Paul Scherrer Institut, Swiss Light Source

Frithjof Nolting
X-ray absorption spectroscopy
Surface Science, FS 2011

Surface Science lecture

Di, 22.02.2010 Fixing Dates, Intro to Vacuum Technology, Labvisits Basel (Thomas Jung, Roland Steiner)
Di, 01.03.2010 Introduction, Concepts Samples and Structure (Thomas Jung)
Di, 08.03.2010 Adsorption / Desorption (Thomas Jung)
Di, 15.03.2010 Fasnacht
Di, 22.03.2010 Electronic Properties and Surface Electron Spectroscopies: XPS/UPS, Auger, ARPES (Nirmalya Ballav)
Di, 29.03.2010 Electron Diffraction Methods, in particular RHEED, LEED (Bert Müller)
Di, 05.04.2010 Diffusion and Growth (Thomas Jung)
Di, 12.04.2010 X-ray Absorption Spectroscopy (Frithjof Nolting)
Di, 19.04.2010 Surface Magnetism XMCD / PEEM (Frithjof Nolting)
Di, 26.04.2010 Local Probes and Experiments I, STM, Inelastic tunneling and STS (Silvia Schintke and Thomas Jung)
Di, 03.05.2010 Local Probes and Experiments II, AFM FIM (Thomas Jung)
Di, 10.05.2010 Surface Optics, Kelvin Probe (Thilo Glatzel)
Di, 17.05.2010 Applications of Surface Science in Industry (M. de Wild)
Di, 24.05.2010 Schlussprüfung (Christian Wäckerlin, Thomas Jung)
Di, 31.06.2010 Excursion (Thomas Jung)

Di, 12.04. 2011 X-ray Absorption Spectroscopy (F. Nolting)
Di, 19.04. 2011 PEEM and X-ray Microscopy (F. Nolting)
Both with an emphasis of magnetism

Repetition IV

- Winkelaufgeloeste Photoelektronenspektroskopie ARPES / Fermi Surface Mapping
- Diffusion / Random Walk in 2D
- Fick's Laws
- Atomistic Diffusion Mechanisms / Defects / Steps
- Mass Transfer / Anisotropy
- Cluster Diffusion

Surface Science – Interface science

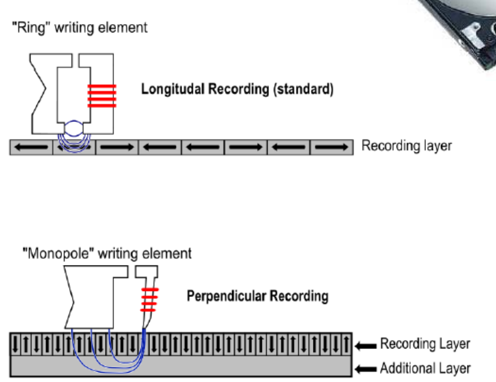
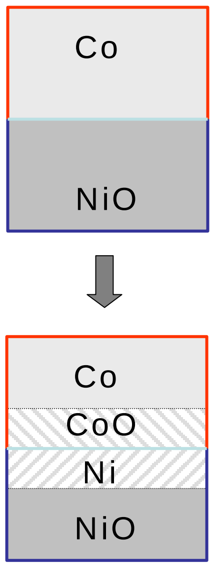


Diagram of perpendicular recording. Note how the magnetic flux travels through the second layer of the platter.

Surface Science – Interface science



Outline

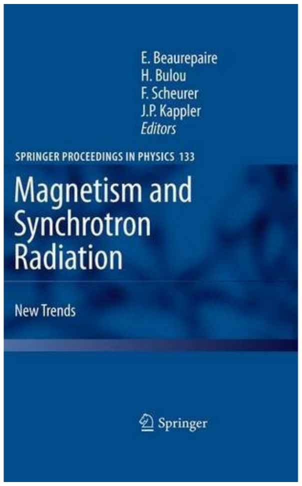
X-ray absorption spectroscopy (XAS)
- Absorption process
- Total electron yield mode
- Examples

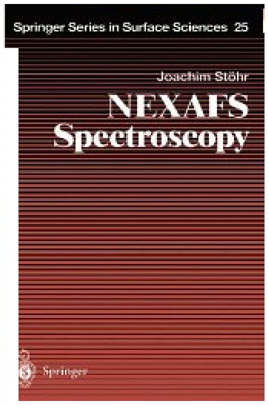
X-ray Magnetic Circular Dichroism (XMCD)
- Basics
- Example: Magnetocrystalline Anisotropy

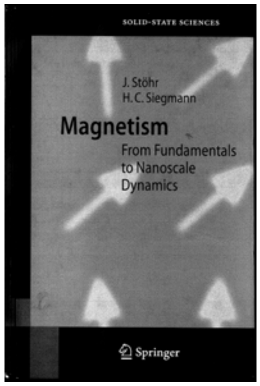
Closer look at the absorption process
- Mulitplet effects
- Example: Interface effect in Exchange Bias system

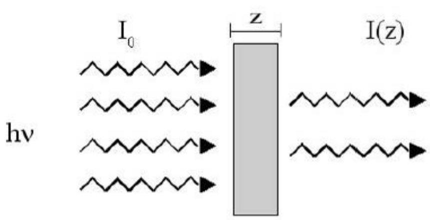
X-ray Magnetic Linear Dichroism (XMLD)
- Basics

Some good books



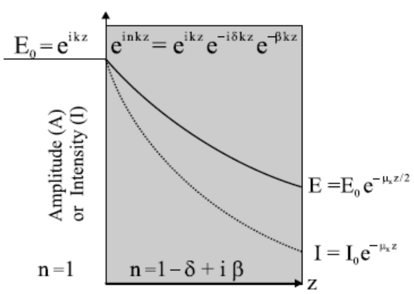




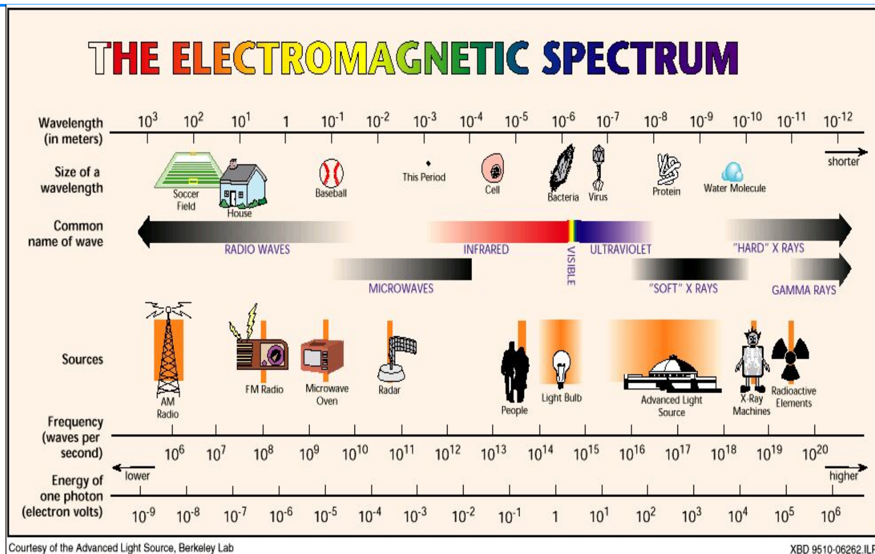


Lambert-Beer

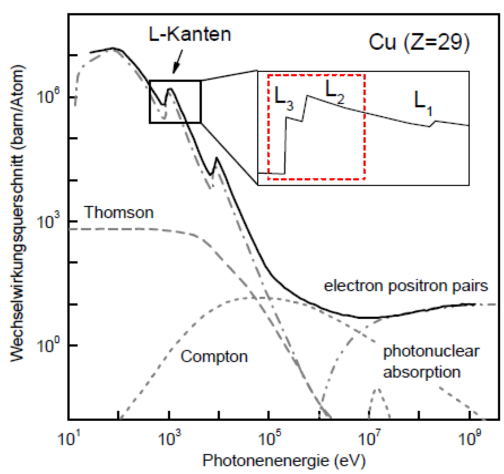
$$\frac{I}{I_0} = e^{-z\mu}$$



$$I(z) = I_0 \, e^{-\mu_x z}$$

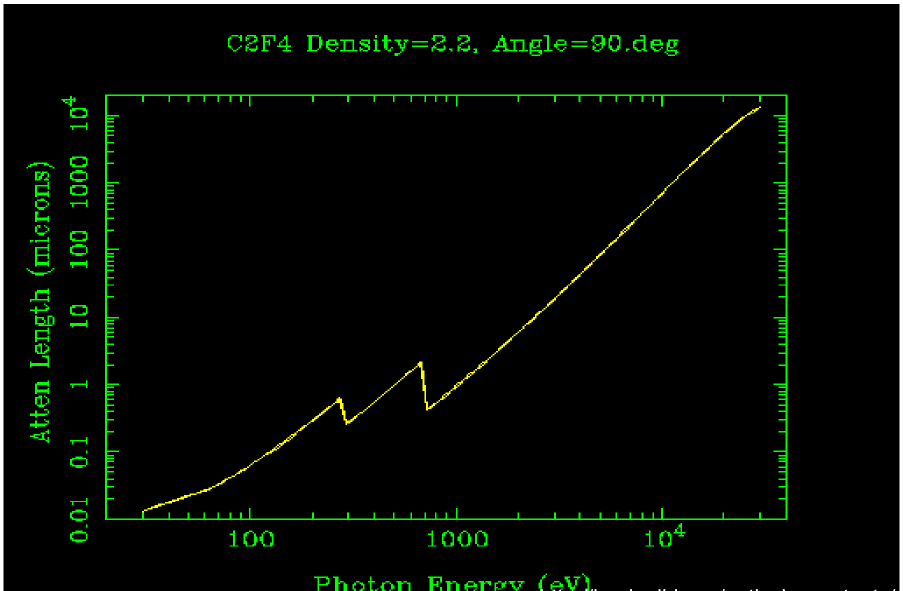


$$E = h\nu = hc/\lambda, \qquad \lambda\,[\text{Å}] = \frac{12.3984}{E\,[\text{keV}]}.$$



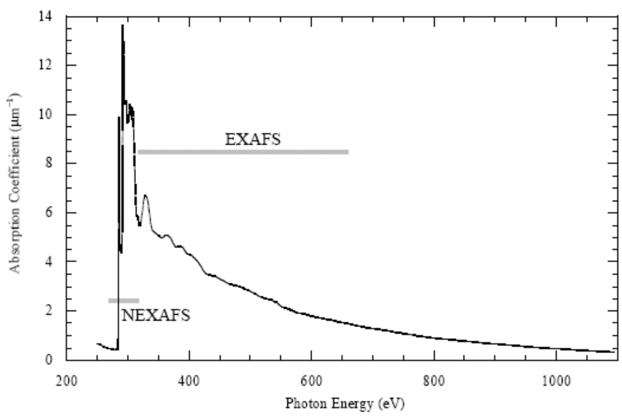
J. H. Hubbel, H. A. Gimm und I. Øverbø, *Pair, triplet, and total atomic cross sections (and mass attenuation coefficients) for 1 MeV-100 GeV photons in elements Z = 1 to 100*, J. Phys. Chem. Ref. Data **9**, 1023 (1980).

Absorption - Teflon



http://henke.lbl.gov/optical_constants/

Absorption of Photons in the Soft X-ray Range



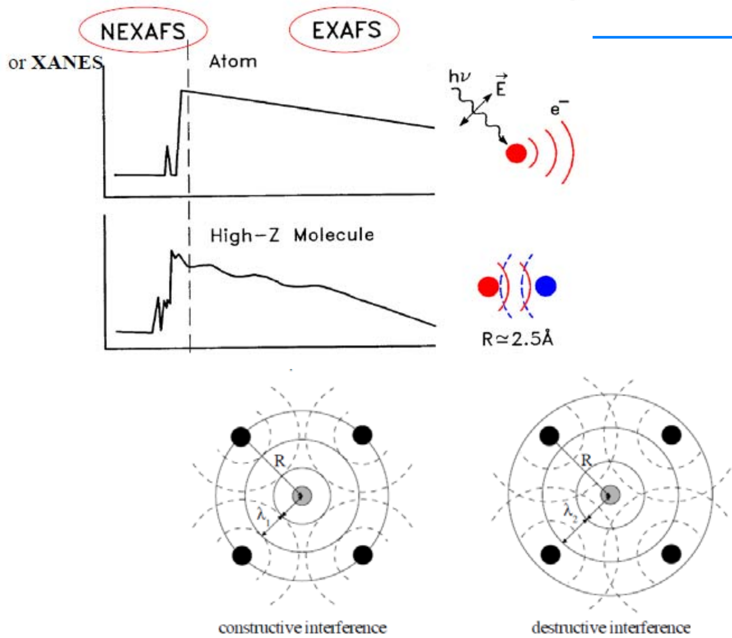
Near Edge X-ray Absorption Fine Structure

reflects density of unoccupied states

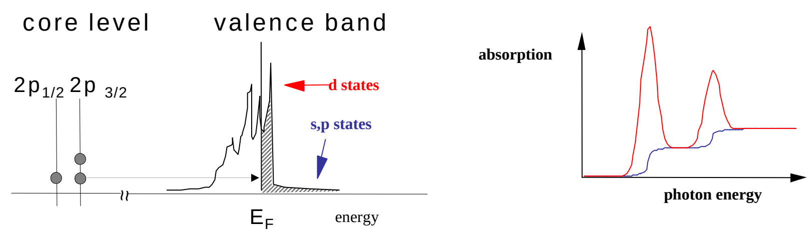
Also called XANES

Extended X-ray Absorption Fine Structure

reflects spatial location of neighboring atoms



Interaction of electromagnetic wave with charge

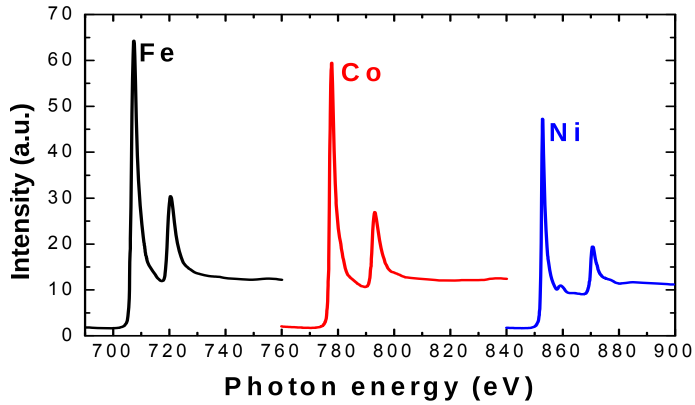


Absorption ~ (Transition matrix: Final state, Initial state) (Density of final states)

Fermi's golden rule
in dipole approximation
wavelength is large compared to charge
1000 eV corresponds to 1.2 nm
2p core radius is about 0.01 nm

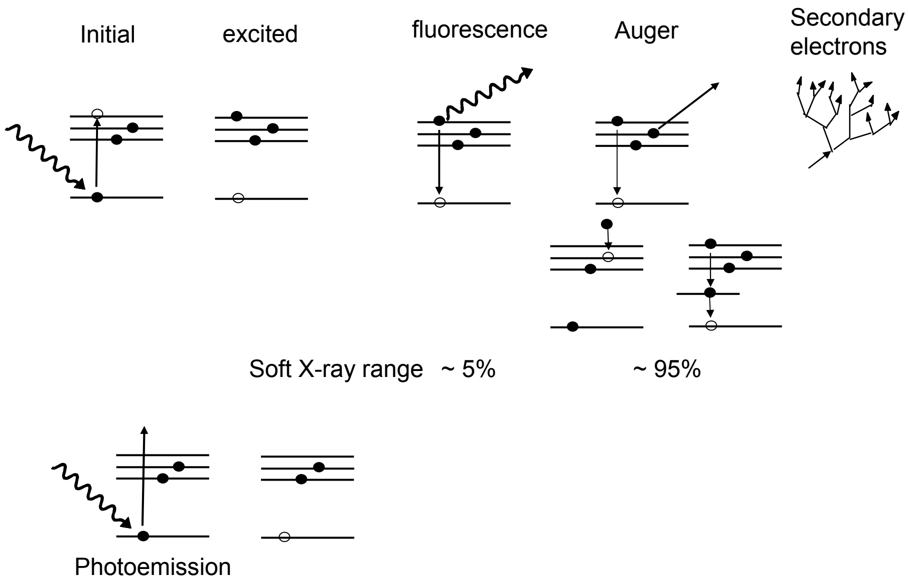
$$\mu \propto \left|\langle f | e \cdot p | i \rangle\right|^2 \rho(E)$$

Element specific



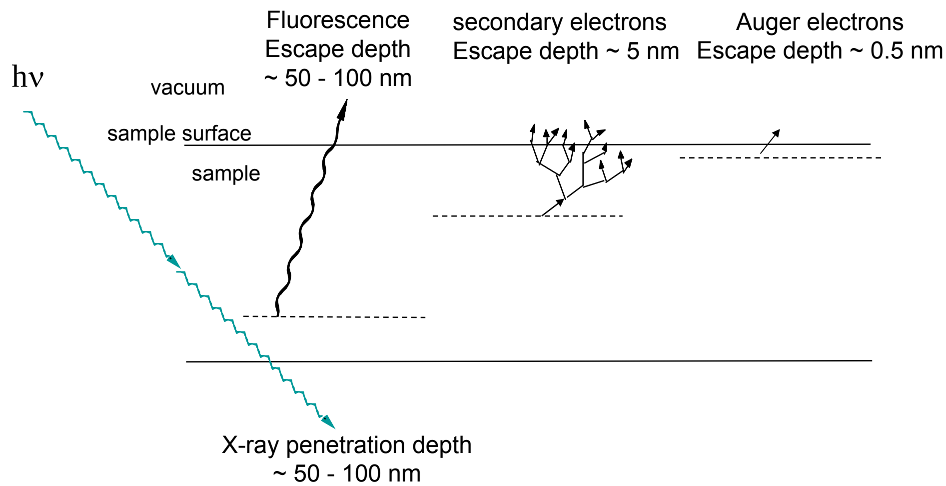
F. Nolting Surface Science FS 2011

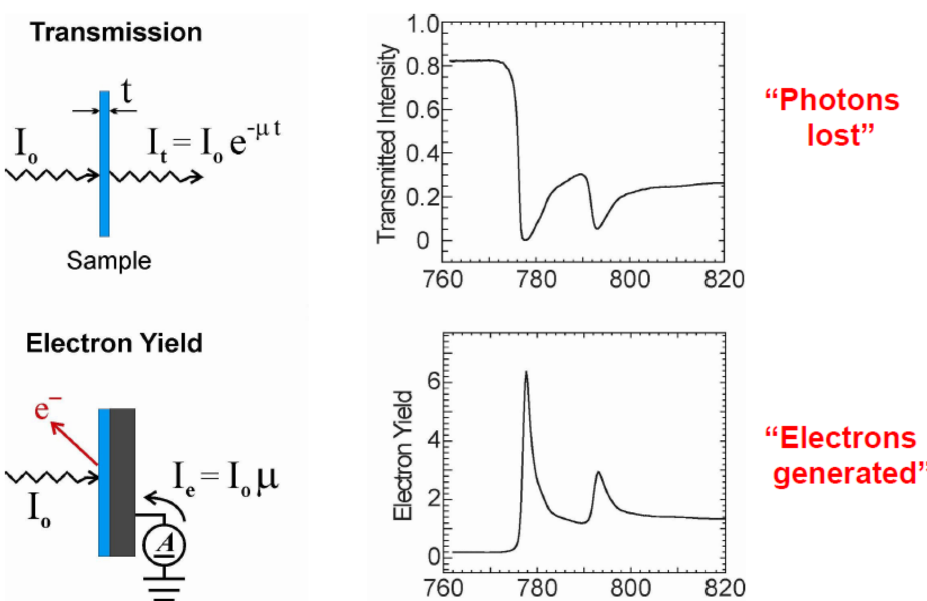
Decay channels



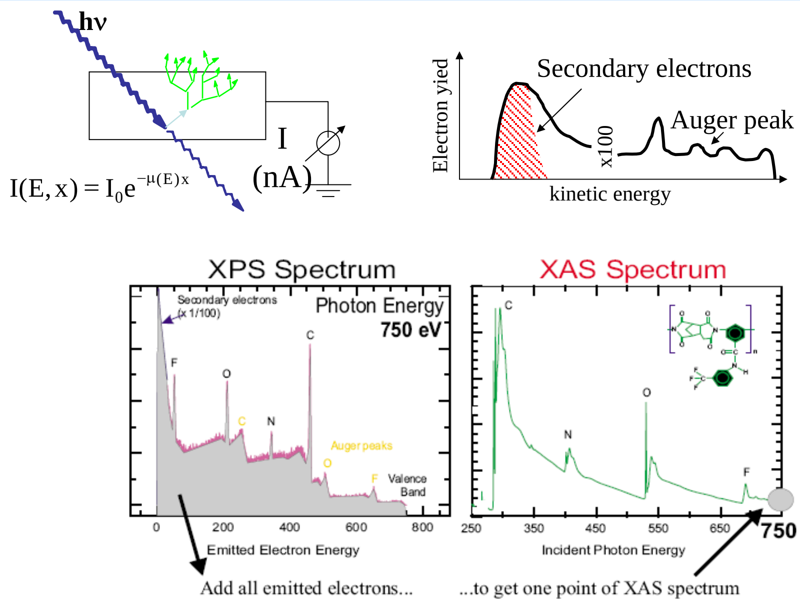
F. Nolting Surface Science FS 2011

Sampling depth

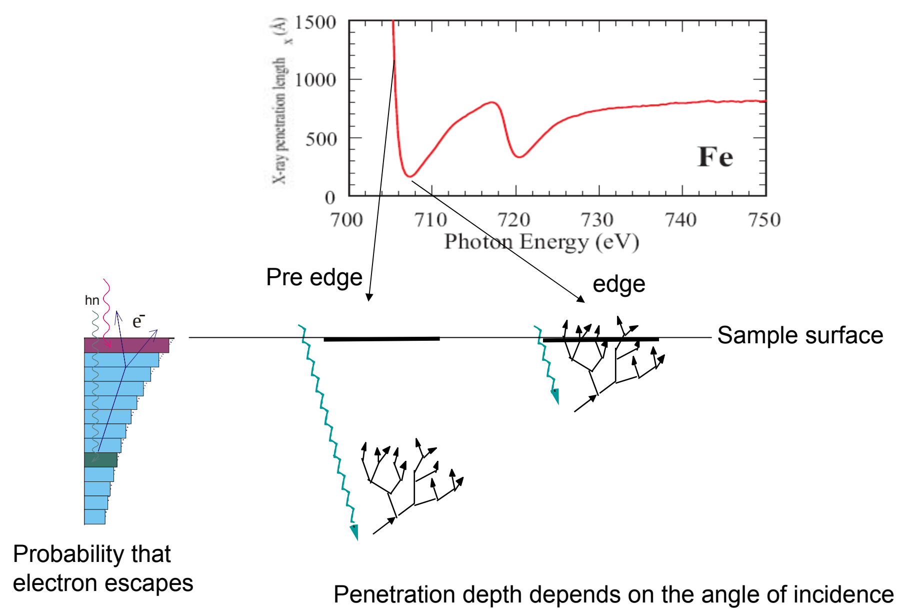




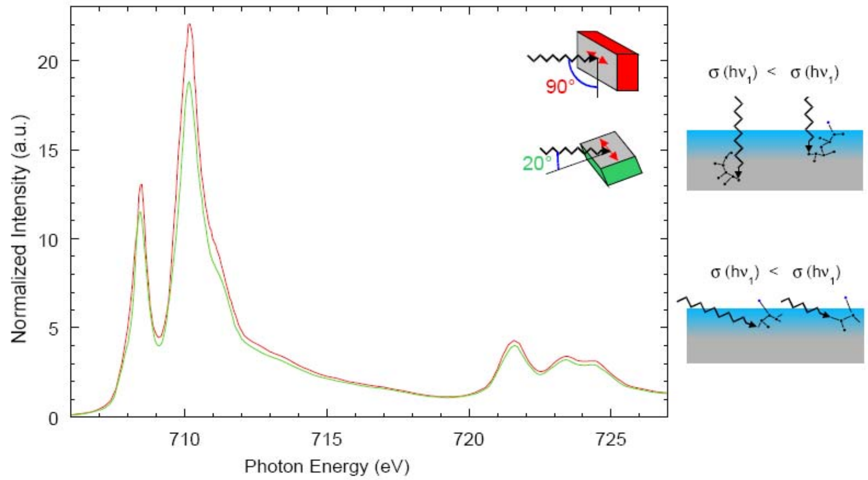
Total electron yield (TEY)



Why is TEY proportional to absorption coefficient

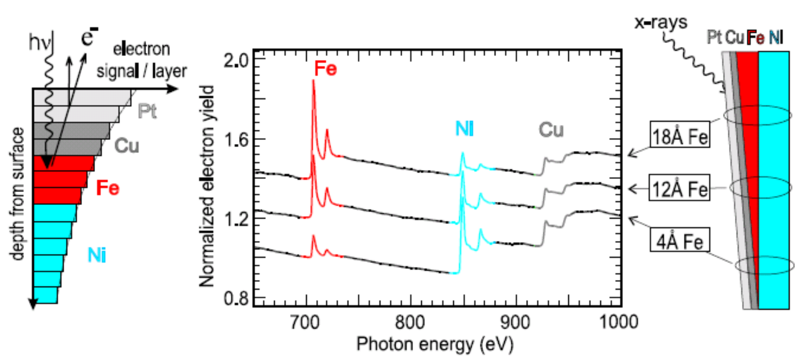


Saturation Effects in TEY Detection



J. Lüning et al, PRB 67, 214433 (2003)

"Dismantle" a Multilayer

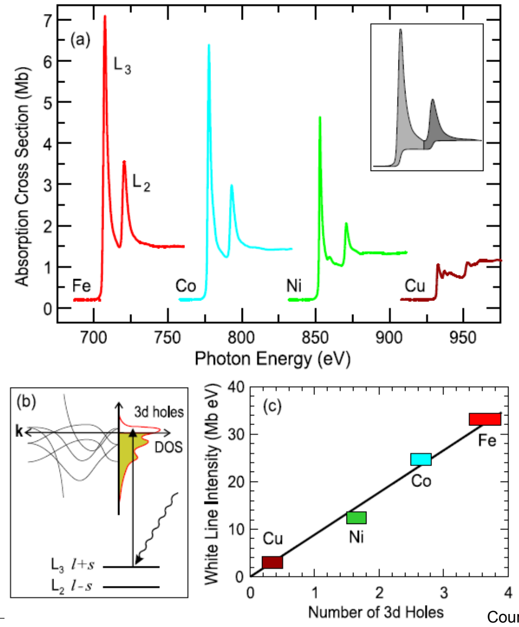


Courtesy J. Stöhr

Determine number of 3d holes

Charge sum rule

Integrated intensity is proportional to number of empty valance states



Courtesy J. Stöhr

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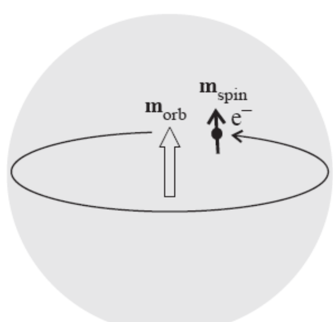
X-ray Magnetic Linear Dichroism (XMLD)
- Basics

Crash class nanomagnetism probed with X-rays

Source of magnetism (atomic)



Spin moment	~ 1.5 μ_B / atom	isotropic
Orbital moment	~ 0.1 μ_B / atom	isotropic/anisotropic

They interact via the spin-orbit coupling L · S

Switching on the interaction

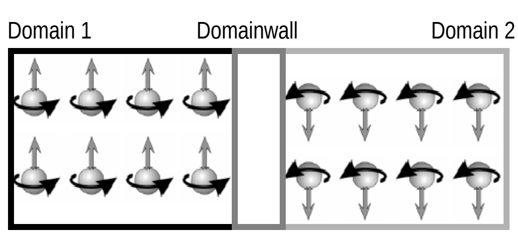
Atoms have an magnetic moment

Without interaction (and no applied magnetic field) they point in random directions and no macroscopic magnetic field is created

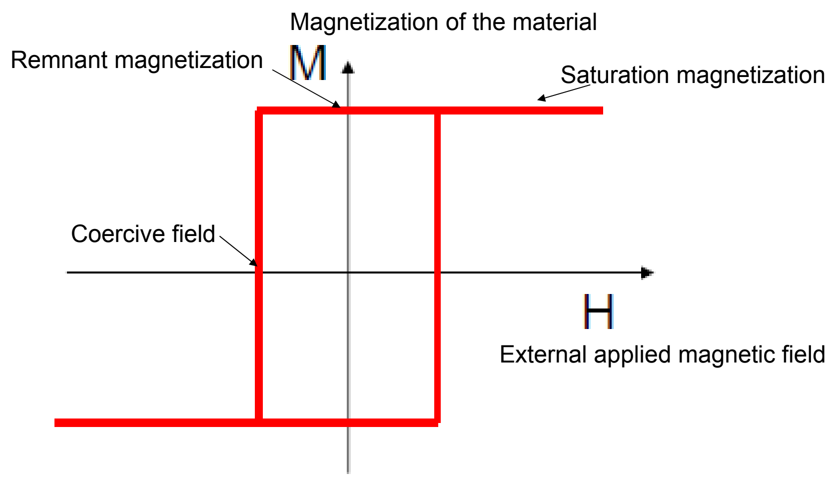
Switching on the interaction

Atoms have an magnetic moment

With interaction they can align to each other and can create macroscopic magnetic field



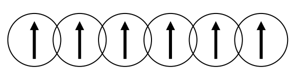
Hysteresis loop



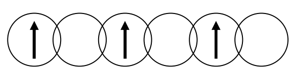
Responses of a material to an applied magnetic field is described by the hysteresis loop

Different magnetic interactions

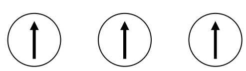
Direct exchange
Overlapping wavefunctions



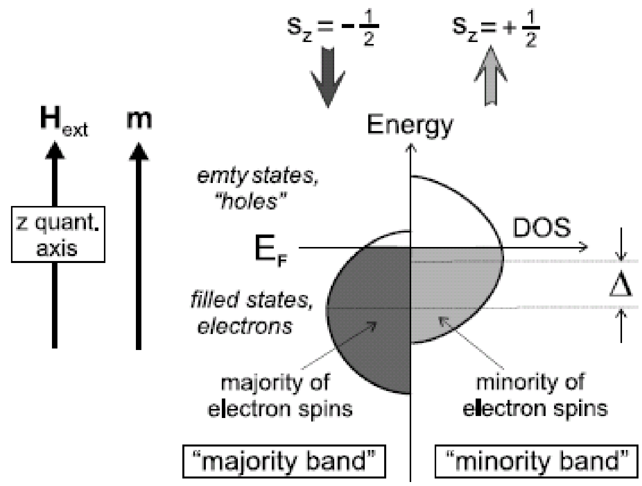
superexchange
Overlapping wavefunctions via
non-magnetic atoms



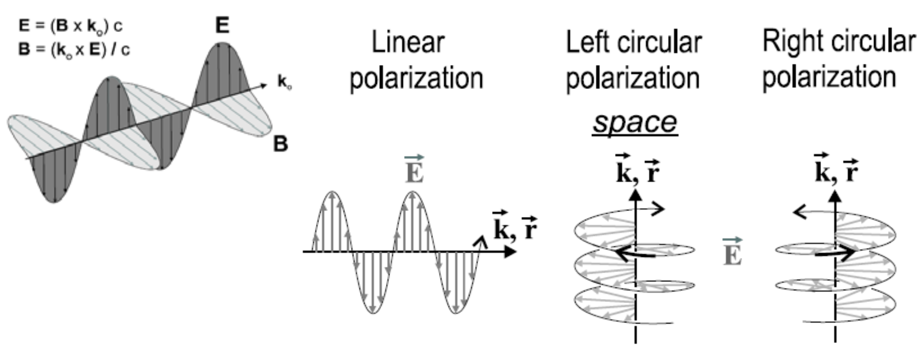
Indirect exchange
Exchange via delocalised electrons



Stoner Model for *3d* Band and Nomenclature

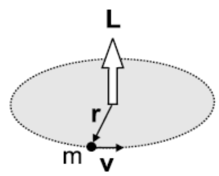


Polarized Photons



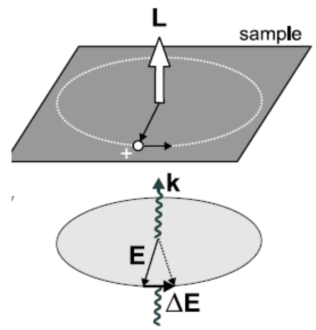
Polarized Photons

Angular moment of orbiting mass



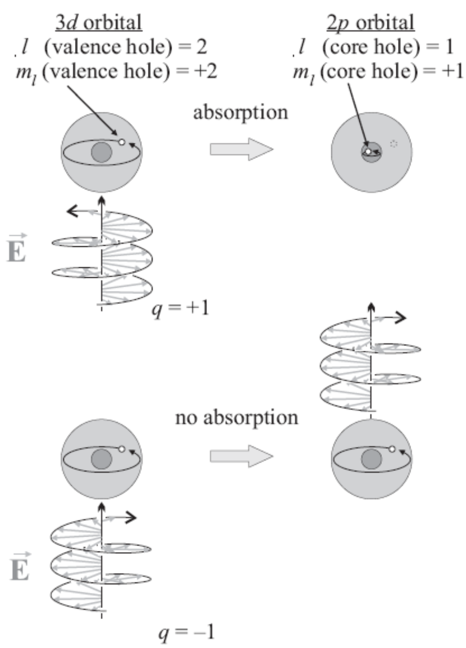
$\mathbf{L} = m\, \mathbf{r} \times \mathbf{v}$

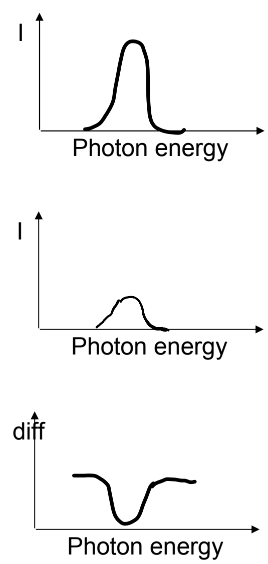
Photon angular moment



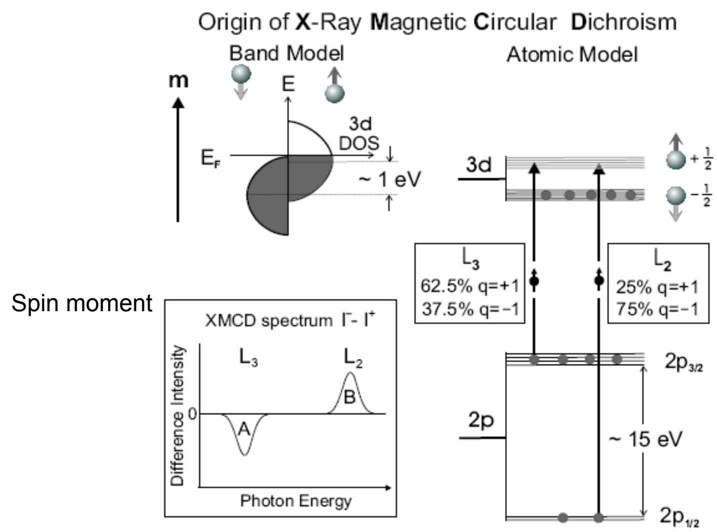
Angular momentum conservation

Polarized Photons

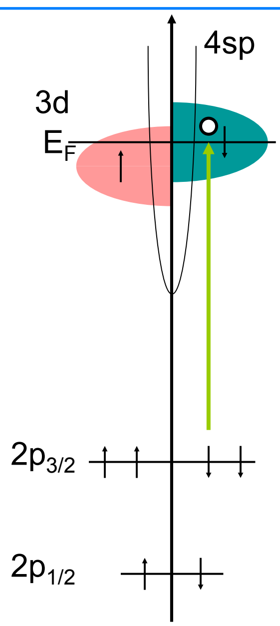




Origin of XMCD



Dipole selection rules



Fermi's golden rule :

$$\mu \propto |\langle f|e \cdot p|i\rangle|^2 \rho(E), \qquad \text{dipole transition}$$

Dipole selection rules:

ΔL = -1, +1

Δ J = -1, 0, +1

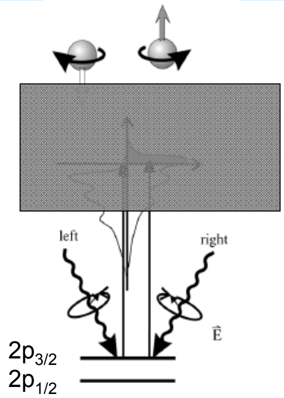
Δ M_J = -1, 0, +1

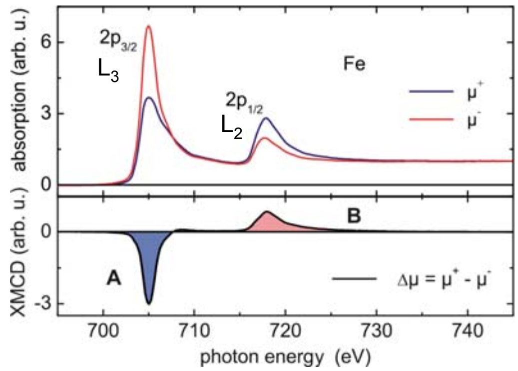
Polarization q +1, 0, -1 (s^+, p, s^-)

L2: $2p_{1/2}$□4s, $3d_{3/2}$

L3: $2p_{3/2}$□4s, $3d_{3/2}$, $3d_{5/2}$

Two-step Model of XMCD



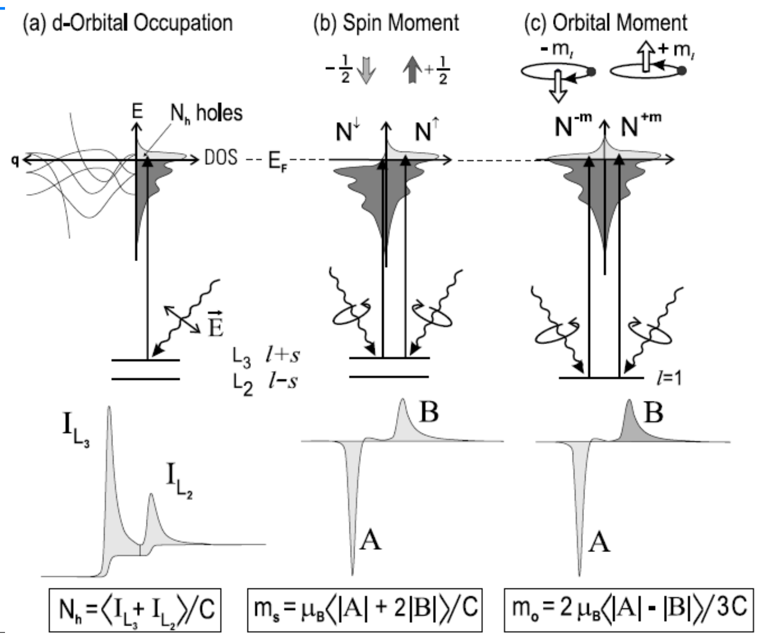


1. Step
Circ. Pol. X-rays generate spin-polarized electrons from inner shell

2. Step
Spin-split 3d bands act as spin analyser

$$\Delta I_{XMCD} \propto P_{circ}\, \boldsymbol{m} \cdot \boldsymbol{L}_{ph} \propto P_{circ} \langle \boldsymbol{m} \rangle \cos\alpha$$

Sum rules



... more complex ... of course

$$m_{\text{orb}} = -\frac{4\int_{L_3+L_2}(\mu_+ - \mu_-)\,d\omega}{3\int_{L_3+L_2}(\mu_+ + \mu_-)\,d\omega}(10 - n_{3d}), \quad (1)$$

Electron occupation

$$m_{\text{spin}} = -\frac{6\int_{L_3}(\mu_+ - \mu_-)\,d\omega - 4\int_{L_3+L_2}(\mu_+ - \mu_-)\,d\omega}{\int_{L_3+L_2}(\mu_+ + \mu_-)\,d\omega} \times (10 - n_{3d})\left(1 + \frac{7\langle T_z\rangle}{2\langle S_z\rangle}\right)^{-1}, \quad (2)$$

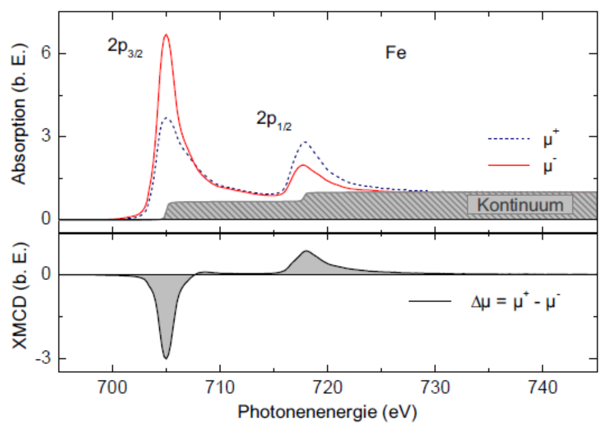
magnetic dipole moment

$\langle T_z \rangle$ is the expectation value of the intra-atomic magnetic dipole operator, accounting for a possible asphericity of the spin density distribution.

effective spin magnetic moment

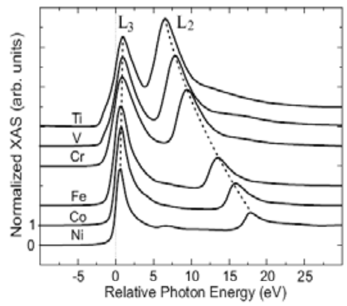
$$\mu_S^{\text{eff}} = \mu_S + 7\mu_T$$

Only contribution to the resonance absorption should be considered



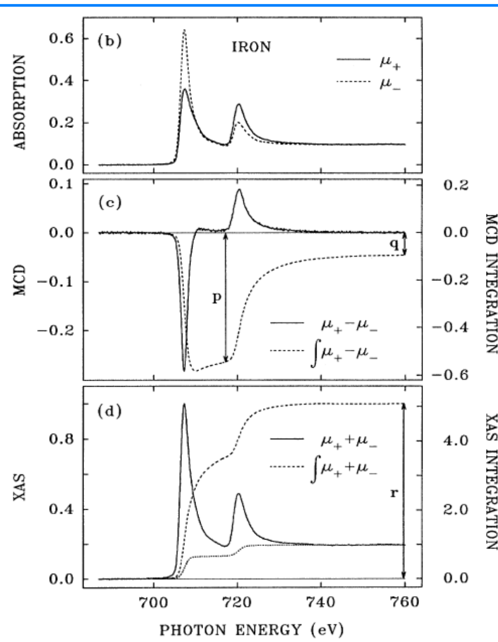
Taken from PhD Thesis Armin Kleibert, 2005

... more complex ... of course



L_3 and L_2 must be separated

calculating



Normalize Spectra
Corrected for
- incident angle
- Polarization degree
- saturation effects

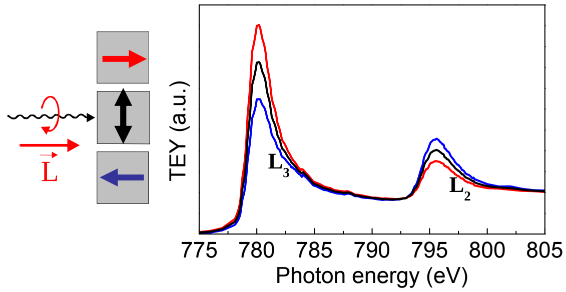
MCD
- difference
- integrate

XAS
- sum spectra
- correct background
- non resonant

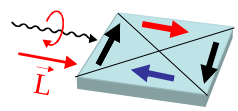
Calculate/neglect
- $\langle T_Z \rangle$
- $\langle Sz \rangle$

C.T. Chen et al. PRL 75(1), 152 (1995)

X-ray Magnetic Circular Dichroism (XMCD)



XMCD ~ <**M**> cos(**M**,**L**)



Photons
- no mass
- no spin
- angular momentum

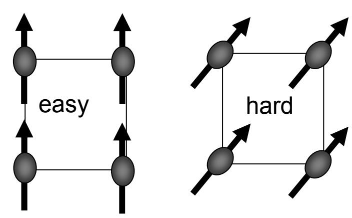
Magnetism 3d metals
- small orbital moment
- large spin moment

XMCD in action

Study Magneto-crystalline anisotropy

Magnetic Anisotropy
preferential magnetization along axes
easy / hard axis

(magneto-crystalline anisotropy)

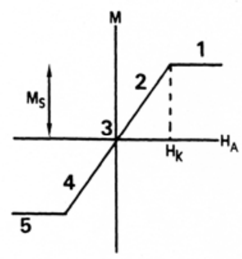


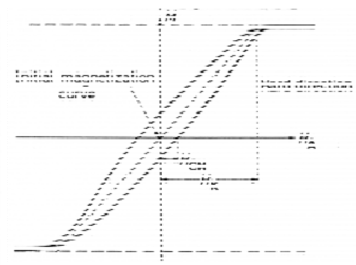
The magneto-crystalline anisotropy is the energy that it takes to rotate the magnetization from the “easy” direction into the “hard” direction

J. Stöhr, JMMM 200 (1999) 470 – 497
Reiko Nakajima PhD Thesis 1998

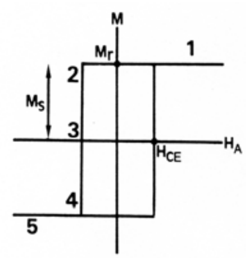
Hysteresis loop – anisotropy

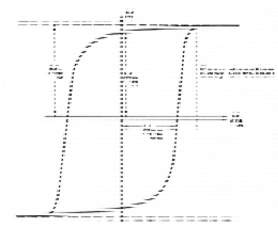
hard axis



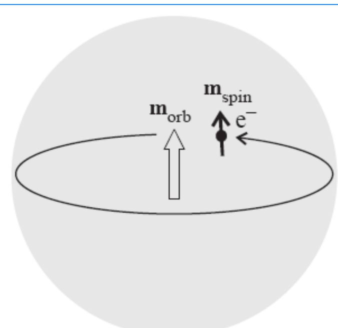


easy axis





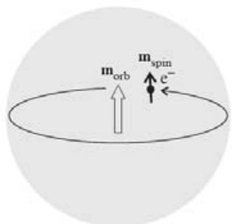
Magneto-crystalline anisotropy

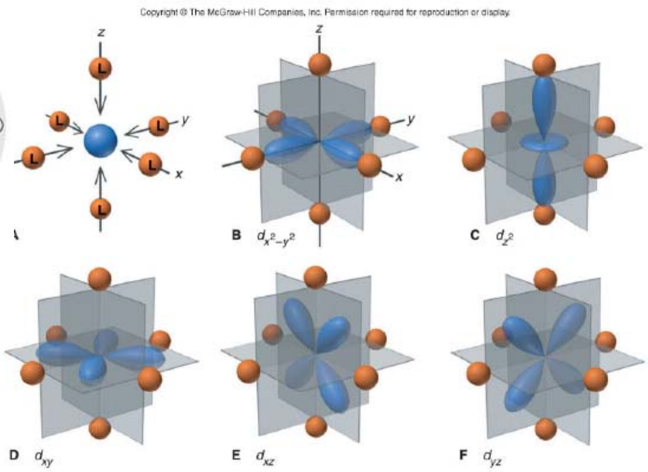


Spin moment	~ 1.5 μ_B / atom	isotropic
Orbital moment	~ 0.1 μ_B / atom	isotropic/anisotropic

They interact via the spin-orbit coupling L · S

Anisotropy





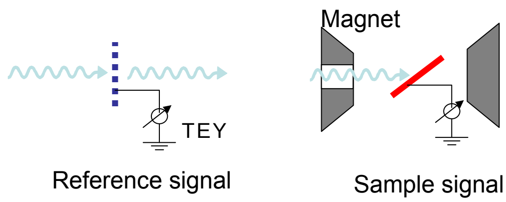
Bruno model

The Bruno model states that the orbital moment is larger along the easy magnetization direction, and that the difference between the orbital moments along the easy and hard directions is proportional to the magneto-crystalline anisotropy

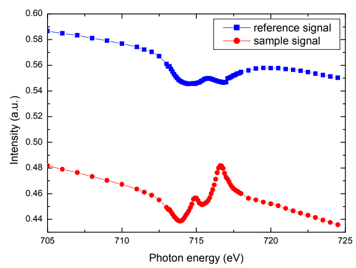
$$\Delta E_{so} = \zeta \left[\langle \boldsymbol{L} \cdot \boldsymbol{S} \rangle_{hard} - \langle \boldsymbol{L} \cdot \boldsymbol{S} \rangle_{easy} \right] = \frac{\zeta}{4\mu_B} (m_o^{easy} - m_o^{hard}) > 0$$

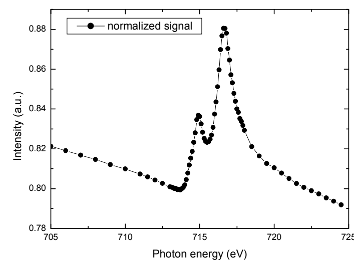
P. Bruno, PRB 39, 865 (1989)

How do we measure

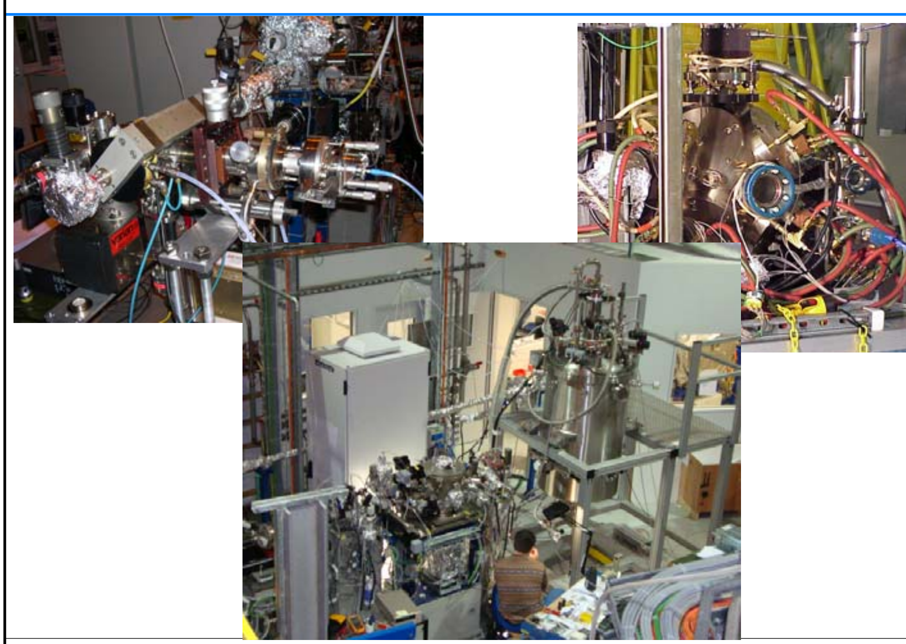


$$\frac{\text{Sample}}{\text{Reference}} = \text{Norm}$$



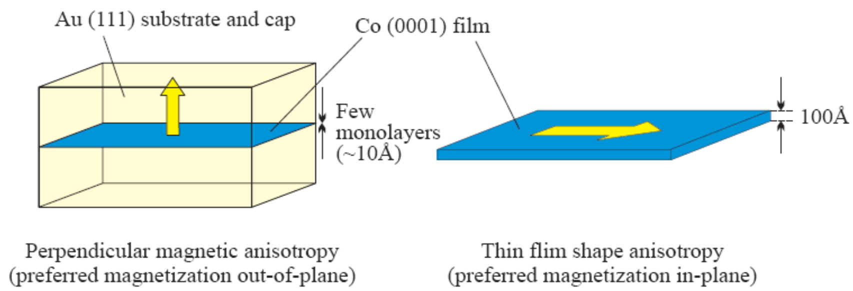


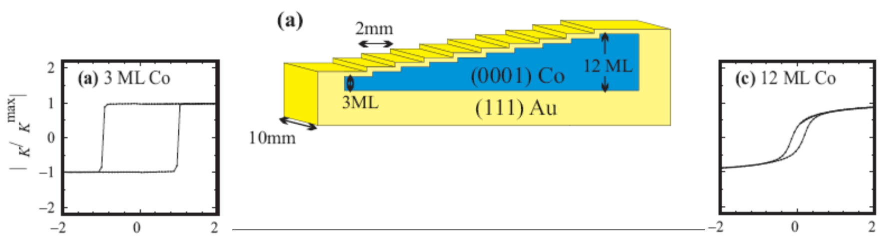
How do we measure



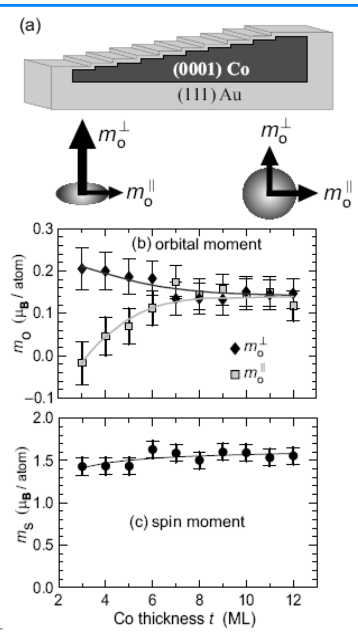
Test system

Magnetic anisotropy in Co (0001) films





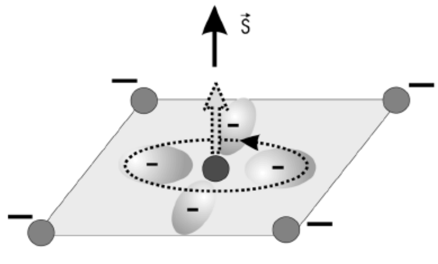
Results



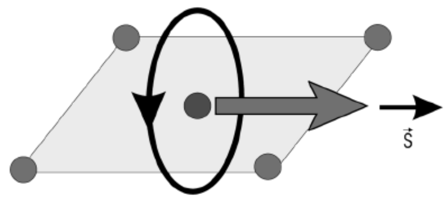
Thin film
Orbital moment is anisotropic and larger out-of-plane

Thick film
Orbital moment is isotropic
shape anisotropy is dominating

Simple picture – Ligand fields



in-plane orbits are quenched



out-of-plane orbits are less perturbed

Free monolayer — in-plane moment

Mulitlayer with stronger out-of-plane bonding — out-of-plane moment

Ferromagnetism in one-dimensional monatomic metal chains

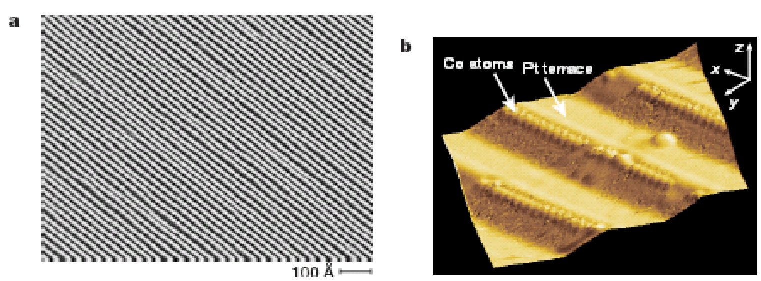
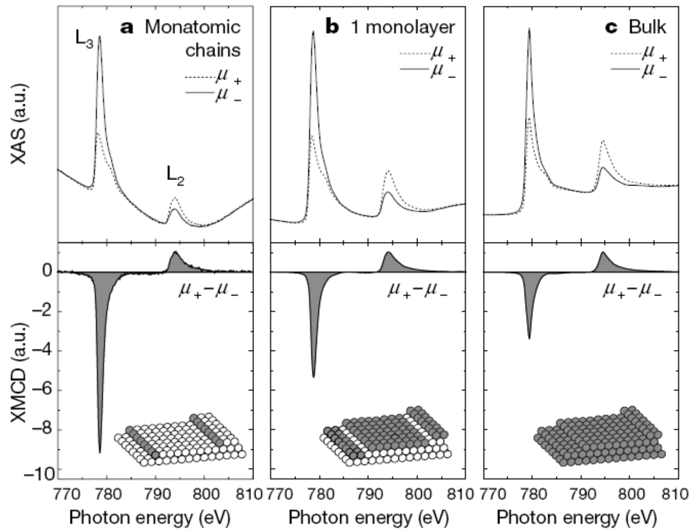


Figure 1 STM topographs of the Pt(997) surface. **a**, Periodic step structure (each white line represents a single step). The surface has a 6.45° miscut angle relative to the (111) direction; repulsive step interactions result in a narrow terrace width distribution centred at 20.2 Å with 2.9 Å standard deviation. **b**, Co monatomic chains decorating the Pt step edges (the vertical dimension is enhanced for better contrast). The monatomic chains are obtained by evaporating 0.13 monolayers of Co onto the substrate held at $T = 260$ K and previously cleaned by ion sputtering and annealing cycles in ultrahigh vacuum (UHV). The chains are linearly aligned and have a spacing equal to the terrace width.

P. Gambardella et al. Nature 416, 301 (2002)

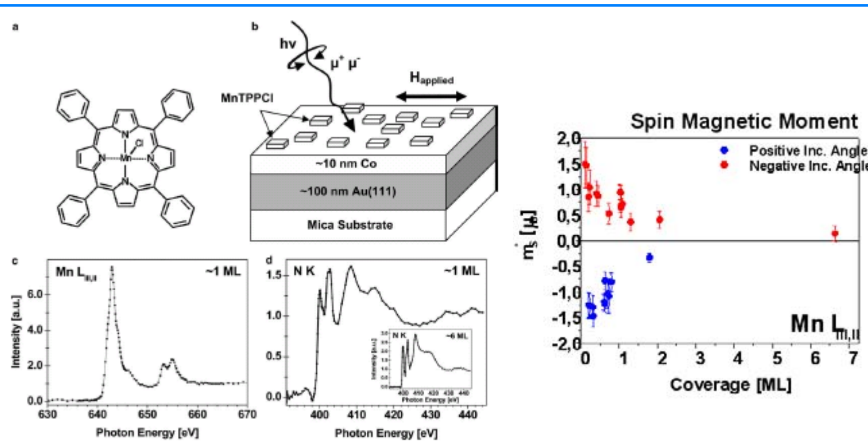
Increased orbital moment in Co chains



$m_l \sim 0.68\ \mu_B$ / atom $m_l \sim 0.31\ \mu_B$ / atom $m_l \sim 0.14\ \mu_B$ / atom

P. Gambardella et al. Nature 416, 301 (2002)

Induced magnetic ordering in a molecular monolayer



A. Scheybal, T. Ramsvik, R. Bertschinger, M. Putero, F. Nolting, and T.A. Jung, Chemical Physics Letters 411, 214 (2005)

Outline

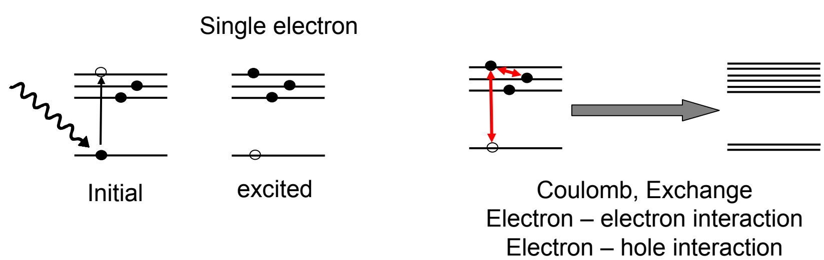
X-ray absorption spectroscopy (XAS)
- Absorption process
- Total electron yield mode
- Examples

X-ray Magnetic Circular Dichroism (XMCD)
- Basics
- Example: Magnetocrystalline Anisotropy

Closer look at the absorption process
- Mulitplet effects
- Example: Interface effect in Exchange Bias system

X-ray Magnetic Linear Dichroism (XMLD)
- Basics

Interactions

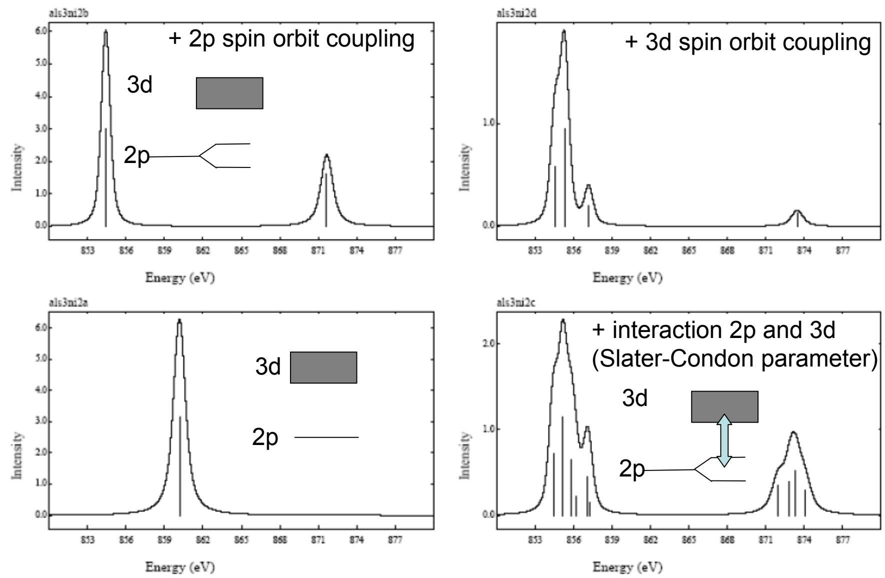


Valence – Valence interaction : many body effects

Valence – Core interaction : multiplet effects

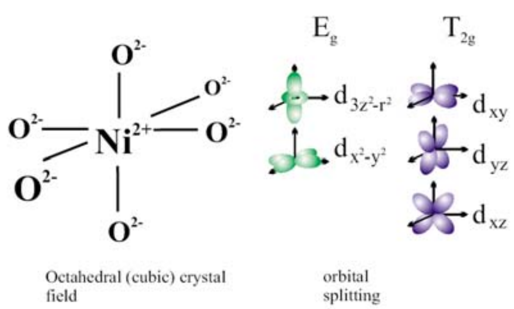
Hybridization between ground state and final state leads to a multiplet structure of the spectrum

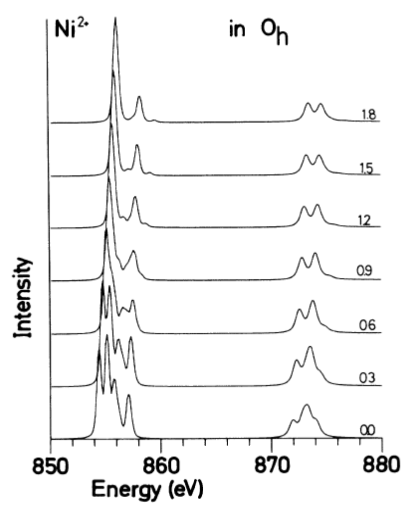
Interactions – NiO (Ni 2+)



F. de Groot

Crystal field

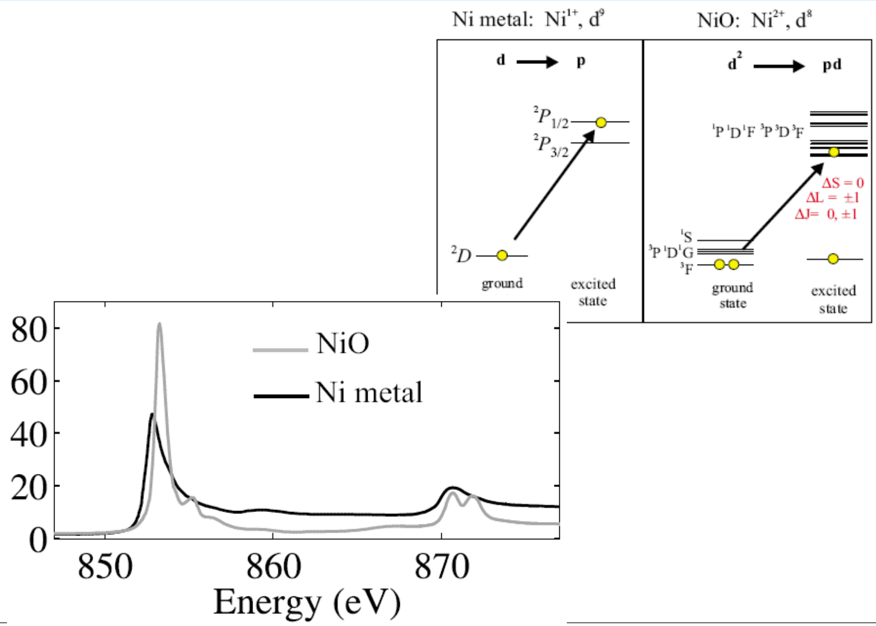




Further parameter is charge transfer

F. de Groot et al. PRB 42, 5459 (1990)

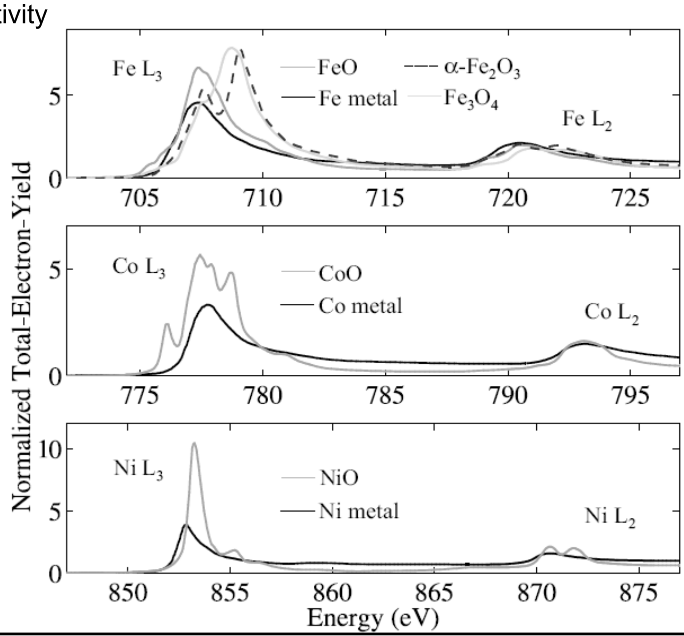
Ni metal vs NiO



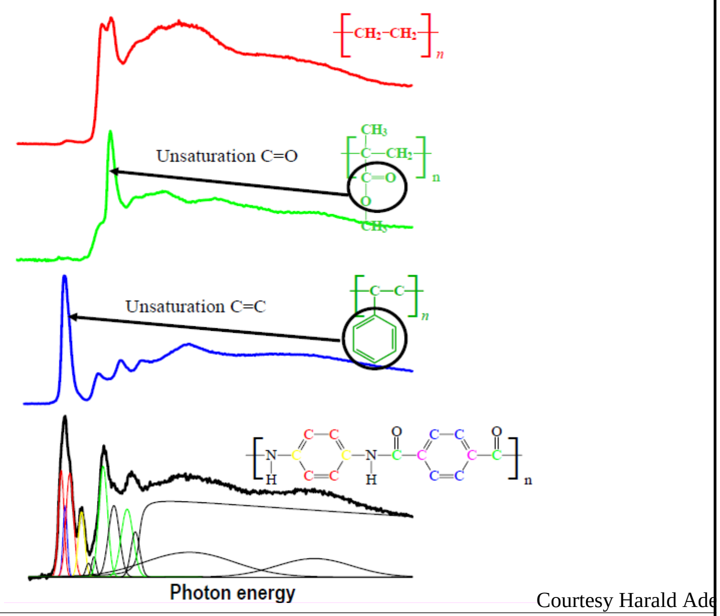
F. Nolting Surface Science FS 2011

Complex but good for us

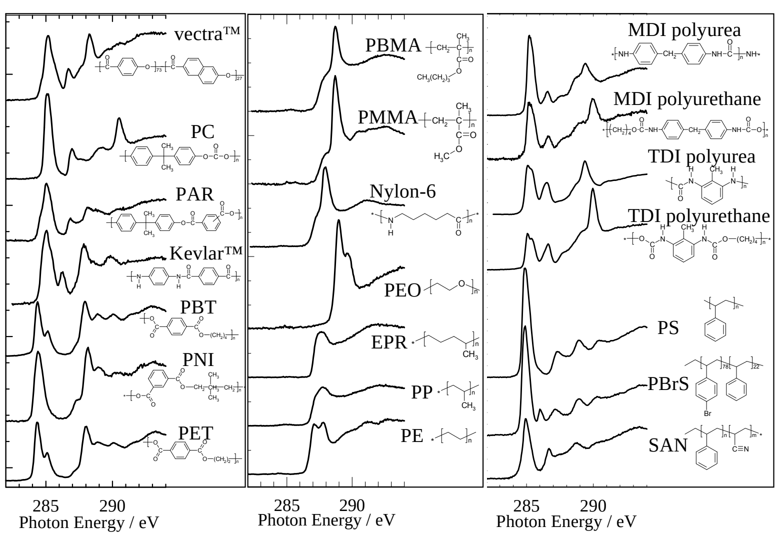
Chemical sensitivity



Footprint of complex bindings

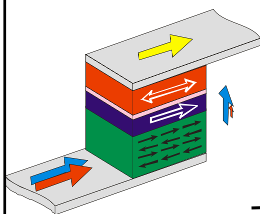


Absorption spectroscopy library



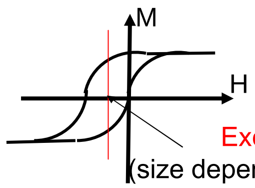
Dhez, Ade, and Urquhart J. Electron Spectrosc. 128, 85 (2003)

Exchange Bias



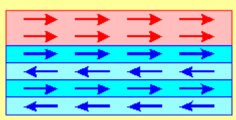
Unidirectional anisotropy in FM adjacent to AFM

discovered 1956 by Meiklejohn and Bean

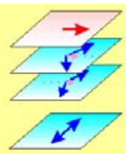


Effect of exchange bias is still poorly understood

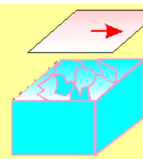
Ideal Interface Model



Spin Flop Model



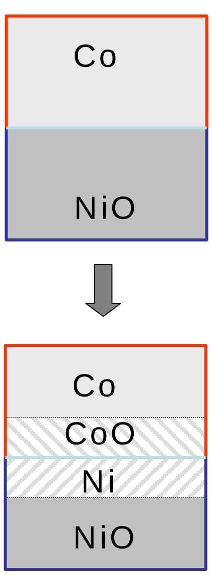
Domain Size Model

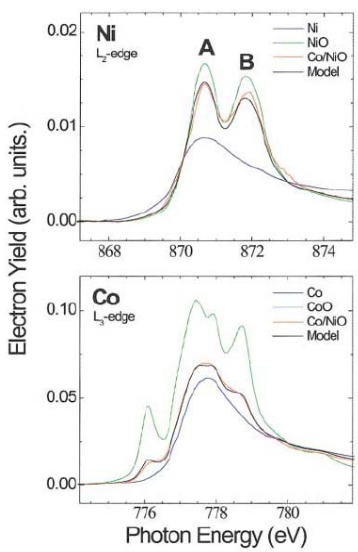


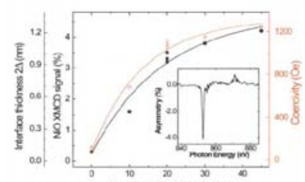
Uncompen-sated spins at AF domain boundaries

Reviews: A.E. Berkowitz and K. Takano, J. Magn. Magn. Mater. 200(1-3), 552 (1999).
J. Nogues and I.K. Schuller, J. Magn. Magn. Mater. 192, 203 (1999)

Exchange biased Co/NiO multilayer



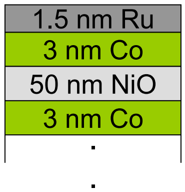




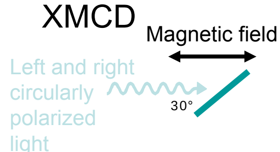
Oxidation/reduction at the interface is responsible for increased coercivity

Tom Regan et al, Phys. Rev. B 64, 214422 (2001)

Exchange biased Co/NiO multilayer

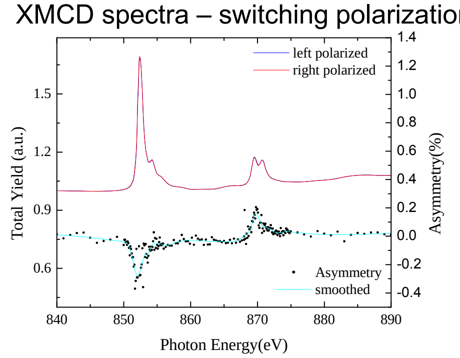


XMCD

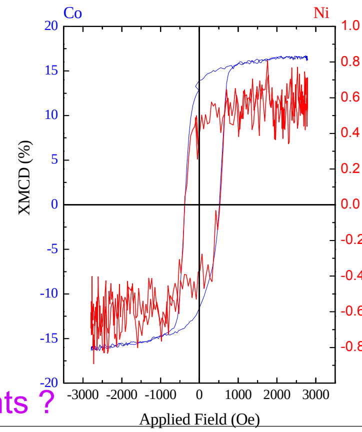


EPU beamline 4 at ALS,
Elke Arenholz, Tony Young

XMCD spectra – switching polarization



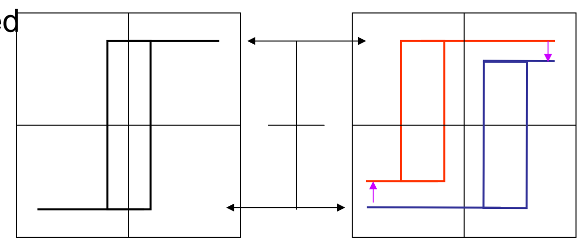
Hysteresis of Co and NiO



Pinned Moments ?

Pinned Moments

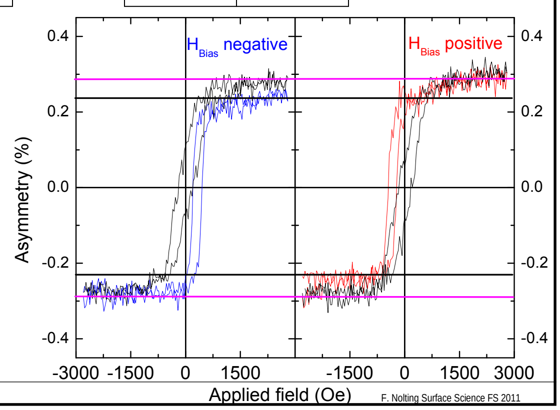
unbiased



biased

Pinned Moments

Co/IrMn multilayer
Field grown, H_c = 600 Oe
Matt Carey at IBM, Almaden, USA



H. Ohldag et al, PRL 91, 017203 (2003)

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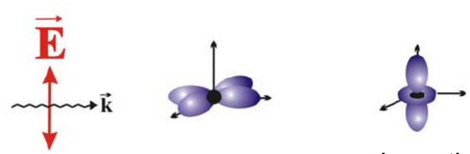
- Basics

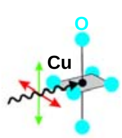
Interaction with linear light - charge

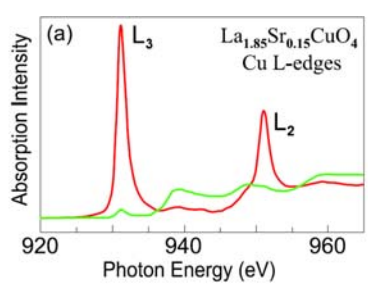
Excitation into 3d band



No absorption   absorption

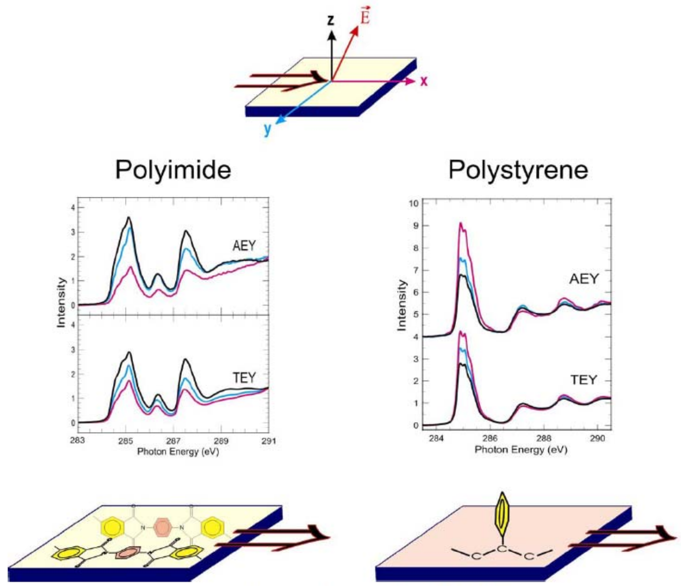
X-ray Natural linear dichroism
“search light effect”





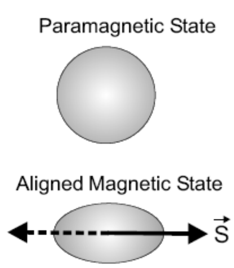
C.T. Chen et al PRL 68, 2543 (1998)

Polarization Dependent NEXAFS Probes Bond Anisotropy at Surface



J. Stöhr et al., Science **292**, 2299 (2001)

Interaction with linear light - magnetic

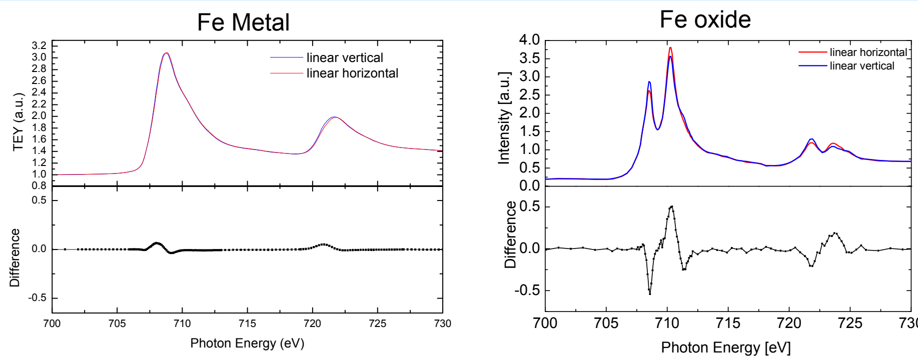


Electron charge density is isotropic
no linear dichroism

Preferred spin axis
spin orbit coupling changes charge density
linear dichroism

XMLD X-ray Magnetic Linear Dichroism

XMLD



XMLD enhanced by mulitplet

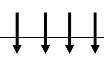
Enables to measure antiferromagnetic systems!

XMCD ~ **M** cos(**M**,**S**)

XMLD ~ <**M**²> cos²(**M**,**E**)

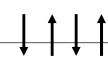
Ferromagnet (FM)

Net magnetic moment



Antiferromagnet (AFM)

No net magnetic moment



Some pioneering papers on XMCD and XMLD

Strong magnetic dichroism predicted in the $M_{4,5}$ X-ray absorption spectra of magnetic rare-earth materials,
B.T. Thole, G. van der Laan, and G.A. Sawatzky, Phys. Rev. Lett. 55, 2086 (1985).

Experimental proof of magnetic x-ray dichroism,
G. van der Laan, B.T. Thole, G.A. Sawatzky, J.B. Goekoop, J.C. Fuggle, J.-M. Esteva, R. Karnatak, J.P. Remeika, and H.A. Dabkowska, Phys. Rev. B 34, 6529 (1986).

Absorption of Circularly Polarized X-rays in Ion,
G. Schütz, W. Wagner, W. Wilhelm, P. Kienle, R. Zeller, R. Frahm, G. Materlik, Phys. Rev. Lett. 58, 737 (1987).

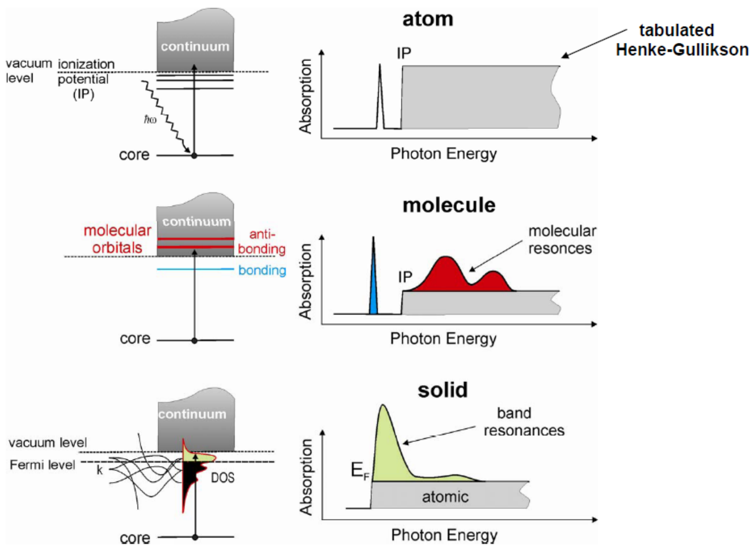
Soft X-ray magnetic circular dichroism at the $L_{2,3}$ edges of nickel,
C.T. Chen, F. Sette, Y. Ma, and S. Modesti, Phys. Rev. B 42, 7262 (1990).

X-ray circular dichroism as a probe of orbital magnetization,
B.T. Thole, P. Carra, F. Sette, and G. van der Laan, Phys. Rev. Lett, 1943 (1992).

Magnetic X-ray dichroism – general features of dipolar and quadrupolar spectra,
P. Carra, H. König, B.T. Thole, and M. Altarelli, Physica B 192, 182 (1993).

Determination of Spin- and Orbital-Moment Anisotropies in Transition Metals by Angle-Dependent X-Ray Magnetic Circular Dichroism,
J. Stöhr, H. König, Phys. Rev. Lett. 75, 3748 (1995)

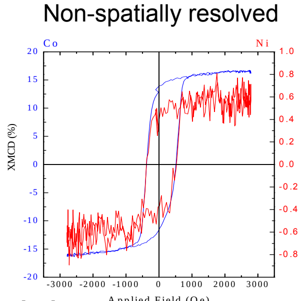
X-ray Absorption Spectra in a Nutshell



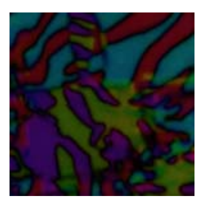
Conclusions

Polarization depend soft X-ray absorption spectroscopy is a powerful tool to study elemental resolved ferromagnetic and anitferromagnetic thin films and interfaces

Non-spatially resolved



spatially resolved …next time



The technique

is sensitive to

- elemental composition
- chemical bonds
- structural parameters
- electronic structure
- magnetic properties

has a very broad range of application

- Magnetic multilayers
- Diluted systems
- Nanoparticles
- Molecular magnets
- …