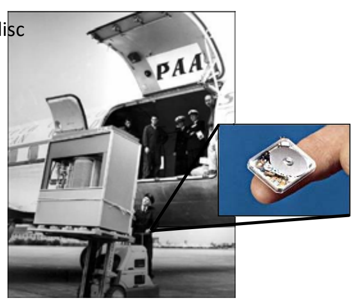
Frithjof Nolting :: Head of LSC :: Paul Scherrer Institut

Polarization dependent X-ray absorption

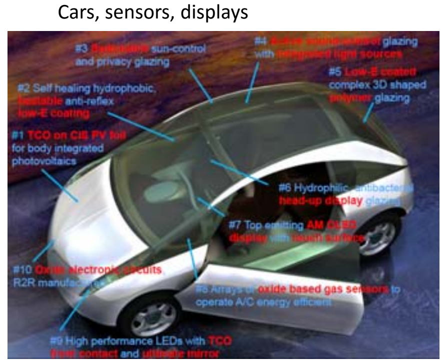
PSI Master School 2017

Basic research – electronic devices

Hard disc



Cars, sensors, displays



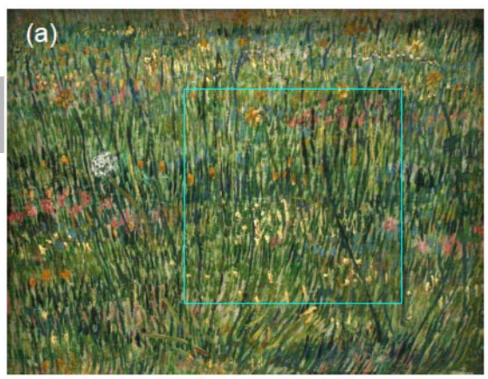
Modern communication devices are full of fascinating physics and advanced materials

Aim of the lecture

Basic concepts of X-ray absorption spectroscopy to probe electronic and magnetic states

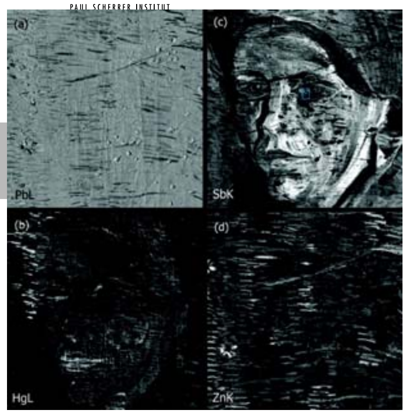
- Absorption process
- Polarization dependency
- Example for XMCD
- Multiplet structure
- XMLD
- Other techniques
- Polarized X-rays

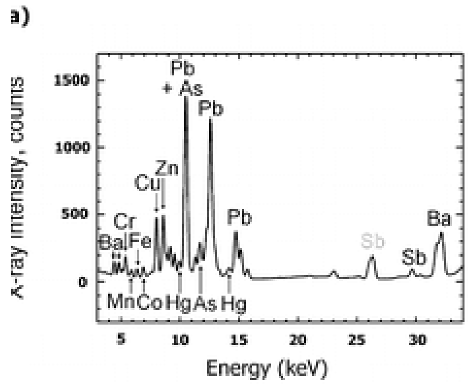
"Seeing the invisible"



The 1887 floral painting by van Gogh, "Patch of Grass".

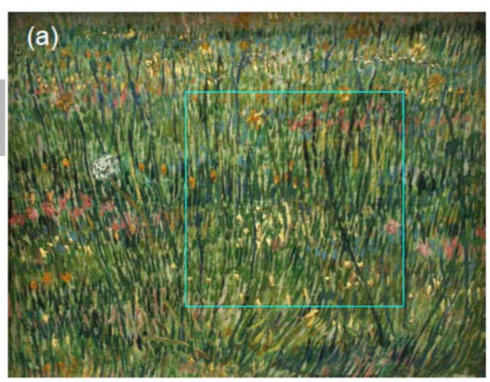
Dik et al., Anal. Chem. 80 6436 (2008).





(a) Distribution of Pb L measured with SR-based XRF (black, low intensity; white, high intensity). (b) Hg L showing distribution of vermillion (Zinnoberrot). (c) Sb (Antimon) K showing distribution of Naples yellow, paint sample location indicated in the blue frame (Figure 4). (d) Zn K showing distribution of zinc white, mostly corresponding with surface painting but some overlap with concentrations of SbK (nose, ear, neck).

Joris Dik; Koen Janssens; Geert Van Der Snickt; Luuk van der Loeff; Karen Rickers; Marine Cotte; *Anal. Chem.* **2008,** 80, 6436-6442.



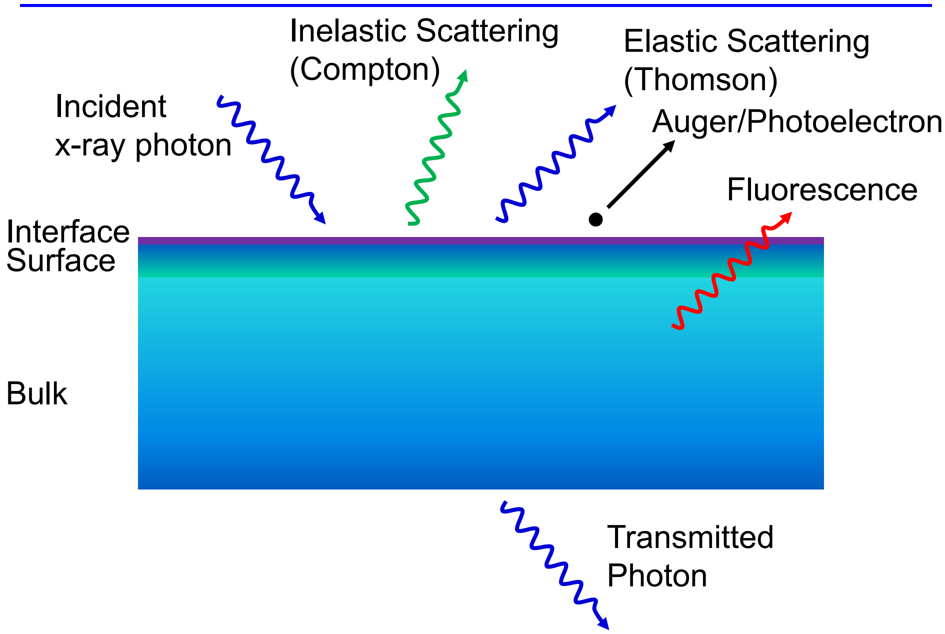
The 1887 floral painting by van Gogh, “Patch of Grass”. XRF analysis within the area bounded by the blue box revealed details of a hidden face of a peasant woman from an earlier painting (ca. 1884 – 1885). (b) A tritonal reconstruction from Sb (yellow-white) and Hg (vermillion) elemental distribution maps of the hidden portrait. From Dik et al., Anal. Chem. 80 6436 (2008).

Aim of the lecture

Basic concepts of X-ray absorption spectroscopy to probe electronic and magnetic states

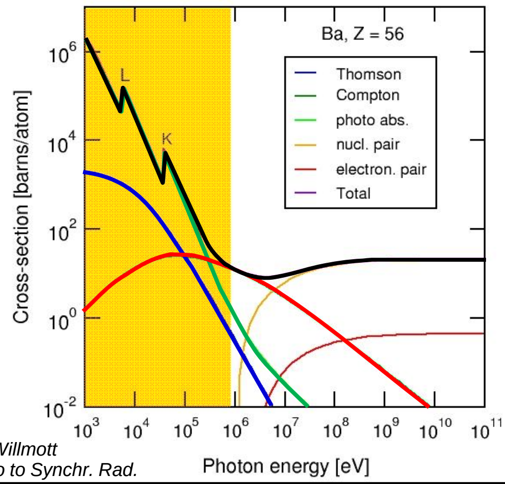
- Absorption process
- Polarization dependency
- Example for XMCD
- Multiplet structure
- XMLD
- Other techniques
- Polarized X-rays

Key Phenomena



X-ray Scattering Processes

- Cross-sections for various processes involving interaction of x-rays with matter - primary scatterer is the **electron**
- Plot for Ba; orange area highlights upper energy range covered by synchrotron sources



P. Willmott
Intro to Synchr. Rad.

Key scattering processes:

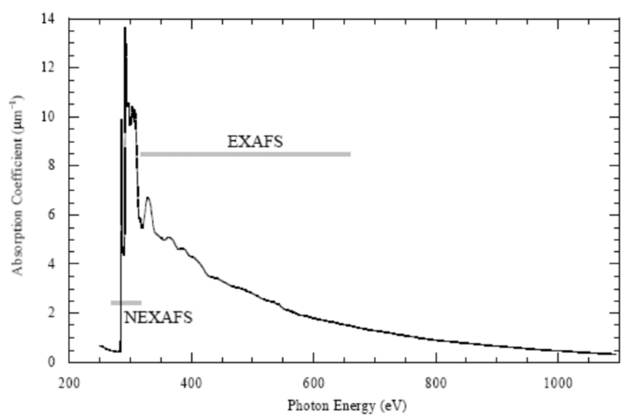
- **Photoelectric Absorption**
- **Thomson Scattering (elastic)**
- **Compton Scattering (inelastic)**

➔ **Total !**

1 barn = 10^{-24} cm^2
= 10^{-28} m^2

PAUL SCHERRER INSTITUT

Absorption of Photons in the Soft X-ray Range



Near Edge X-ray Absorption Fine Structure

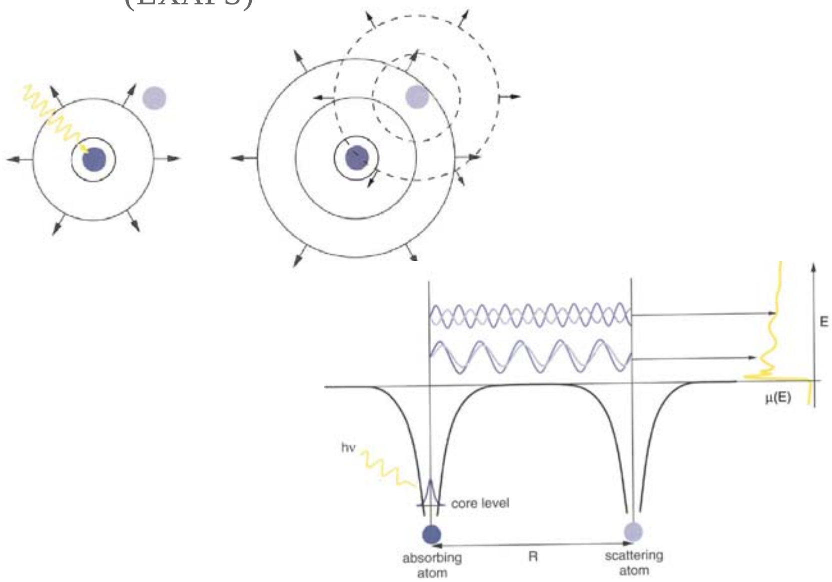
reflects density of unoccupied states

Also called XANES

Extended X-ray Absorption Fine Structure

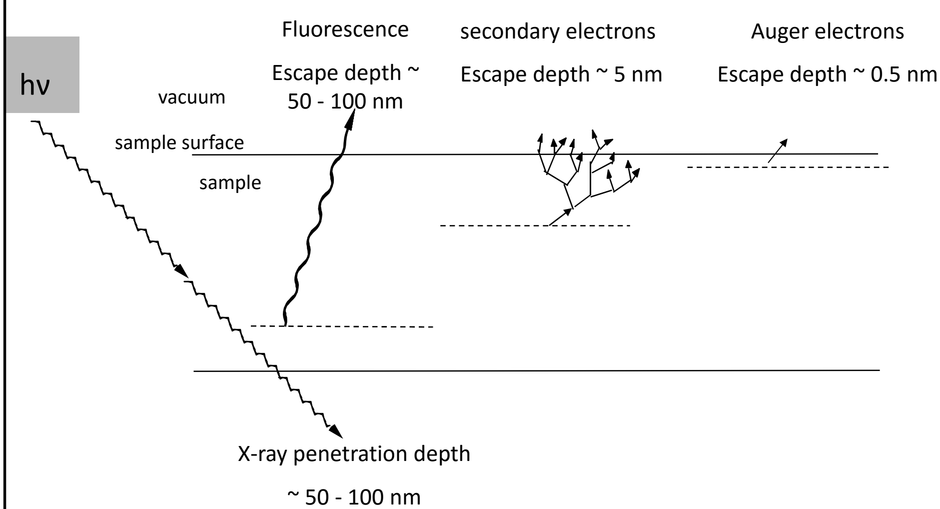
reflects spatial location of neighboring atoms

Extended X-ray Absorption Fine Structure (EXAFS)



Page 11

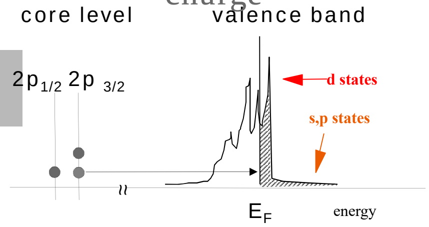
Sampling depth (soft-Xrays)

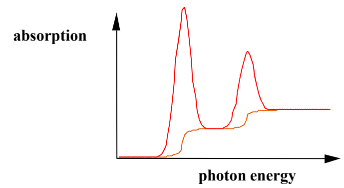


Page 12

PAUL SCHERRER INSTITUT

Interaction of electromagnetic wave with charge





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

Fermi's Golden rule

$$P_{fi} \propto \sum_{f,i} M_{fi}^2 \cdot (1 - n(E_f)) \cdot \delta(\hbar\omega - (E_f - E_i))$$

In dipole approximations

$M_{fi}^2 = |< f \,|\, P A \,|\, i >$

P momentum operator

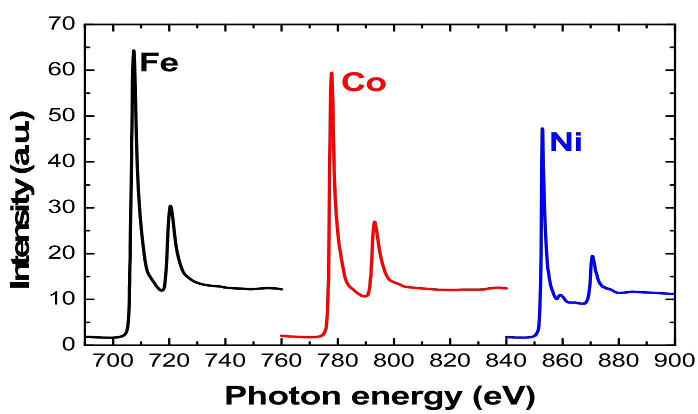
A electric field vector

$\Delta m_s = 0$

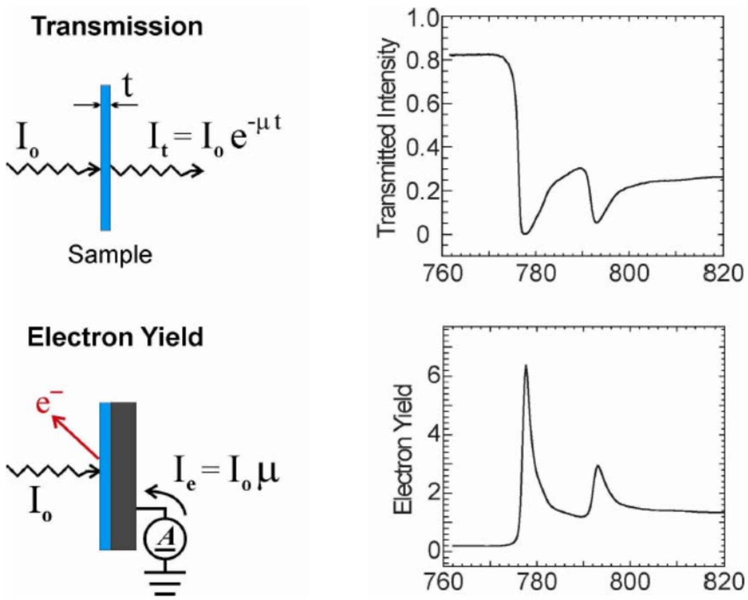
$\Delta m_l = +/- 1$

PAUL SCHERRER INSTITUT

Element specific



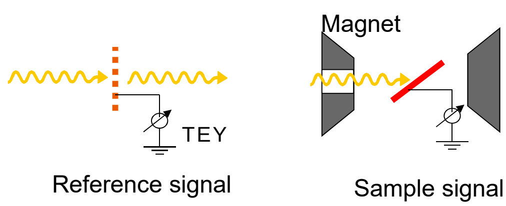
How do we measure

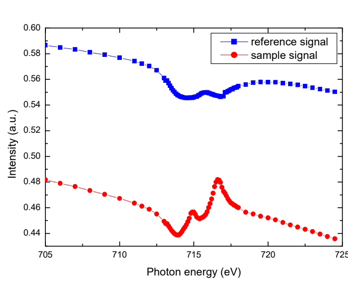


"Photons lost"

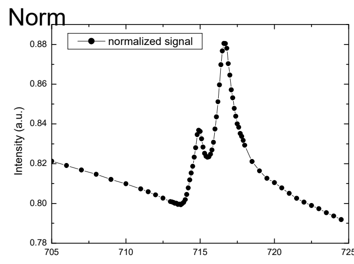
"Electrons generated"

How do we measure





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



PAUL SCHERRER INSTITUT

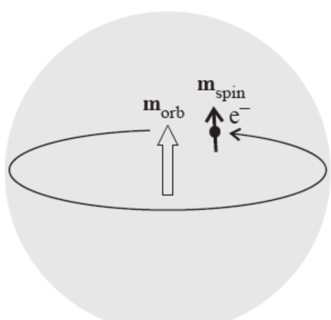
Aim of the lecture

Basic concepts of X-ray absorption spectroscopy to probe electronic and magnetic states

- Absorption process
- Polarization dependency
- Example for XMCD
- Multiplet structure
- XMLD
- Other techniques
- Polarized X-rays

PAUL SCHERRER INSTITUT

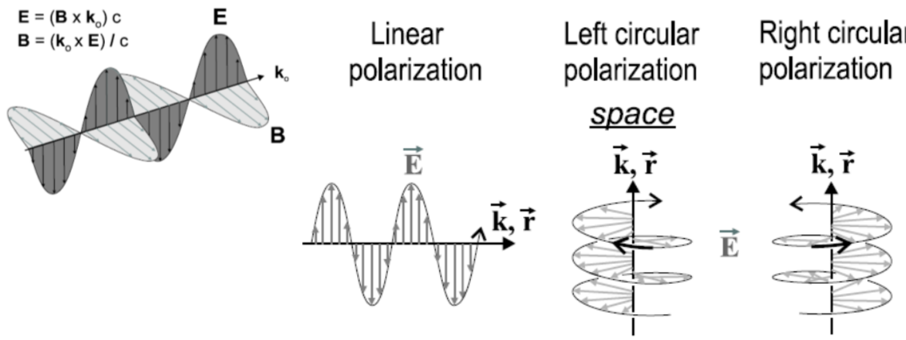
Source of magnetism (atomic)



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

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

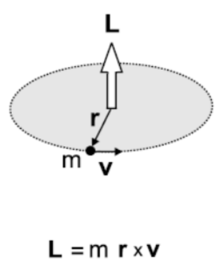
Polarized Photons

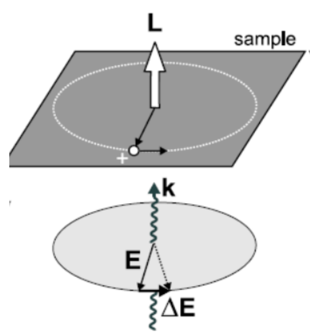


Polarized Photons

Angular moment of orbiting mass

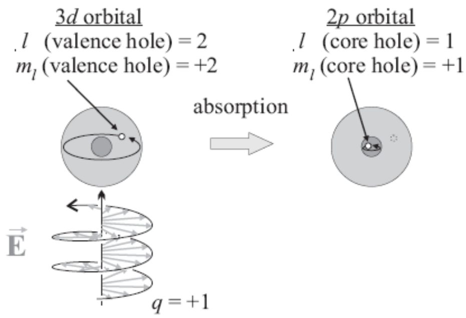
Photon angular moment

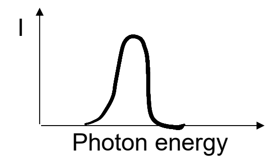




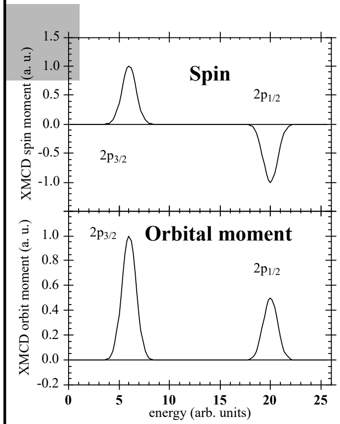
Angular momentum conservation

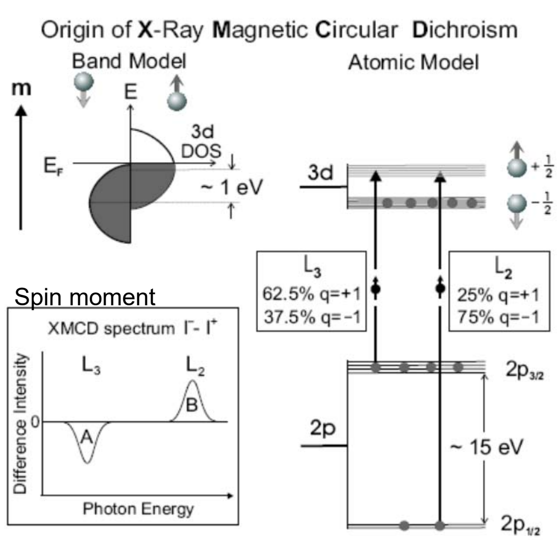
Polarized Photons



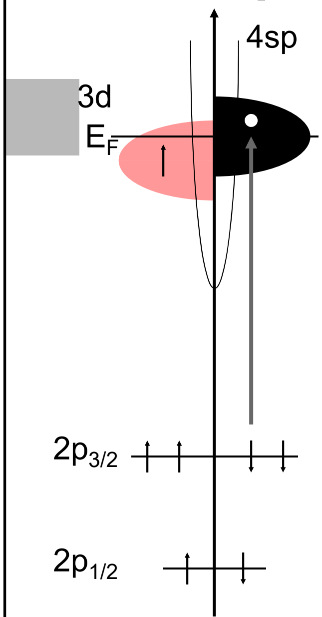


Origin of XMCD





Dipole selection rules



Fermi's golden rule :

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

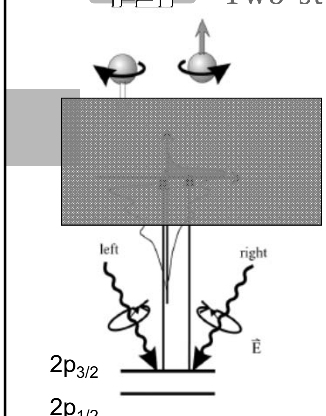
Dipole selection rules:

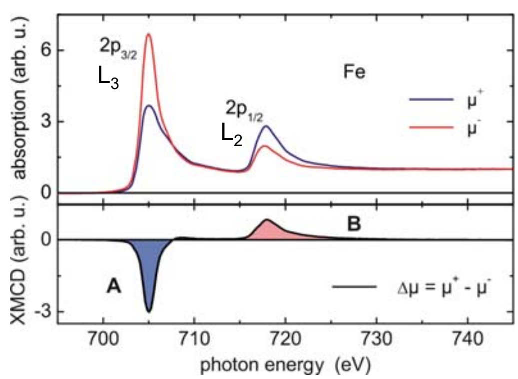
ΔL	=	-1, +1
ΔJ	=	-1, 0, +1
ΔM_J	=	-1, 0, +1
Polarization q		+1, 0, -1 (s⁺, p, s⁻)

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

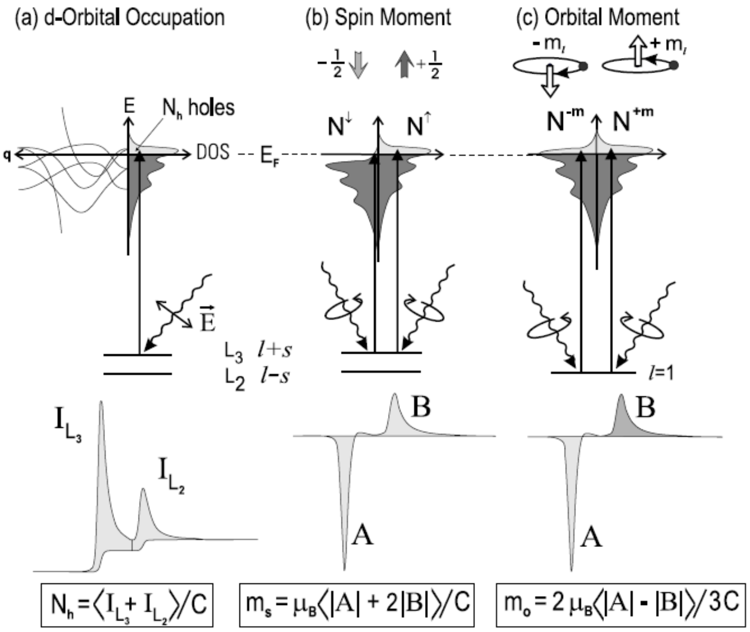
Circ. Pol. X-rays generate spin-polarized electrons from inner shell

2. Step

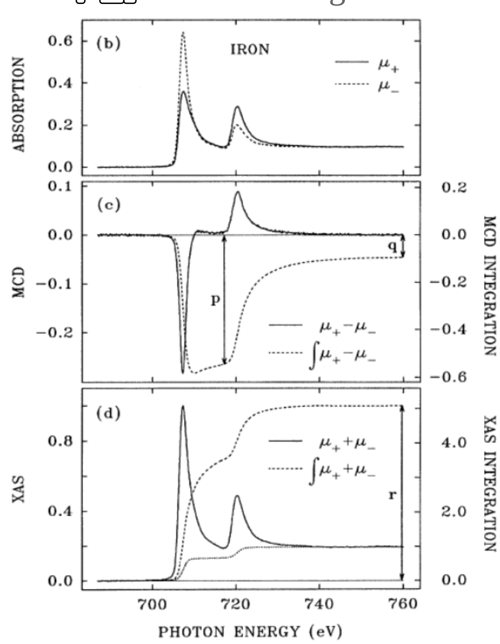
Spin-split 3d bands act as spin analyser

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

Sum rules



calculating



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

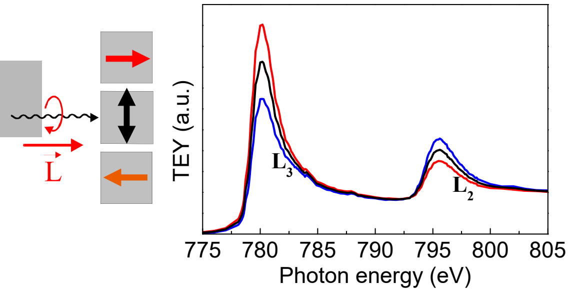
MCD
- difference
- integrate

XAS
- sum spectra
- correct background
- non resonant

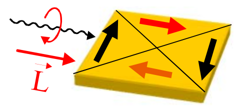
Calculate/neglect
- $\langle T_Z \rangle$
- $\langle Sz \rangle$

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

Aim of the lecture

Basic concepts of X-ray absorption spectroscopy to probe electronic and magnetic states

- Absorption process
- Polarization dependency
- Example for XMCD
- Multiplet structure
- XMLD
- Other techniques
- Polarized X-rays

XMCD in action

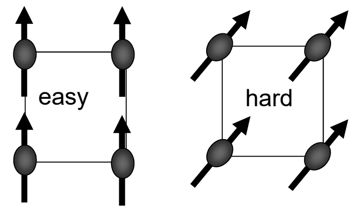
Study Magneto-crystalline anisotropy

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

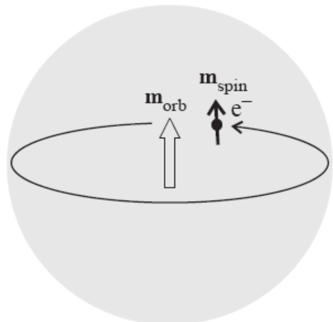
Bruno model

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)

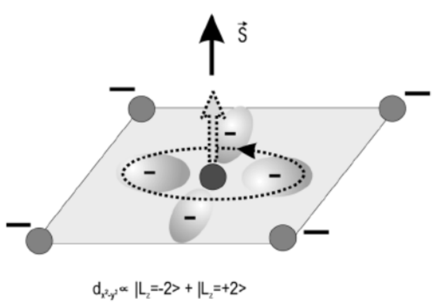
Magneto-crystalline anisotropy



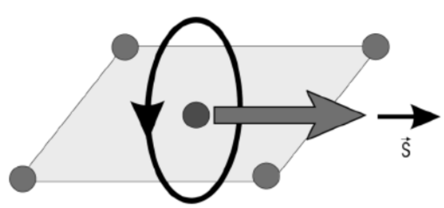
Spin moment	~ 1.5 μ_B / atom	isotropic
Orbital moment	~ 0.1 μ_B / atom	isotropic/anisotropic

They interact via the spin-orbit coupling L · S

Simple picture – Ligand fields



in-plane orbits are quenched

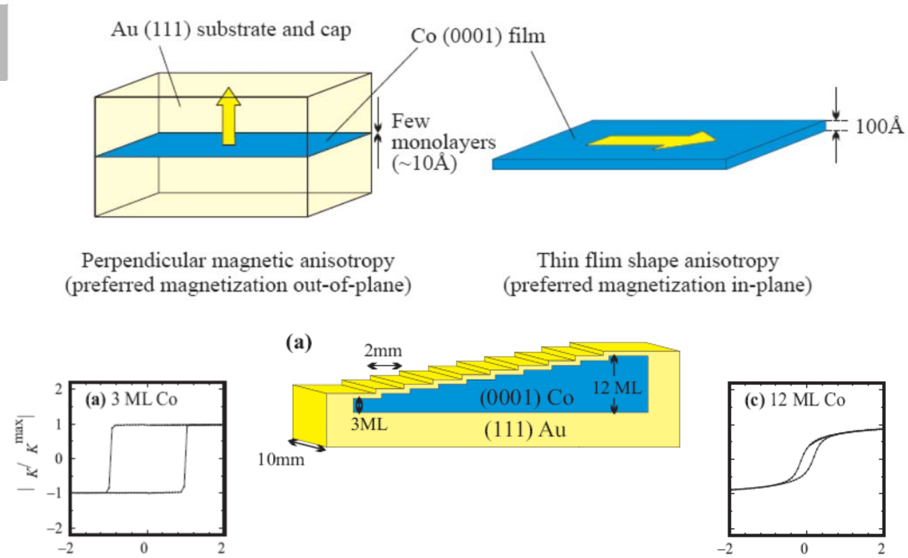


out-of-plane orbits are less perturbed

Free monolayer	in-plane moment
Mulitlayer with stronger out-of-plane bonding	out-of-plane moment

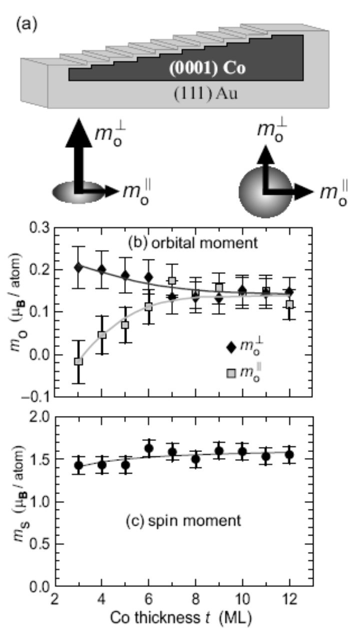
Test system

Magnetic anisotropy in Co (0001) films



Page 33

Results



Thin film

Orbital moment is anisotropic and larger out-of-plane

Thick film

Orbital moment is isotropic

shape anisotropy is dominating

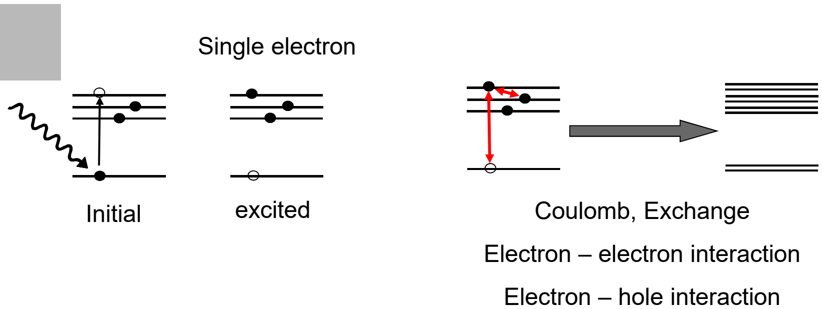
Page 34

Aim of the lecture

Basic concepts of X-ray absorption spectroscopy to probe electronic and magnetic states

- Absorption process
- Polarization dependency
- Example for XMCD
- Multiplet structure
- XMLD
- Other techniques
- Polarized X-rays

Interactions

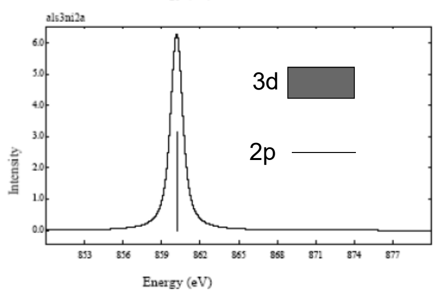


Valence – Valence interaction : many body effects

Valence – Core interaction : multiplet effects

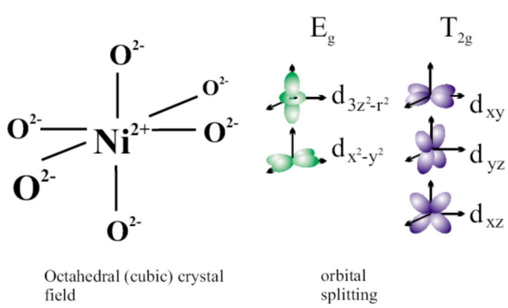
Hybridization between ground state and final state leads to a multiplet structure of the spectrum

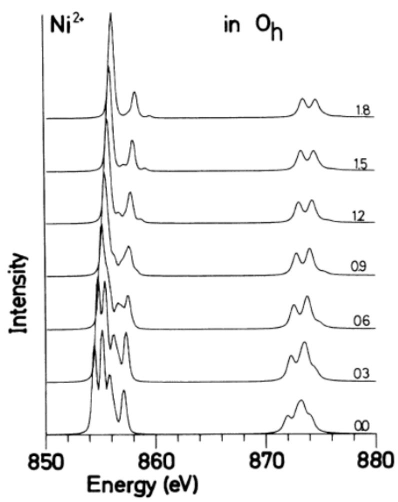
Interactions – NiO (Ni 2+)



F. de Groot

Crystal field

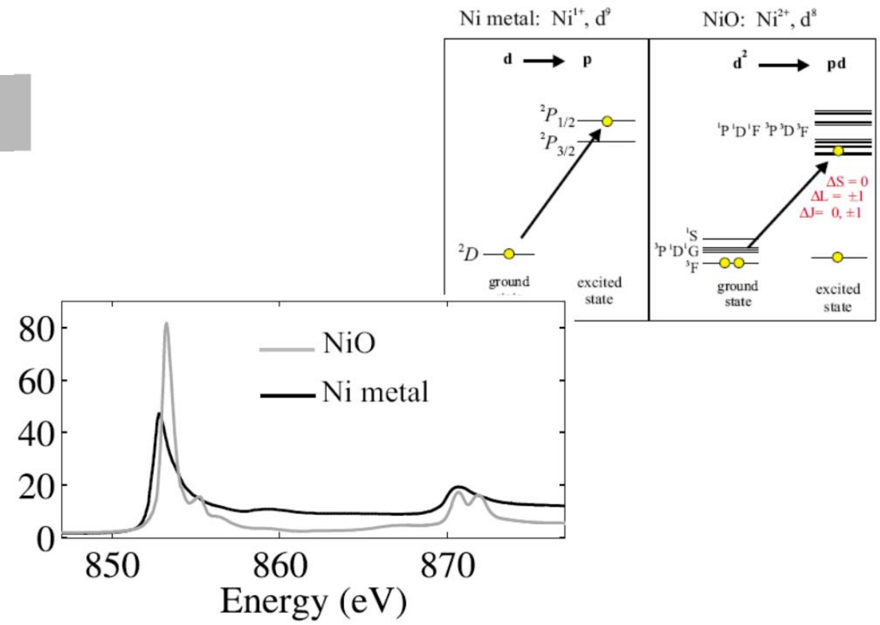




Further parameter is charge transfer

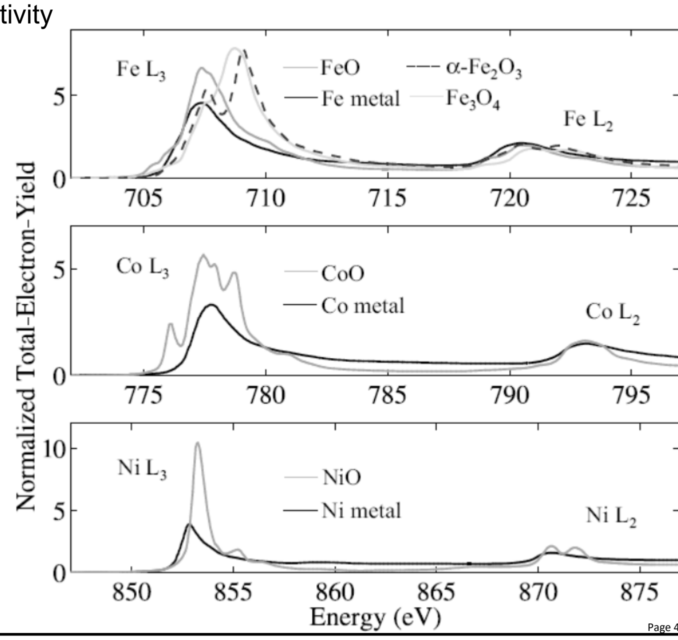
F. de Groot et al. PRB 42, 5459 (1990)

Ni metal vs NiO



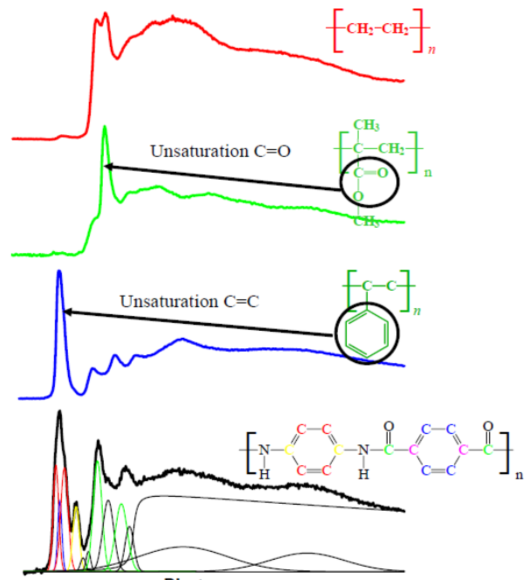
Complex but good for us

Chemical sensitivity



PAUL SCHERRER INSTITUT

Footprint of complex bindings



Courtesy Harald Ade

PAUL SCHERRER INSTITUT

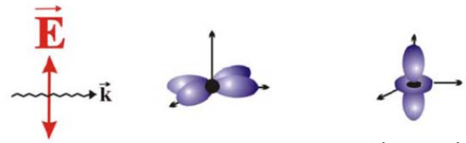
Aim of the lecture

Basic concepts of X-ray absorption spectroscopy to probe electronic and magnetic states

- Absorption process
- Polarization dependency
- Example for XMCD
- Multiplet structure
- XMLD
- Other techniques
- Polarized X-rays

Interaction with linear light - charge

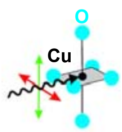
Excitation into 3d band

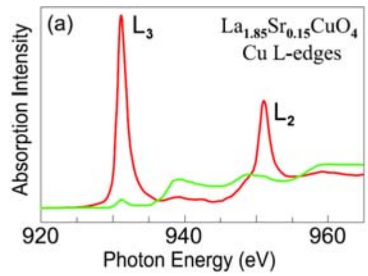


No absorption   absorption

X-ray Natural linear dichroism

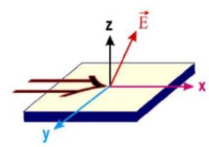
“search light effect”

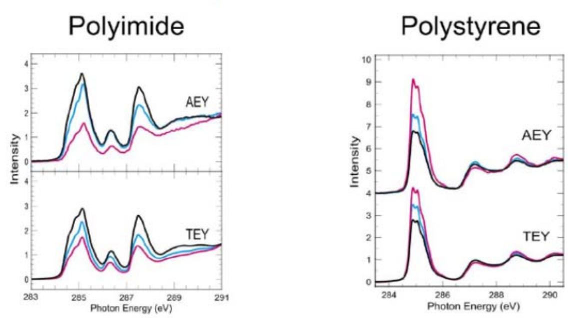


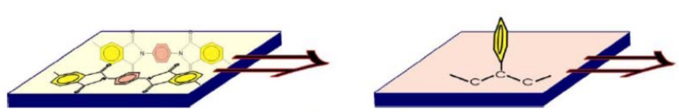


C.T. Chen et al PRL 68, 2543 (1998)

Polarization Dependent NEXAFS Probes Bond Anisotropy at Surface



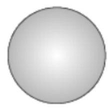




J. Stöhr et al., Science **292**, 2299 (2001)

Interaction with linear light - magnetic

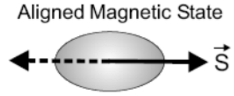
Paramagnetic State



Electron charge density is isotropic

no linear dichroism

Aligned Magnetic State



Preferred spin axis

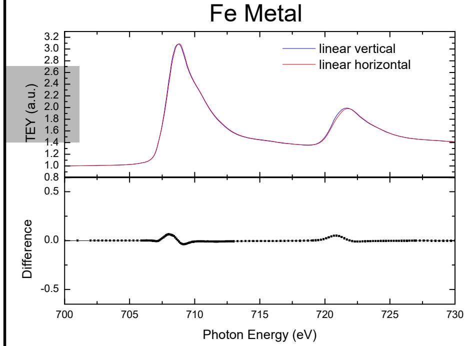
spin orbit coupling changes charge density

linear dichroism

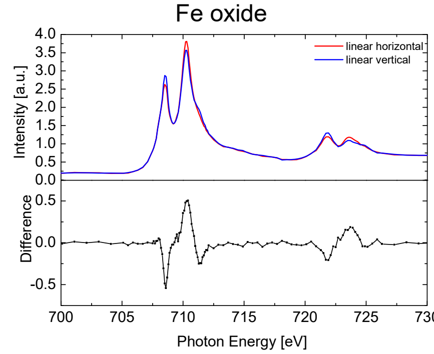
XMLD X-ray Magnetic Linear Dichroism

XMLD

Fe Metal



Fe oxide



XMLD enhanced by mulitplet

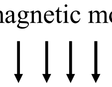
Enables to measure antiferromagnetic systems!

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

XMLD ~ <**M**²> cos²(**M**,**E**)

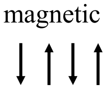
Ferromagnet (FM)

Net magnetic moment



Antiferromagnet (AFM)

No net magnetic moment



PAUL SCHERRER INSTITUT PSI

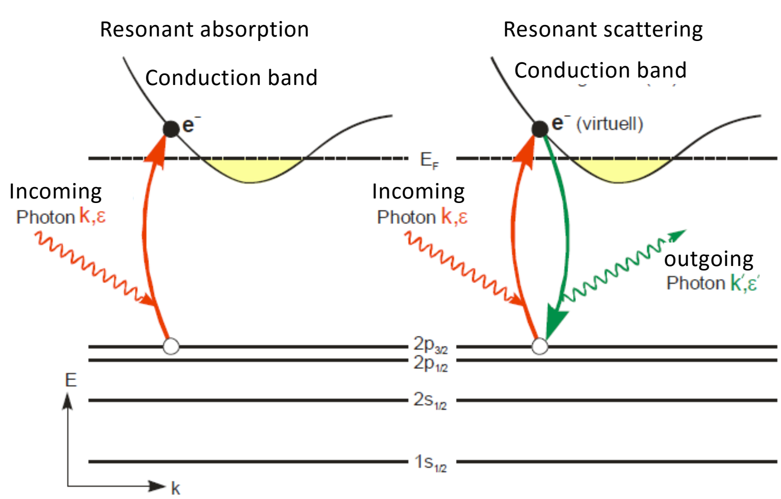
Aim of the lecture

Basic concepts of X-ray absorption spectroscopy to probe electronic and magnetic states

- Absorption process
- Polarization dependency
- Example for XMCD
- Multiplet structure
- XMLD
- Other techniques
- Polarized X-rays

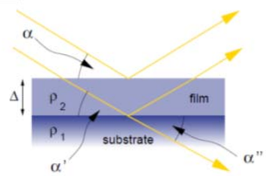
PAUL SCHERRER INSTITUT PSI

Scattering



Soft X-ray resonant magnetic scattering

Ultrathin fcc Fe on Cu(001)



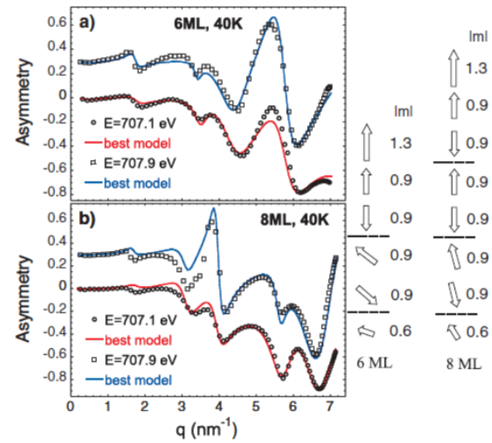
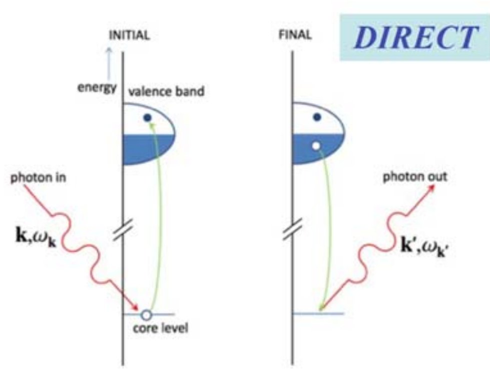


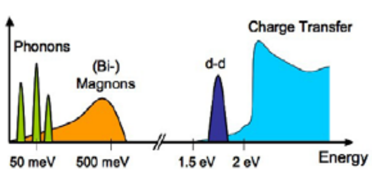
FIG. 3 (color). Experimental (symbols) and calculated (lines) $A(q_z)$ for 6 (a) and 8 ML (b) at 40 K measured in remanence after applying a perpendicular field of $\mu_0 H = 0.4$ T. Magnetization profiles are shown on the right. Dashed lines separate strongly coupled spin units.

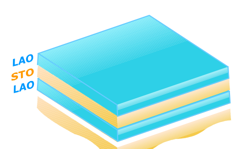
Meyerheim et. Al, PRL 103, 267202 (2009)

Page 49

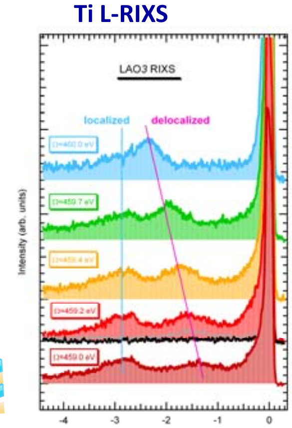
Resonant inelastic X-ray scattering (RIXS)







Ti L-RIXS



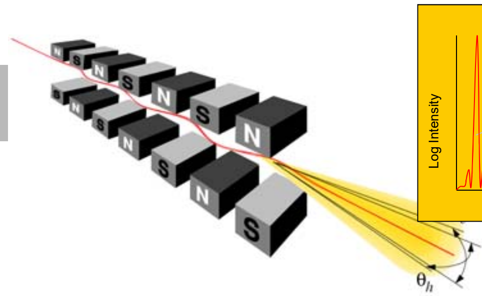
Page 50

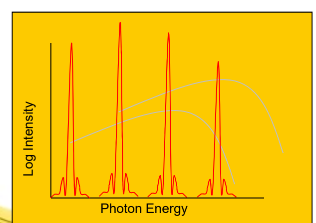
Aim of the lecture

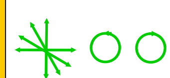
Basic concepts of X-ray absorption spectroscopy to probe electronic and magnetic states

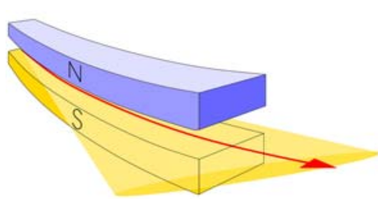
- Absorption process
- Polarization dependency
- Example for XMCD
- Multiplet structure
- XMLD
- Other techniques
- Polarized X-rays

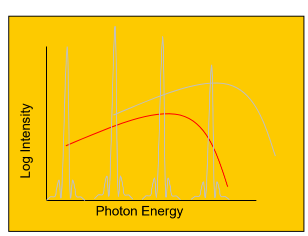
Polarized X-rays

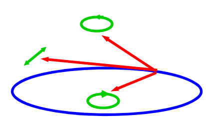




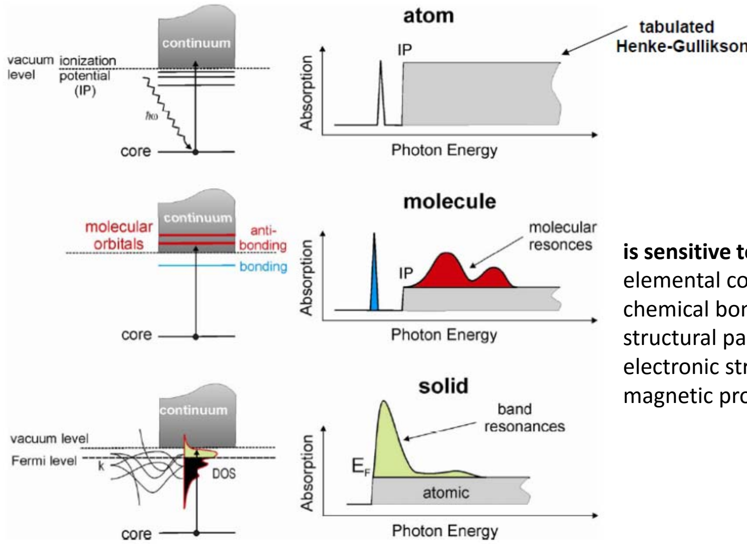








Conclusion: X-ray Absorption Spectra in a Nutshell



is sensitive to
elemental composition
chemical bonds
structural parameters
electronic structure
magnetic properties

Some good books