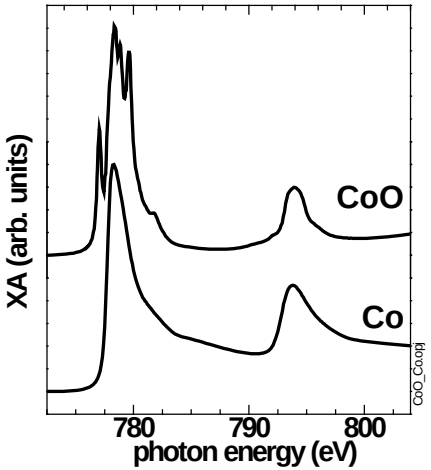
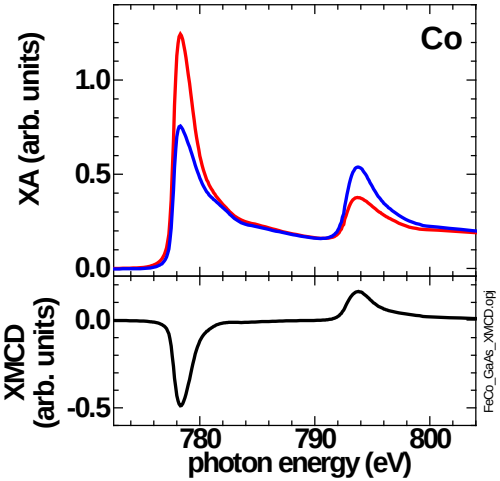
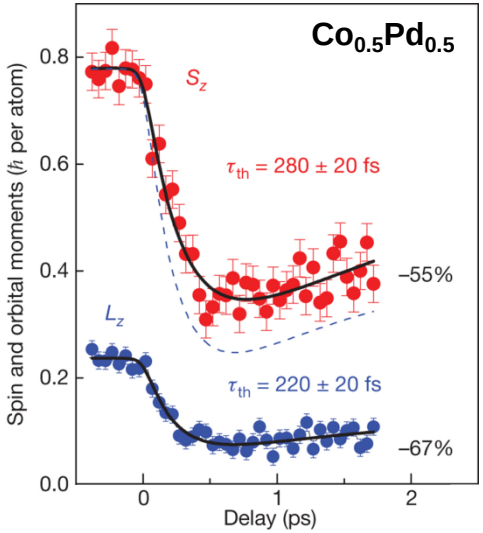
MAGNETIC SPECTROSCOPY

Elke Arenholz, Advanced Light Source

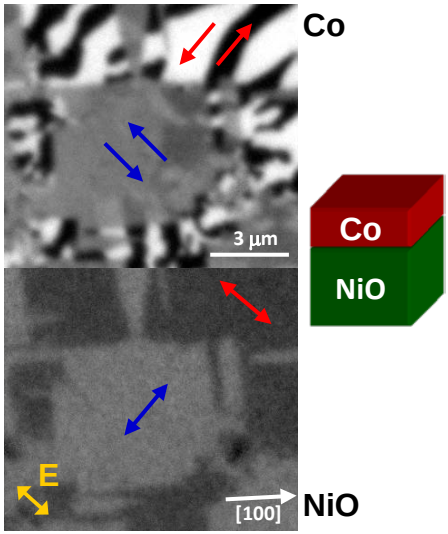


+ X ray absorption, XA
+ X ray magnetic circular dichoism, XMCD
+ X ray magnetic linear dichroism, XMLD
+ X ray magnetic microscopy
+ Magnetization Dynamics

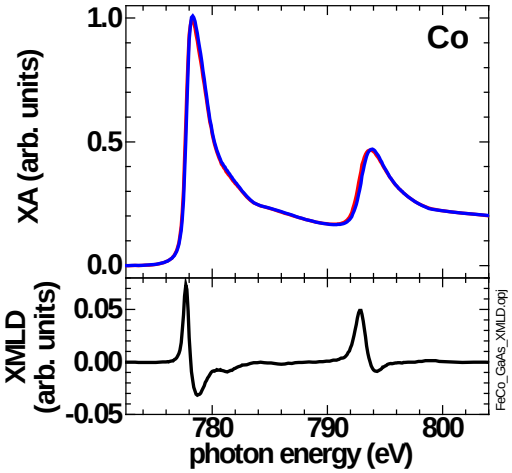




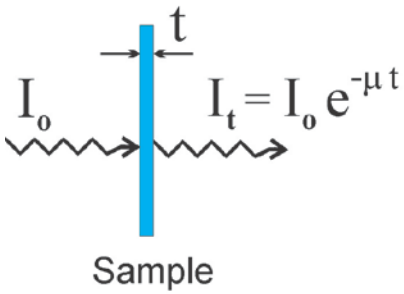
C. Boeglin *et al.*, Nature 465, 458 (2011)



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



X-RAY ABSORPTION – THE SIMPLEST X RAY TECHNIQUE

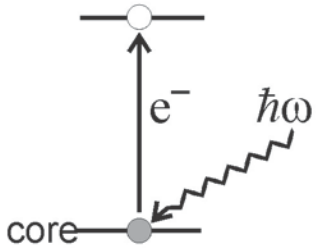


Experiment/Measurement:

Reduction in x ray flux transmitted through a sample.

X-ray absorption:

+ Electrons excited from core shells to unoccupied valence states through the 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

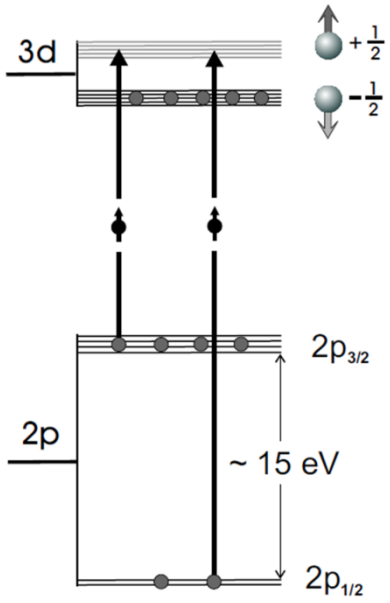
Configuration model, e.g. *L* edge absorption :

+ 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)

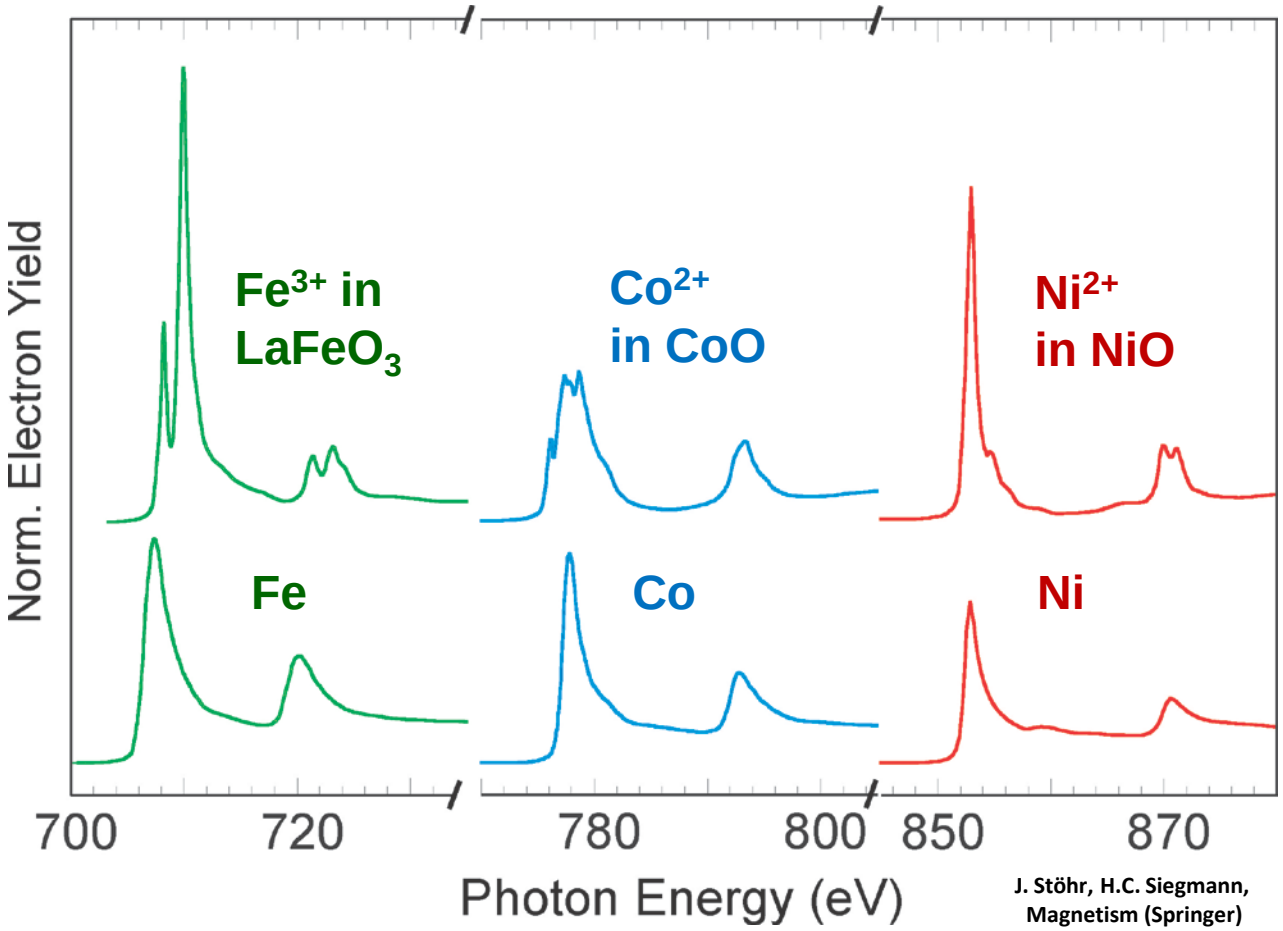
+ Takes into account correlation effects
in the ground state as well as
in the excited state

+ Leads to multiplet effects/structure



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

X-RAY ABSORPTION



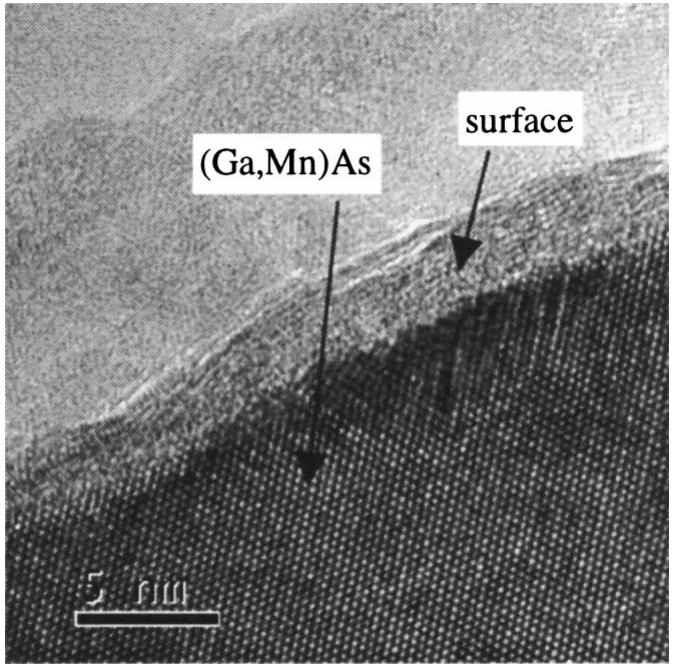
J. Stöhr, H.C. Siegmann, Magnetism (Springer)

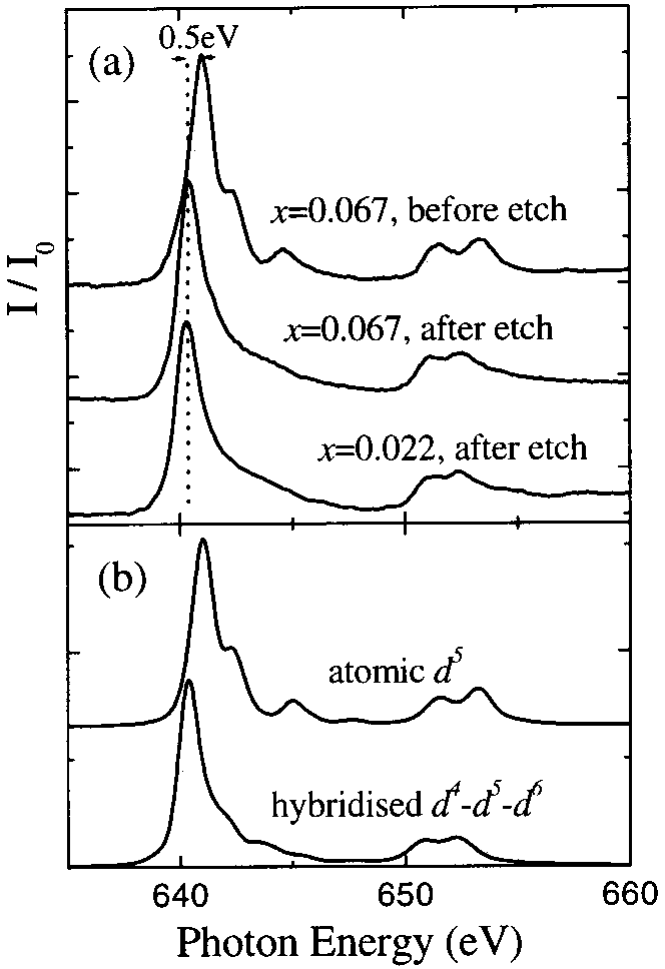
XA provides

+ elemental specificity

+ sensitivity to valence shell properties, i.e. valence state and lattice site symmetry

SURFACE EFFECTS IN (Ga,Mn)As

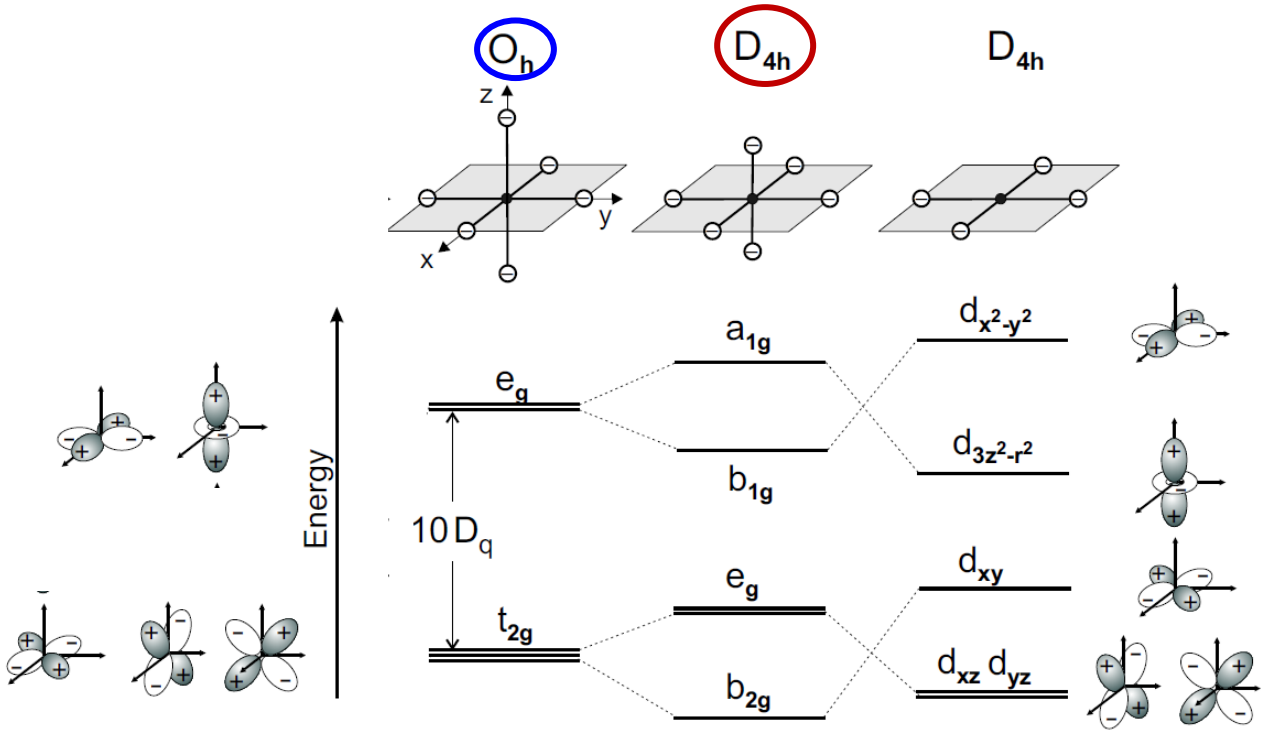




+ As grown/before etch:
  - Multiplet structure characteristic of MnO
+ After removal of the surface layer:
  - Multiplet structure is less pronounced
  - Spectrum shifted to 0.5 eV lower photon energy.
+ Comparison with calculated spectra:
  - localized Mn ground state for the untreated sample
  - hybridized ground state after etching.

K. Edmonds *et al.*,
Appl. Phys. Lett. 84, 4065(2004)

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**

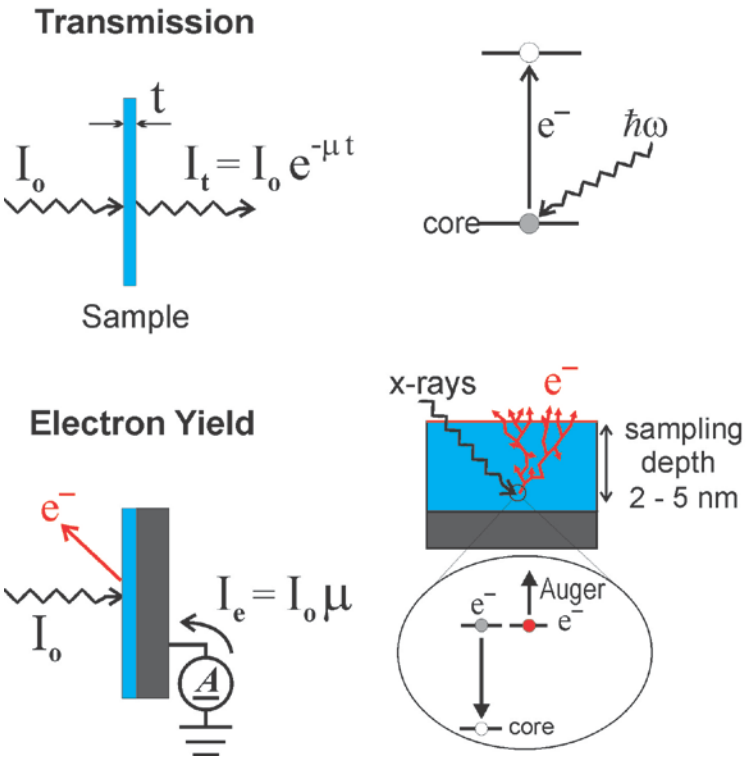
t_2 orbitals between ligands → lower energy

Tetragonal symmetry:

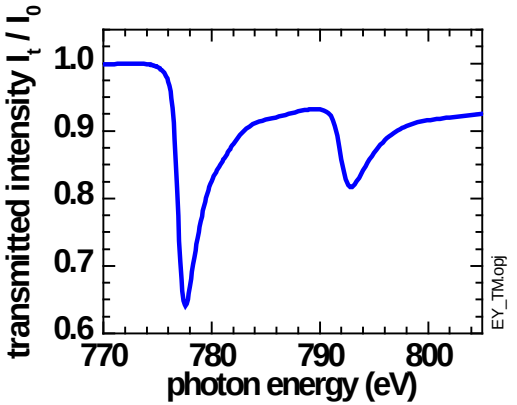
***e* orbitals → $b_2 = d_{xy}$, $e = d_{yz}, d_{yz}$**

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

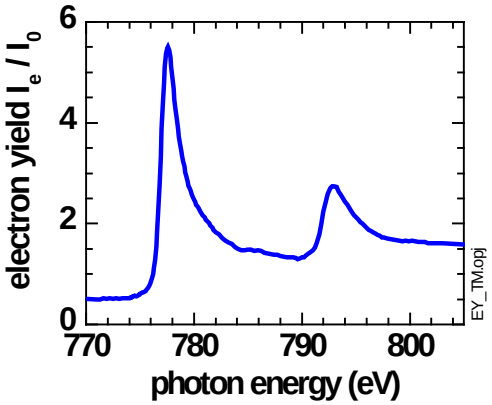
X-RAY ABSORPTION – MEASUREMENTS



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



photons absorbed

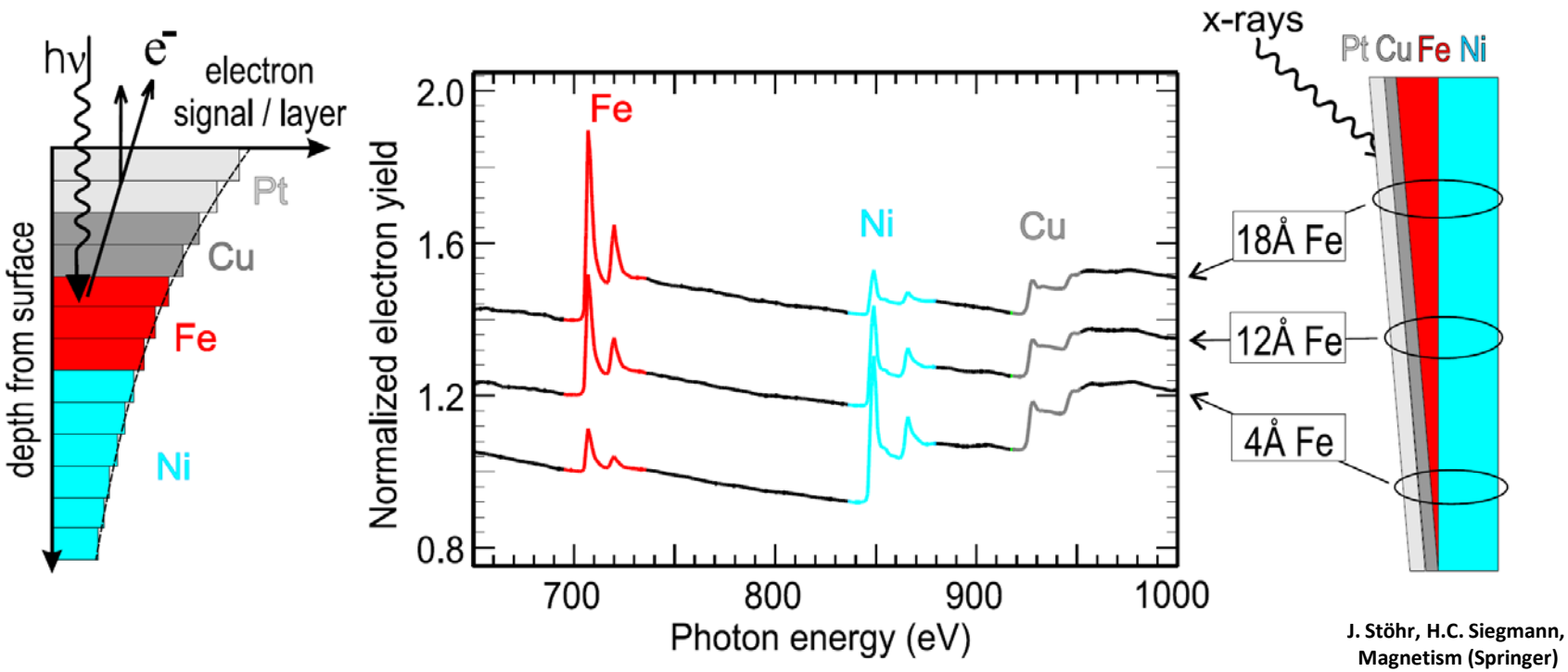


electrons generated

Electron yield:

+ Absorbed photons create core holes that are 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

SAMPLING DEPTH OF ELECTRON YIELD



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

+ **Electron sample depth: 2nm in Fe, Co, Ni**

  ⇒ 60% of the electron yield originates form the topmost 2nm

+ **X ray absorption length: 500nm before the absorption edge**

  20nm at the L_3 edge

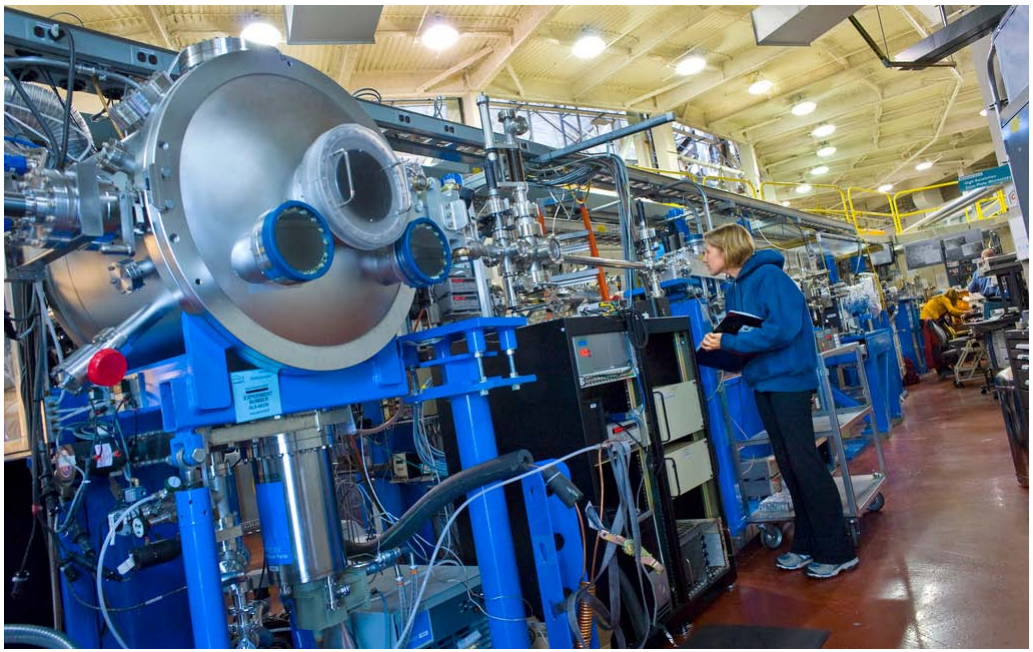
PHOTON SOURCES AND MONOCHROMATORS

Advanced Light Source

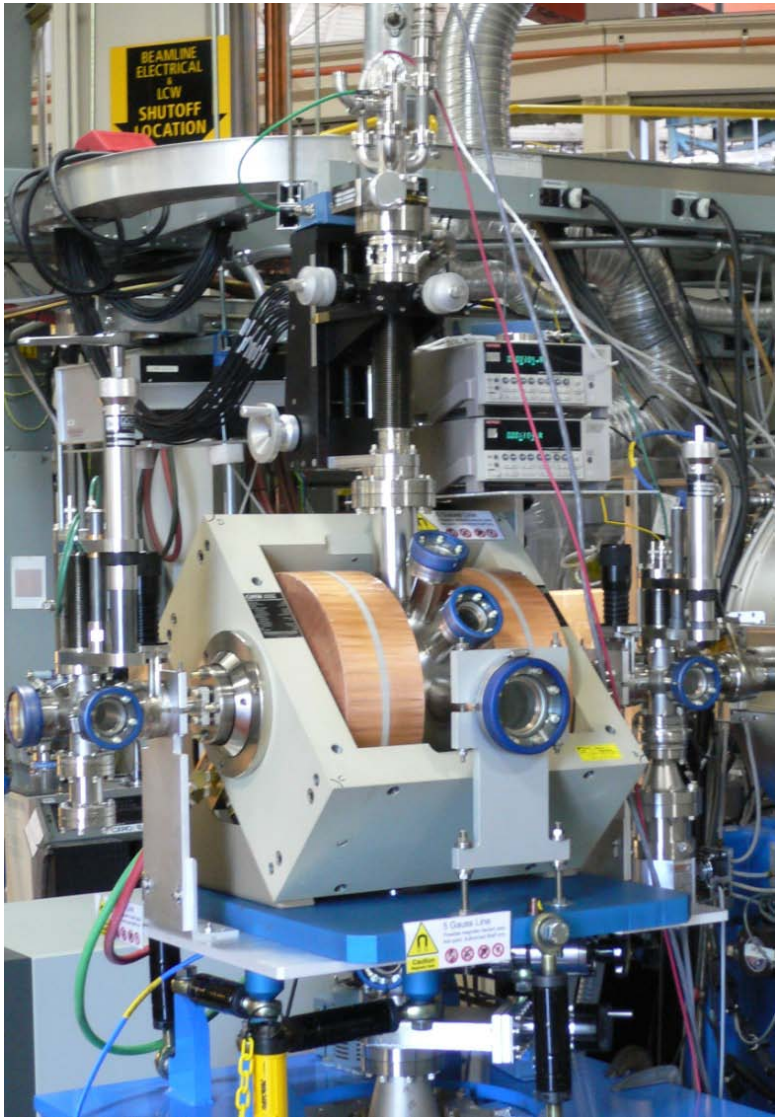
+ **Tunable photon source in the soft x ray range, 200-2000eV, i.e. undulator or bend magnet, at synchrotron.**

+ **Beamlines/Monochromators provide photons with well defined characteristics:**
  - tunable energy/wavelength
  - fixed polarization: (variable) linear, circular, elliptical, …

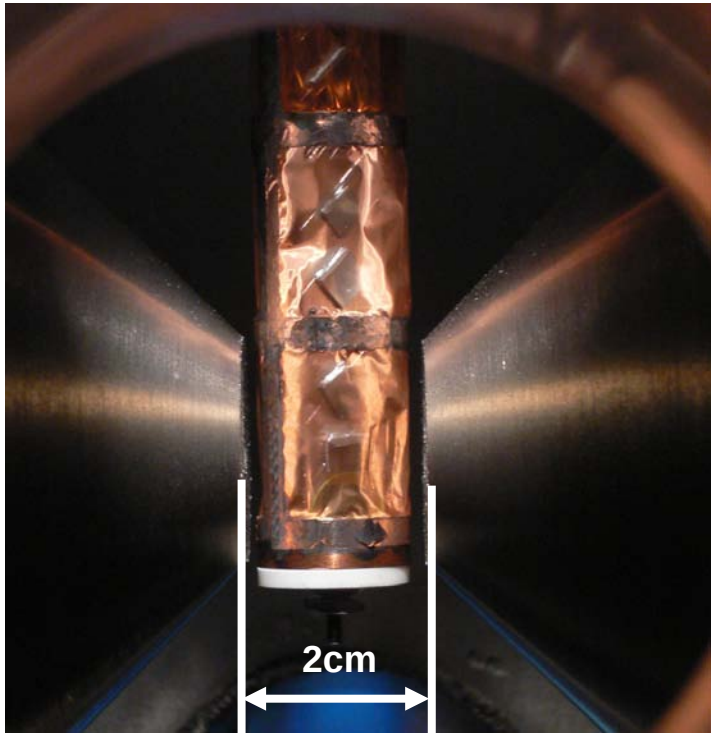
BL6.3.1



ENDSTATIONS

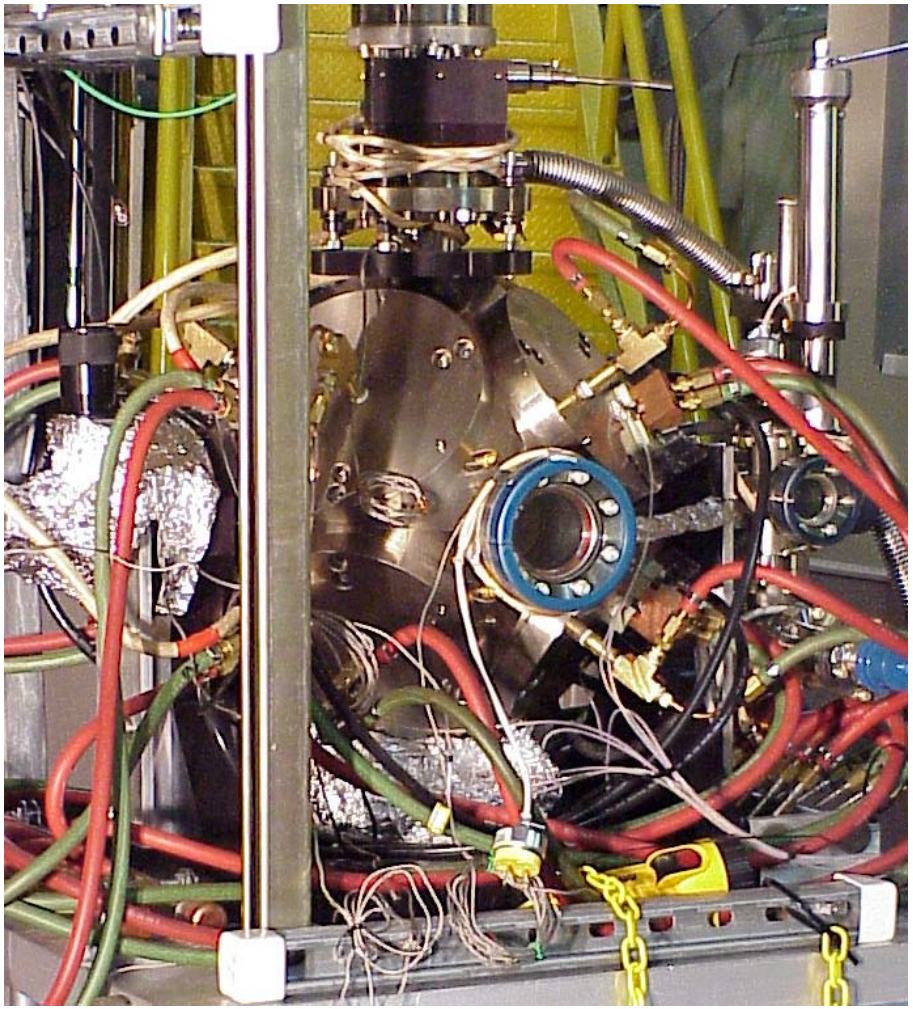


+ **Endstations provide well defined sample environments for the interaction with photons:**
  - **precisely defined experimental geometries**
  - **sample temperature**
  - **external magnetic and electric fields**
  - **…**



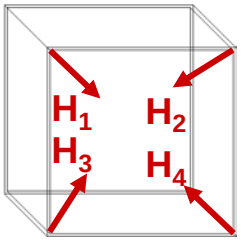
2T magnet at ALS BL6.3.1

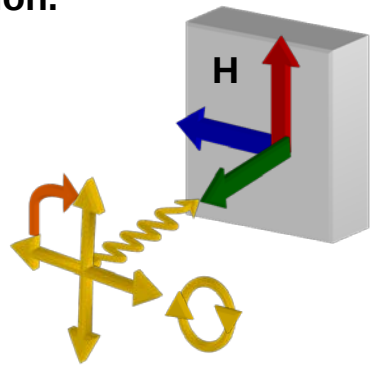
ENDSTATIONS

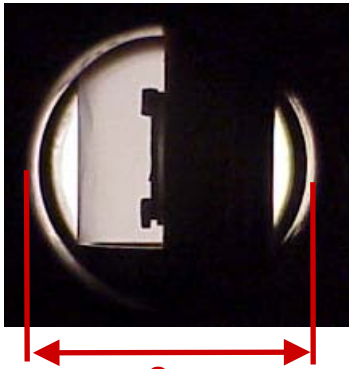


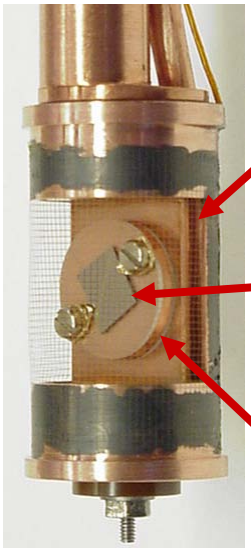
Vector magnet at ALS BL4.0.2

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

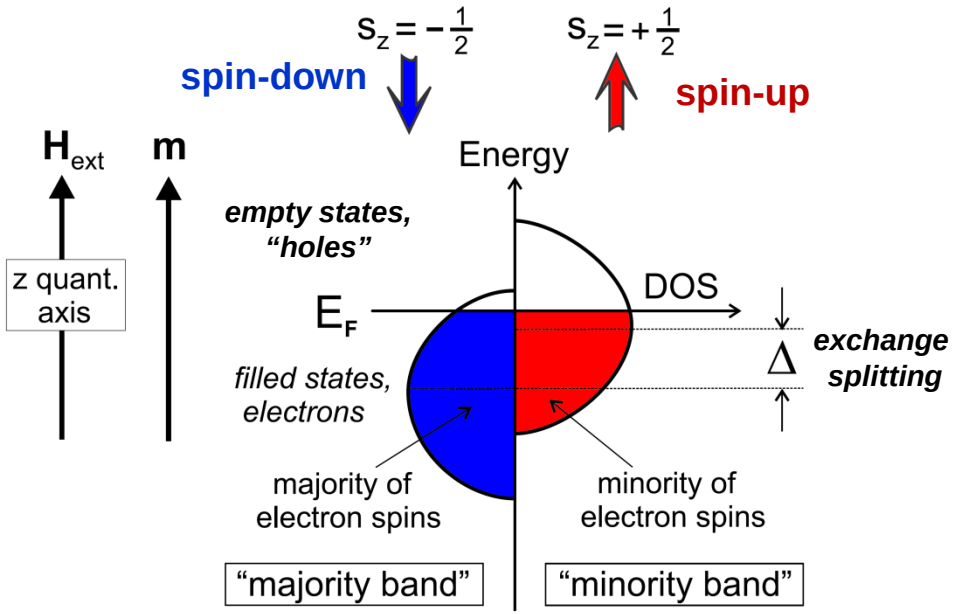








STONER MODEL FOR FERROMAGNETIC TRANSITION METALS



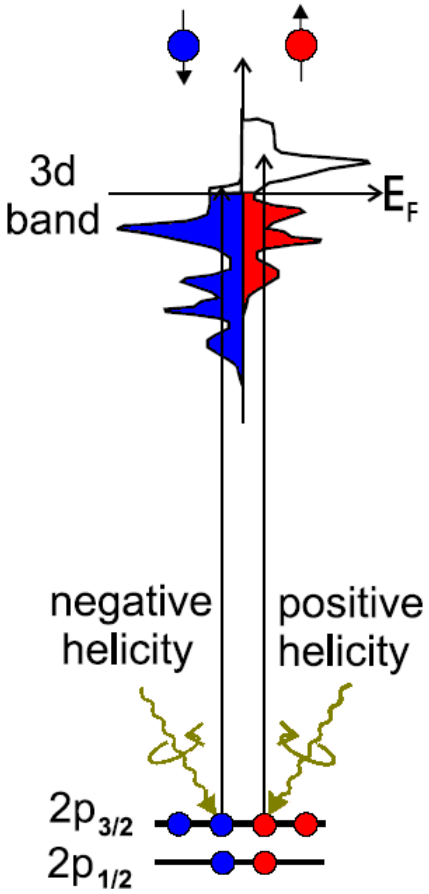
J. Stöhr, H.C. Siegmann, Magnetism (Springer)

3*d* shell

+ **Magnetic moments in Fe, Co, Ni are well described by the 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 the difference in number of electrons in majority and minority bands**

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

TWO-STEP MODEL OF XMCD



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

Photoelectrons excited from $2p_{3/2}$, $2p_{1/2}$ 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 act on the spin and

$\Rightarrow$ No spin flips during excitation.

+ Conservation of angular momentum

$\Rightarrow$ transfer of angular momentum ($\pm\hbar$) from photon to electron

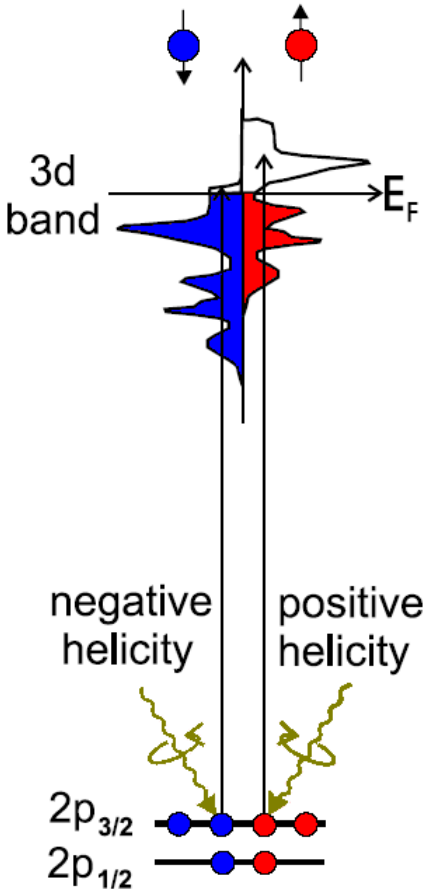
+ Spin-orbit coupling: Angular momentum of photon transferred in part to electron spin

$\Rightarrow$ Excited photoelectrons are spin polarized

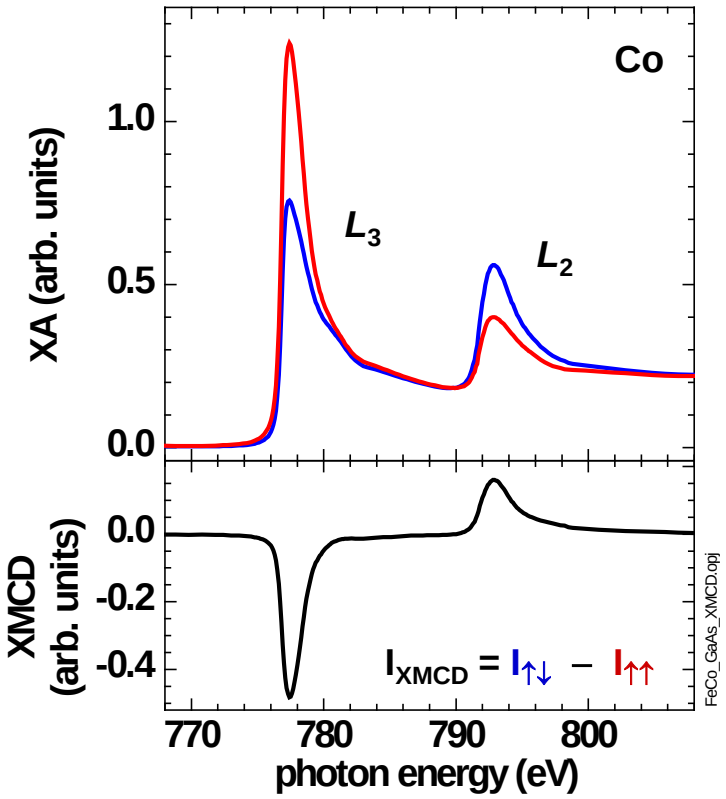
Second step:

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

TWO-STEP MODEL OF XMCD



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



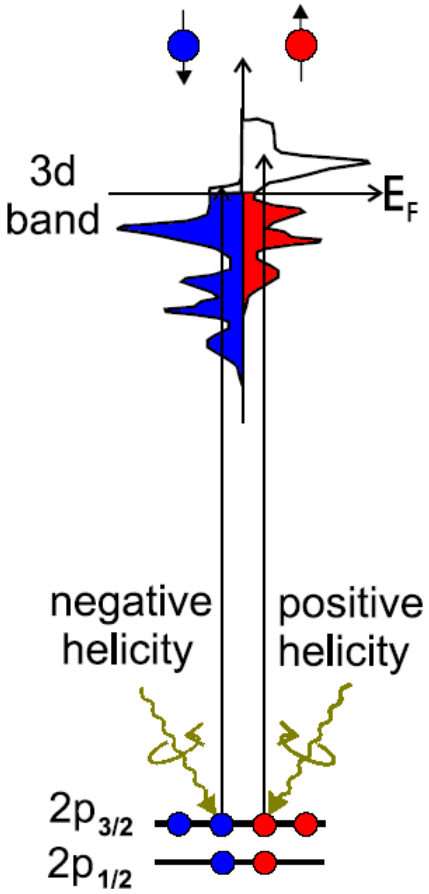
Magnitude of the dichroism effect depends on

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

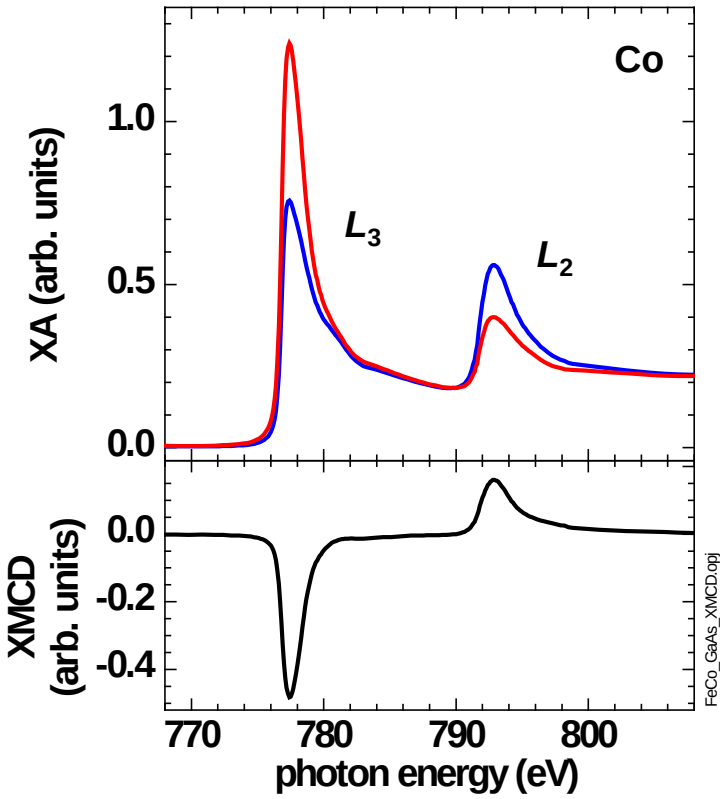
$$I_{XMCD} \propto P_{circ} \langle m \rangle \cos\theta$$

- **XMCD allows studying ferri- and ferromagnets.**

TWO-STEP MODEL OF XMCD

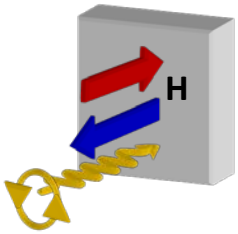


J. Stöhr, H.C. Siegmann,
Magnetism (Springer)

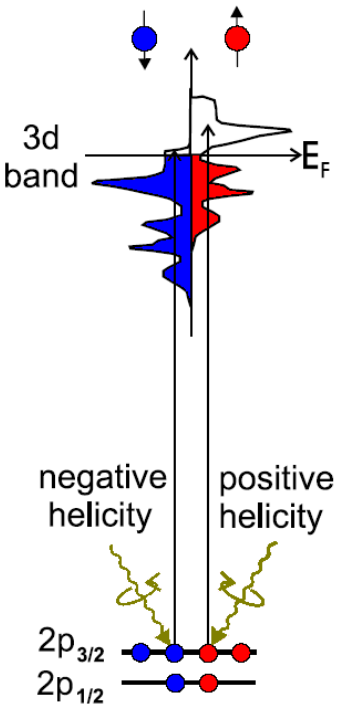


+ $2p_{3/2}$ and $2p_{1/2}$ have opposite spin orbit coupling (l+s, l –s)
  ⇒ Spin polarization and XMCD have opposite sign at two edges
+ Spin polarization opposite for x rays with opposite helicity, i.e. photon spin, ±ħ
  ⇒ XMCD reverses sign with polarization
+ Reversing the x ray polarization is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

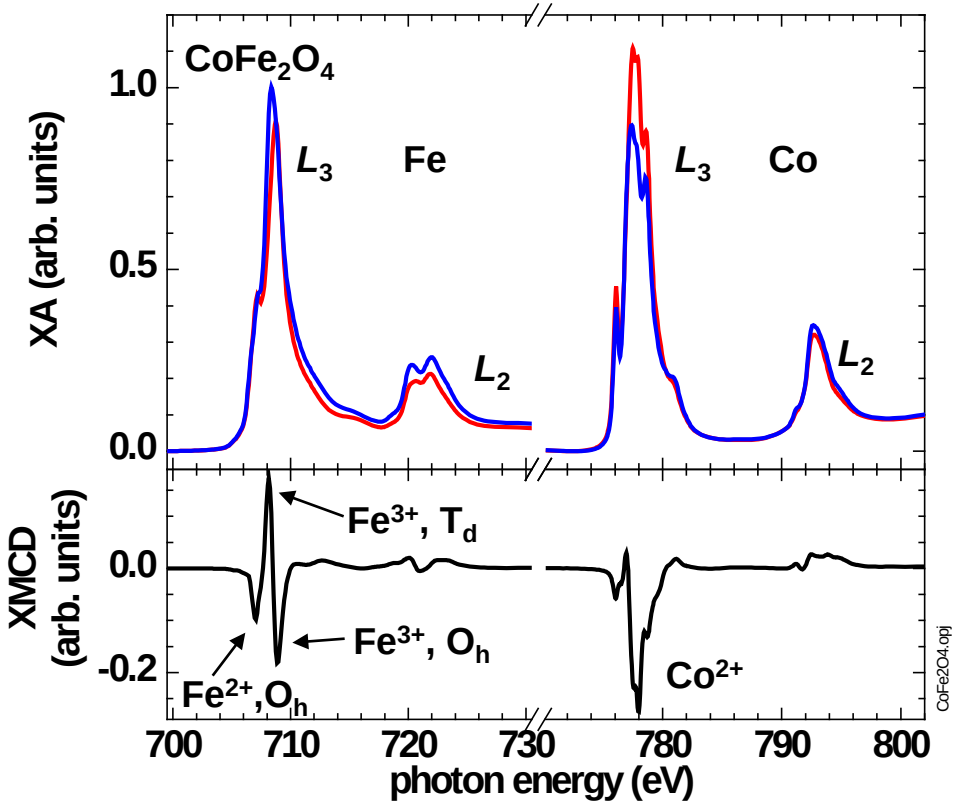
X RAY MAGNETIC CIRCULAR DICHROISM (XMCD)



circularly polarized



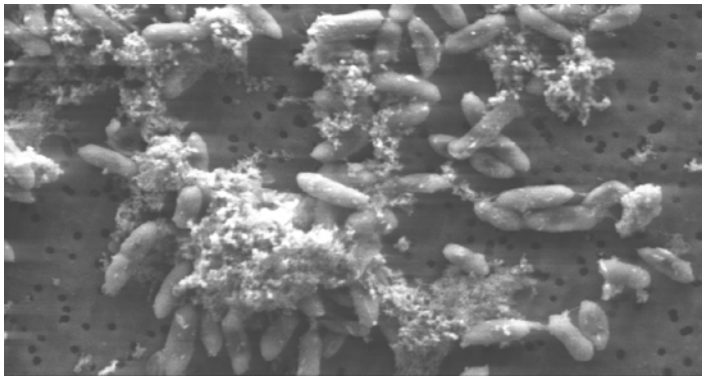
J. Stöhr, H.C. Siegmann, Magnetism (Springer)



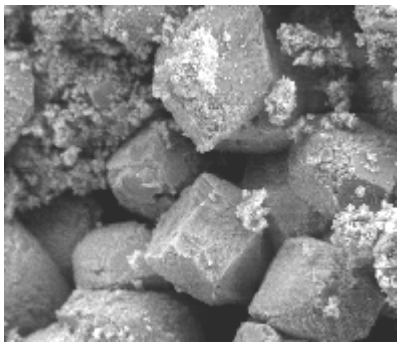
+ XMCD provides magnetic information resolving elements Fe, Co, …
valence states: Fe^{2+}, Fe^{3+}, …
lattice sites: octahedral, O_h, tetrahedral, T_d, …

CHARACTERISTICS OF MAGNETIC BIONANOSPINELS

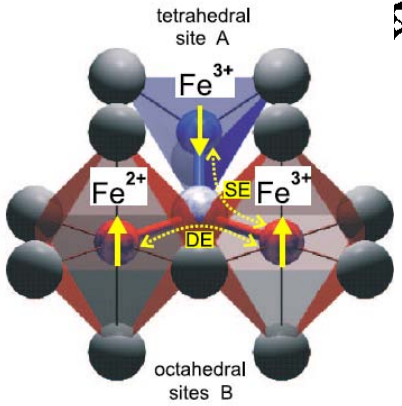
+ **Geobacter sulfurreducens bacteria form magnetite via extracellular reduction of amorphous Fe(III)-bearing minerals**

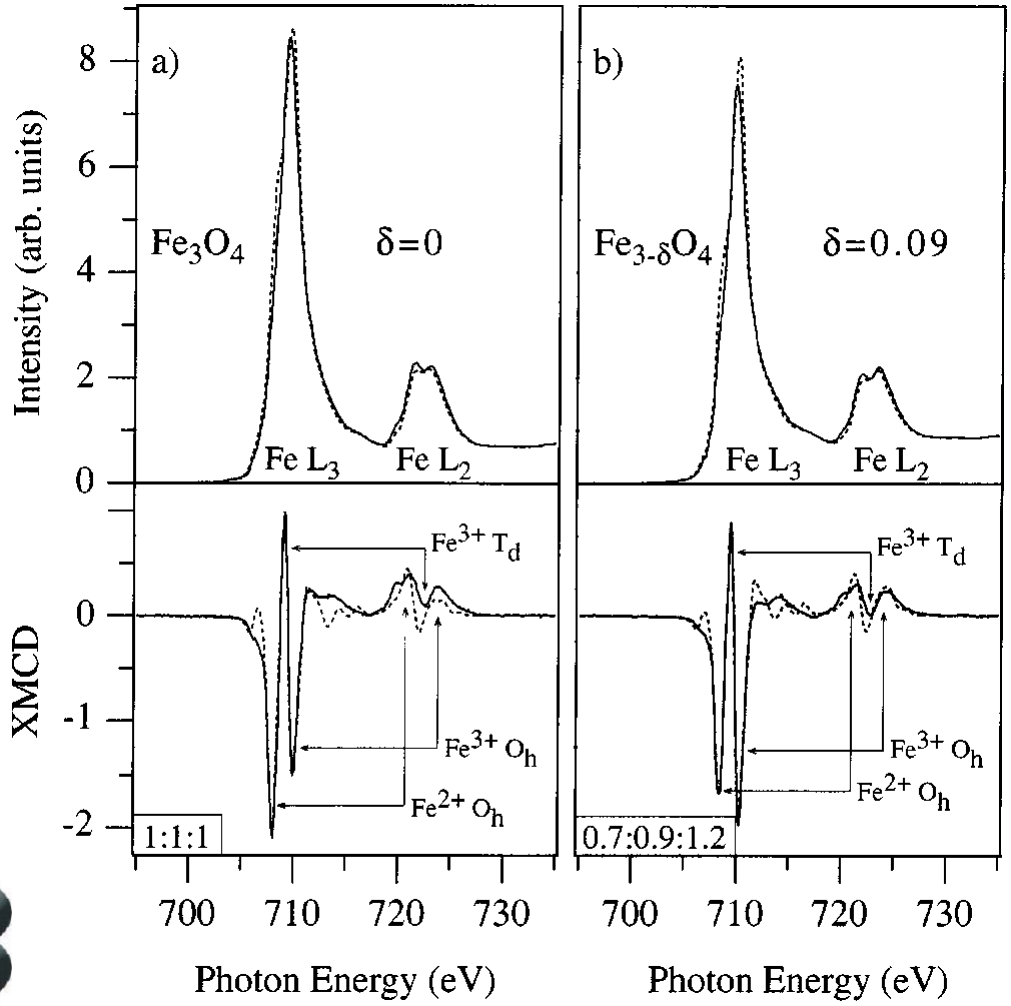


V. Cocker *et al*.,
Eur. J. Mineral. 19, 707–716 (2007)



The Department of Geology and Geophysics, University of Wisconsin-Madison



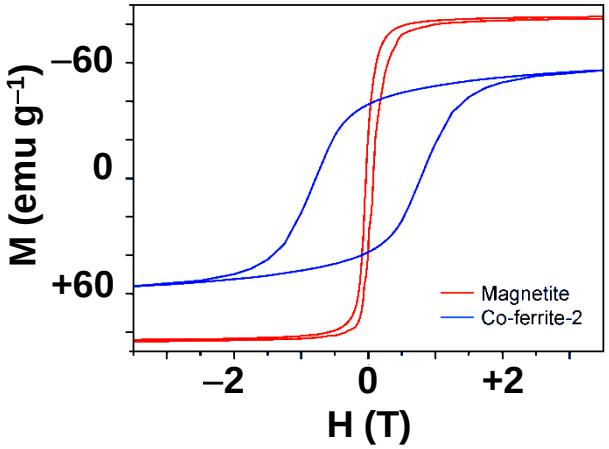


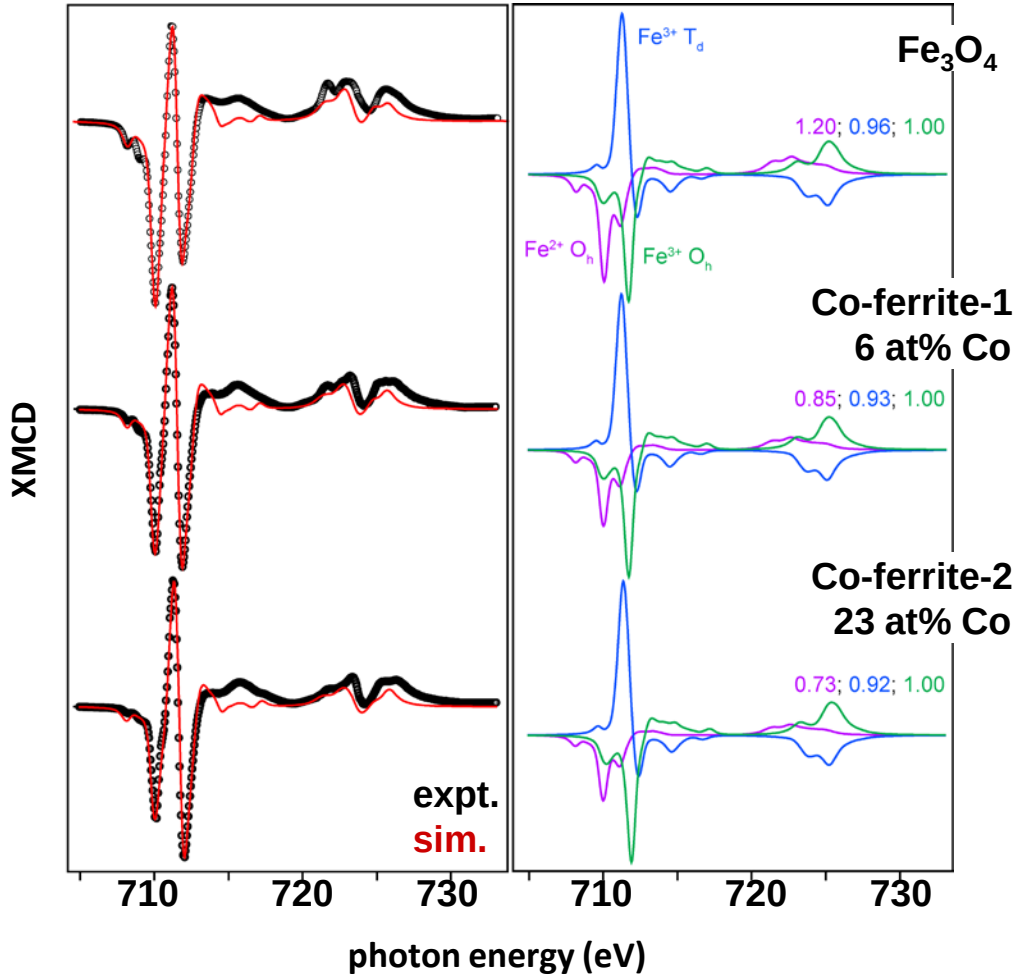
P. Morrall *et al*.,
Phys. Rev. B 67, 214408 (2003)

CHARACTERISTICS OF MAGNETIC BIONANOSPINELS

Magnetite and Co ferrites produced from Co(II) containing Fe(III)-oxyhydroxides using metal-reducing bacterium (*Geobacter sulfurreducens)*

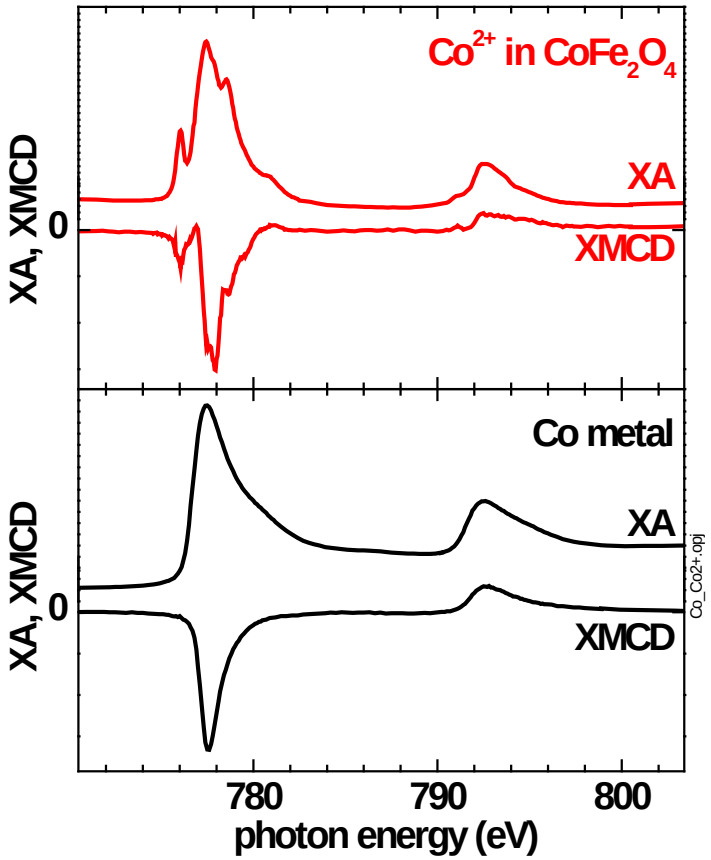
- **+ Up to 23at% Co^{2+} incorporated (compared to 1at% using magnetotactic bacteria)**
- **+ Co^{2+} in Fe^{2+} O_h sites**
- **+ 10fold increase in magnetic anisotropy**

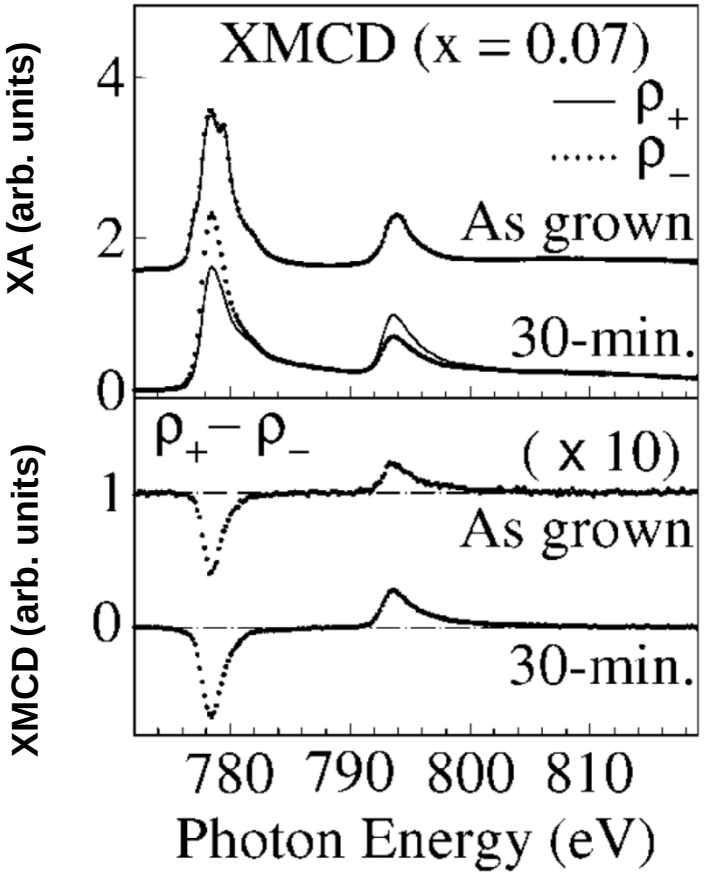




V. Cocker *et al.*,
Eur. J. Mineral. 19, 707–716 (2007)

Co-DOPED TiO_2



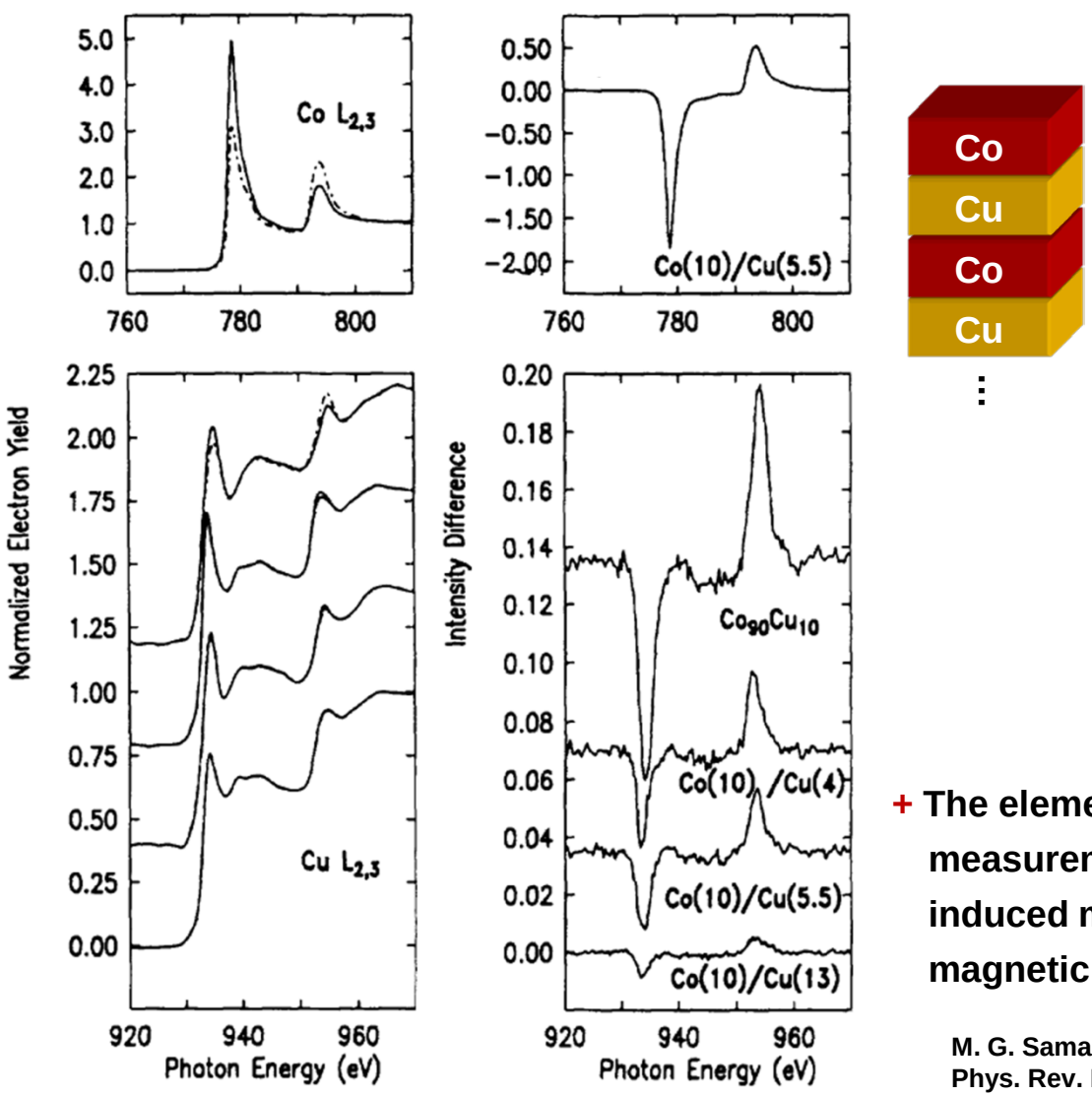


+ Comparing XMCD spectra with model compounds and/or theoretical multiplet calculations allows

⇒ Identifying the contributions to the magnetic phase of a system.

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

INDUCED MOMENTS AT Co/Cu INTERFACES

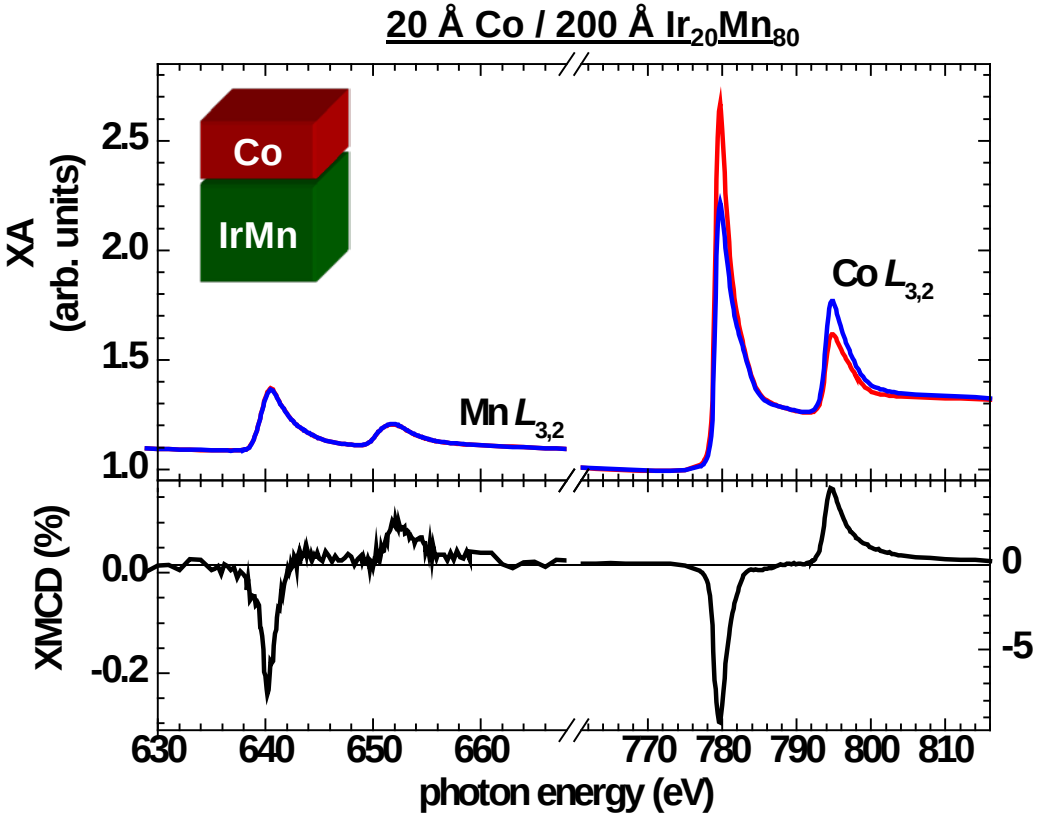


+ **The element-specificity makes XMCD measurements an ideal tool to determine induced moments at interfaces between magnetic and non-magnetic elements.**

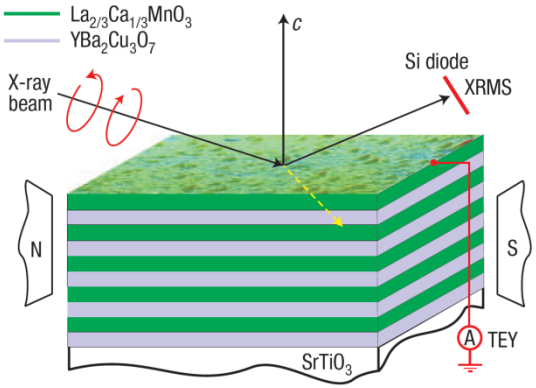
M. G. Samant *et al.*,
Phys. Rev. Lett. 72, 1112 (1994)

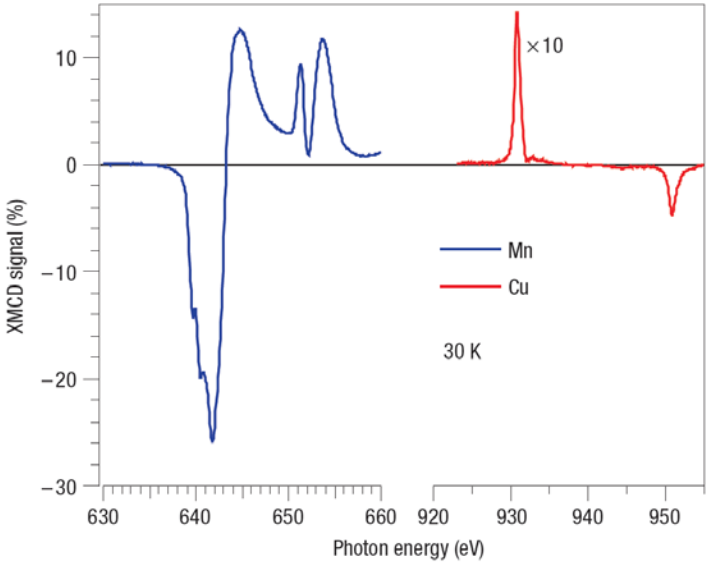
ANTIFERROMAGNET/FERROMAGNETIC INTERFACES

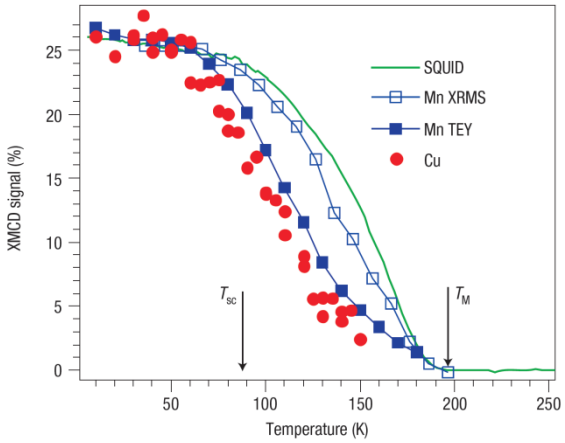
+ The weak Mn XMCD signal indicates uncompensated Mn at the Co/IrMn interface.
+ The same sign of XMCD signal for Co and Mn and indicates parallel coupling.
+ The nominal thickness of uncompensated interface moments is (0.5±0.1)ML for Co/$Ir_{20}Mn_{80}$.

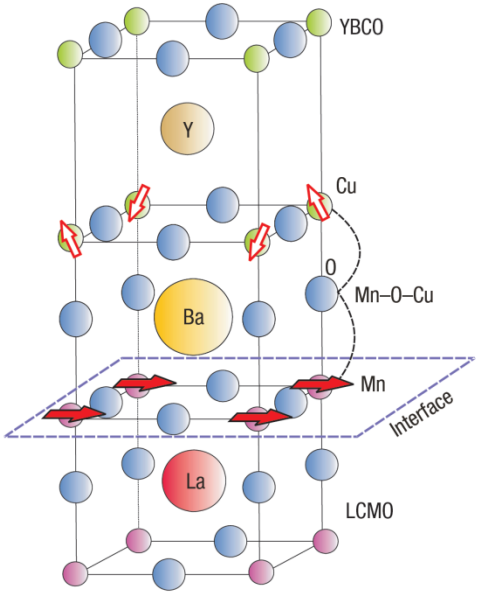


MAGNETISM AT FERROMAGNET/SUPERCONDUCTOR INTERFACES









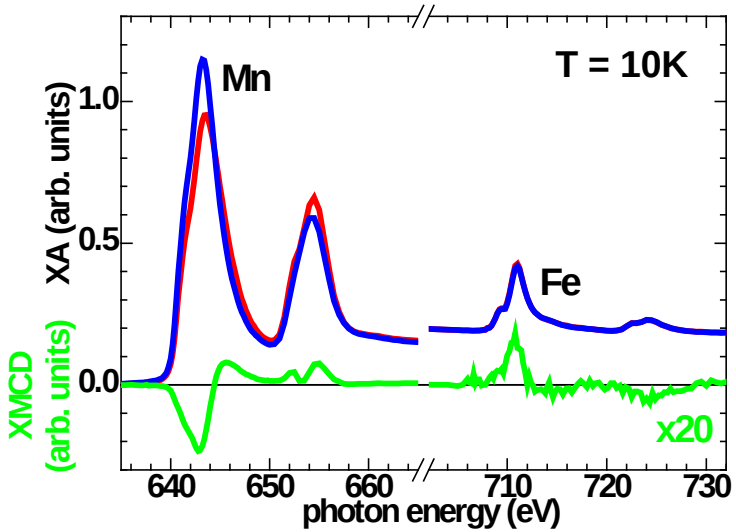
J. Chakhalian *et al.*,
Nature Phys. 2, 244 (2006)

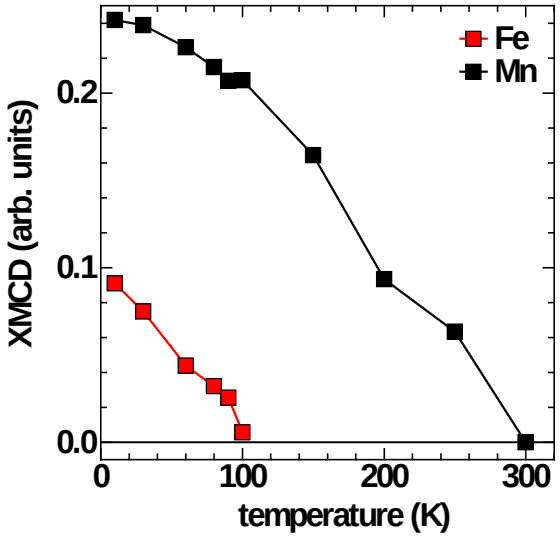
+ **LCMO : significant Mn $L_{3,2}$ XMCD at T = 30K**
  ferromagnetic transition ~180 K

+ **YBCO: Weak Cu $L_{3,2}$ XMCD**
  ⇔ **net ferromagnetic polarization on Cu**
  i.e. presence of uncompensated induced magnetic moment in the YBCO layer close to LCMO interface.

+ **opposite sign of Cu and Mn XMCD**
  ⇔ **antiparallel orientation of Cu and Mn moments**

$La_{0.7}Sr_{0.3}MnO_3$ / $BiFeO_3$ INTERFACE

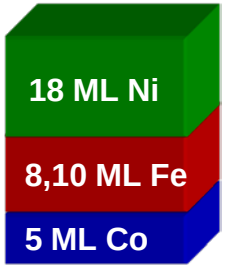


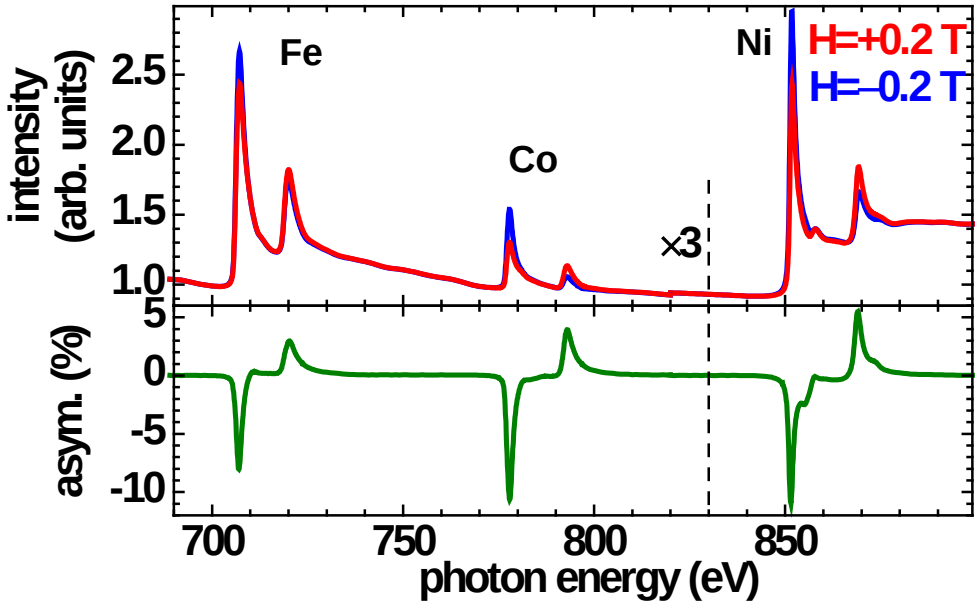


+ $La_{0.7}Sr_{0.3}MnO_3$: significant Mn $L_{3,2}$ XMCD at T = 10K
  ferromagnetic transition ~300 K
+ $BiFeO_3$: Weak Fe $L_{3,2}$ XMCD
  ⇔ net ferromagnetic polarization on Fe
  i.e. presence of uncompensated induced magnetic moment in the $BiFeO_3$ layer close to $La_{0.7}Sr_{0.3}MnO_3$ interface.
+ opposite sign of Fe and Mn XMCD
  ⇔ antiparallel orientation of Fe and Mn moments
+ Transition temperature of the magnetic phase in BiFeO3 significantly lower than $La_{0.7}Sr_{0.3}MnO_3$

P. Yu *et al.*,
Phys. Rev. Lett. 105, 027201 (2010)

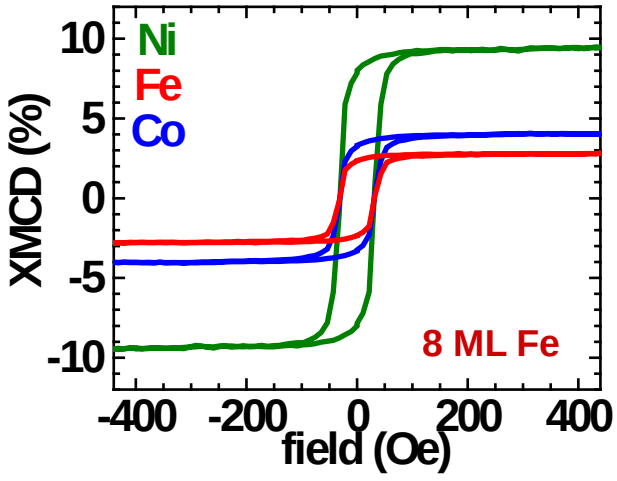
ELEMENT-SPECIFIC MAGNETIZATION REVERSAL

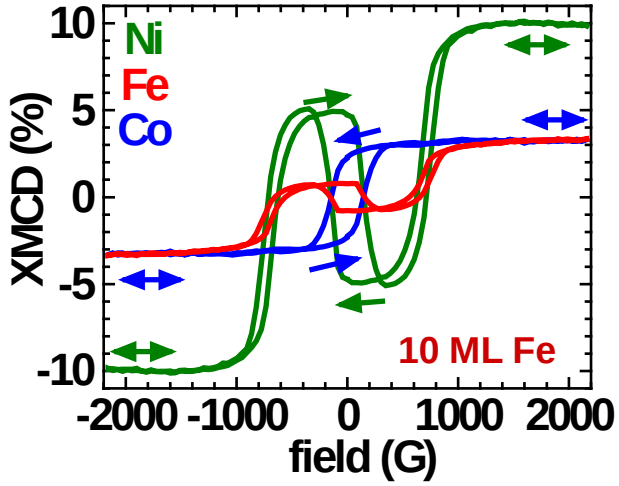




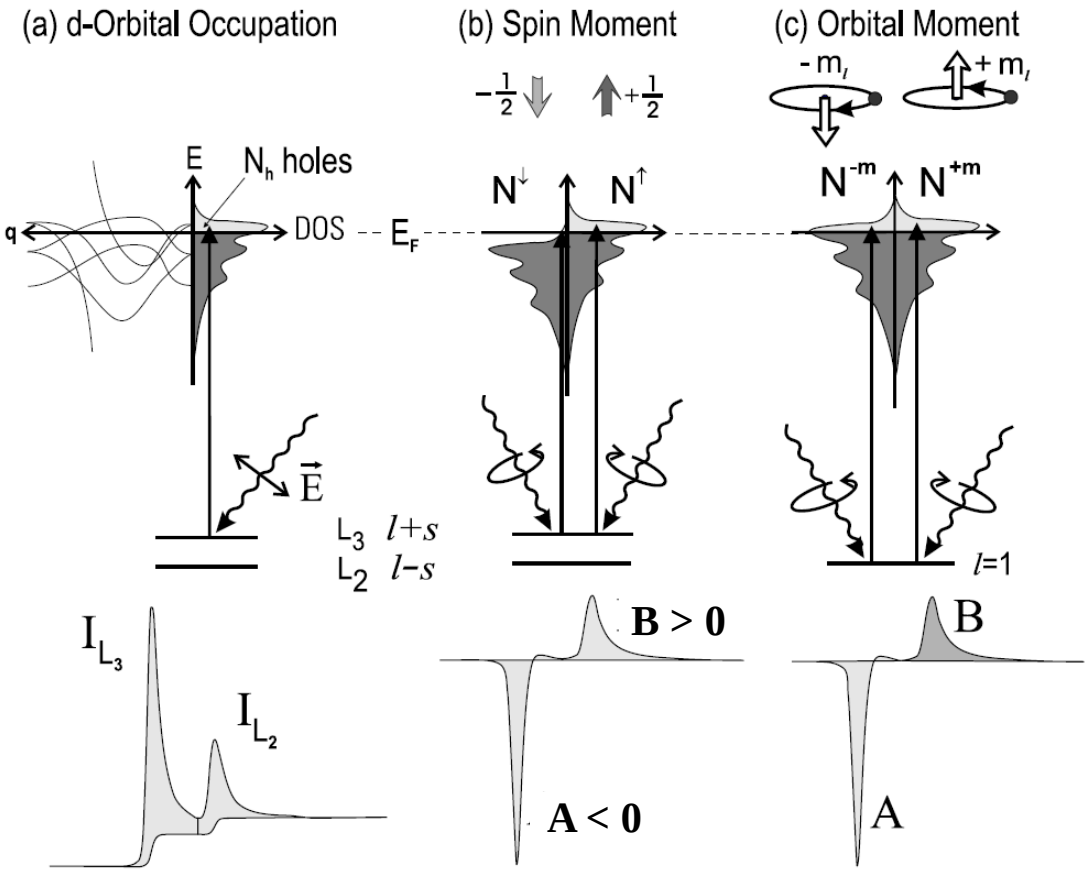
+ Monitoring the field dependence of the XMCD signal

⇒ Detailed information on magnetization reversal in complex magnetic hetero-structures





SUM RULES



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

$N_h = \langle I_{L3} + I_{L2} \rangle / C$ $\quad m_S = \mu_B \langle -A + 2B \rangle / C$ $\quad m_L = -2\mu_B \langle A + B \rangle / 3C$

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

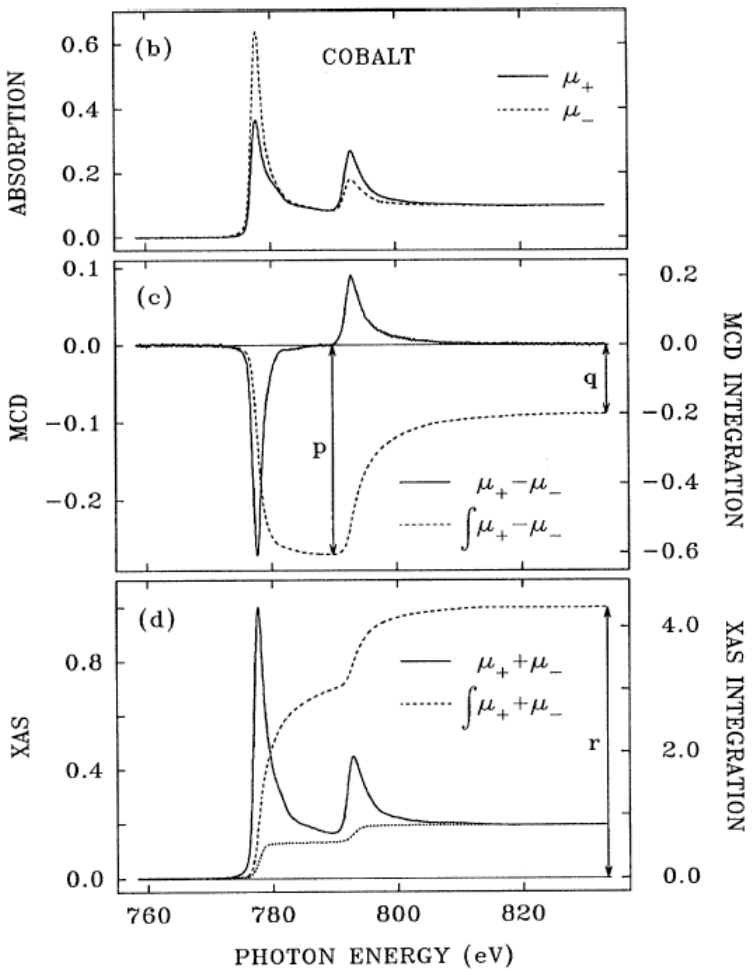
SUM RULES

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

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

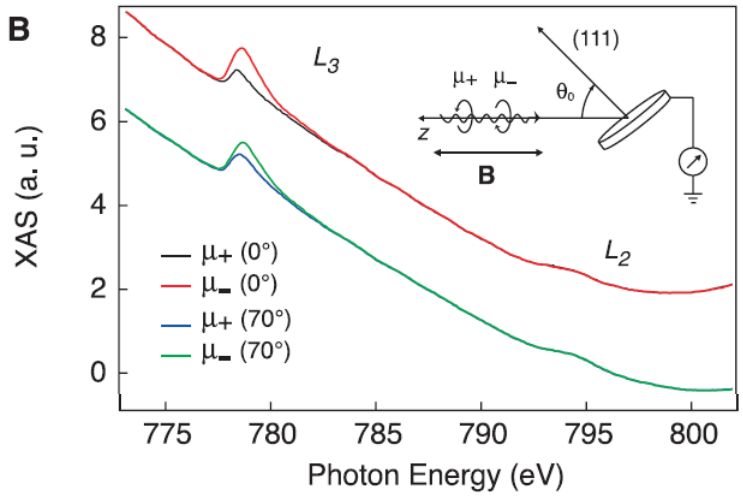
$$m_{orb} = -\frac{4q\,(10 - n_{3d})}{3r}$$

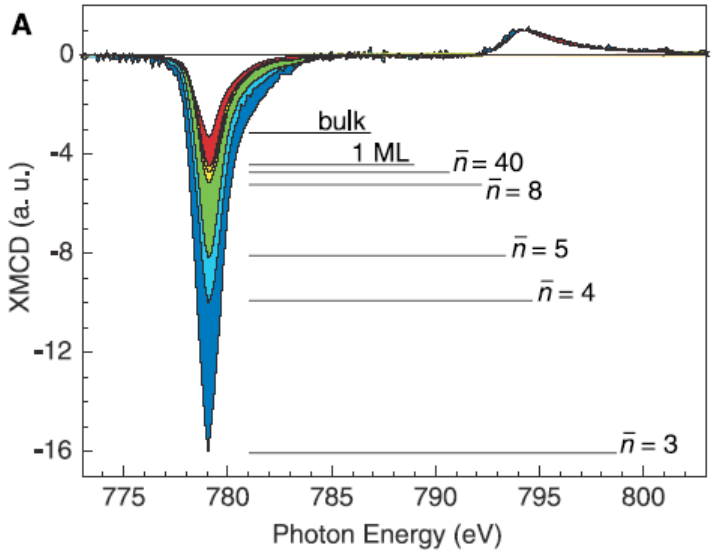
$$m_{spin} = -\frac{(6p - 4q)\,(10 - n_{3d})}{r}$$

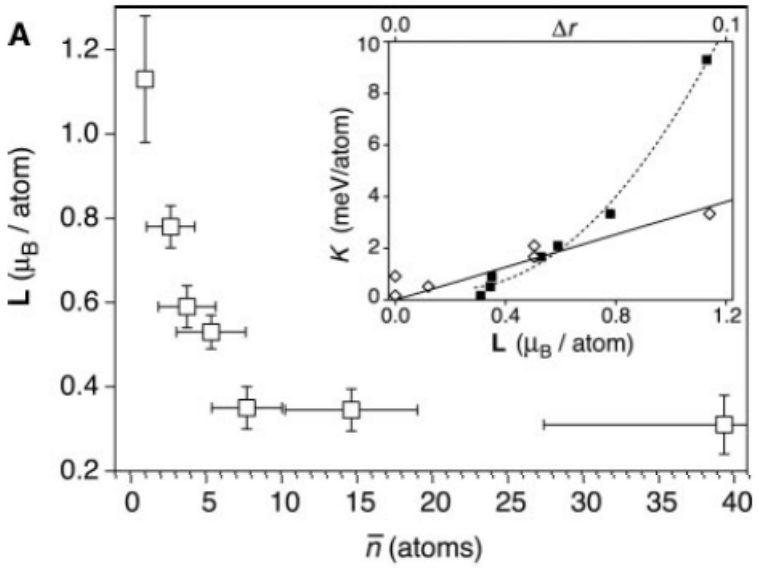


C.T. Chen *et al.*,
Phys. Rev. Lett. 75, 152(1995)

ORBITAL MOMENT OF Co NANOPARTICLES



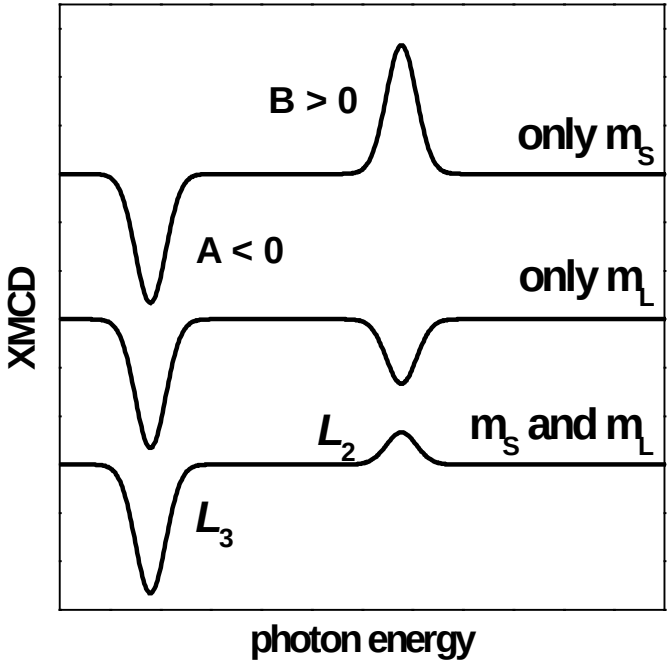




+ **Strong variation of orbital and spin magnetic moment observable as change in L_3 and L_2 in the XMCD spectrum.**
+ **Co atoms and nanoparticles on Pt have enhanced orbital moments up to 1.1 μ_B**

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

SUM RULES



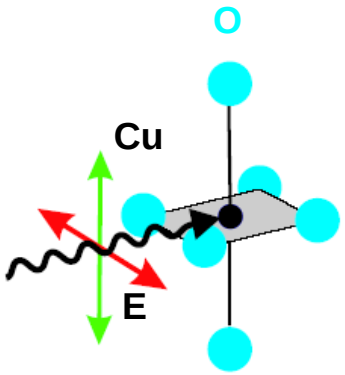
+ Spin and orbital moment only systems have distinct XMCD spectra:

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

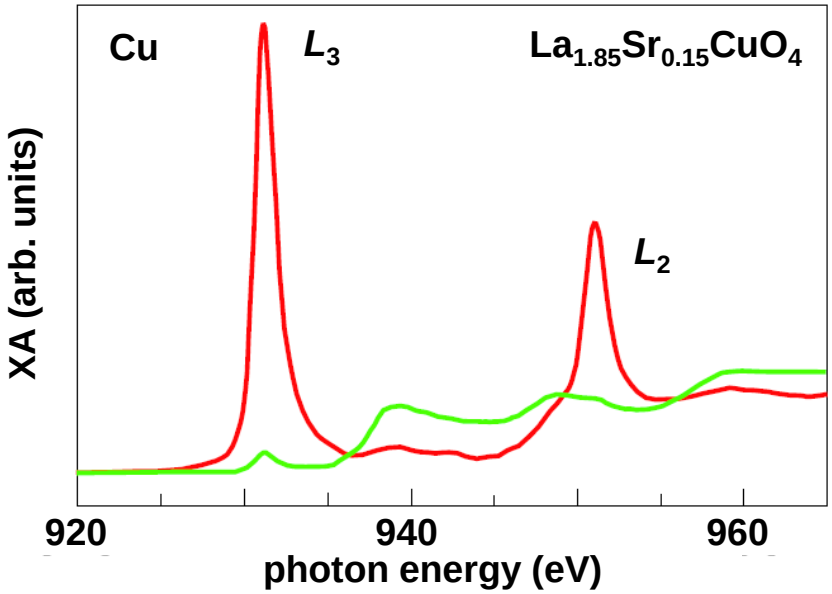
$$m_S = \mu_B\langle -A + 2B\rangle / C = 0 \quad \text{for } A = 2B$$

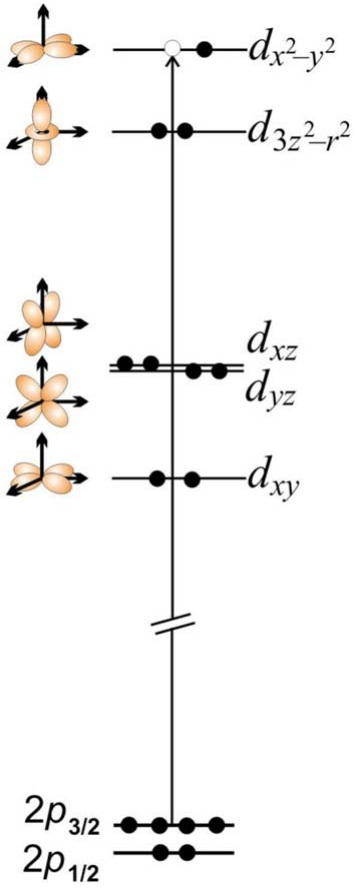
X-RAY LINEAR DICHROISM

+ **Linear dichroism: difference in x-ray absorption for different polarization direction relative to crystalline and/or spin axis.**
+ **Linear dichroism is 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.

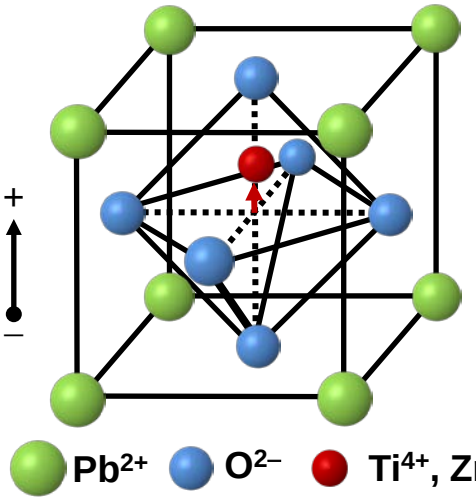


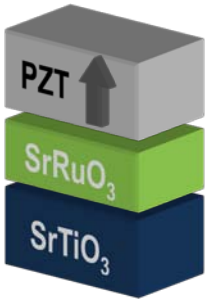
C. T. Chen *et al.*
PRL 68, 2543 (1992)



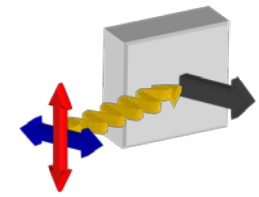


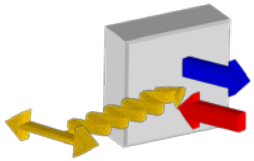
STRUCTURAL CHANGES IN $PbZr_{0.2}Ti_{0.8}O_3$

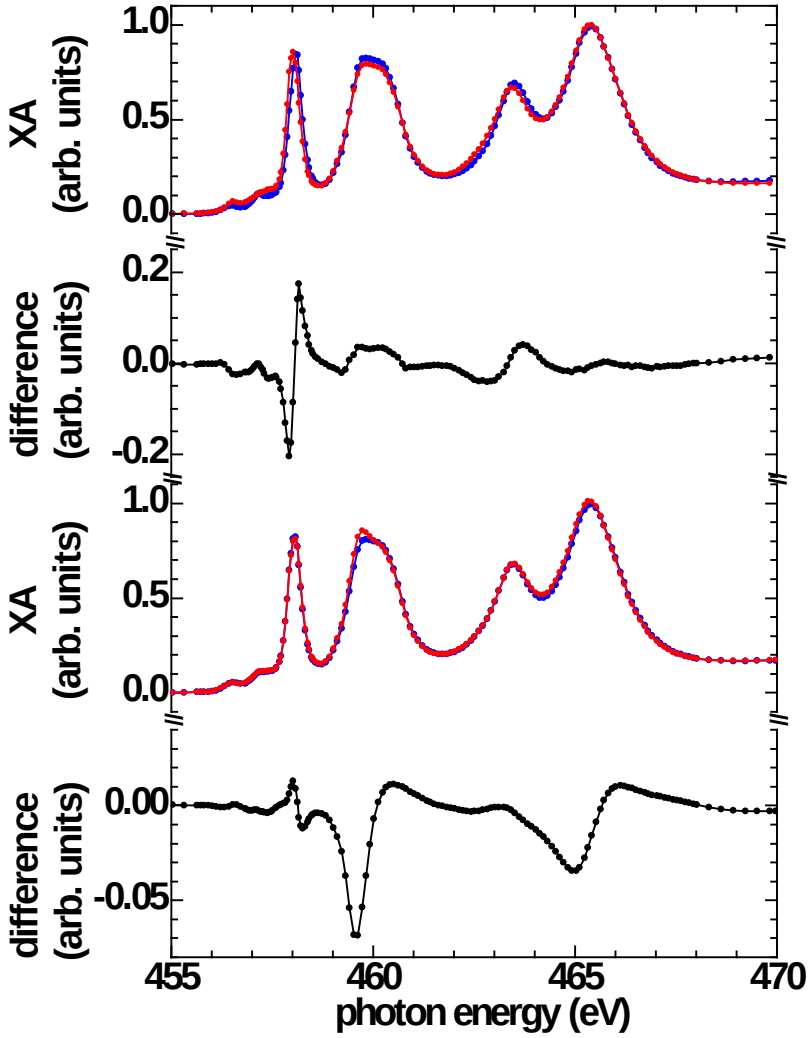




ferroelectric polarization





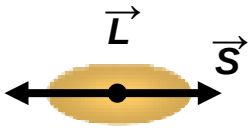


+ Spontaneous electric polarization due to off-center shift of Ti^{4+}, Zr^{4+} ; associated with tetragonal distortion ⇔ linear dichroism

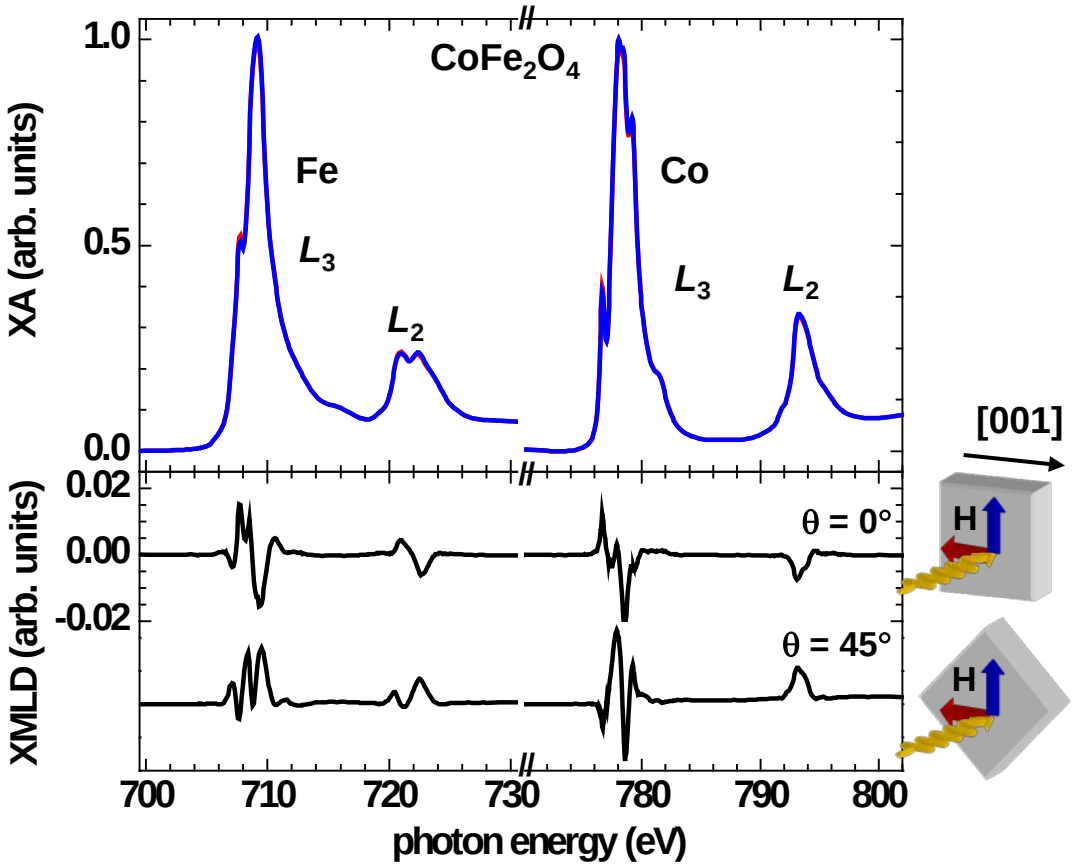
+ Reversing the polarization changes XA ⇔ Change in tetragonal distortion

X-RAY MAGNETIC LINEAR DICHROISM

Isotropic *d* electron charge density
⇒ No polarization dependence



magnetically aligned
Spin-orbit coupling distorts
charge density
⇒ polarization dependence

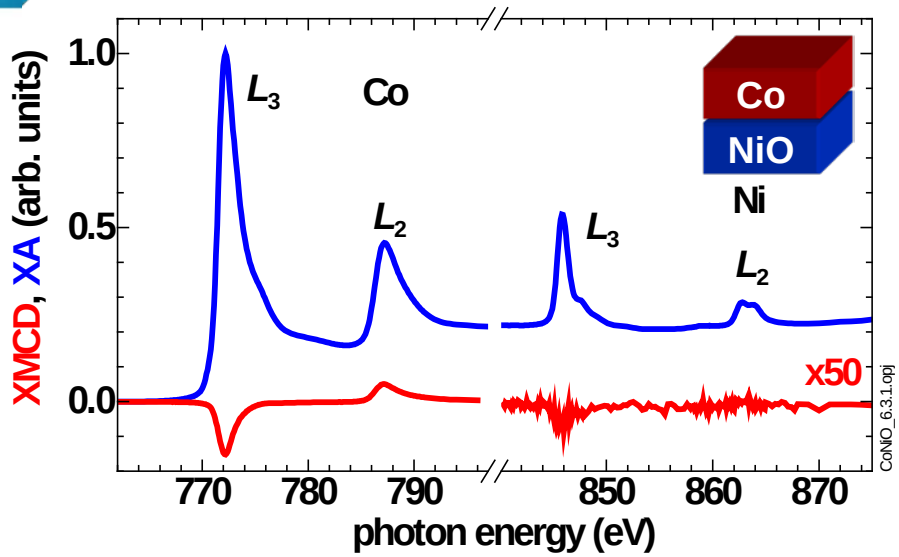


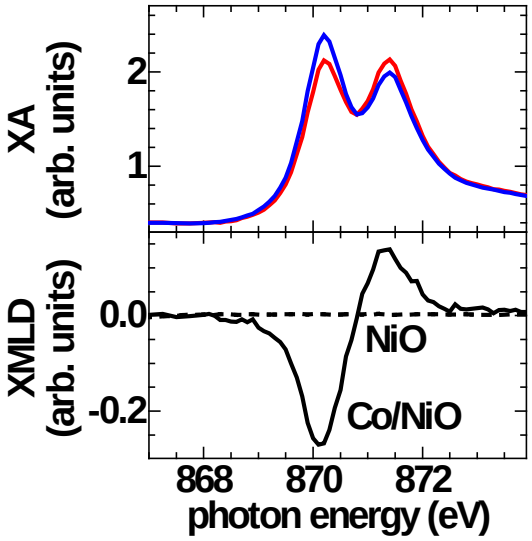
+ $I_{XMLD} = I_{||} - I_{\perp} \propto \langle m^2 \rangle$, $\langle m^2 \rangle$ = expectation value of the square of the atomic magnetic moment

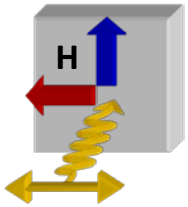
+ XMLD allows investigating ferri- and ferromagnets as well as antiferromagnets.

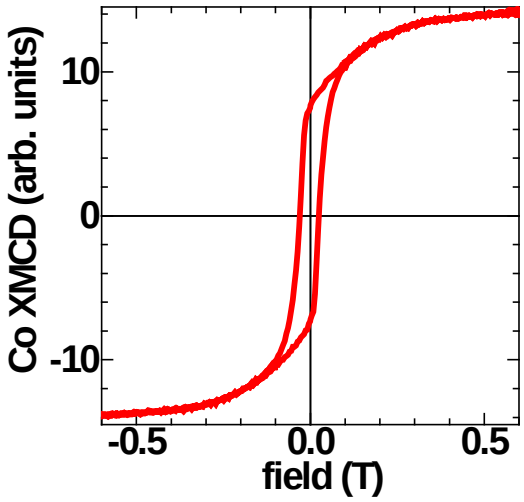
+ XMLD spectral shape and angular dependence are determined by magnetic order and lattice symmetry.

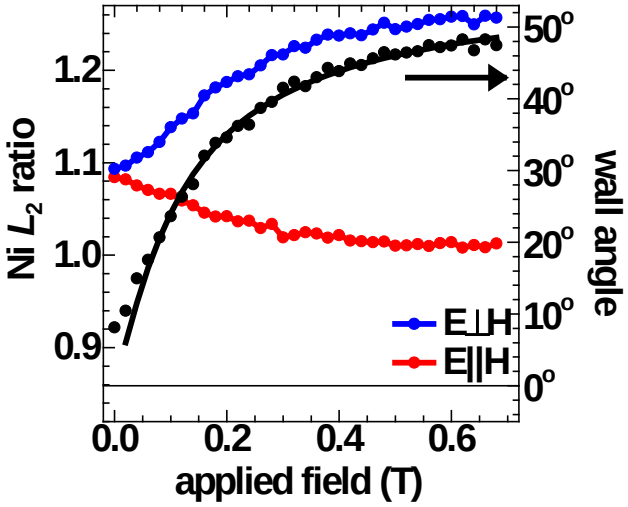
PLANAR DOMAIN WALL NEAR Co/NiO INTERFACES

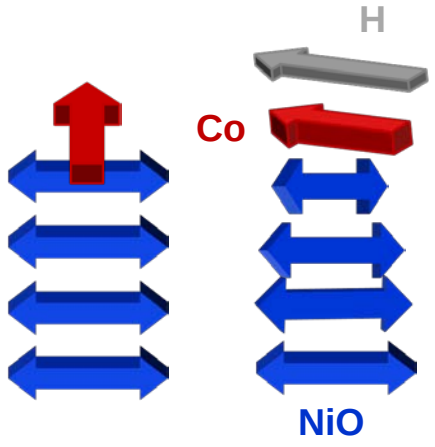






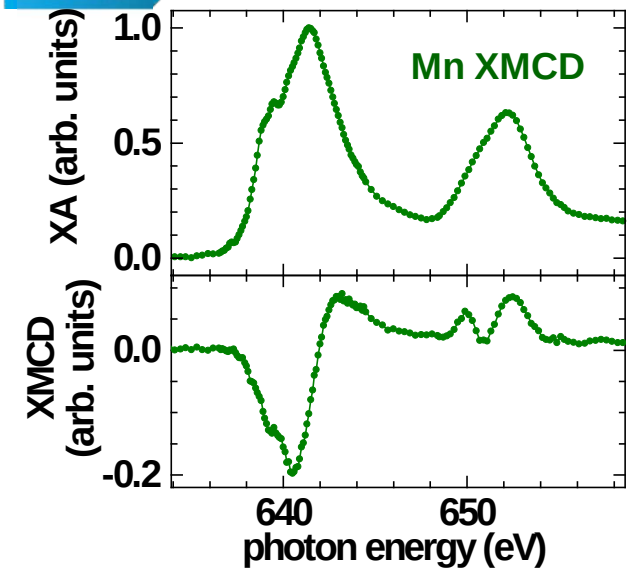


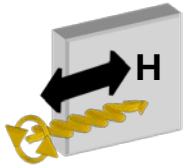




A. Scholl *et al.*,
Phys. Rev. Lett. 92, 247201 (2004)

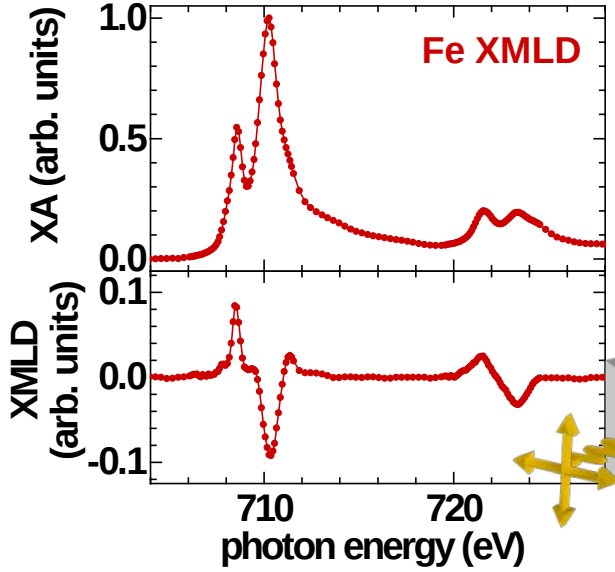
MAGNETIC COUPLING AT $La_{0.7}Sr_{0.3}MnO_3/La_{0.7}Sr_{0.3}FeO_3$ INTERFACES

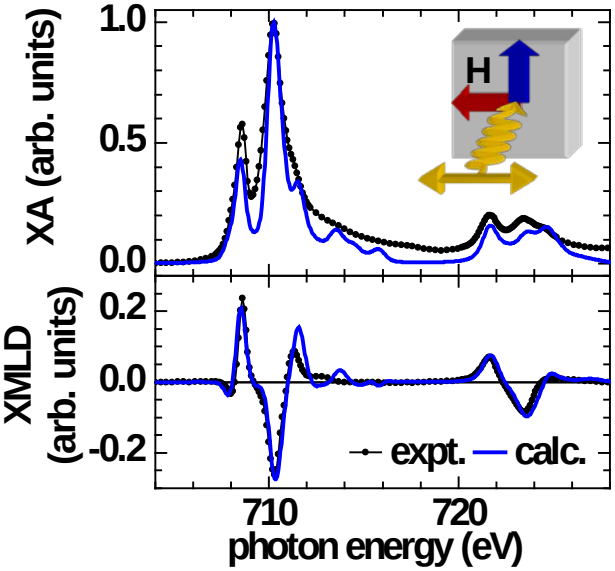


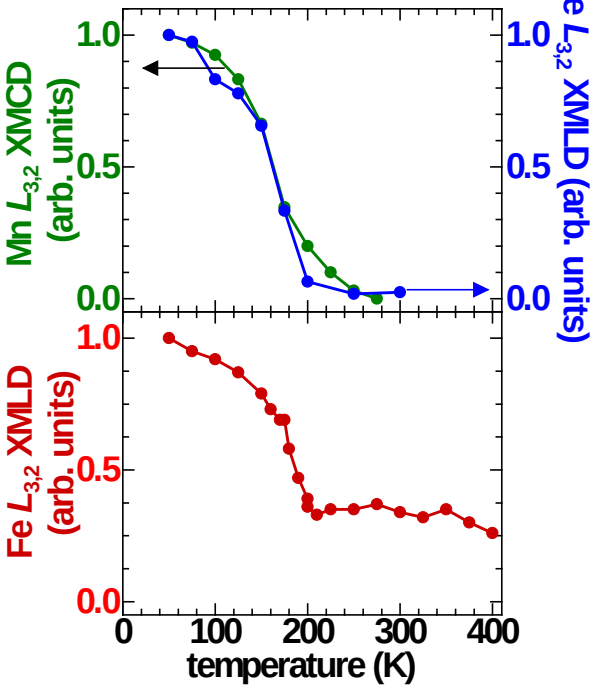


$La_{0.7}Sr_{0.3}MnO_3$ (LSMO)
ferromagnet

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

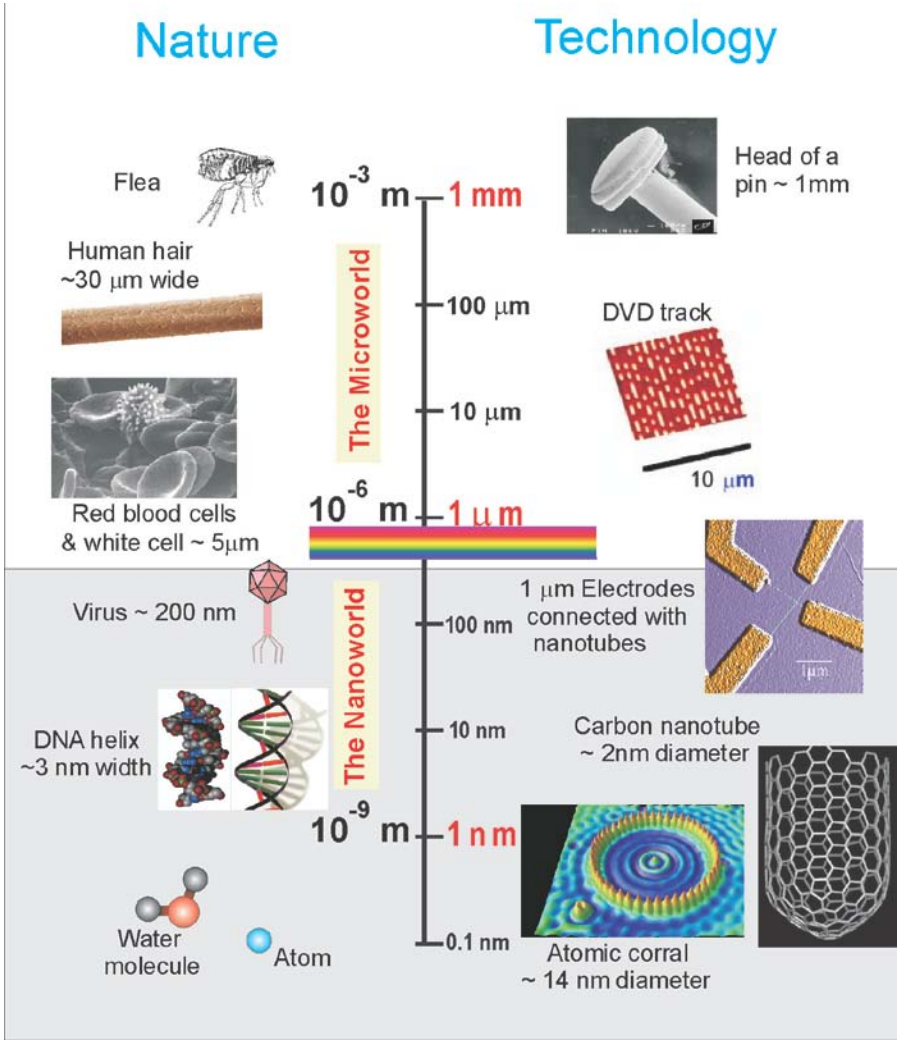


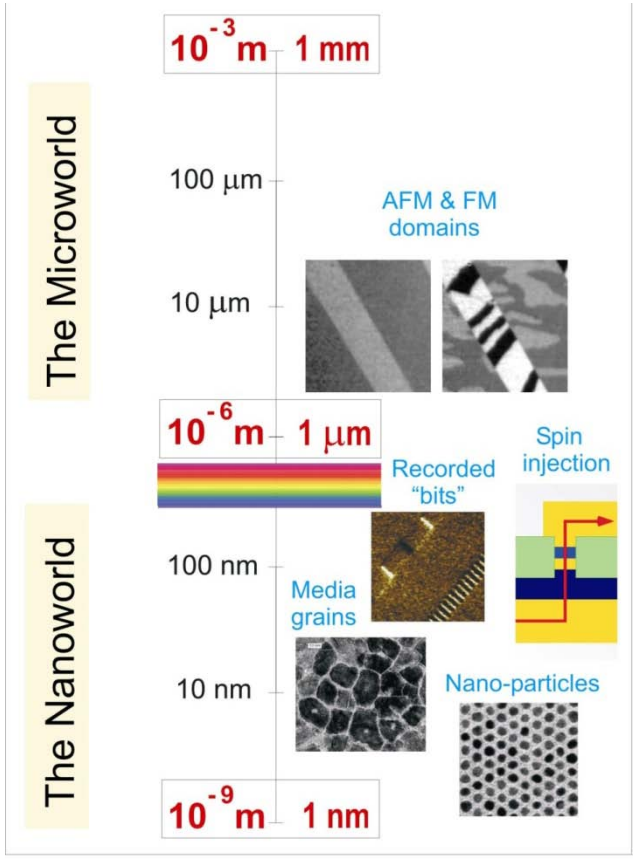




⇒ Perpendicular coupling at LSMO/LSFO interface

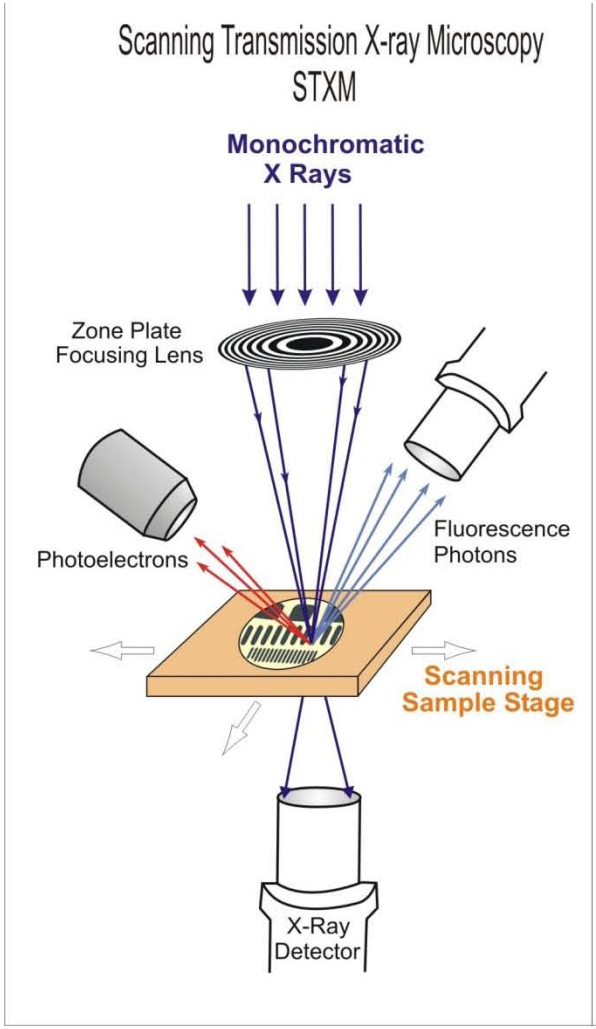
MAGNETIC MICROSCOPY

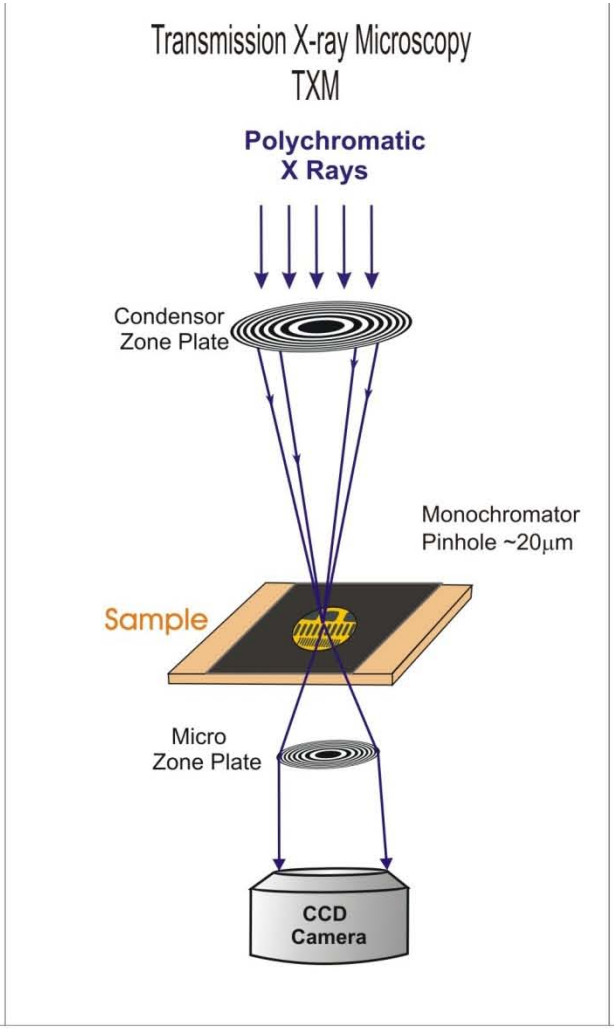


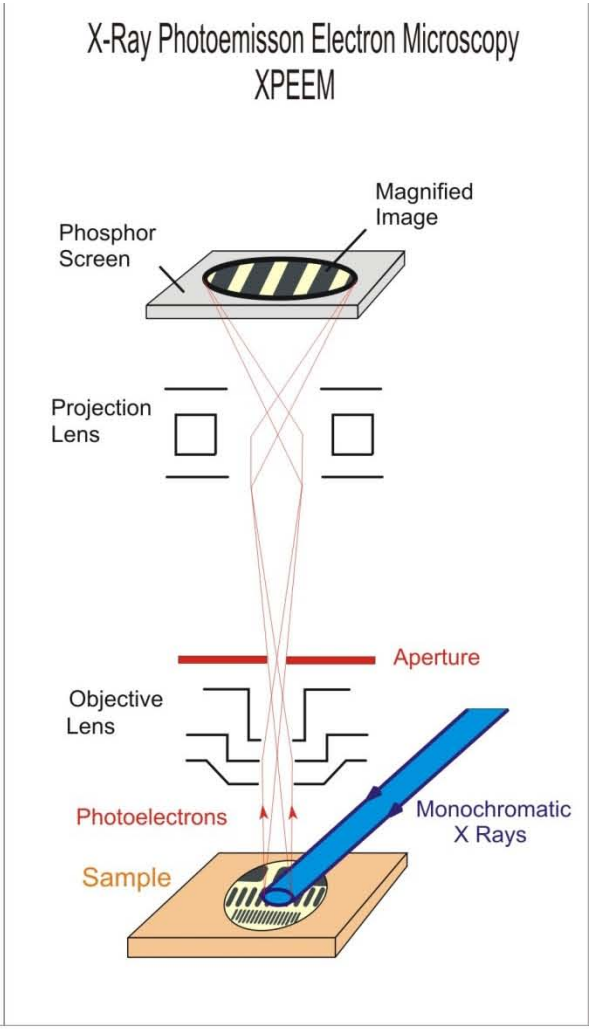


J. Stöhr, H.C. Siegmann,
Magnetism (Springer)

MAGNETIC MICROSCOPY



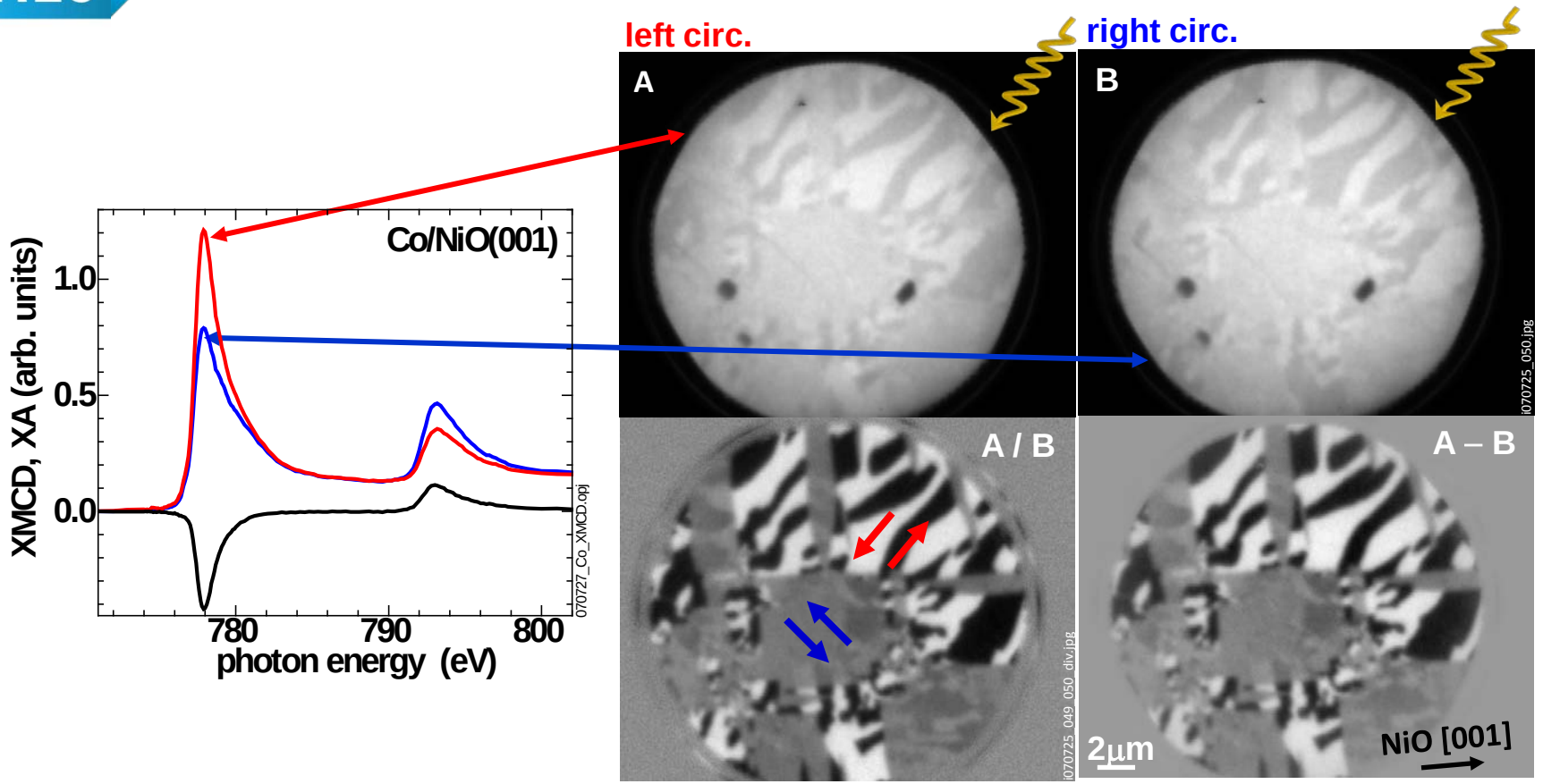




10-50 nm spatial resolution

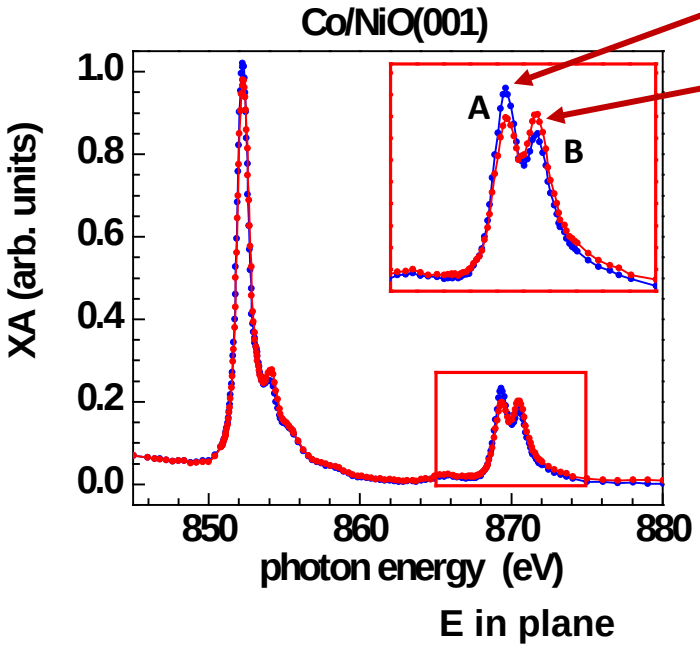
J. Stöhr, H.C. Siegmann, Magnetism (Springer)

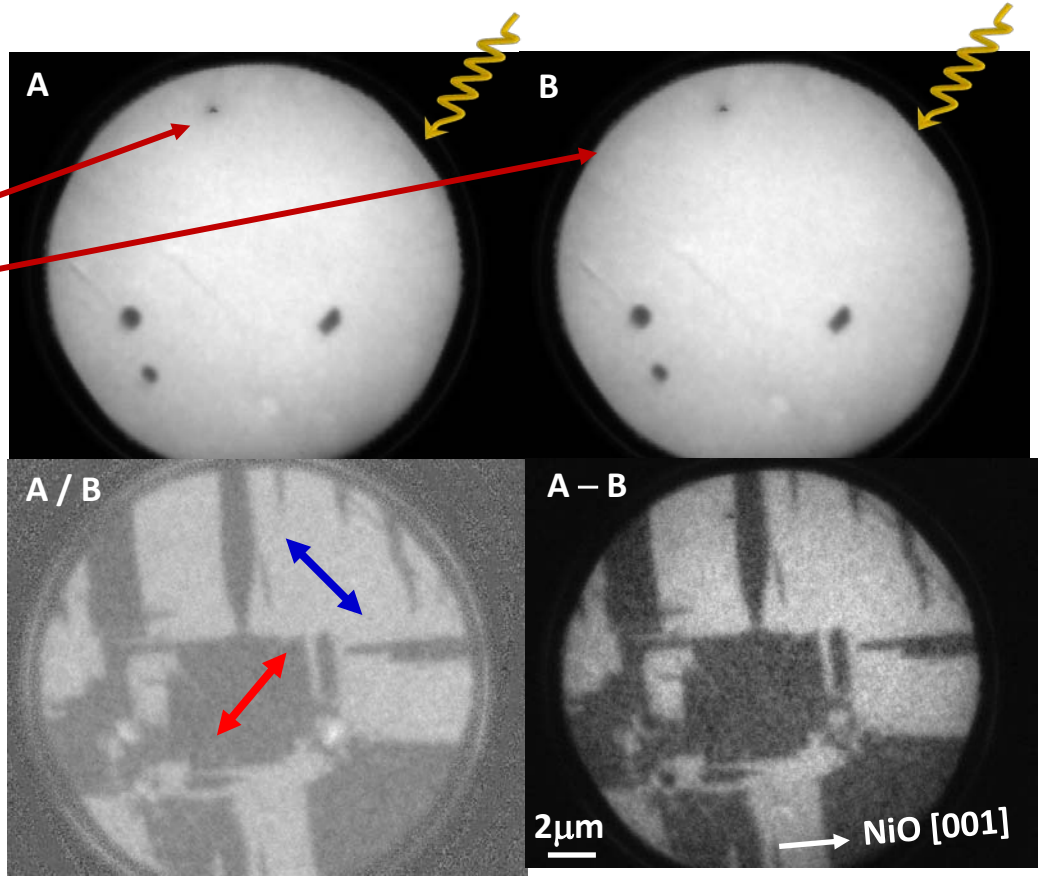
IMAGING FERROMAGNETIC DOMAINS USING XMCD



+ 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

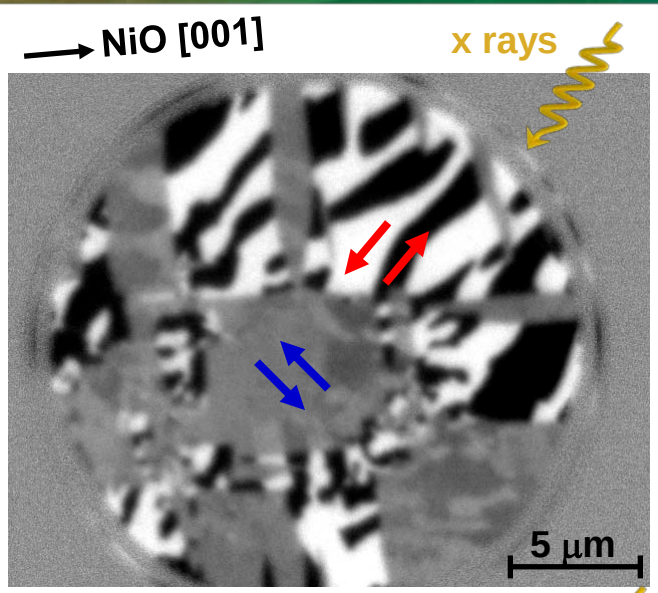




+ Images taken with linearly polarized x-rays at photon energies with XMLD, i.e. Ni L_2 edge, provide magnetic contrast and domain images.

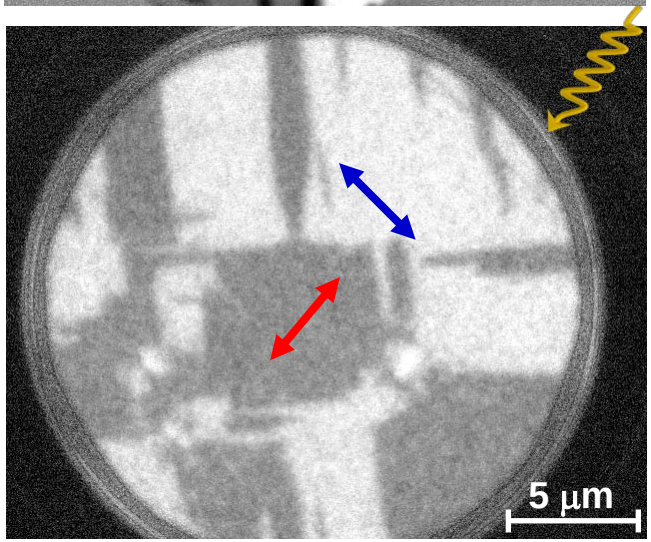
MAGNETIC COUPLING AT Co/NiO INTERFACE

Co XMCD

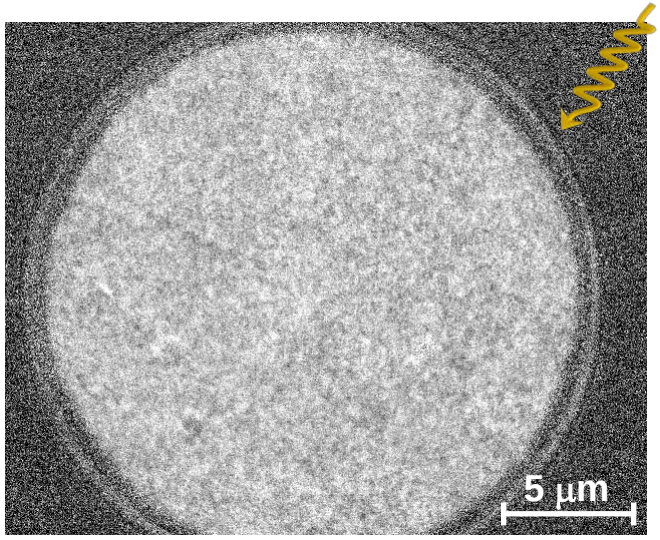


+ Taking into account the geometry dependence of the Ni XMLD signal
⇒ perpendicular coupling of Co and NiO moments at the interface.

Ni XMLD



probing in-plane

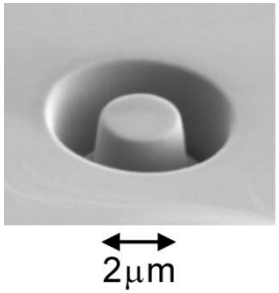


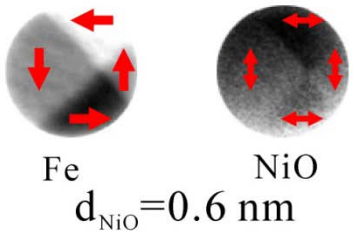
probing out-of-plane

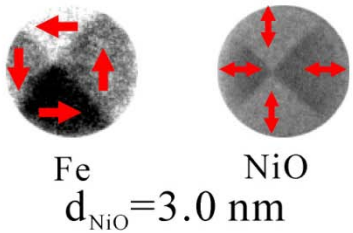
OBSERVATION OF ANTIFERROMAGNETIC VORTICES

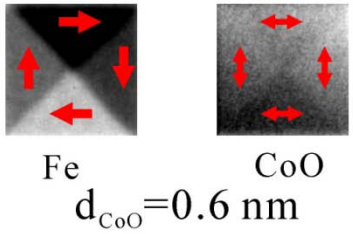
+ First direct observation of vortex state in antiferromagnetic CoO and NiO disks in Fe/CoO and Fe/NiO bilayers using XMCD and XMLD.

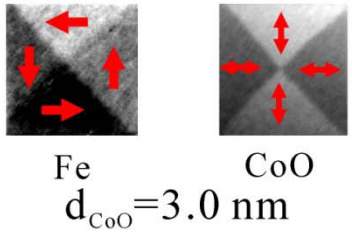
+ Two types of AFM vortices:
  - conventional curling vortex as in ferromagnets
  - divergent vortex, forbidden in ferromagnets
  - thickness dependence of magnetic interface coupling

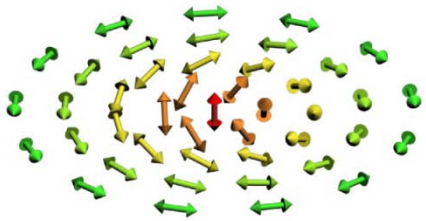




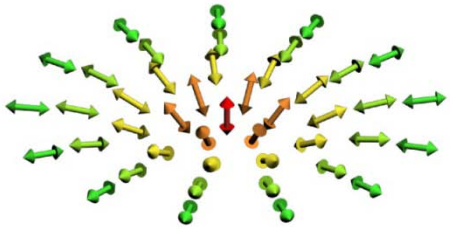








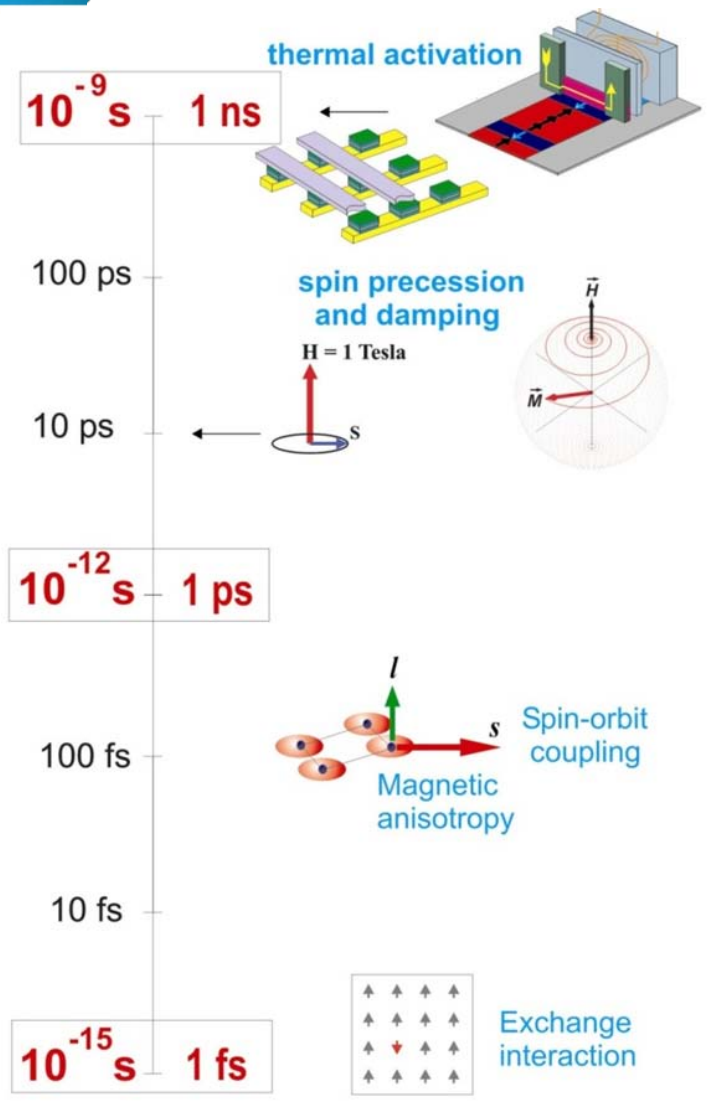
conventional curling vortex



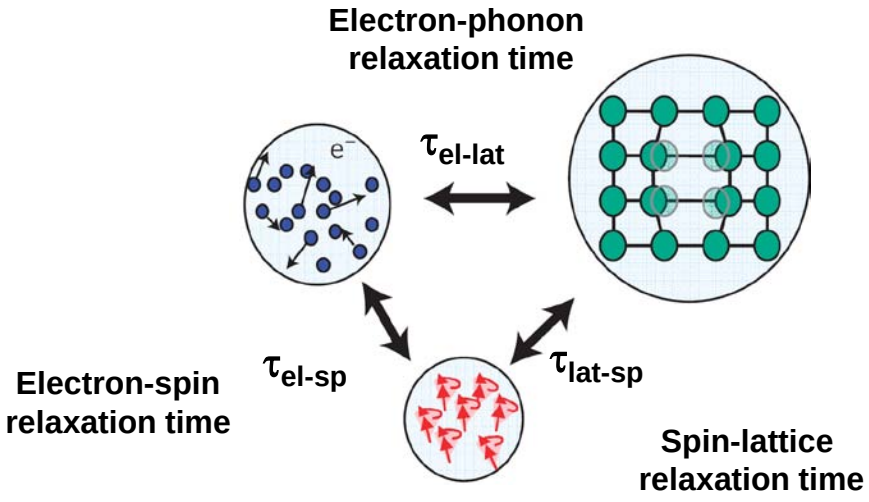
divergent vortex

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

ULTRAFAST MAGNETISM

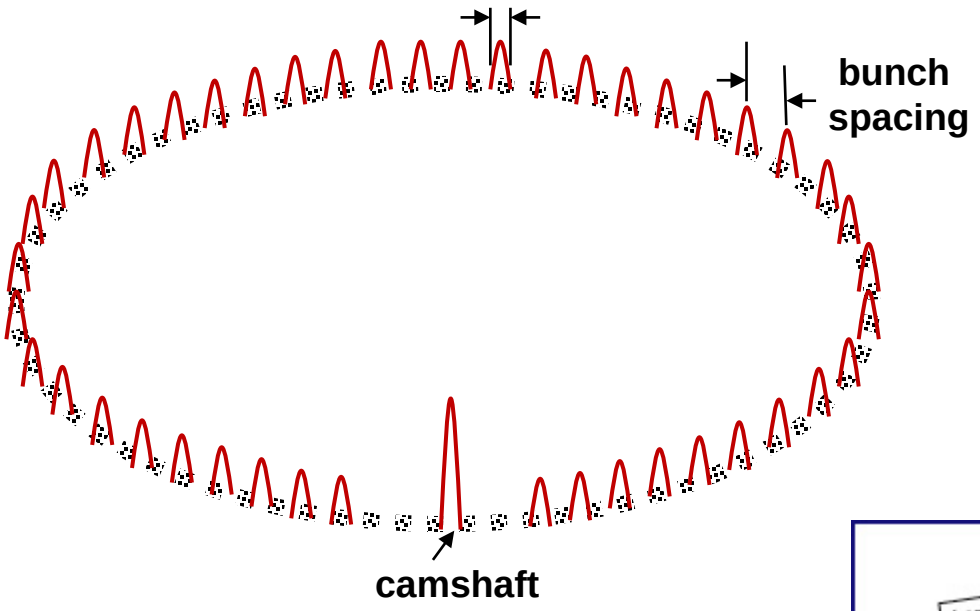


J. Stöhr, H.C. Siegmann, Magnetism (Springer)

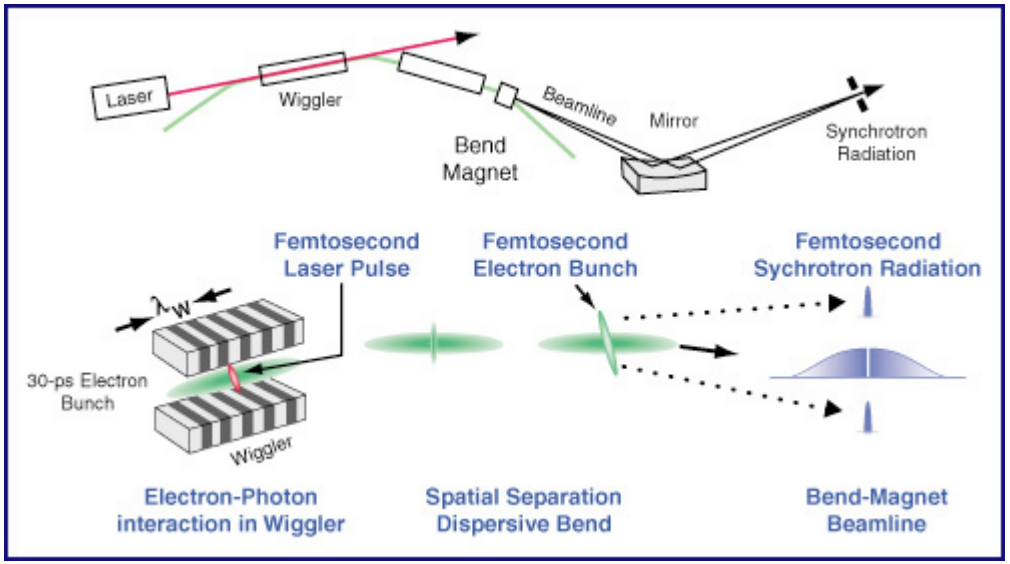


+ Energy reservoirs in a ferromagnetic metal
+ Deposition of energy in one reservoir
⇒ Non-equilibrium distribution and subsequent relation through energy and angular momentum exchange

ALS TIME STRUCTURE

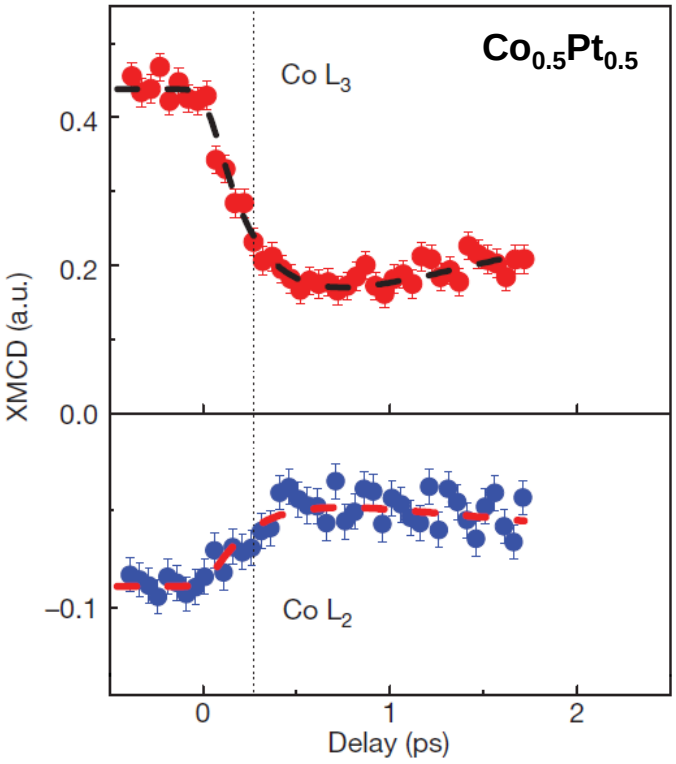


+ 256-320 bunches for 500mA beam current
+ Possibility of one or two 5mA "camshaft" bunches in filling gaps
+ Bunch spacing:
  multibunch mode: 2 ns
  two-bunch mode: 328 ns
+ Pulse length 70ps



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

ULTRAFAST DYNAMICS OF SPIN AND ORBITAL MOMENTS

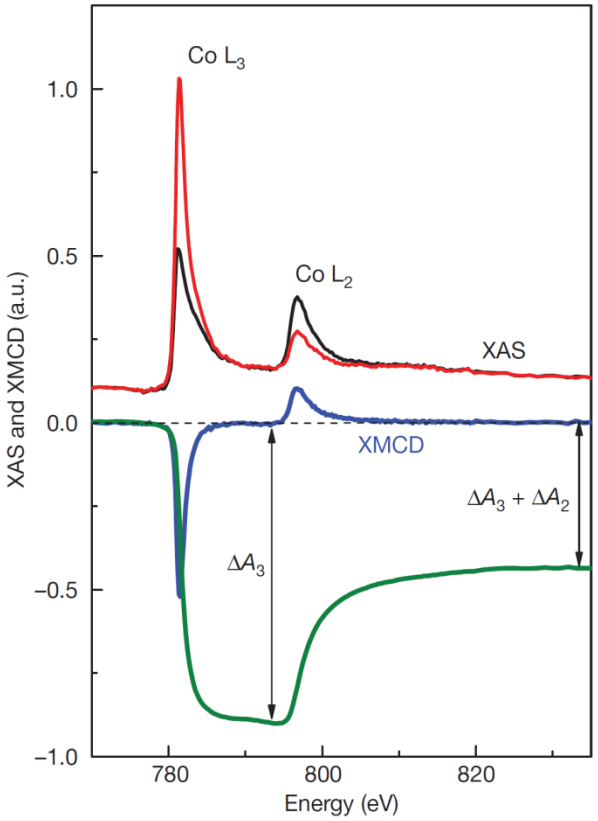


C. Boeglin, *et al.*,
Nature 465, 458 (2010)

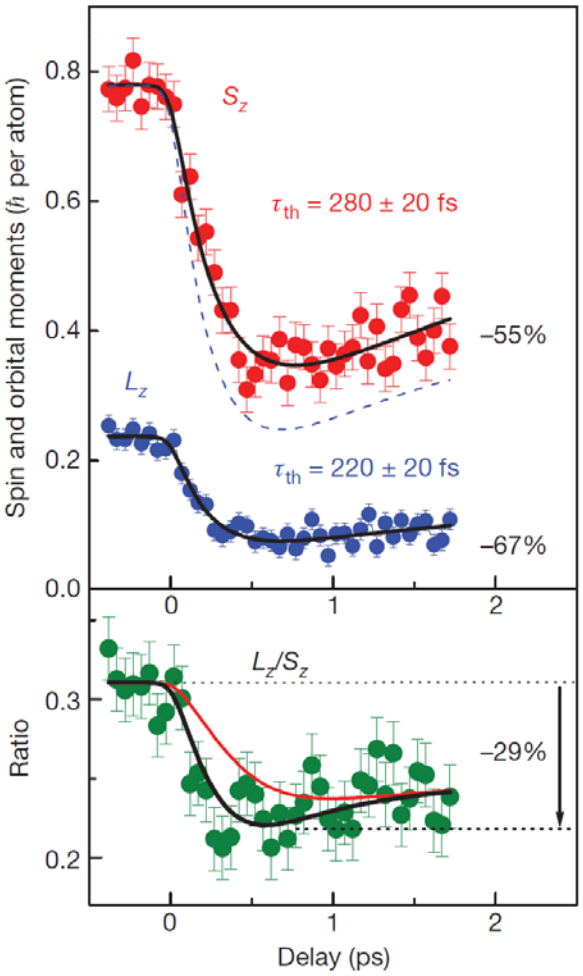
+ Orbital (*L*) and spin (*S*) magnetic moments can change with total angular momentum is conserved.
+ Efficient transfer between *L* and S through spin–orbit interaction in solids
+ Transfer between *L* and *S* occurs on fs timescales.

+ $Co_{0.5}Pt_{0.5}$ 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



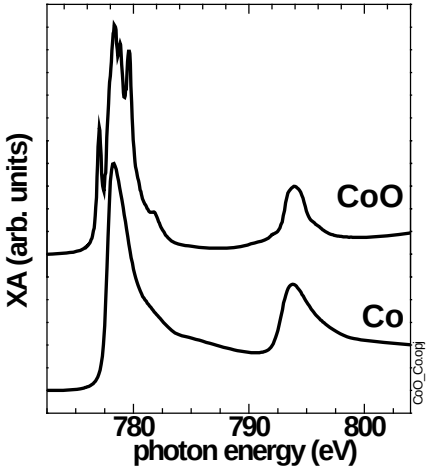
ULTRAFAST DYNAMICS OF SPIN AND ORBITAL MOMENTS



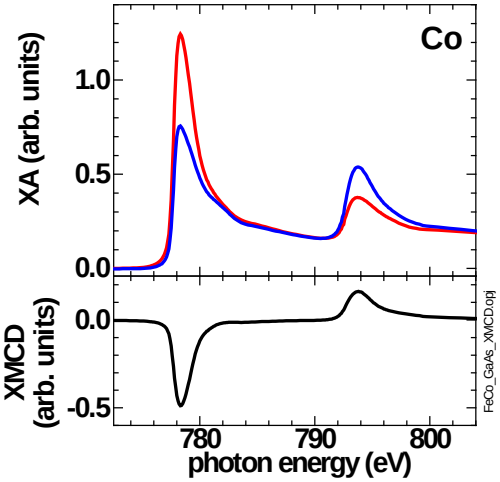
C. Boeglin, *et al.*,
Nature 465, 458 (2010)

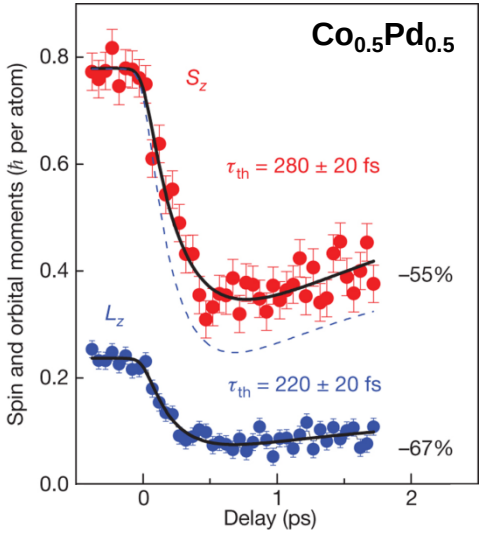
+ **Characteristic thermalization:**
  Faster decrease of orbital moment
+ **Theory:**
  Orbital magnetic moment strongly correlated with magnetocrystalline anisotropy
+ **Reduction in orbital moment**
  ⇔ Reduction in magnetocrystalline anisotropy
+ **Typically observed at elevated temperatures in static measurements as well**
+ **Further studies needed**

MAGNETIC SPECTROSCOPY

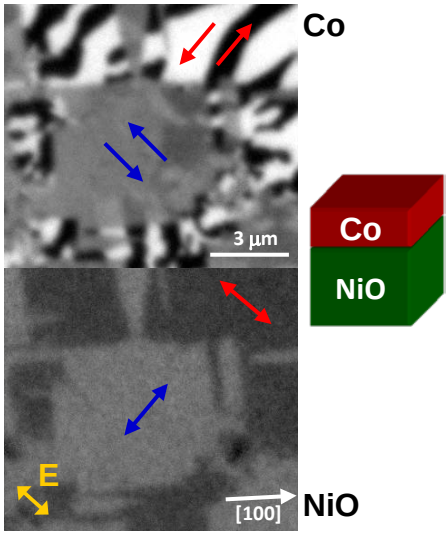


+ X ray absorption
+ X ray magnetic circular dichoism, XMCD
+ X ray magnetic linear dichroism, XMLD
+ X ray magnetic microscopy
+ Magnetization Dynamics

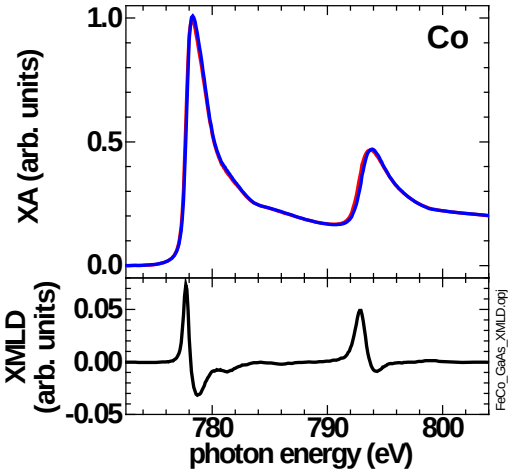




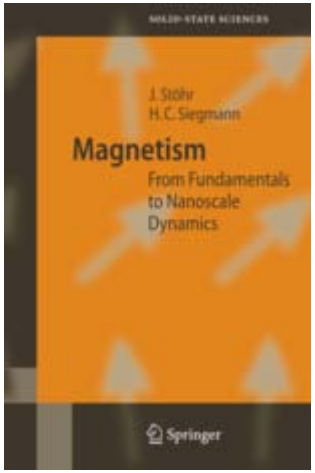
C. Boeglin *et al.*, Nature 465, 458 (2011)



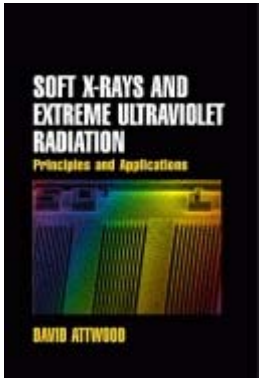
E. Arenholz *et al.*,
Appl. Phys. Lett. 93, 162506 (2008)



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