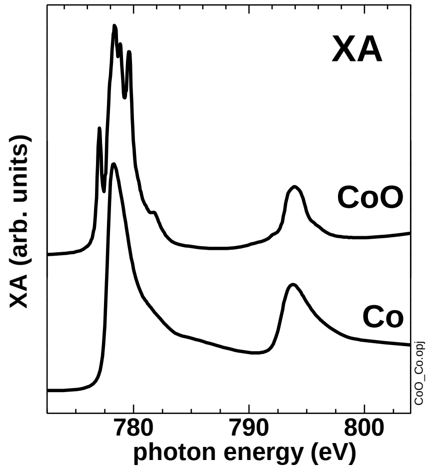
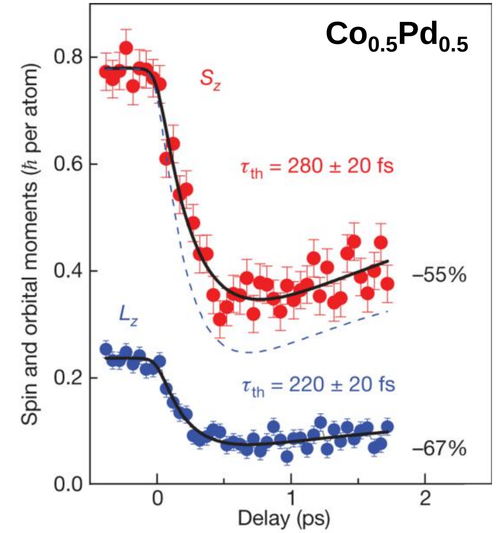
MAGNETIC SPECTROSCOPY

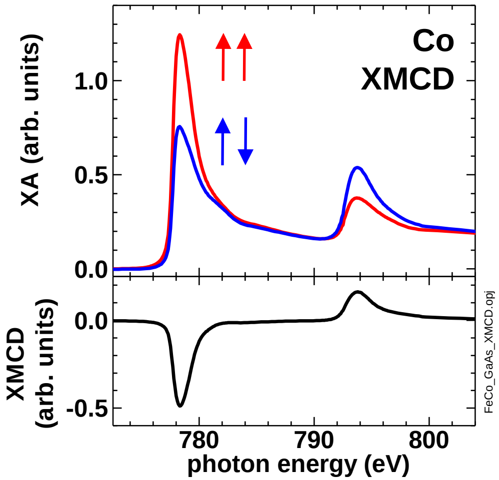
Elke Arenholz, Advanced Light Source

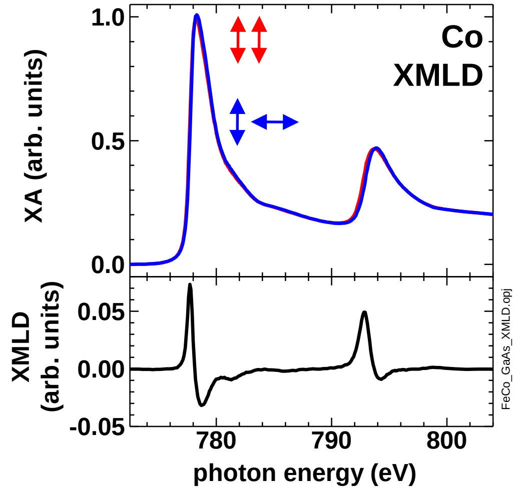


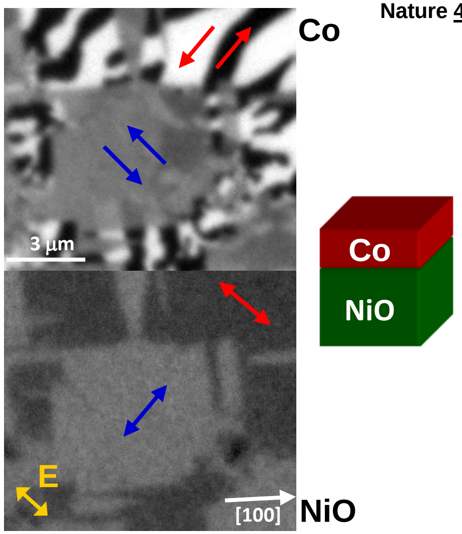
- + X-ray absorption, XA
- + X-ray magnetic circular dichoism, XMCD
- + X-ray magnetic linear dichroism, XMLD
- + X-ray magnetic microscopy
- + Magnetization Dynamics



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

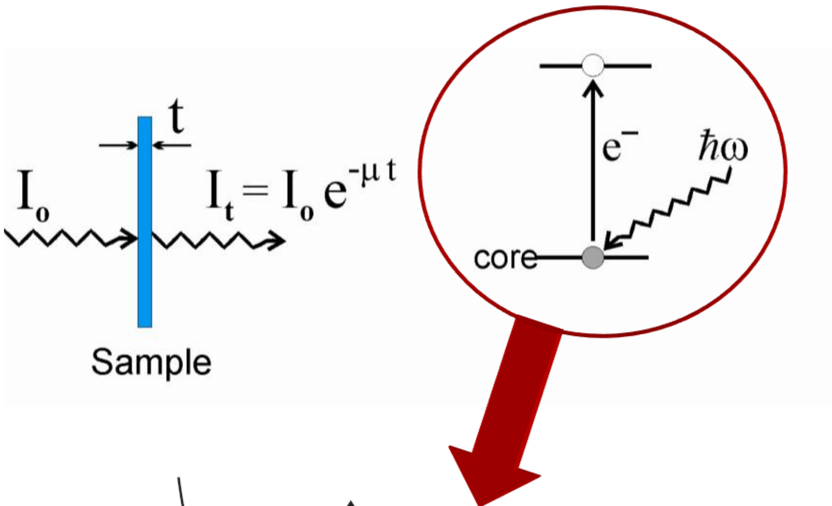






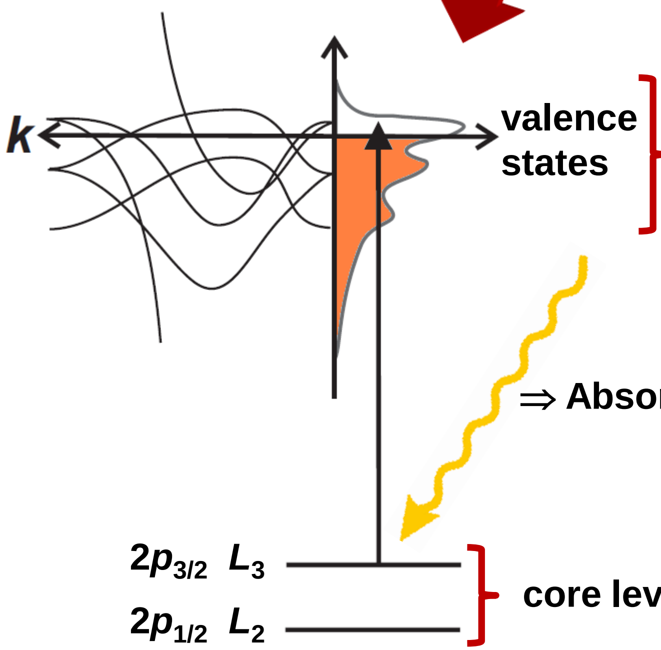
E. Arenholz *et al.*,
Appl. Phys. Lett. 93, 162506 (2008)

X-RAY ABSORPTION



Experimental Concept:

Monitor the reduction in x-ray flux transmitted through sample as function of x-ray photon energy

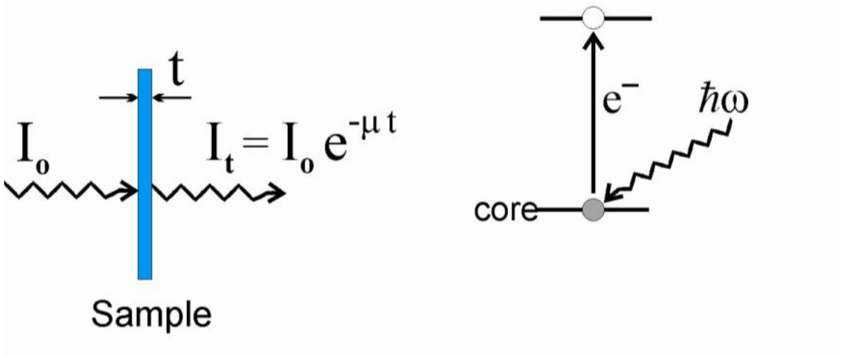


- ⇒ charge state of absorber Fe^{2+}, Fe^{3+}
- ⇒ symmetry of lattice site of absorber: O_h, T_d
- ⇒ sensitive to magnetic order

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

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

X-RAY ABSORPTION



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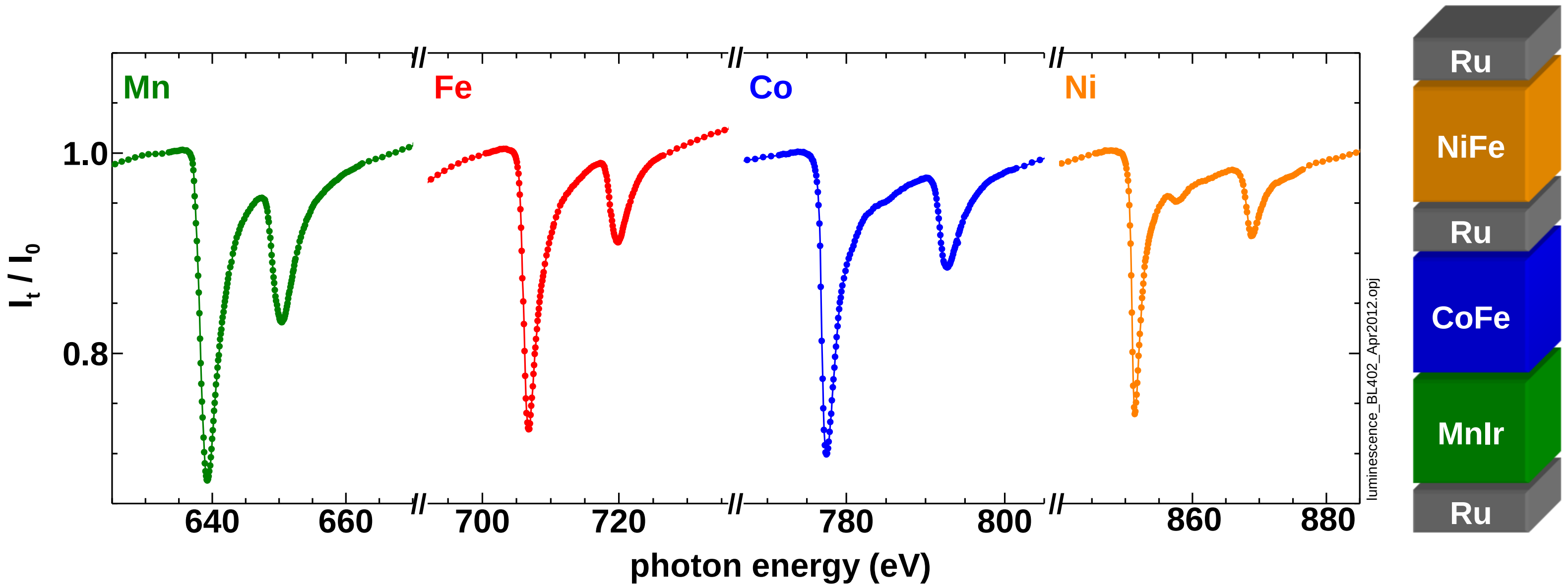
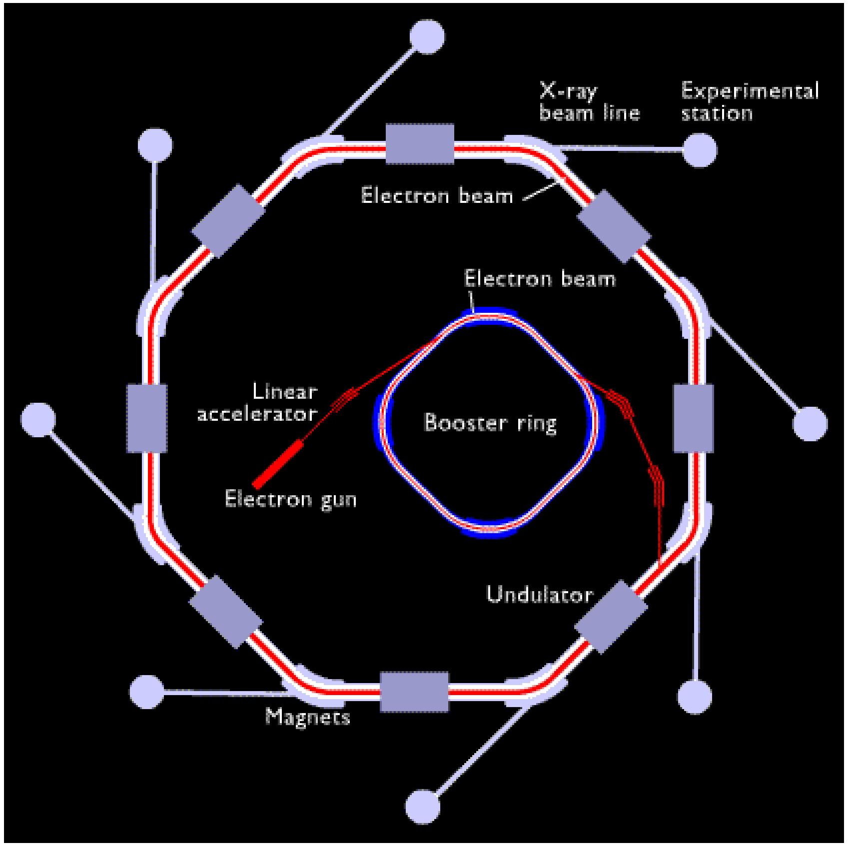


TUNABLE PHOTON SOURCE FOR SOFT X-RAYS: SYNCHROTRON

+ **Change velocity of electrons near the speed of light**

⇒ **Emission of wide wavelength range of electromagnetic spectrum (IR, UV, soft x-rays, hard x-rays)**

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



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

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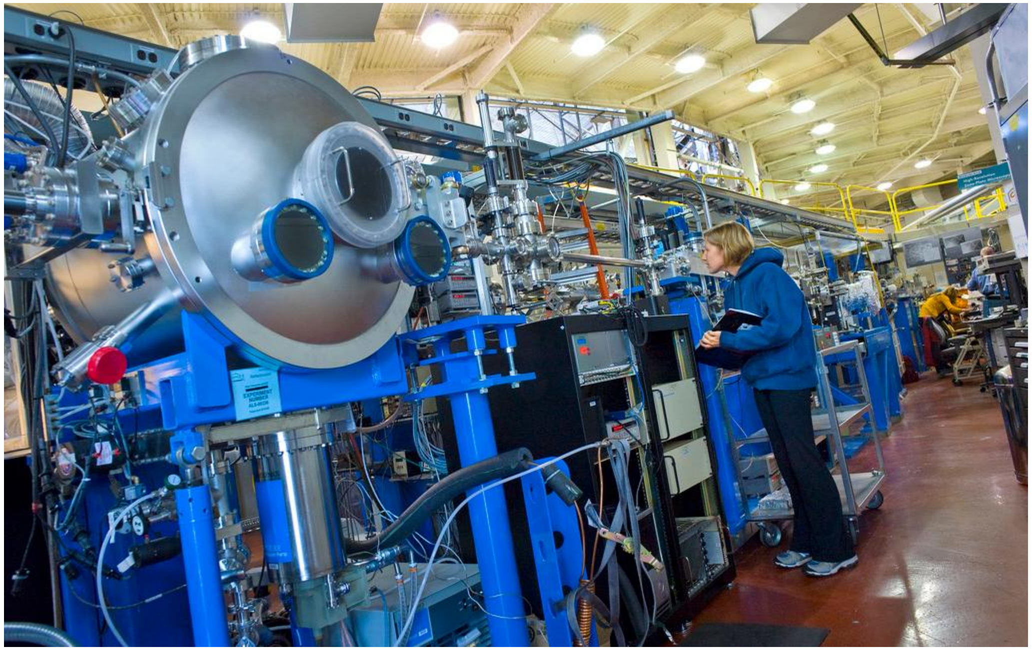
Advanced Light Source

Elliptically Polarized Undulator

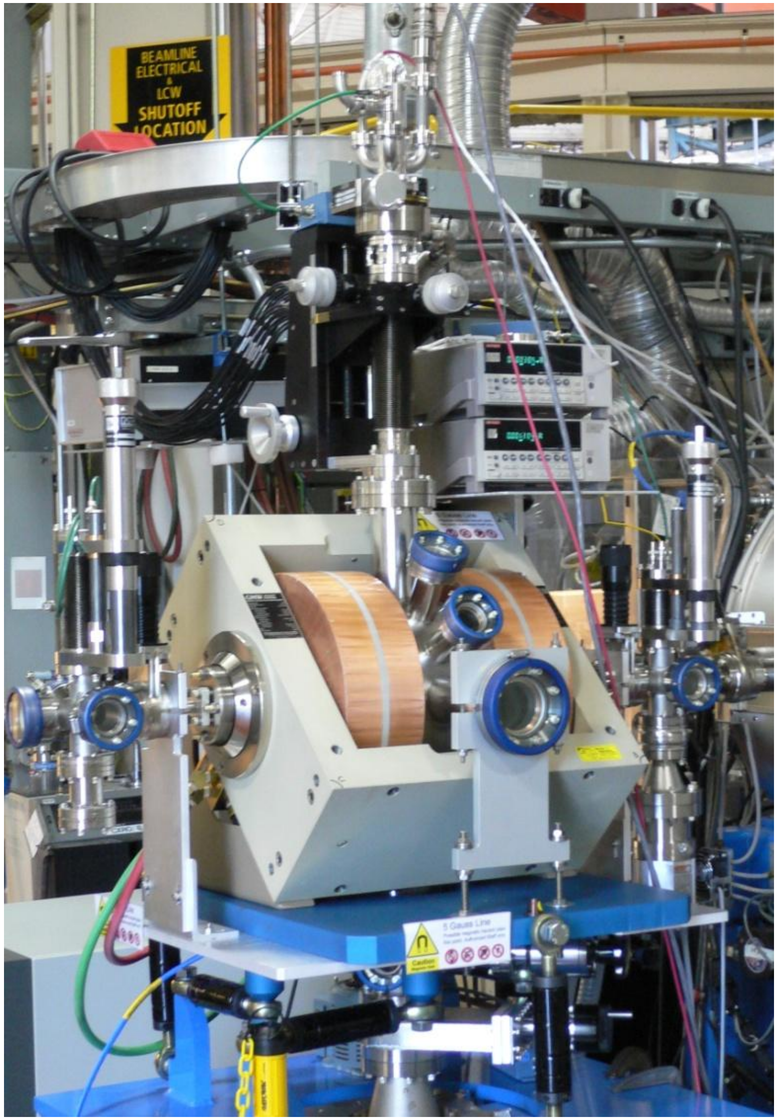
+ Beamlines/Monochromators provide photons with well defined characteristics:

- **tunable energy/wavelength**
- **band width**
- **fixed polarization: (variable) linear, circular, …**

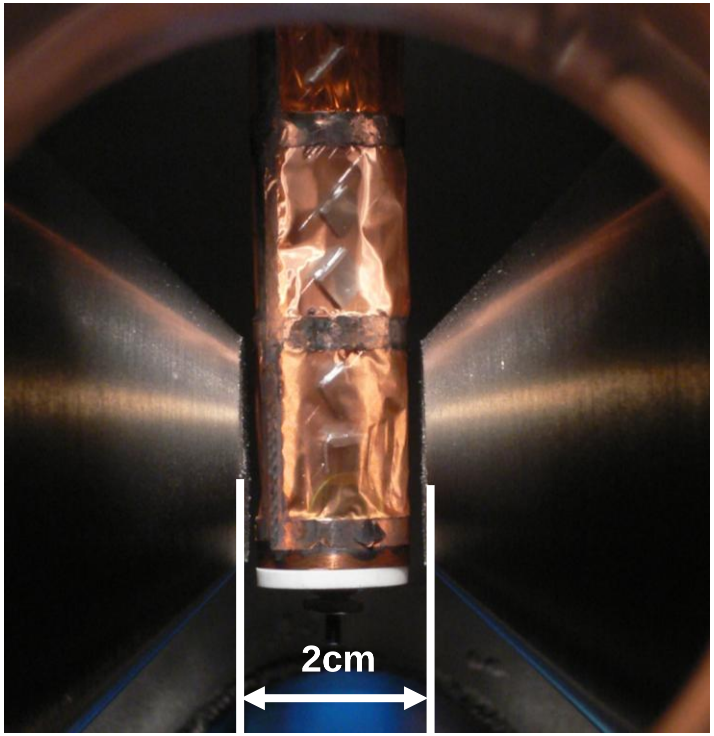
BL6.3.1



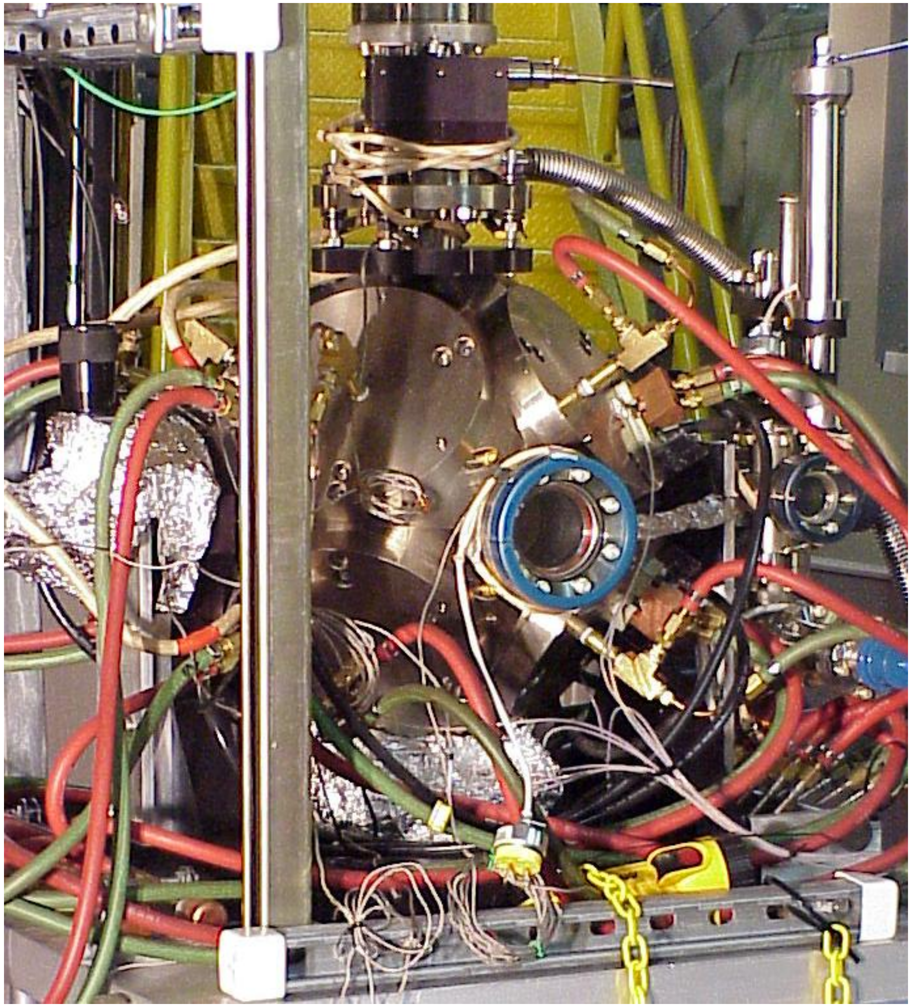
ENDSTATIONS



+ **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**

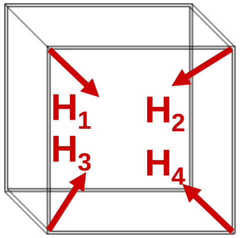


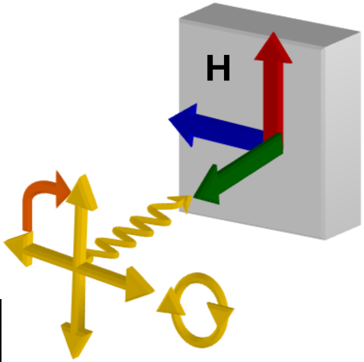
2T magnet at ALS BL6.3.1

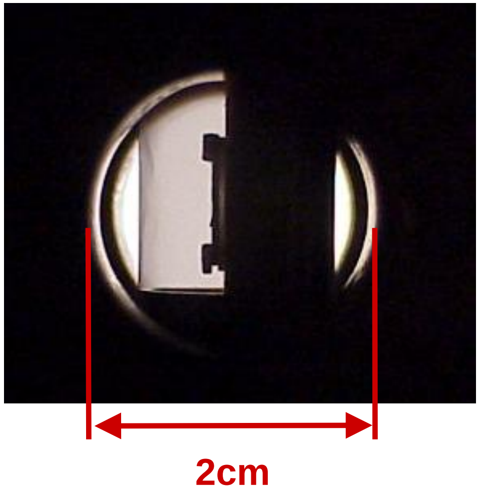


Vector magnet at ALS BL4.0.2

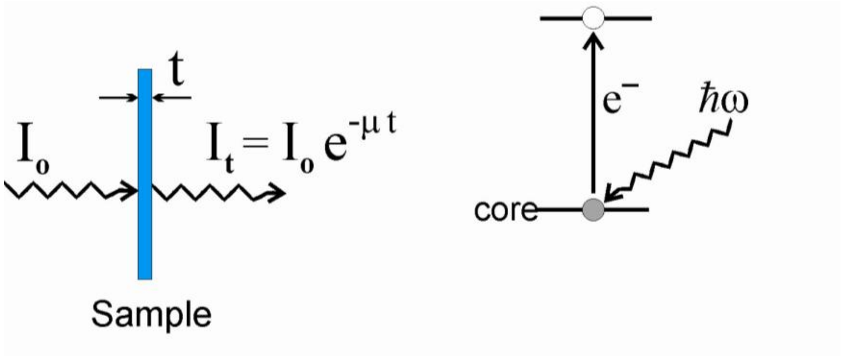
+ **Magnetic fields in arbitrary directions obtained through superposition of fields generated by 4 dipole pairs in octahedral configuration.**







X-RAY ABSORPTION



Experimental Concept:

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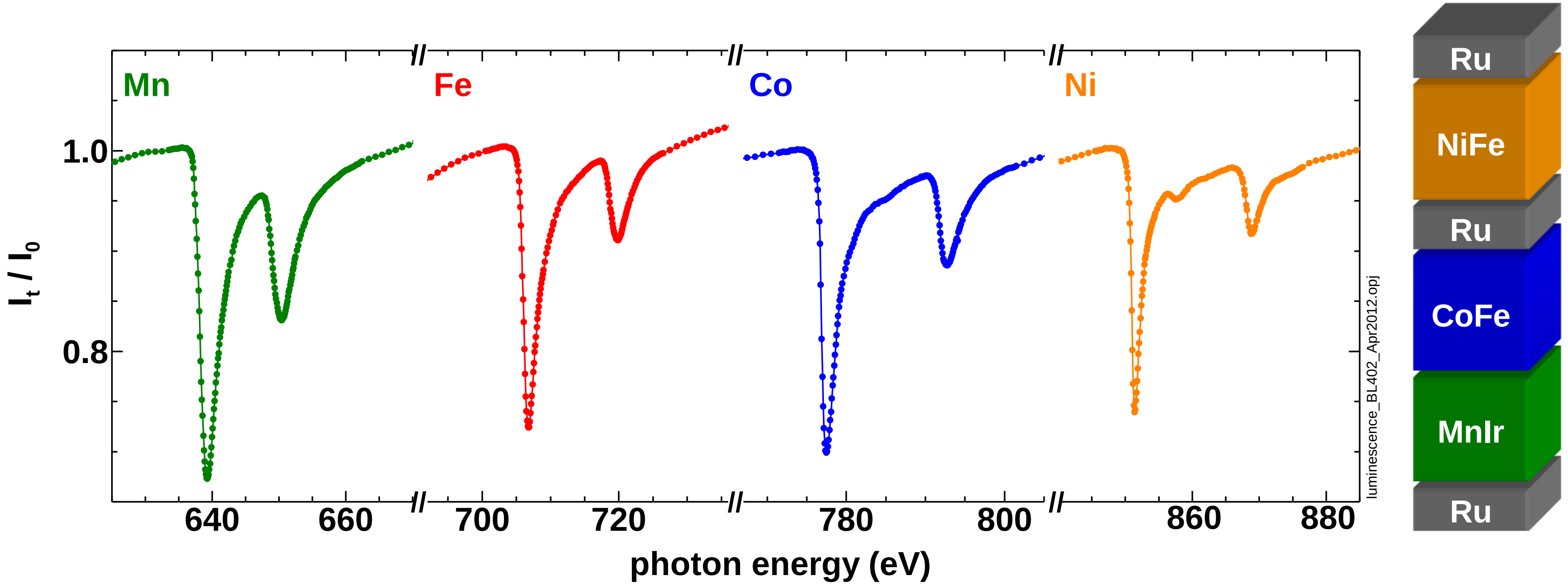
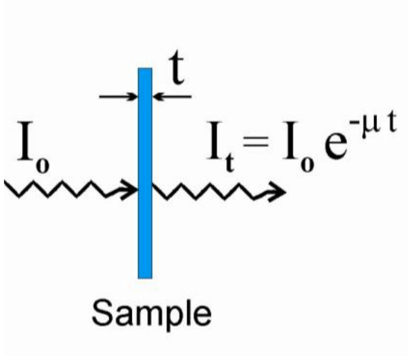
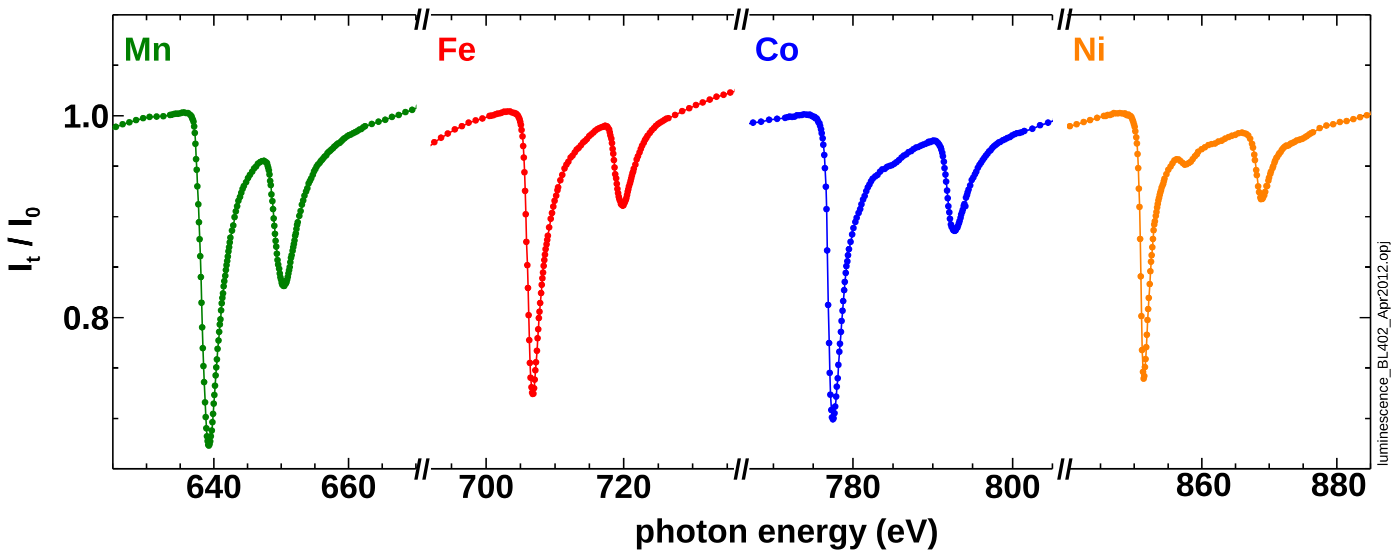
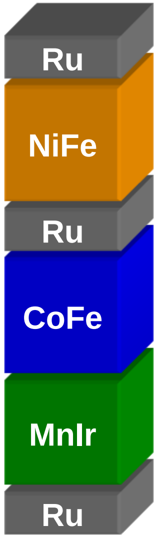


X-RAY ABSORPTION

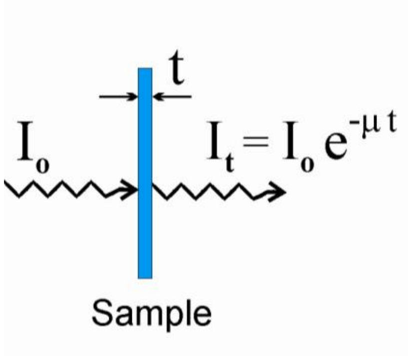


Element	10eV below L_3 μ [nm^{-1}]	at L_3 μ [nm^{-1}]	40 eV above L_3 μ [nm^{-1}]
Fe	1.8x10^{-3}	6.0x10^{-2}	1.2x10^{-2}
Co	1.8x10^{-3}	5.8x10^{-2}	1.2x10^{-2}
Ni	1.6x10^{-3}	4.2x10^{-2}	1.2x10^{-2}

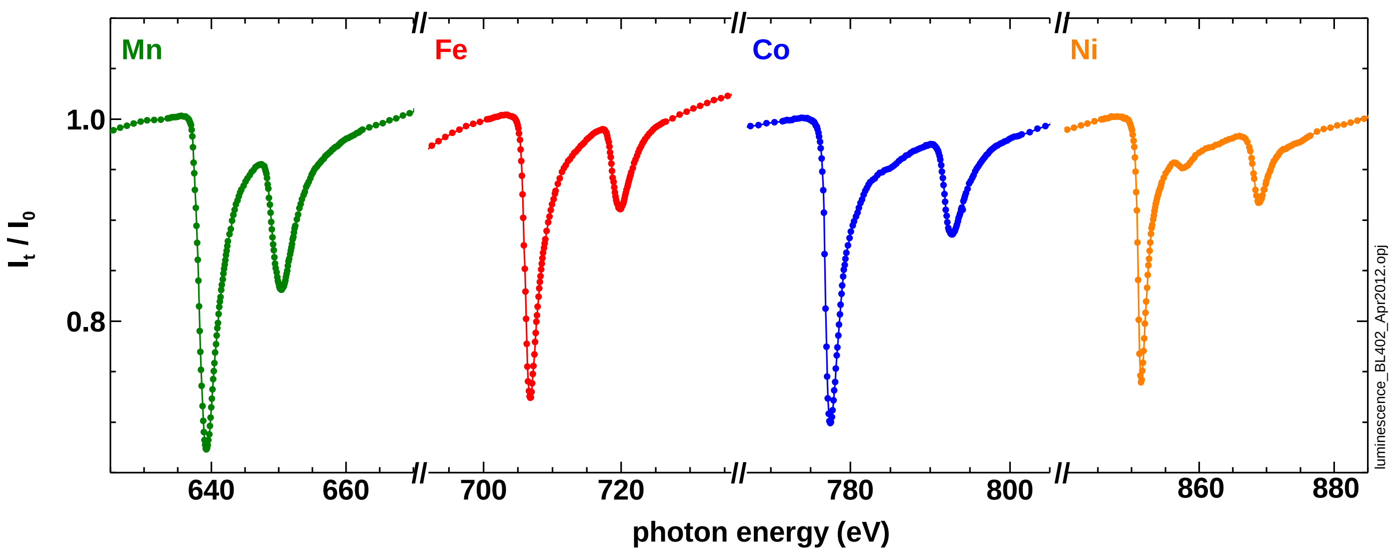


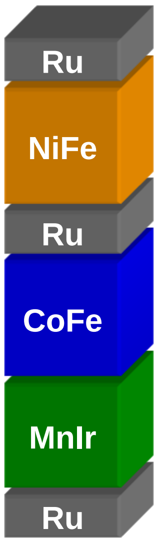


X-RAY ABSORPTION



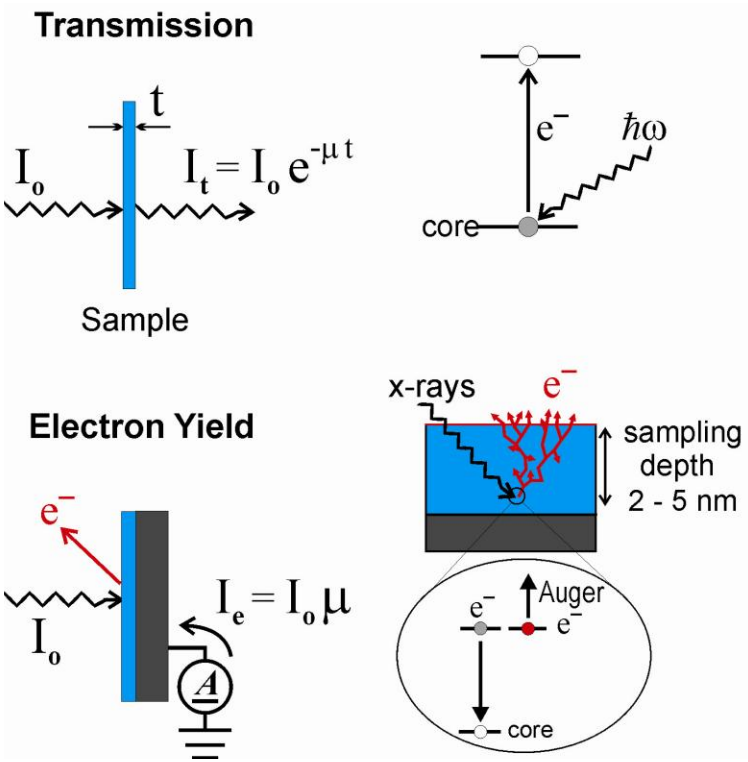
Element	10eV below L_3 1/μ [nm]	at L_3 1/μ [nm^{-1}]	40 eV above L_3 1/μ [nm^{-1}]
Fe	550	17	85
Co	550	17	85
Ni	625	24	85



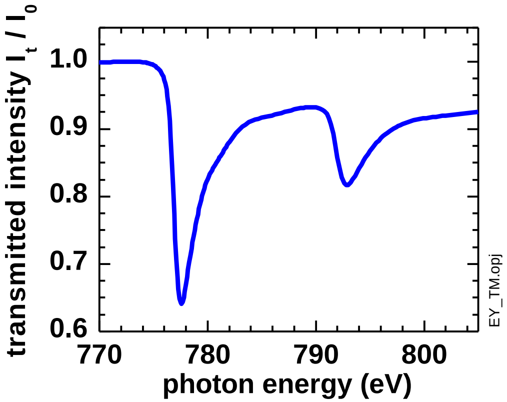


~10-20 nm layer thick films supported by substrates transparent to soft x-rays

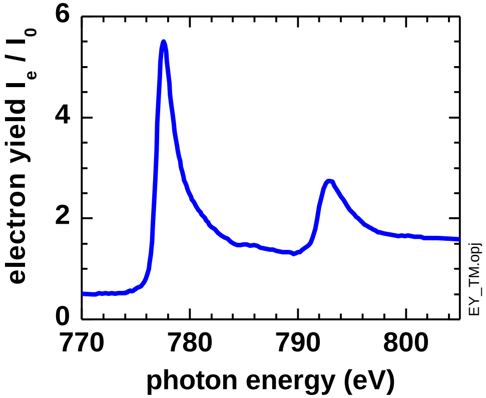
X-RAY ABSORPTION – MEASUREMENTS



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



photons absorbed

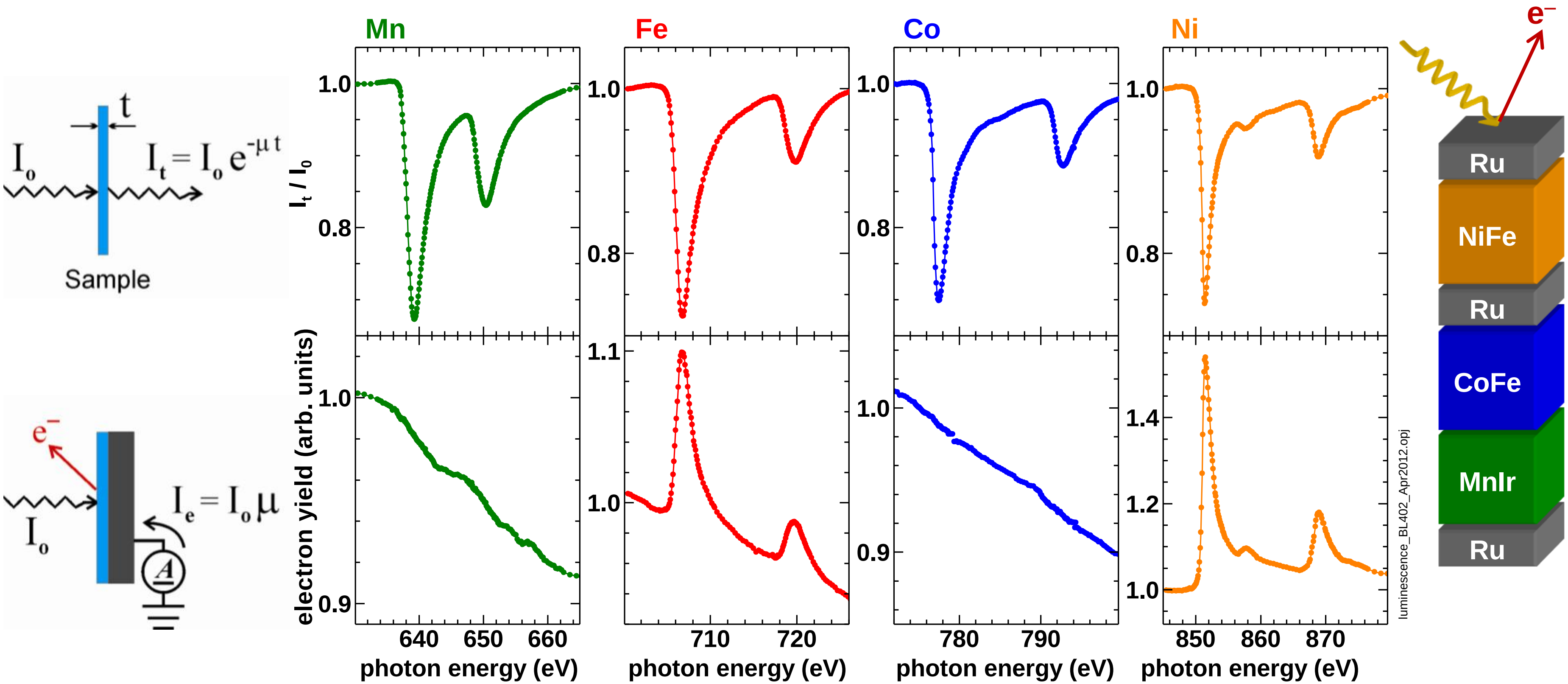


electrons generated

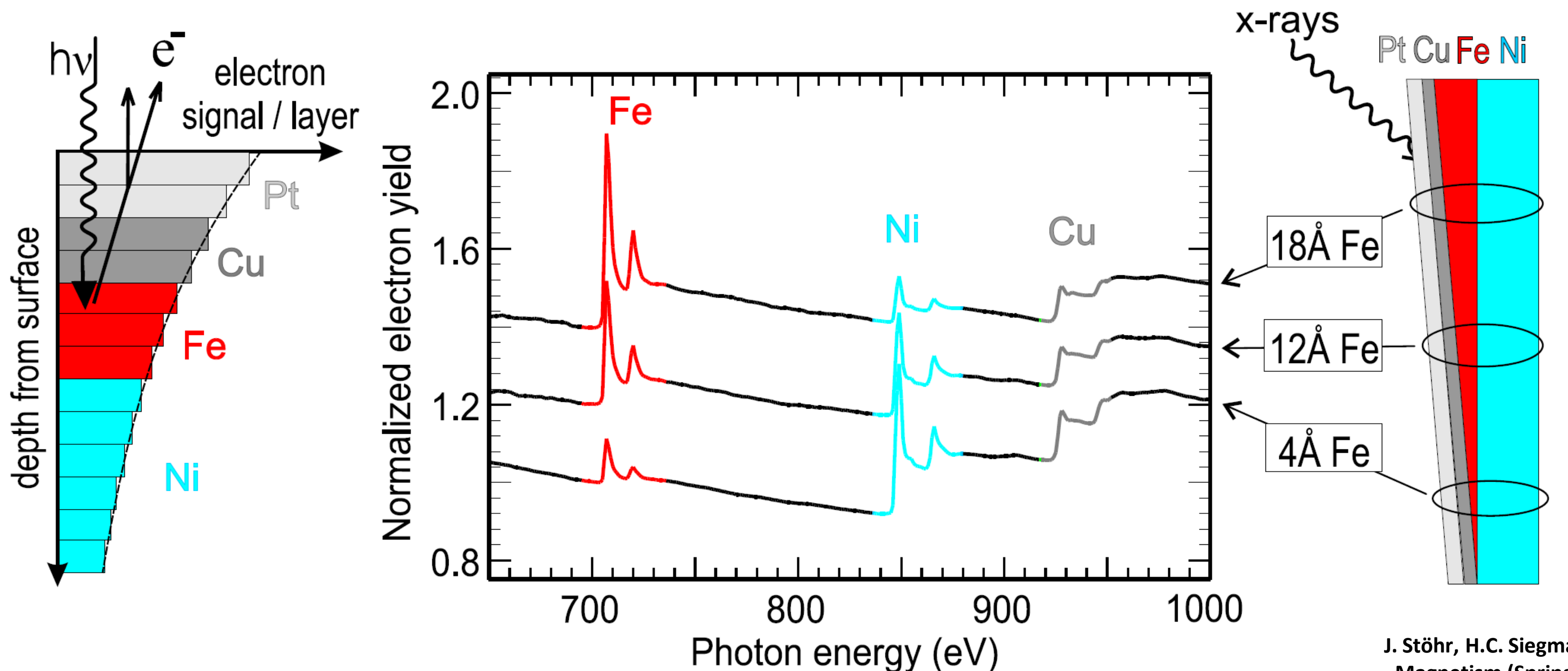
Electron yield:

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

X-RAY ABSORPTION – MEASUREMENTS



SAMPLING DEPTH OF ELECTRON YIELD



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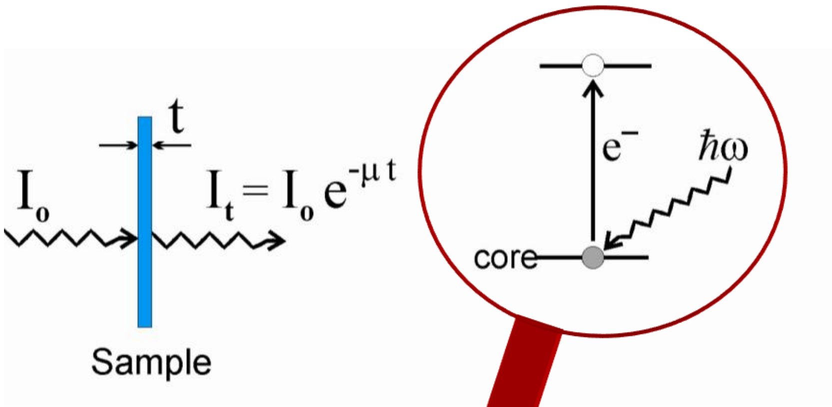
+ **Electron sample depth: 2-5 nm in Fe, Co, Ni**
  ⇒ **60% of the electron yield originates form the topmost 2-5 nm**

X-RAY ABSORPTION



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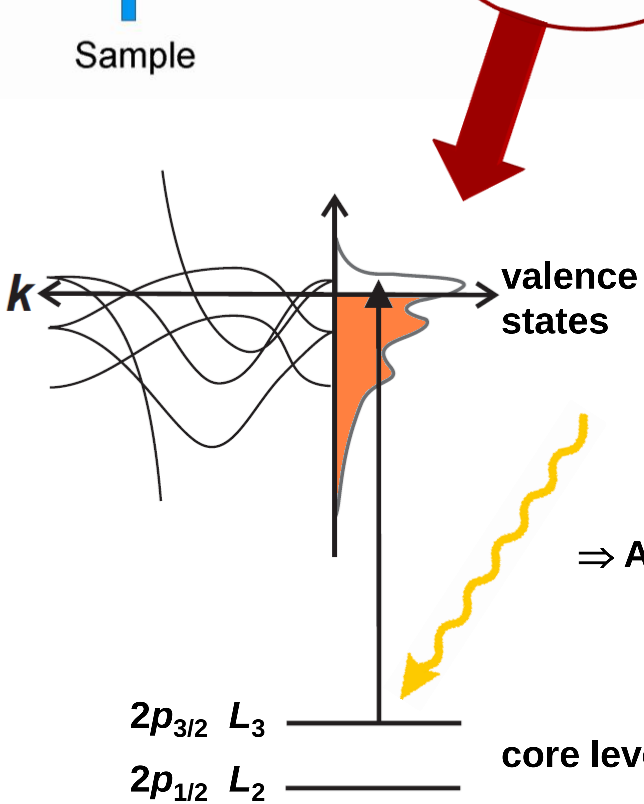
Monitor the reduction in x-ray flux transmitted through sample as function of x-ray photon energy



⇒ charge state of absorber Fe^{2+}, Fe^{3+}

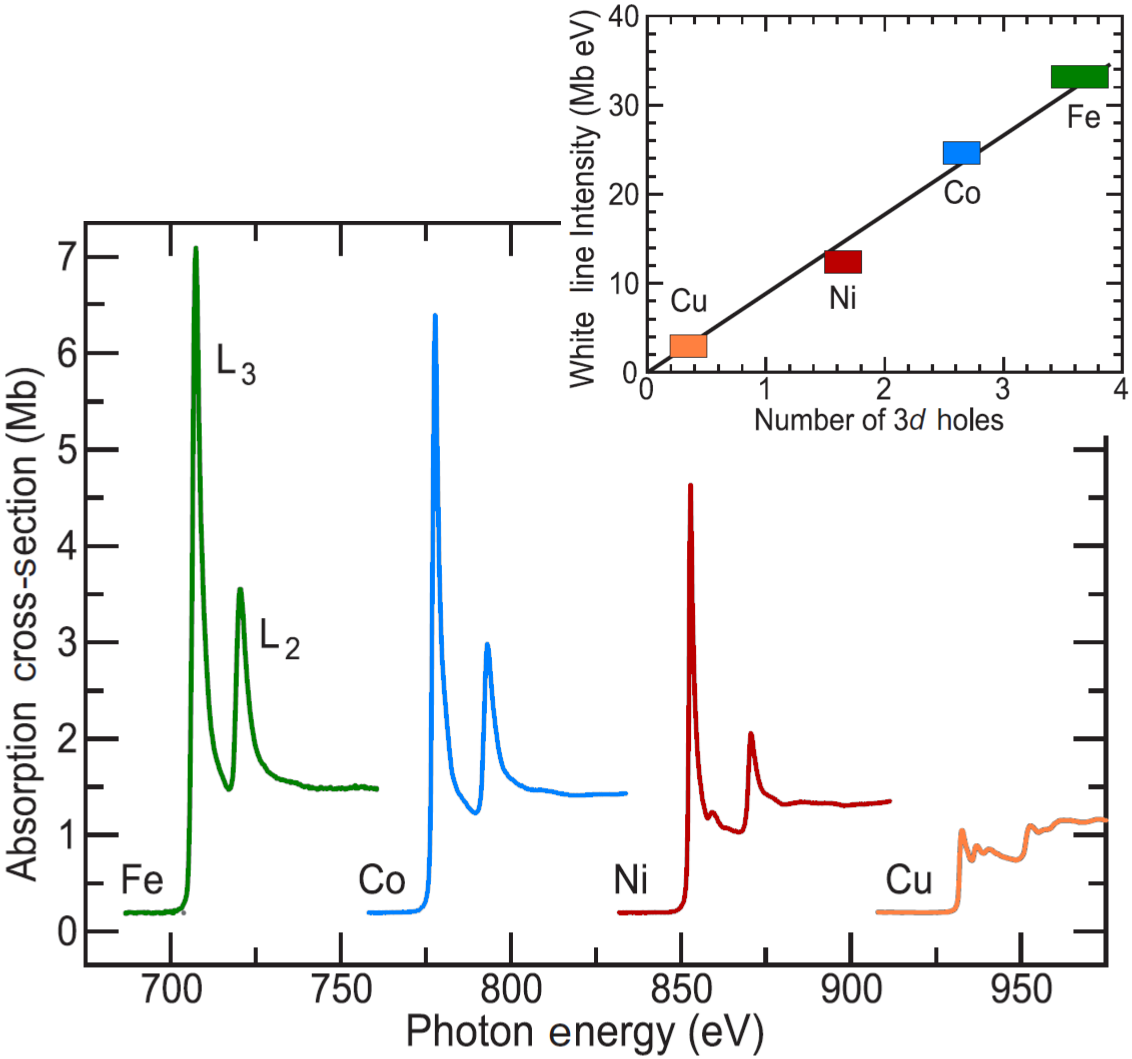
⇒ symmetry of lattice site of absorber: O_h, T_d

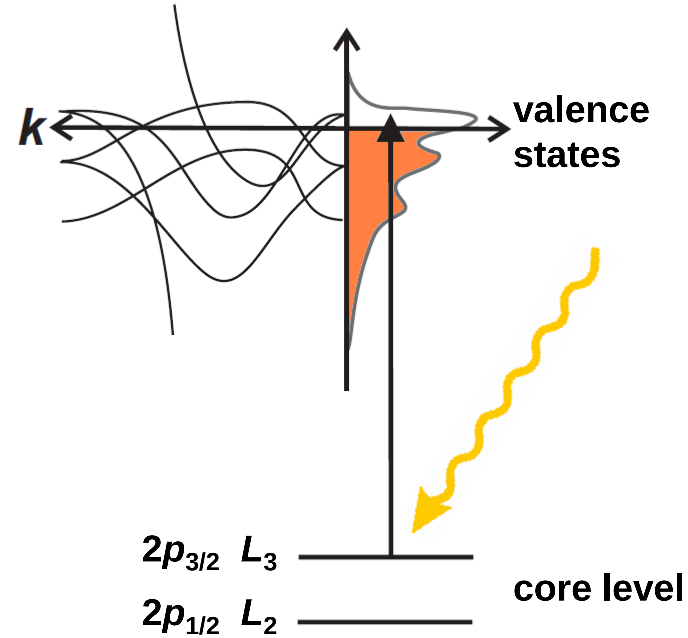
⇒ sensitive to magnetic order

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

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

'WHITE LINE' INTENSITY

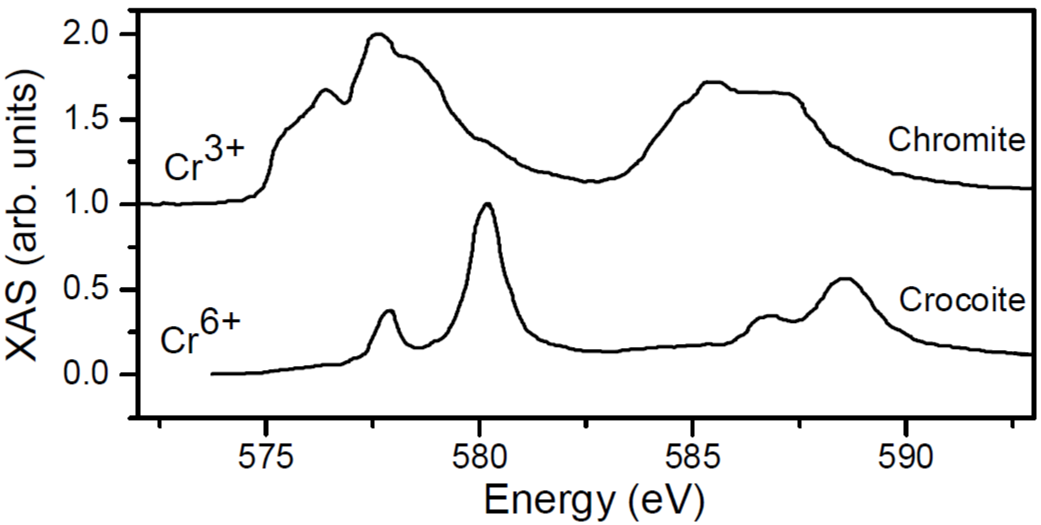




The intensity of the $L_{3,2}$ resonances is proportional to the number of *d* states above the Fermi level, i.e. the number of holes in the *d band.*

X-RAY ABSORPTION

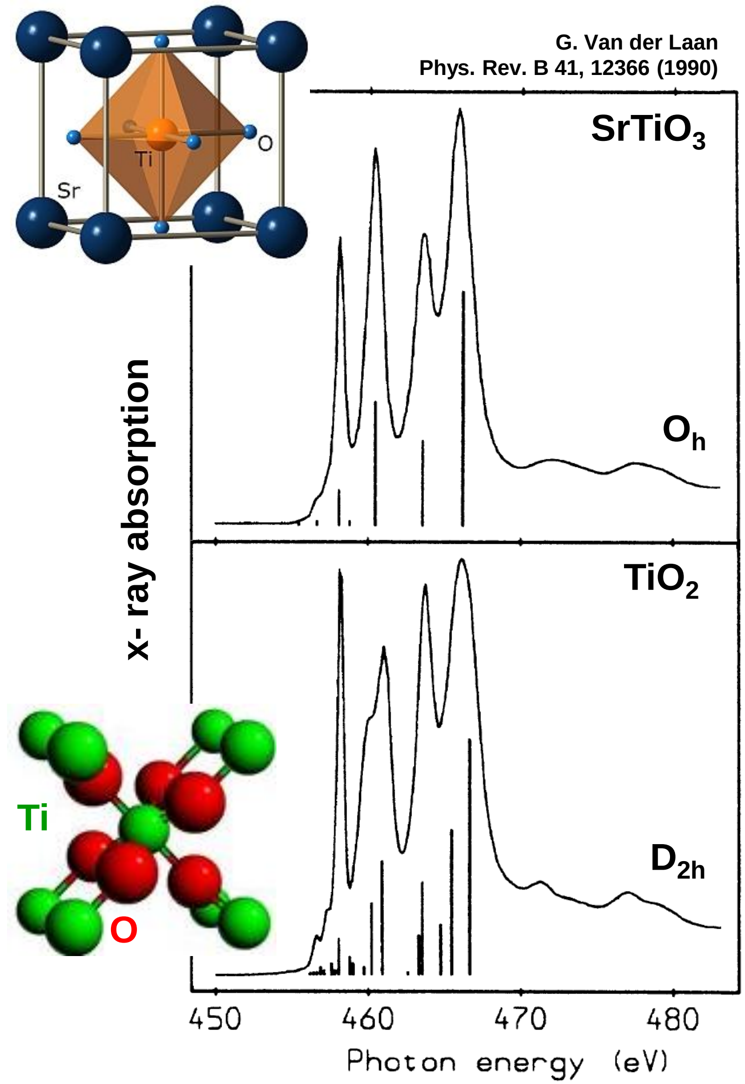
Influence of the charge state of the absorber



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

Influence of lattice site symmetry at the absorber

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



X-RAY ABSORPTION – ONE ELECTRON PICTURE

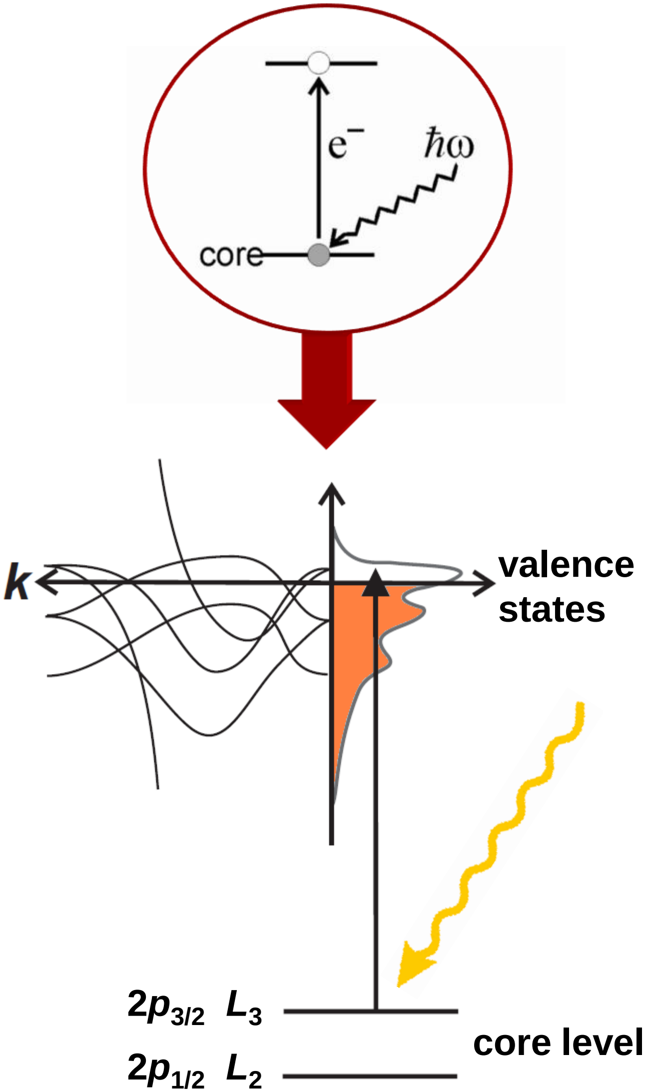
X-ray absorption:

+ **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.**

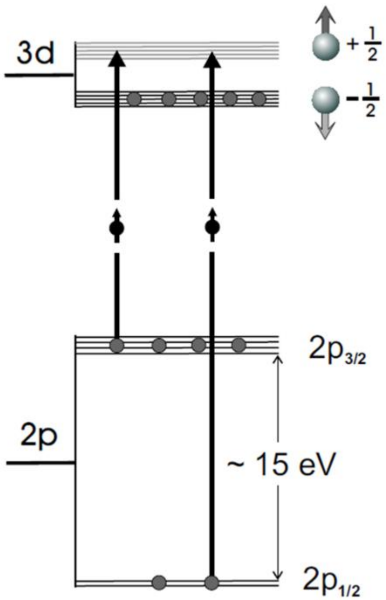
+ **However: Not directly excited electrons also influenced by electron excitation, i.e. hole in core shell**



X-RAY ABSORPTION – CONFIGURATION MODEL

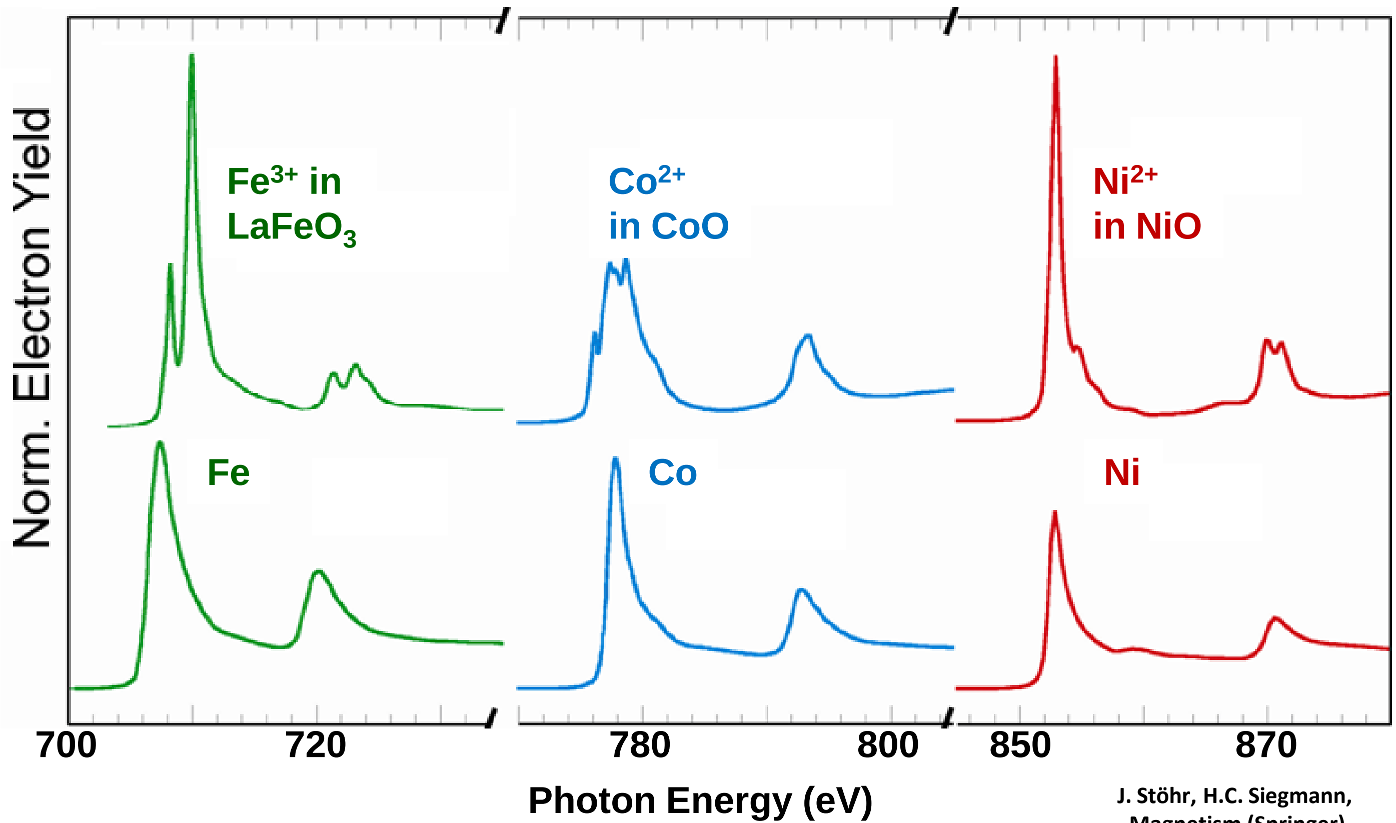
Configuration model, e.g. *L* edge absorption :

+ **Atom is 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**



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

X-RAY ABSORPTION – MULTIPLET EFFECTS



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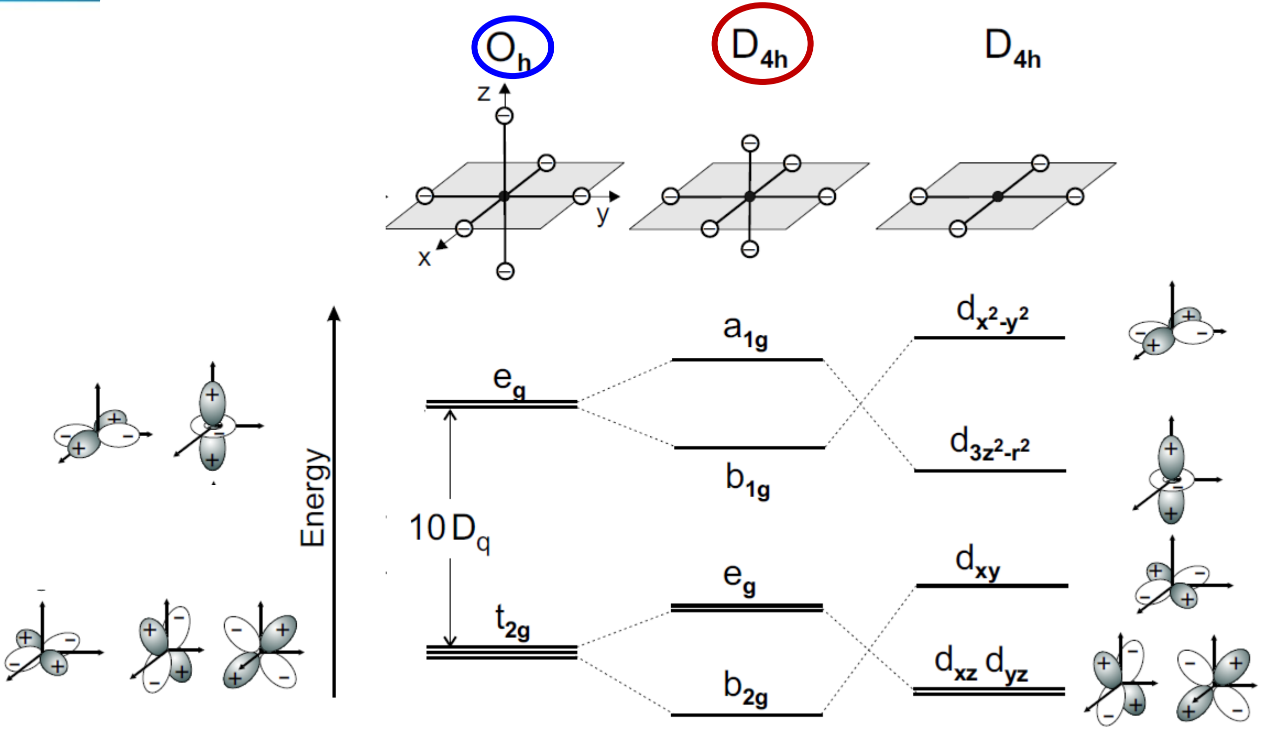
SENSITIVITY TO SITE SYMMETRY: Ti^{4+} $L_{3,2}$



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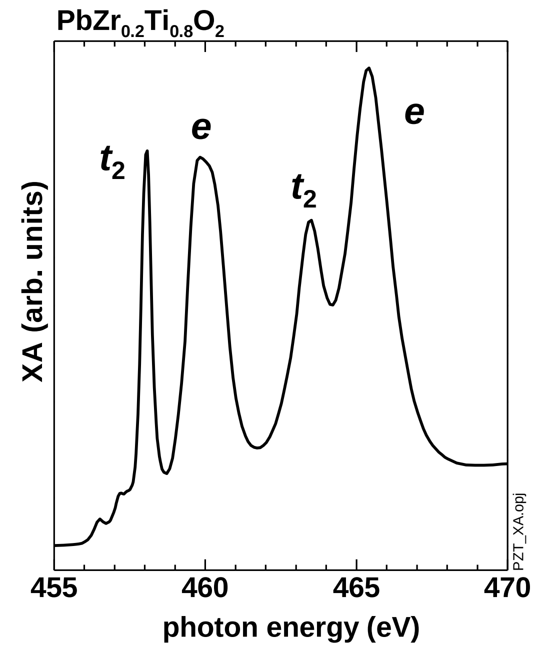


+ **Electric dipole transitions: $d^0 \rightarrow 2p^5 3d^1$**

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

Octahedral symmetry:

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

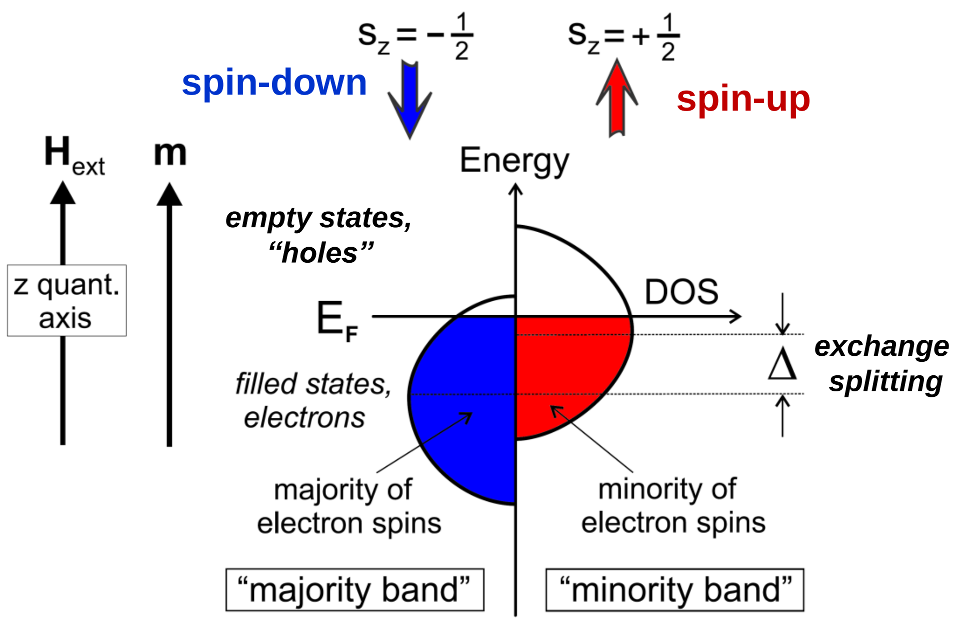
t_2 orbitals between ligands → lower energy

Tetragonal symmetry:

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

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

STONER MODEL FOR FERROMAGNETIC TRANSITION METALS



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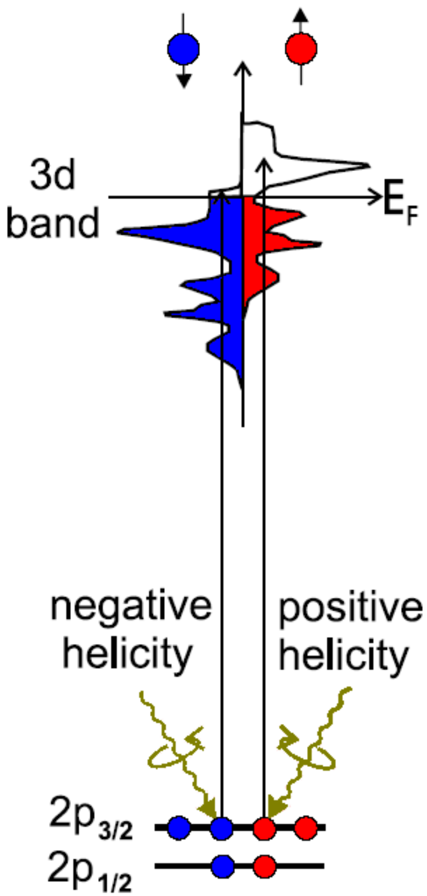
3*d* shell

- **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**

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

TWO-STEP MODEL OF XMCD



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Magnetism (Springer)

Photoelectrons excited from 2$p_{3/2}$, 2$p_{1/2}$ to 3*d* states

First step:

+ Excitation of electron from 2*p* states by absorption of circularly polarized x rays

+ Note: Dipole operator does not affect spin

⇒ No spin flips during excitation

+ Conservation of angular momentum

⇒ Transfer of angular momentum (±ħ) from photon to electron

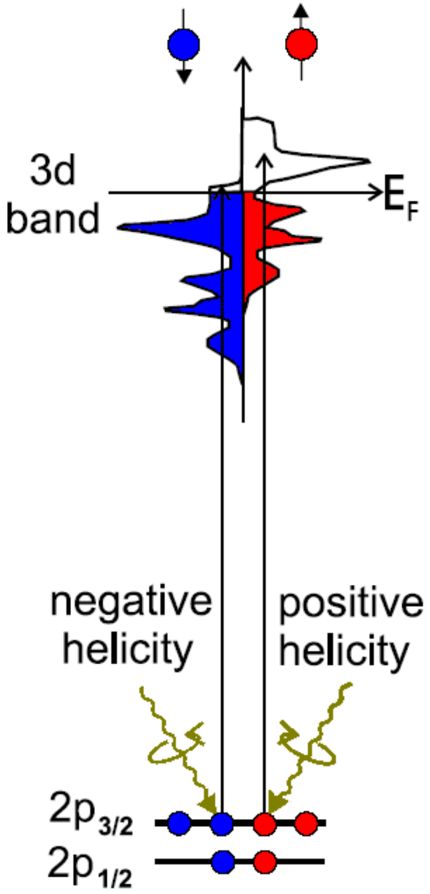
+ Spin-orbit coupling: Angular momentum of photon transferred in part to electron spin

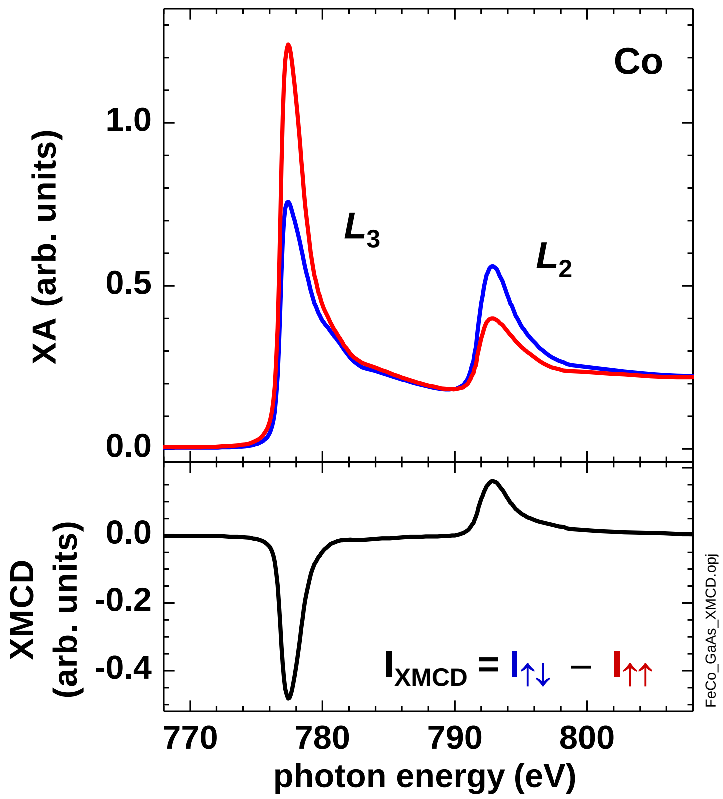
⇒ Excited photoelectrons are spin polarized

Second step:

+ Unequal spin-up and spin-down populations determine spin or orbital momentum of possible excitations

TWO-STEP MODEL OF XMCD





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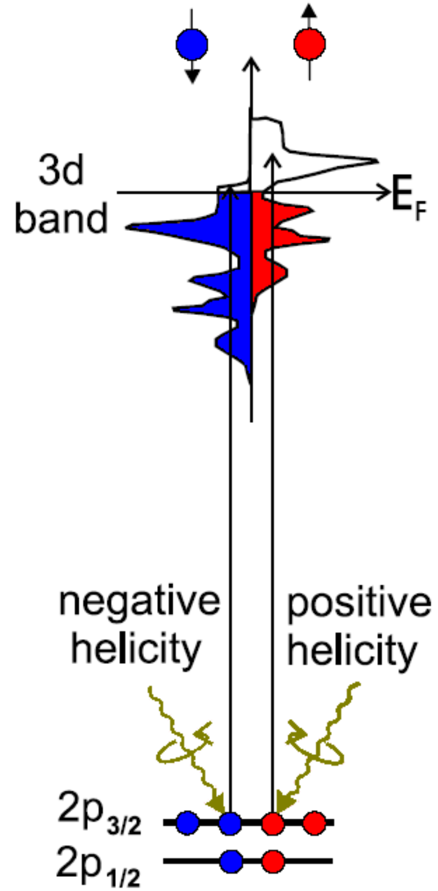
Magnitude of dichroism depends on

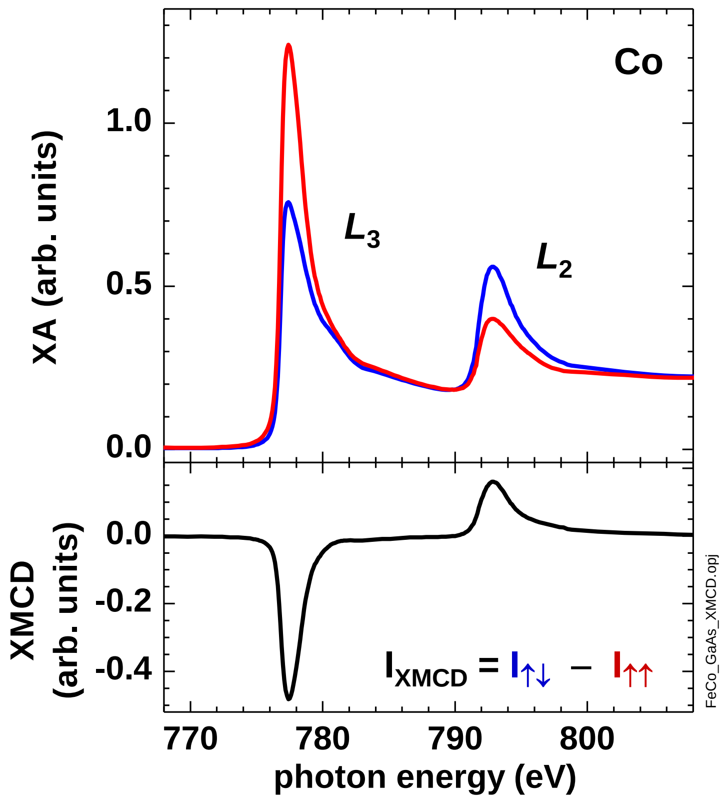
- **+ degree of circular photon polarization, P_{circ}**
- **+ angle θ between photon angular momentum, L_{ph} and magnetic moment, *m***
- **+ expectation value of 3*d* magnetic moment**

$$I_{XMCD} \propto P_{circ} \langle m \rangle \cos\theta$$

TWO-STEP MODEL OF XMCD

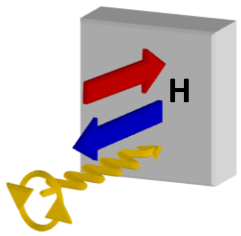


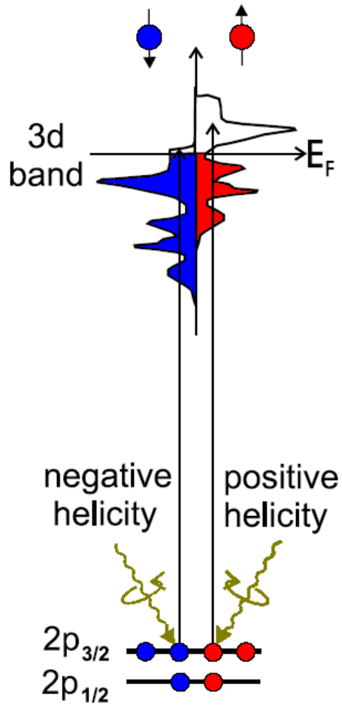
J. Stöhr, H.C. Siegmann,
Magnetism (Springer)



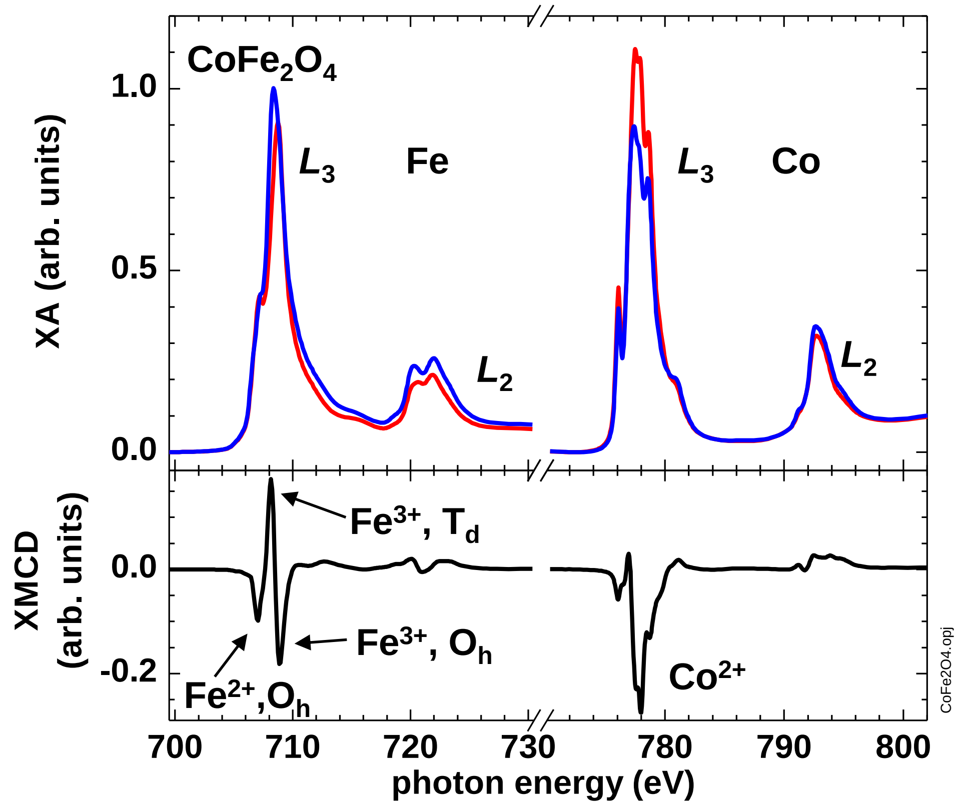
- **+ $2p_{3/2}$ and $2p_{1/2}$ have opposite spin orbit coupling (l+s, l –s)**
  ⇒ Spin polarization and XMCD have opposite sign at two edges
- **+ Spin polarization opposite for x rays with opposite helicity, i.e. photon spin, ±ħ**
  ⇒ XMCD reverses sign with polarization
- **+ Reversing x ray polarization is equivalent to reversing magnetization/spin direction**

X-RAY MAGNETIC CIRCULAR DICHROISM (XMCD)





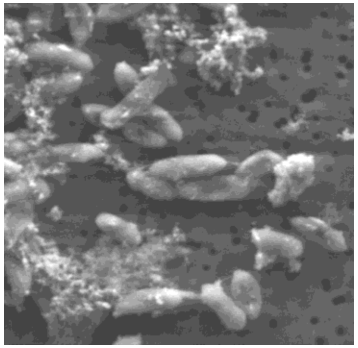
J. Stöhr, H.C. Siegmann, Magnetism (Springer)

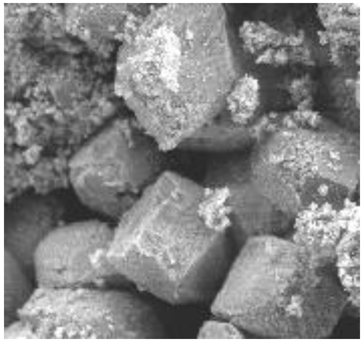


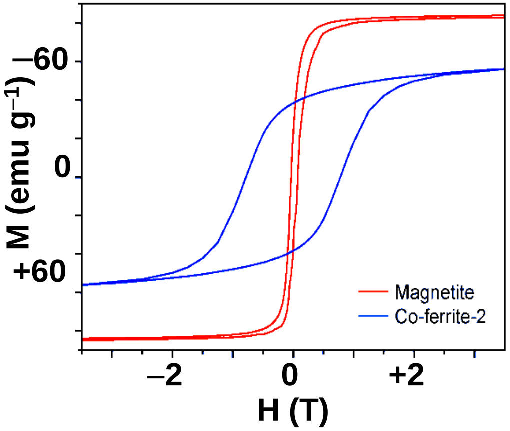
+ **XMCD provides magnetic information resolving elements Fe, Co, …**
valence states: Fe^{2+}, Fe^{3+}, …
lattice sites: octahedral, O_h, tetrahedral, T_d, …

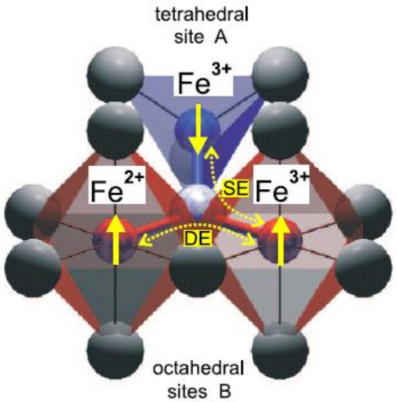
CHARACTERISTICS OF MAGNETIC BIONANOSPINELS

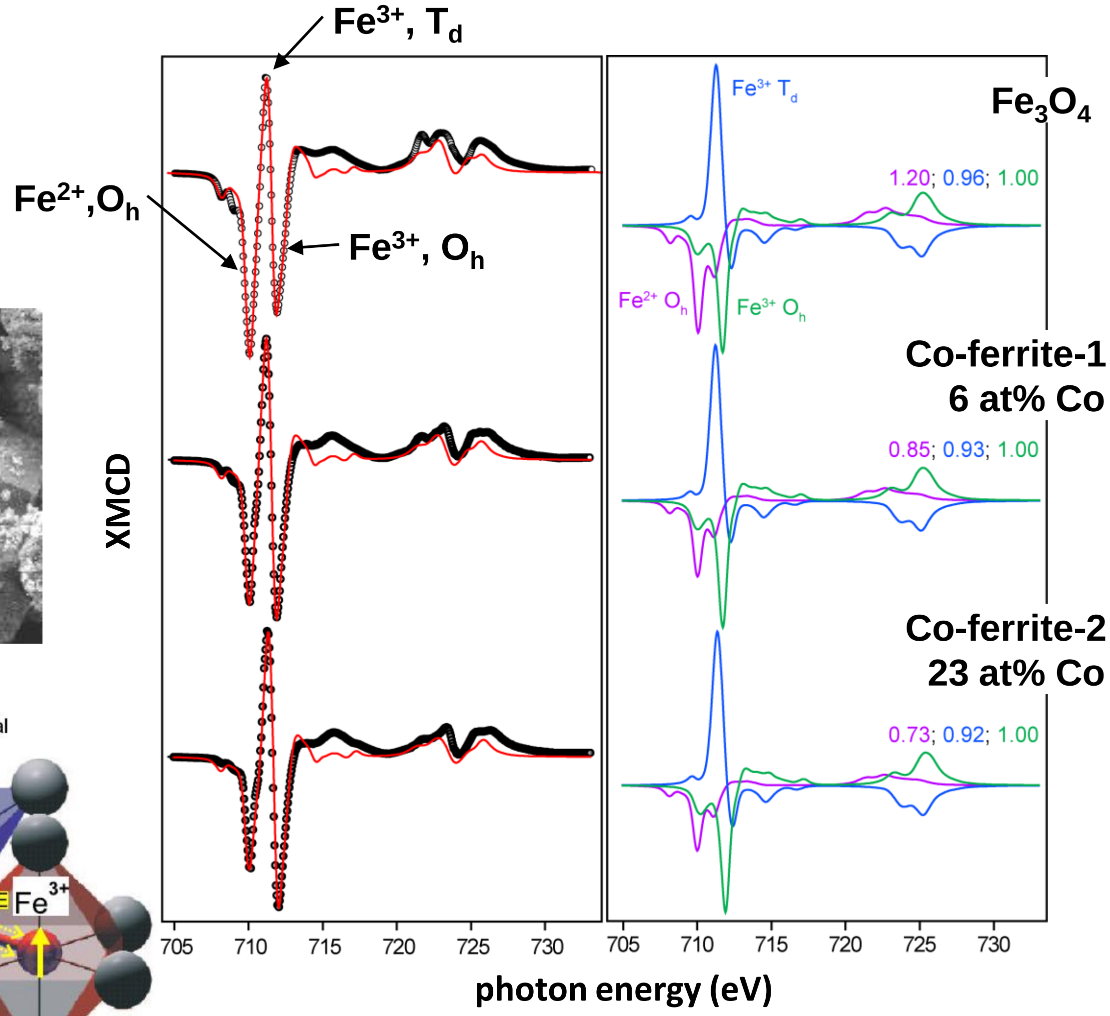
- Geobacter sulfurreducens bacteria form magnetite nanocrystals (15nm) via extracellular reduction of amorphous Fe(III)-bearing minerals





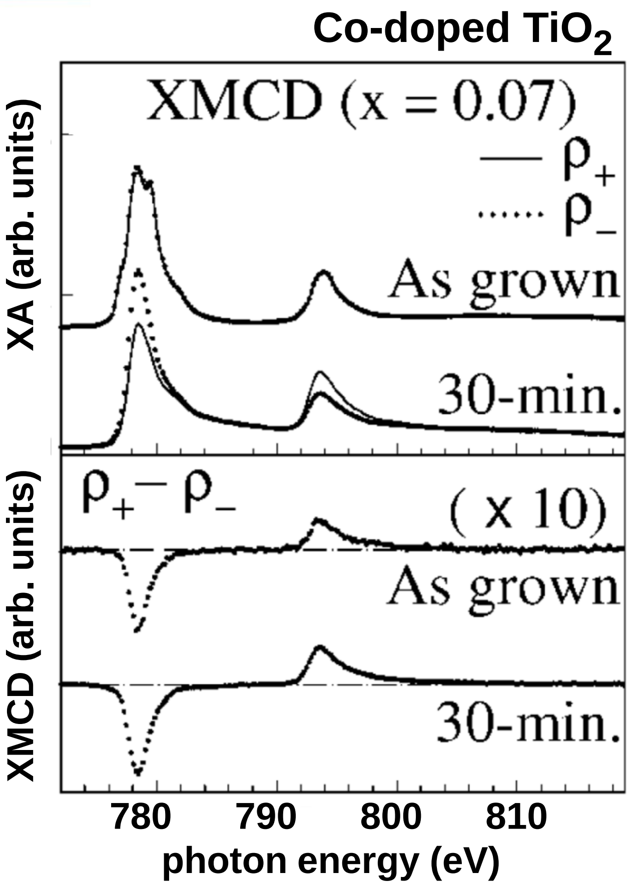




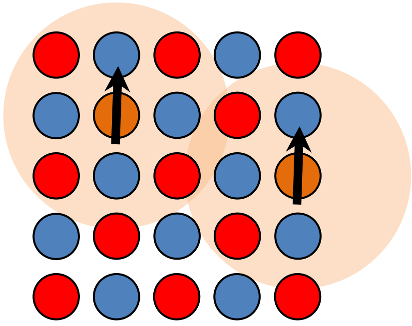


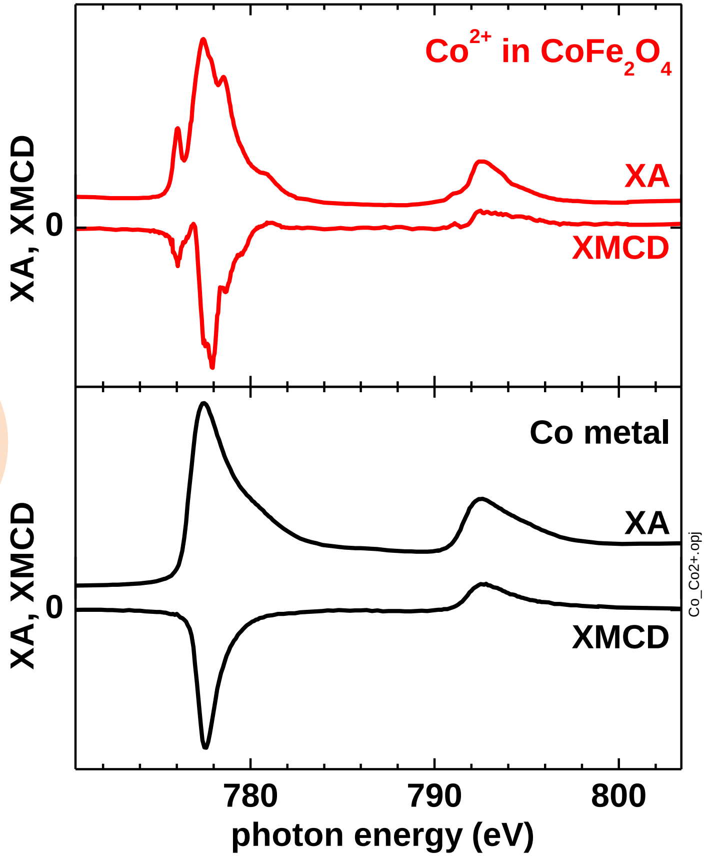
V. Cocker *et al.*,
Eur. J. Mineral. 19, 707–716 (2007)

Co-DOPED TiO_2



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



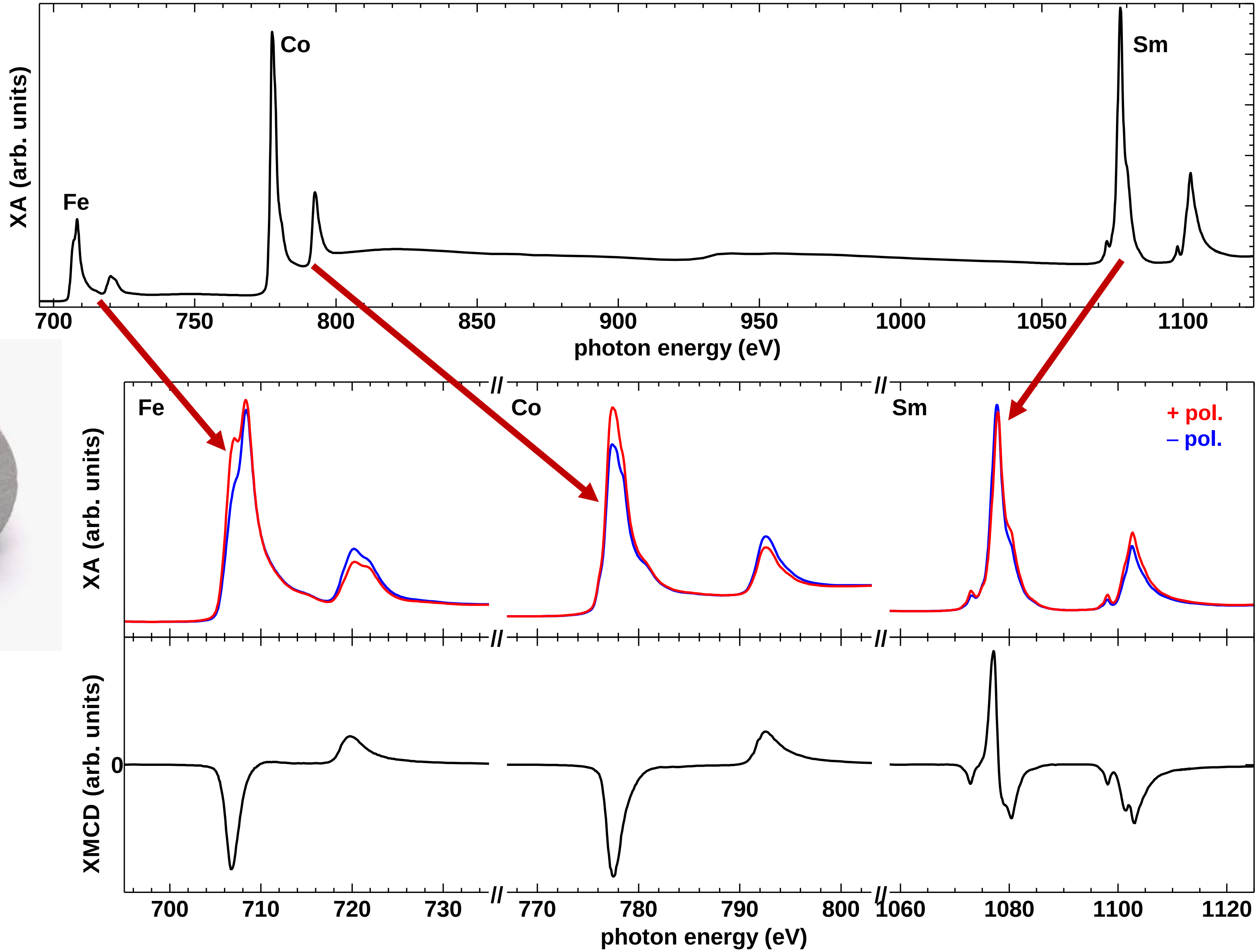


+ Comparing XMCD spectra with model compounds and/or calculations

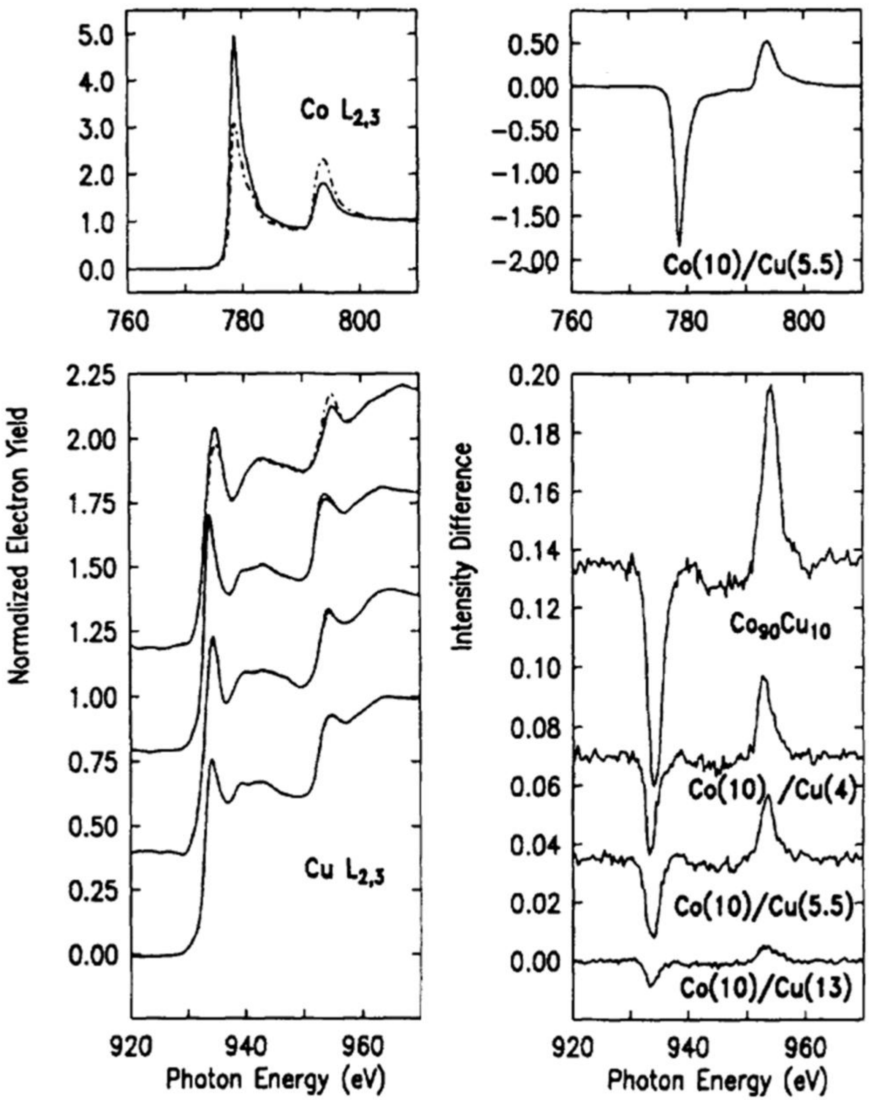
⇒ Identifying magnetic phases

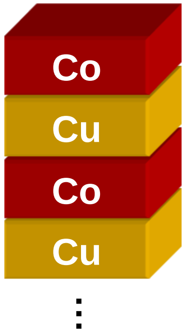
SINTERED CoSm PERMANENT MAGNETS

'CoSm'



INDUCED MOMENTS AT Co/Cu INTERFACES



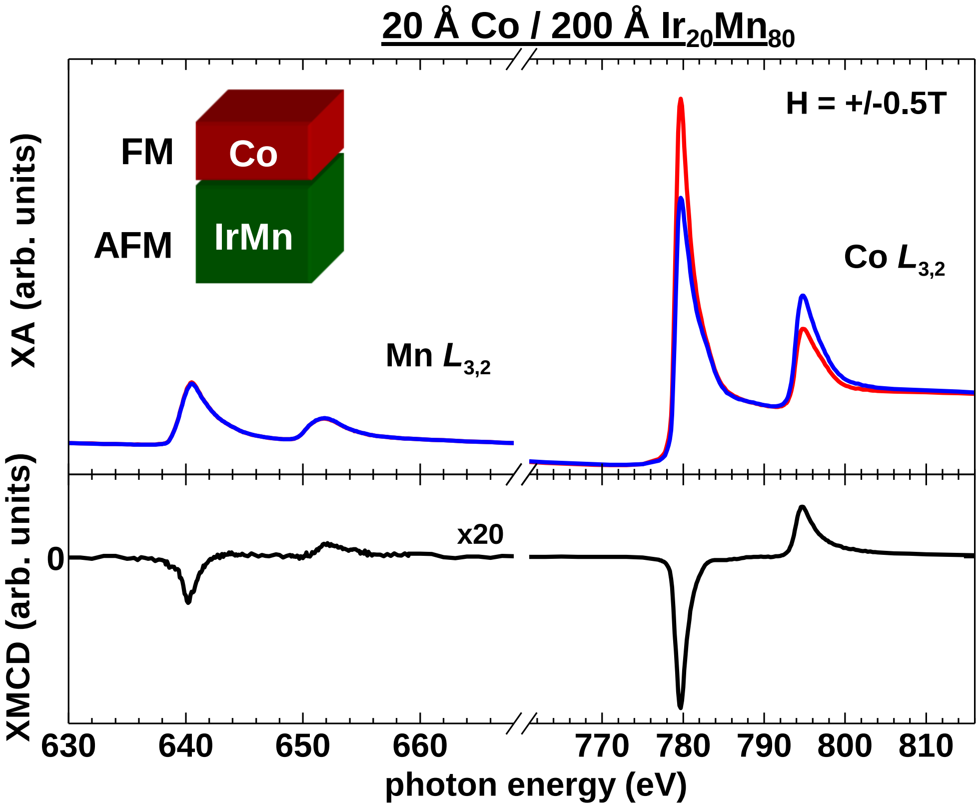


+ **The element-specificity makes XMCD measurements an ideal tool to determine induced moments at interfaces between magnetic and non-magnetic elements.**

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

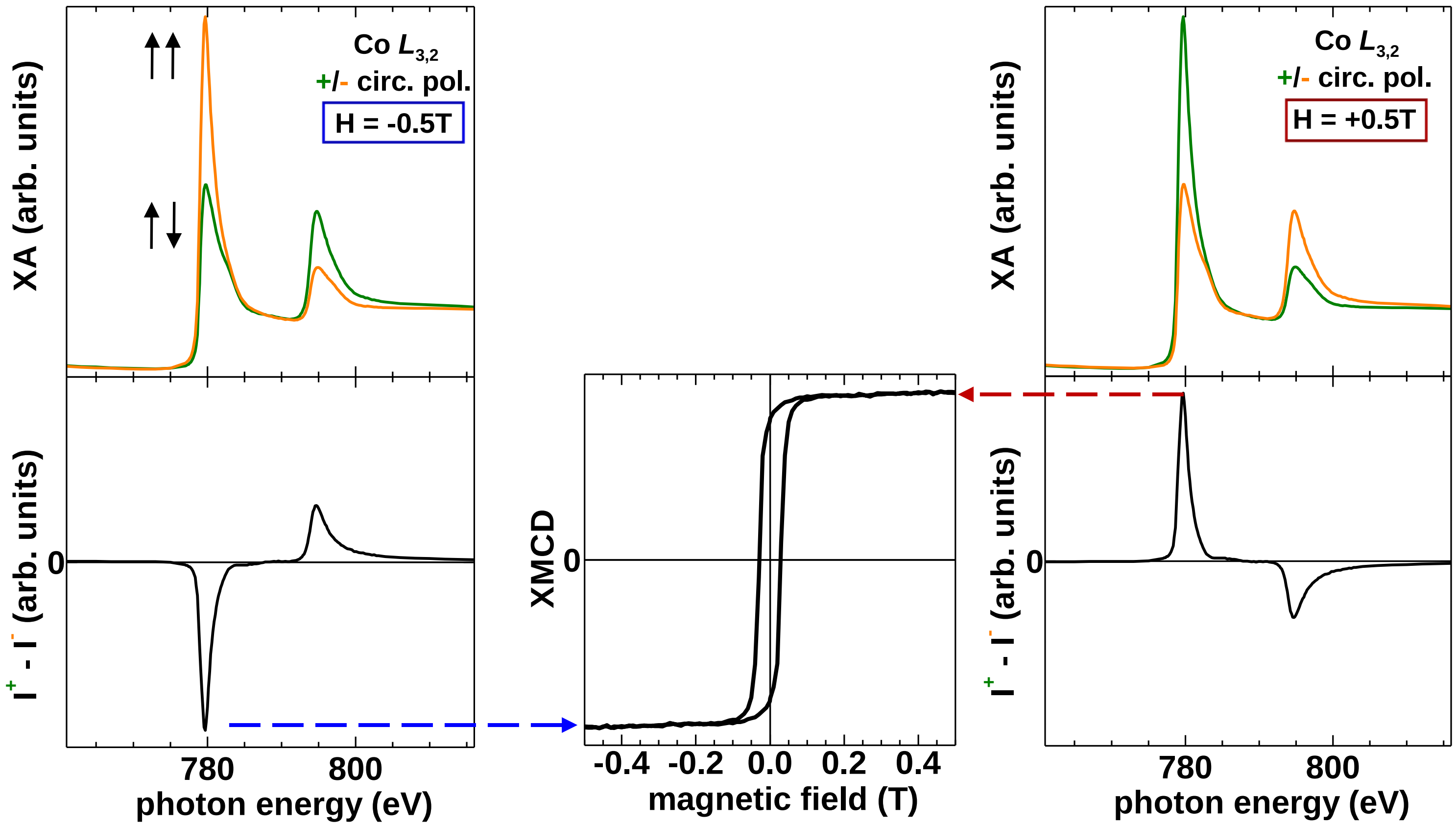
ANTIFERROMAGNET/FERROMAGNETIC INTERFACES

- + 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 for Co/$Ir_{20}Mn_{80}$.



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

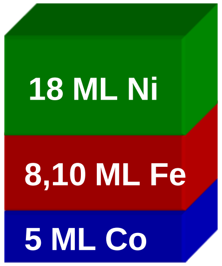
ELEMENT-SPECIFIC MAGNETIZATION REVERSAL

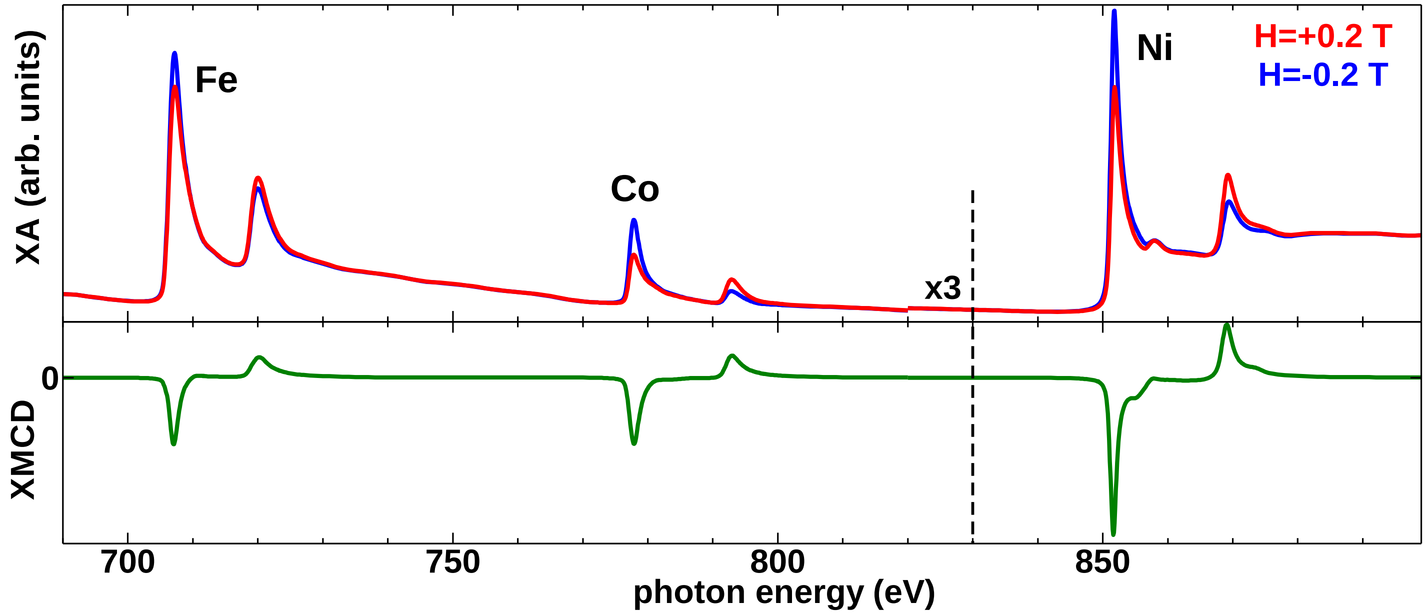


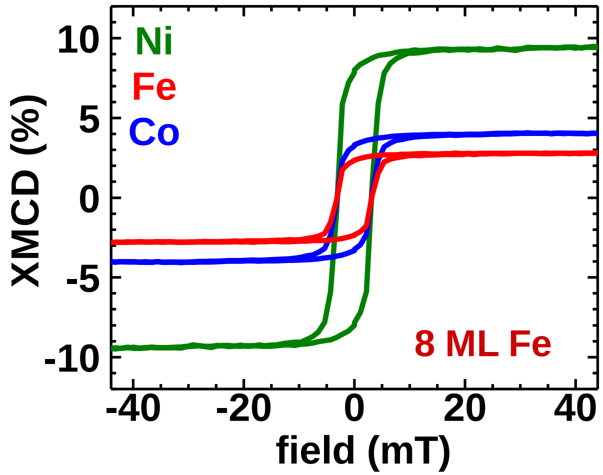
+ Monitoring field dependence of XMCD

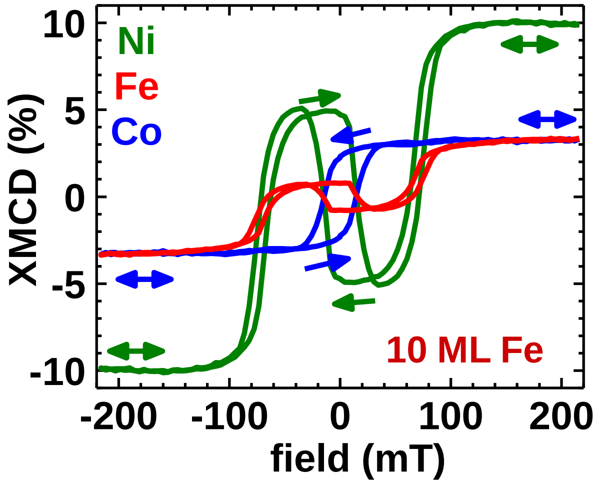
⇒ Element-specific information on magnetization reversal in complex magnetic nanostructures.

ELEMENT-SPECIFIC MAGNETIZATION REVERSAL





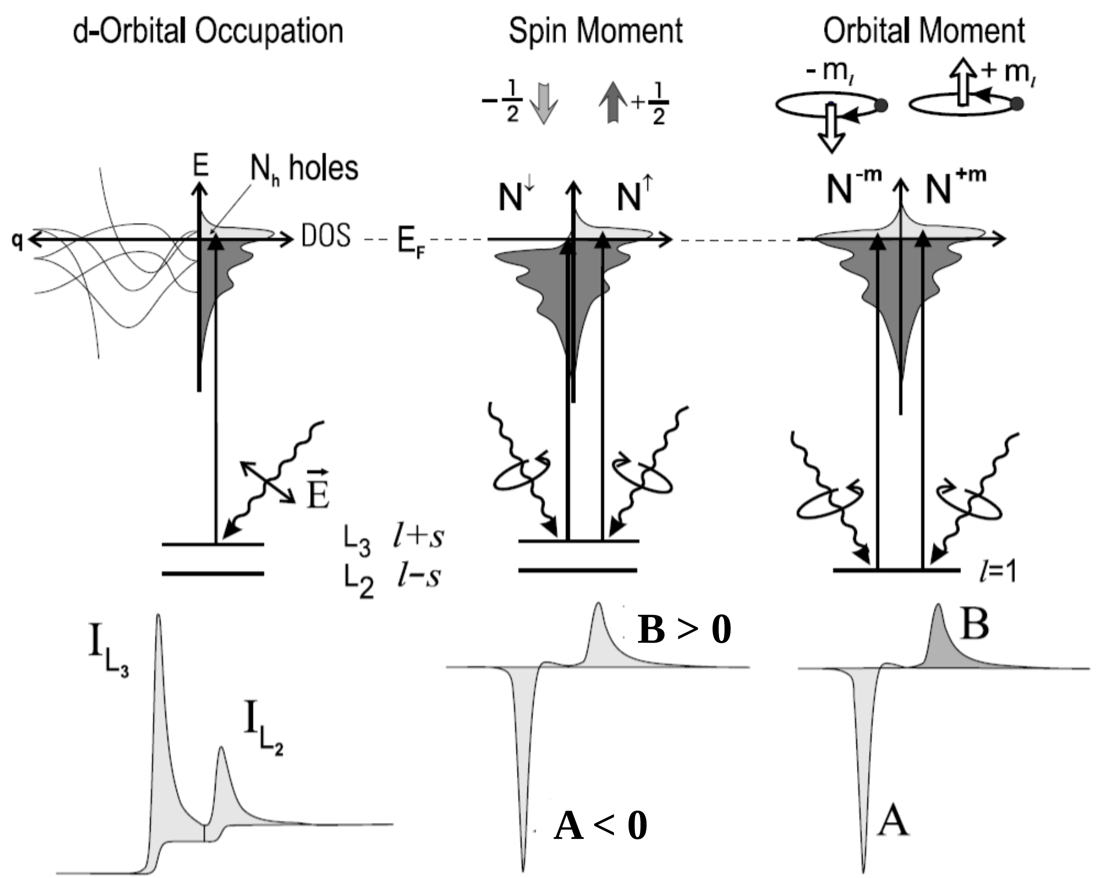




+ Monitoring field dependence of XMCD

⇒ Detailed information on magnetization reversal in complex magnetic heterostructures

SUM RULES



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

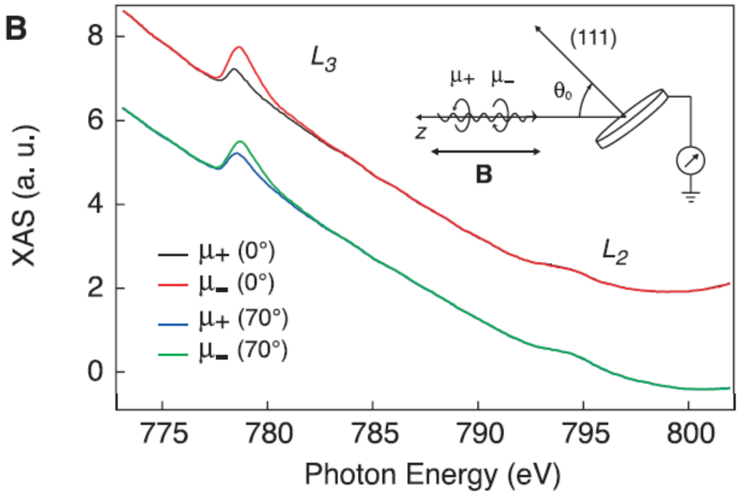
$$N_h = \langle I_{L3} + I_{L2} \rangle / C$$

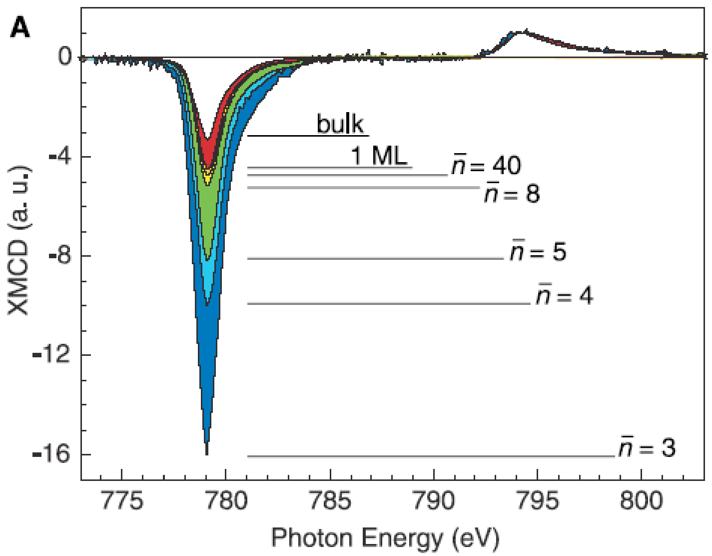
$$m_L = -2\mu_B \langle A + B \rangle / 3C$$

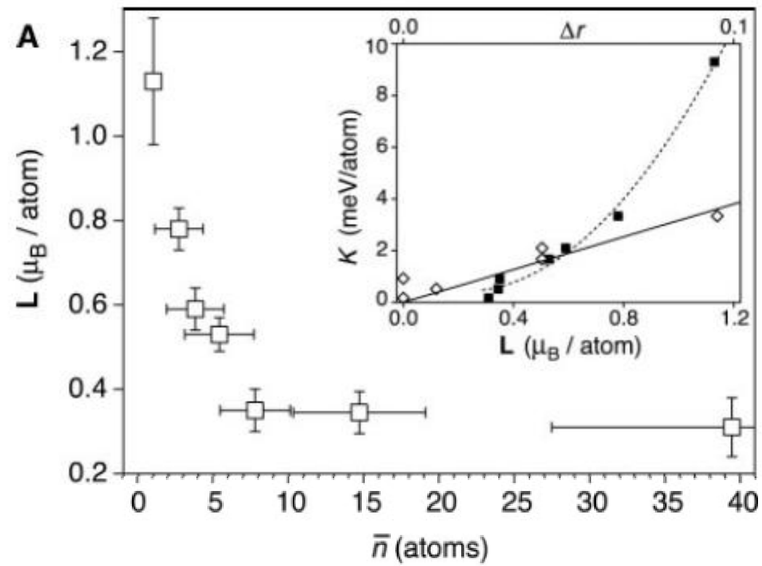
$$m_S = \mu_B \langle -A + 2B \rangle / C$$

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

ORBITAL MOMENT OF Co NANOPARTICLES



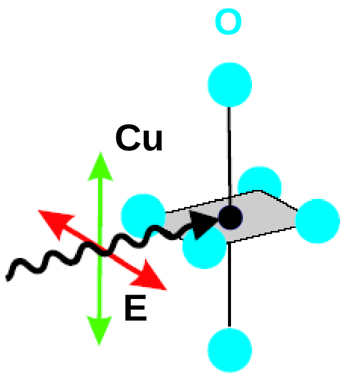




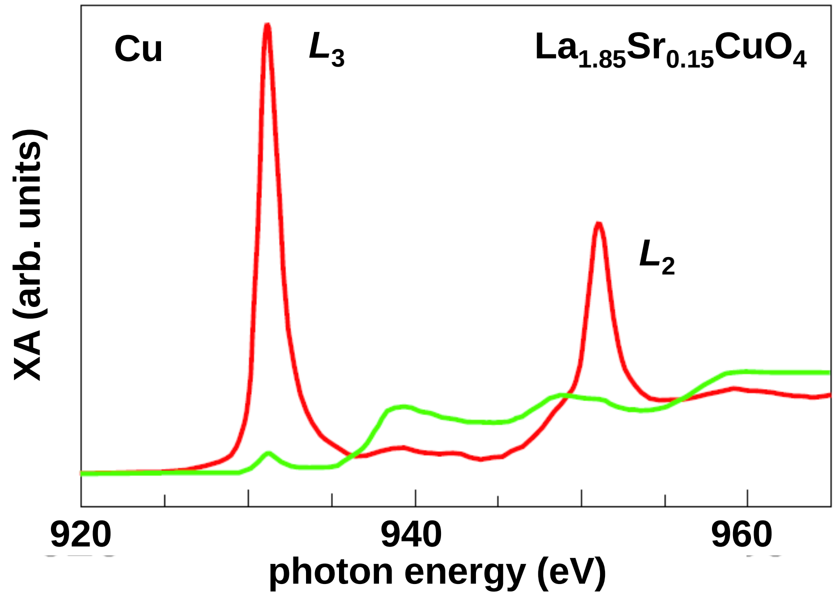
+ **Strong variation of orbital and spin magnetic moment observable as change in relative L_3 and L_2 intensity in XMCD spectrum.**
+ **Co atoms and nanoparticles on Pt have enhanced orbital moments up to 1.1 μ_B**

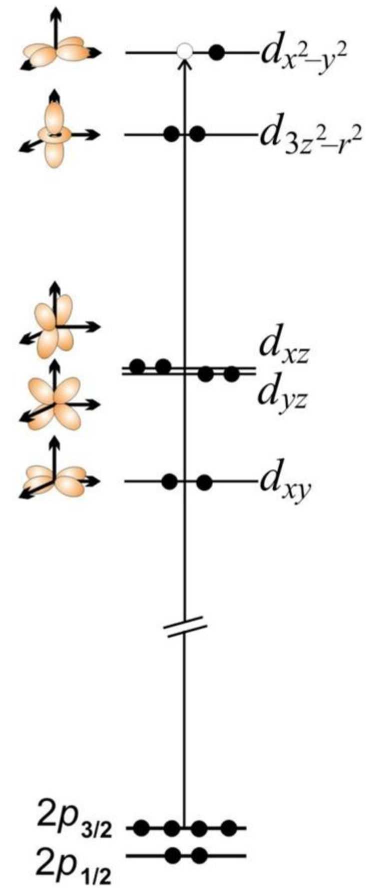
**P. Gambardella *et al.*,
Science 300, 1130 (2003)**

X-RAY LINEAR DICHROISM



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





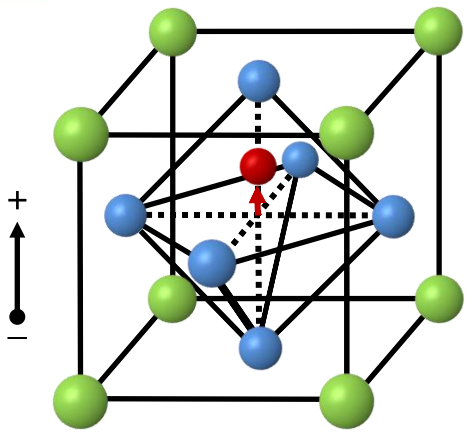
X-Ray Linear Dichroism:

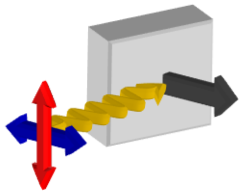
+ Difference in x-ray absorption for different linear polarization direction relative to crystalline and/or spin axis.

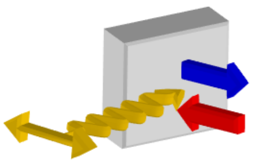
+ Due to the anisotropic charge distribution about the absorbing atom caused by bonding and/or magnetic order.

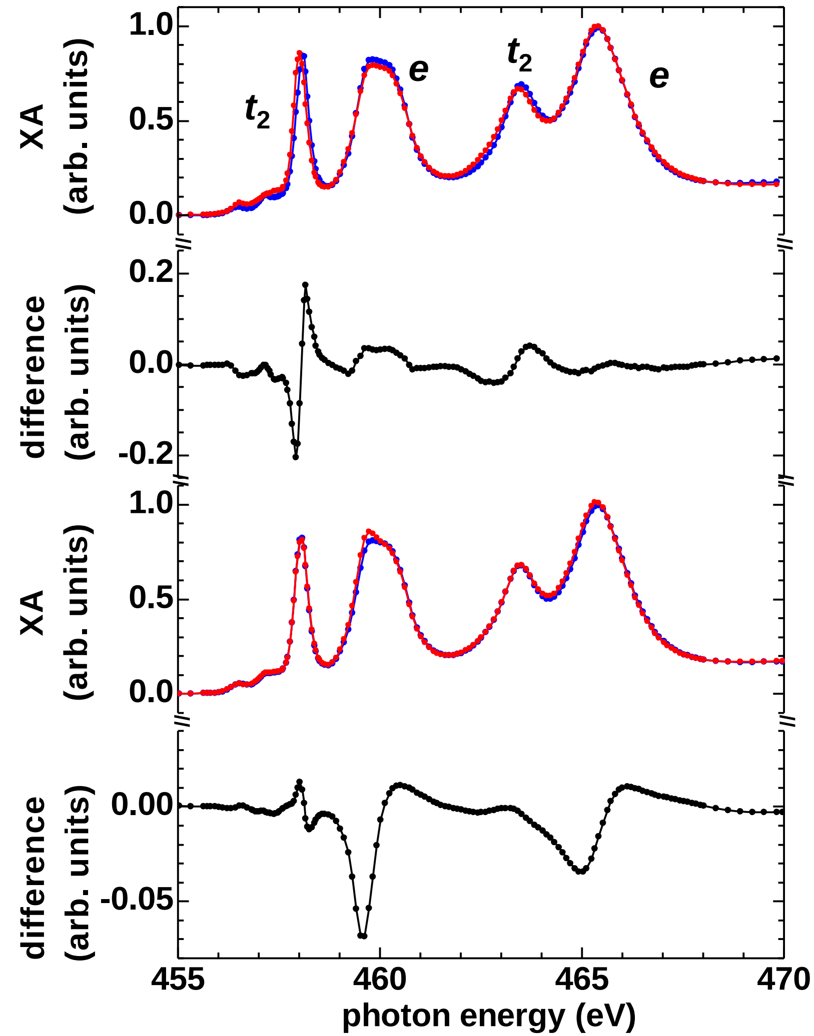
+ “Search Light Effect”: X-ray absorption of linear polarized x rays proportional to density of empty valence states in direction of electric field vector E.

STRUCTURAL CHANGES IN $PbZr_{0.2}Ti_{0.8}O_3$







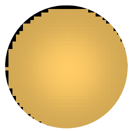


E. Arenholz *et al.*,
Phys. Rev. B 82, 140103 (2010)

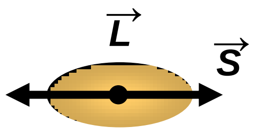
+ Spontaneous electric polarization due to off-center shift of Ti^{4+}, Zr^{4+} associated with tetragonal distortion ⇔ linear dichroism

+ Reversing ferroelectric polarization changes XA ⇔ Change in tetragonal distortion

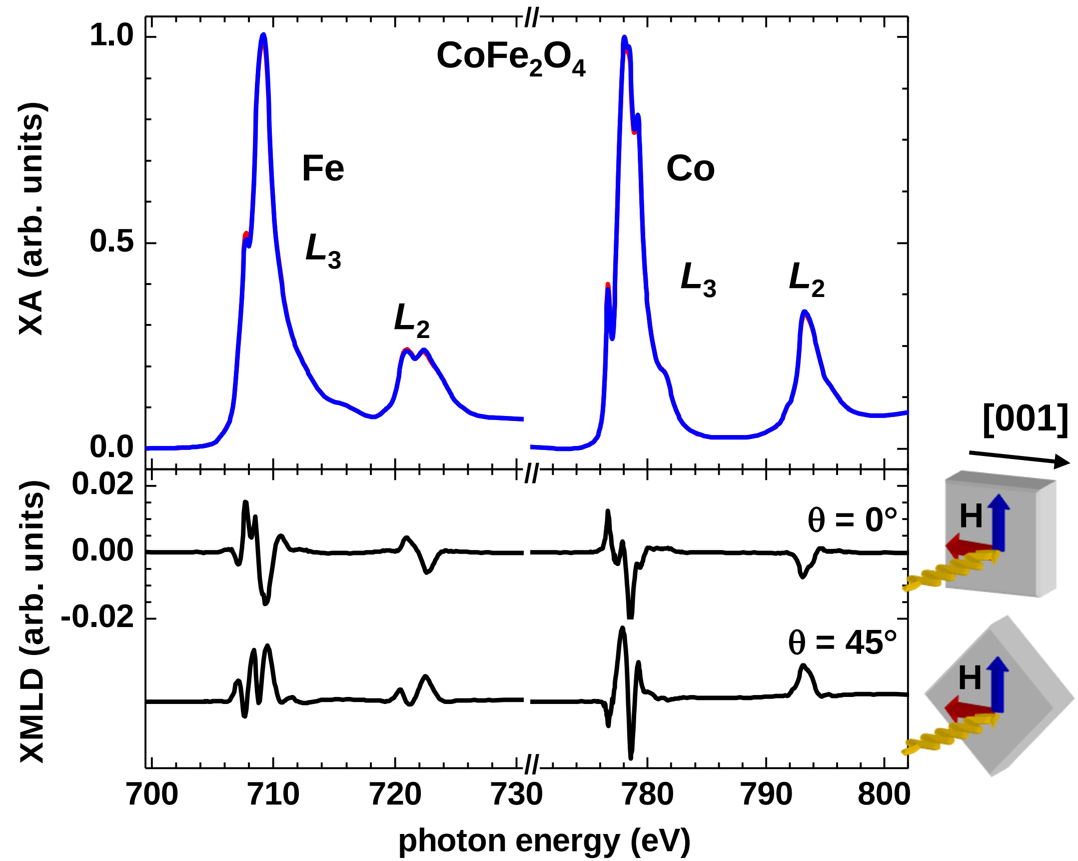
X-RAY MAGNETIC LINEAR DICHROISM



Isotropic *d* electron charge density
⇒ No polarization dependence

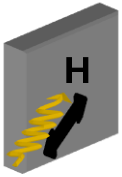


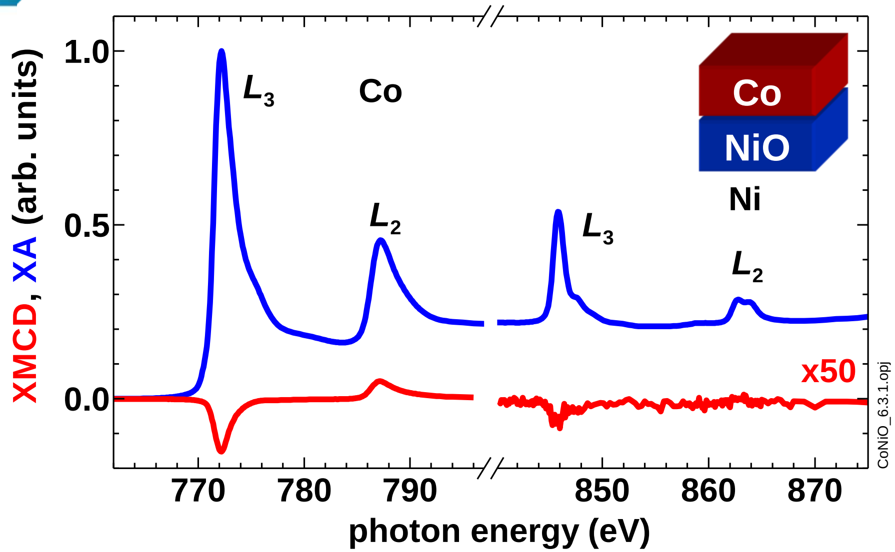
Magnetically aligned system
⇒ Spin-orbit coupling distorts charge density
⇒ Polarization dependence

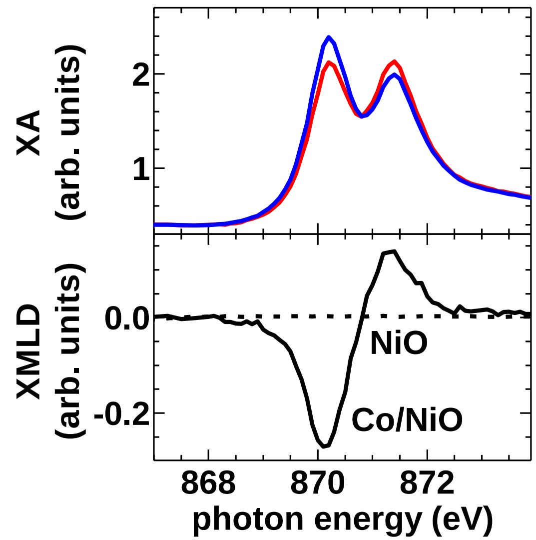


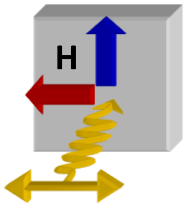
+ $I_{XMLD} = I_{||} - I_{\perp} \propto \langle m^2 \rangle$, $\langle m^2 \rangle$ = expectation value of the square of the atomic magnetic moment
+ XMLD allows investigating ferri- and ferromagnets as well as antiferromagnets
+ XMLD spectral shape and angular dependence are determined by magnetic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

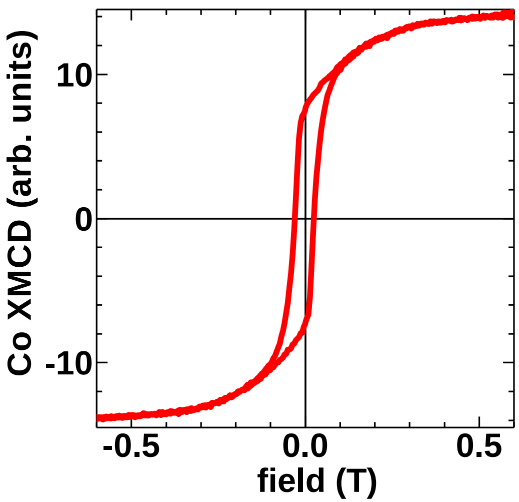
PLANAR DOMAIN WALL NEAR Co/NiO INTERFACES

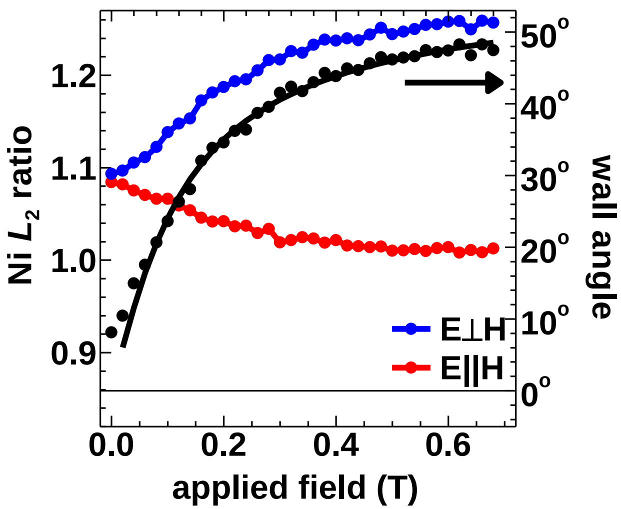


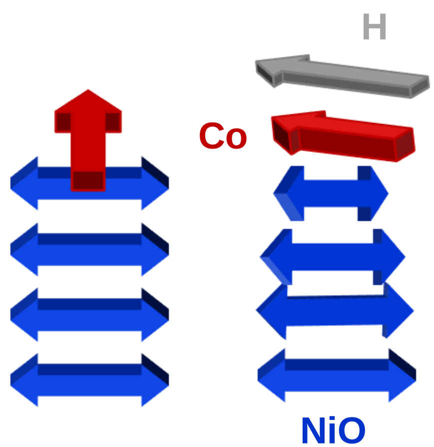






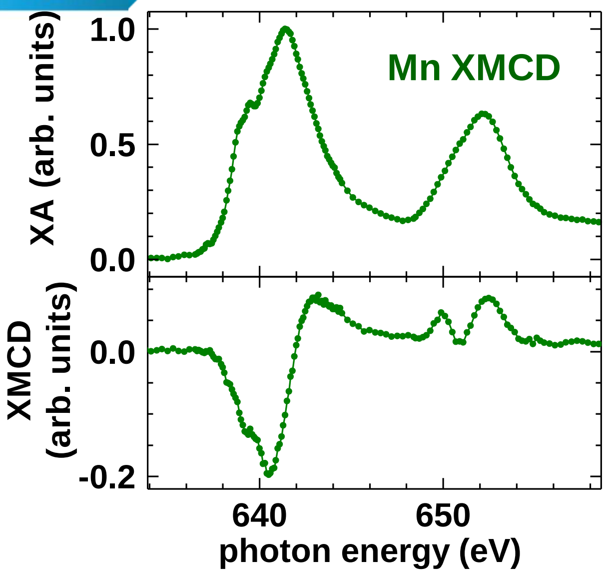


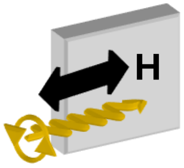




A. Scholl *et al*.,
Phys. Rev. Lett. 92, 247201 (2004)

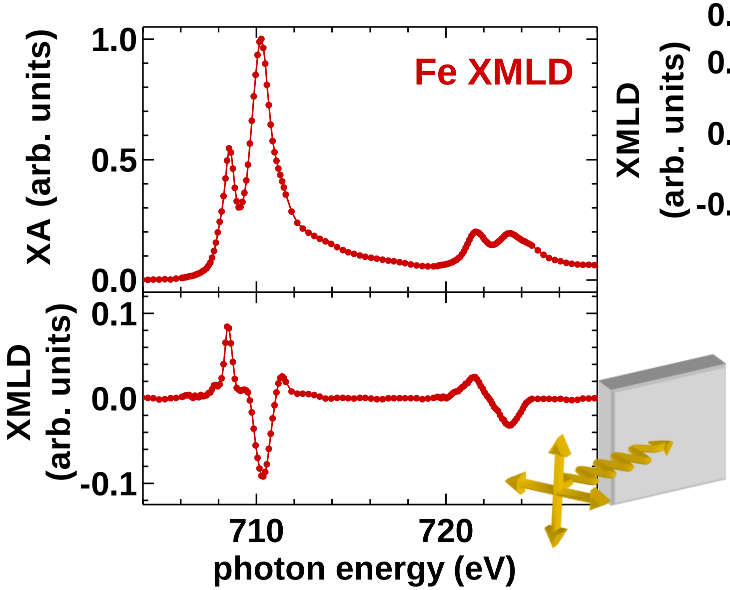
MAGNETIC COUPLING AT INTERFACES

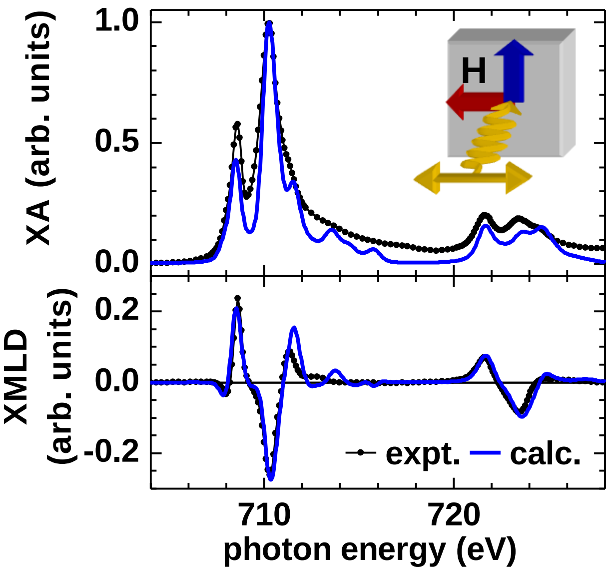


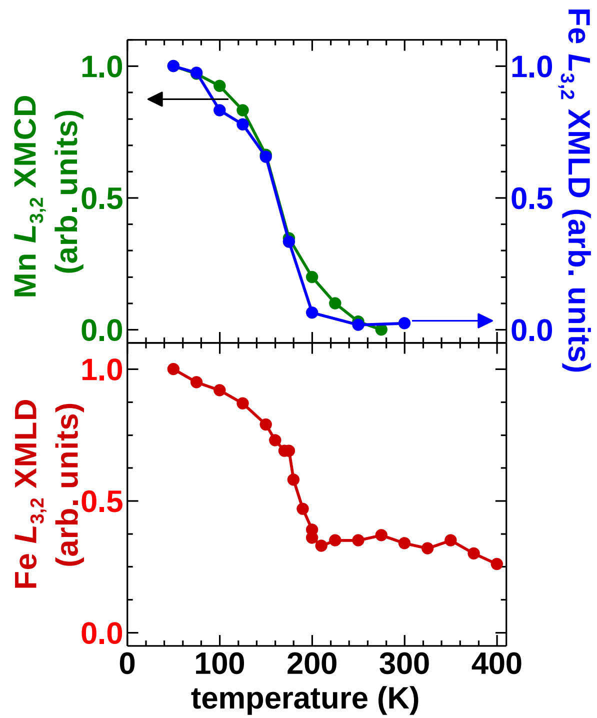


$La_{0.7}Sr_{0.3}MnO_3$ (LSMO)
ferromagnet

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



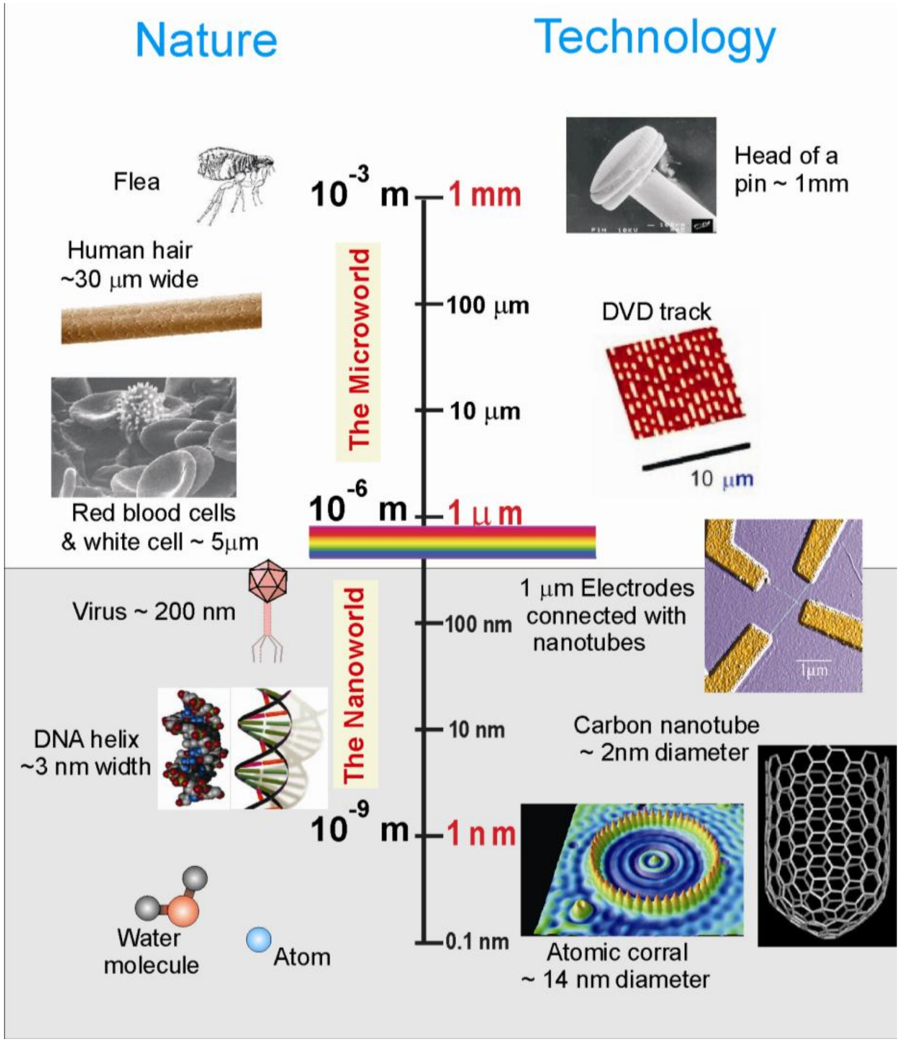




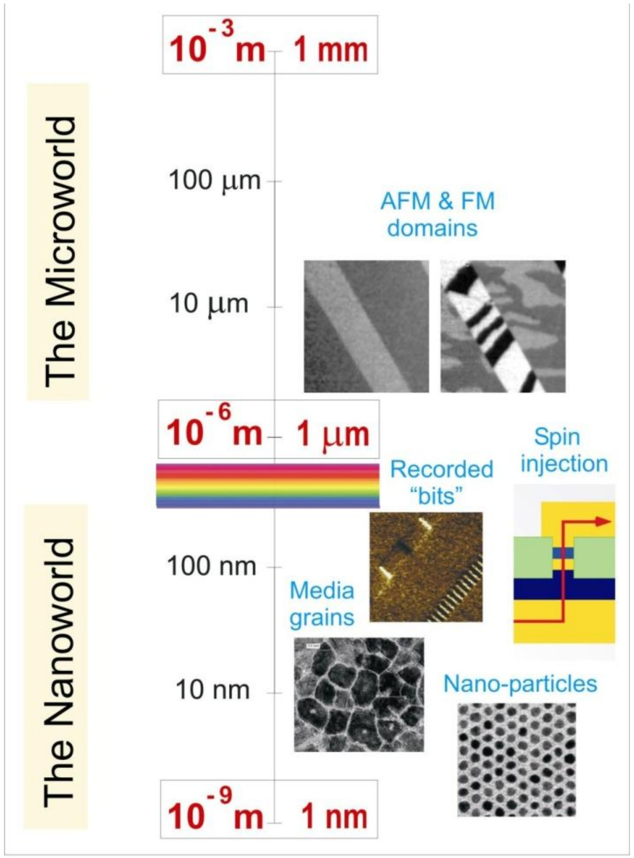
⇒ **Perpendicular coupling at LSMO/LSFO interface**

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

MAGNETIC MICROSCOPY

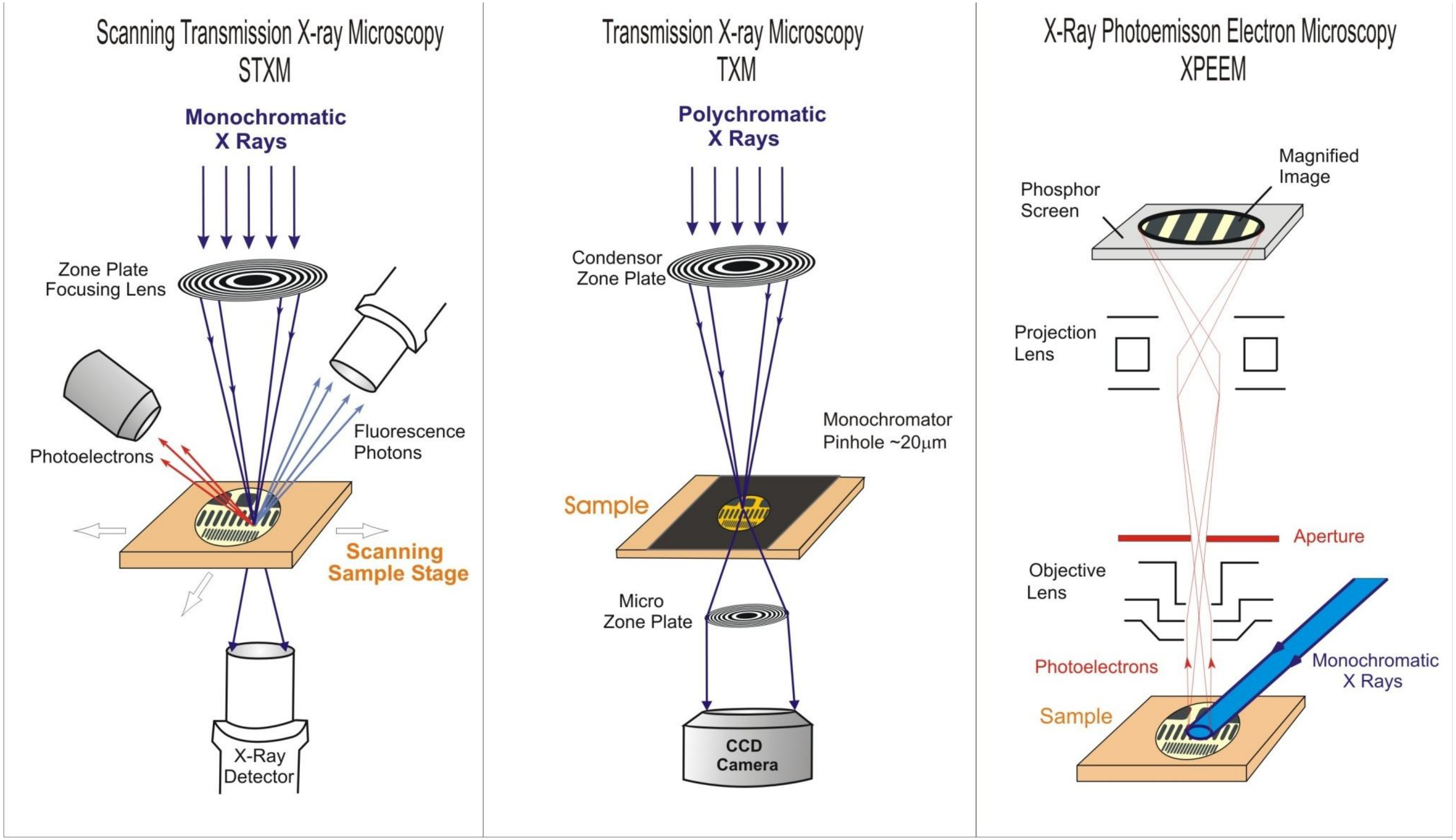


Magnetism



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

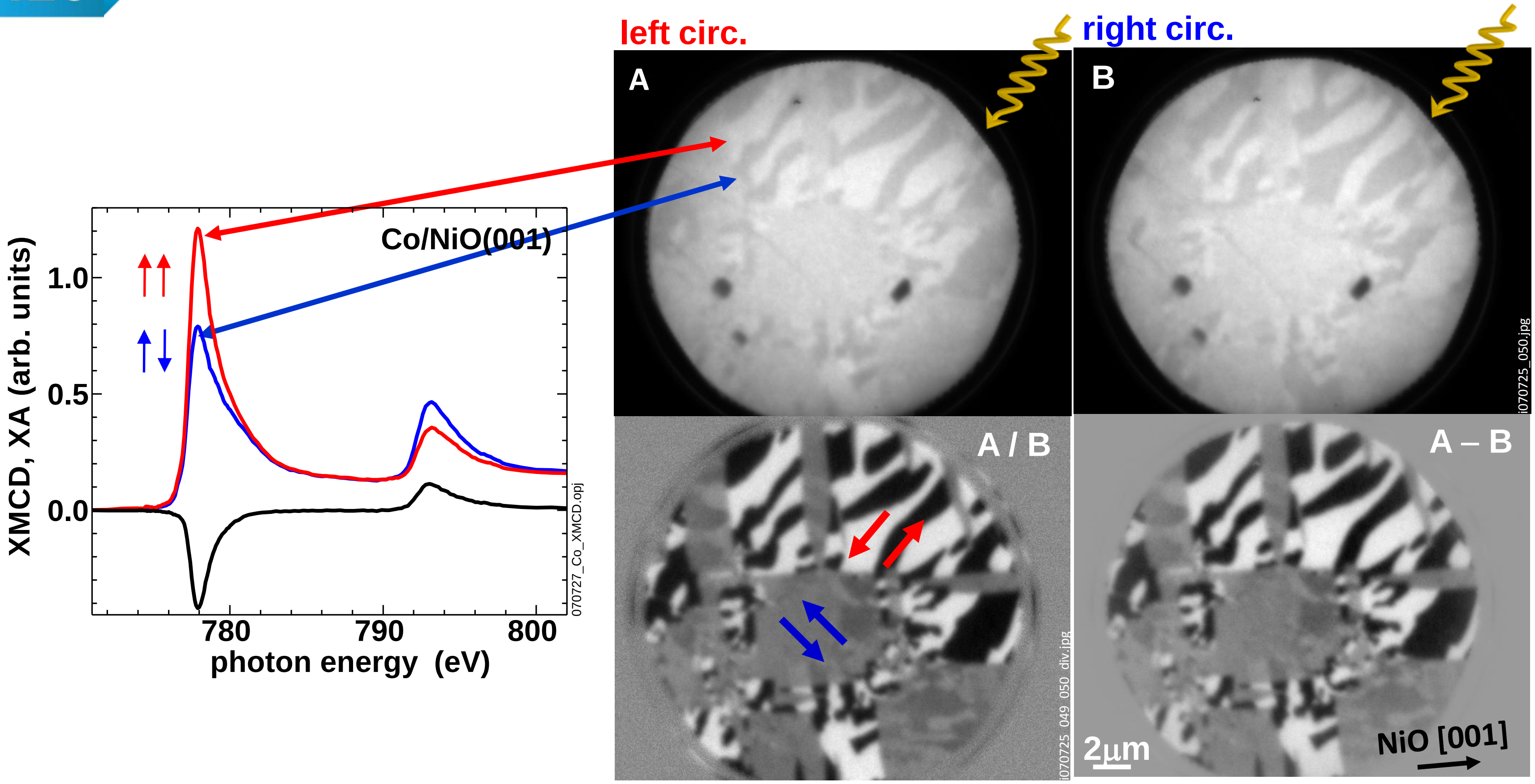
MAGNETIC MICROSCOPY



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

10-50 nm spatial resolution

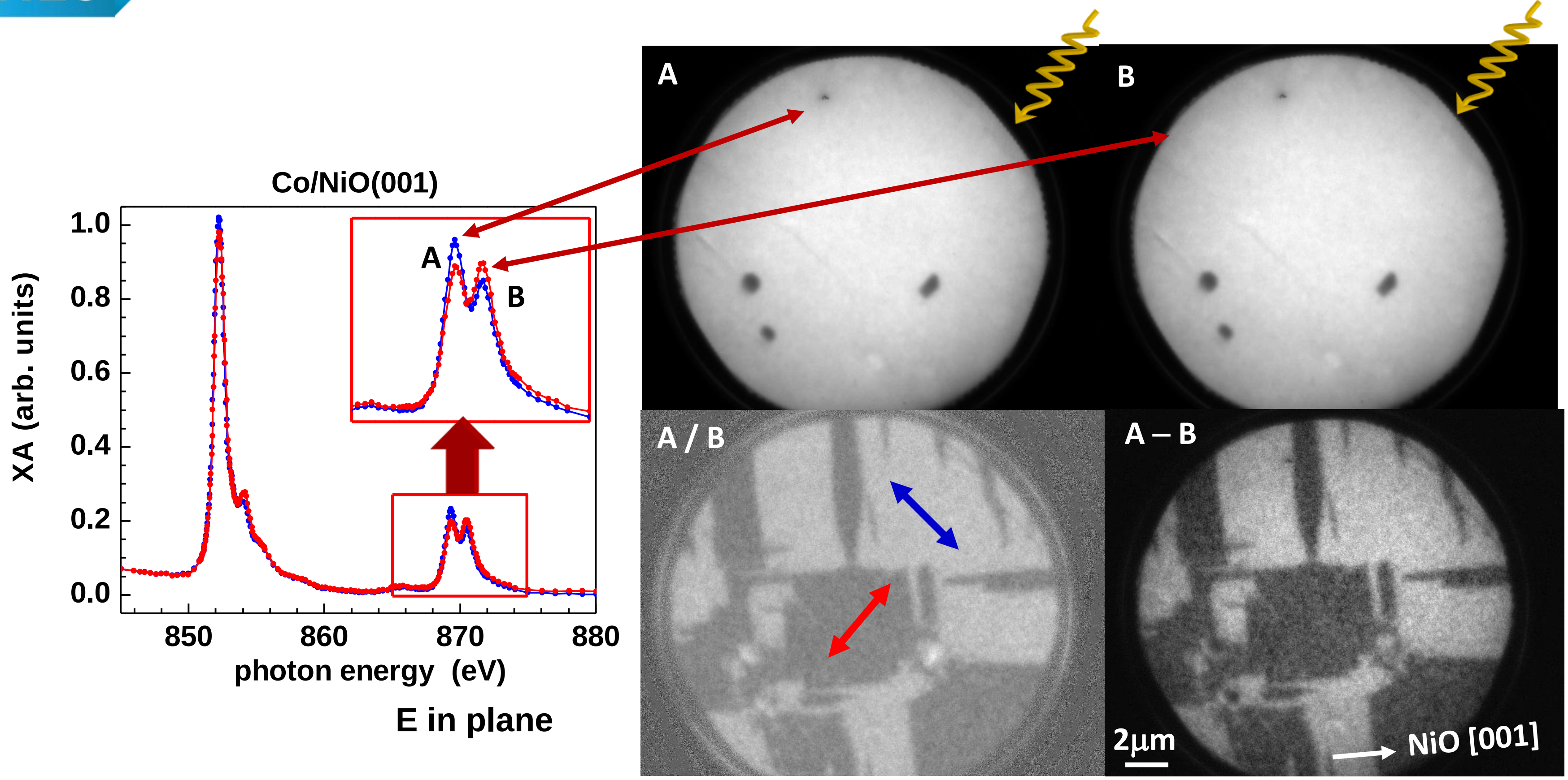
IMAGING FERROMAGNETIC DOMAINS USING XMCD



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.**

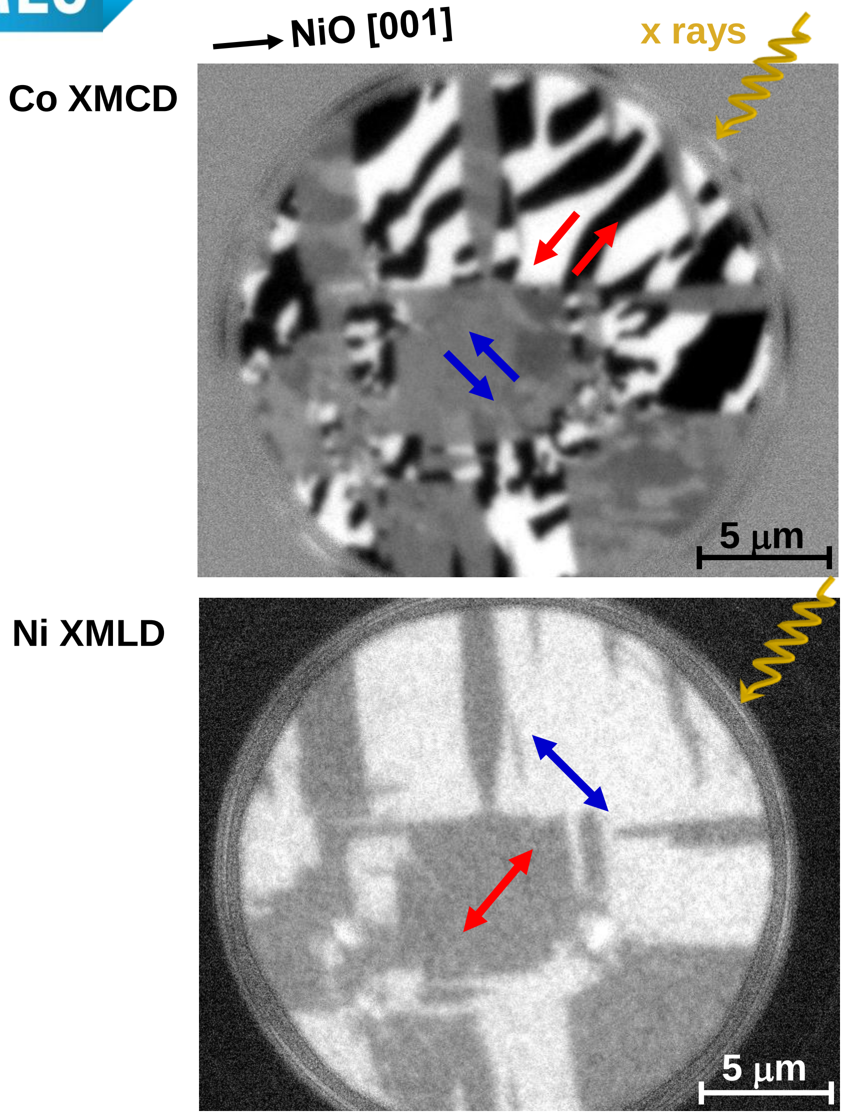
IMAGING ANTIFERROMAGNETIC DOMAINS USING XMLD



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

+ **Images taken with linearly polarized x-rays at photon energies with XMLD, i.e. Ni L_2 edge, provide magnetic contrast and domain images.**

MAGNETIC COUPLING AT Co/NiO INTERFACE



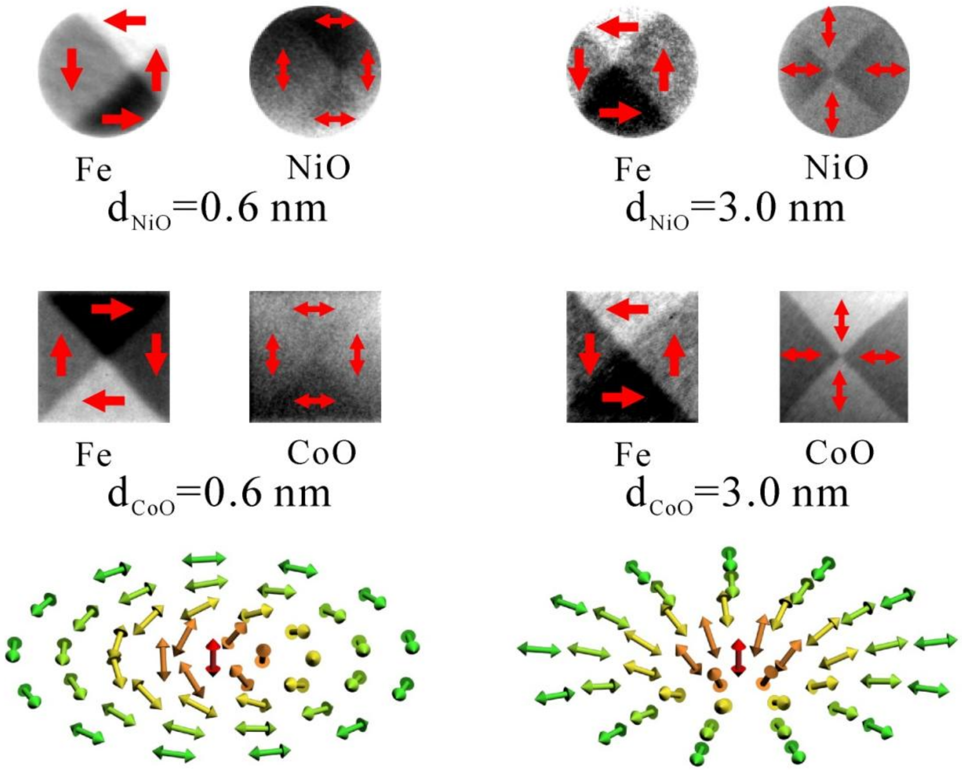
probing in-plane

- Taking into account the geometry dependence of the Ni XMLD signal
  ⇒ Perpendicular coupling of Co and NiO moments at the interface.

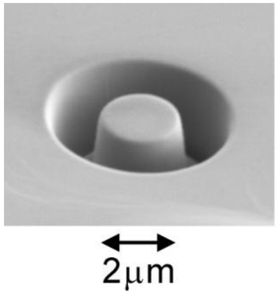
E. Arenholz *et al.*,
Appl. Phys. Lett. <u>93</u>, 162506 (2008)

OBSERVATION OF ANTIFERROMAGNETIC 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

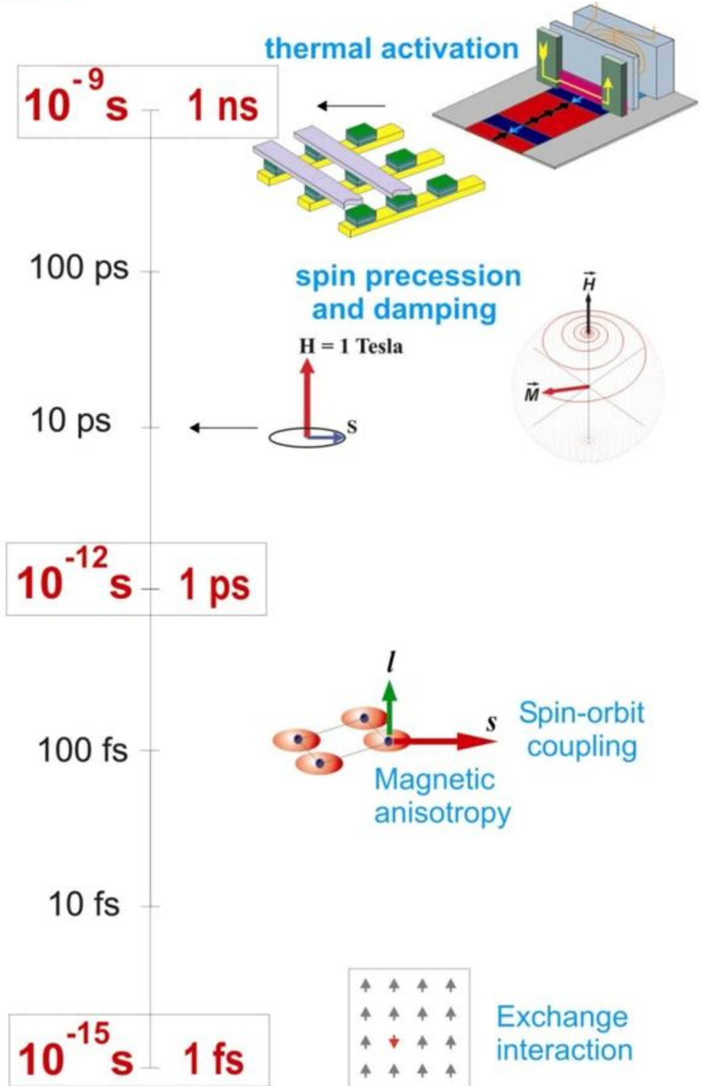


conventional curling vortex **divergent vortex**



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

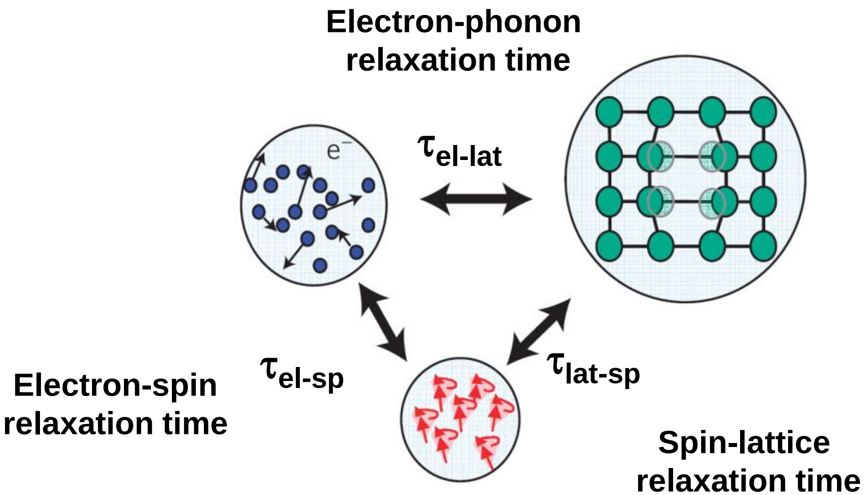
ULTRAFAST MAGNETISM



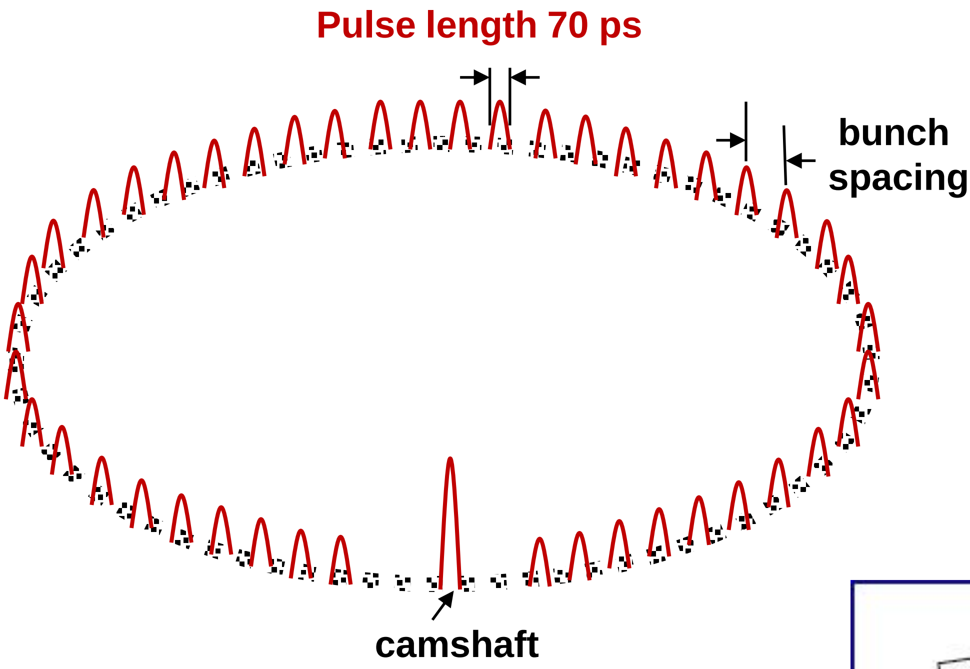
J. Stöhr, H.C. Siegmann, Magnetism (Springer)

+ Energy reservoirs in a ferromagnetic metal
+ Deposition of energy in one reservoir

⇒ Non-equilibrium distribution and subsequent relation through energy and angular momentum exchange

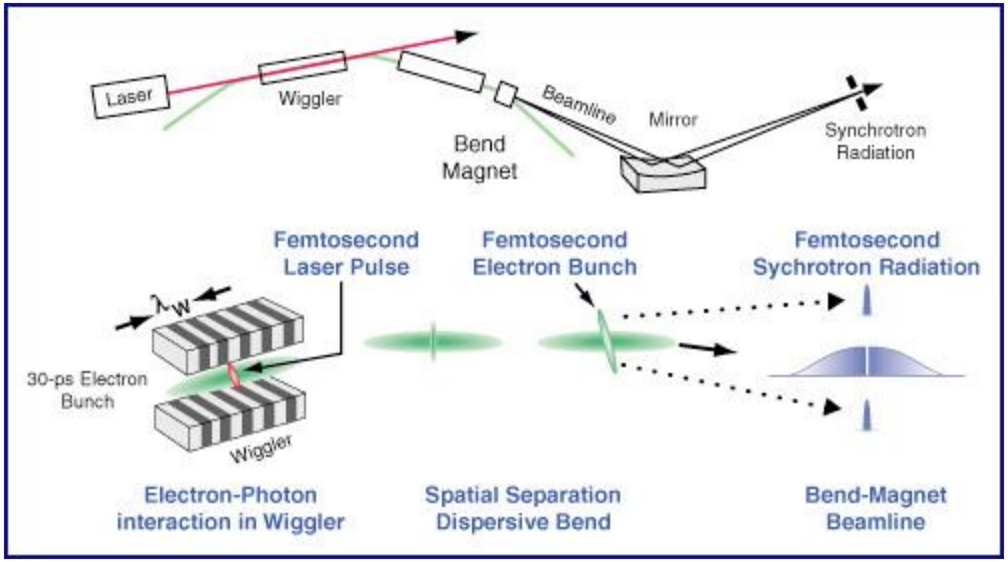


ALS TIME STRUCTURE

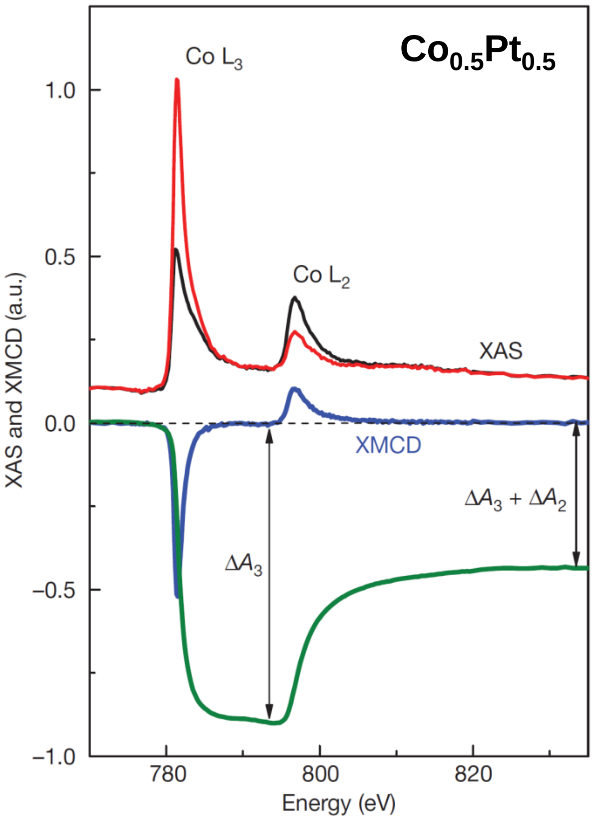


- 256-320 bunches for 500mA beam current
- Possibility of one or two 5mA "camshaft" bunches in filling gaps
- Bunch spacing:
  multibunch mode: 2 ns
  two-bunch mode: 328 ns
- Pulse length 70ps

- <300 fs x ray pulses though “laser bunch-slicing technique”



ULTRAFAST DYNAMICS OF SPIN AND ORBITAL MOMENTS

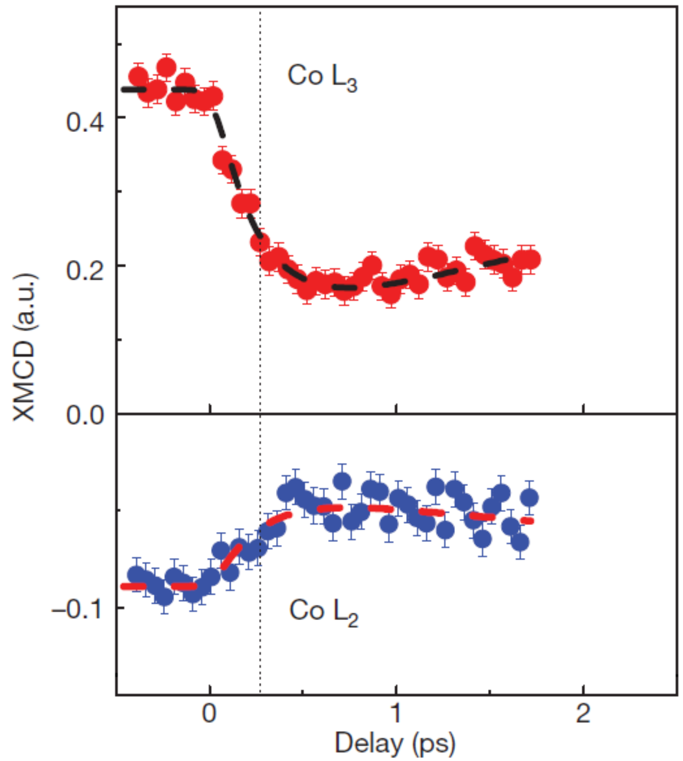


C. Boeglin, *et al.*,
Nature 465, 458 (2010)

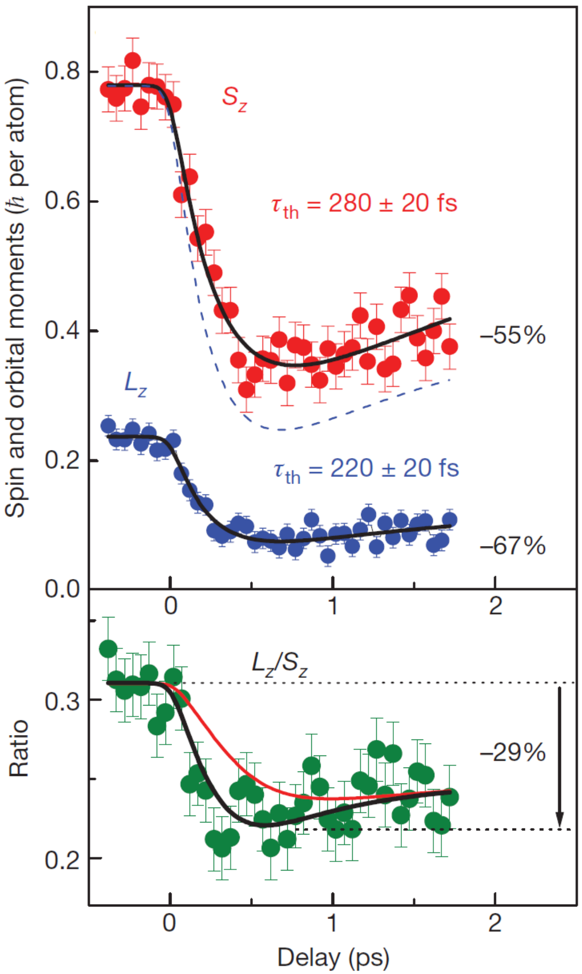
- **Orbital (*L*) and spin (*S*) magnetic moments can change with total angular momentum is conserved.**
- **Efficient transfer between *L* and S through spin–orbit interaction in solids**
- **Transfer between *L* and *S* occurs on fs timescales.**

- **$Co_{0.5}Pt_{0.5}$ with perpendicular 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**

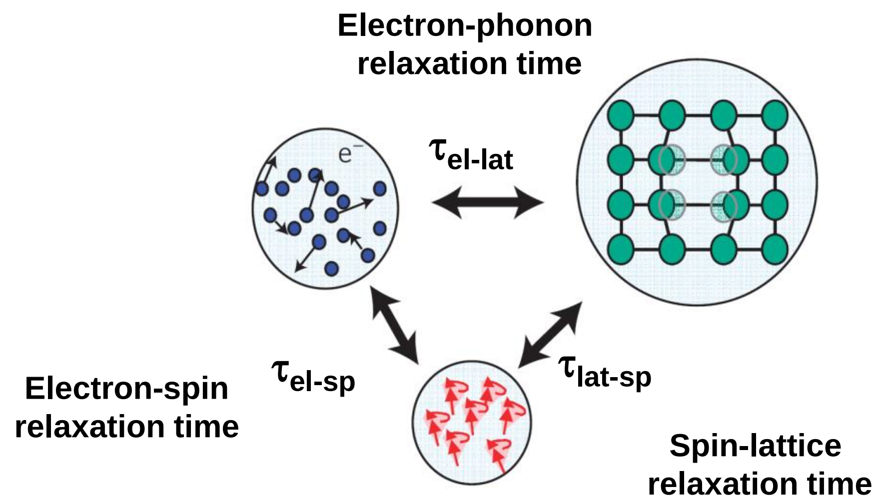


ULTRAFAST DYNAMICS OF SPIN AND ORBITAL MOMENTS

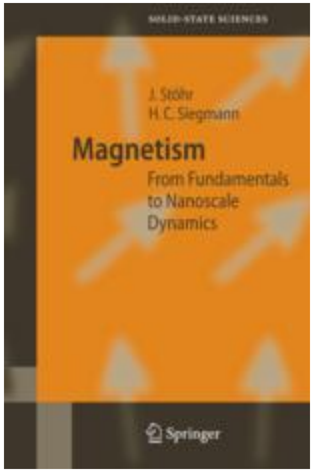


C. Boeglin, *et al.*,
Nature 465, 458 (2010)

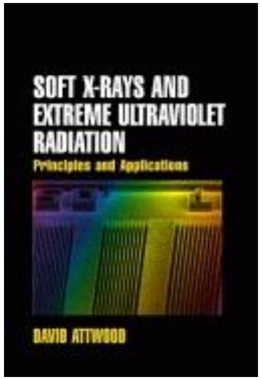
+ Thermalization: Faster decrease of orbital moment
+ Theory: Orbital magnetic moment strongly correlated with magnetocrystalline anisotropy
+ Reduction in orbital moment
  ⇔ Reduction in magnetocrystalline anisotropy
+ Typically observed at elevated temperatures in static measurements as well



REFERENCES AND FURTHER READING



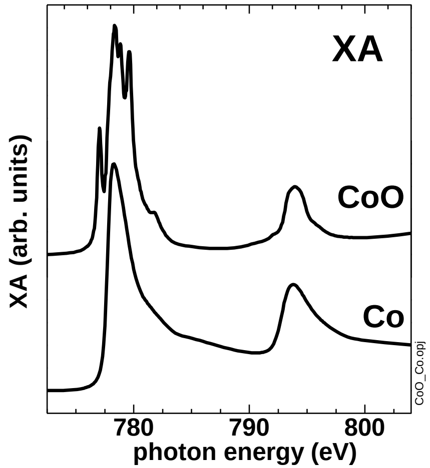
J. Stöhr, H.C. Siegmann
Magnetism– From Fundamentals to Nanoscale Dynamics
Springer



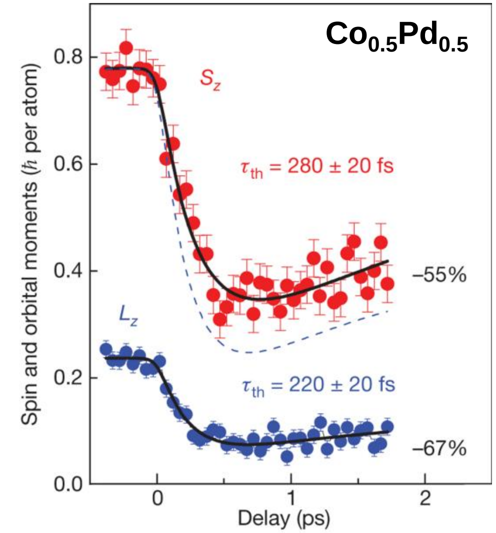
D. Attwood
Soft X-Rays and Extreme Ultraviolet Radiation:
Principles and Applications

MAGNETIC SPECTROSCOPY

Elke Arenholz, Advanced Light Source



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



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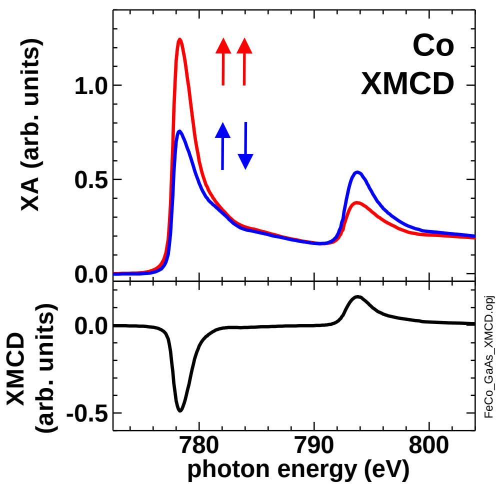

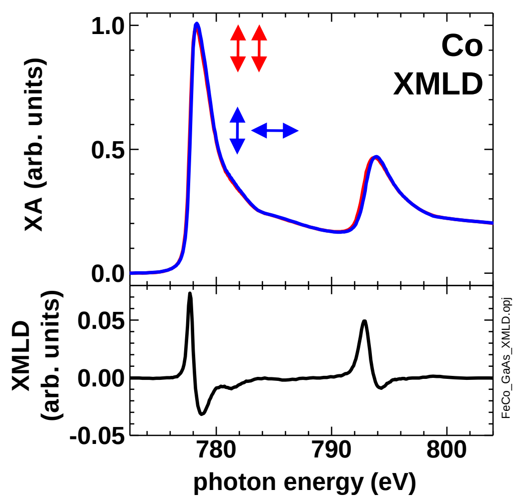

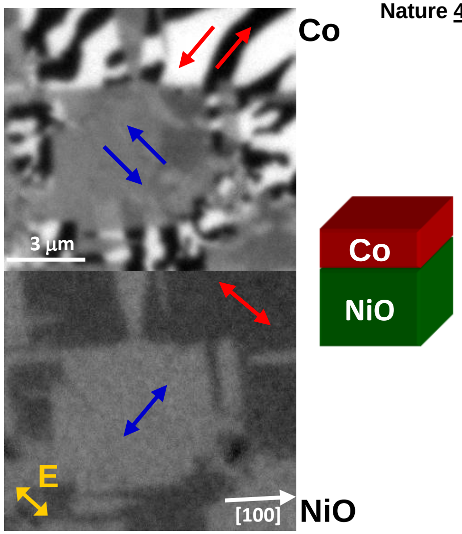

E. Arenholz *et al.*, Appl. Phys. Lett. 93, 162506 (2008)