Paul Scherrer Institut, Swiss Light Source

Frithjof Nolting
X-ray absorption spectroscopy
Surface Science, FS 2012

## Surface Science lecture

Di, 21.02.2012 Fixing Dates, Intro to Vacuum Technology, Labvisits Basel (Toni Ivas, Sylwia Nowakowska, Roland Steiner)
Di, 28.02.2012 Introduction, Concepts Samples and Structure (Thomas Jung)
Di, 06.03.2012 Adsorption / Desorption (Thomas Jung)
Di, 13.03.2012 Electron Diffraction Methods, in particular RHEED, LEED (Bert Müller)
Di, 20.03.2012 Electronic Properties and Surface Electron Spectroscopies: XPS/UPS, Auger, ARPES (Andrij Romaniyuk)
Di, 27.03.2012 FASNACHT
Di, 03.04.2012 Diffusion and Growth (Thomas Jung)
Di, 10.04.2012 Local Probes and Experiments I, STM, Inelastic tunneling and STS (Thomas Jung)
Di, 17.04.2012 X-ray Absorption Spectroscopy (Frithjof Nolting)
Di, 24.04.2012 Surface Magnetism XMCD / PEEM (Frithjof Nolting)
Di, 01.05.2012 Surface Optics, Kelvin Probe (Thilo Glatzel)
Di, 08.05.2012 Local Probes and Experiments II, AFM FIM (Thomas Jung)
Di, 15.05.2012 Applications of Surface Science in Industry (M. de Wild)
Di, 22.05.2012 Schlussprüfung (Jan Girovsky, Thomas Jung)
Di, 29.05.2012 Excursion (Thomas Jung)

Di, 17.04. 2011 X-ray Absorption Spectroscopy (F. Nolting)
Di, 24.04. 2011 PEEM and X-ray Microscopy (F. Nolting)
Both with an emphasis of magnetism

## Repetition VII

•Scanning Tunneling Microscopy

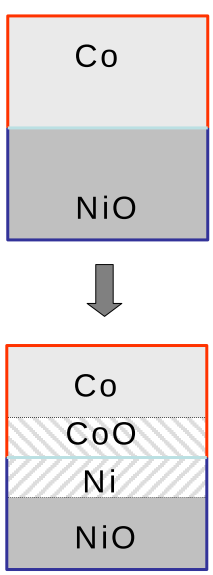
•Principle, Creep, Non-linearities, Tip Artefacts tip preparation

•Beyond Microscopy: Imaging, Mapping, Manipulation

•Quantum mechanical Tunneling: Tip and Surface States: Spectroscopy



## Surface Science – Interface science




•Look through Co layer
•Sensitive to the interface region
•Distinguish Co and NiO
•Distinguish Co and CoO and Ni and NiO

## Outline

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

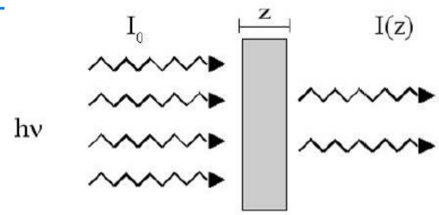
**X-ray Magnetic Circular Dichroism (XMCD)**
- Basics
- Example: Magnetocrystalline Anisotropy

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

**X-ray Magnetic Linear Dichroism (XMLD)**
- Basics

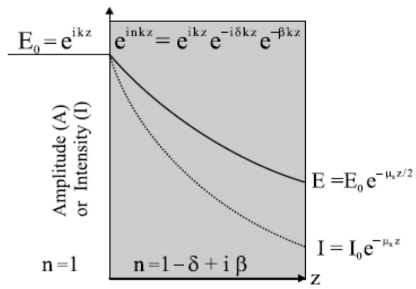


## Some good books



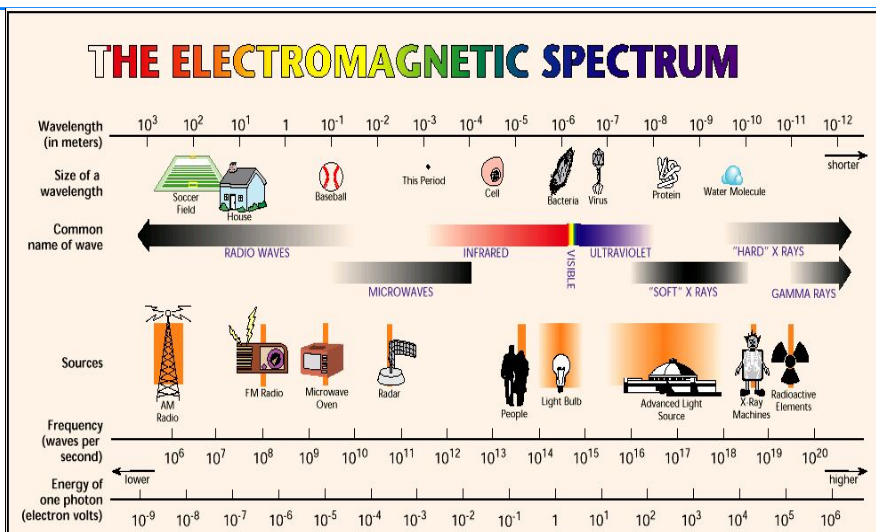

Lambert-Beer

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




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

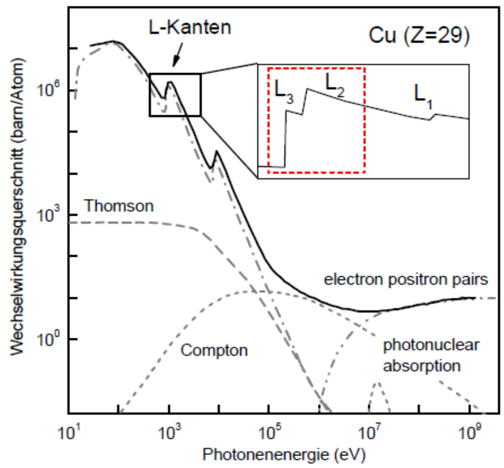





Courtesy of the Advanced Light Source, Berkeley Lab

XBD 9510-06262.ILR

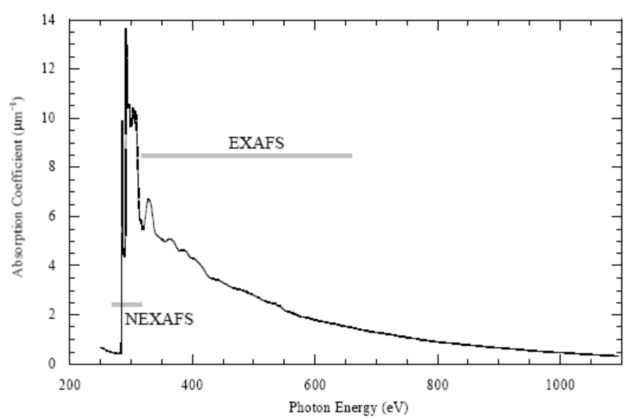
$$E = h\nu = hc/\lambda, \qquad \lambda\,[\text{Å}] = \frac{12.3984}{E\,[\text{keV}]}.$$




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 of Photons in the Soft X-ray Range



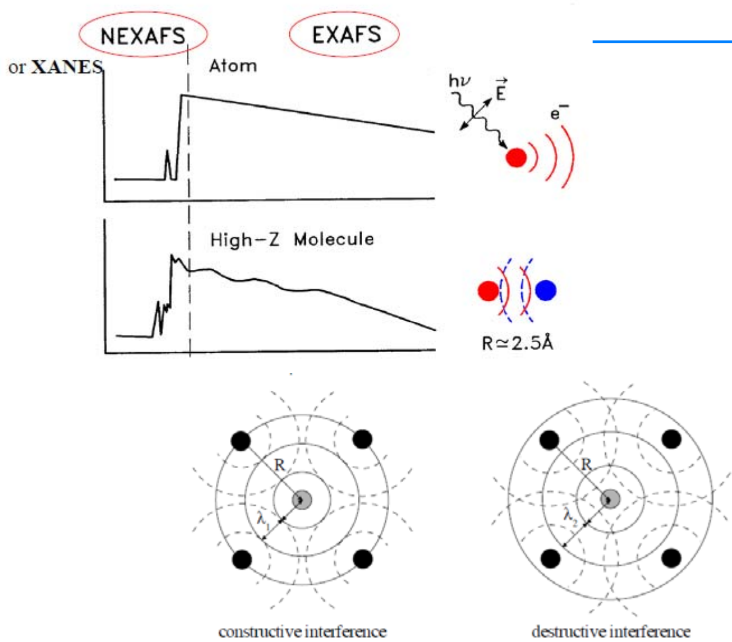

**Near Edge X-ray Absorption Fine Structure**

reflects density of unoccupied states

Also called XANES

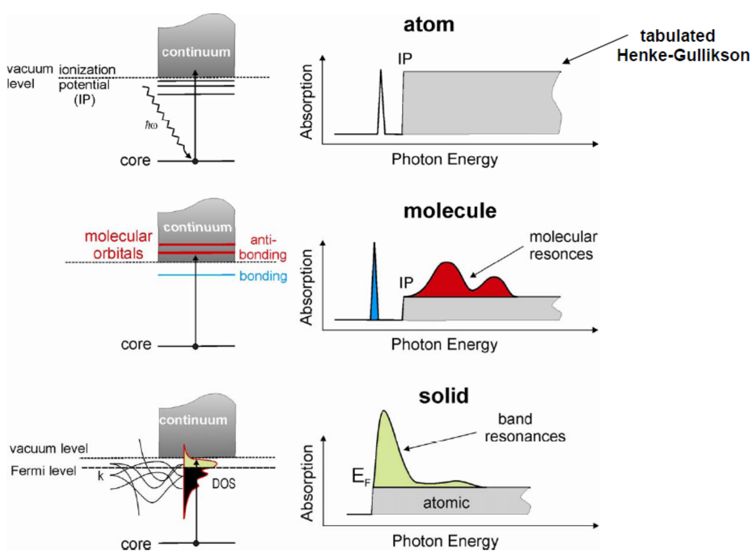
**Extended X-ray Absorption Fine Structure**

reflects spatial location of neighboring atoms

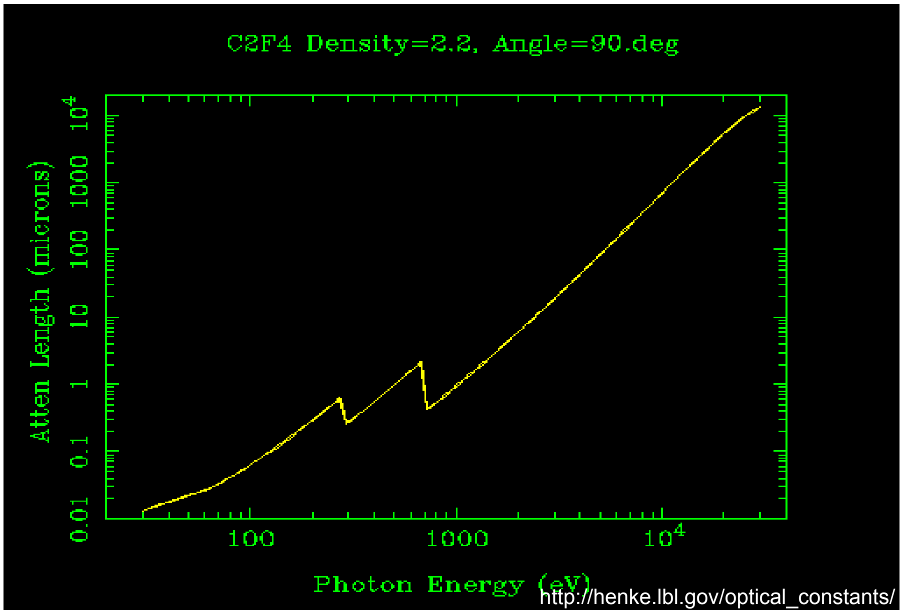





## X-ray Absorption Spectra in a Nutshell



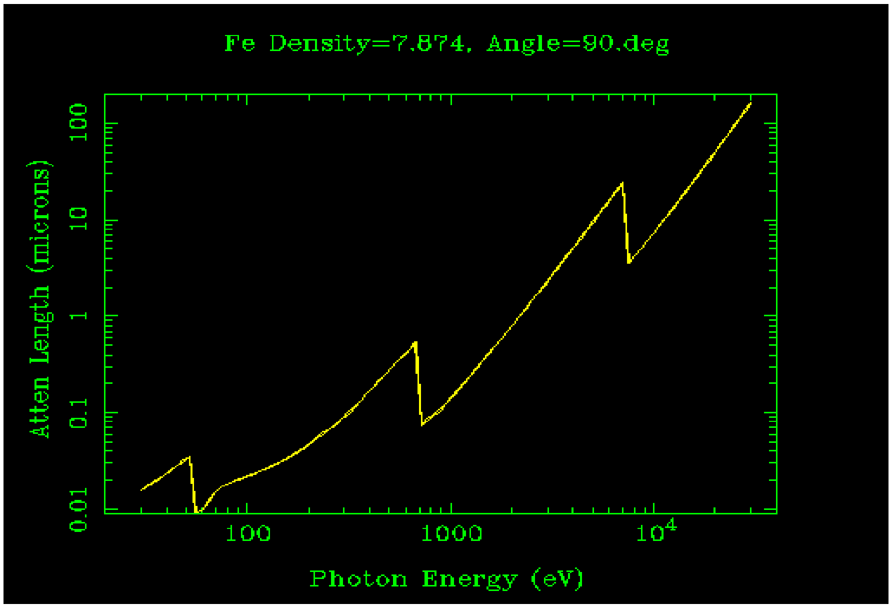
## Absorption - Teflon



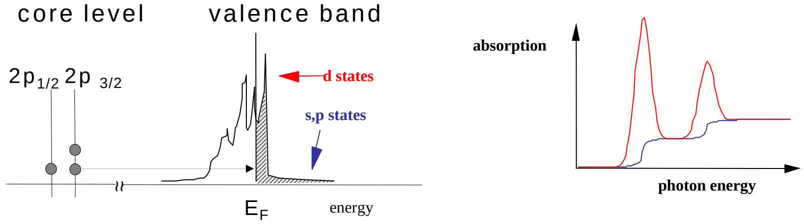

http://henke.lbl.gov/optical_constants/



## Absorption - Iron



## Interaction of electromagnetic wave with charge



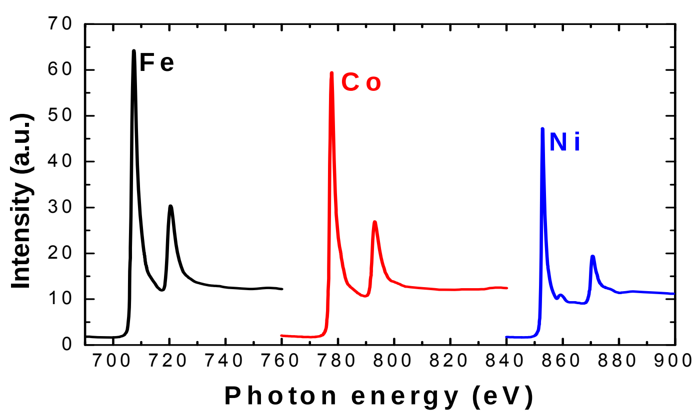

Absorption ~ (Transition matrix: Final state, Initial state) (Density of final states)

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

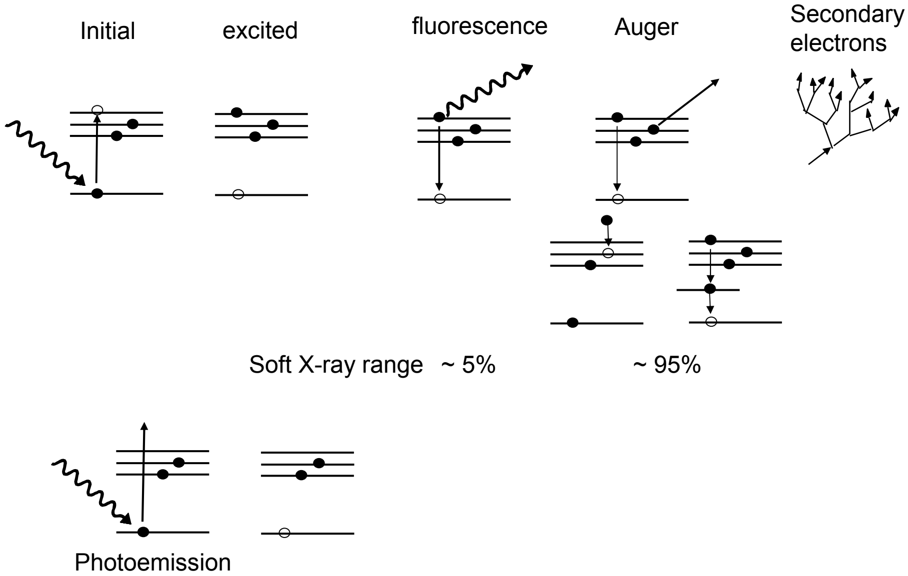
$$\mu \propto \left|\langle f | e \cdot p | i \rangle\right|^2 \rho(E)$$



## Element specific

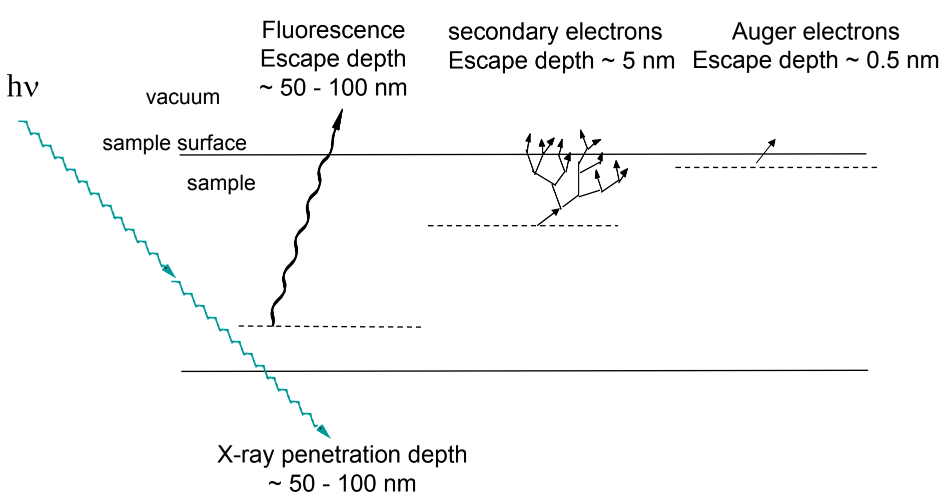


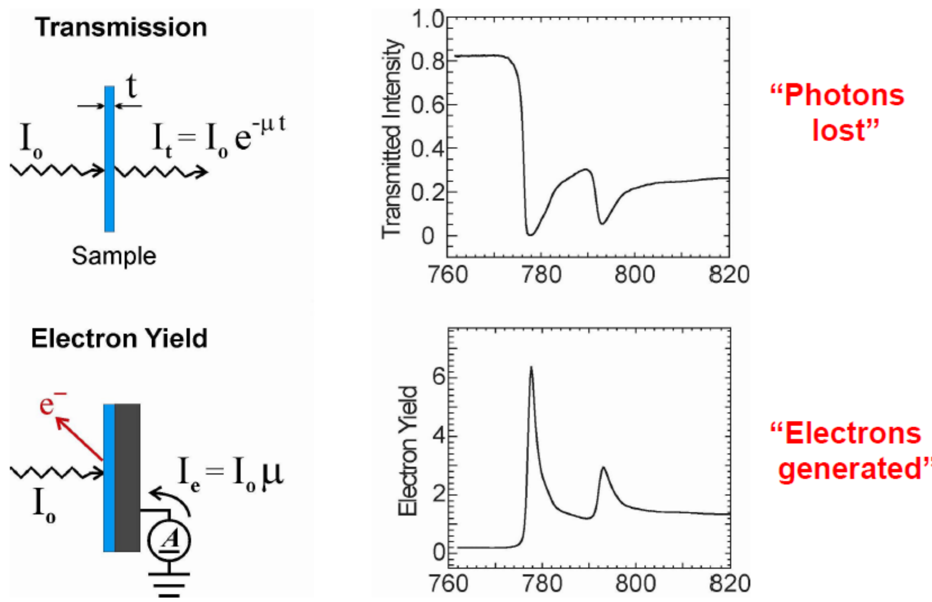
## Decay channels





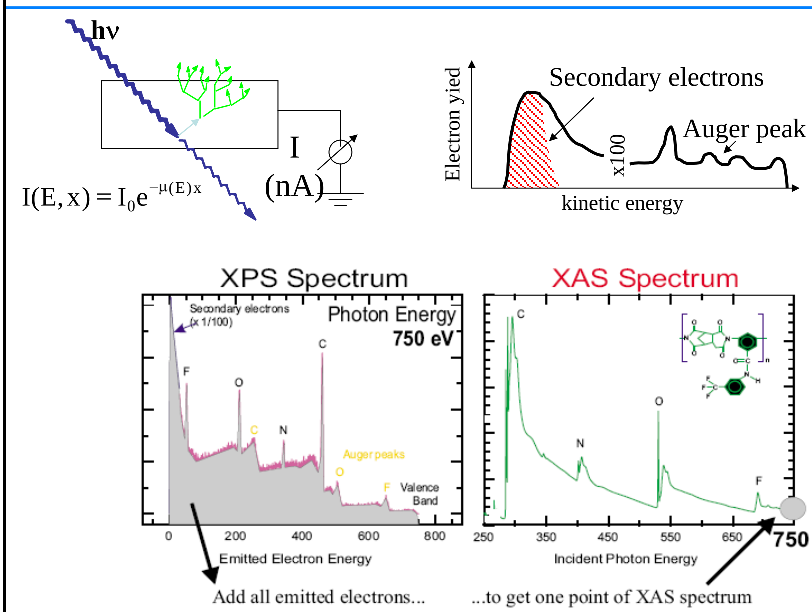

## Sampling depth



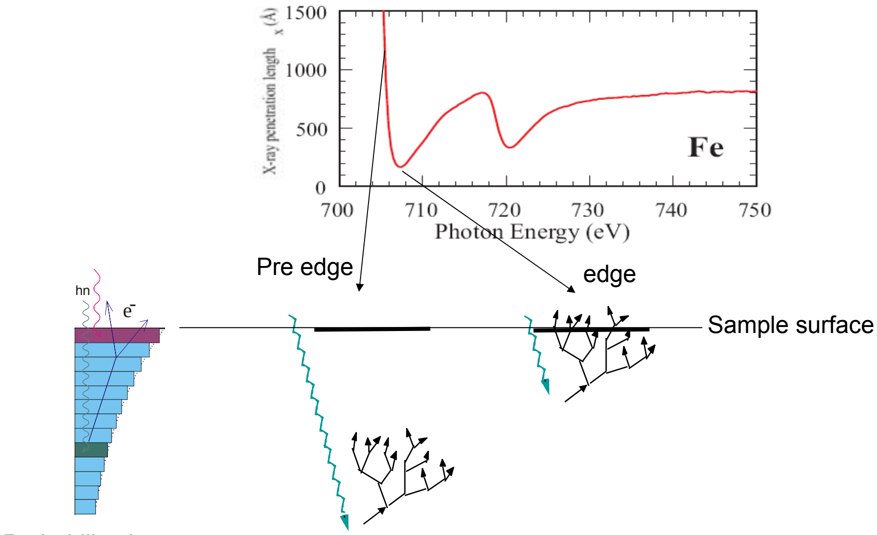





## Total electron yield (TEY)



## Why is TEY proportional to absorption coefficient

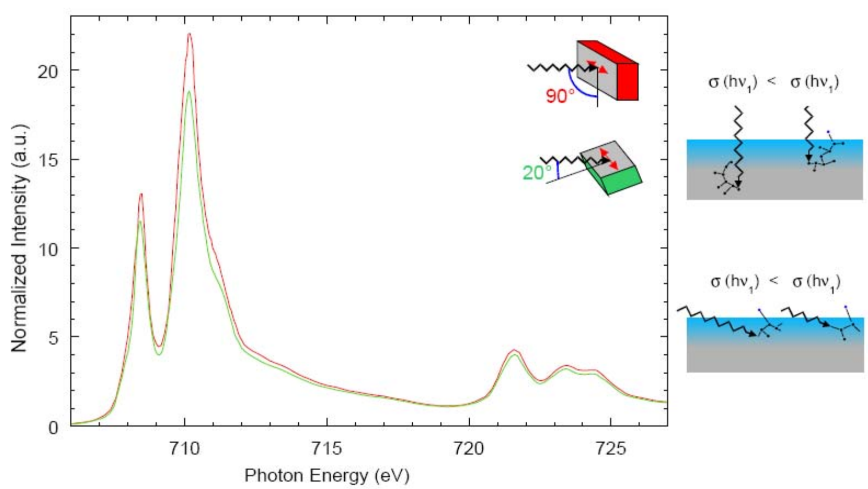



Probability that electron escapes

Penetration depth depends on the angle of incidence

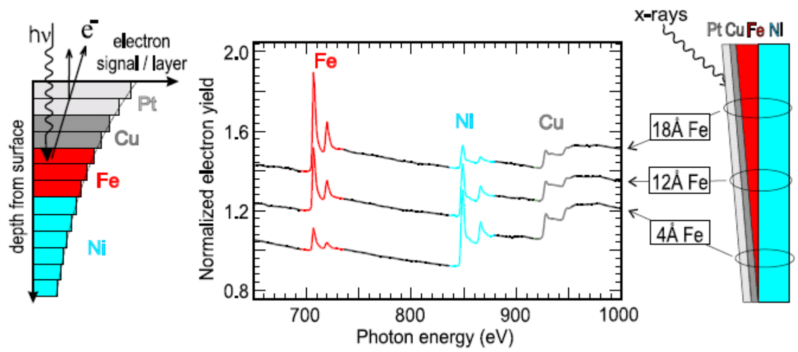


## Saturation Effects in TEY Detection




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

## "Dismantle" a Multilayer




The probability that an electron generated at depth t is ~e(-t/λ)
With λ the electron escape length typically a few nm

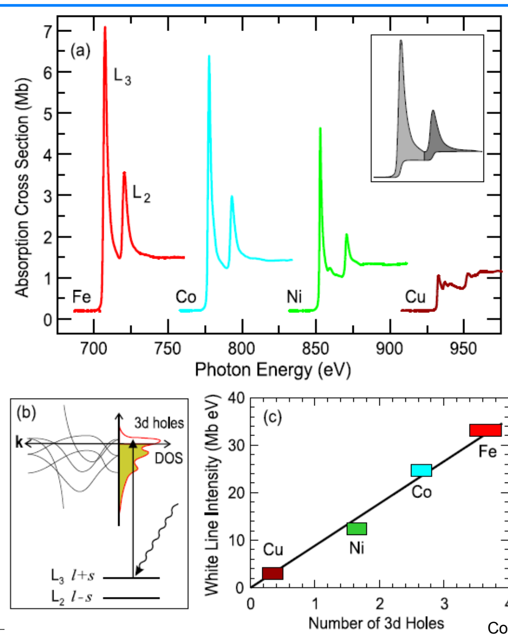
Courtesy J. Stöhr



## Determine number of 3d holes

Charge sum rule

Integrated intensity is proportional to number of empty valance states




Courtesy J. Stöhr

## Outline

**X-ray absorption spectroscopy (XAS)**

Absorption process
Total electron yield mode
Examples

**X-ray Magnetic Circular Dichroism (XMCD)**

Crash class nanomagnetism probed with X-rays
Basics
Example: Magnetocrystalline Anisotropy

**Closer look at the absorption process**

Mulitplet effects
Example: Interface effect in Exchange Bias system

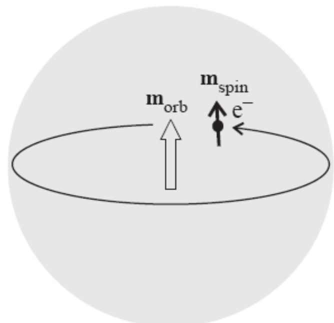
**X-ray Magnetic Linear Dichroism (XMLD)**

Basics



Crash class nanomagnetism probed with X-rays

## Source of magnetism (atomic)




| | | |
|---|---|---|
| Spin moment | ~ 1.5 $\mu_B$ / atom | isotropic |
| Orbital moment | ~ 0.1 $\mu_B$ / atom | isotropic/anisotropic |

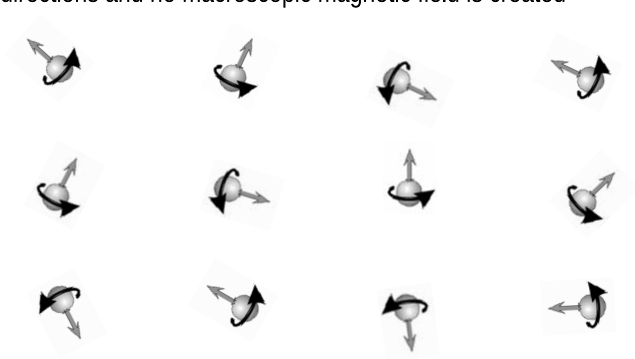
They interact via the spin-orbit coupling   $L \cdot S$



## Switching on the interaction

Atoms have an magnetic moment

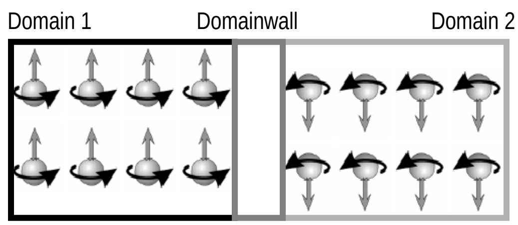
Without interaction (and no applied magnetic field) they point in random directions and no macroscopic magnetic field is created



## Switching on the interaction

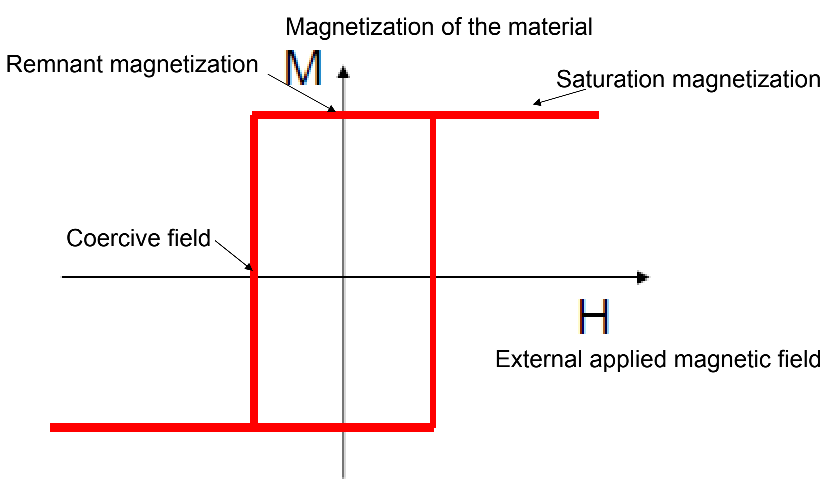
Atoms have an magnetic moment

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





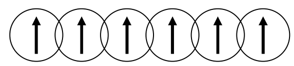

## Hysteresis loop



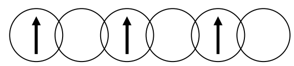

Responses of a material to an applied magnetic field is described by the hysteresis loop

## Different magnetic interactions

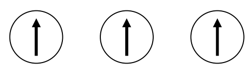
Direct exchange
Overlapping wavefunctions



superexchange
Overlapping wavefunctions via non-magnetic atoms

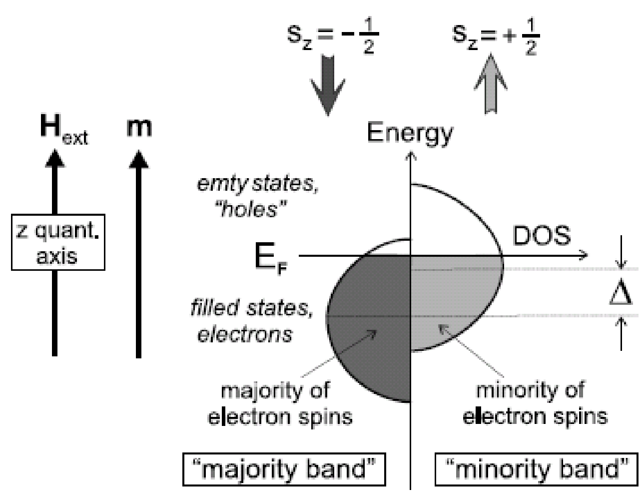


Indirect exchange
Exchange via delocalised electrons

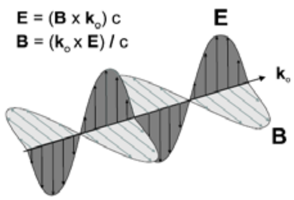


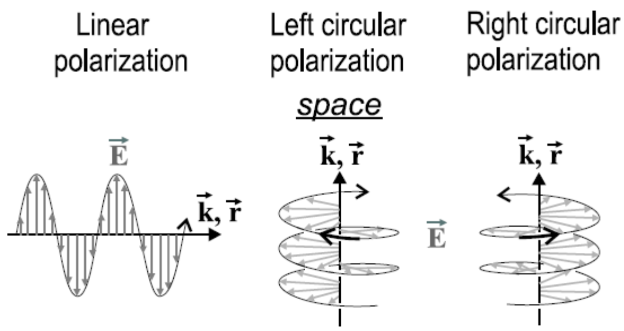


## Stoner Model for *3d* Band and Nomenclature



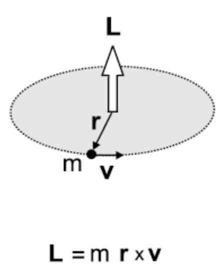
## Polarized Photons

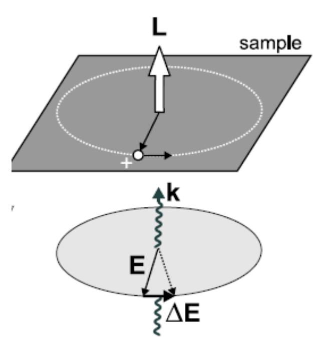




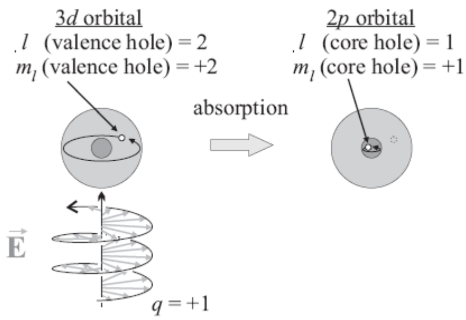

## Polarized Photons

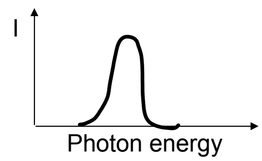



Angular momentum conservation

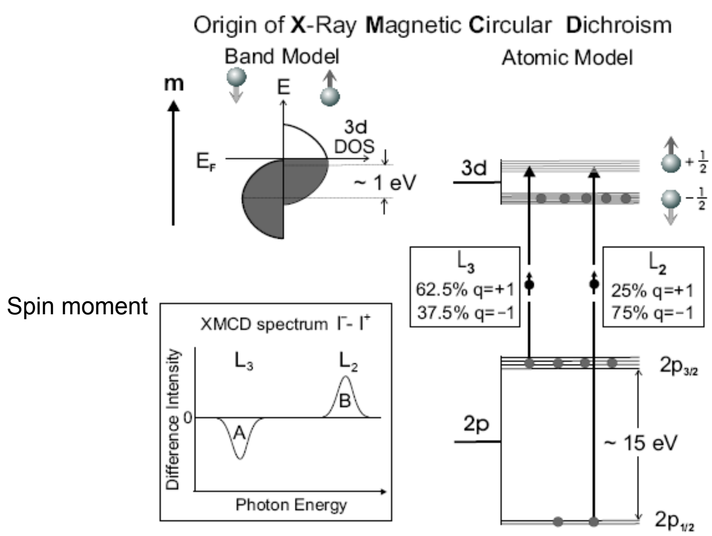
## Polarized Photons



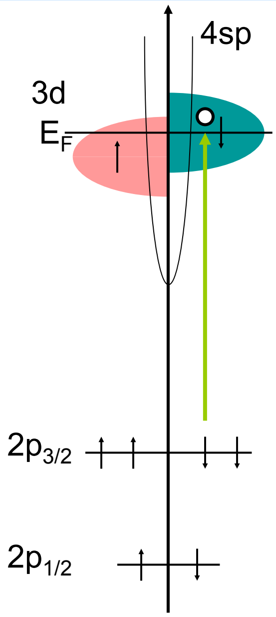






## Origin of XMCD



## 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:**

$\Delta L$ = -1, +1

$\Delta J$ = -1, 0, +1

$\Delta M_J$ = -1, 0, +1

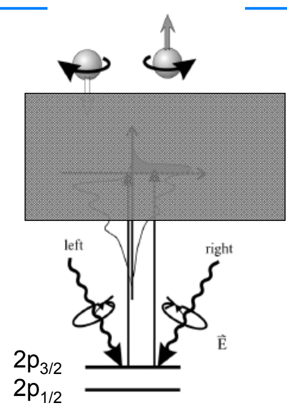
Polarization q +1, 0, -1 ($s^+$, p, $s^-$)

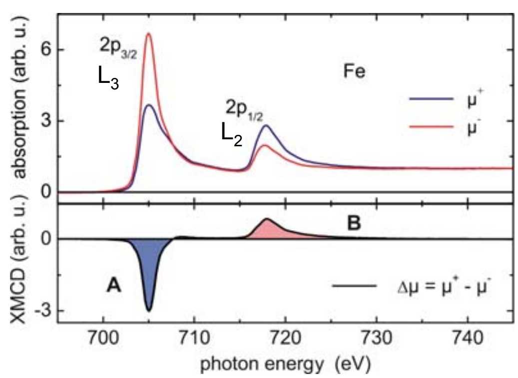
**L2**: $2p_{1/2}$□4s, $3d_{3/2}$

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



## Two-step Model of XMCD



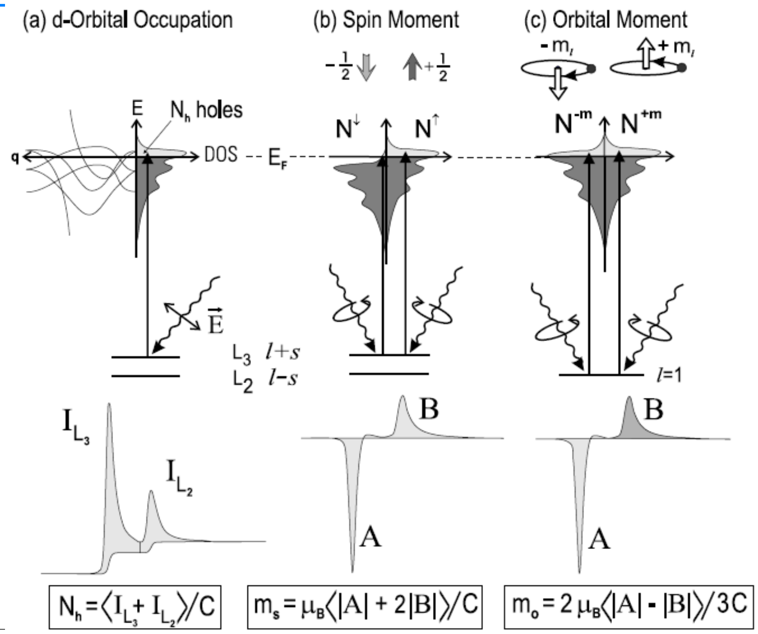




1. Step
Circ. Pol. X-rays generate spin-polarized electrons from inner shell

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

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

Electron occupation

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

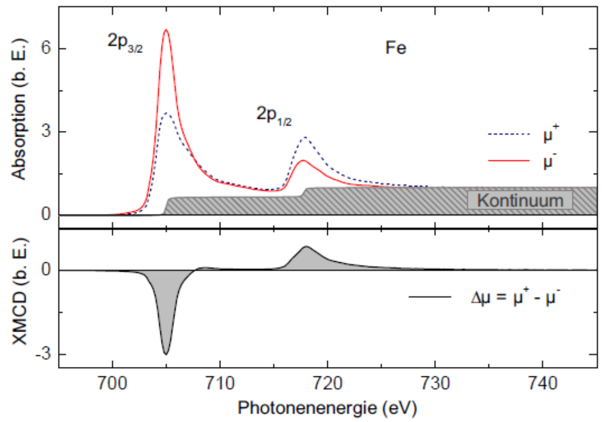
magnetic dipole moment

$\langle T_z \rangle$ 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

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

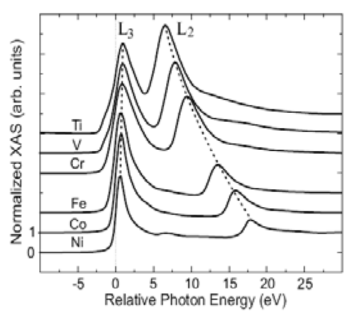
Only contribution to the resonance absorption should be considered




Taken from PhD Thesis Armin Kleibert, 2005

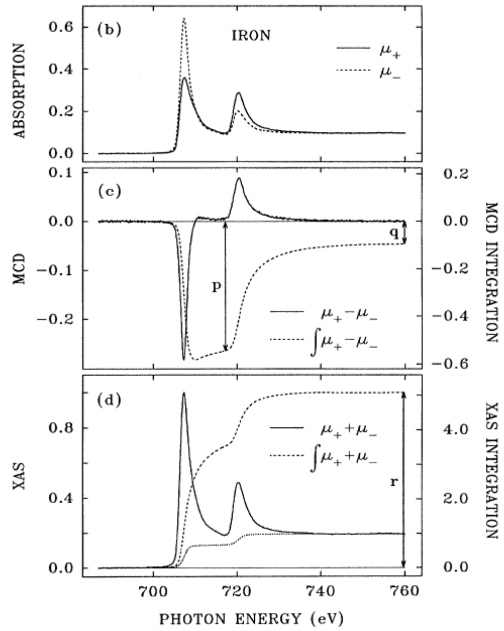


## ... more complex ... of course




$L_3$ and $L_2$ must be separated

## calculating




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

MCD
- difference
- integrate

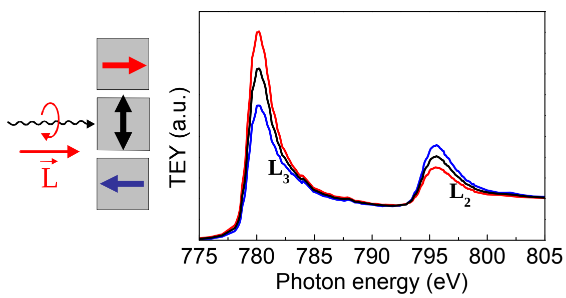
XAS
- sum spectra
- correct background
- non resonant

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

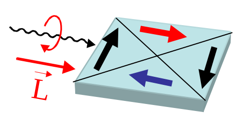
C.T. Chen et al. PRL 75(1), 152 (1995)



## X-ray Magnetic Circular Dichroism (XMCD)




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




Photons
- no mass
- no spin
- angular momentum

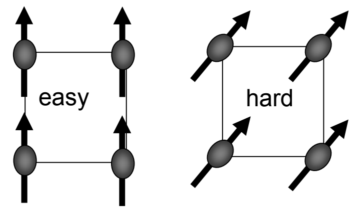
Magnetism 3d metals
- small orbital moment
- large spin moment

## 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

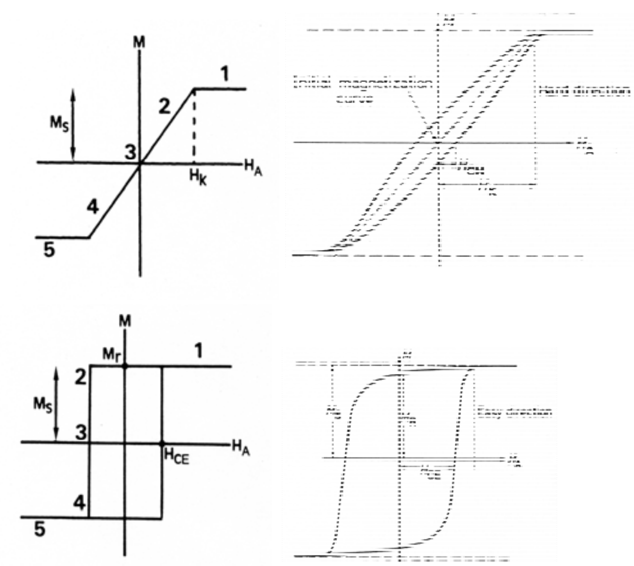
J. Stöhr, JMMM 200 (1999) 470 – 497
Reiko Nakajima PhD Thesis 1998



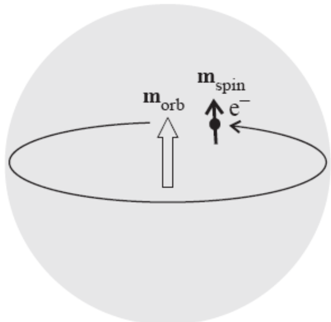
## Hysteresis loop – anisotropy

hard axis

easy axis



## Magneto-crystalline anisotropy

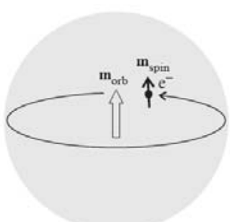


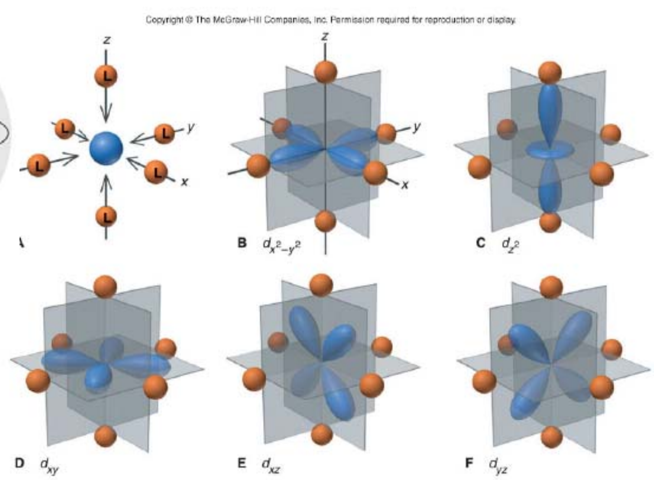

| | | |
|---|---|---|
| Spin moment | ~ 1.5 $\mu_B$ / atom | isotropic |
| Orbital moment | ~ 0.1 $\mu_B$ / atom | isotropic/anisotropic |

They interact via the spin-orbit coupling L · S

F. Nolting Surface Science FS 2012

## Anisotropy




F. Nolting Surface Science FS 2011

## Bruno model

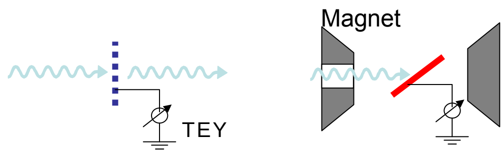
The Bruno model states that the orbital moment is larger along the easy magnetization direction, and that the difference between the orbital moments along the easy and hard directions is proportional to the magneto-crystalline anisotropy

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

P. Bruno, PRB 39, 865 (1989)

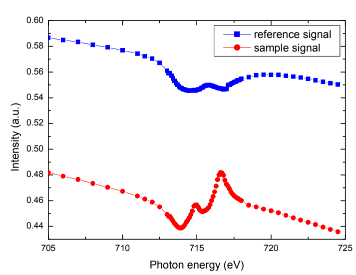


## How do we measure

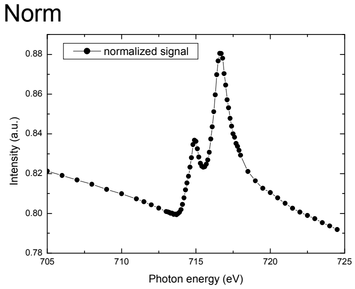



Reference signal

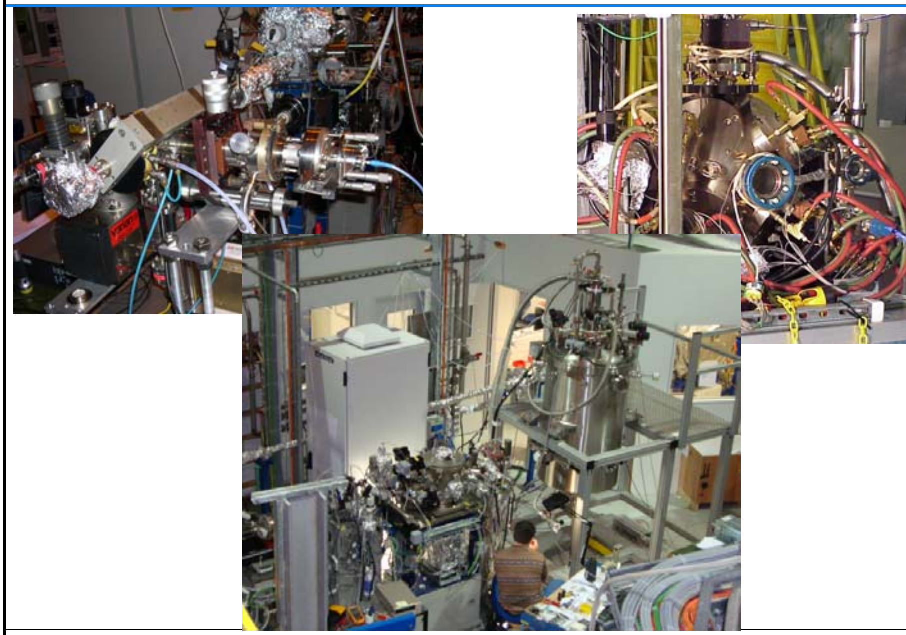
Sample signal




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



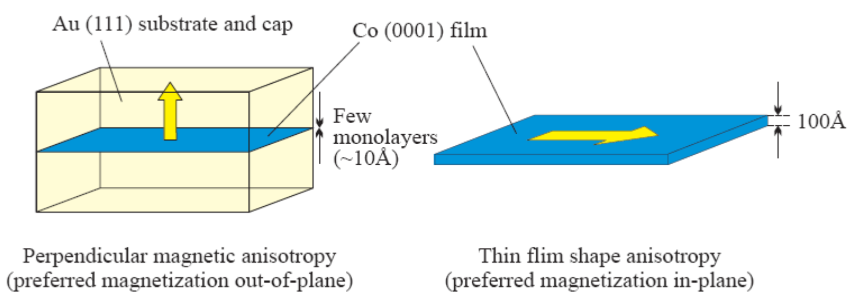
## How do we measure

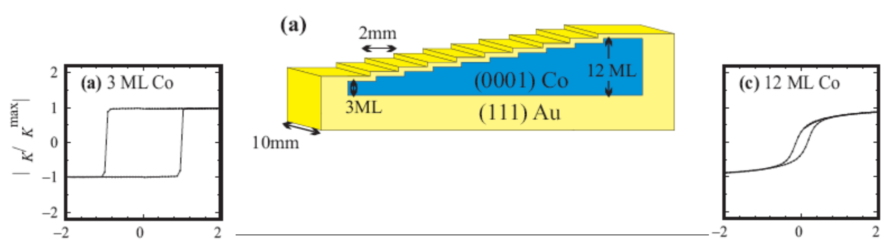




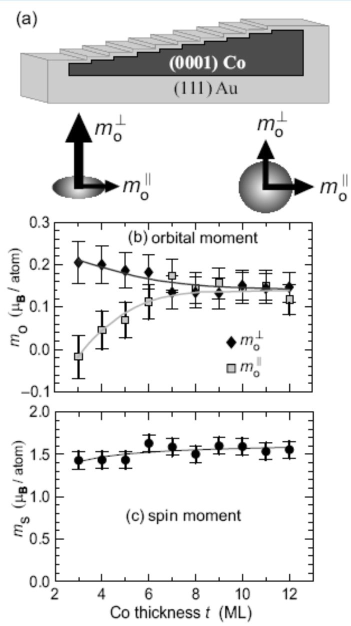
## Test system

Magnetic anisotropy in Co (0001) films



## Results

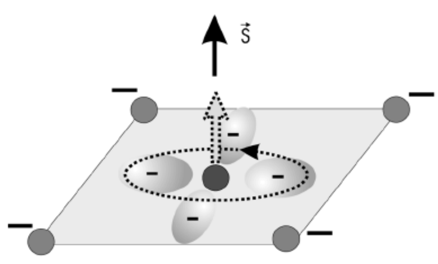



**Thin film**
Orbital moment is anisotropic and larger out-of-plane

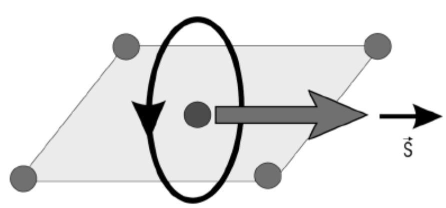
**Thick film**
Orbital moment is isotropic
shape anisotropy is dominating



## 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

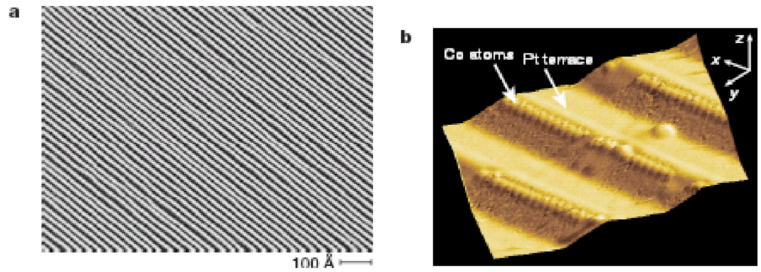
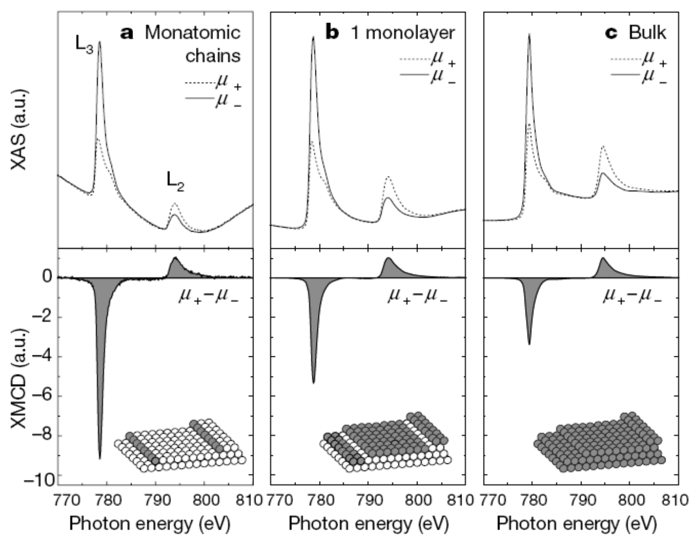



**Figure 1** STM topographs of the Pt(997) surface. **a**, Periodic step structure (each white line represents a single step). The surface has a 6.45° miscut angle relative to the (111) direction; repulsive step interactions result in a narrow terrace width distribution centred at 20.2 Å with 2.9 Å standard 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)



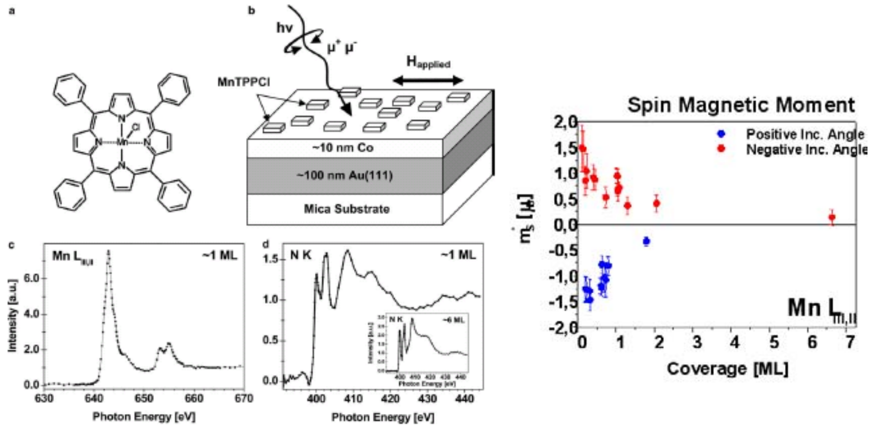
## Increased orbital moment in Co chains




$m_l \sim 0.68\ \mu_B$ / 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

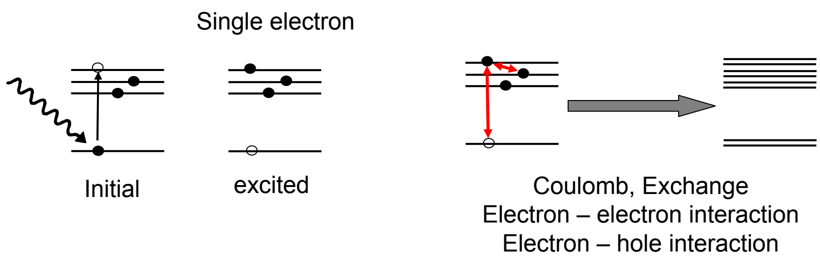
**X-ray absorption spectroscopy (XAS)**
- Absorption process
- Total electron yield mode
- Examples

**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



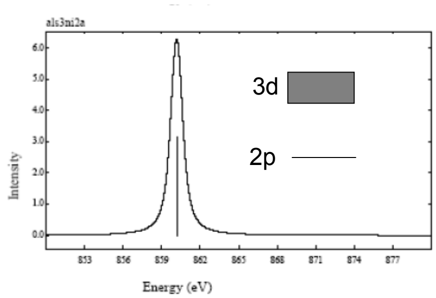

**Valence – Valence interaction** : many body effects

**Valence – Core interaction** : multiplet effects

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

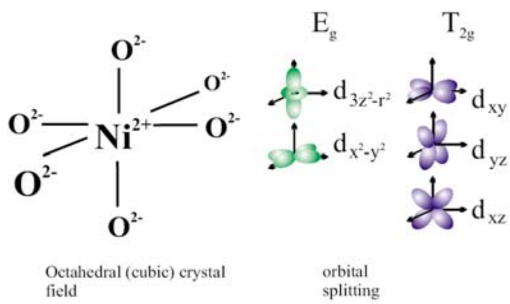


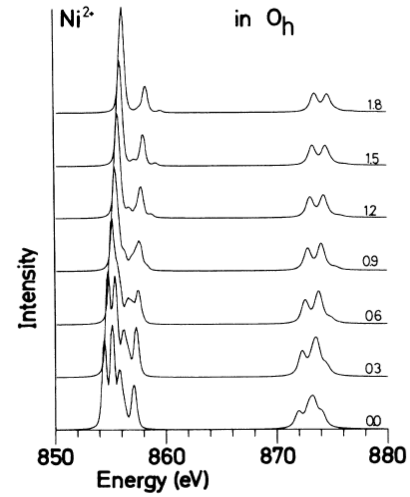
## Interactions – NiO (Ni 2+ )




F. de Groot

## Crystal field



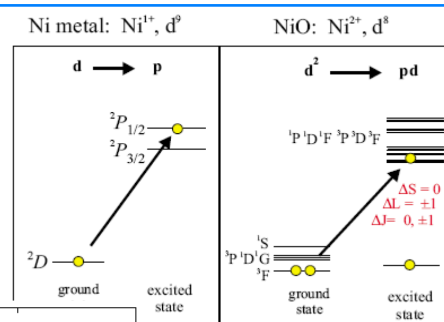



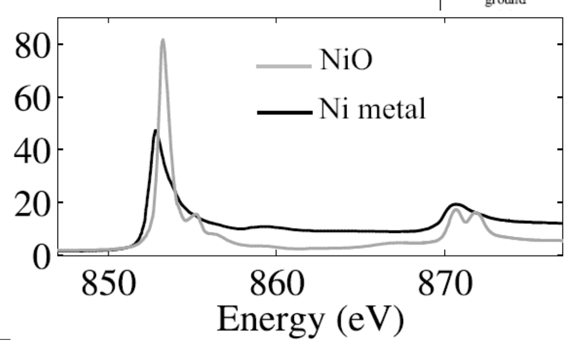

Further parameter is charge transfer

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



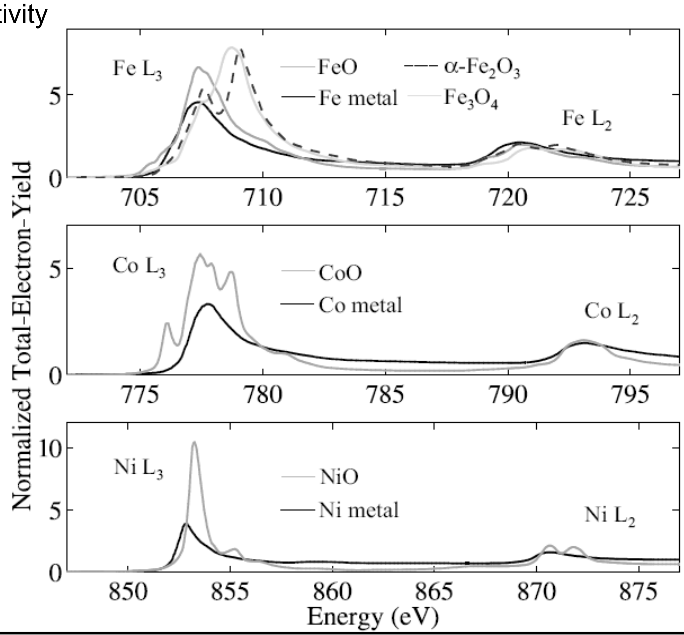
## Ni metal vs NiO



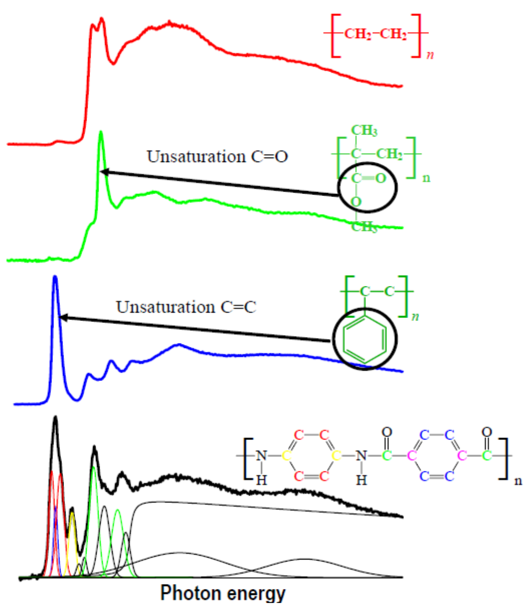



## Complex but good for us

Chemical sensitivity



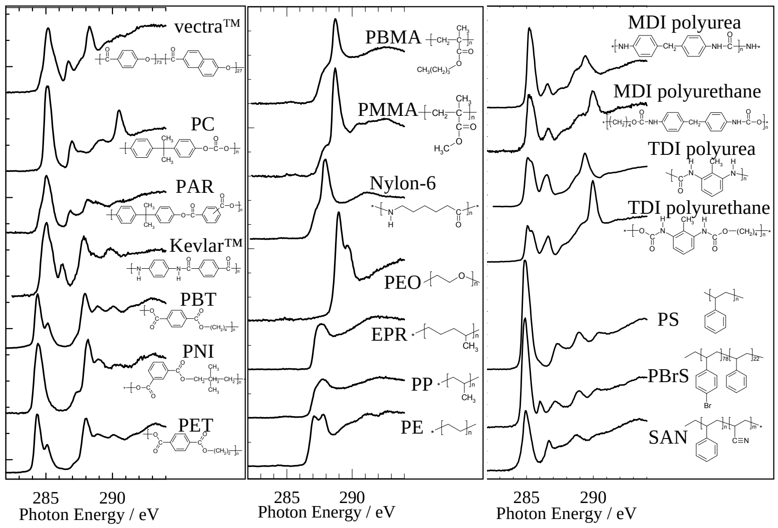

## Footprint of complex bindings




Courtesy Harald Ade

F. Nolting Surface Science FS 2012

## Absorption spectroscopy library




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



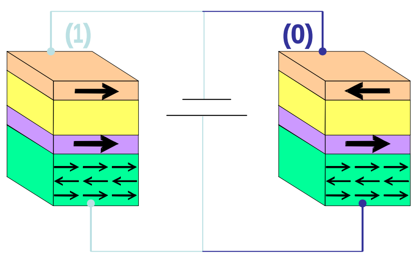
## Example magnetic recording

GMR Element

Ferromagnet

Ferromagnet

Antiferromagnet



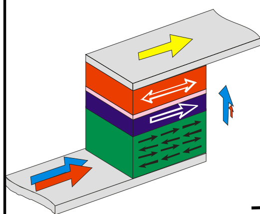

Top layer "free" can be switched

Bottom layer "pinned" *Hard layer or Exchange coupling*

Low resistance

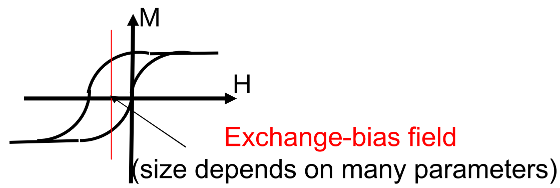
high resistance

## Exchange Bias



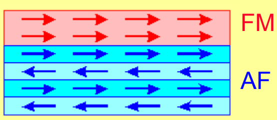
### Unidirectional anisotropy in FM adjacent to AFM

discovered 1956 by Meiklejohn and Bean

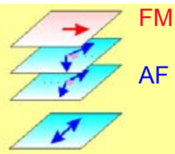



Effect of exchange bias is still poorly understood

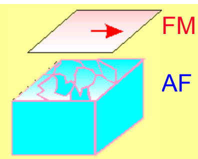
**Ideal Interface Model**




**Spin Flop Model**




**Domain Size Model**

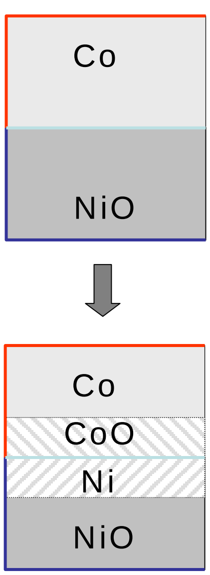



Uncompen-sated spins at AF domain boundaries

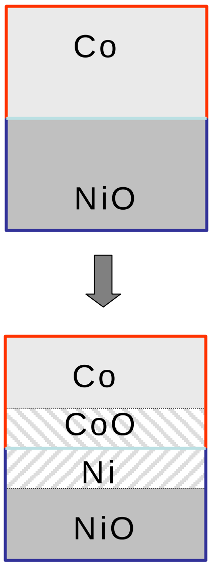
Reviews: A.E. Berkowitz and K. Takano, J. Magn. Magn. Mater. 200(1-3), 552 (1999).
J. Nogues and I.K. Schuller, J. Magn. Magn. Mater. 192, 203 (1999)

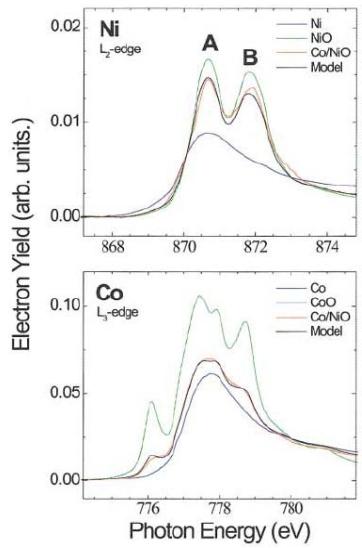


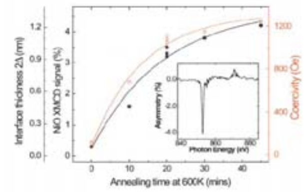
## Exchange biased Co/NiO multilayer



## Exchange biased Co/NiO multilayer



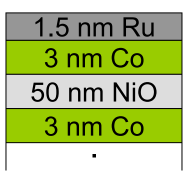




Oxidation/reduction at the interface is responsible for increased coercivity

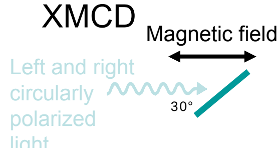
Tom Regan et al, Phys. Rev. B 64, 214422 (2001)



## Exchange biased Co/NiO multilayer

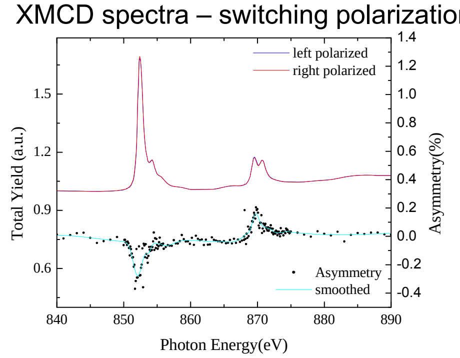



XMCD

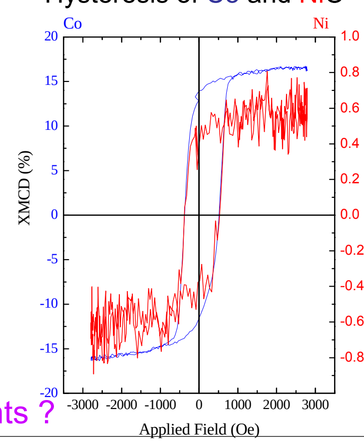



EPU beamline 4 at ALS, Elke Arenholz, Tony Young

XMCD spectra – switching polarization



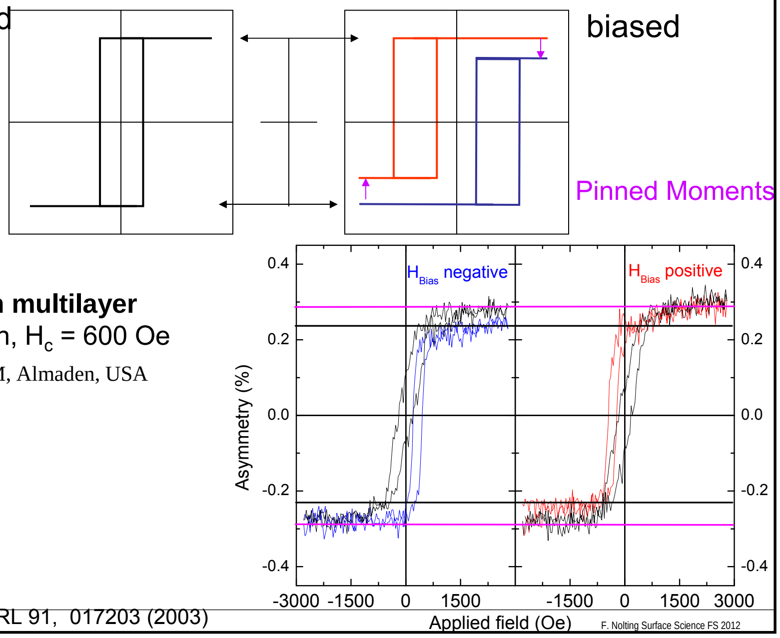

Hysteresis of Co and NiO




Pinned Moments ?

## Pinned Moments

unbiased




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

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



## Outline

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- Basics
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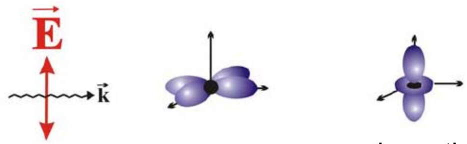
- Example: Interface effect in Exchange Bias system

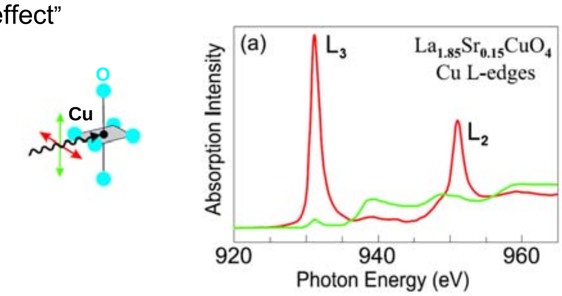
**X-ray Magnetic Linear Dichroism (XMLD)**
- Basics

## Interaction with linear light - charge

Excitation into 3d band



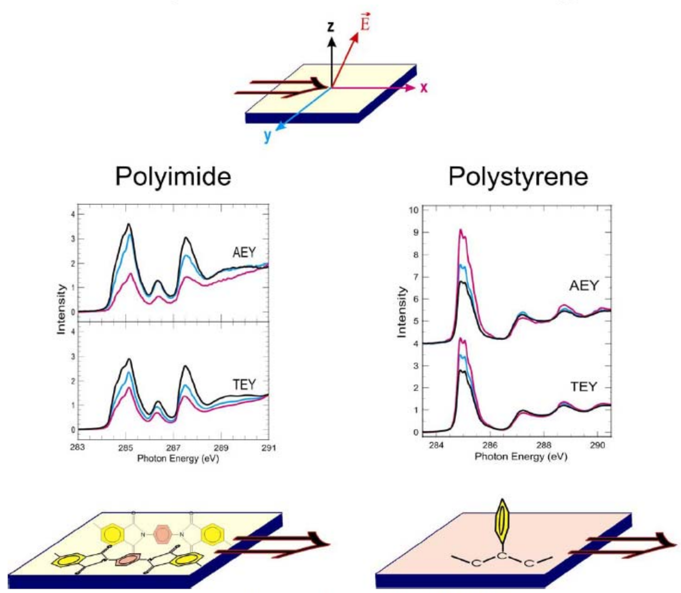

X-ray Natural linear dichroism
“search light effect”




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



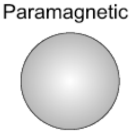
## Polarization Dependent NEXAFS Probes Bond Anisotropy at Surface




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

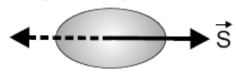
## Interaction with linear light - magnetic

Paramagnetic State



Electron charge density is isotropic
no linear dichroism

Aligned Magnetic State



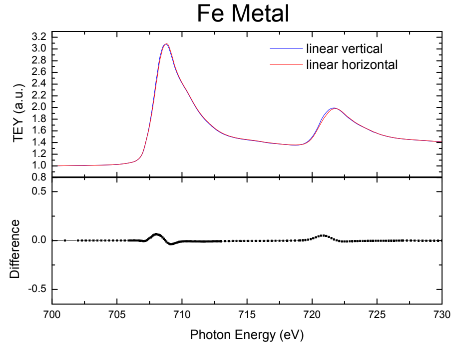

Preferred spin axis
spin orbit coupling changes charge density
linear dichroism

XMLD X-ray Magnetic Linear Dichroism

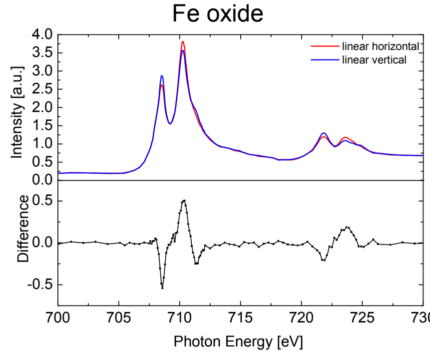


## XMLD

Fe Metal




Fe oxide



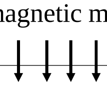

XMLD enhanced by mulitplet

Enables to measure antiferromagnetic systems!

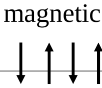
XMCD ~ **M** cos(**M**,**S**)

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).

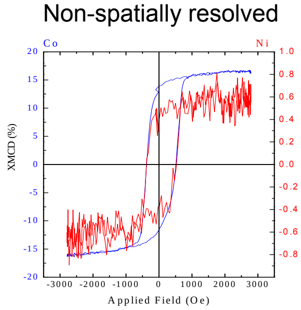
Determination of Spin- and Orbital-Moment Anisotropies in Transition Metals by Angle-Dependent X-Ray Magnetic Circular Dichroism,
J. Stöhr, H. König, Phys. Rev. Lett. 75, 3748 (1995)



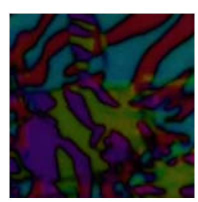
## Conclusions

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
- …