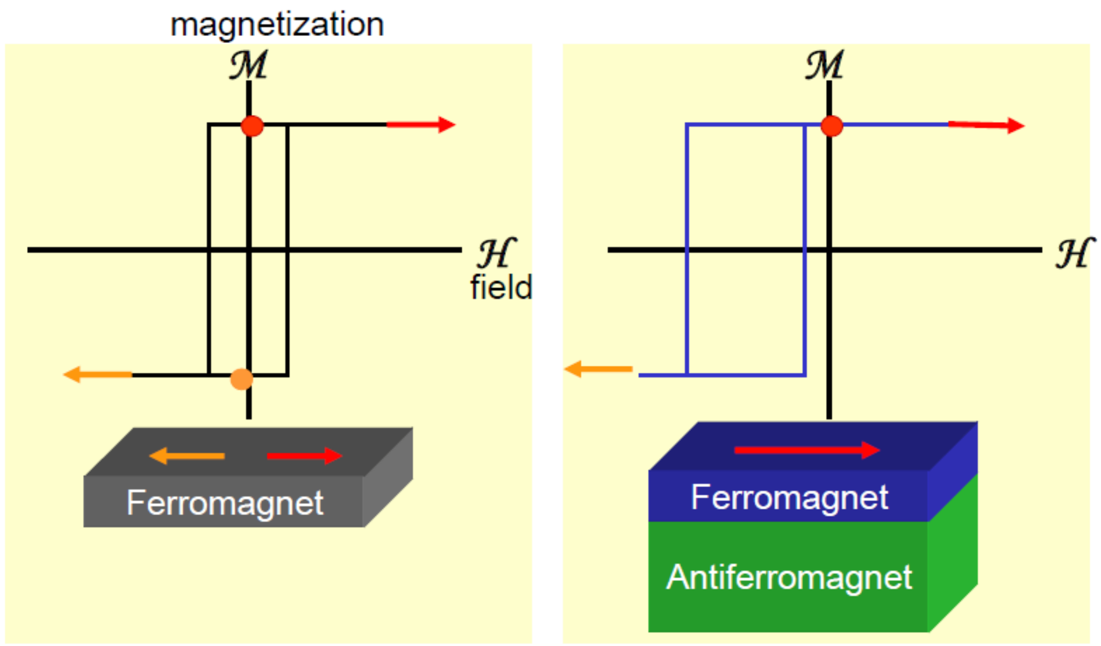
Powerful in studying antiferromagnetic spintronics



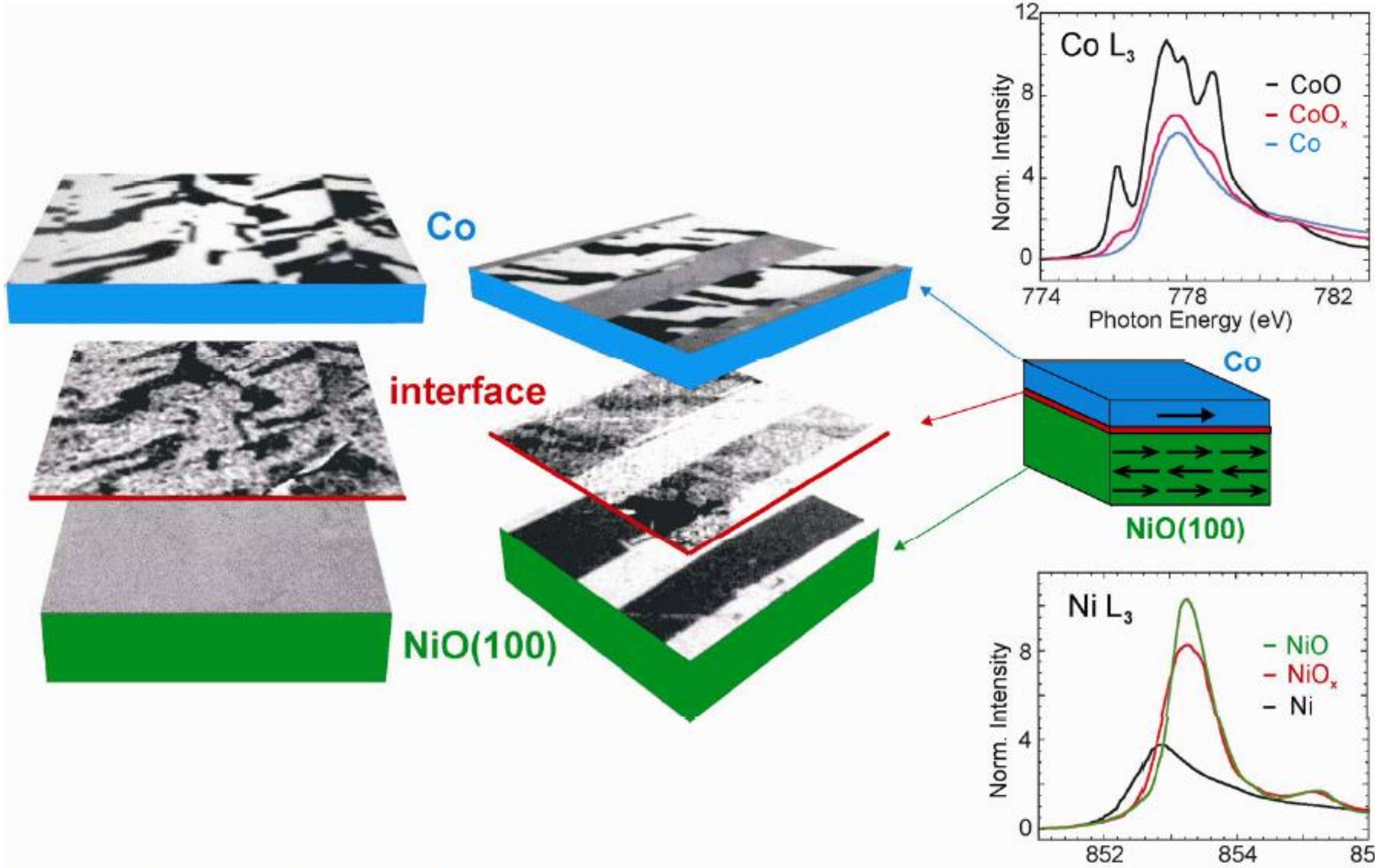
X. Marti et al. Nature Materials, 2014



AFM is “neutral” AFM is “magnetic” at surface



Images of the Ferromagnet-Antiferromagnet Interface



Ohldag *et al.*, PRL **87**, 247201 (2001)

Summary:

- XMCD and XMLD exploits advantages of XAS
- Provide sensitivity to the spin and orbital degrees of freedom
- Particularly suitable for complex magnetic materials and structures
- Can be used to probe different magnetic orders
- Relatively easy to implement magnetic field
- Compatible with imaging techniques