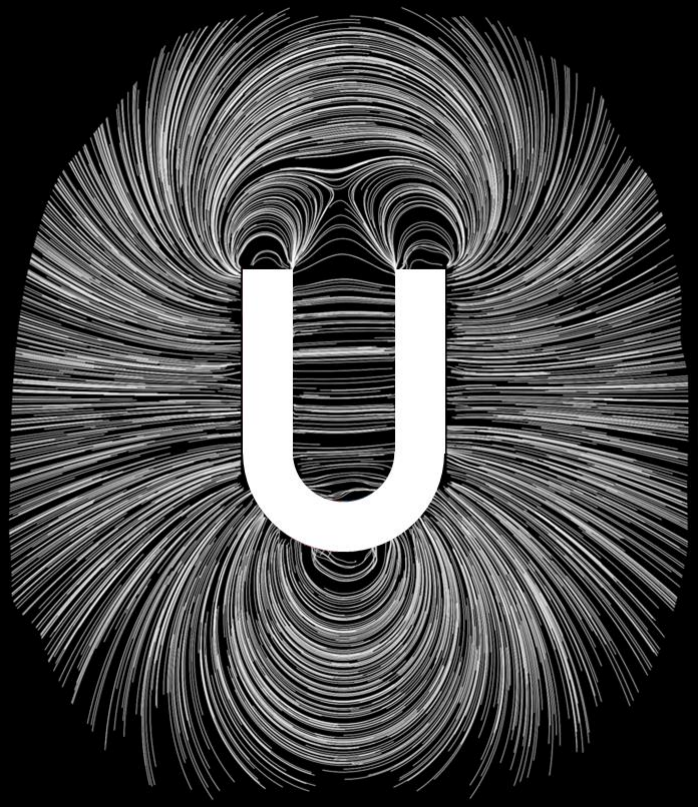
Magnetism as seen with X-Rays



Elke Arenholz

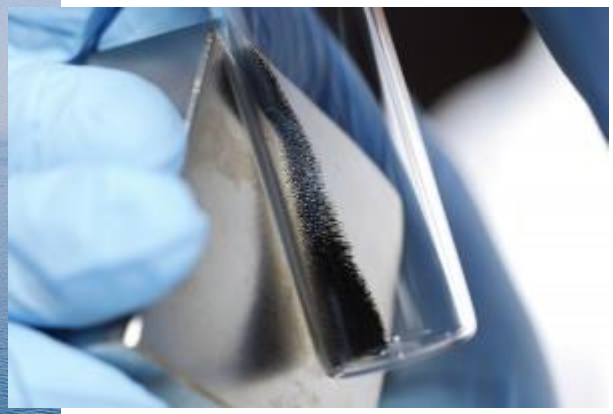
Lawrence Berkeley National Laboratory

and

Department of Material Science and Engineering, UC Berkeley

Magnetic Materials Today

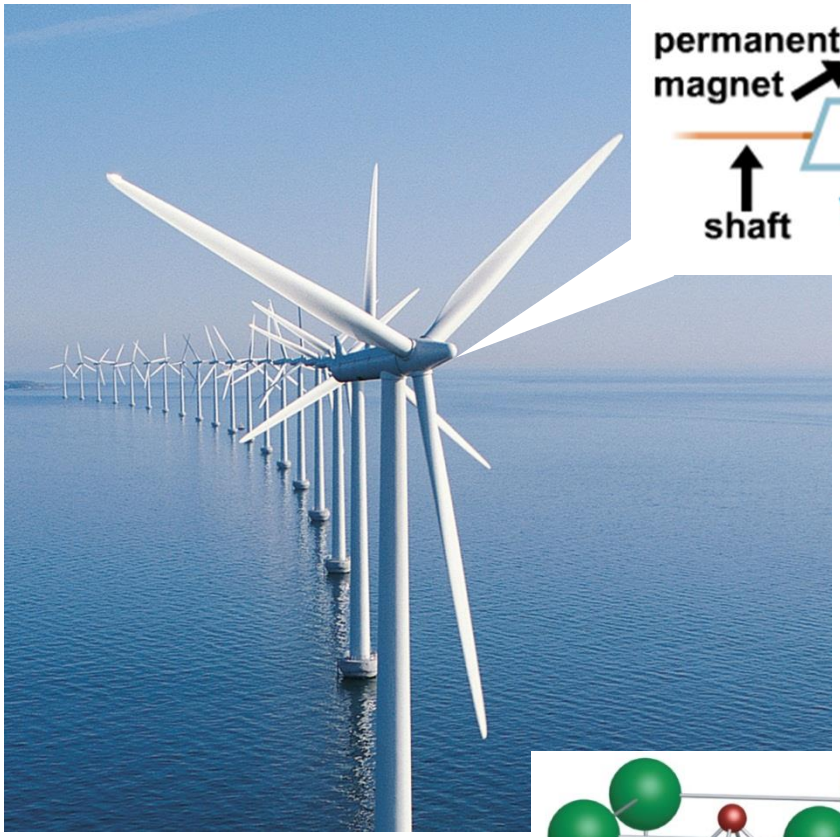
Magnetic materials
for
energy applications

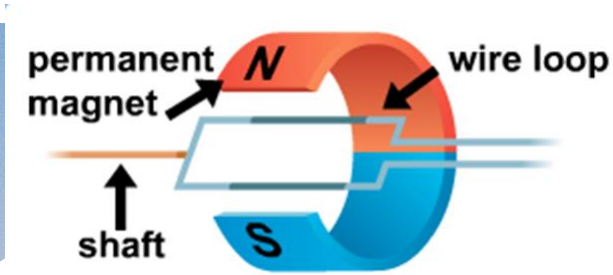


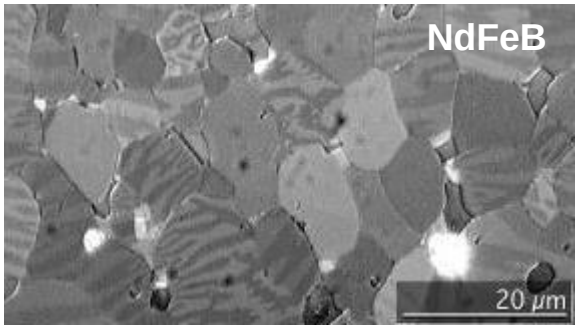
Magnetic
nanoparticles
for
biomedical
applications

Magnetic thin films
for
information storage
and processing

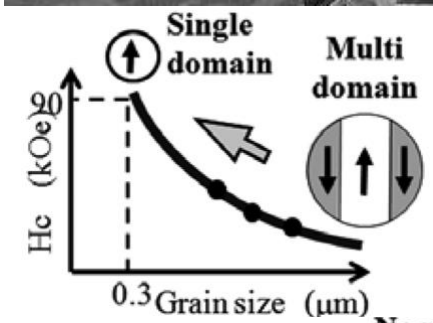
Permanent and Hard Magnetic Materials

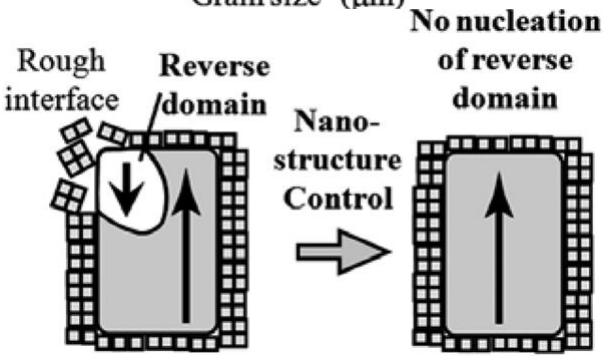




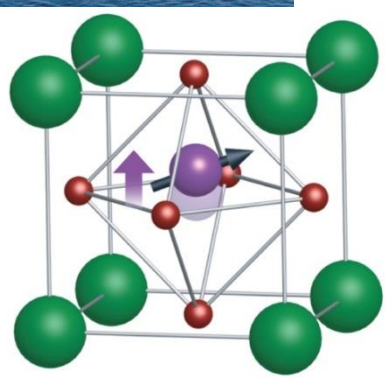


Controlling grain and domain structure on the micro- and nanoscale

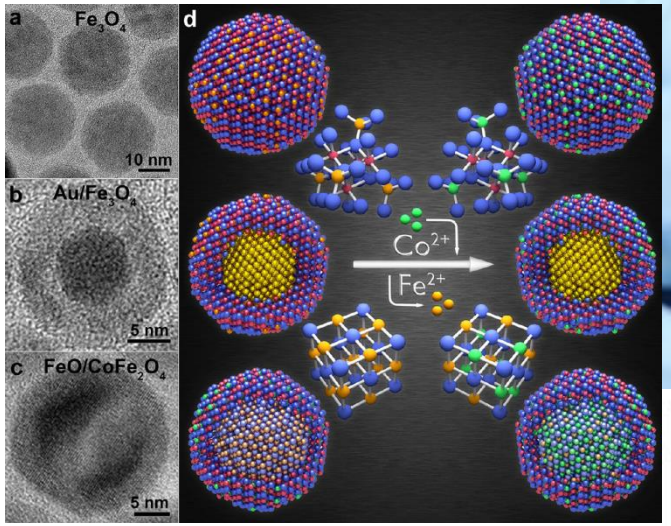


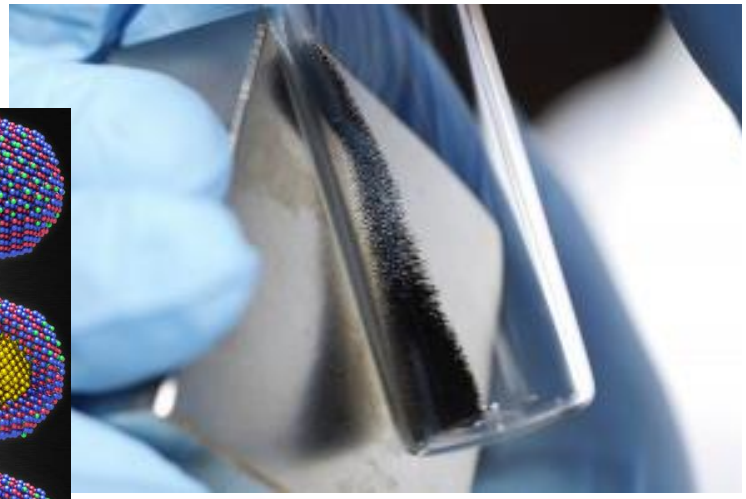


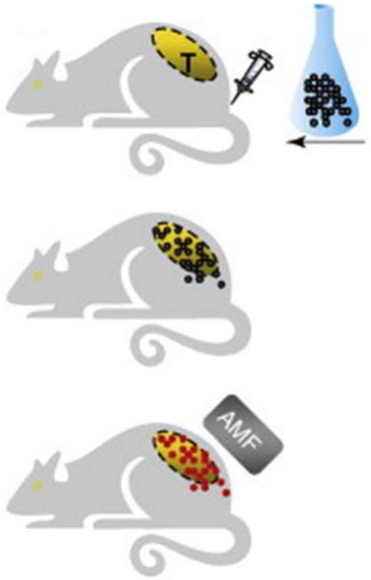
Engineering magnetic anisotropy on the atomic scale

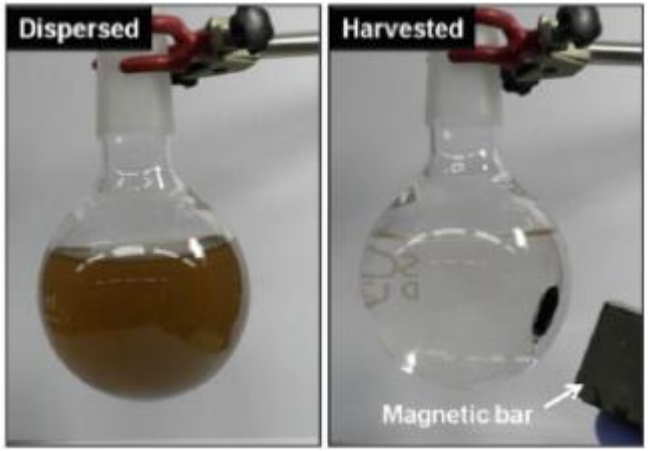


MAGNETIC NANOPARTICLES





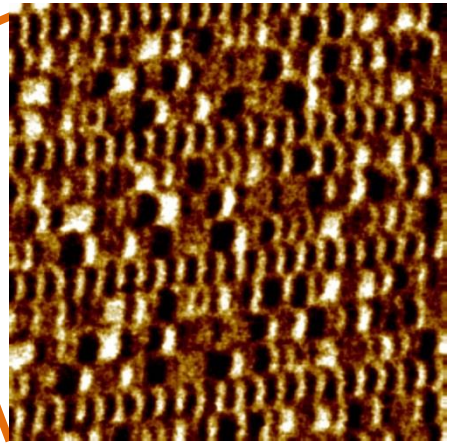




Tailoring magnetic nanoparticles for environmental applications

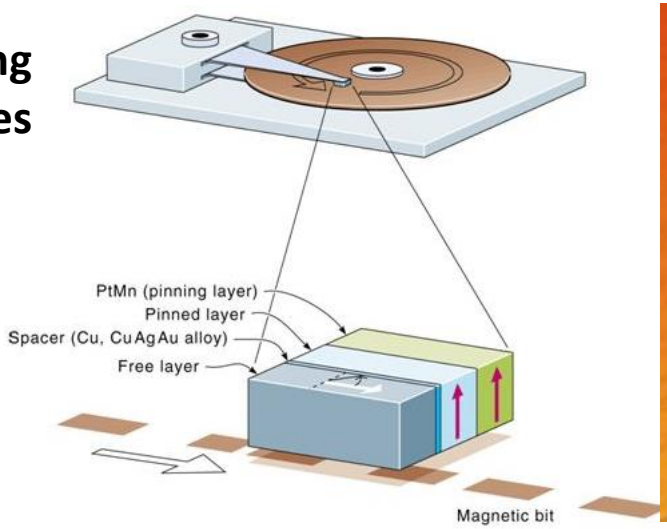
Optimizing magnetic nanoparticles for biomedical applications

Magnetic Thin Films



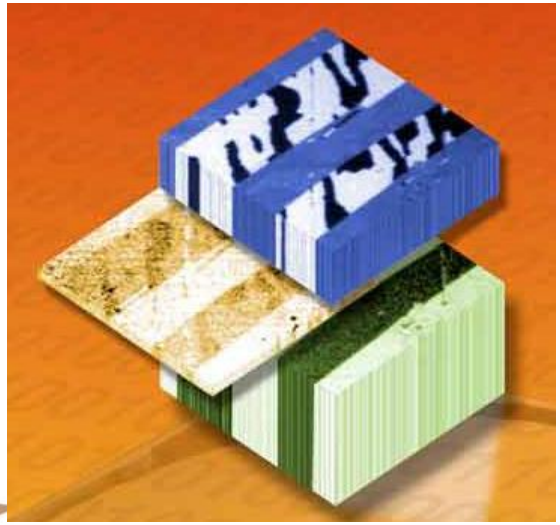
Magnetic domain structure on the nanometer scale

Magnetic coupling at interfaces



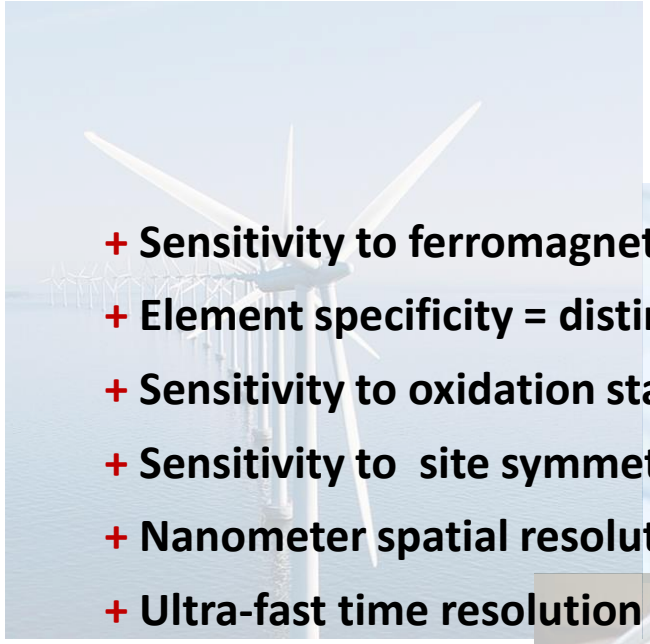
Ultrafast magnetization reversal dynamics

GMR Read Head Sensor



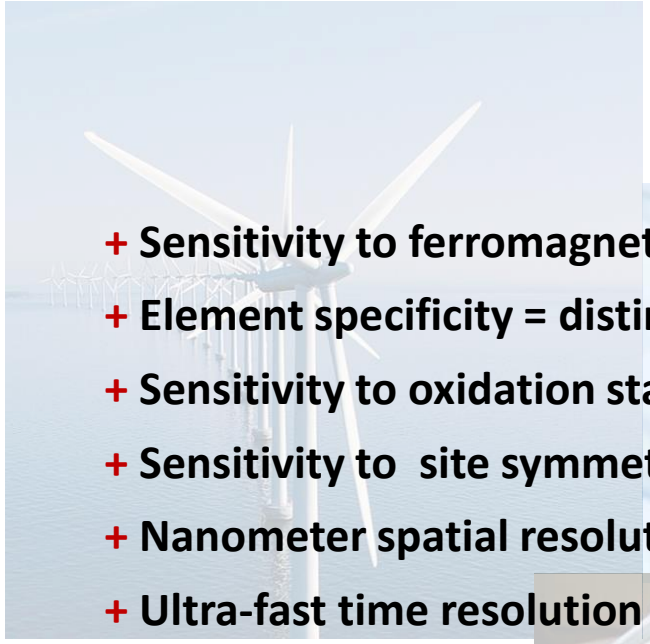
Unique magnetic phases at interfaces

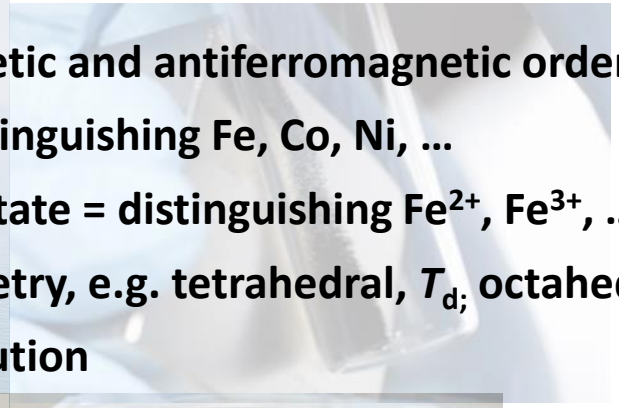
Magnetic Materials Characterization Wish List

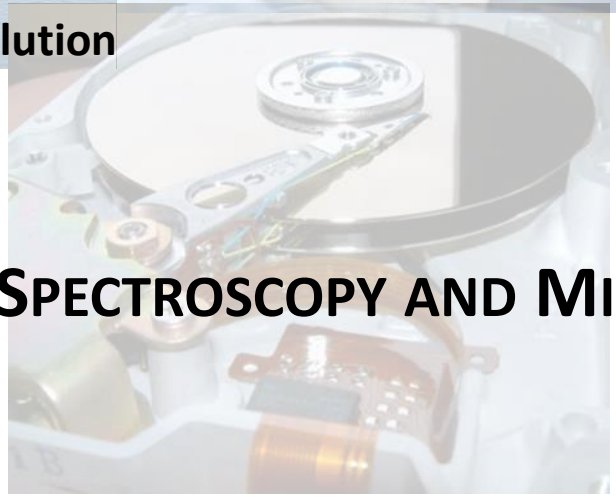


+ Sensitivity to ferromagnetic and antiferromagnetic order
+ Element specificity = distinguishing Fe, Co, Ni, …
+ Sensitivity to oxidation state = distinguishing Fe^{2+}, Fe^{3+}, …
+ Sensitivity to site symmetry, e.g. tetrahedral, T_d; octahedral, O_h
+ Nanometer spatial resolution
+ Ultra-fast time resolution

Magnetic Materials Characterization Wish List







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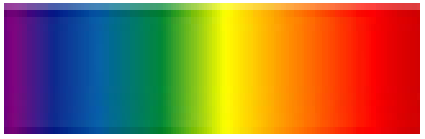
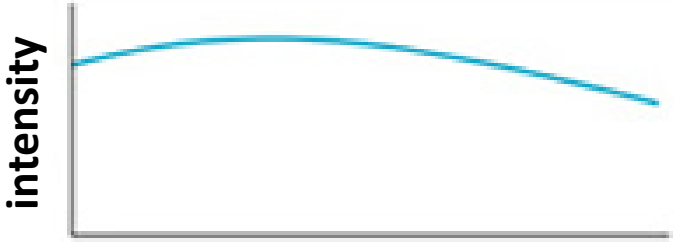
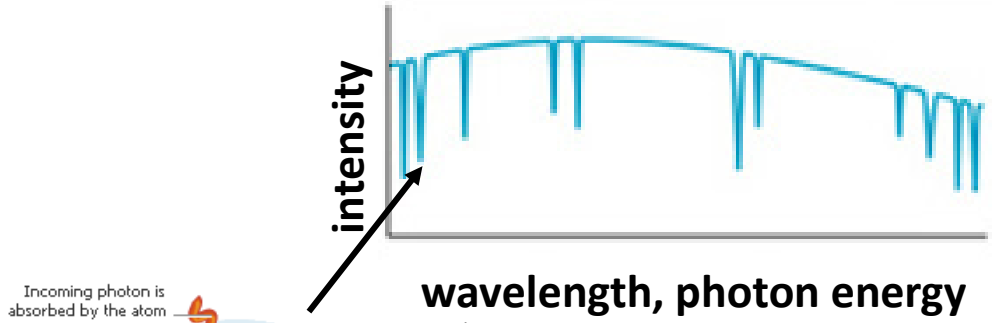
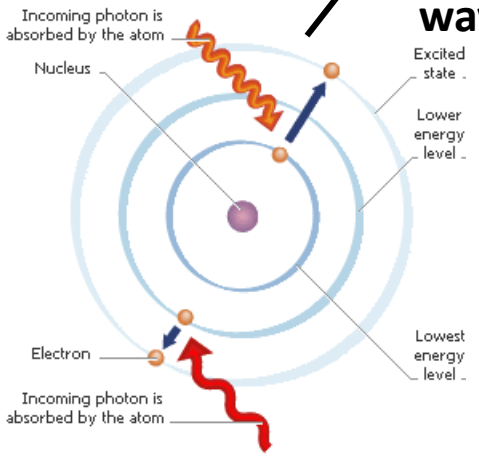
Soft X-Ray Spectroscopy and Microscopy

SPECTROSCOPY



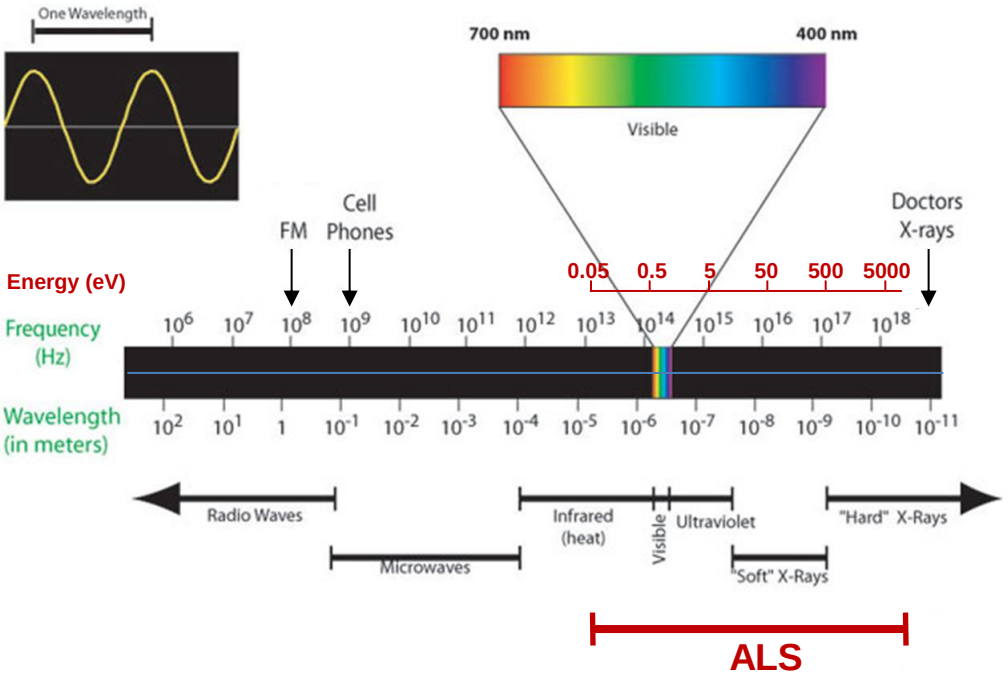






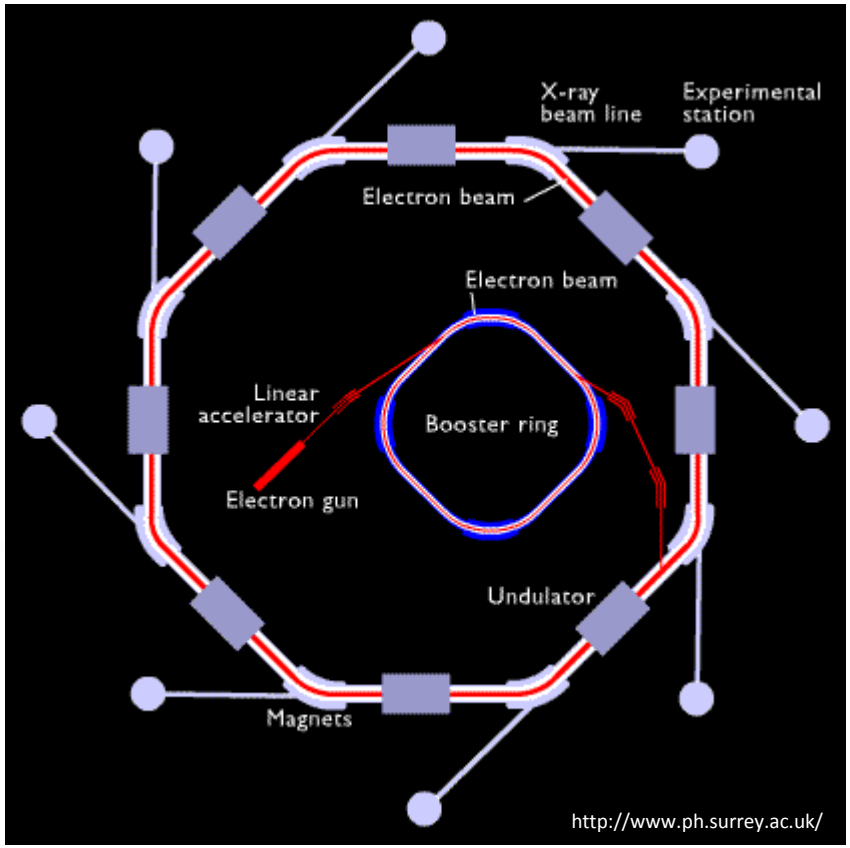
Tunable Photon Source for Spectroscopy

Electromagnetic Spectrum



http://www.src.wisc.edu/about/tutorial.htm

Synchrotron Light Sources



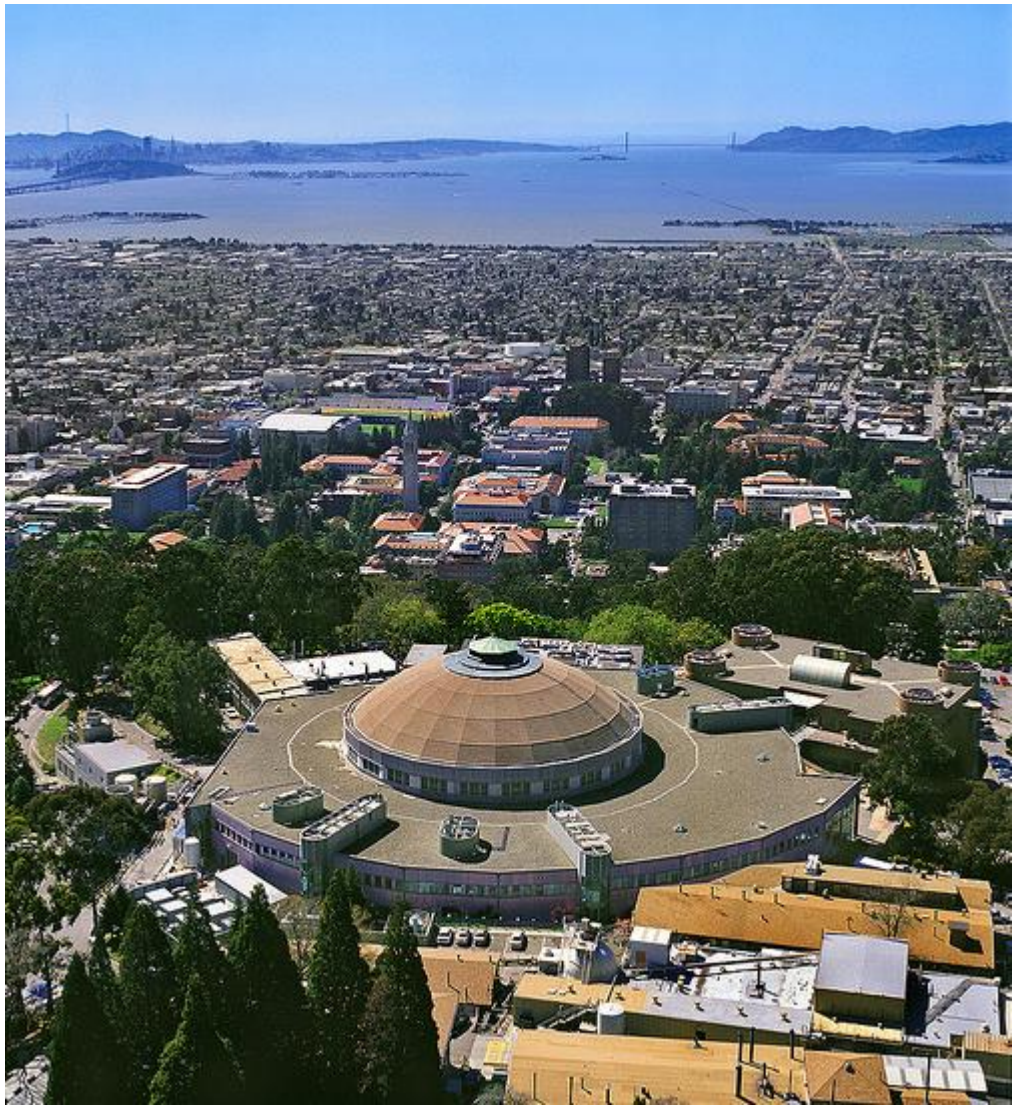
http://www.ph.surrey.ac.uk/

+ Change velocity of electrons near the speed of light

⇒ Emission of wide wavelength range of electromagnetic spectrum

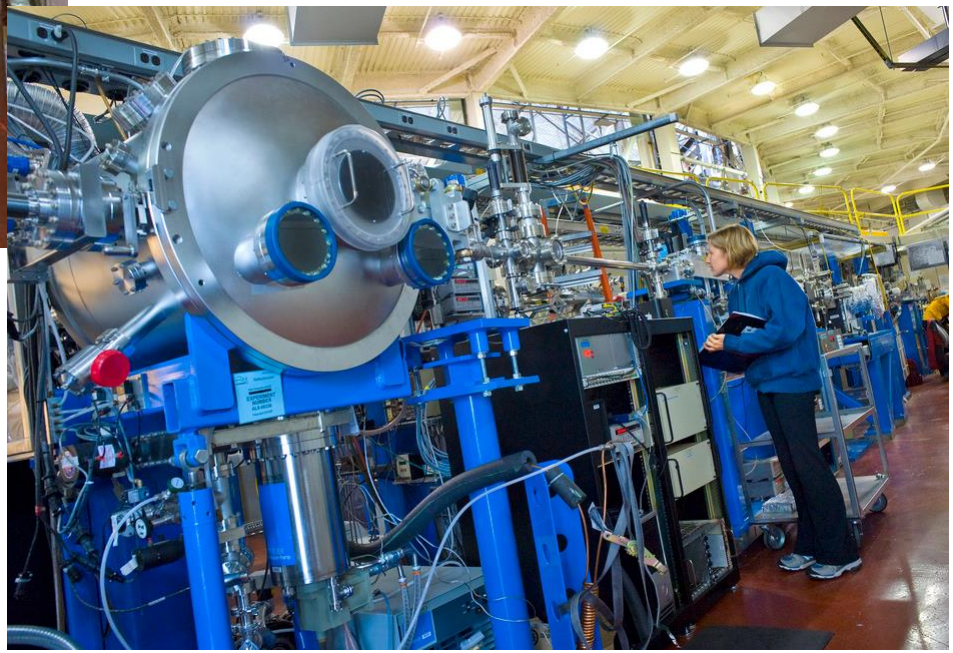
⇒ Tunable source in the soft x-ray range for x-ray absorption spectroscopy

ADVANCED LIGHT SOURCE



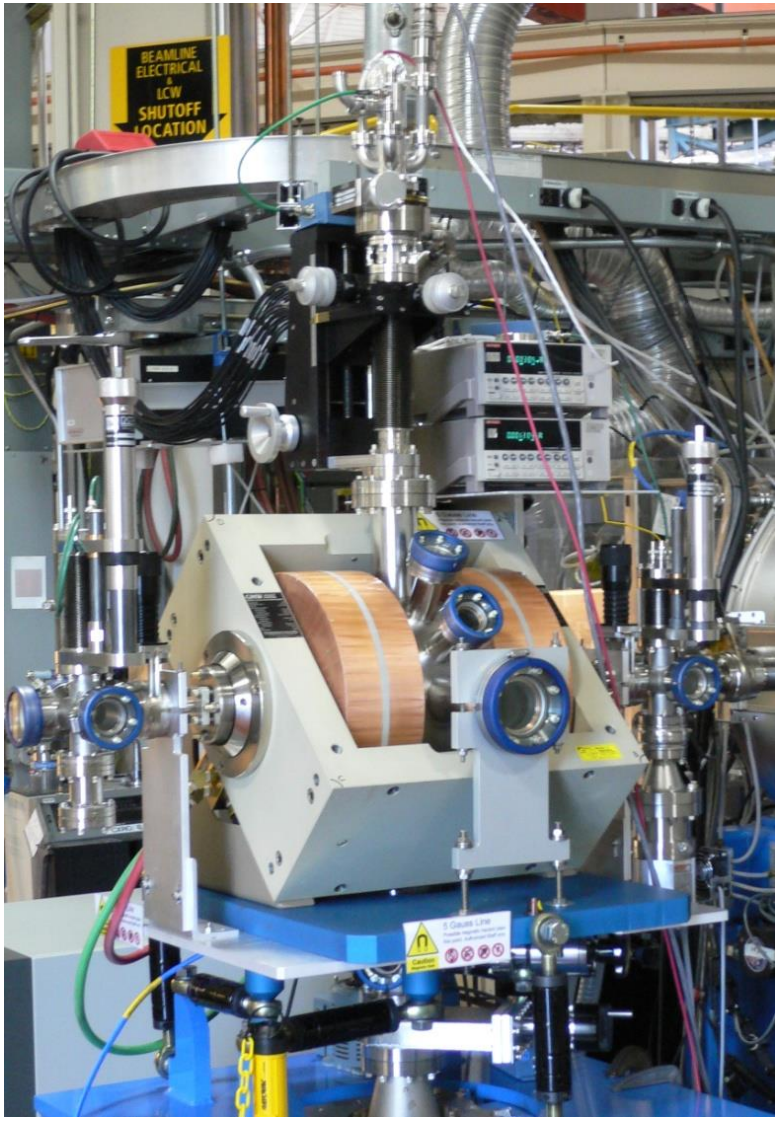
Electron Storage Ring and Monochromators

Inside the ALS storage ring

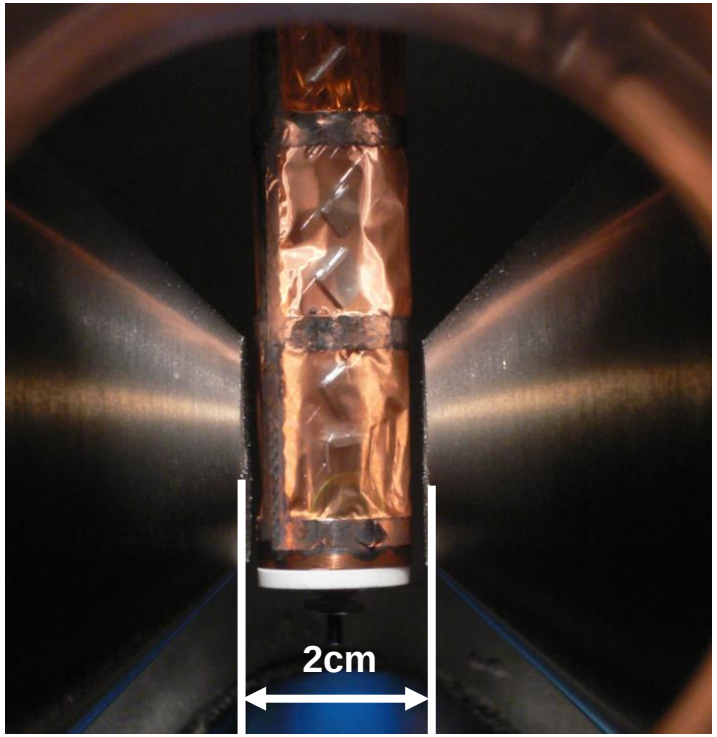


+ Monochromators provide photon beams with well defined characteristics:
  - tunable energy/wavelength
  - polarization: linear, circular, …
  - x-ray spot size …

2T Magnet Endstation

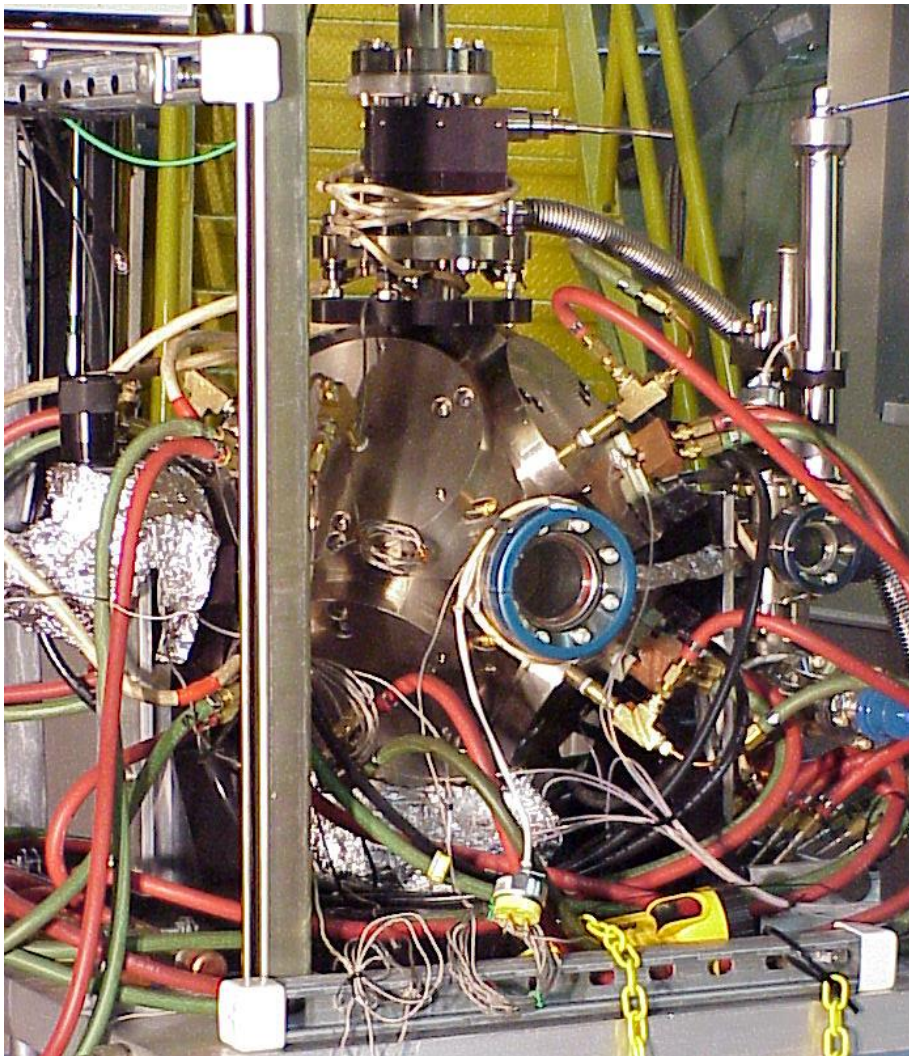


+ Endstations provide well defined environments for the interaction of samples and photons:
  - precisely defined experimental geometries, i.e. angle of x ray beam to sample
  - sample temperature
  - external magnetic and electric fields



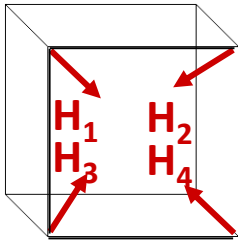
2T magnet at ALS BL6.3.1

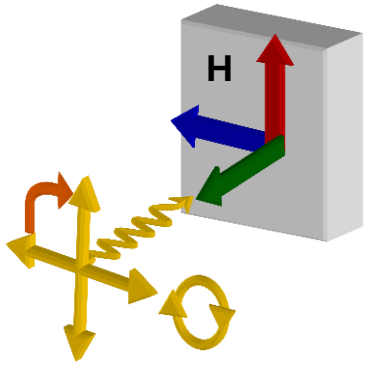
Vector Magnet Endstation

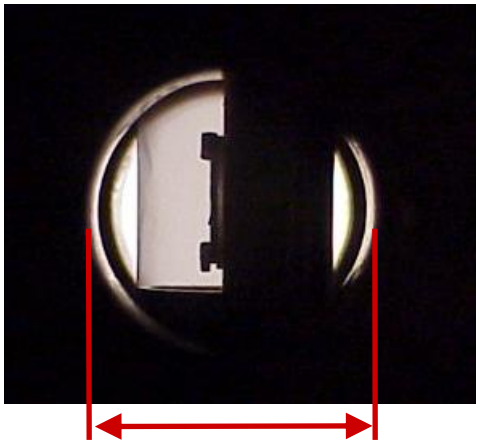


Vector magnet at ALS BL4.0.2

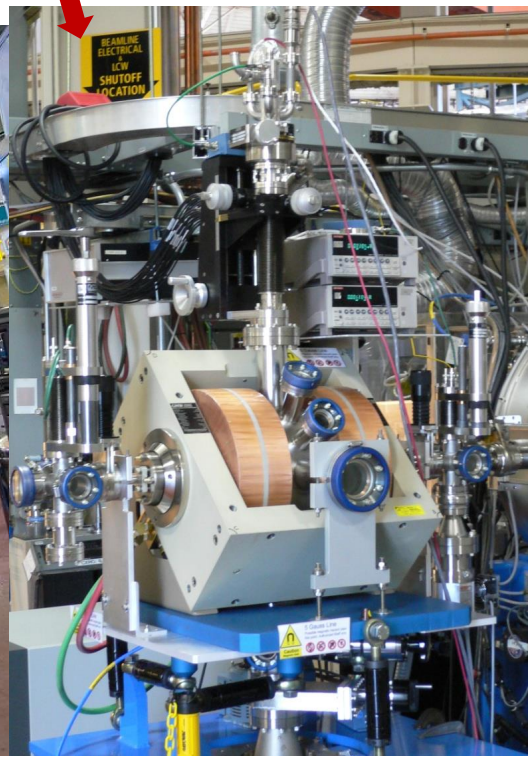
+ Magnetic fields in arbitrary directions obtained through superposition of fields generated by 4 dipole pairs in octahedral configuration.



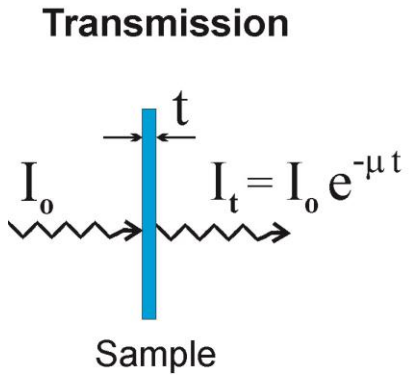


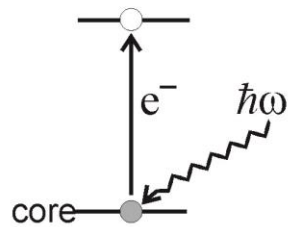


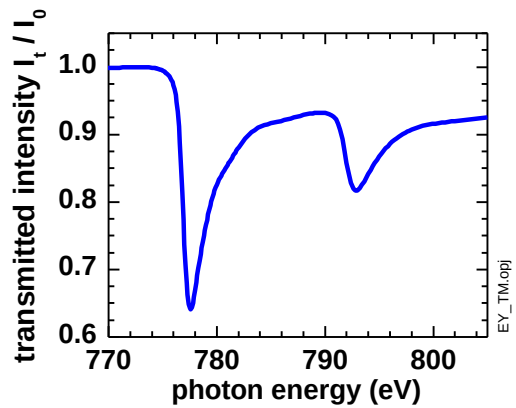
Soft X-Ray Spectroscopy (hν ≈ 500-1000eV, λ ≈ 1-2nm)



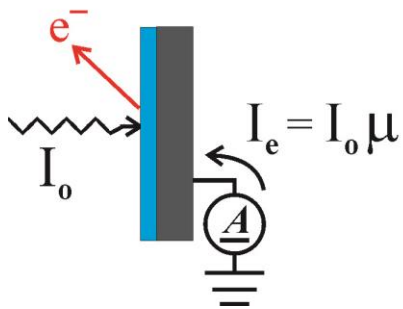
X-Ray Absorption – Detection Modes

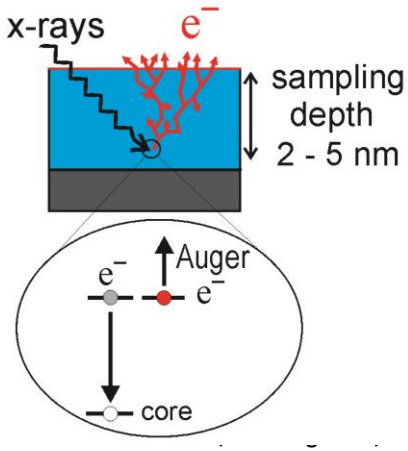




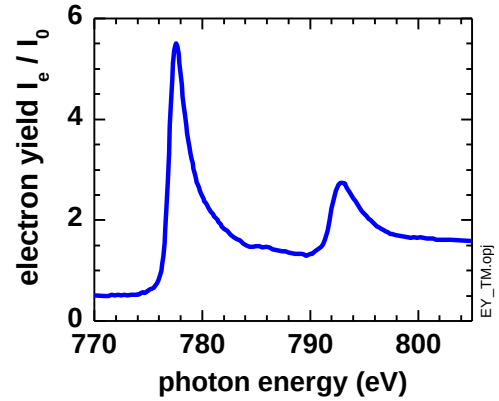


photons absorbed





Magnetism (Springer)

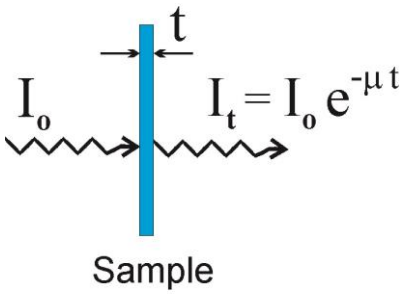


electrons generated

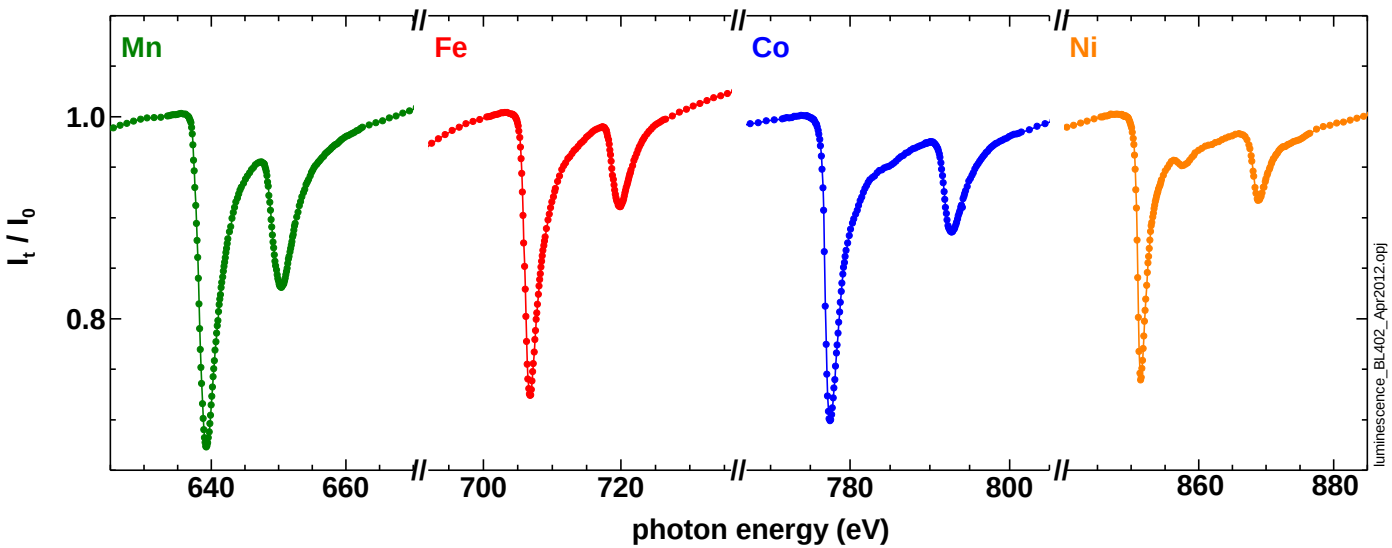
Electron yield:

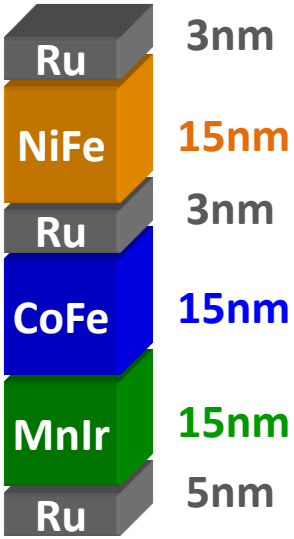
+ **Absorbed photons create core holes subsequently filled by Auger electron emission**
+ **Auger electrons create low-energy secondary electron cascade through inelastic scattering**
+ **Emitted electrons ∝ probability of Auger electron creation ∝ absorption probability**

Soft X-Ray Absorption – Probing Depth



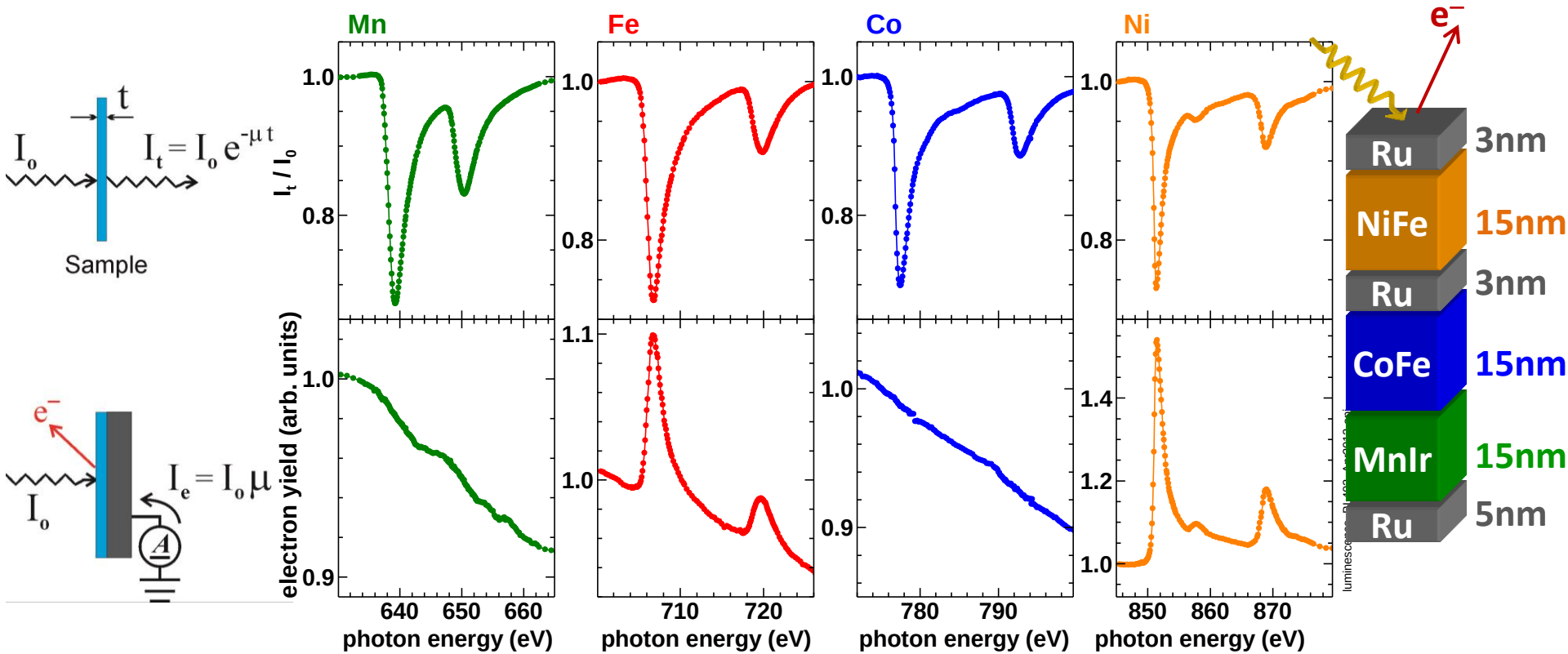
Element	10eV below L_3 1/μ [nm]	at L_3 1/μ [nm]	40 eV above L_3 1/μ [nm]
Fe	550	17	85
Co	550	17	85
Ni	625	24	85



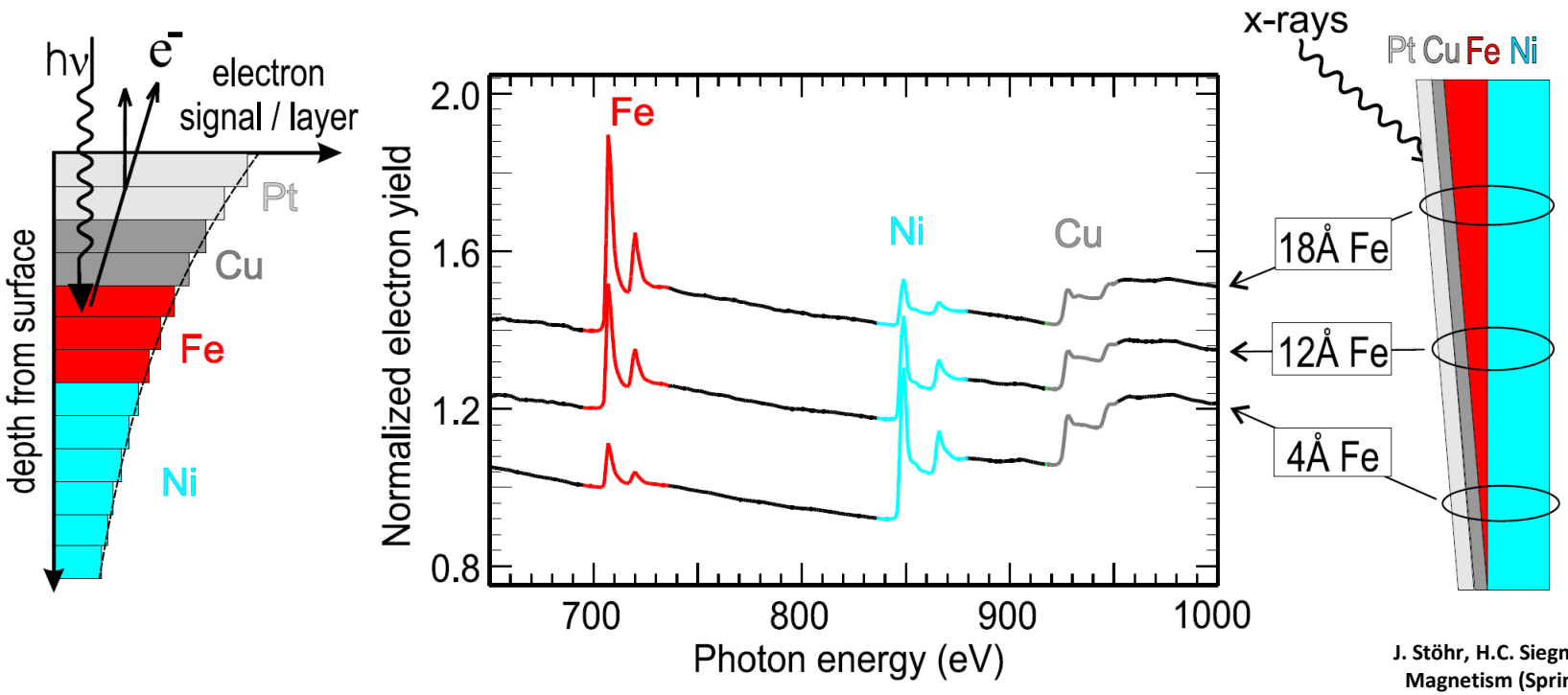


~10-20 nm layer thick films supported by substrates transparent to soft x-rays

X-Ray Absorption – Detection Modes and Probing Depth



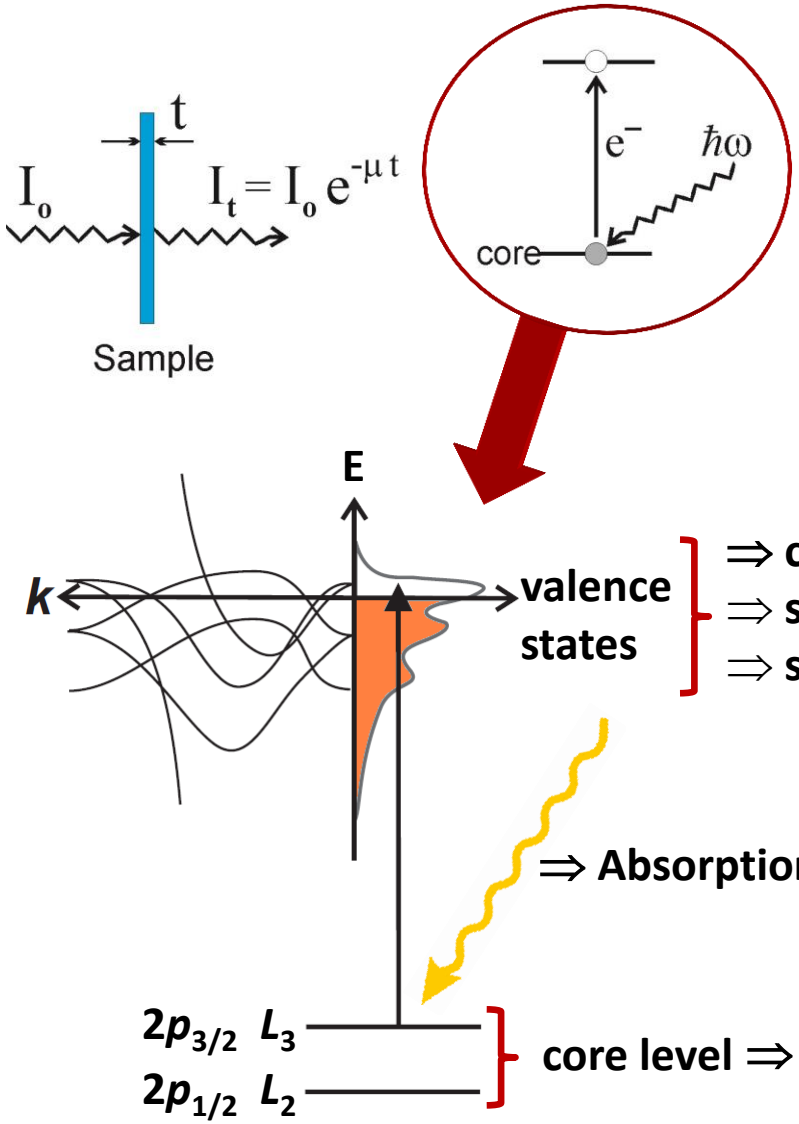
Probing Depth Of Electron Yield



J. Stöhr, H.C. Siegmann, Magnetism (Springer)

+ **Electron sample depth: 2-5 nm in Fe, Co, Ni**
  ⇒ **60% of the electron yield originates form the topmost 2-5 nm**

X-Ray Absorption – Fundamentals



Experimental Concept:
Monitor reduction in x-ray flux transmitted through sample as function of photon energy

⇒ charge state of absorber Fe^{2+}, Fe^{3+}
⇒ symmetry of lattice site of absorber: O_h, T_d
⇒ sensitive to magnetic order

⇒ Absorption probability: x-ray energy, x-ray polarization, experimental geometry

core level ⇒ atomic species of absorber Fe, Co, Ni, ….

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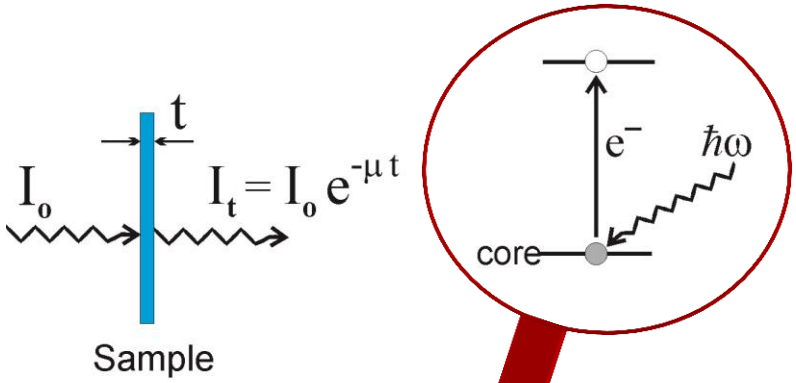

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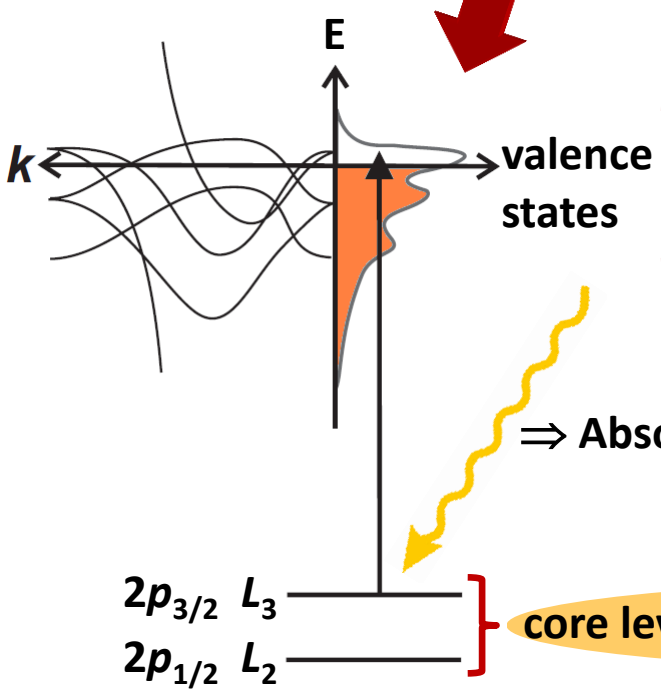

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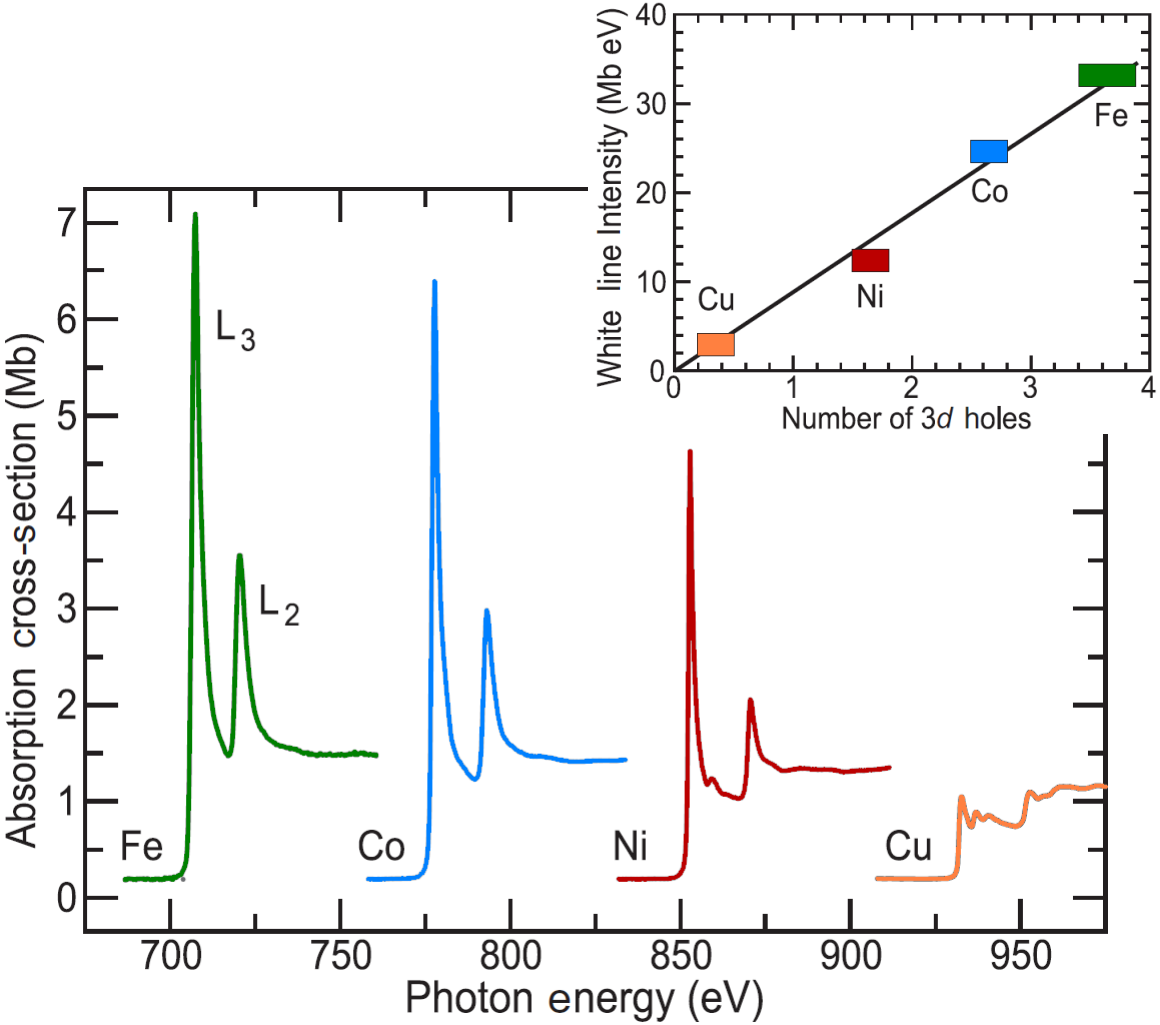
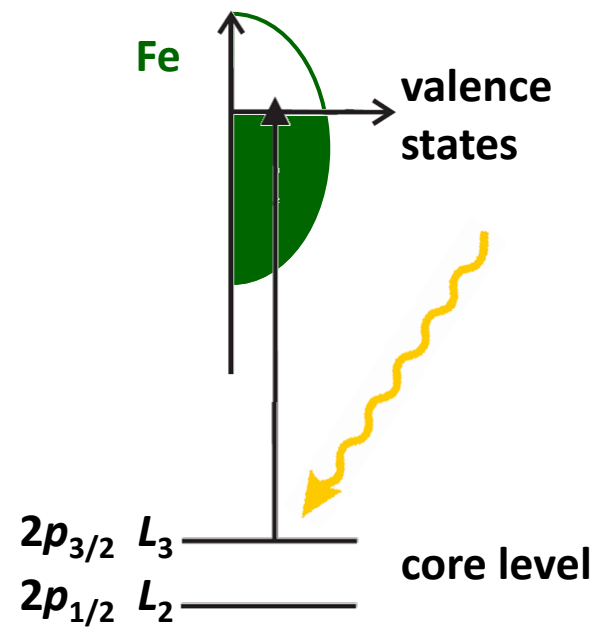
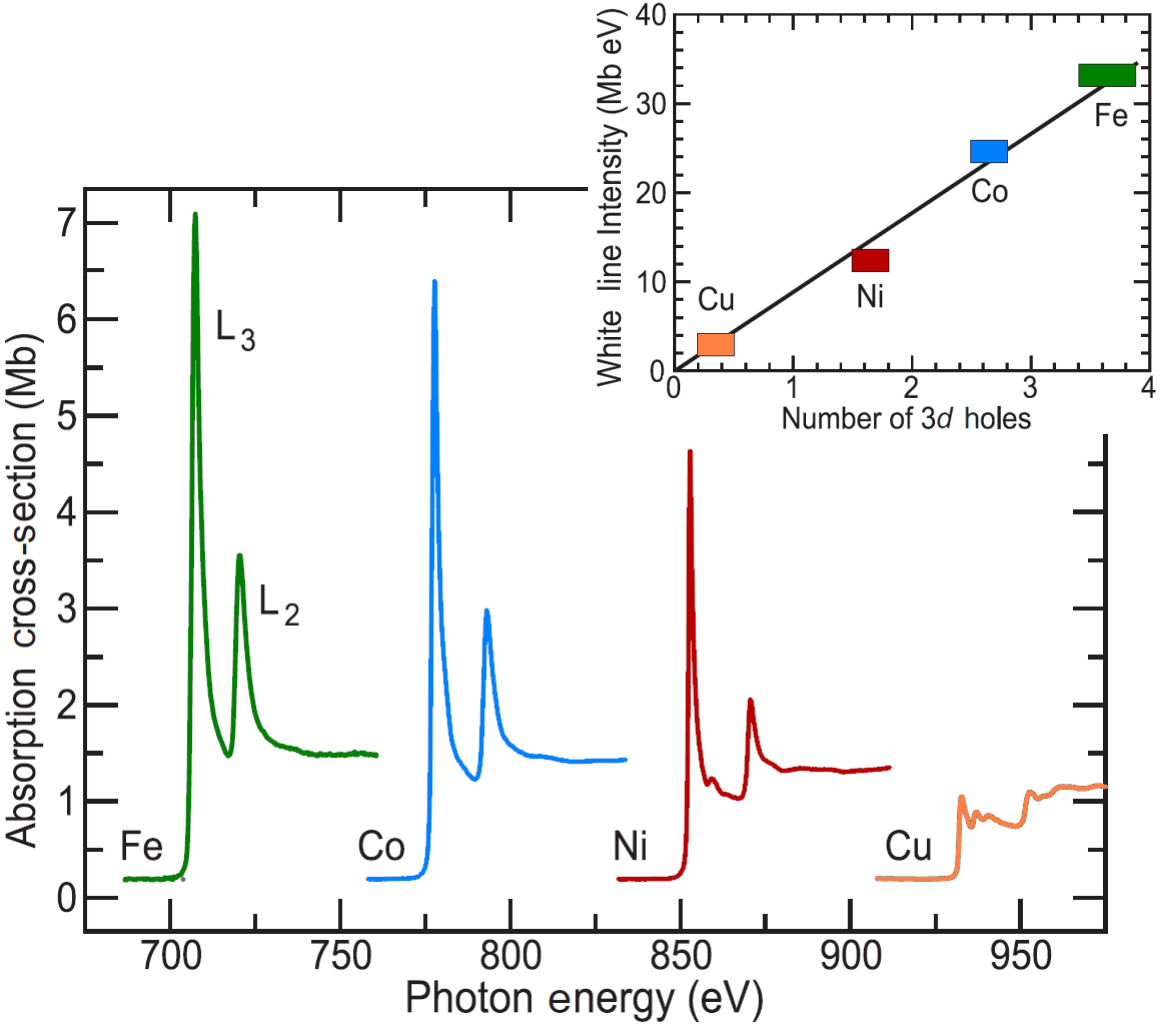
'White Line' Intensity

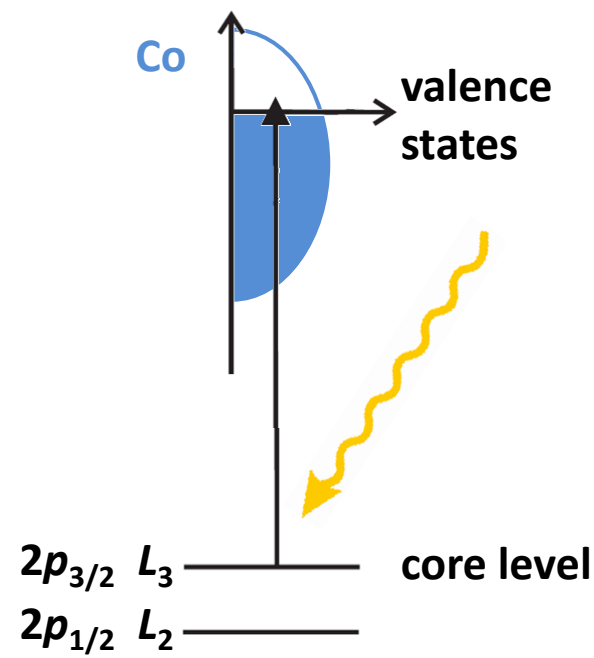




Intensity of $L_{3,2}$ resonances is proportional to number of *d* states above the Fermi level, i.e. number of holes in the *d band.*

'White Line' Intensity





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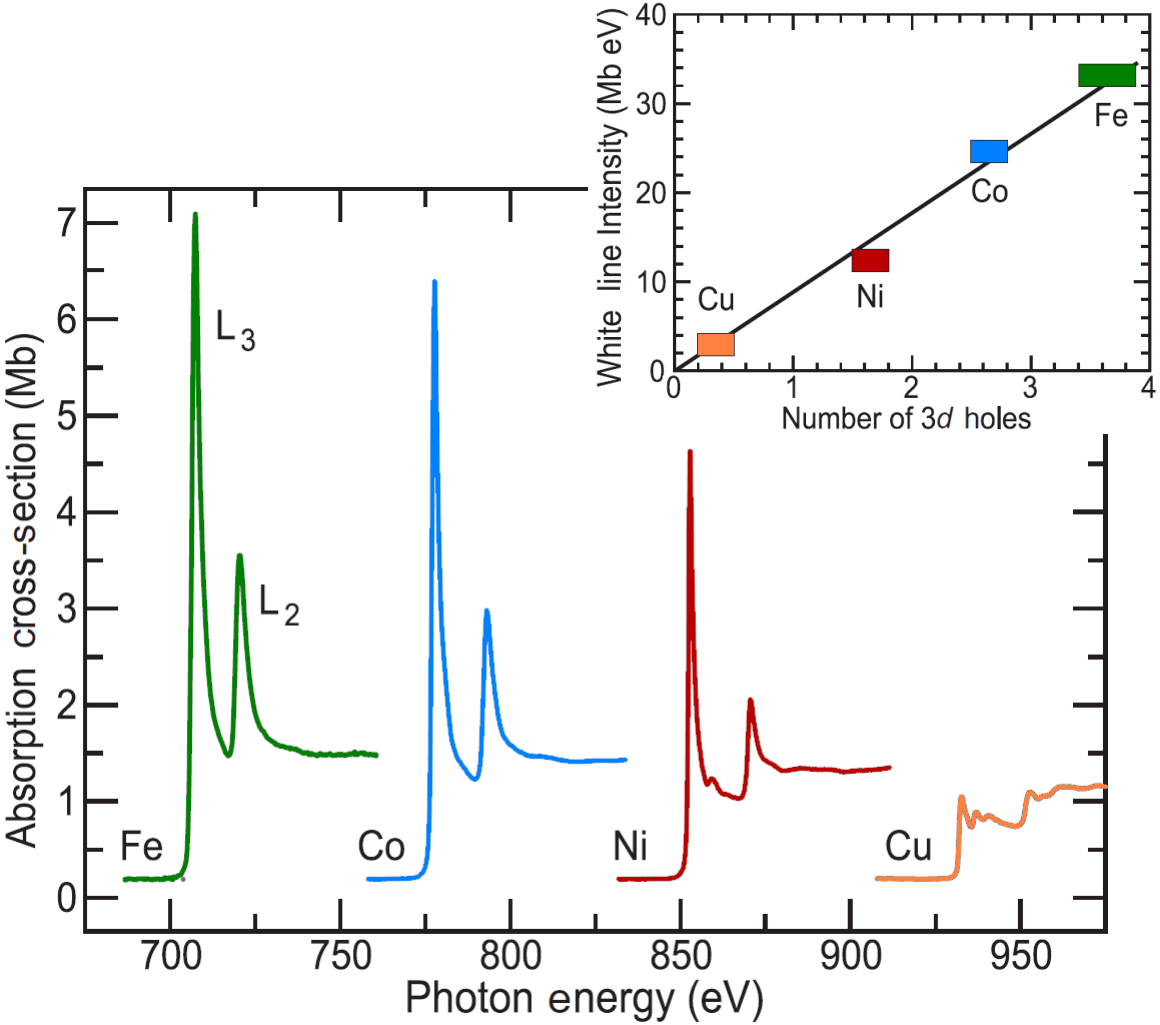
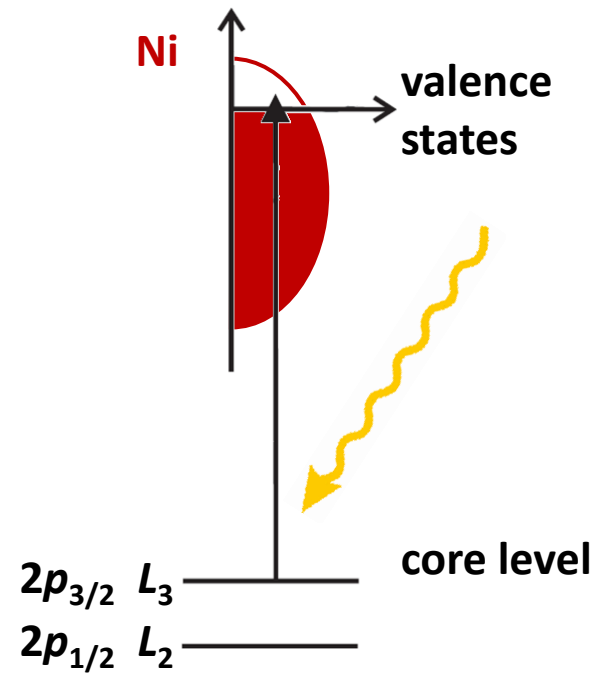
'White Line' Intensity





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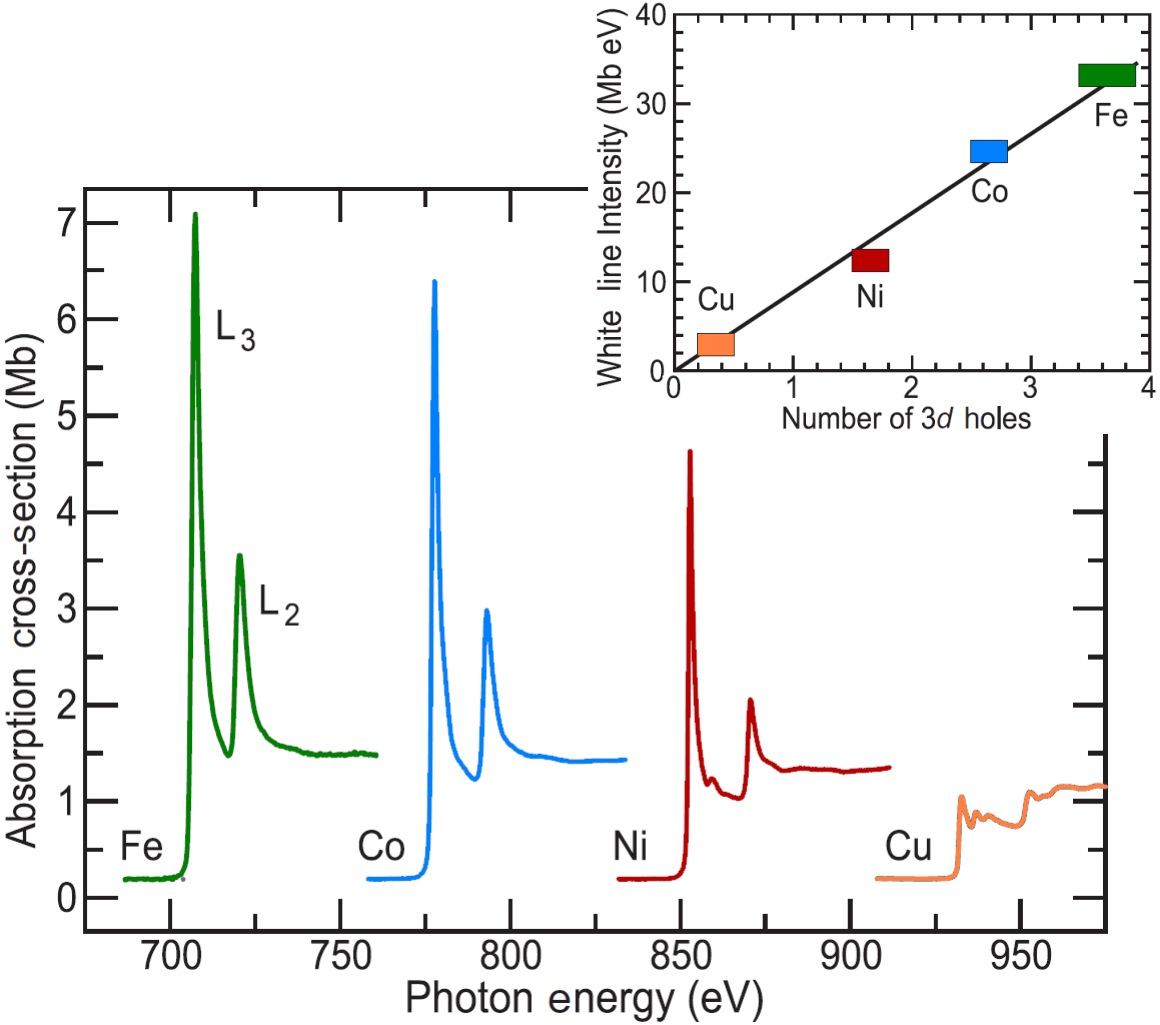

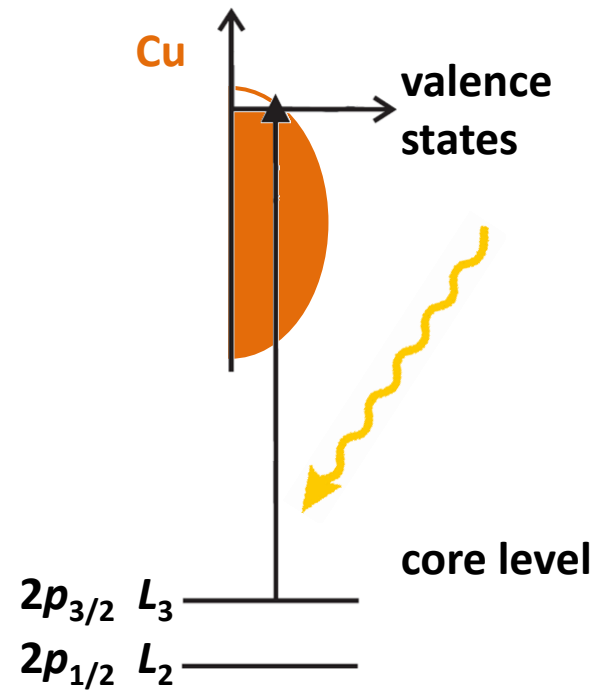

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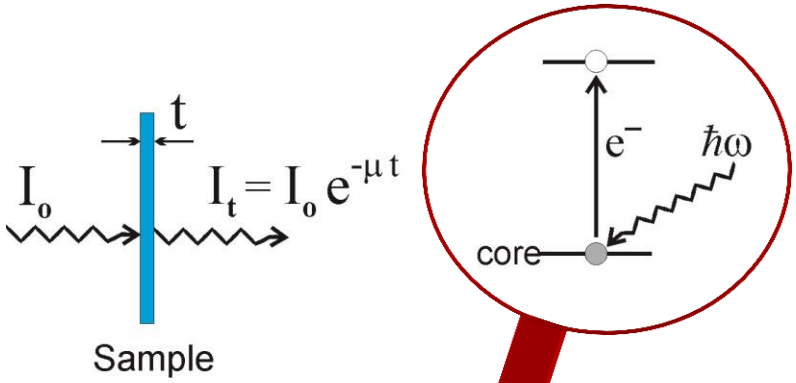
X-Ray Absorption – Fundamentals



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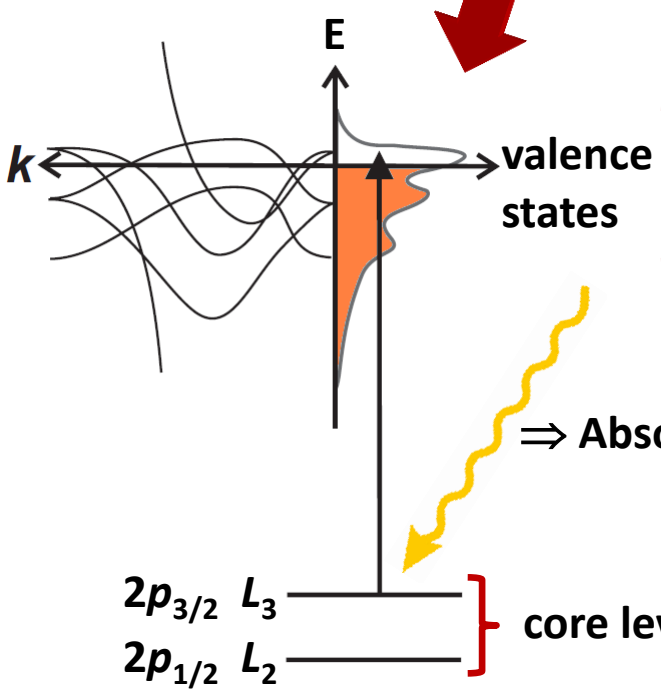
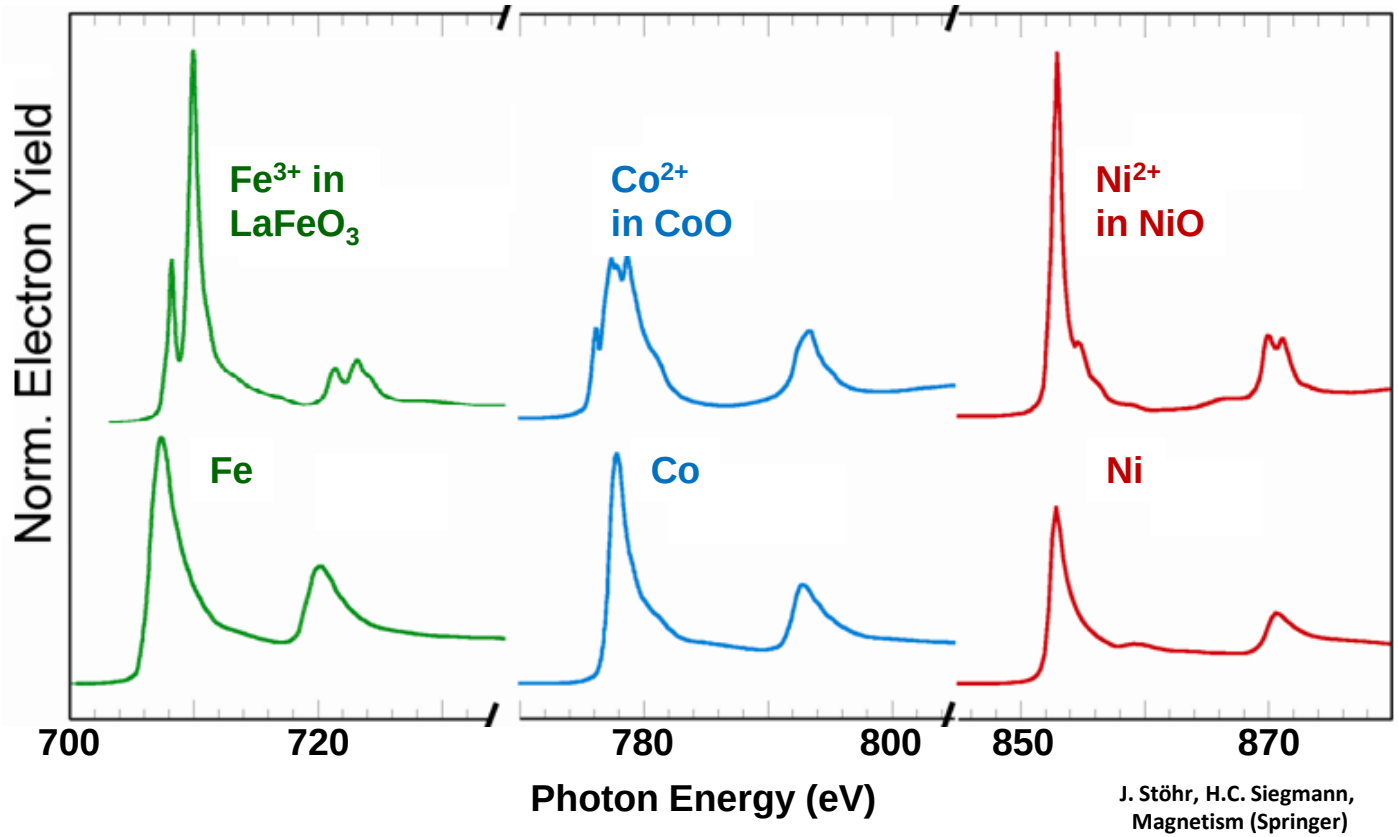


- ⇒ **charge state of absorber Fe^{2+}, Fe^{3+}, …**
- ⇒ **symmetry of lattice site of absorber: O_h, T_d**
- ⇒ **sensitive to magnetic order**

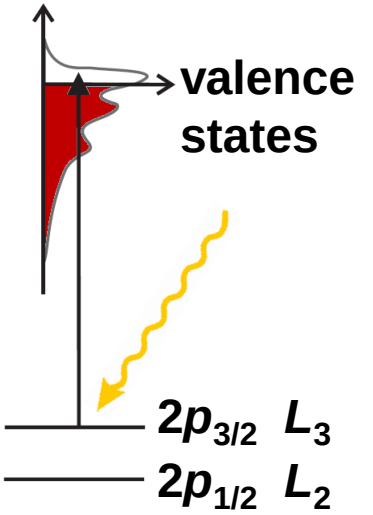
⇒ **Absorption probability: x-ray energy, x-ray polarization, experimental geometry**

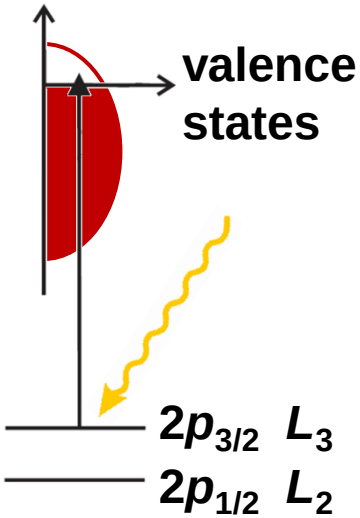
core level ⇒ atomic species of absorber Fe, Co, Ni, ….

X-RAY ABSORPTION – VALENCE STATE



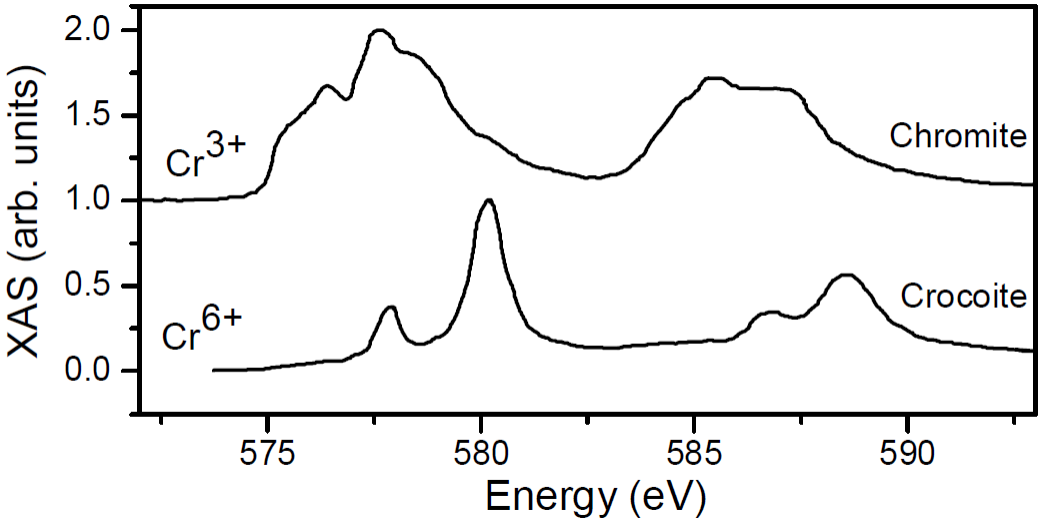
J. Stöhr, H.C. Siegmann, Magnetism (Springer)



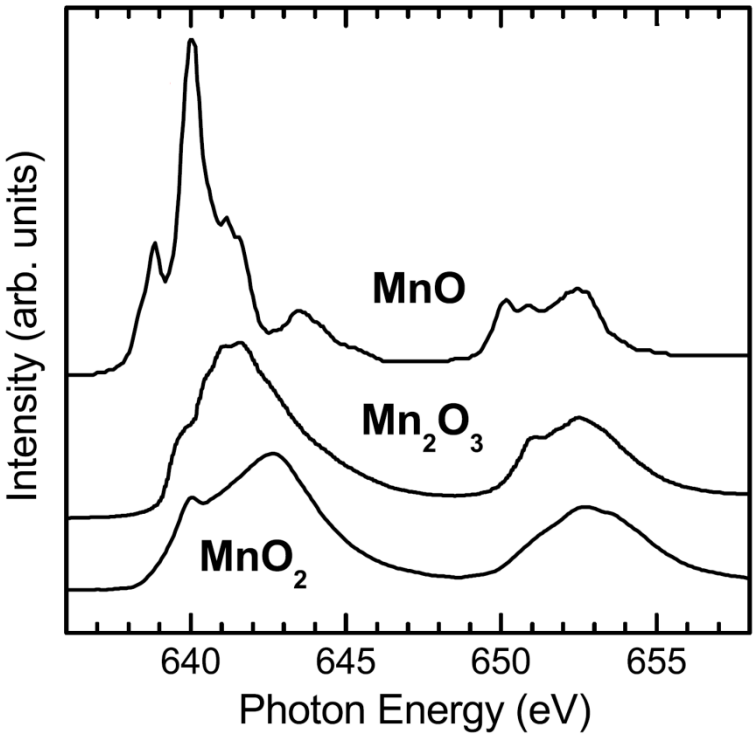


X-RAY ABSORPTION – VALENCE STATE

Influence of the charge state of the absorber



N. Telling *et al.*,
Appl. Phys. Lett. 95, 163701 (2009)



J.-S. Kang et al., Phys. Rev. B 77, 035121 (2008)

X-Ray Absorption – One Electron Picture

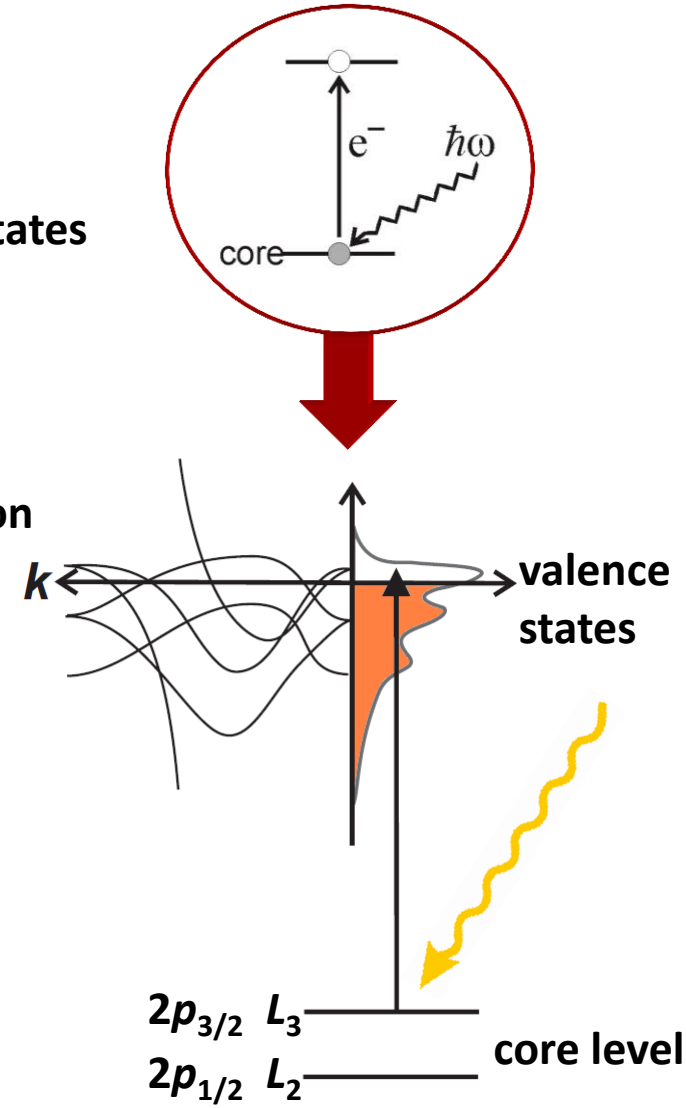
X-ray absorption:

+ Electrons excited from core shells to unoccupied valence states through absorption of a photon determined by energy and angular momentum conservation

Simplest model: One electron picture

+ Photon transfers its energy and momentum to core electron
+ Core electron excited into unoccupied electronic state.

+ However: Not directly excited electrons also influenced by electron excitation, i.e. hole in core shell

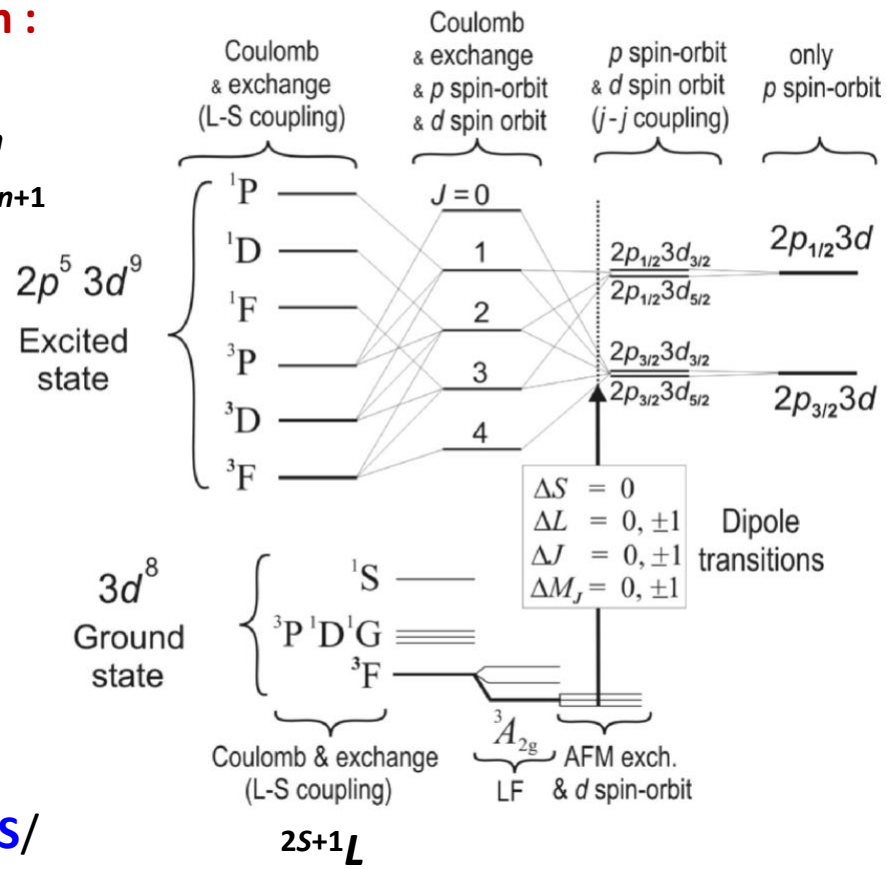


X-Ray Absorption – Configuration Model

Ni^{2+} in NiO: $2p^6\,3d^8 \rightarrow 2p^5\,3d^9$

Configuration model, e.g. *L* edge absorption :

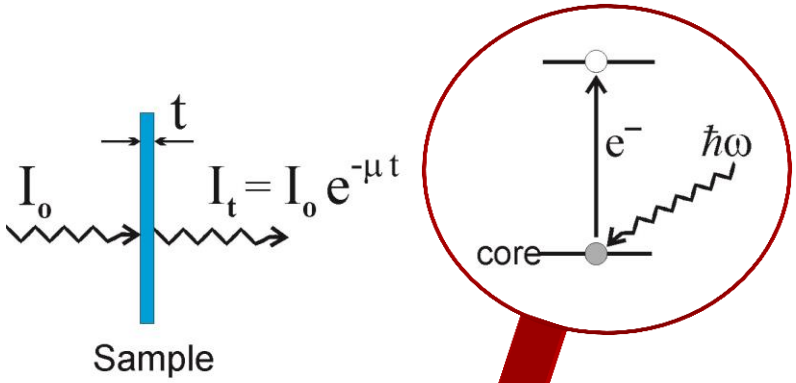
- **Excited from ground/initial state configuration, $2p^6 3d^n$ to exited/final state configuration, $2p^5 3d^{n+1}$**
- **Omission of all full subshells (spherical symmetric)**
- **Takes into account correlation effects in the ground state as well as in the excited state**
- **Leads to multiplet effects/structure**



http://www.anorg.chem.uu.nl/CTM4XAS/

J. Stöhr, H.C. Siegmann, Magnetism (Springer)

X-Ray Absorption – Fundamentals



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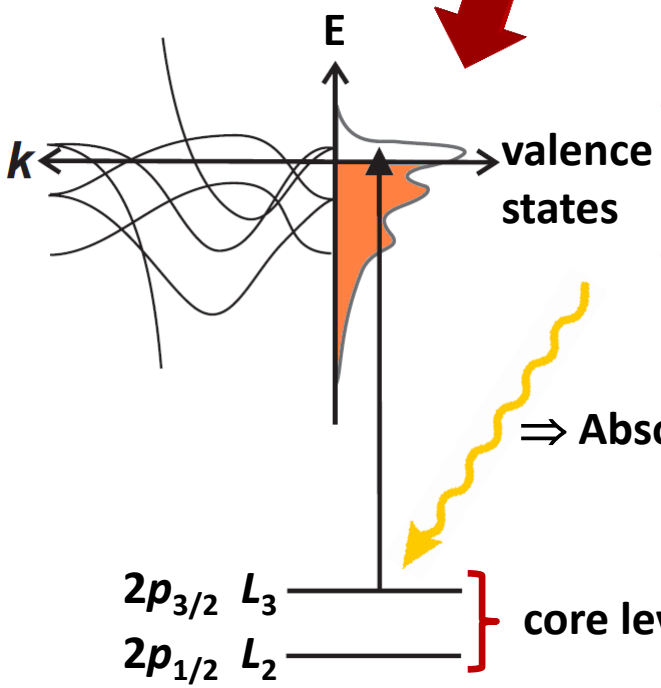

- ⇒ **charge state of absorber Fe^{2+}, Fe^{3+}**
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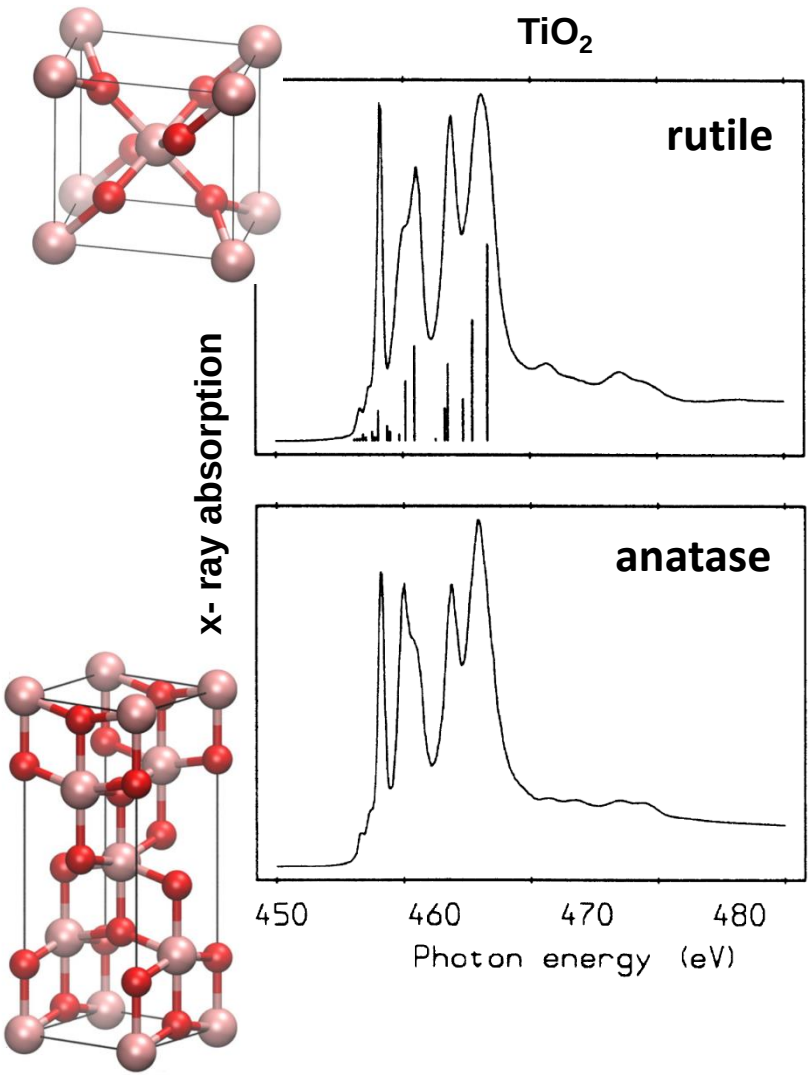
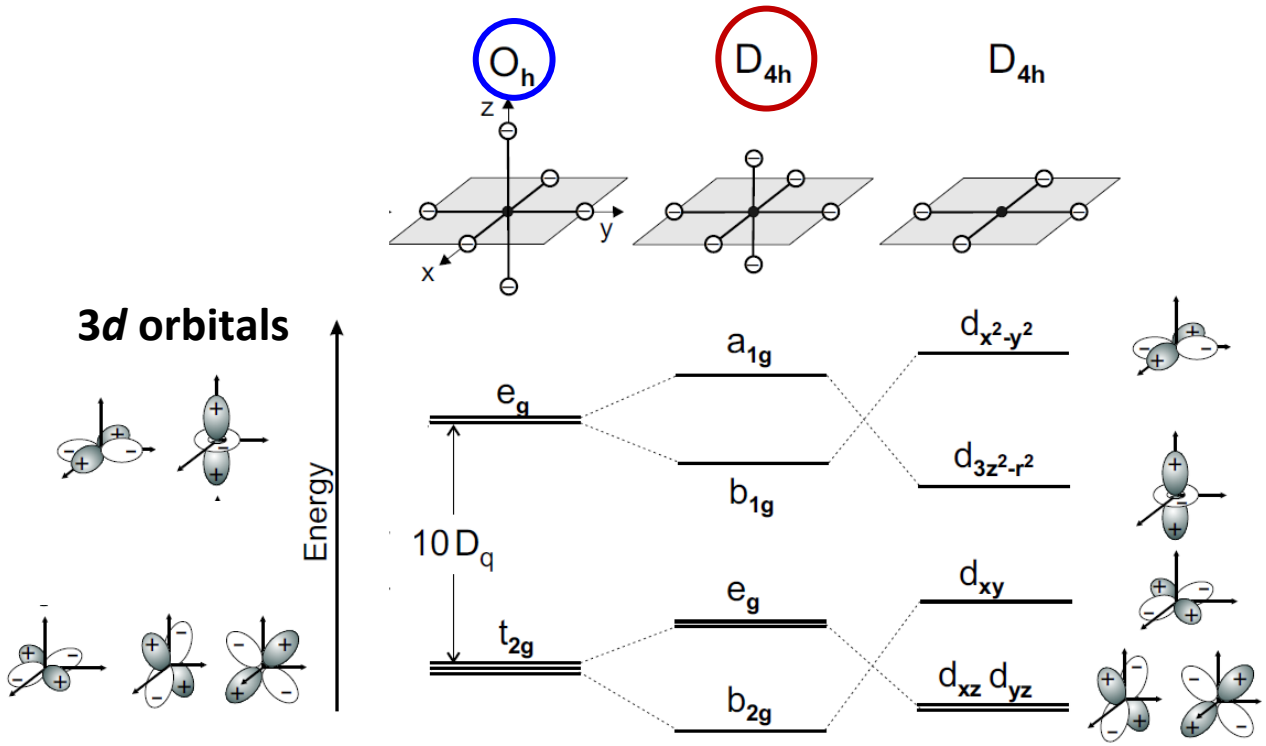
X-Ray Absorption – Lattice Symmetry



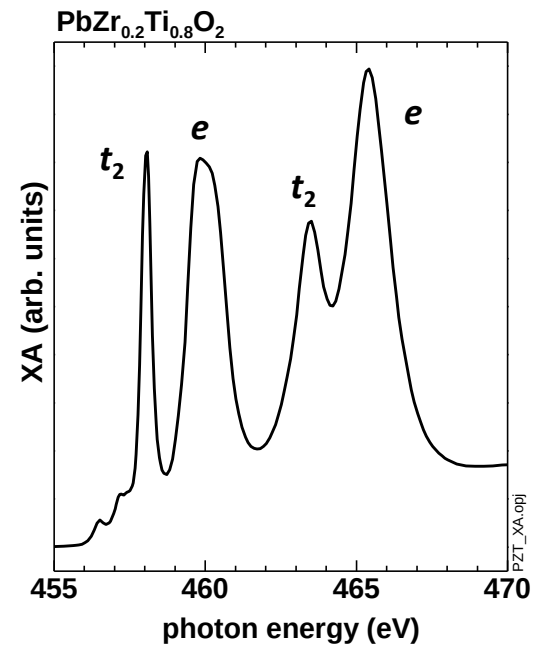
Influence of lattice site symmetry at the absorber

G. Van der Laan
Phys. Rev. B 41, 12366 (1990)

Sensitivity To Site Symmetry: Ti^{4+} $L_{3,2}$



J. Stöhr, H.C. Siegmann, Magnetism (Springer)



+ **Electric dipole transitions: $d^0 \rightarrow 2p^5 3d^1$**

+ **Crystal field splitting 10*Dq* acting on 3*d* orbitals:**

Octahedral symmetry:

***e* orbitals towards ligands → higher energy**

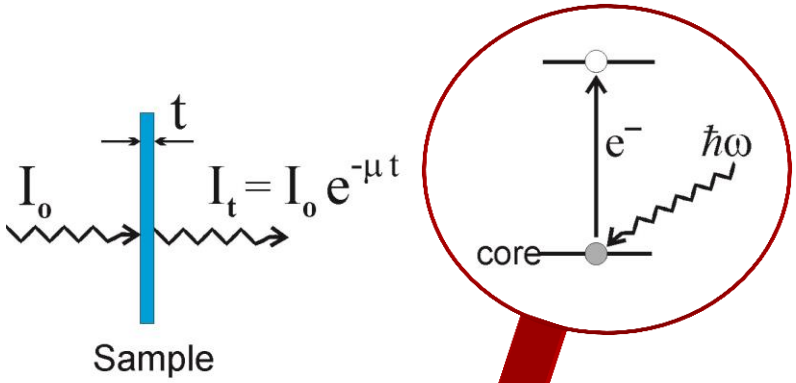
t_2 orbitals between ligands → lower energy

Tetragonal symmetry:

***e* orbitals → $b_2 = d_{xy}$, $e = d_{yz}, d_{yz}$**

t_2 orbitals → $b_1 = d_{x^2-y^2}$, $a_1 = d_{3z^2-r^2}$

X-Ray Absorption – Fundamentals



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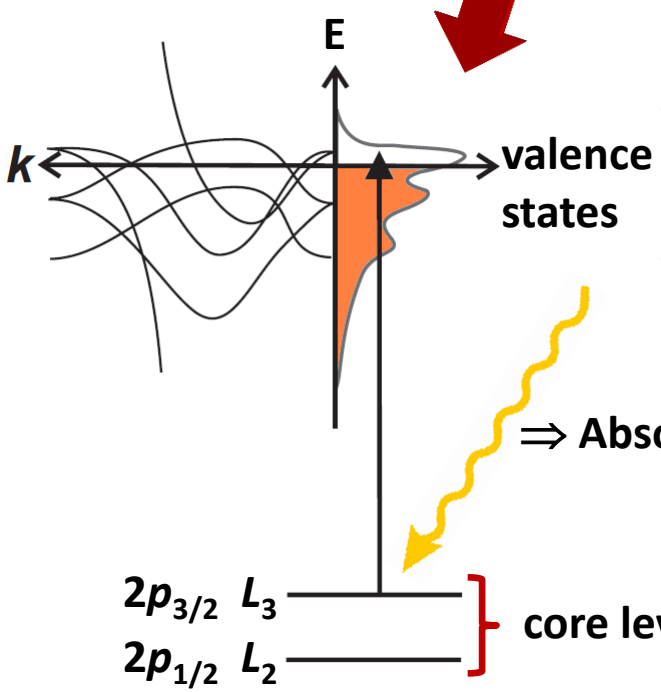

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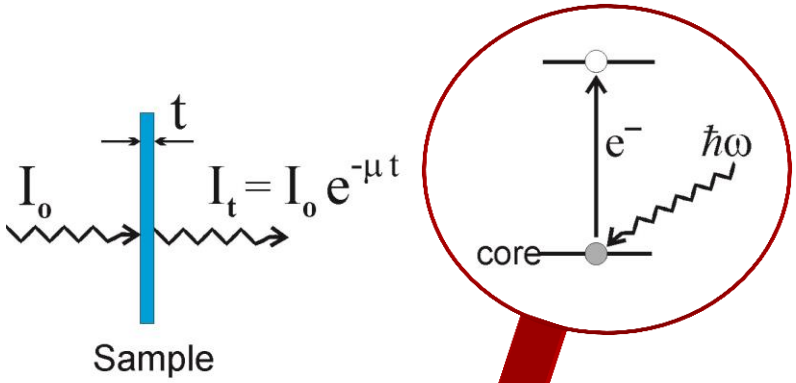

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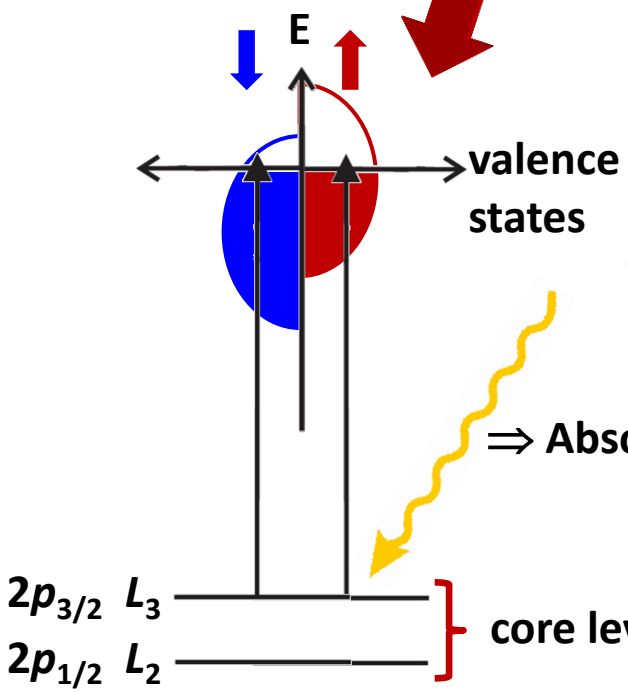

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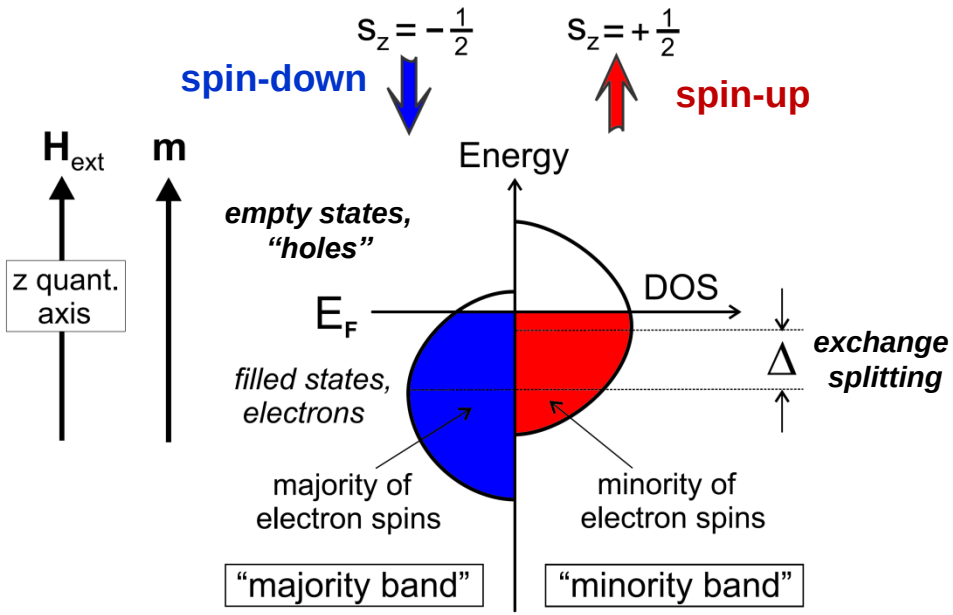
Stoner Model For Ferromagnetic Metals



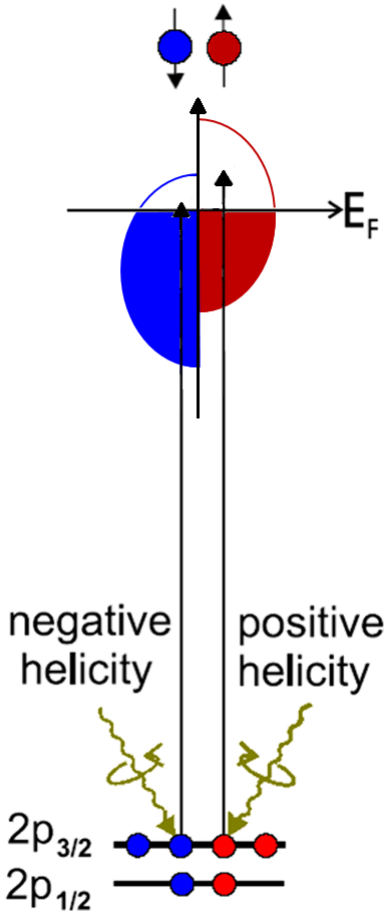
J. Stöhr, H.C. Siegmann, Magnetism (Springer)

3*d* shell

- **Magnetic moments in Fe, Co, Ni well described by Stoner model: *d*-bands containing up and down spins shifted relative to each other by "exchange splitting"**
- **Spin- up and spin-down bands filled according to Fermi statistics**
- **Magnetic moment |m| determined by difference in number of electrons in majority and minority bands**

$$|m| = \mu_B (n_e^{maj} - n_e^{min})$$

X-Ray Magnetic Circular Dichroism (XMCD)



Photoexcitation of electron from $2p_{3/2}$, $2p_{1/2}$ to $3d$ states by absorption of circularly polarized x rays:

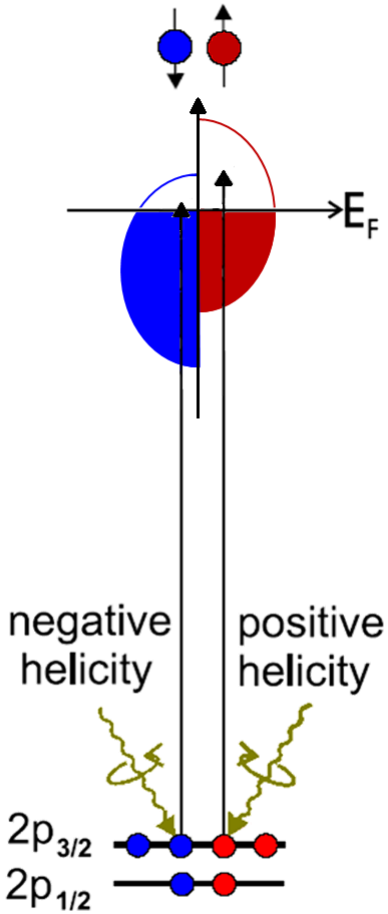
- **Transfer of angular momentum of incident circular polarized x ray to excited electrons (angular momentum conservation)**
- **Excitation from spin-orbit split $2p_{3/2}$, $2p_{1/2}$ level**

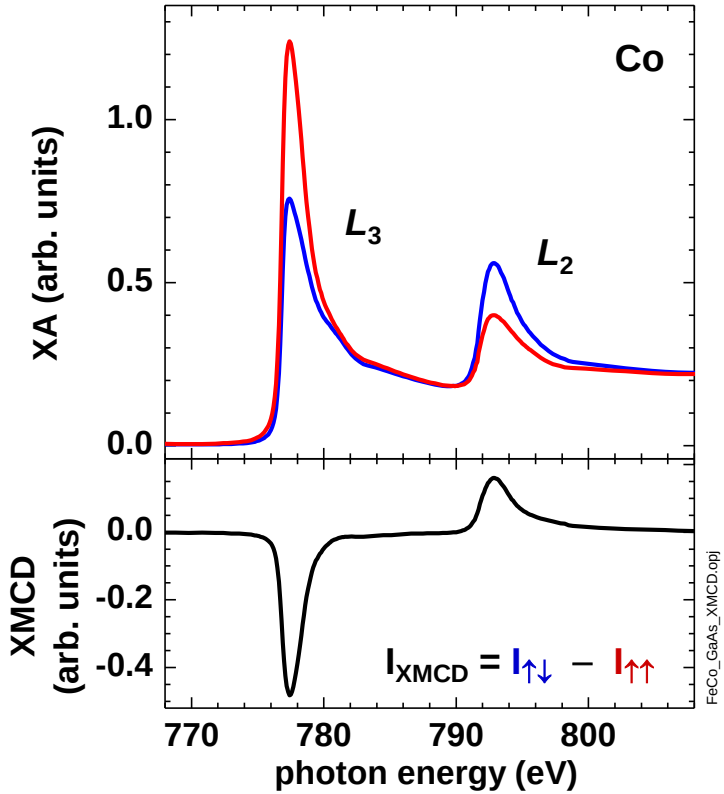
  ⇒ **Transfer of angular momentum ($\pm\hbar$) from photon to electron spin through spin-orbit coupling**

  ⇒ **Spin polarization opposite for incident x rays with positive ($+\hbar$) and negative ($-\hbar$) photon spin**
- **$2p_{3/2}$ and $2p_{1/2}$ levels have opposite spin orbit coupling ($l+s$, $l-s$)**

  ⇒ **Spin polarization opposite for two levels**
- **Unequal spin-up and spin-down populations in exchange split valence shell acts as detector for spin of excited electrons**

X-Ray Magnetic Circular Dichroism (XMCD)

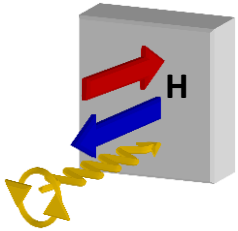




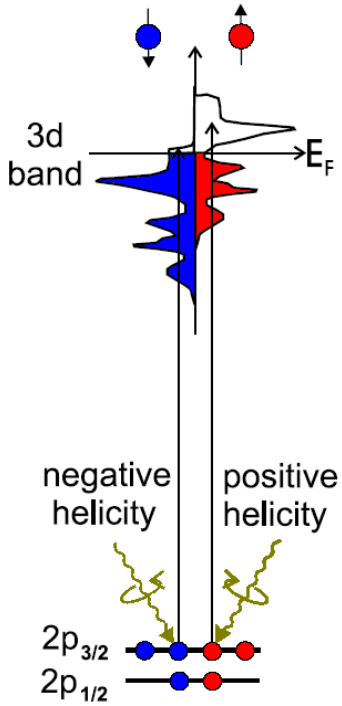
Magnitude of dichroism depends on

- **+ expectation value of 3*d* magnetic moment**
- **+ degree of circular photon polarization, P_{circ}**
- **+ …**

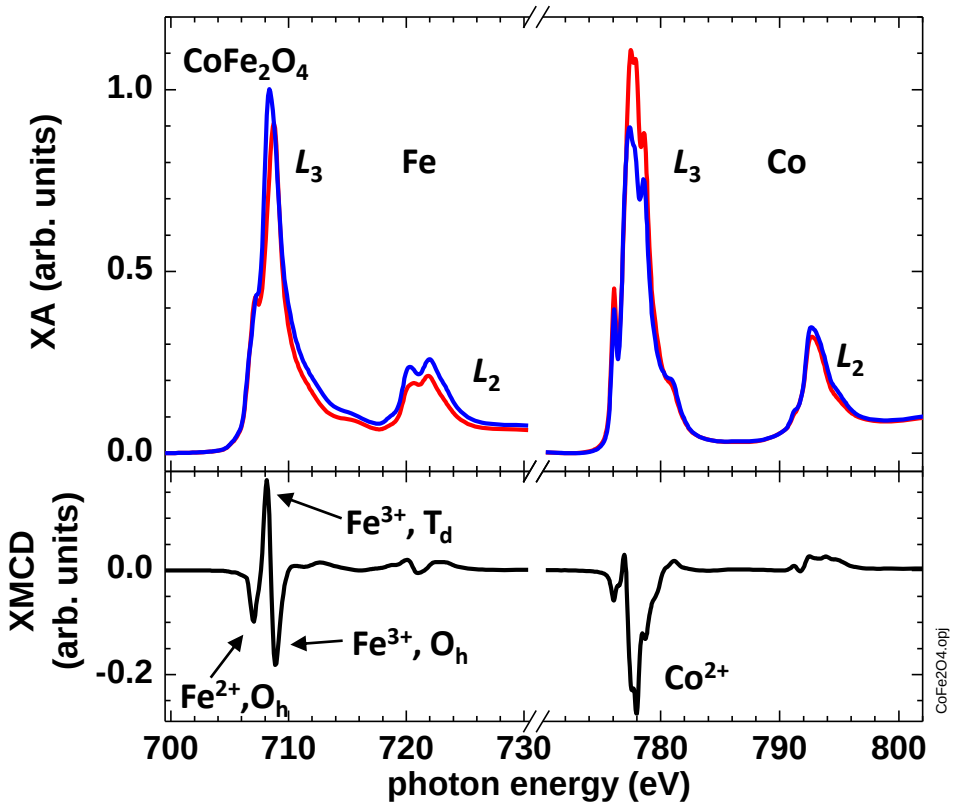
X-Ray Magnetic Circular Dichroism (XMCD)



circularly polarized



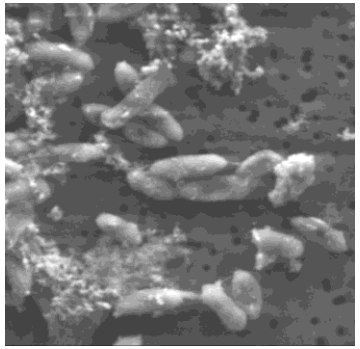
J. Stöhr, H.C. Siegmann, Magnetism (Springer)

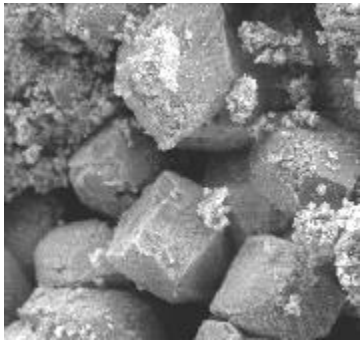


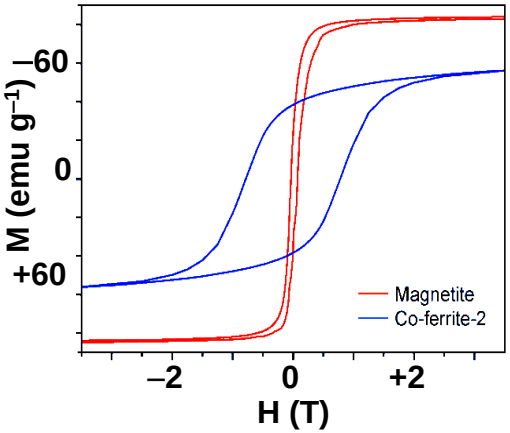
+ XMCD provides magnetic information resolving elements Fe, Co, …
valence states: Fe^{2+}, Fe^{3+}, …
lattice sites: octahedral, O_h, tetrahedral, T_d, …

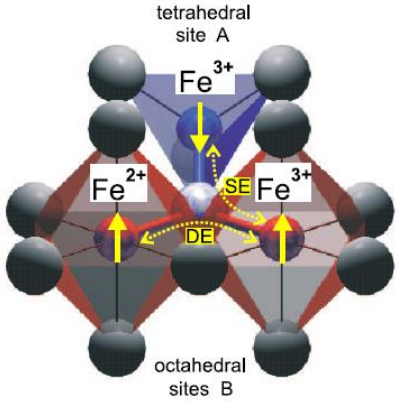
MAGNETIC BIONANOSPINELS

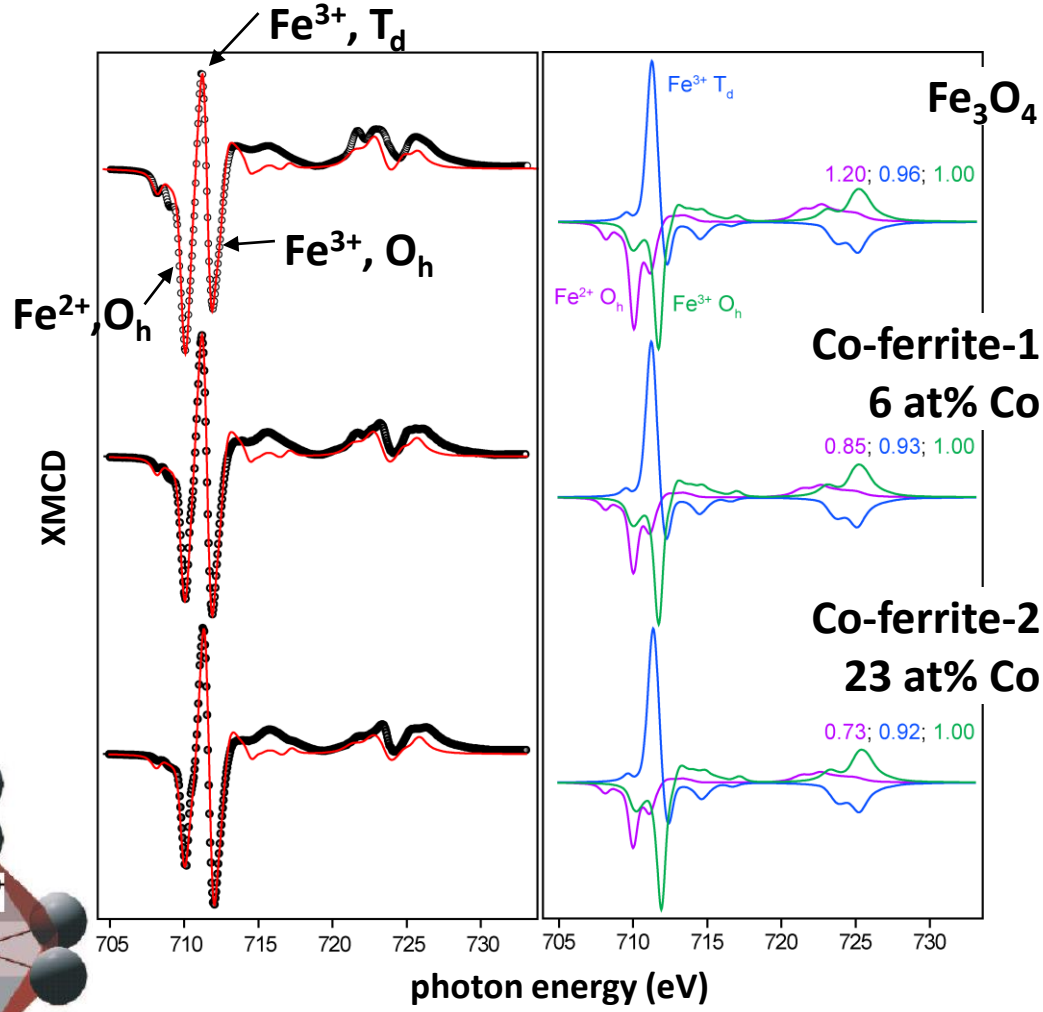
+ Geobacter sulfurreducens bacteria form magnetite nanocrystals (15nm) via extracellular reduction of amorphous Fe(III)-bearing minerals







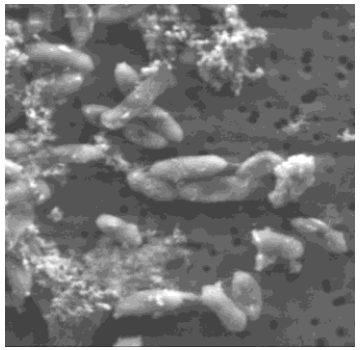


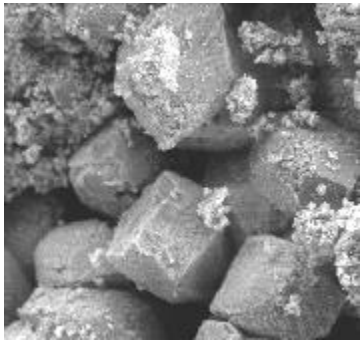


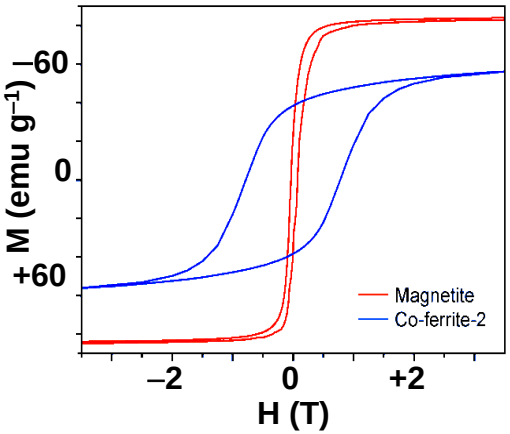
V. Cocker *et al.*,
Eur. J. Mineral. 19, 707–716 (2007)

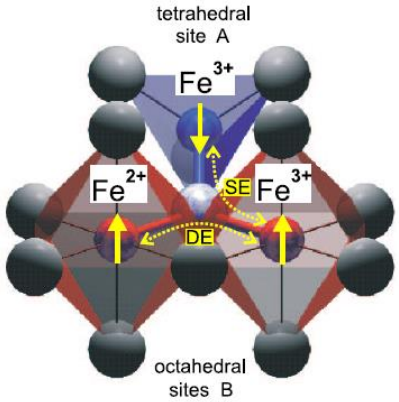
MAGNETIC BIONANOSPINELS

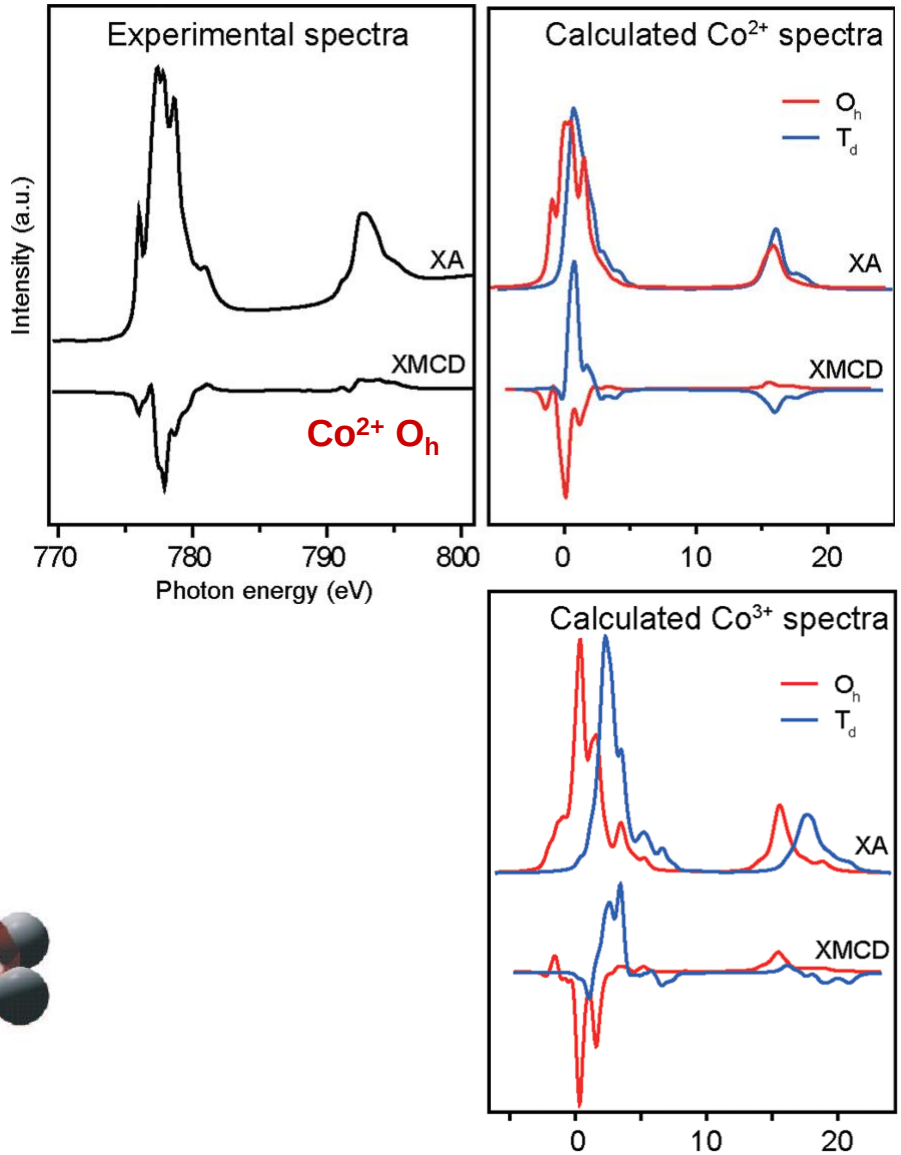
+ **Geobacter sulfurreducens bacteria form magnetite nanocrystals (15nm) via extracellular reduction of amorphous Fe(III)-bearing minerals**



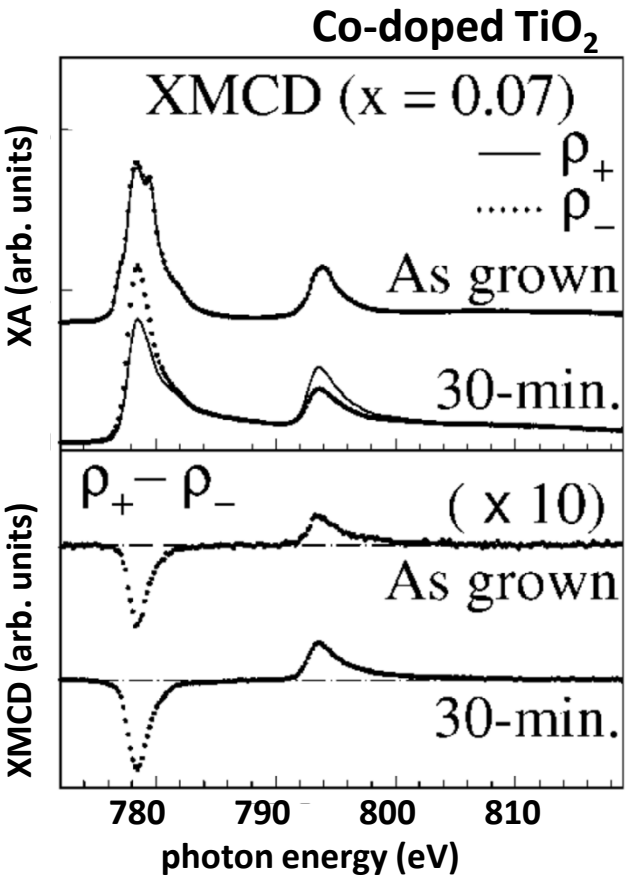






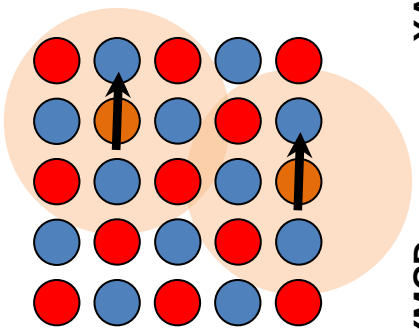


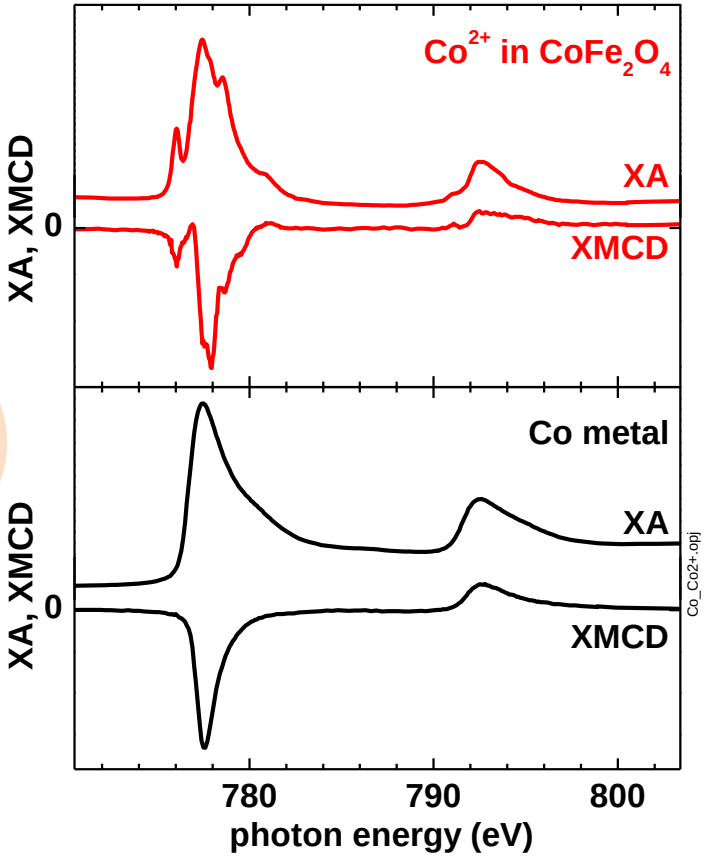
Co-DOPED TiO_2



J.-Y. Kim *et al.*,
Phys. Rev. Lett. 90, 017401 (2003)

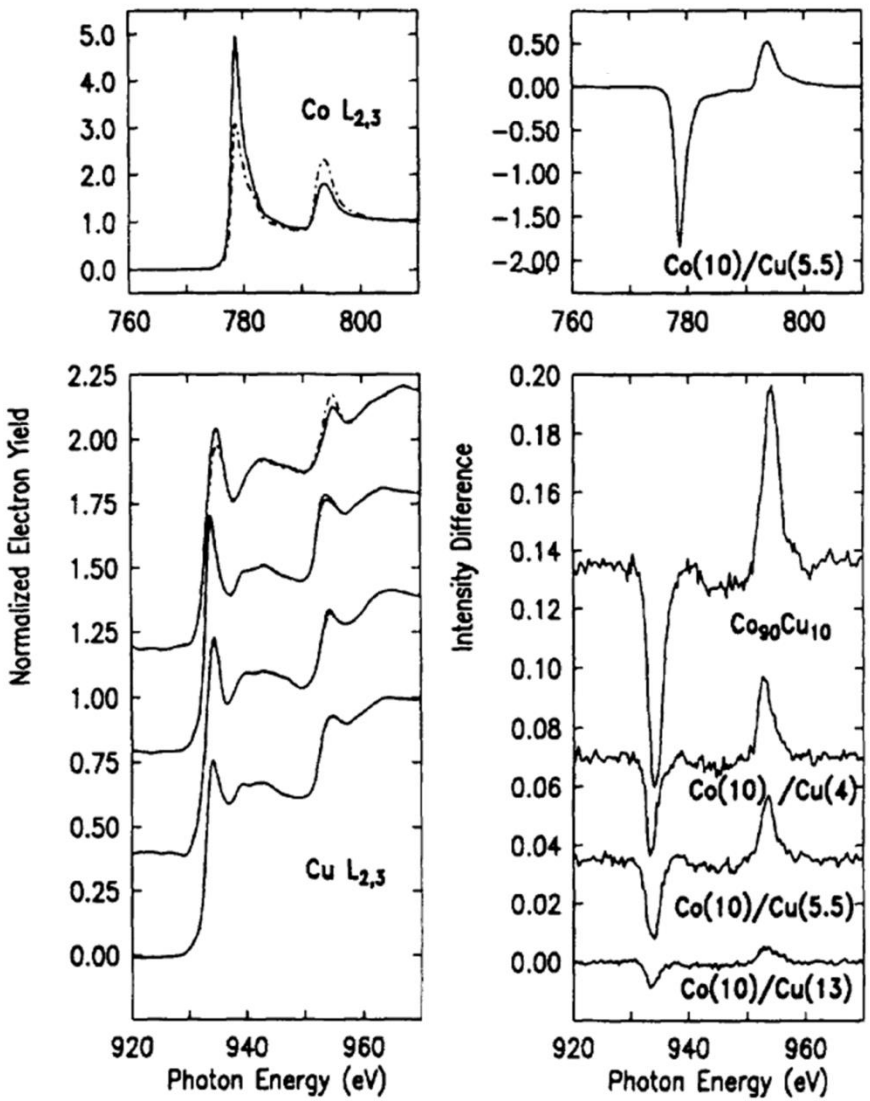
dilute magnetic semiconductors

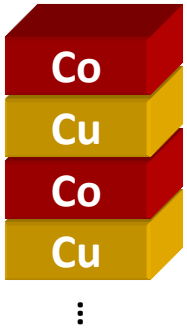




+ Comparing XMCD spectra with model compounds and/or calculations
⇒ Identifying magnetic phases

Induced Moments At Co/Cu Interfaces

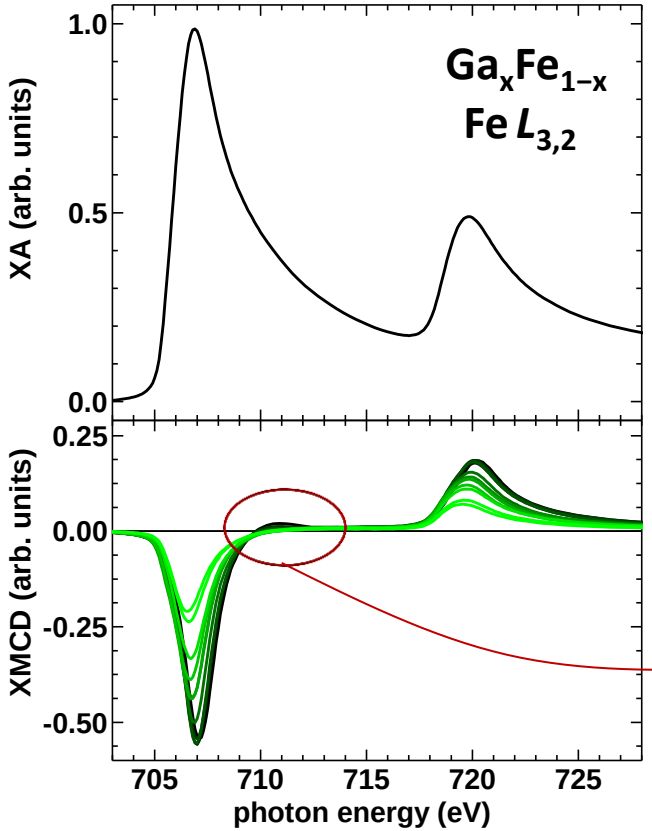


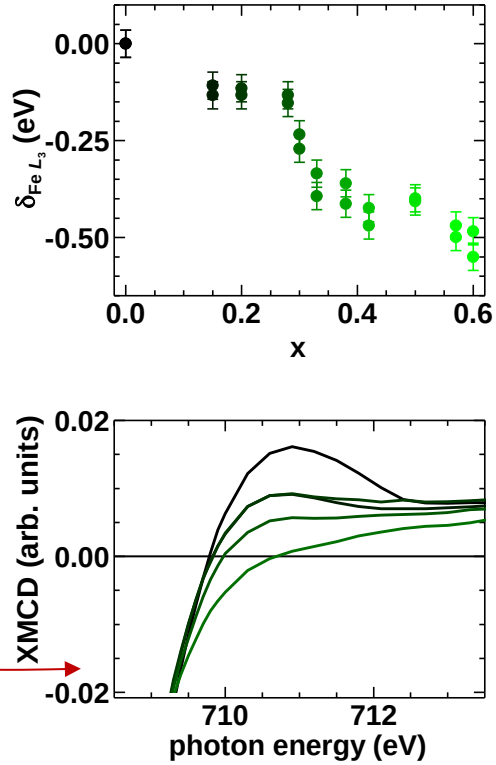


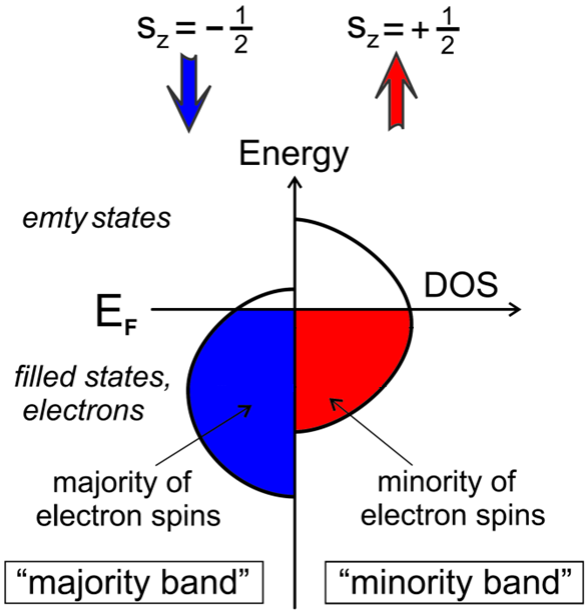
+ **The element-specificity makes XMCD measurements an ideal tool to determine induced moments at interfaces between magnetic and non-magnetic elements.**

M. G. Samant *et al.*,
Phys. Rev. Lett. 72, 1112 (1994)

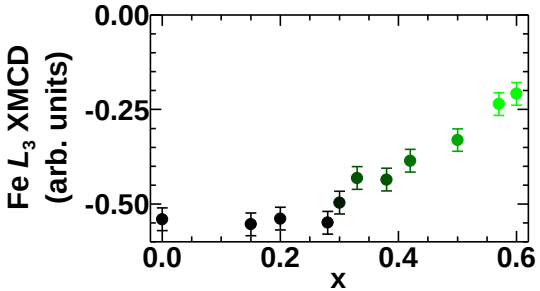
BAND FILLING IN Ga_xFe_{1-x}







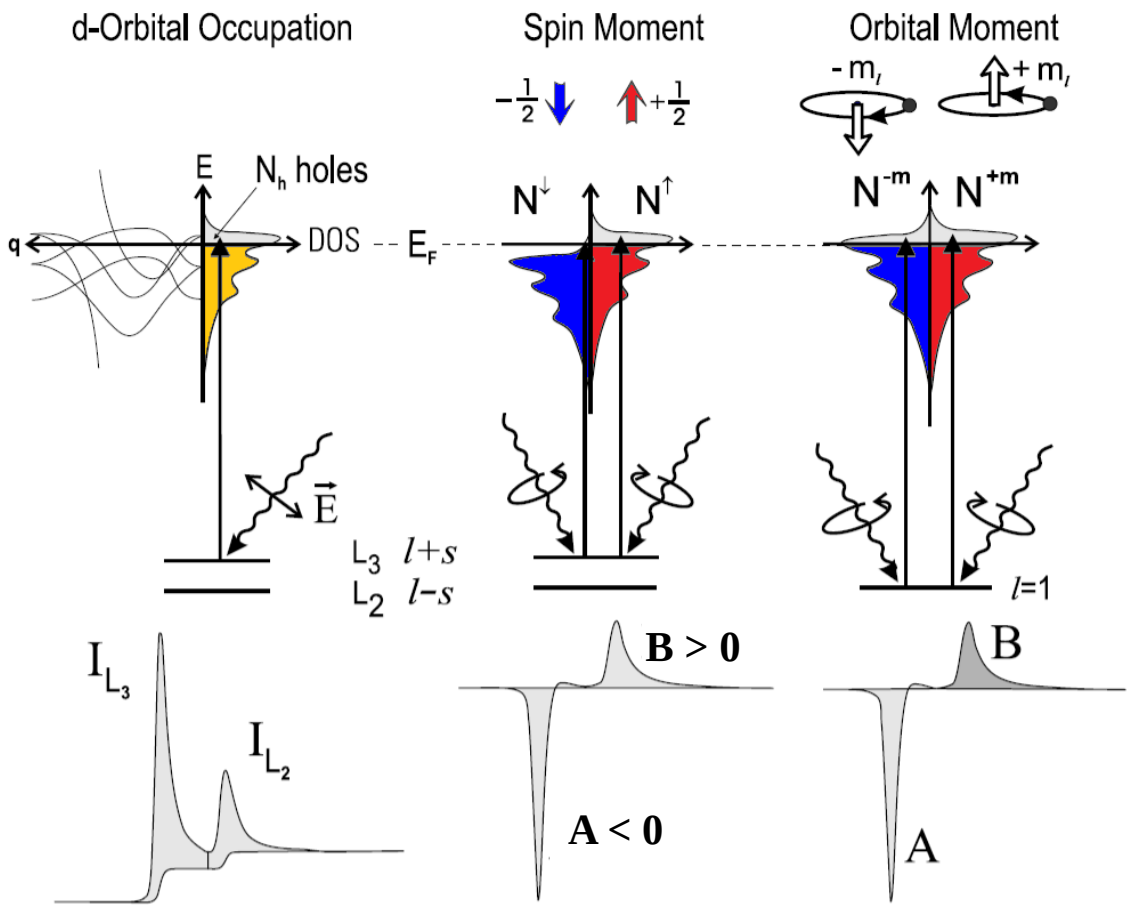
J. Stöhr, H.C. Siegmann, Magnetism (Springer)



E. Arenholz *et al.*, Phys. Rev. B 82, 180405 (2010)

+ Fe majority-spin filled for x=0.3
+ x > 0.3: Fe moment decrease strongly, Formation of D03 precipitates

Sum Rules



$N_h = \langle I_{L3} + I_{L2} \rangle / C$

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

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

+ **Theoretically derived sum rules correlate XMCD spectra with spin and orbital moment providing unique tool for studying magnetic materials.**

J. Stöhr, H.C. Siegmann, Magnetism (Springer)

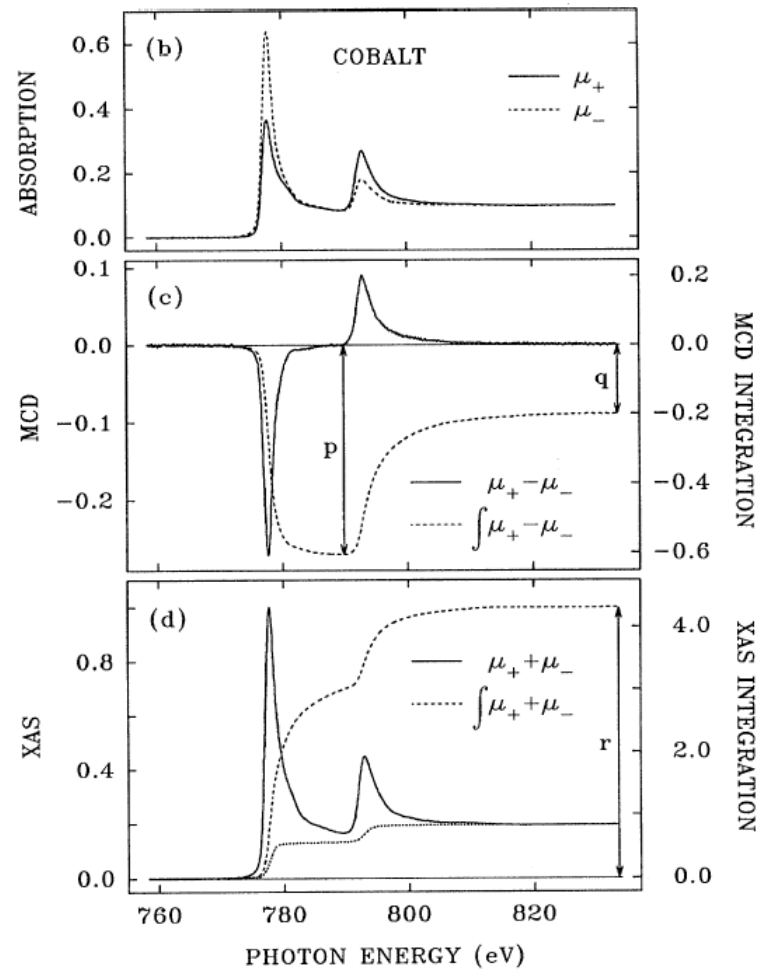
Sum Rules

+ Separation of spin and orbital moments requires very high quality data.

$$\frac{m_{orb}}{m_{spin}} = \frac{2q}{9p - 6q}$$

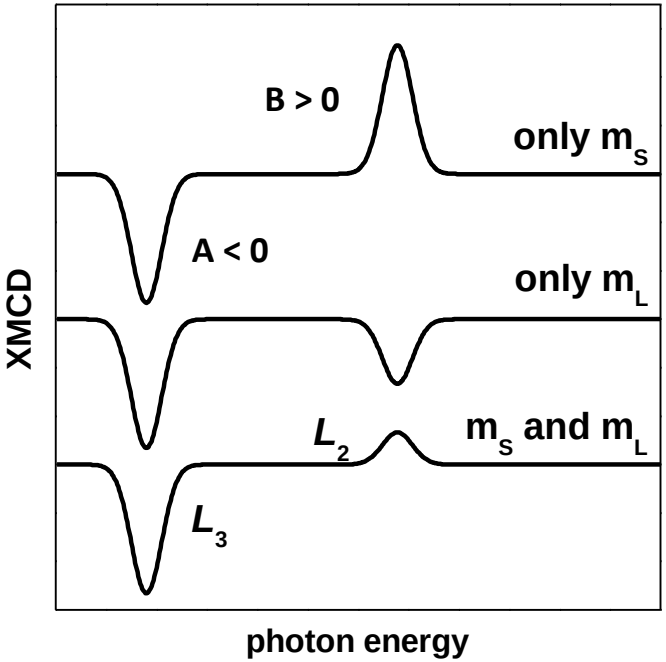
$$m_{orb} = -\frac{4q\,(10 - n_{3d})}{3r}$$

$$m_{spin} = -\frac{(6p - 4q)\,(10 - n_{3d})}{r}$$



C.T. Chen *et al.*,
Phys. Rev. Lett. 75, 152(1995)

SUM RULES

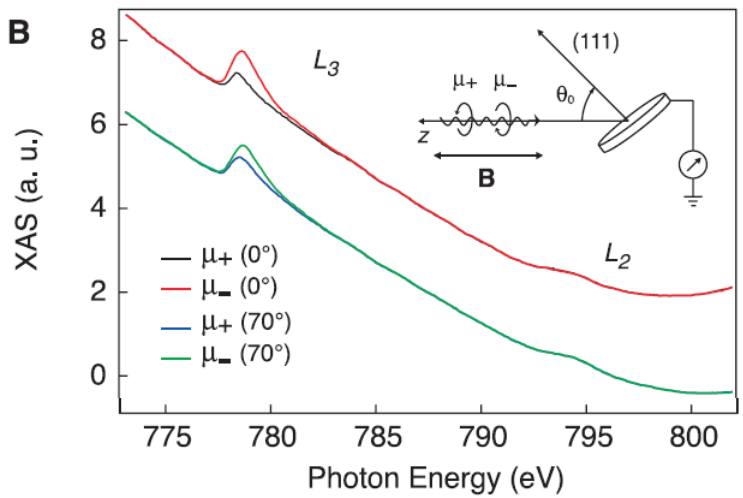


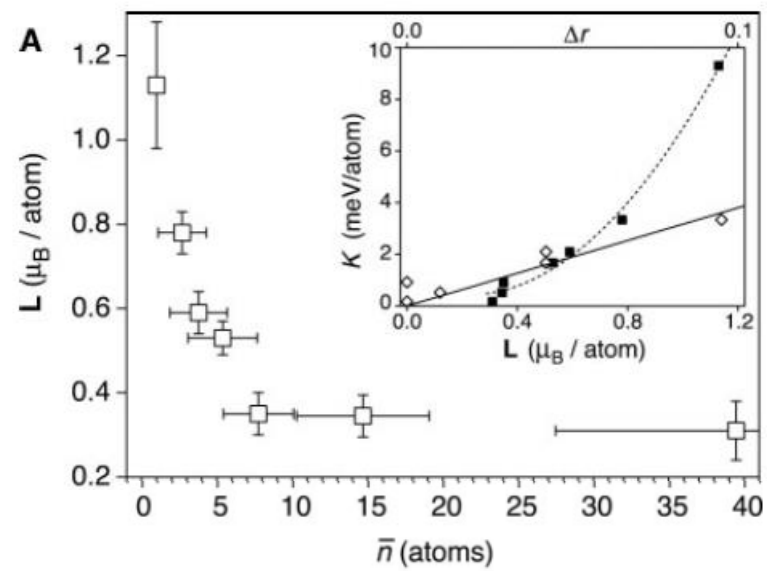
+ Spin and orbital moment only systems have distinct XMCD spectra:

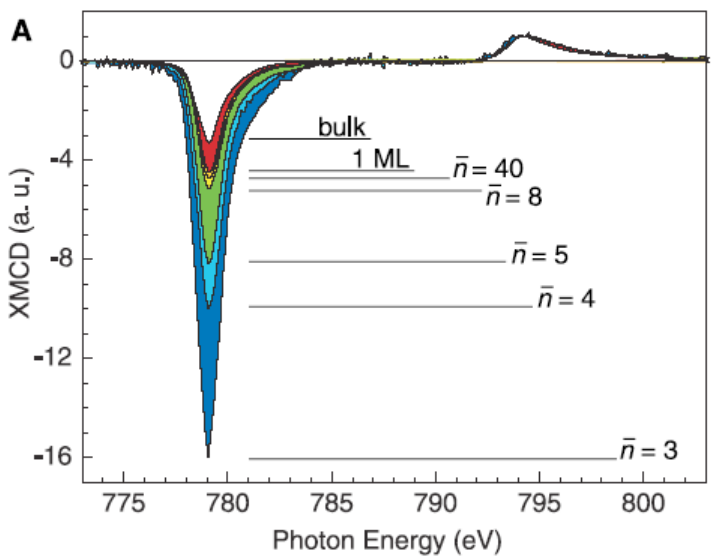
$m_L = -2\mu_B\langle A + B\rangle / 3C = 0$ for $A = -B$

$m_S = \mu_B\langle -A + 2B\rangle / C = 0$ for $A = 2B$

Orbital Moment Of Co Nanoparticles



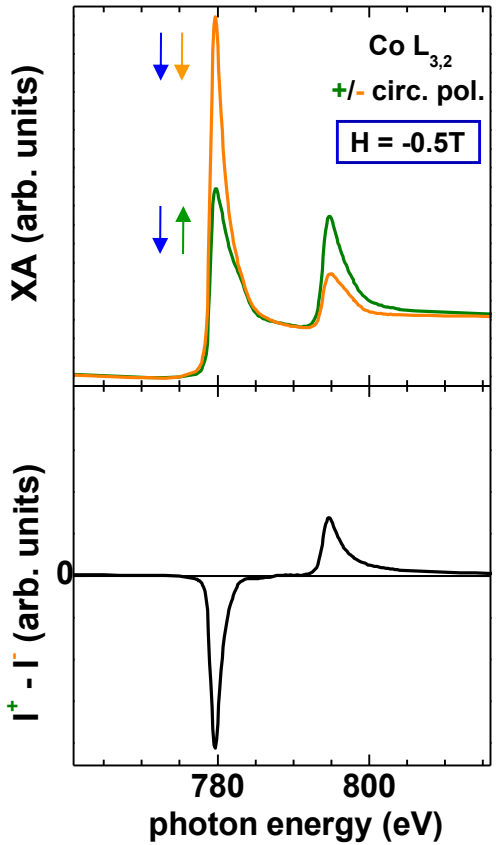




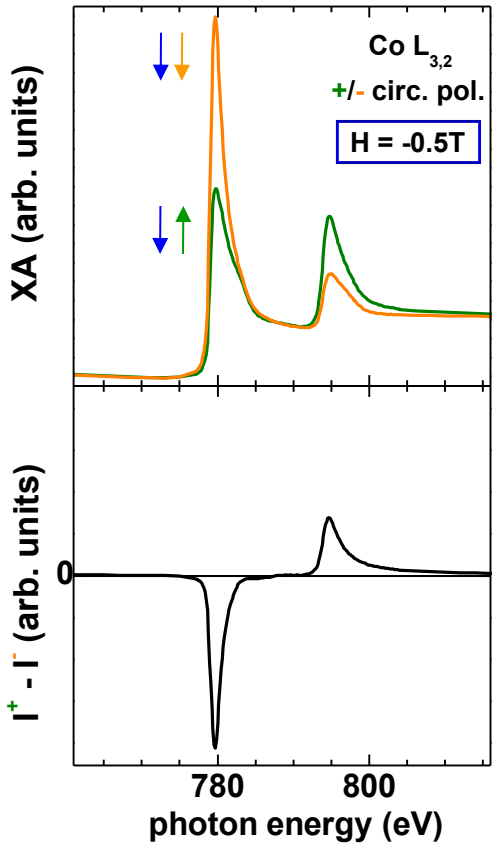
- **Strong variation of orbital and spin magnetic moment observable as change in relative L_3 and L_2 intensity in XMCD spectrum.**
- **Co atoms and nanoparticles on Pt have enhanced orbital moments up to 1.1 μ_B**

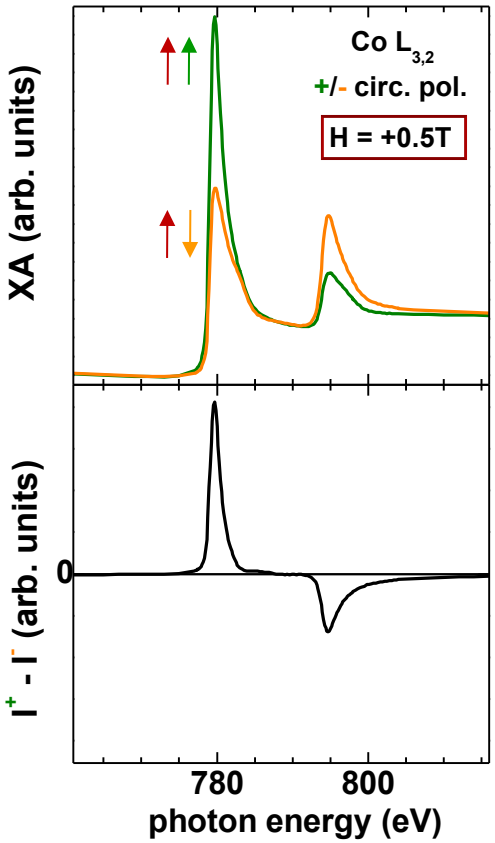
P. Gambardella *et al.*, Science 300, 1130 (2003)

Element-specific Magnetization Reversal

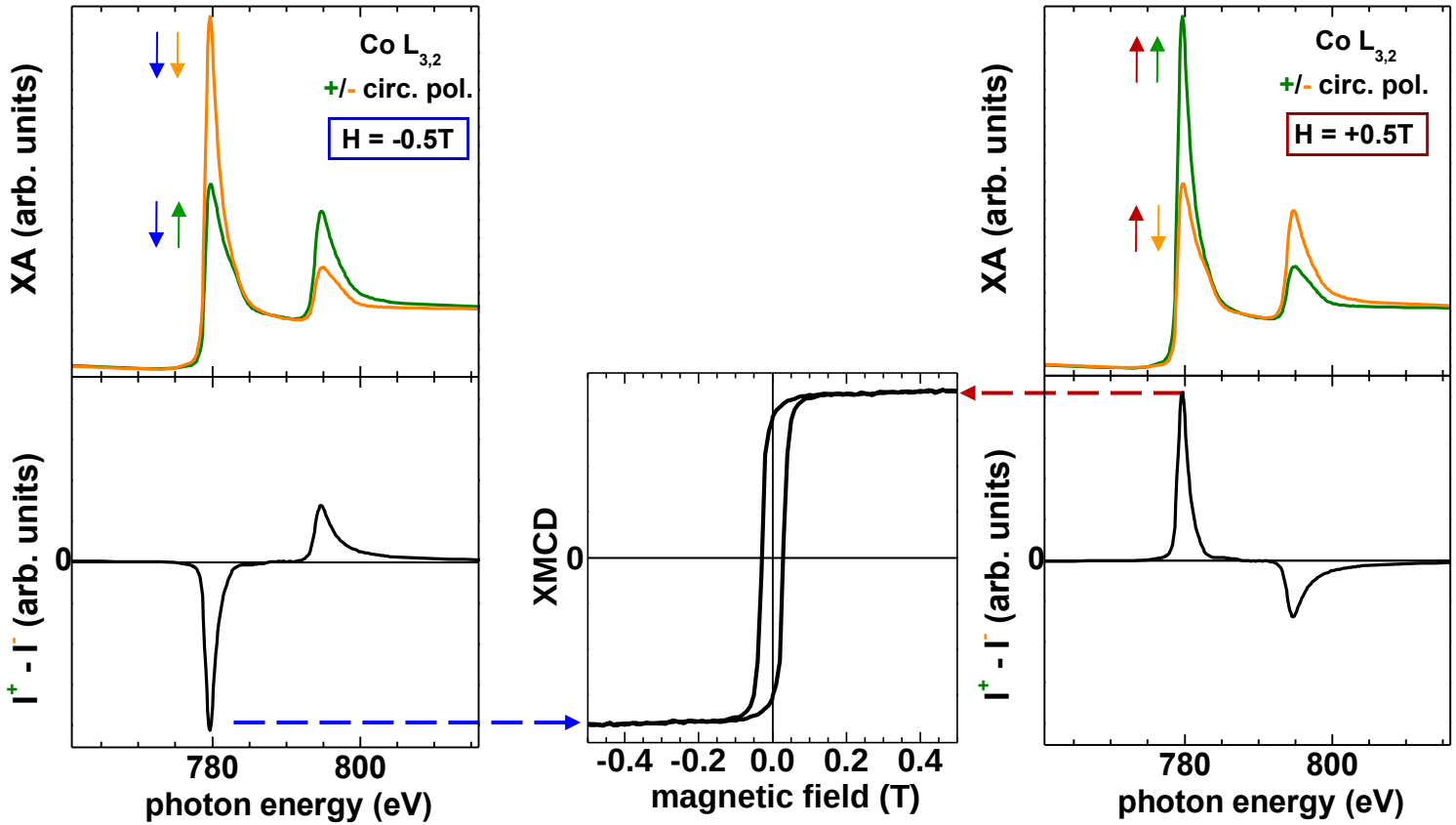


Element-specific Magnetization Reversal





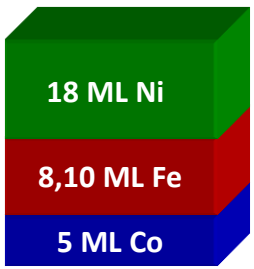
ELEMENT-SPECIFIC MAGNETIZATION REVERSAL

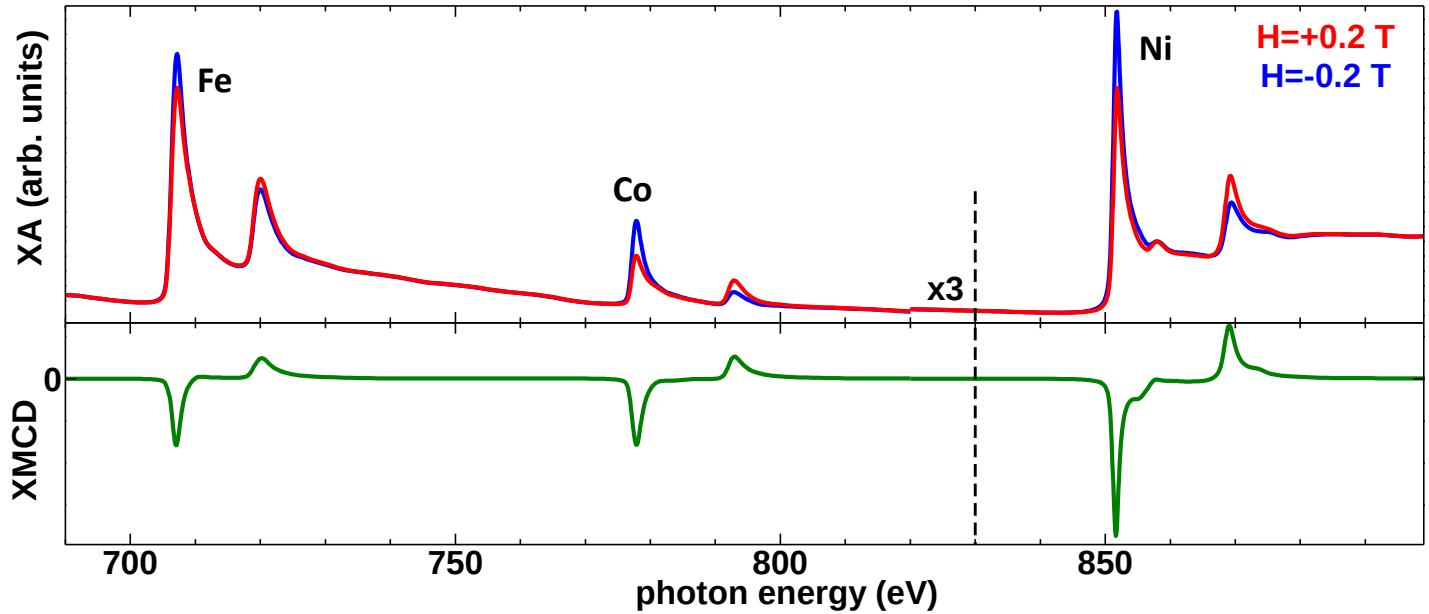


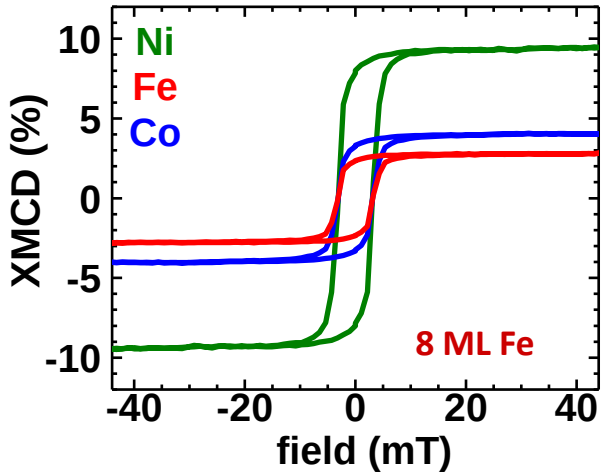
+ **Monitoring field dependence of XMCD**

⇒ **Element-specific information on magnetization reversal in complex magnetic nanostructures.**

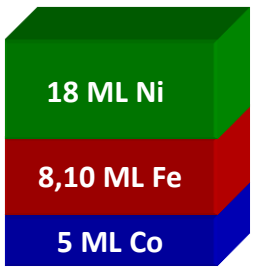
Element-specific Magnetization Reversal

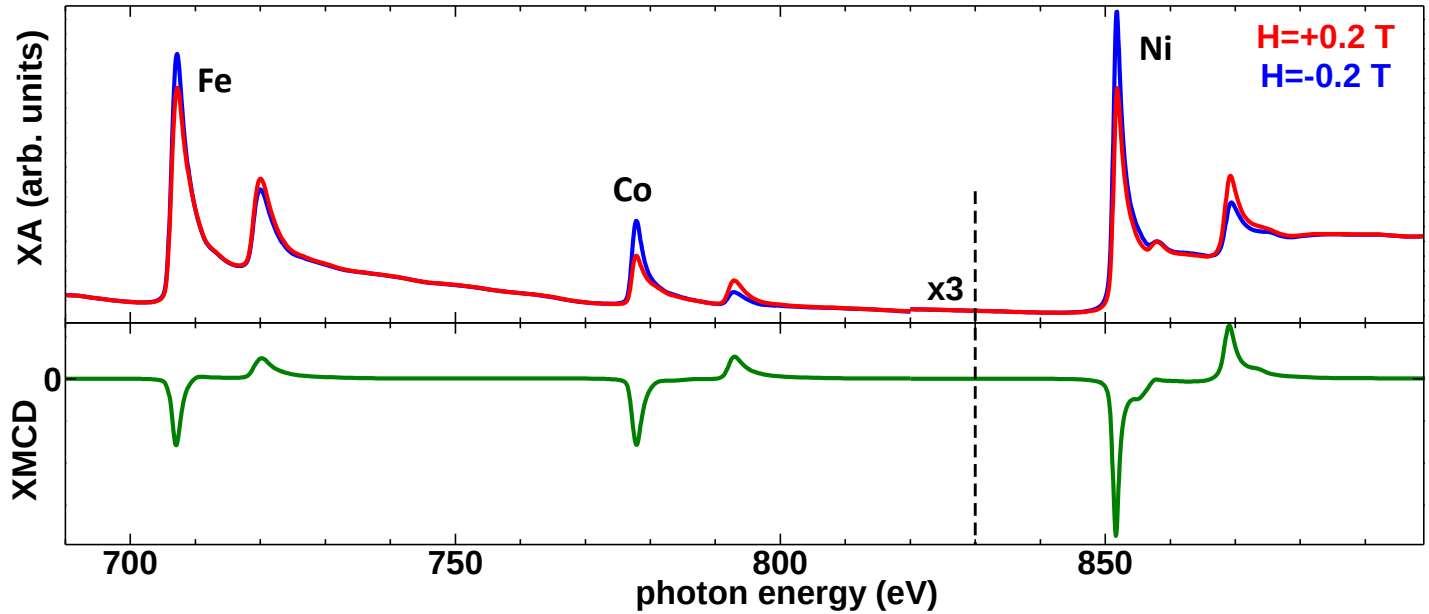


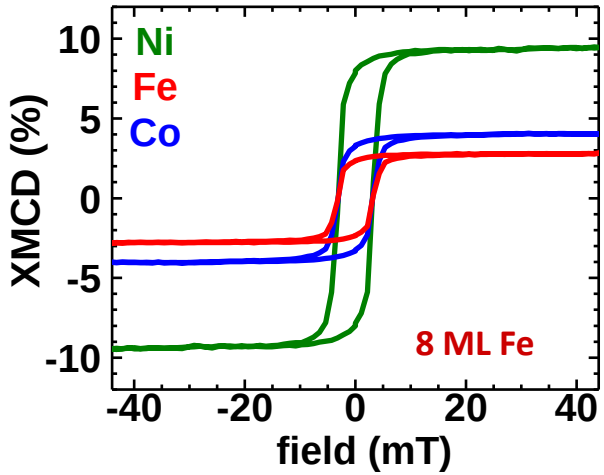


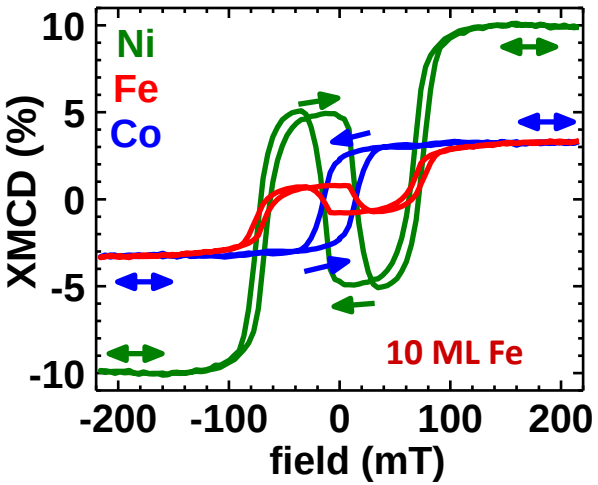


Element-specific Magnetization Reversal









MAGNETIC INTERFACES

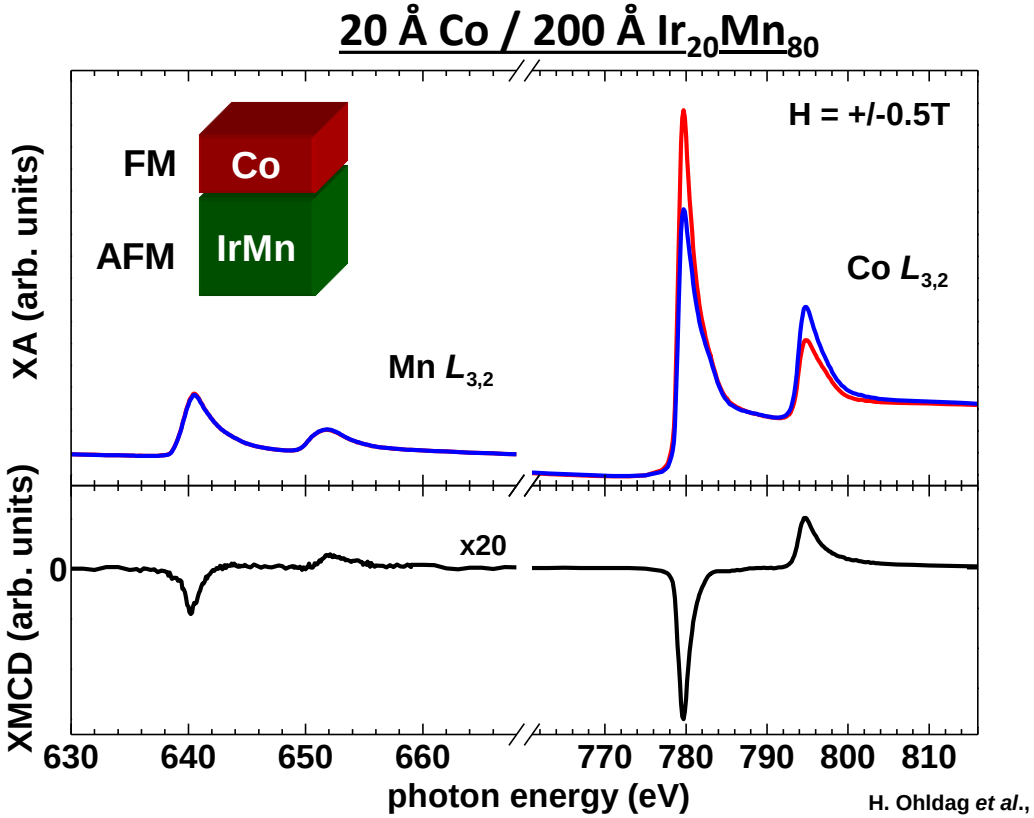
+ Weak Mn XMCD signal

⇒ Uncompensated Mn at Co/IrMn interface

+ Same sign of XMCD signal for Co and Mn

⇒ Parallel coupling of Co and Mn moments

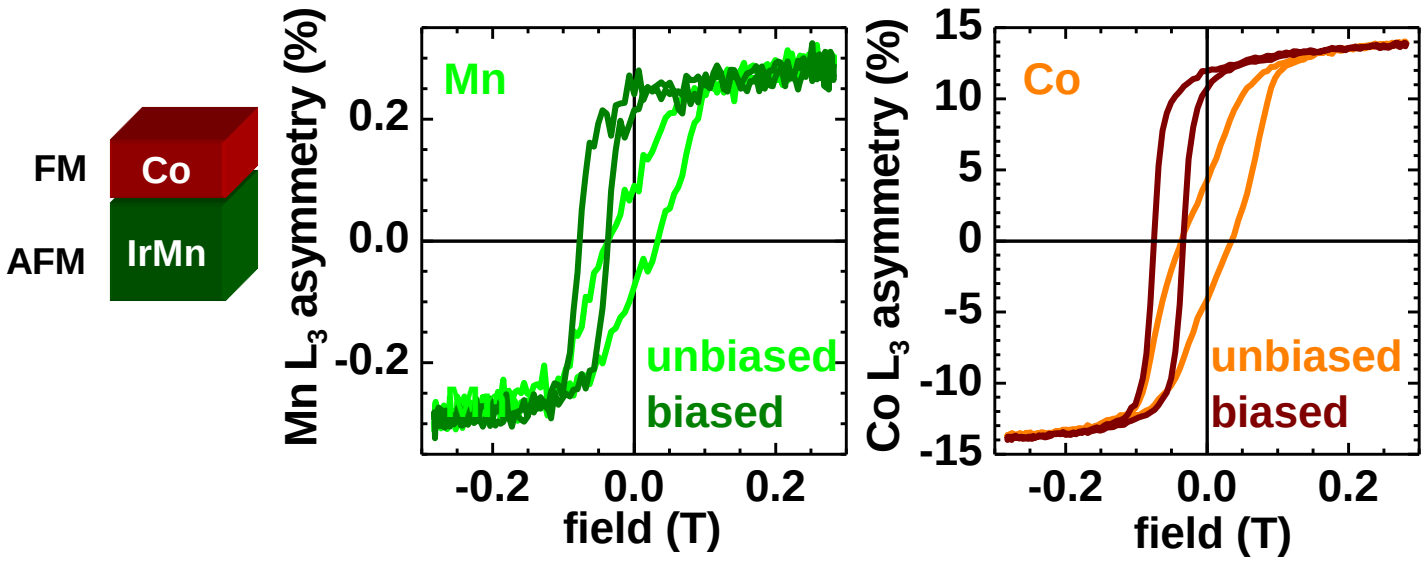
+ Nominal thickness of uncompensated interface moments: (0.5±0.1)ML



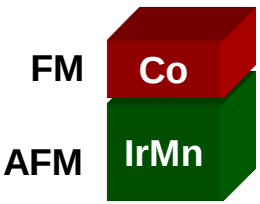
H. Ohldag *et al.*, Phys. Rev. Lett. 91, 017203 (2003)

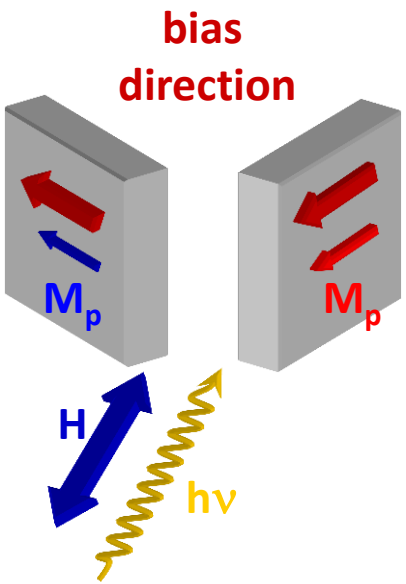
MAGNETIC INTERFACES

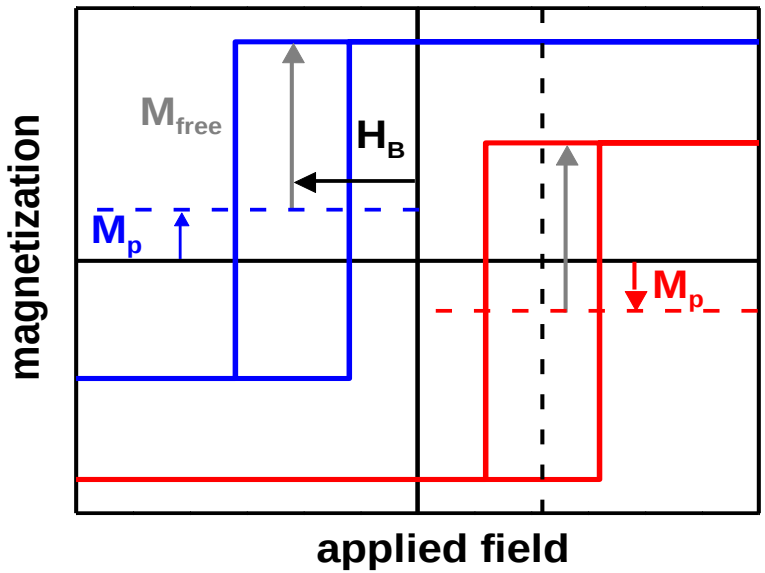
+ Uncompensated interface moments play critical role in exchange bias phenomena
  = field cooling of ferromagnet/antiferromagnet bilayer inducing additional magnetic anisotropy



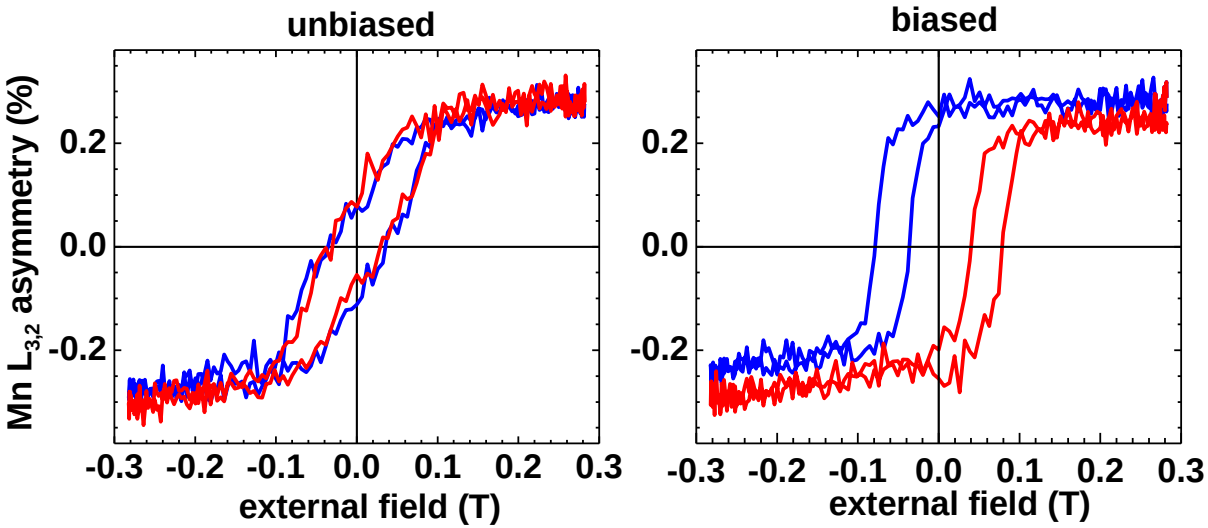
MAGNETIC INTERFACES





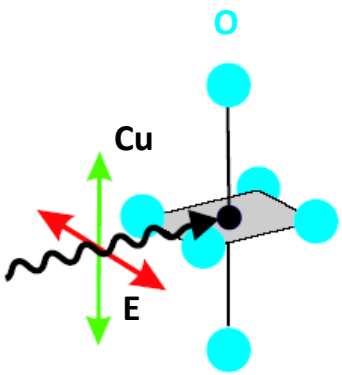


+ **Biased sample:**
  Small vertical loop shift indicating pinned interface moments !
+ **Unbiased sample:**
  no vertical loop shift

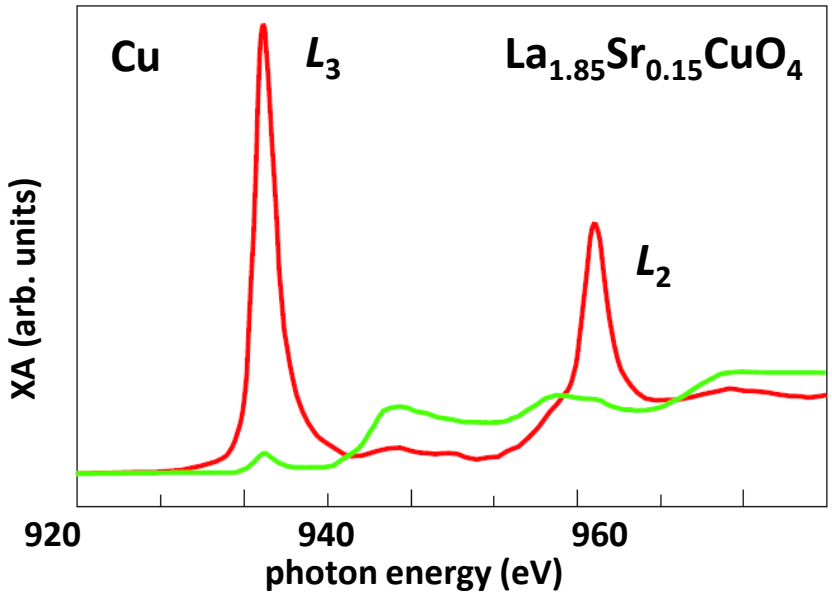


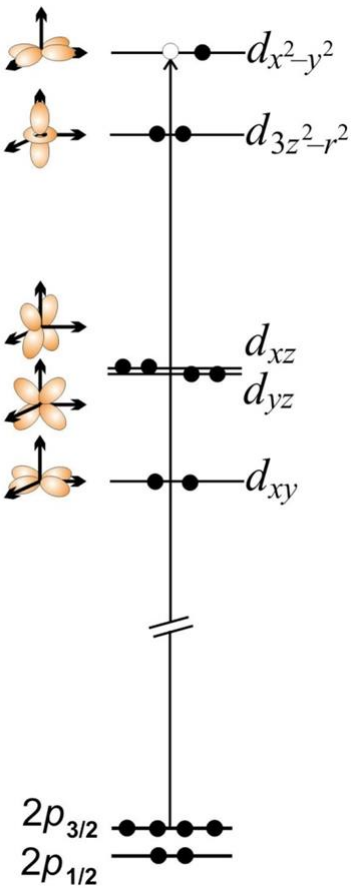
H. Ohldag *et al.*,
Phys. Rev. Lett. 91, 017203 (2003)

X-Ray Linear Dichroism



C. T. Chen *et al.*
PRL 68, 2543 (1992)

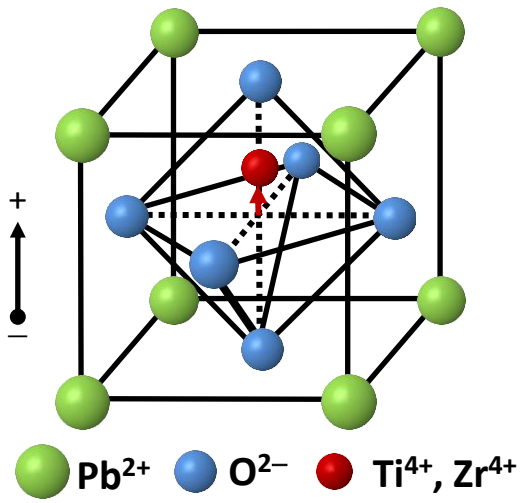


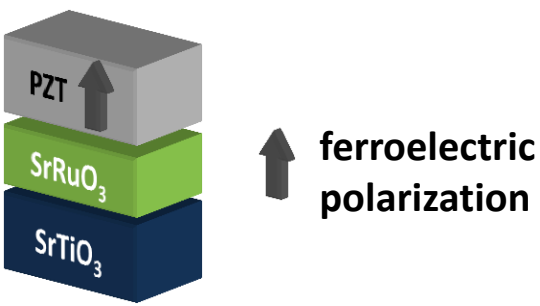


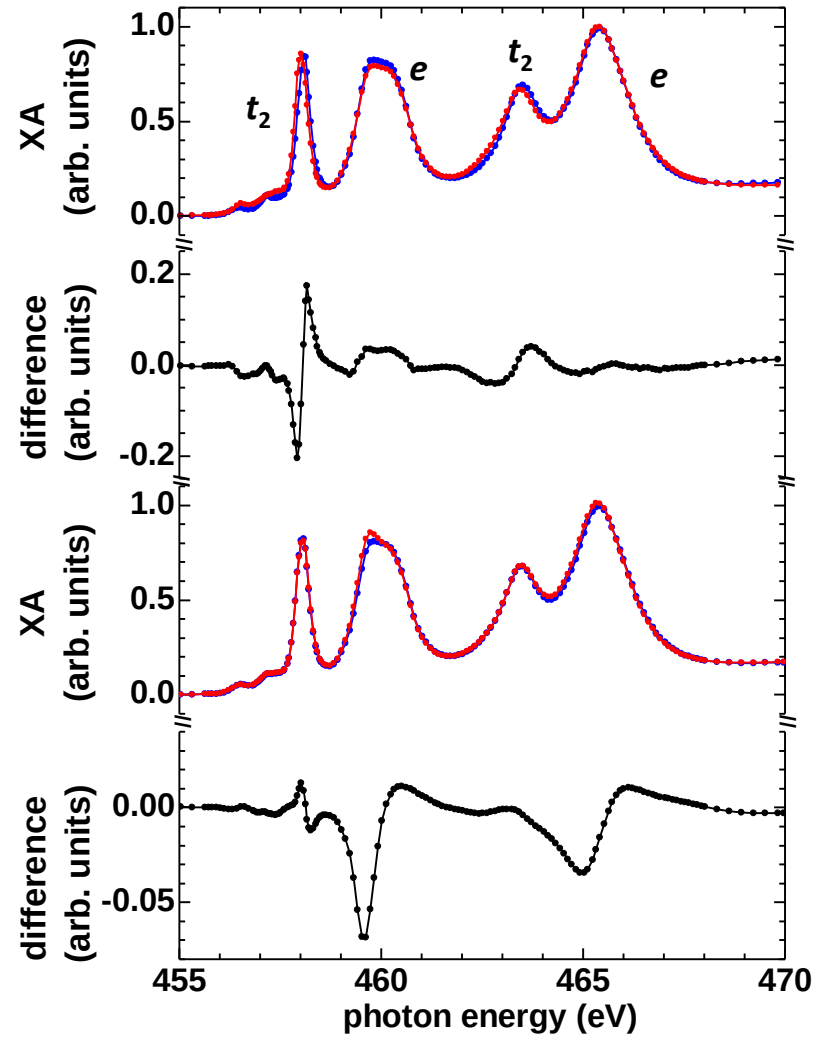
X-Ray Linear Dichroism:

+ **Difference in x-ray absorption for different linear polarization direction relative to crystalline and/or spin axis.**
+ **Due to the anisotropic charge distribution about the absorbing atom caused by bonding and/or magnetic order.**
+ **"Search Light Effect": X-ray absorption of linear polarized x rays proportional to density of empty valence states in direction of electric field vector E.**

Structural Changes In $PbZr_{0.2}Ti_{0.8}O_3$





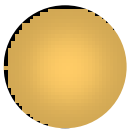


E. Arenholz *et al.*, Phys. Rev. B 82, 140103 (2010)

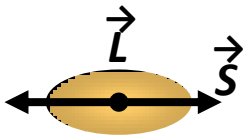
+ Spontaneous electric polarization due to off-center shift of Ti^{4+}, Zr^{4+} associated with tetragonal distortion ⇔ linear dichroism

+ Reversing ferroelectric polarization changes XA ⇔ Change in tetragonal distortion

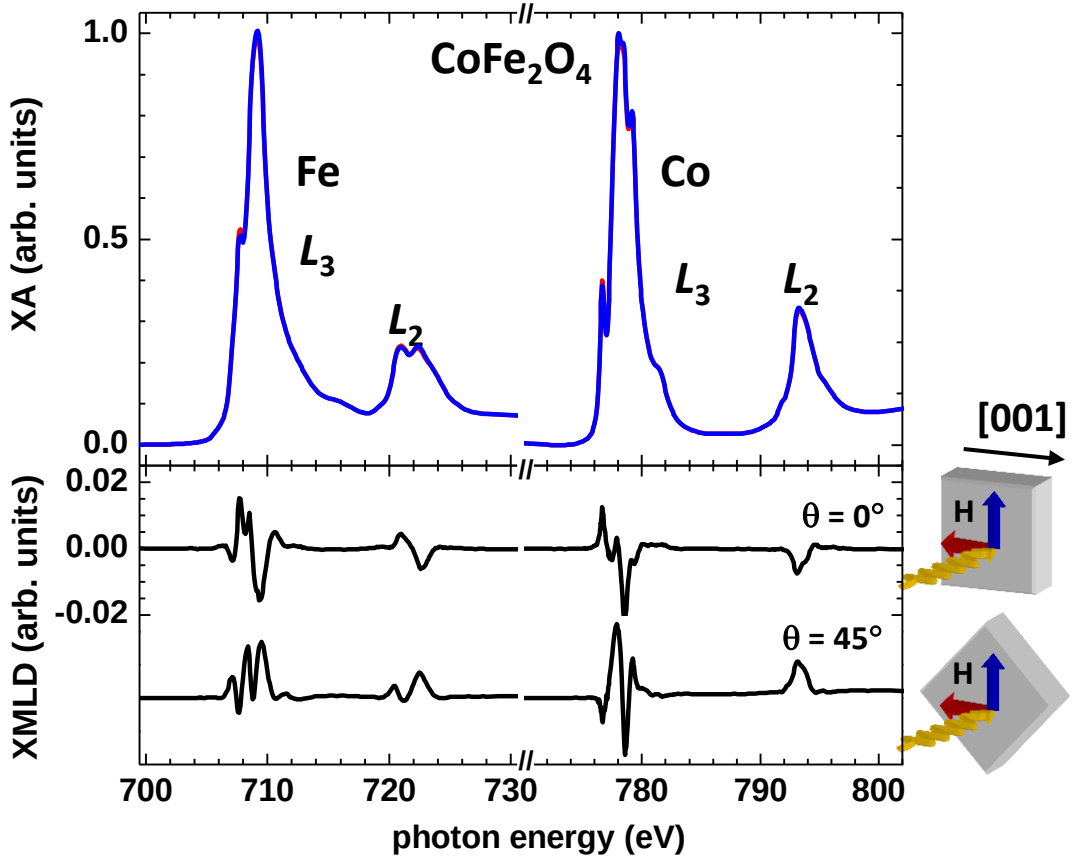
X-Ray Magnetic Linear Dichroism



Isotropic *d* electron charge density
⇒ No polarization dependence

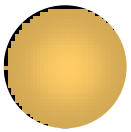


Magnetically aligned system
⇒ Spin-orbit coupling distorts charge density
⇒ Polarization dependence

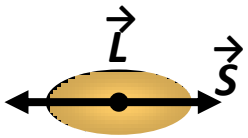


+ $I_{XMLD} = I_{||} - I_{\perp} \propto \langle m^2 \rangle$, $\langle m^2 \rangle$ = expectation value of square of atomic magnetic moment
+ XMLD allows investigating ferri- and ferromagnets as well as antiferromagnets
+ XMLD spectral shape and angular dependence are determined by magnetic order <u>and</u> lattice symmetry

X-Ray Magnetic Linear Dichroism



Isotropic *d* electron charge density
⇒ No polarization dependence



Magnetically aligned system
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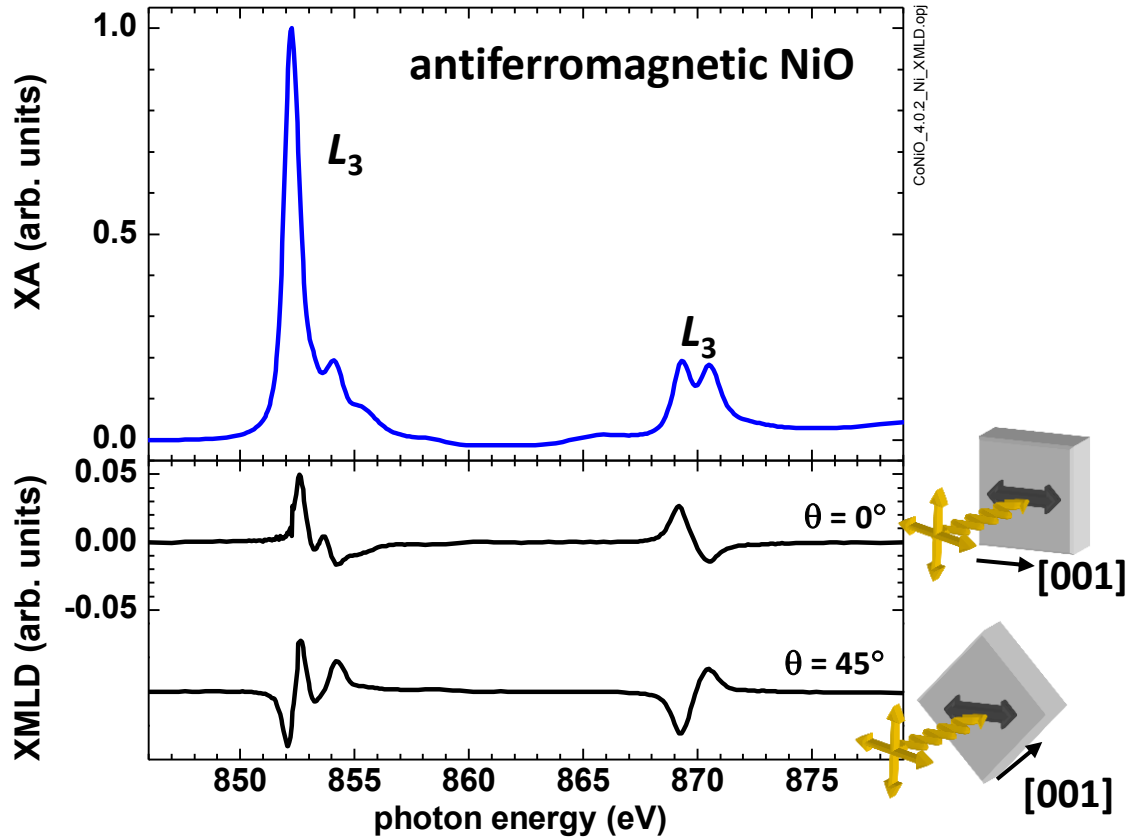
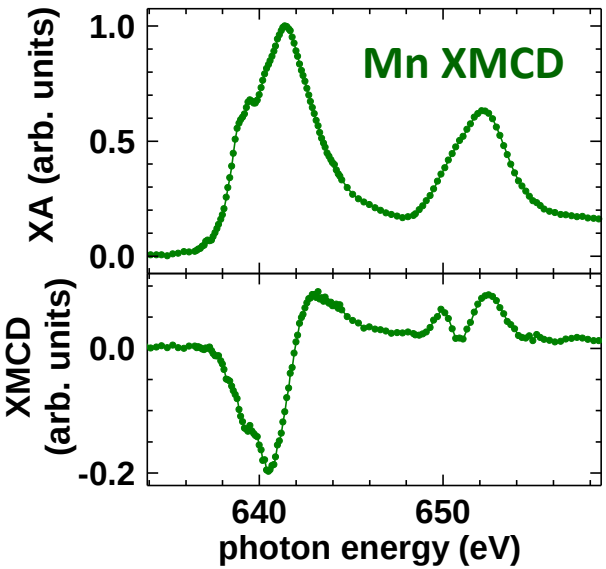
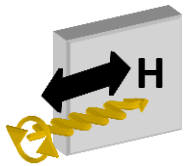


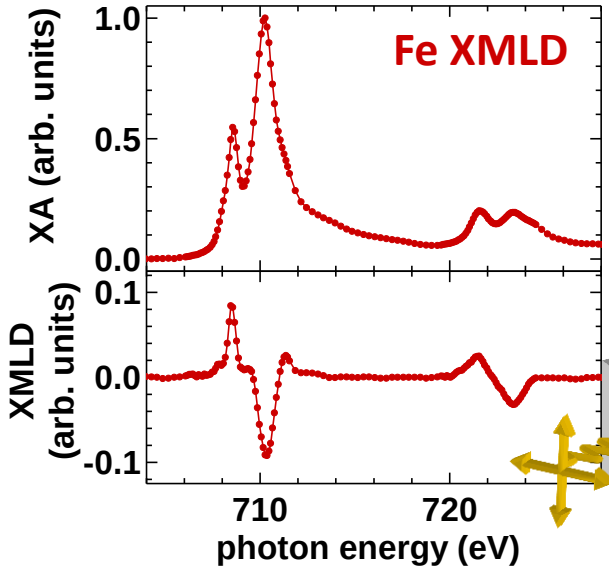
+ $I_{XMLD} = I_{||} - I_{\perp} \propto \langle m^2 \rangle$, $\langle m^2 \rangle$ = expectation value of square of atomic magnetic moment
+ XMLD allows investigating ferri- and ferromagnets as well as antiferromagnets
+ XMLD spectral shape and angular dependence are determined by magnetic order <u>and</u> lattice symmetry

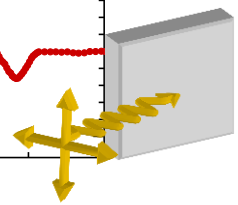
Magnetic Coupling At Interfaces

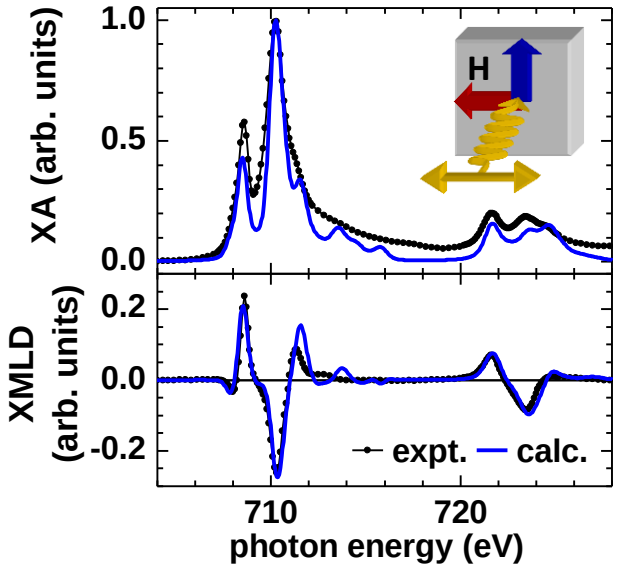


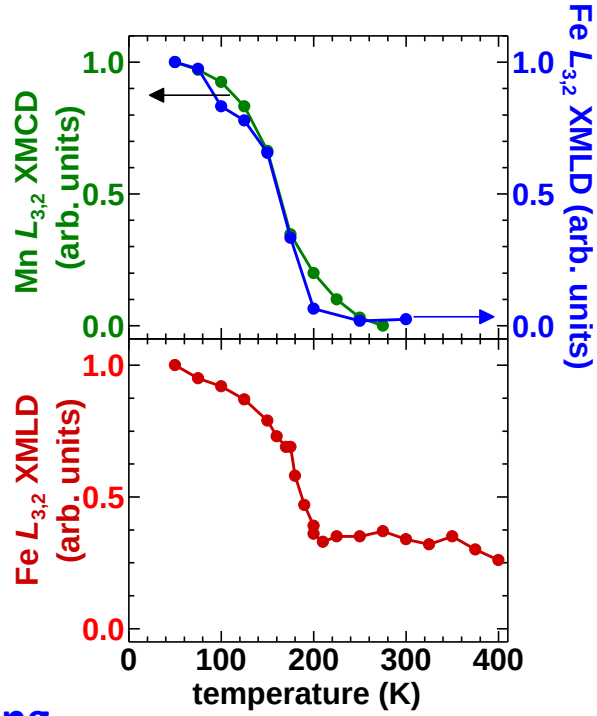


$La_{0.7}Sr_{0.3}MnO_3$ (LSMO)
ferromagnet
$La_{0.7}Sr_{0.3}FeO_3$ (LSFO)
antiferromagnet





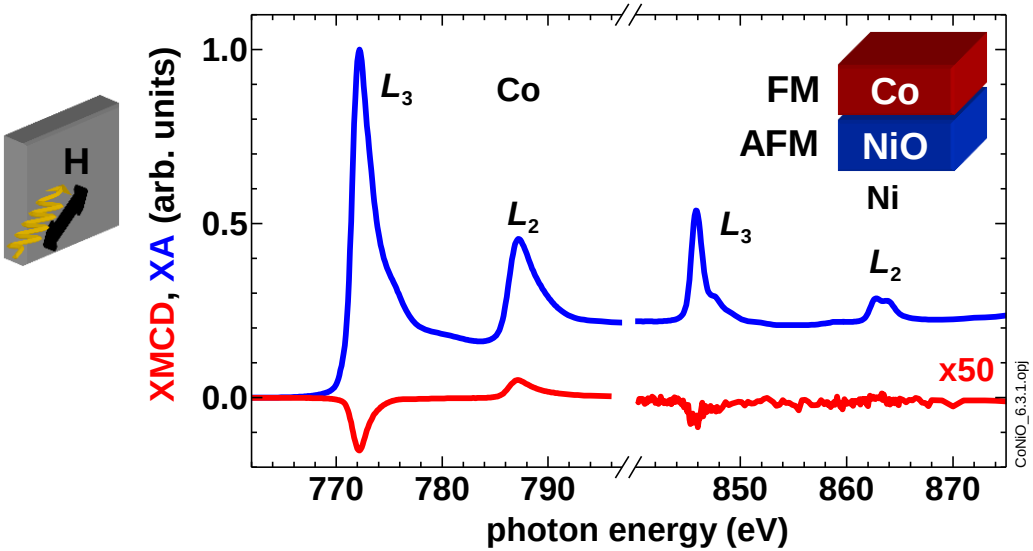


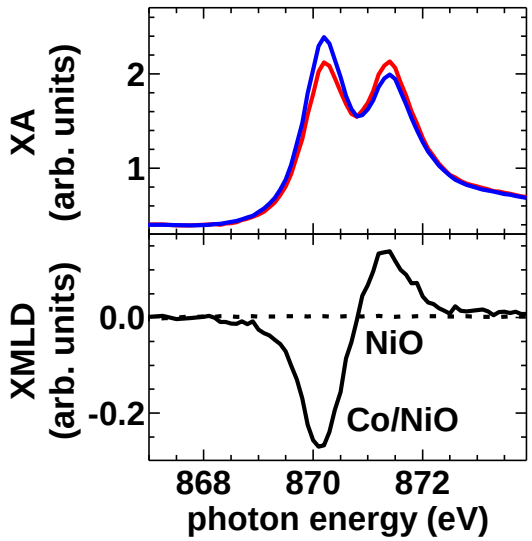


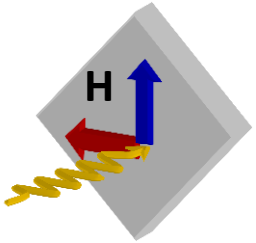
⇒ **Perpendicular coupling at LSMO/LSFO interface**

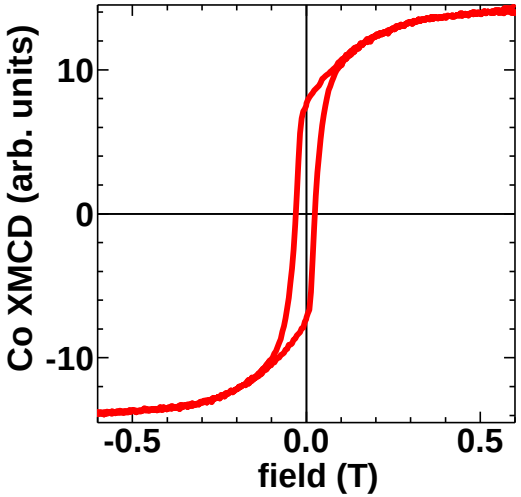
E. Arenholz *et al.*,
Appl. Phys. Lett. 94, 072503 (2009)

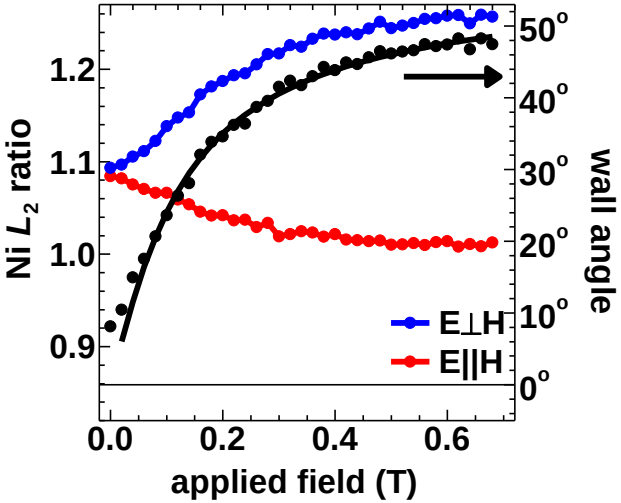
PLANAR DOMAIN WALL

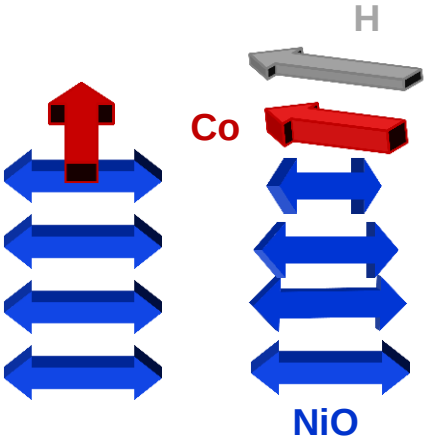






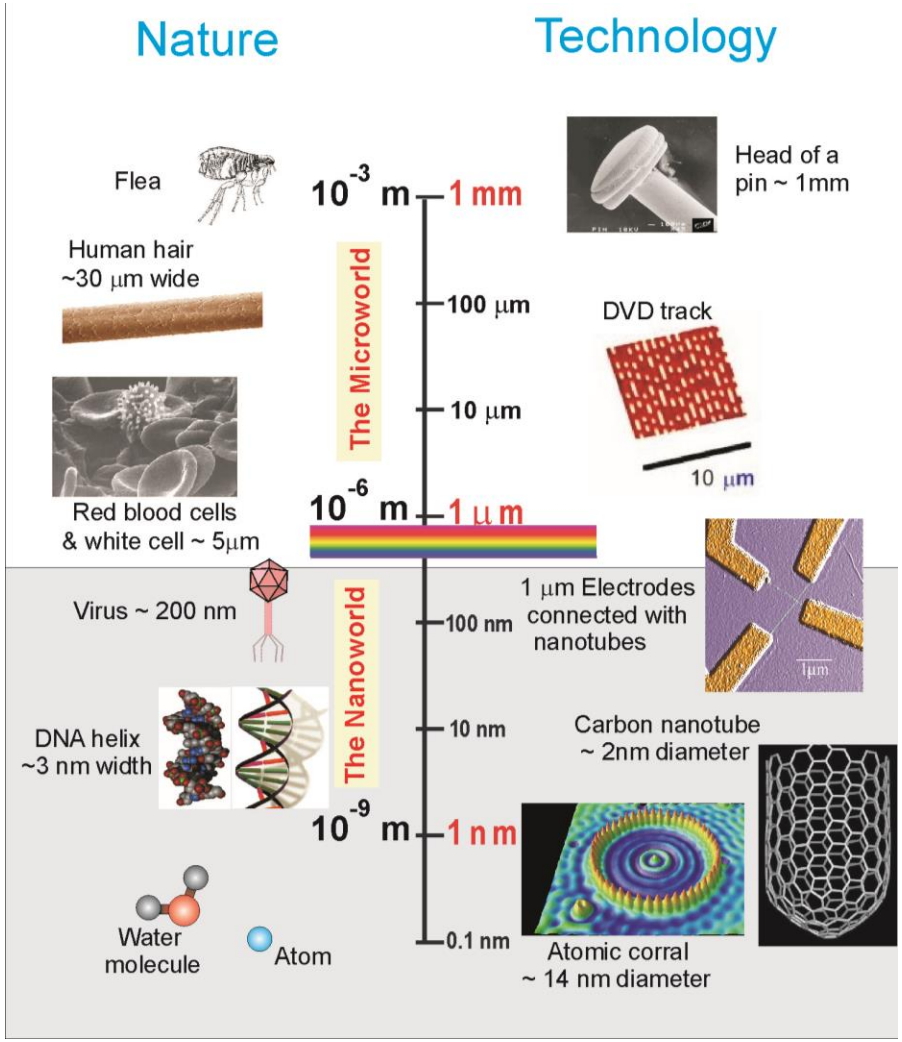


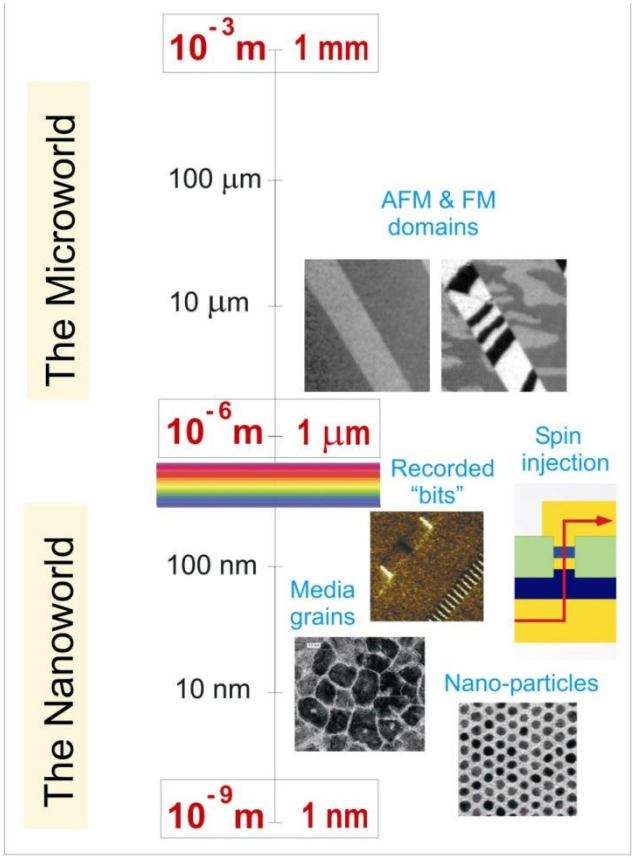




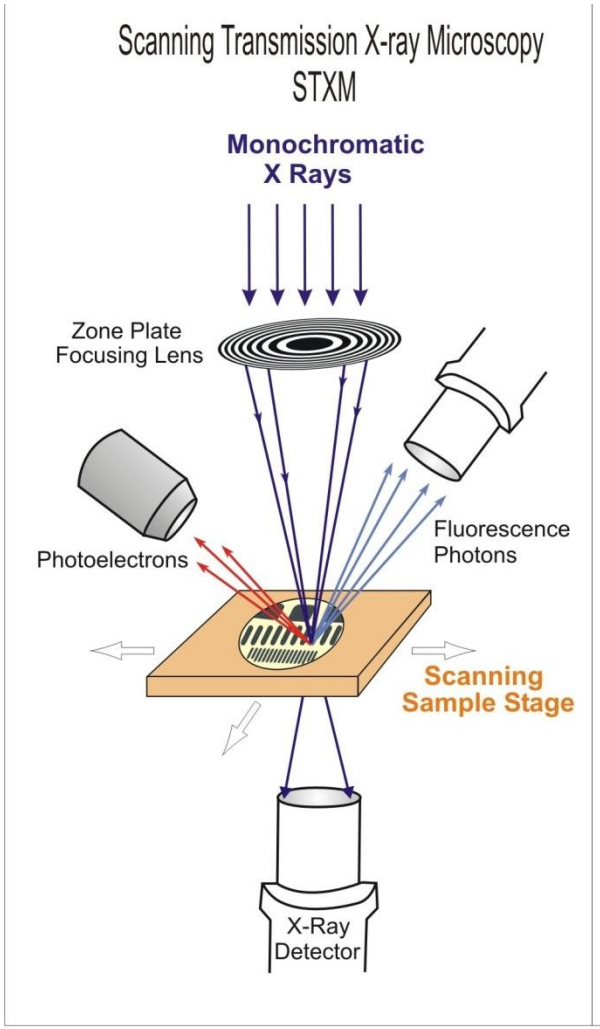
A. Scholl *et al.*,
Phys. Rev. Lett. 92, 247201 (2004)

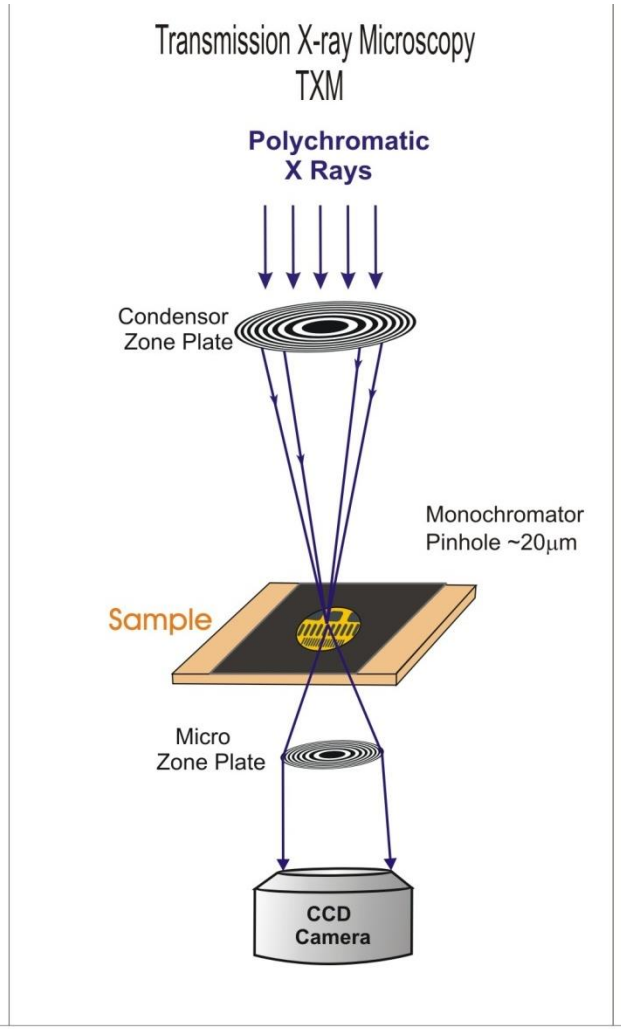
MAGNETIC MICROSCOPY

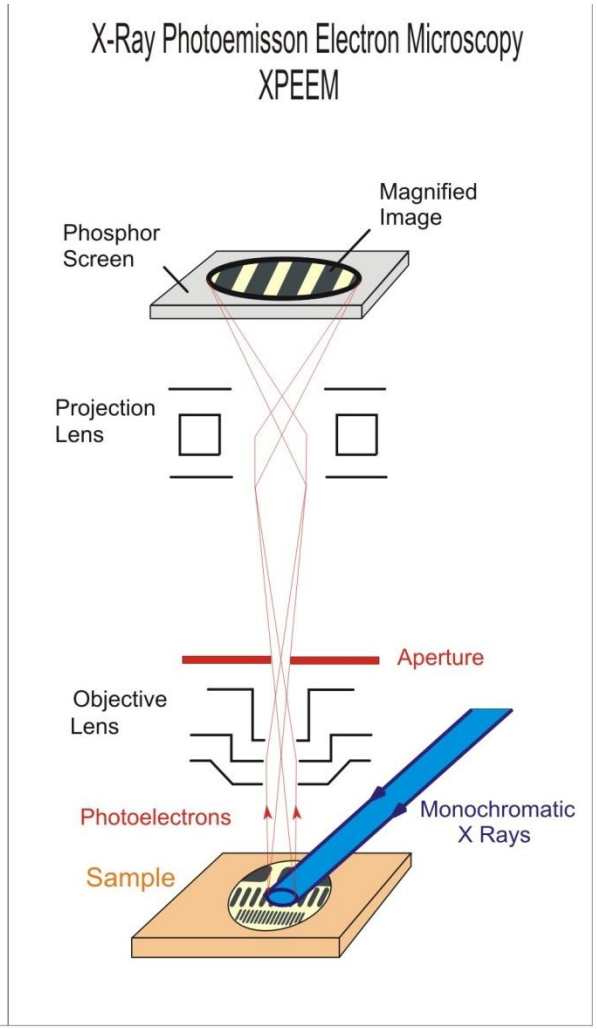




MAGNETIC MICROSCOPY



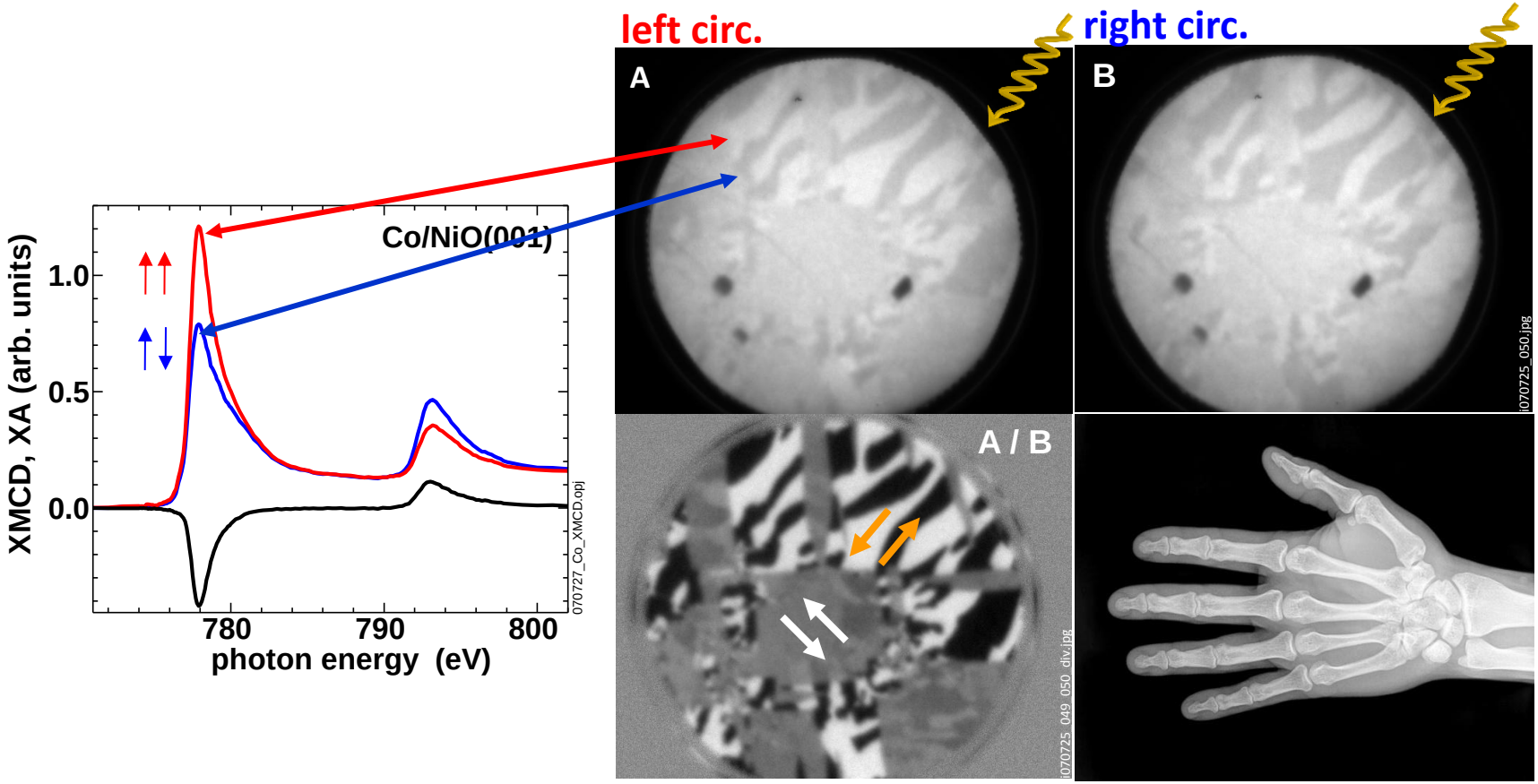




J. Stöhr, H.C. Siegmann,
Magnetism (Springer)

10-50 nm spatial resolution

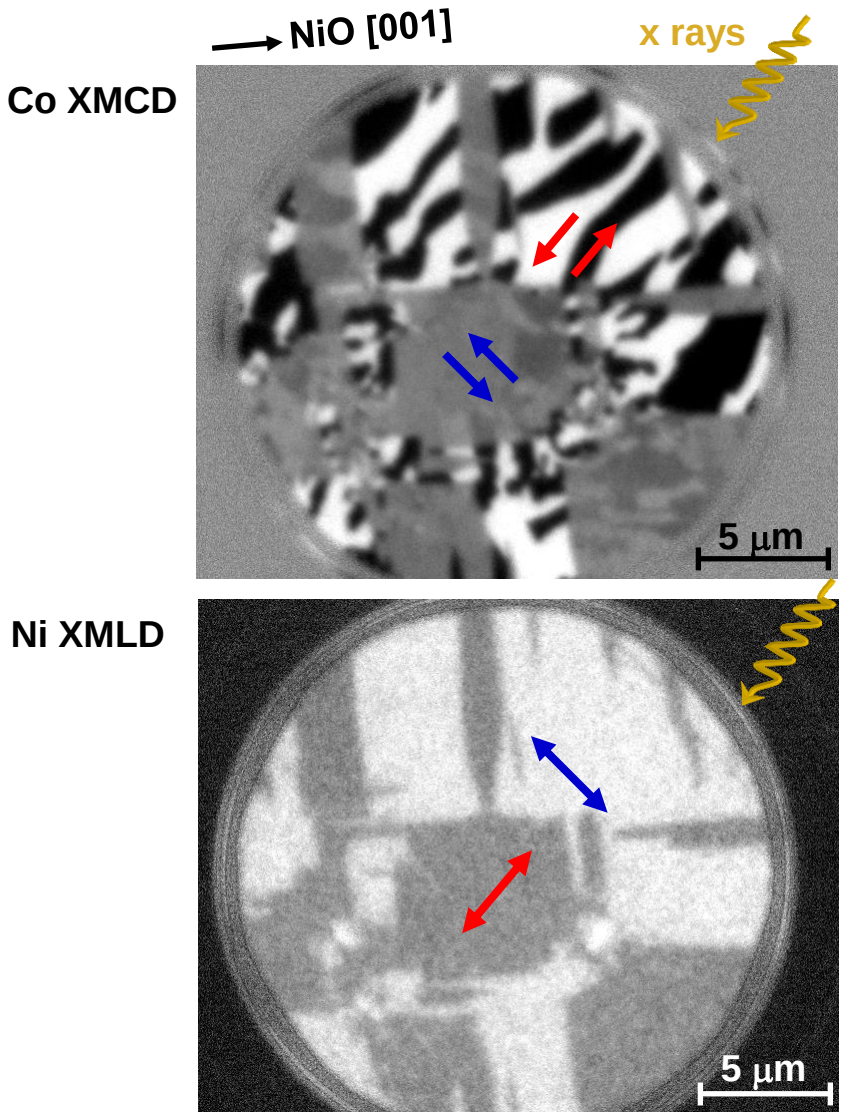
Imaging Magnetic Domains Using X-Rays



E. Arenholz *et al.*,
Appl. Phys. Lett. 93, 162506 (2008)

+ **Images taken with left and right circularly polarized x-rays at photon energies with XMCD, i.e. Co L_3 edge, provide magnetic contrast and domain images.**

Magnetic Coupling At Co/NiO Interface



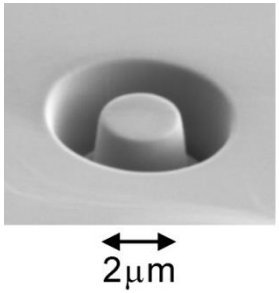
+ Taking into account the geometry dependence of the Ni XMLD signal

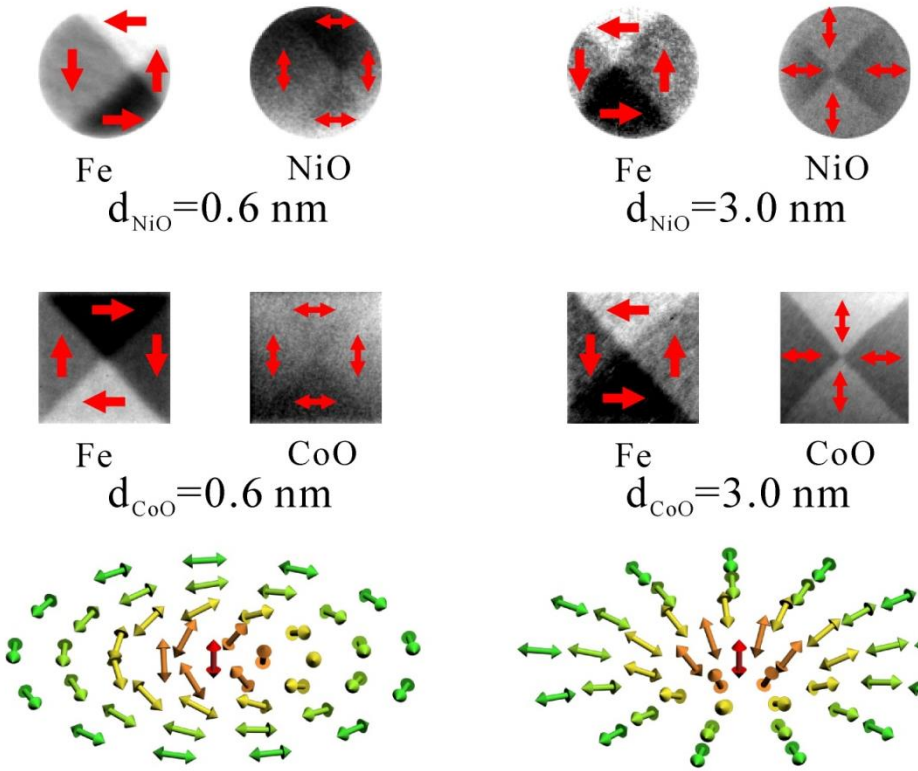
⇒ Perpendicular coupling of Co and NiO moments at the interface.

E. Arenholz *et al.*,
Appl. Phys. Lett. 93, 162506 (2008)

MAGNETIC VORTICES

+ First direct observation of vortex state in antiferromagnetic CoO and NiO disks in Fe/CoO and Fe/NiO bilayers using XMCD and XMLD.
+ Two types of AFM vortices:
  - conventional curling vortex as in ferromagnets
  - divergent vortex, forbidden in ferromagnets
  - thickness dependence of magnetic interface coupling



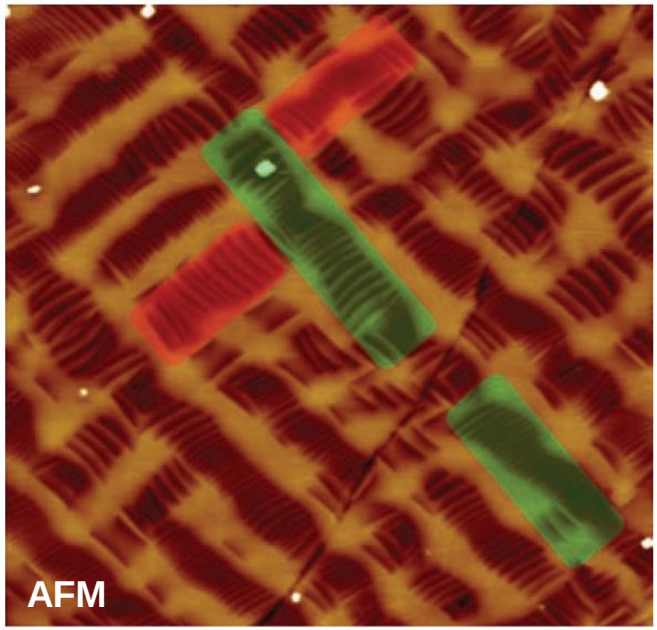


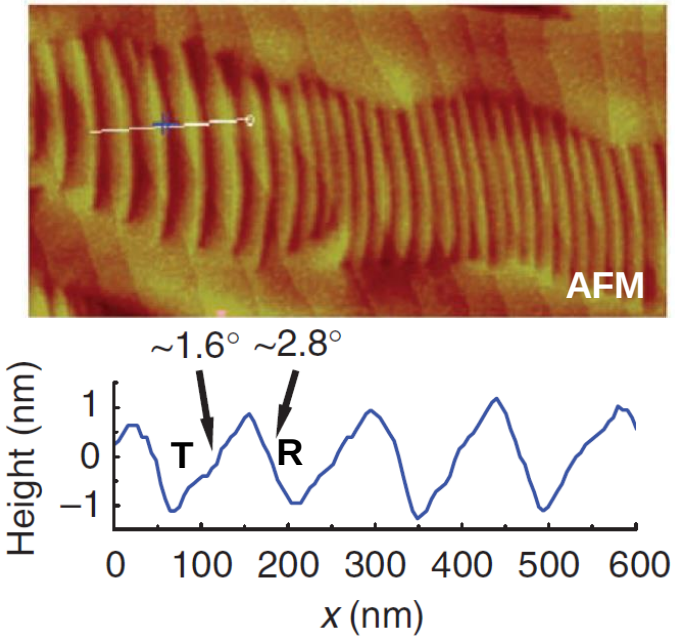
conventional curling vortex

divergent vortex

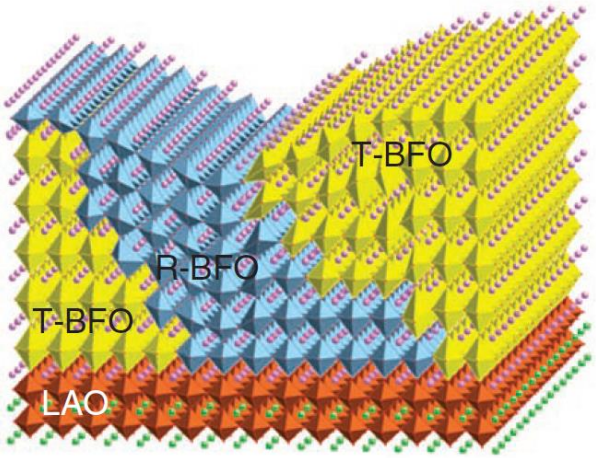
J. Wu *et al.*, Nature Phys. 7, 303 (2011)

Nanoscale Magnetic Phases



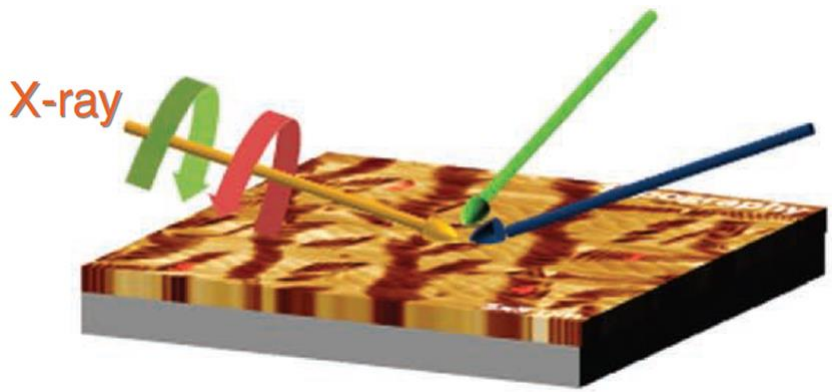


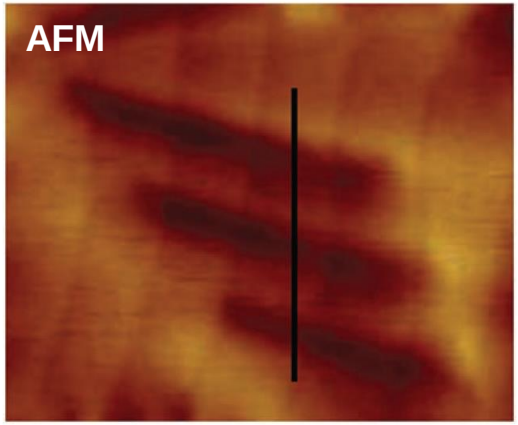
+ $BiFeO_3$ – multiferroic = ferroelectric + antiferromagnetic
+ Compressive strain on rhombohedral phase (R-phase) induced by substrate
⇒ tetragonal-like phase (T-phase)
+ Partial relaxation of epitaxial strain
⇒ Formation of a nanoscale mixture of T- and R-phases

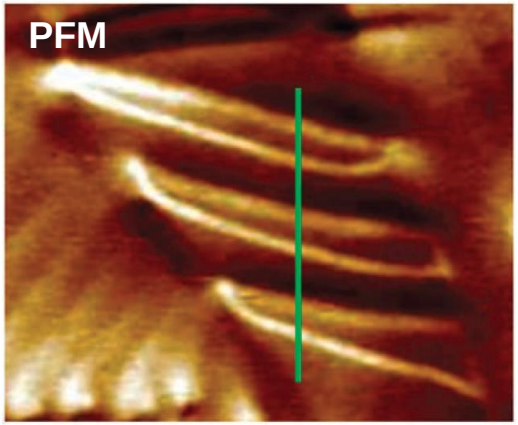


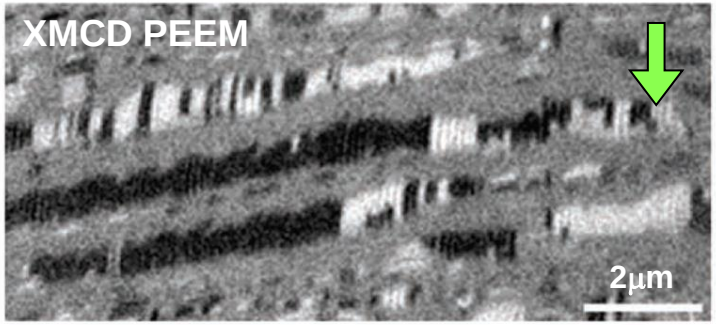
Q. He *et al.*, Nature Comm. 2, 225 (2011)

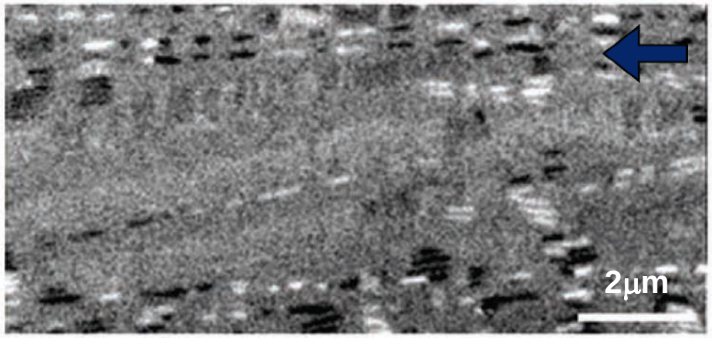
Nanoscale Magnetic Phases



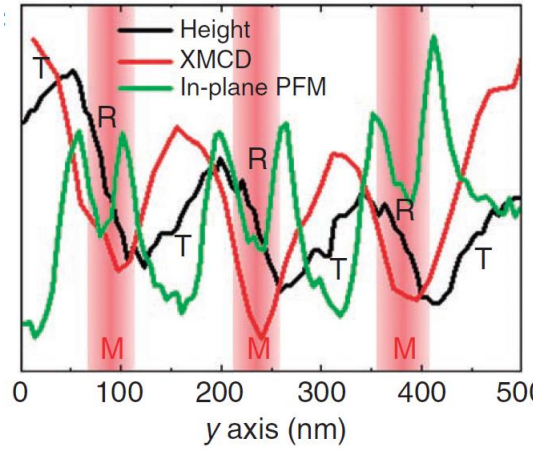


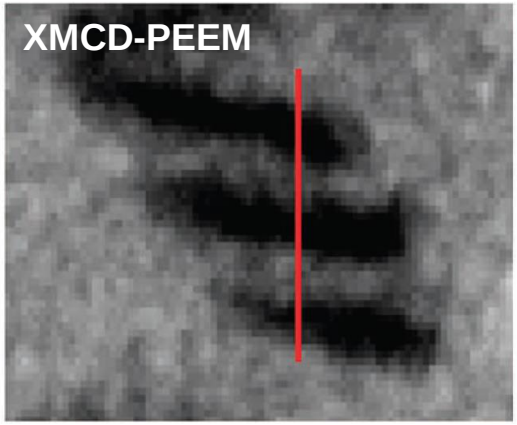






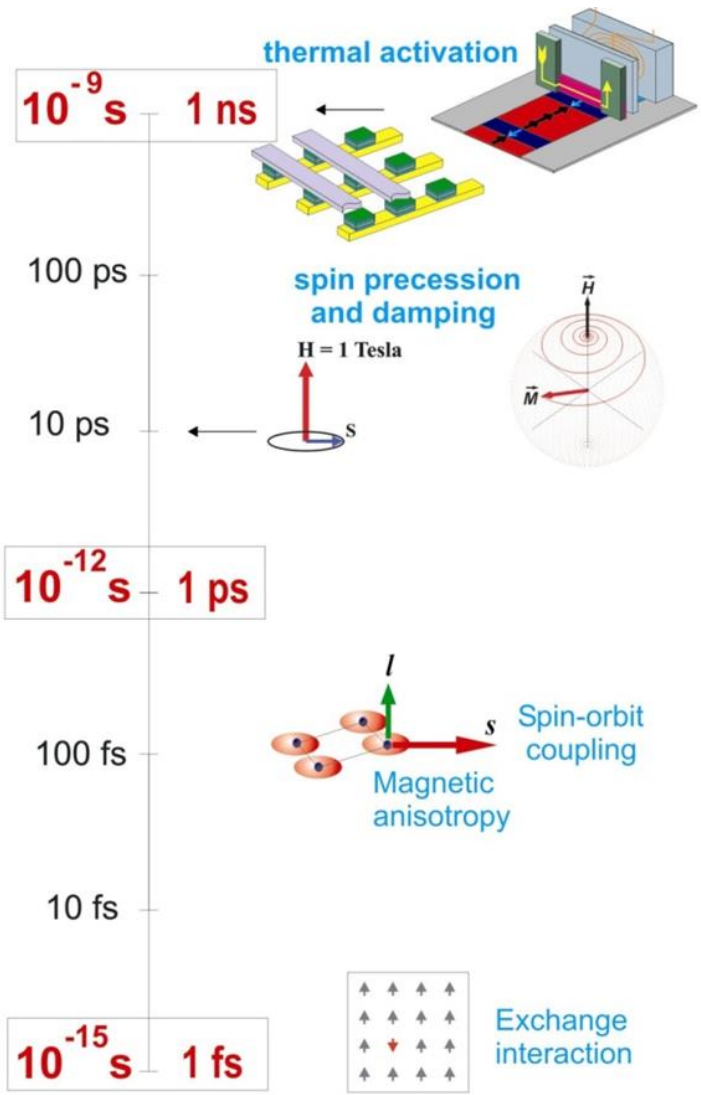
Q. He *et al.*,
Nature Comm. 2, 225 (2011)





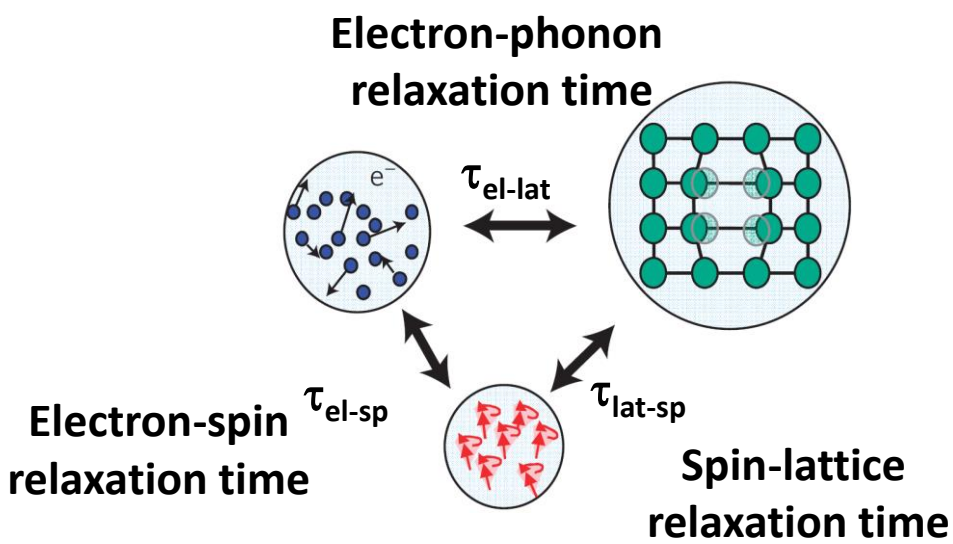
+ **Highly distorted R-phase is the source of enhanced magnetic moment in the XMCD image.**

Ultrafast Magnetism

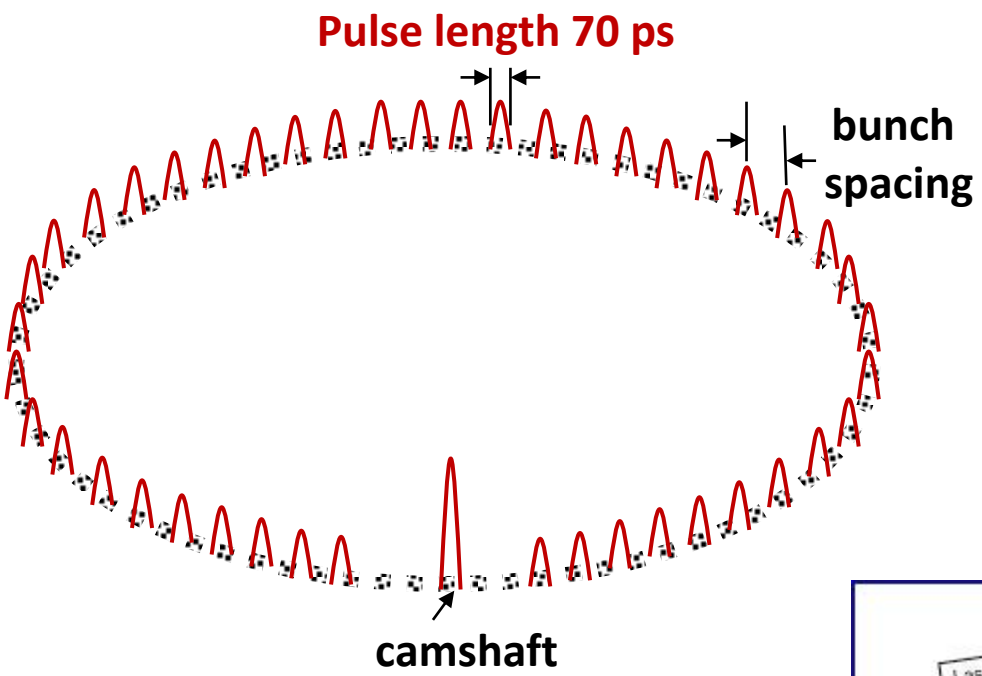


J. Stöhr, H.C. Siegmann, Magnetism (Springer)

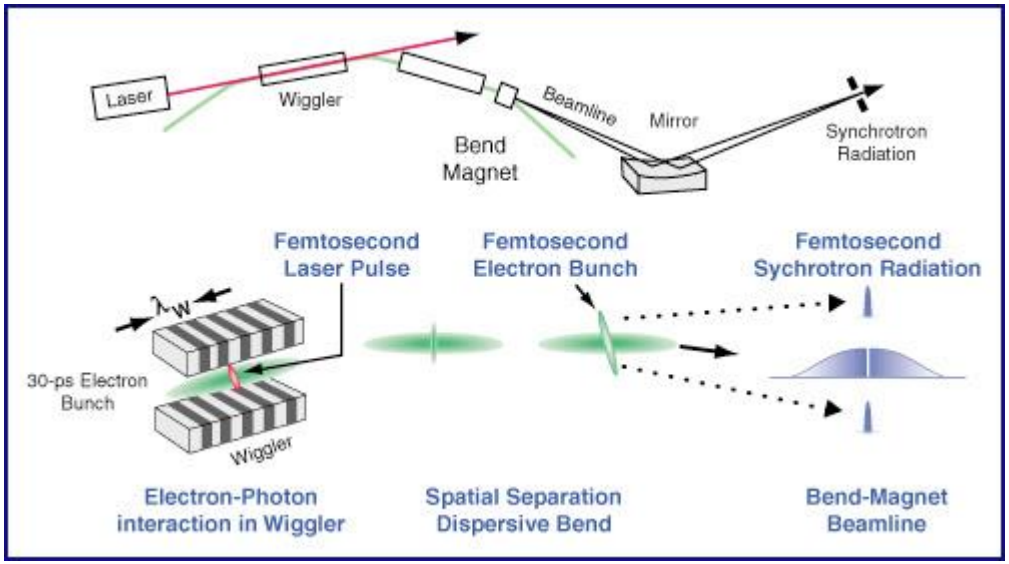
+ Energy reservoirs in a ferromagnetic metal
+ Deposition of energy in one reservoir
⇒ Non-equilibrium distribution and subsequent relation through energy and angular momentum exchange



ALS Time Structure

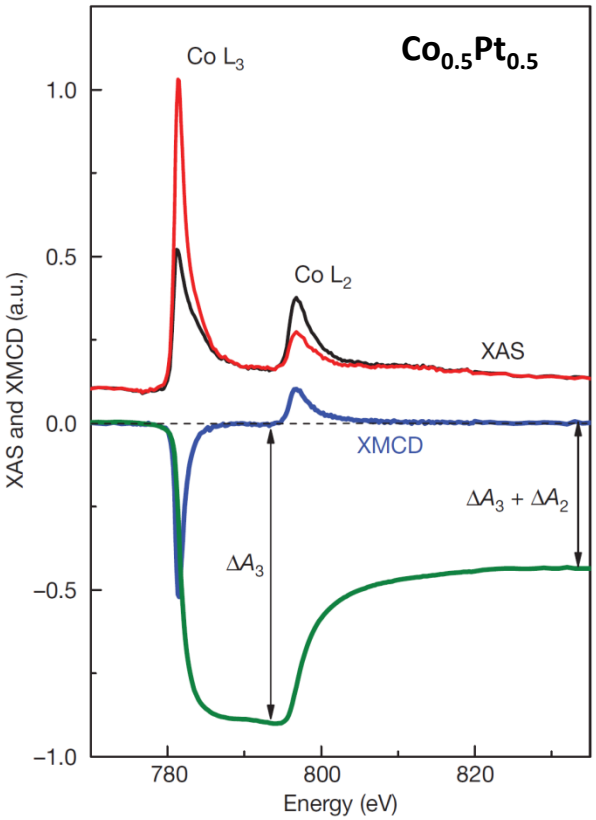


+ 256-320 bunches for 500mA beam current
+ Possibility of one or two 5mA "camshaft" bunches in filling gaps
+ Bunch spacing:
  multibunch mode: 2 ns
  two-bunch mode: 328 ns
+ Pulse length 70ps



+ <300 fs x ray pulses though "laser bunch-slicing technique"

Ultrafast Dynamics Of Spin And Orbital Moments

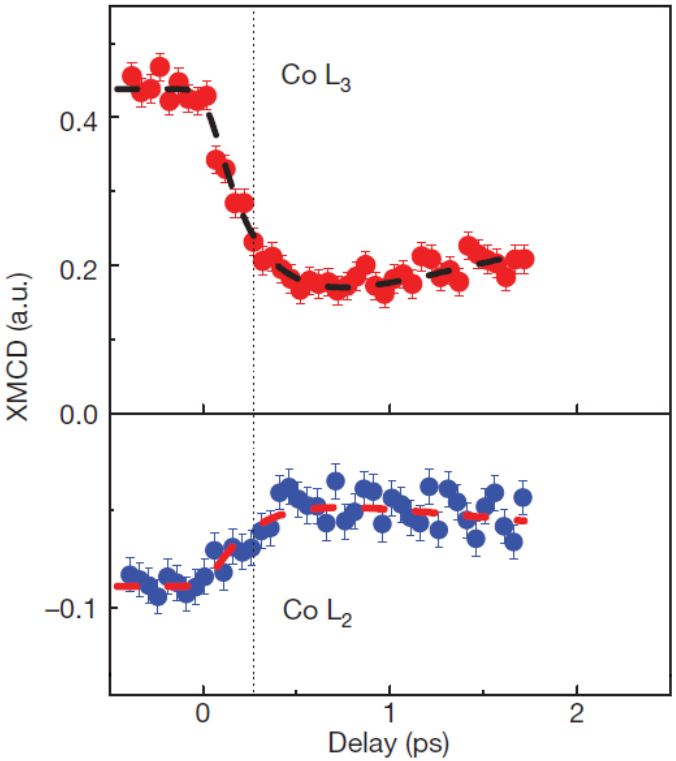


C. Boeglin, *et al.*, Nature 465, 458 (2010)

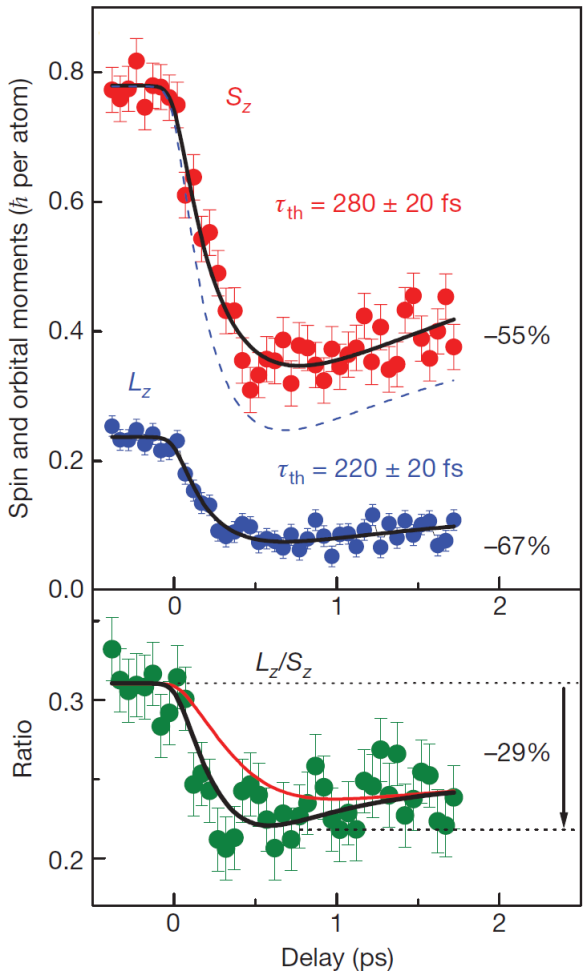
- Orbital (*L*) and spin (*S*) magnetic moments can change with total angular momentum is conserved.
- Efficient transfer between *L* and S through spin–orbit interaction in solids
- Transfer between *L* and *S* occurs on fs timescales.

- $Co_{0.5}Pt_{0.5}$ with perpendicu magnetic anisotropy
- 60 fs optical laser pulses change magnetization
- Dynamics probed with XMCD using 120fs x-ray pulses

- Linear relation connects Co L_3 and L_2 XMCD with L_z and S_z using sum rules

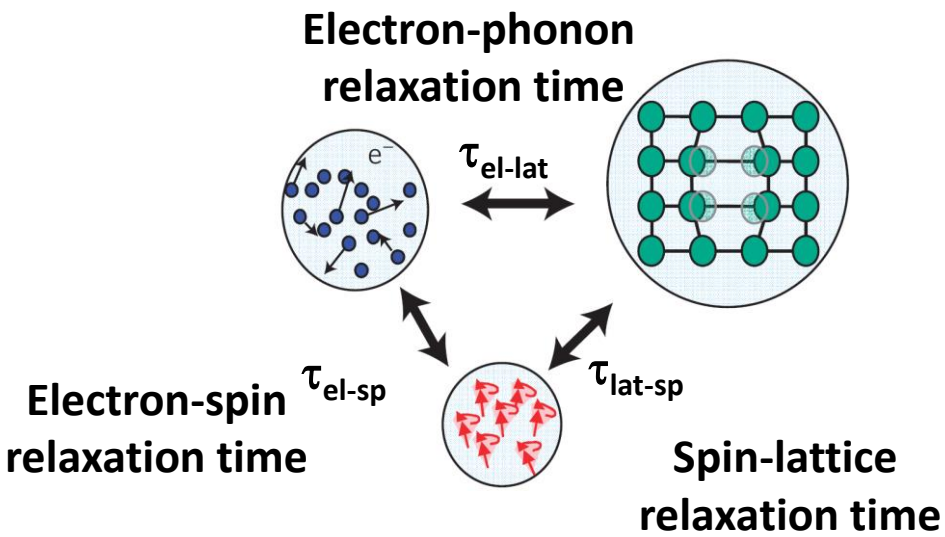


Ultrafast Dynamics Of Spin And Orbital Moments

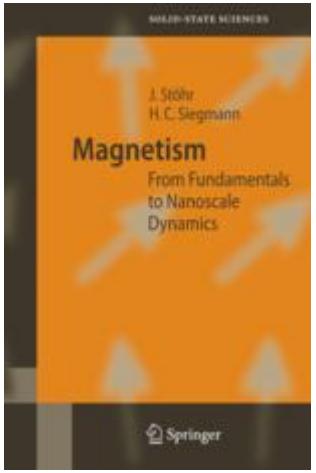


C. Boeglin, *et al.*, Nature 465, 458 (2010)

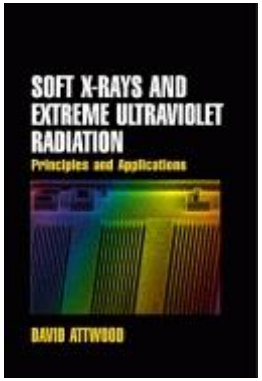
- **Thermalization: Faster decrease of orbital moment**
- **Theory: Orbital magnetic moment strongly correlated with magnetocrystalline anisotropy**
- **Reduction in orbital moment ⇔ Reduction in magnetocrystalline anisotropy**
- **Typically observed at elevated temperatures in static measurements as well**



References And Further Reading



J. Stöhr, H.C. Siegmann
Magnetism– From Fundamentals to Nanoscale Dynamics
Springer



D. Attwood
Soft X-Rays and Extreme Ultraviolet Radiation:
Principles and Applications

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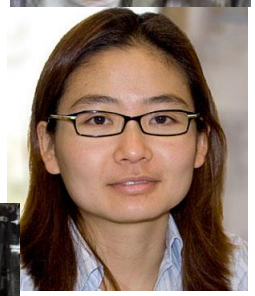

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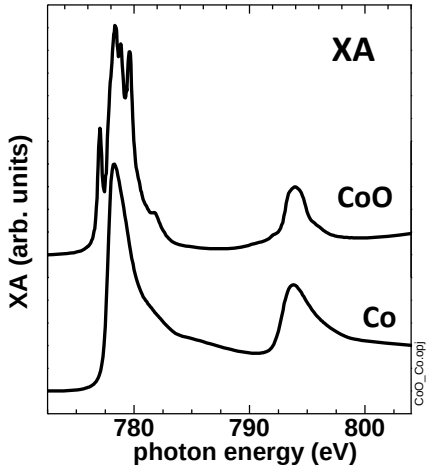
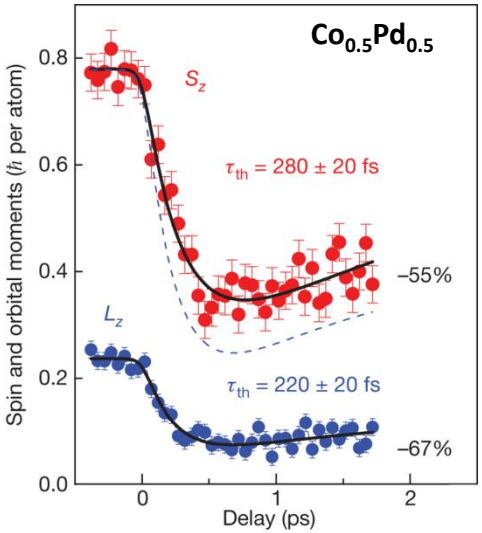
DOE-BES

... and many others !

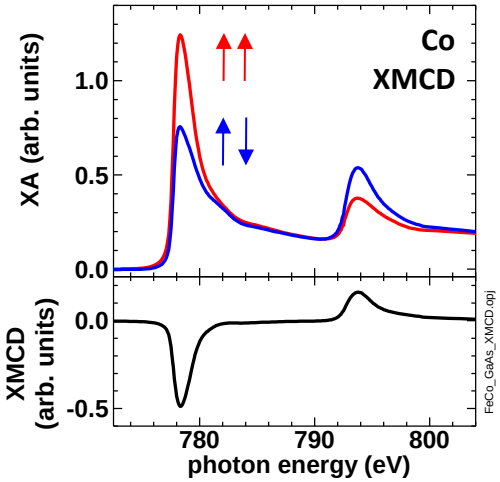
Magnetism as seen with X-Rays

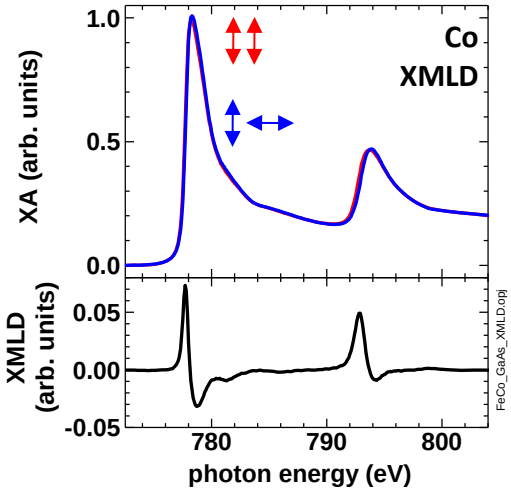


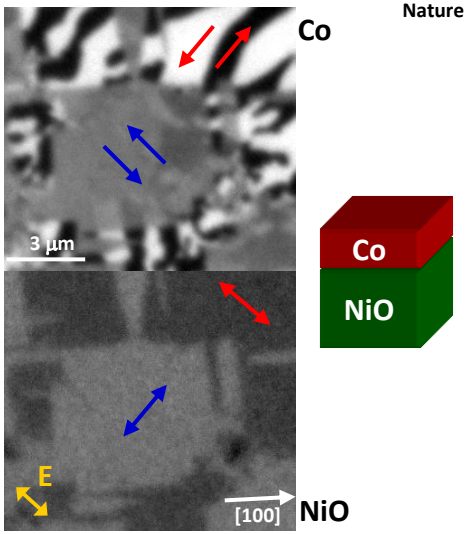
+ X-ray absorption, XA
+ X-ray magnetic circular dichoism, XMCD
+ X-ray magnetic linear dichroism, XMLD
+ X-ray magnetic microscopy
+ Magnetization Dynamics



C. Boeglin *et al.*, Nature 465, 458 (2011)







E. Arenholz *et al.*, Appl. Phys. Lett. 93, 162506 (2008)