Surface Science lecture

Di, 09.03.2010 Introduction, Concepts Samples and Structure (Thomas)
Di, 16.03.2010 Electron Diffraction Methods, in particular RHEED, LEED (Bert Mueller)
Di, 23.03.2010 Adsorption / Desorption (Thomas Jung)

Di, 30.03.2010 X-ray Absorption Spectroscopy (F. Nolting)
Di, 06.04.2010 Surface Magnetism XMCD / PEEM (F. Nolting)

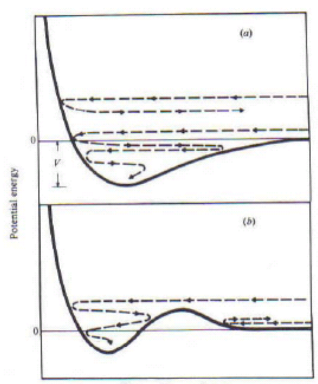
Di, 13.04.2010 Diffusion and Growth (Enrico Gnecco)
Di, 20.04.2010 Electronic Properties and Surface Electron Spectroscopies
XPS/UPS, Auger, ARPES; (Nirmalya Ballav???)
Di, 27.04.2010 Local Probes and Experiments I, STM, Inelastic tunneling and STS (Silvia Schintke)
Di, 04.05.2010 Local Probes and Experiments II, AFM FIM (E. Meyer???)
Di, 11.05.2010 Surface Optics, Kelvin Probe (Thilo Glatzel)
Di, 18.05.2010 Applications of Surface Science in Industry (M. de Wild)
Di, 25.05.2010 Schlusspruefung (Thilo, Christian, Cristian, Enrico, Thomas)
Di, 01.06.2010 Exkursion to e.g. IBM Zurich Research Laboratory (Nanolab, NJ-Lab and Thomas)

Di, 30.03.2010 X-ray Absorption Spectroscopy (F. Nolting)
Di, 06.04.2010 X-ray Microscopy (F. Nolting)

Both with an emphasis of magnetism

Repetition

Adsorption/Desorption



Was geschieht mit einem Atom/Molekül welches aus der Gasphase auf der Oberfläche landet?

(a) Je nach Energie:
Repulsion und Reflexion ins Vakuum oder Umwandlung der kinetischen Energie in Vibrations- und Rotationsfreiheitsgrade und schliesslich Adsorption (Physisorption oder Chemisorption)

(b) Auf gewissen Flächen können auch niederenergetische Teilchen reflektiert werden. Bzw. Verweilen in einem Zwischenzustand.

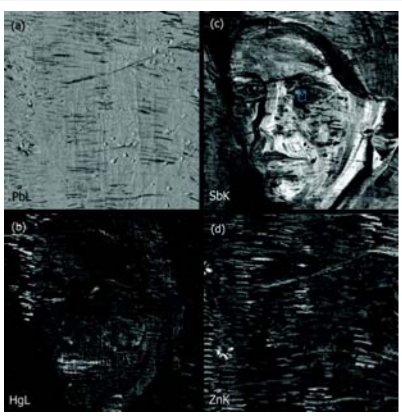
Repetition

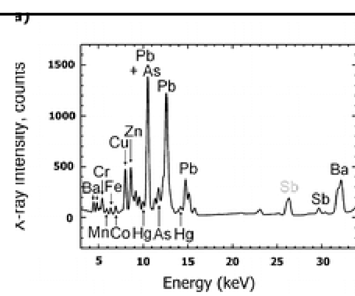
adsorption / desorption
‘take home’ message

- Complex multi – stage process
- T variation affects relaxation
- Important for the formation of interfaces and thin films
- Important for catalysis
- Important for the analysis of interface bonding
- Adsorption can be treated like a chemical reaction:

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

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).





(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).

Published in: Joris Dik; Koen Janssens; Geert Van Der Snickt; Luuk van der Loeff; Karen Rickers; Marine Cotte; *Anal. Chem.* **2008,** 80, 6436-6442.
DOI: 10.1021/ac800965g

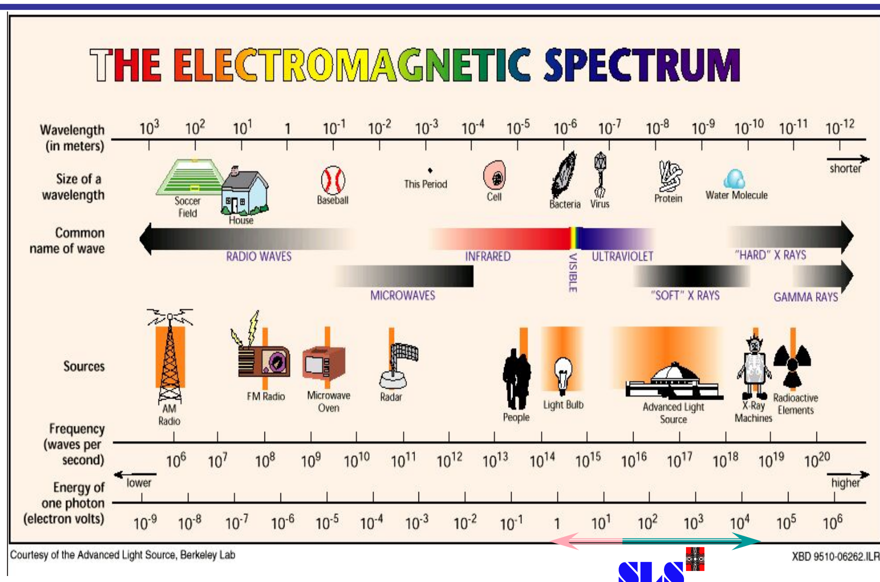
Some things are hidden behind the surface …

- what is surface science?
- interaction at the surface/interface getting more and more important
- combine information

Visible light gives restricted information

- X-ray are an excellent extension

PAUL SCHERRER INSTITUT



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

Some good books

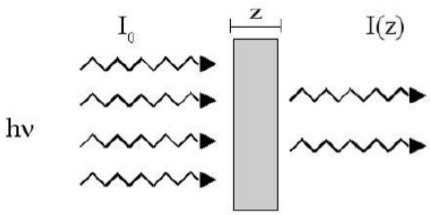
Outline

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

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

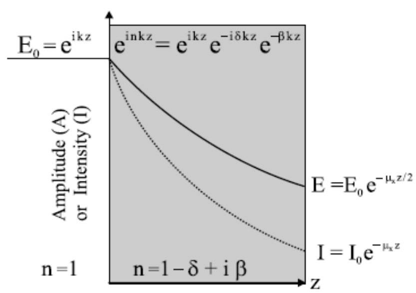
Closer look at the absorption process
- Mulitplet effects
- Example: Interface effect in Exchange Bias system

X-ray Magnetic Linear Dichroism (XMLD)
- Basics

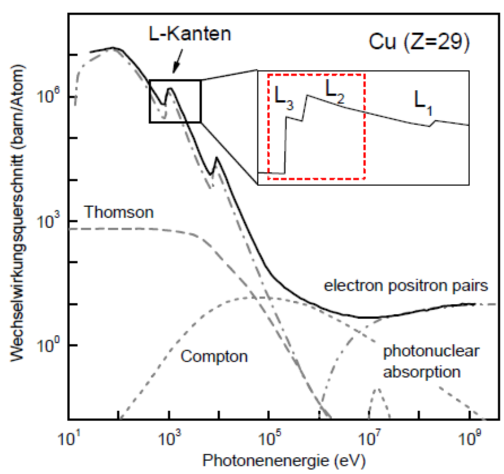


Lambert-Beer

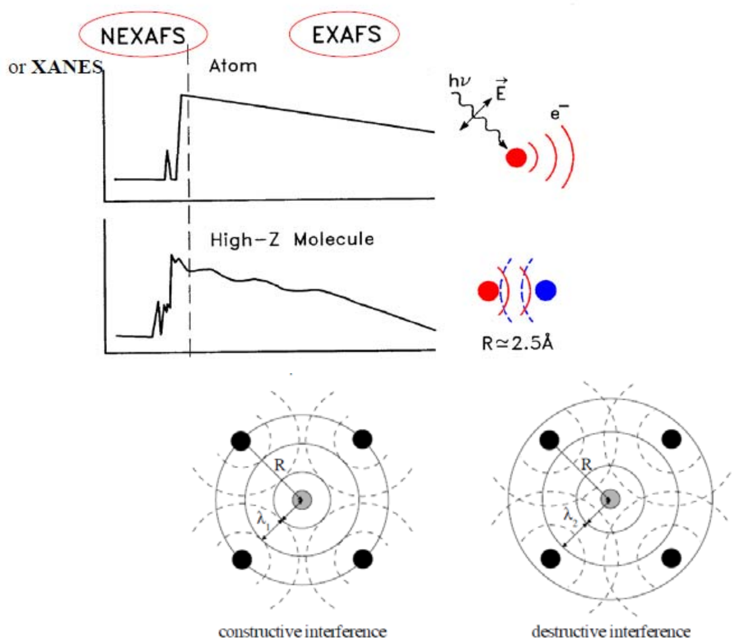
$$\frac{I}{I_o} = e^{-z\mu}$$



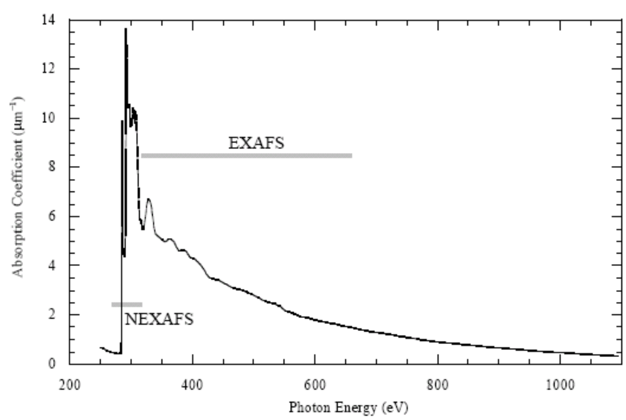
$$I(z) = I_0 \, e^{-\mu_x \, z}$$



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

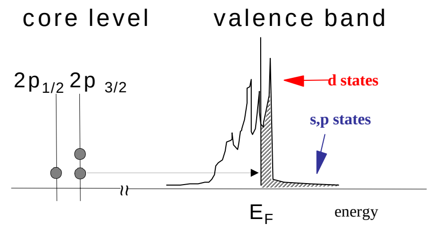
reflects density of unoccupied states

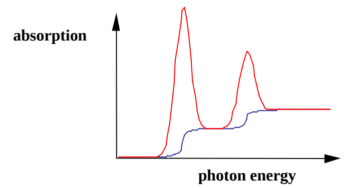
Also called XANES

Extended X-ray Absorption Fine Structure

reflects spatial location of neighboring atoms

Interaction of electromagnetic wave with charge



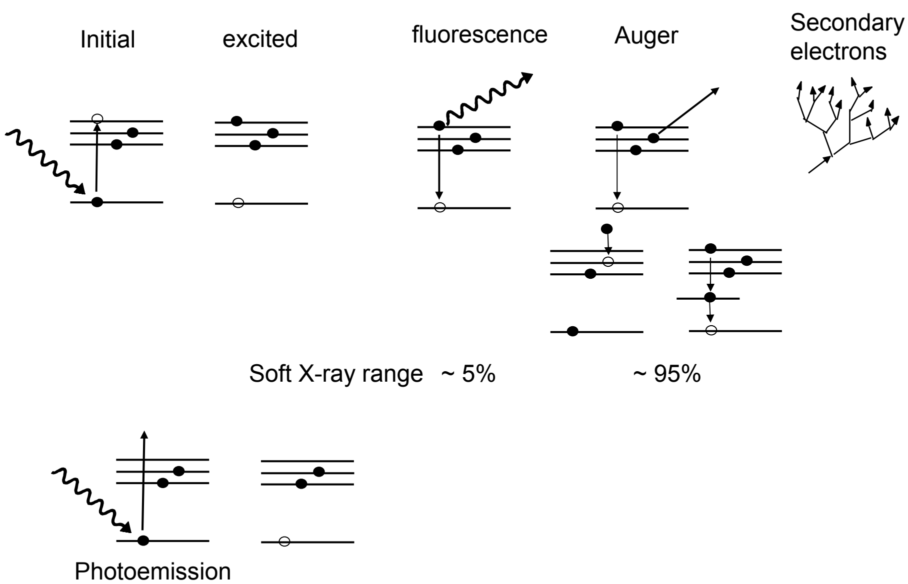


Absorption ~ (Transition matrix: Final state, Initial state) (Density of final states)

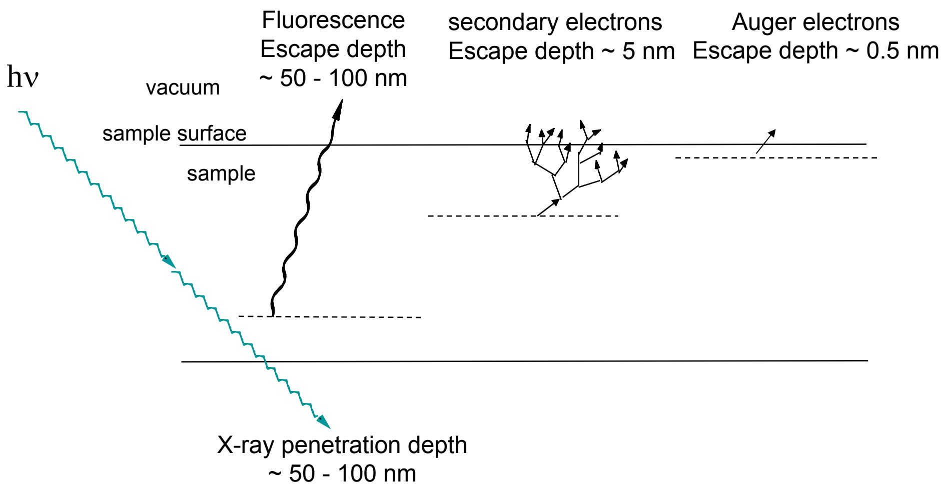
Fermi's golden rule
in dipole approximation
wavelength is large compared to charge
1000 eV corresponds to 1.2 nm
2p core radius is about 0.01 nm

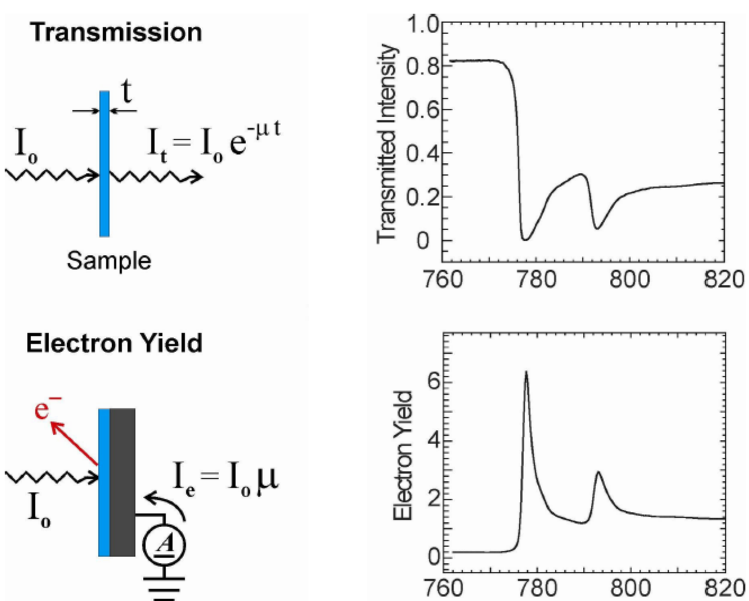
$$\mu \propto \left|\langle f|e \cdot p|i\rangle\right|^2 \rho(E)$$

Decay channels



Sampling depth

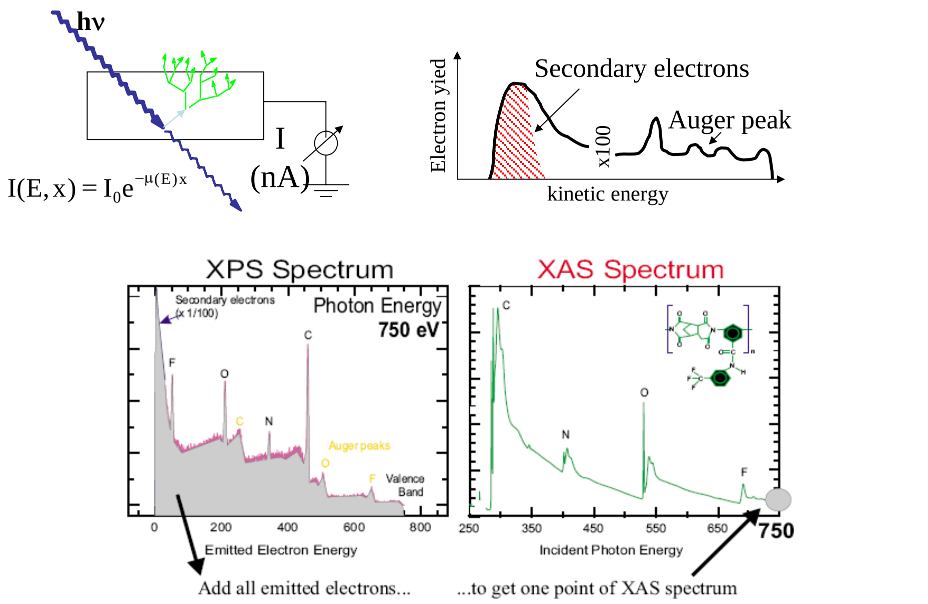




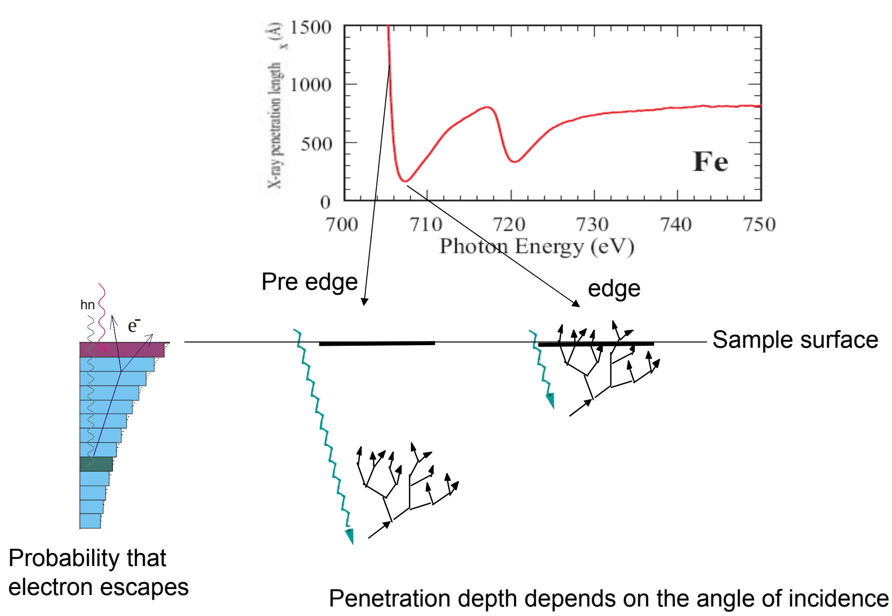
"Photons lost"

"Electrons generated"

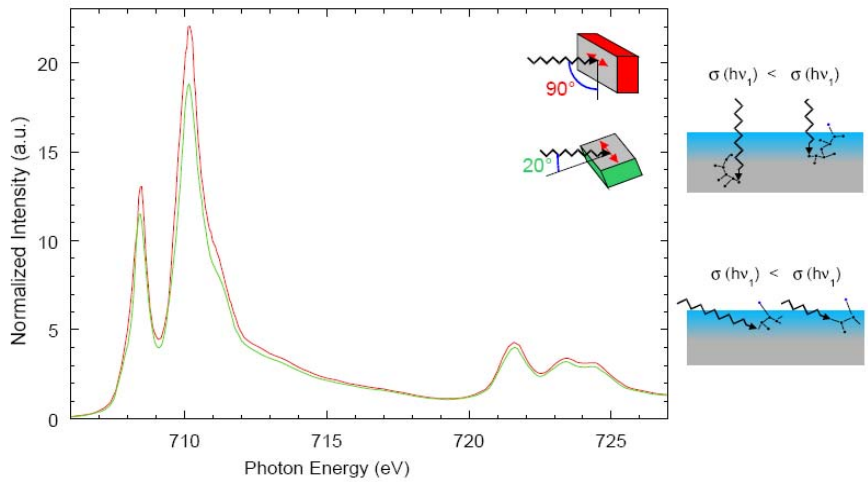
Total electron yield (TEY)



Why is TEY proportional to absorption coefficient

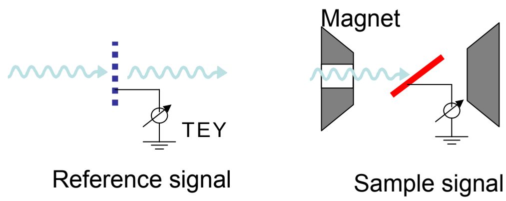


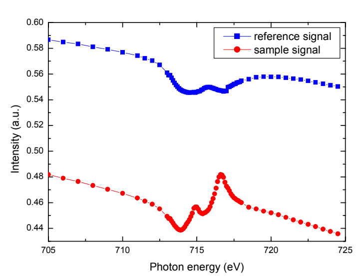
Saturation Effects in TEY Detection



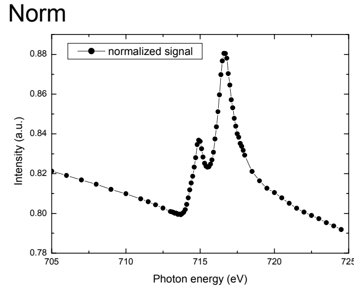
J. Lüning et al, PRB 67, 214433 (2003)

How do we measure

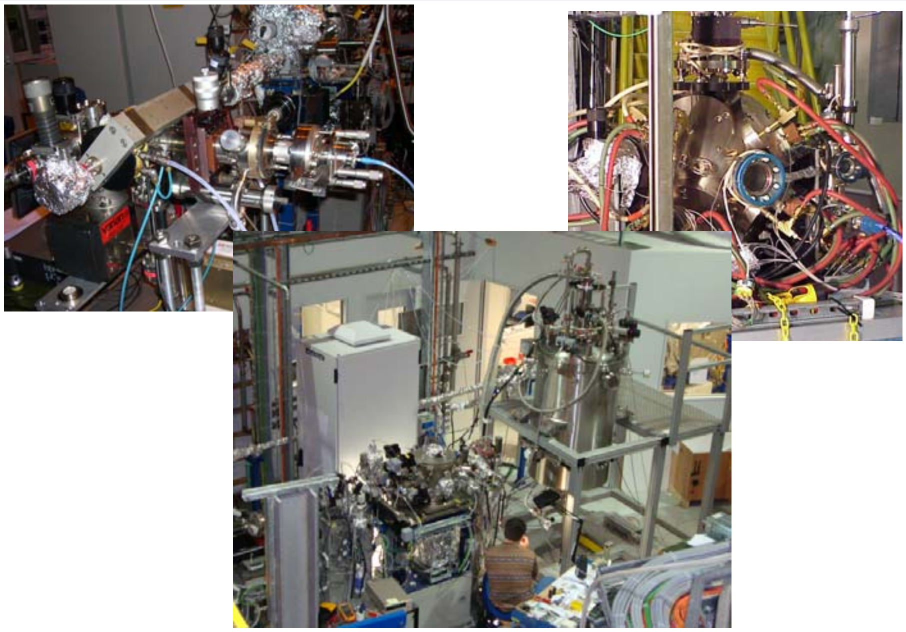




Sample / Reference = Norm



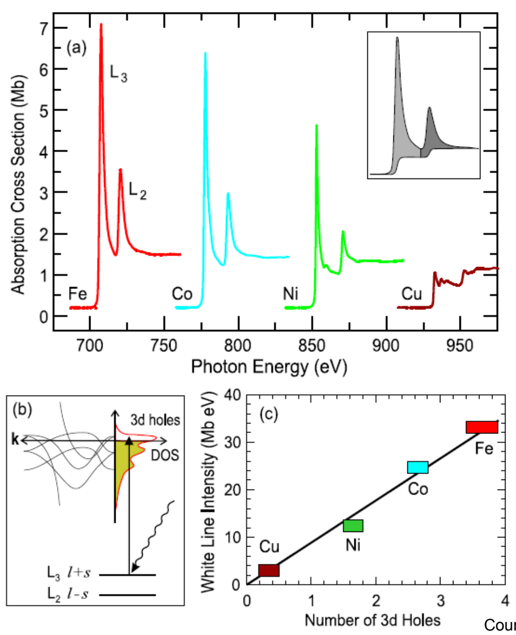
How do we measure



Determine number of 3d holes

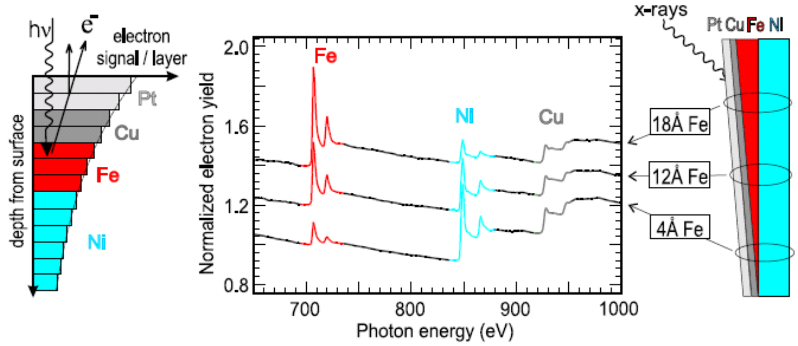
Charge sum rule

Integrated intensity is proportional to number of empty valance states



Courtesy J. Stöhr

“Dismantle” a Multilayer



Courtesy J. Stöhr

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- Example: Magnetocrystalline Anisotropy

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X-ray Magnetic Linear Dichroism (XMLD)
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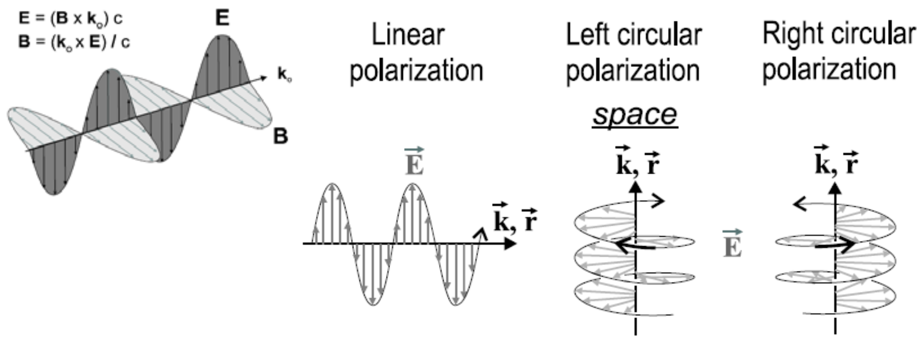
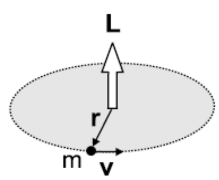
Polarized Photons



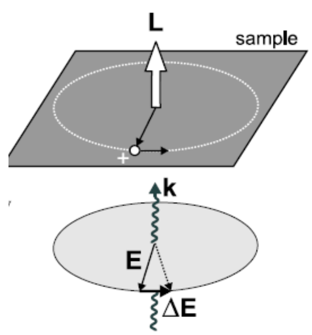
Polarized Photons

Angular moment of orbiting mass



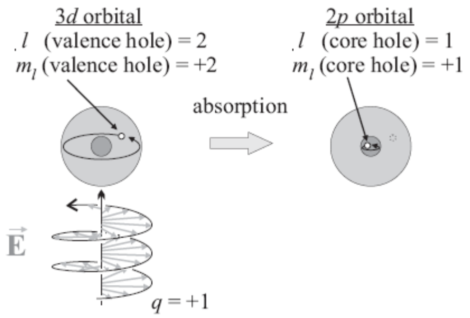
$\mathbf{L} = m\ \mathbf{r} \times \mathbf{v}$

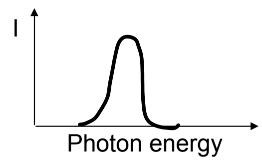
Photon angular moment



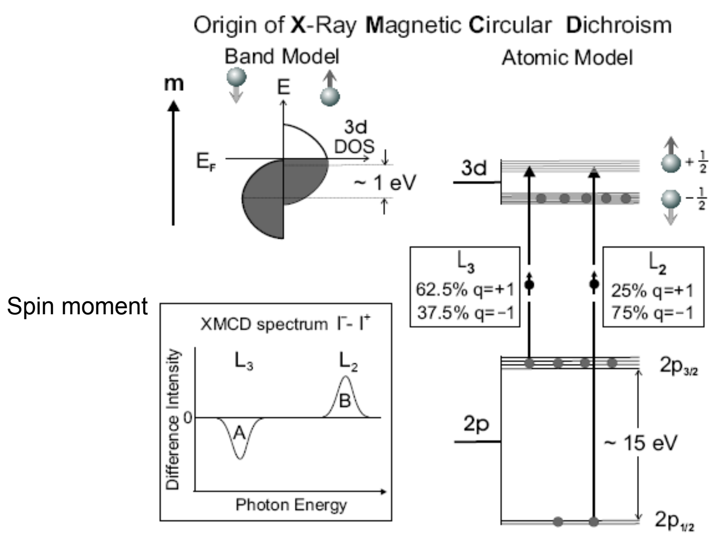
Angular momentum conservation

Polarized Photons

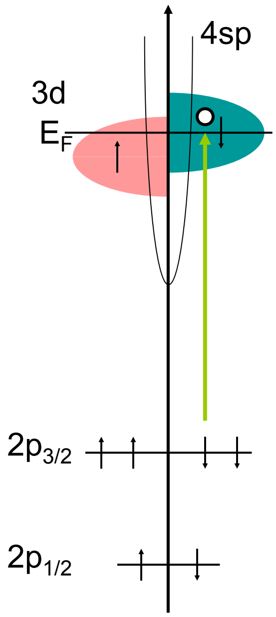




Origin of XMCD



Dipole selection rules



Fermi's golden rule :

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

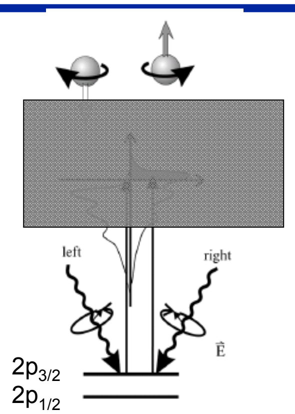
Dipole selection rules:

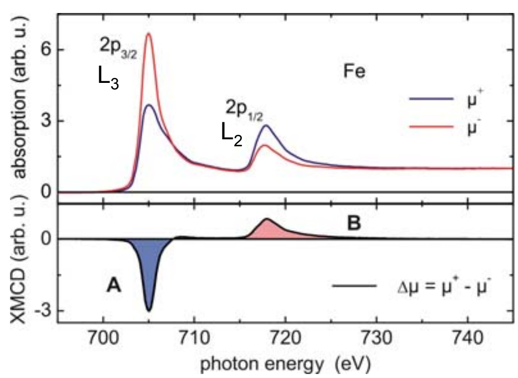
ΔL	=	-1, +1	
ΔJ	=	-1, 0, +1	
ΔM_J	=	-1, 0, +1	
Polarization q		+1, 0, -1	(s^+, p, s^-)

L2: $2p_{1/2}$□4s, $3d_{3/2}$

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

Two-step Model of XMCD



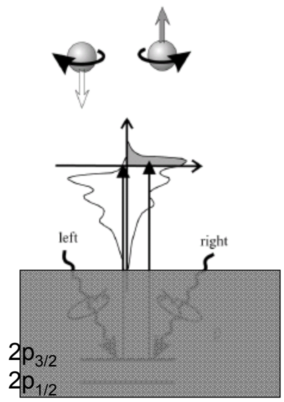


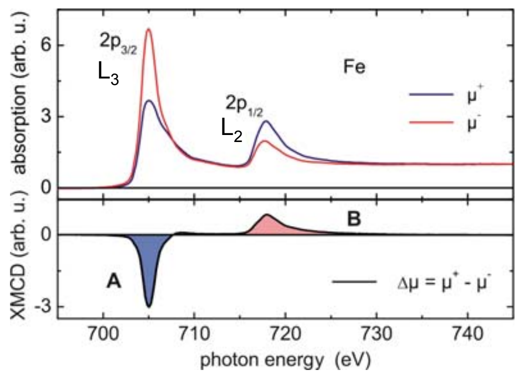
1. Step
Circ. Pol. X-rays generate spin-polarized electrons from inner shell

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

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

Two-step Model of XMCD





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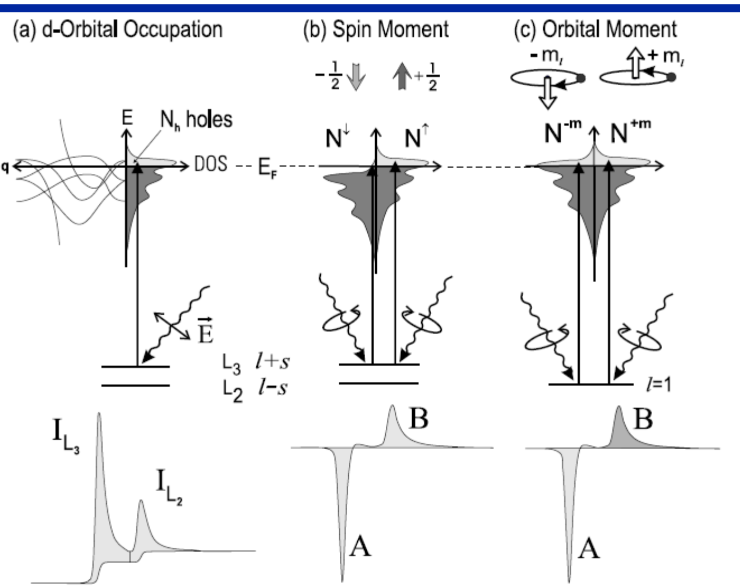
Sum rules



$N_h = \langle I_{L_3} + I_{L_2} \rangle / C$

$m_s = \mu_B \langle |A| + 2|B| \rangle / C$

$m_o = 2\,\mu_B \langle |A| - |B| \rangle / 3C$

… more complex … of course

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

Electron occupation

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

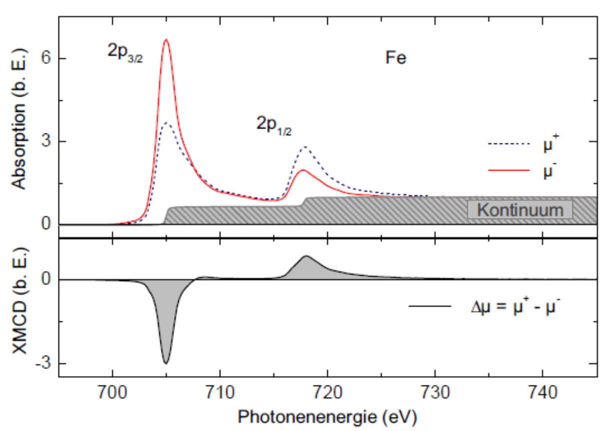
magnetic dipole moment

$\langle T_z \rangle$ 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

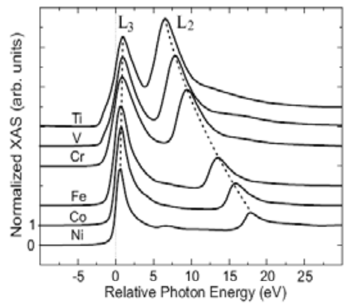
$$\mu_S^{\mathrm{eff}} = \mu_S + 7\mu_T$$

Only contribution to the resonance absorption should be considered



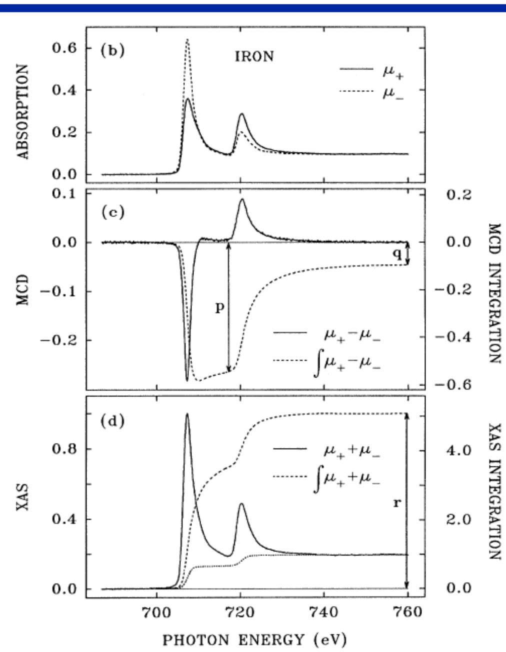
Taken from PhD Thesis Armin Kleibert, 2005

… more complex … of course



L_3 and L_2 must be separated

calculating



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

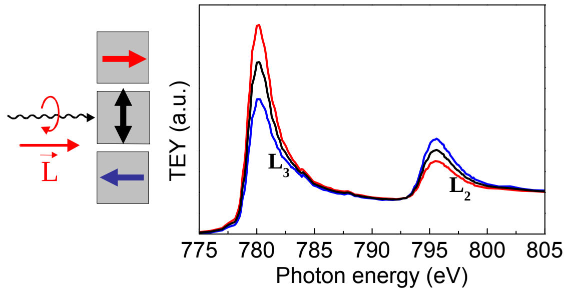
MCD
- difference
- integrate

XAS
- sum spectra
- correct background
- non resonant

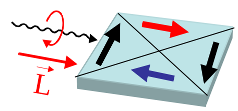
Calculate/neglect
- $\langle T_Z \rangle$
- $\langle Sz \rangle$

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

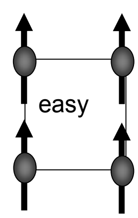
Magnetism 3d metals
- small orbital moment
- large spin moment

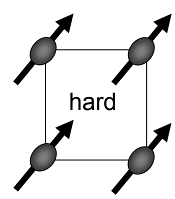
XMCD in action

Study Magneto-crystalline anisotropy

Magnetic Anisotropy
preferential magnetization along axes
easy / hard axis

(magneto-crystalline anisotropy)

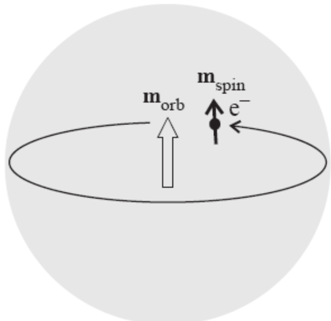




The magneto-crystalline anisotropy is the energy that it takes to rotate the magnetization from the “easy” direction into the “hard” direction

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

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

Bruno model

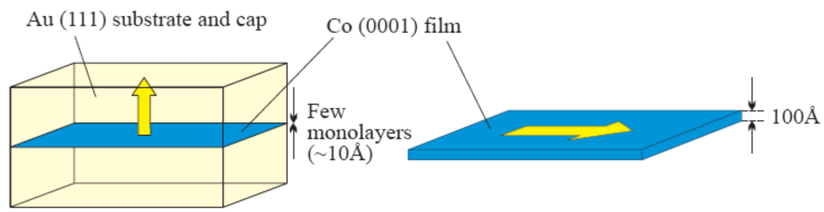
The Bruno model states that the orbital moment is larger along the easy magnetization direction, and that the difference between the orbital moments along the easy and hard directions is proportional to the magneto-crystalline anisotropy

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

P. Bruno, PRB 39, 865 (1989)

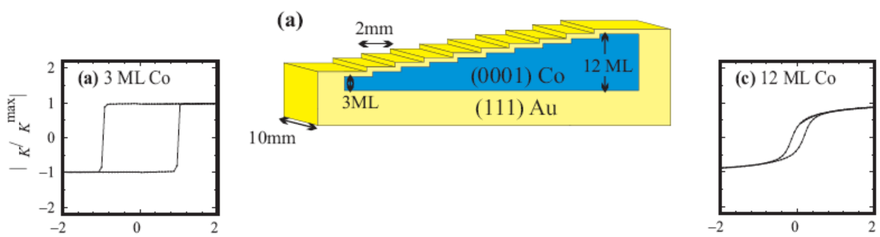
Test system

Magnetic anisotropy in Co (0001) films

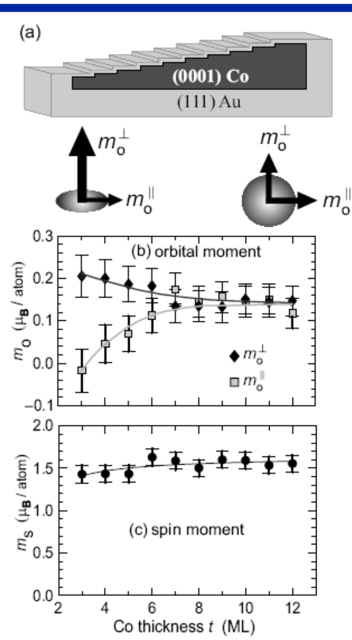


Perpendicular magnetic anisotropy (preferred magnetization out-of-plane)

Thin flim shape anisotropy (preferred magnetization in-plane)



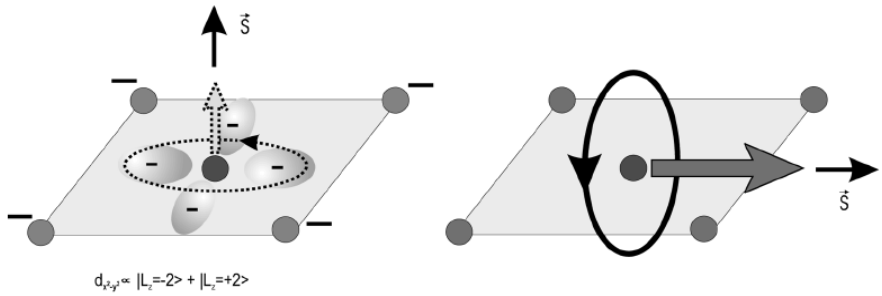
Results



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 monatomicmetal chains

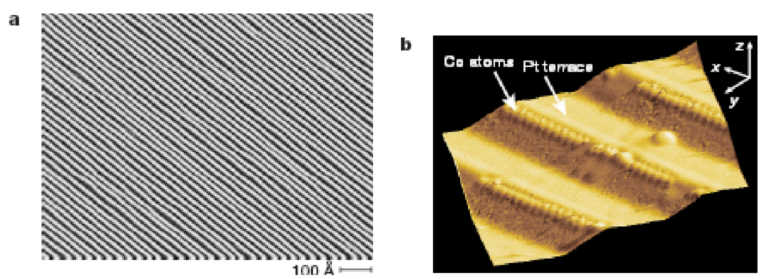
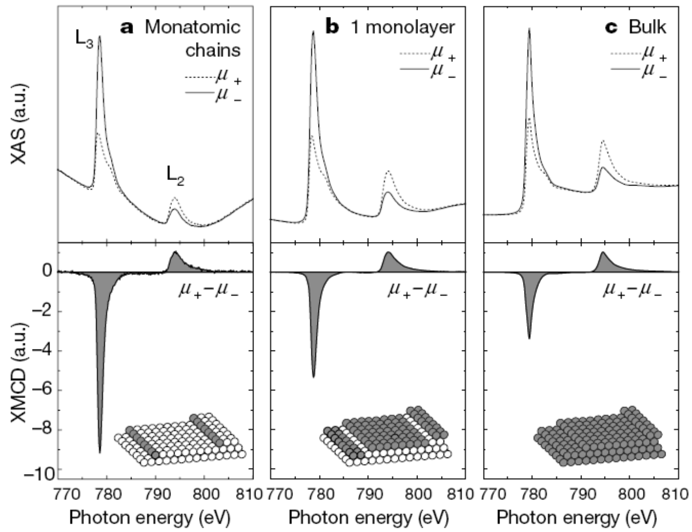


Figure 1 STM topographs of the Pt(997) surface. **a**, Periodic step structure (each white line represents a single step). The surface has a 6.45° miscut angle relative to the (111) direction; repulsive step interactions result in a narrow terrace width distribution centred at 20.2 Å with 2.9 Å standard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

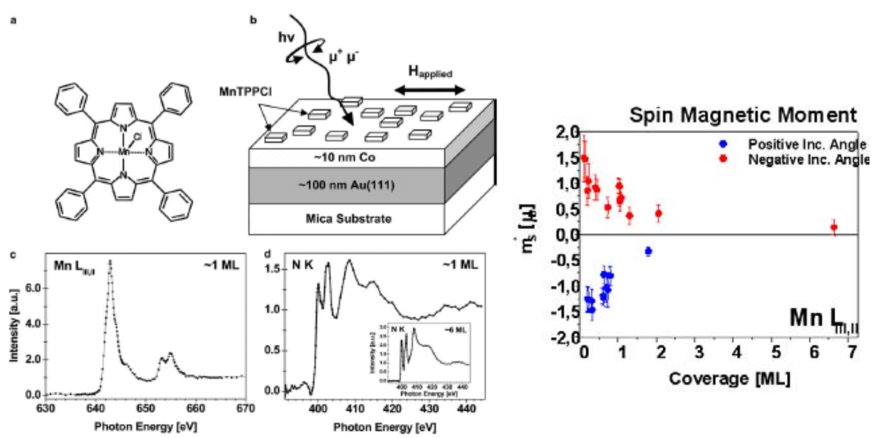
Increased orbital moment in Co chains



$m_l \sim 0.68\ \mu_B$ / 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

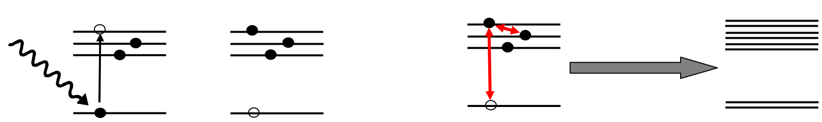
X-ray Magnetic Circular Dichroism (XMCD)
- Basics
- Example: Magnetocrystalline Anisotropy

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

X-ray Magnetic Linear Dichroism (XMLD)
- Basics

Combine it all
- Summary Example: Laser control of an exchange bias system

Interactions



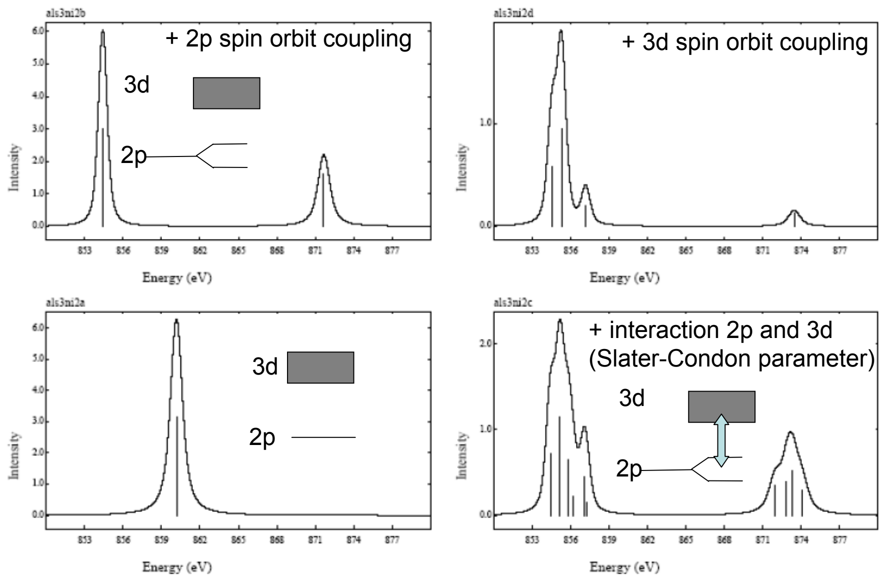
Coulomb, Exchange
Electron – electron interaction
Electron – hole interaction

Valence – Valence interaction : many body effects

Valence – Core interaction : multiplet effects

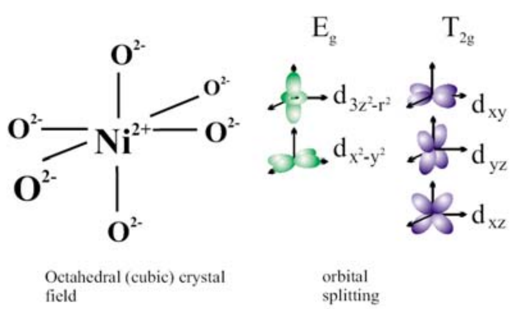
Hybridization between ground state and final state leads to a multiplet structure of the spectrum

Interactions – NiO (Ni^{2+})

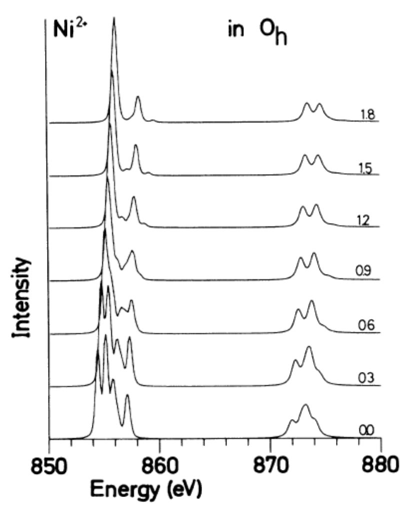


F. de Groot

Crystal field

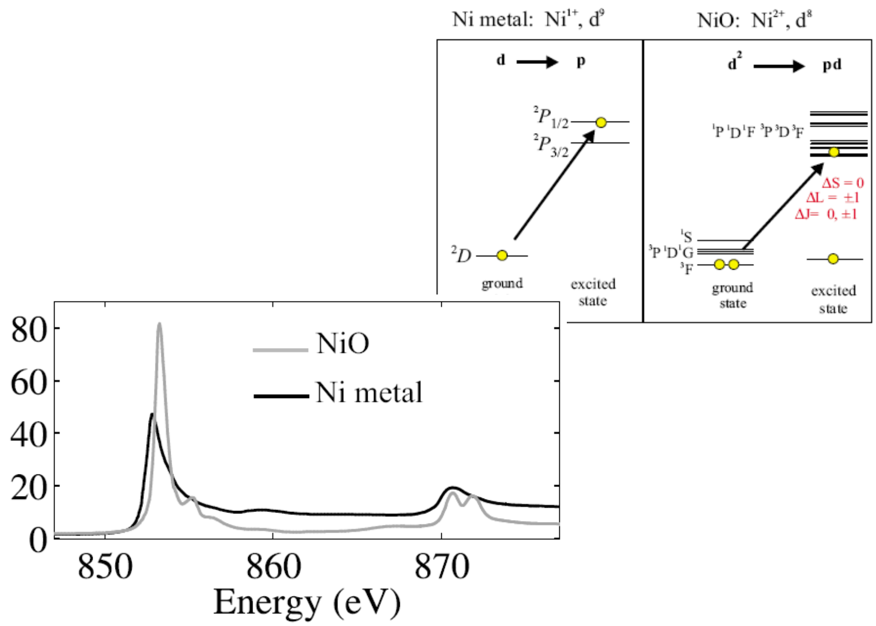


Further parameter is charge transfer



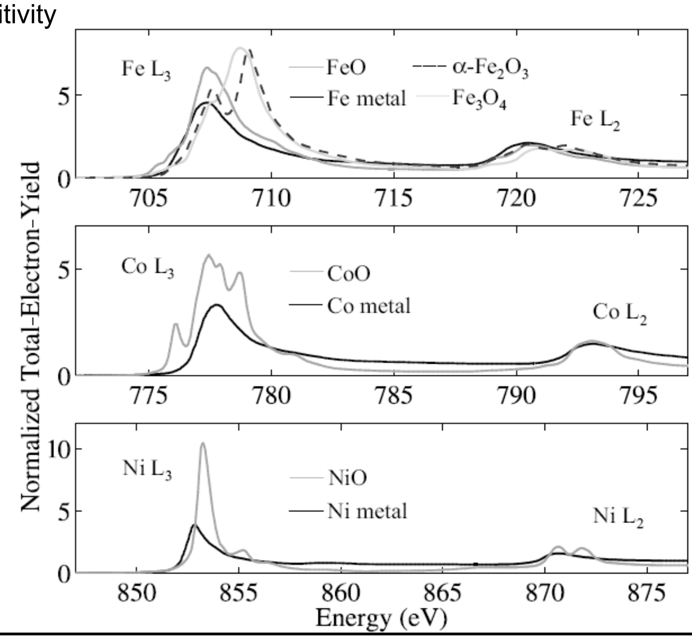
F. de Groot et al. PRB 42, 5459 (1990)

Ni metal vs NiO

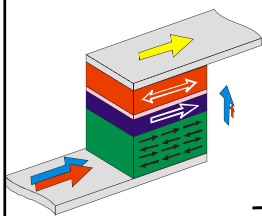


Complex but good for us

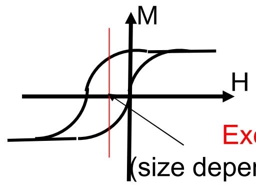
Chemical sensitivity



Exchange Bias

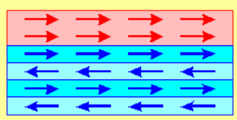


Unidirectional anisotropy in FM adjacent to AFM
discovered 1956 by Meiklejohn and Bean

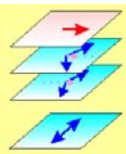


Effect of exchange bias is still poorly understood

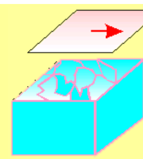
Ideal Interface Model



Spin Flop Model



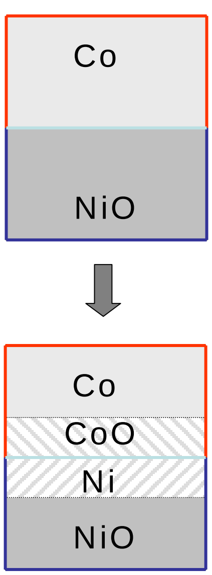
Domain Size Model

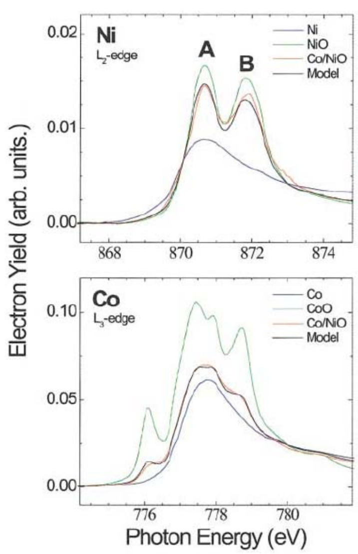


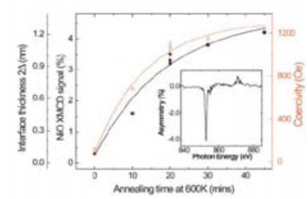
Uncompensated spins at AF domain boundaries

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





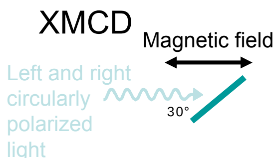


Oxidation/reduction at the interface is responsible for increased coercivity

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

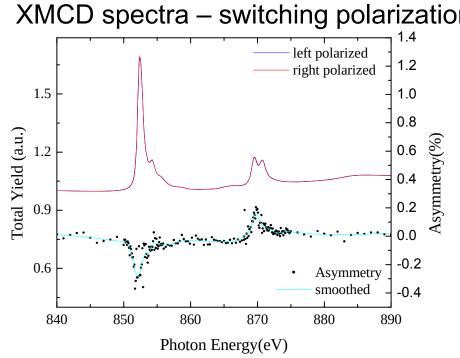
Exchange biased Co/NiO multilayer

1.5 nm Ru
3 nm Co
50 nm NiO
3 nm Co
.
.

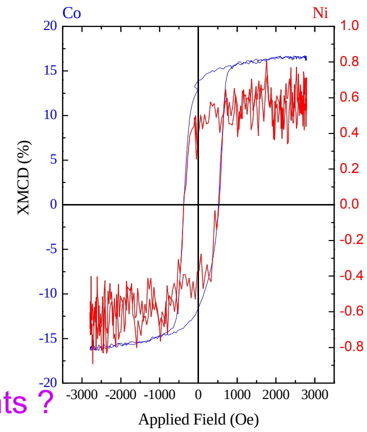


EPU beamline 4 at ALS,
Elke Arenholz, Tony Young

XMCD spectra – switching polarization



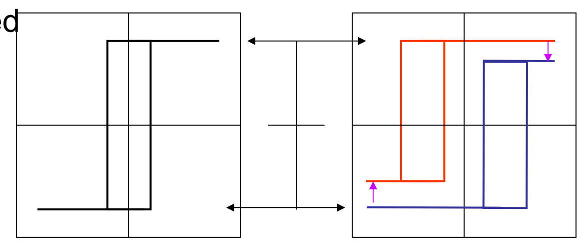
Hysteresis of Co and NiO



Pinned Moments ?

Pinned Moments

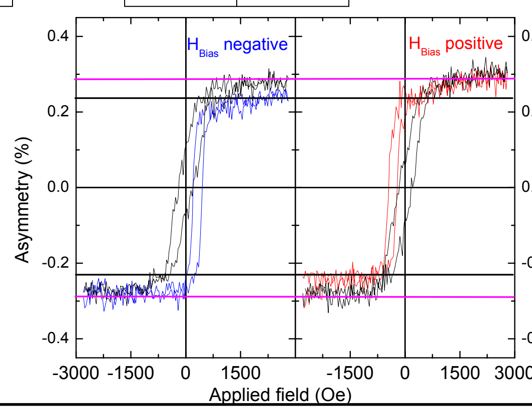
unbiased



biased

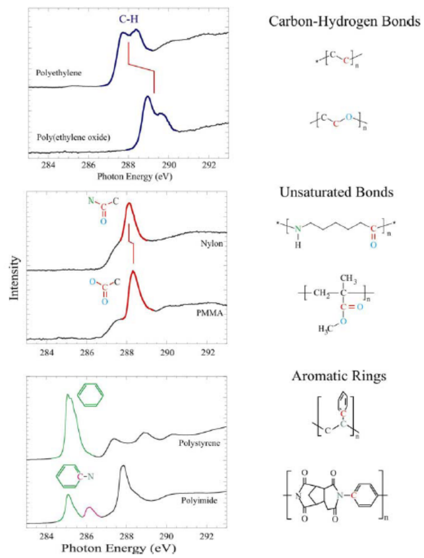
Pinned Moments

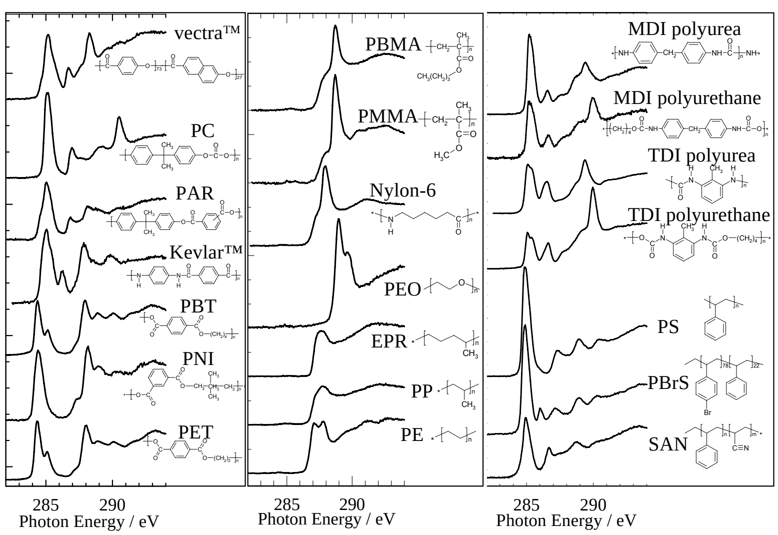
Co/IrMn multilayer
Field grown, H_c = 600 Oe
Matt Carey at IBM, Almaden, USA



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

NEXAFS spectra of polymers: building block picture





Harald Ade (1997)

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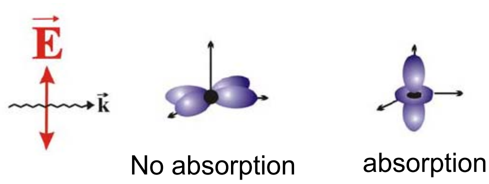
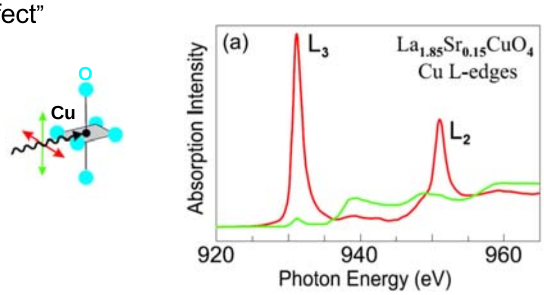
X-ray Magnetic Linear Dichroism (XMLD)
- Basics

Interaction with linear light - charge

Excitation into 3d band

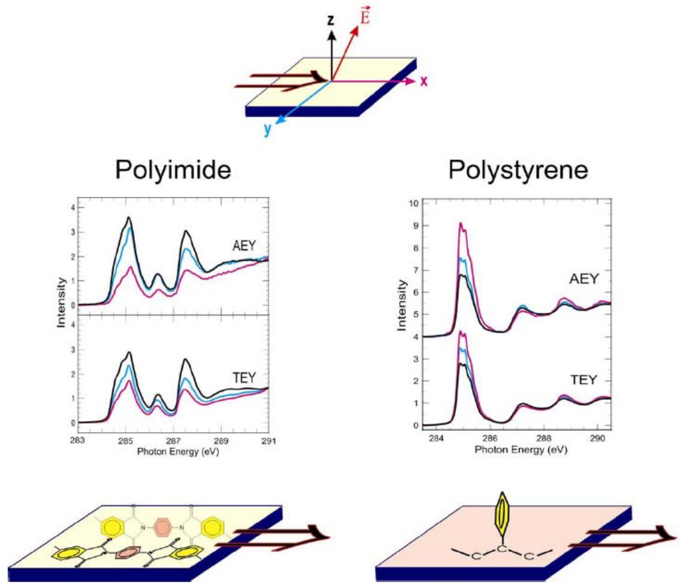


X-ray Natural linear dichroism
"search light effect"



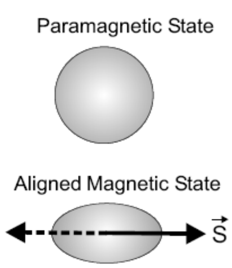
C.T. Chen et al PRL 68, 2543 (1998)

Polarization Dependent NEXAFS Probes Bond Anisotropy at Surface



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

Interaction with linear light - magnetic

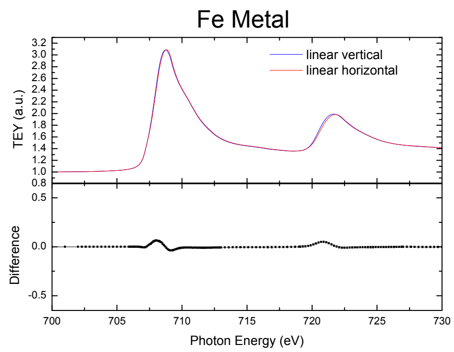


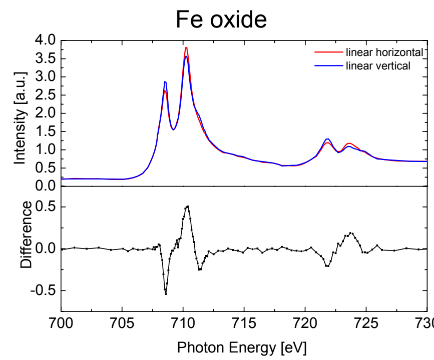
Electron charge density is isotropic
no linear dichroism

Preferred spin axis
spin orbit coupling changes charge density
linear dichroism

XMLD X-ray Magnetic Linear Dichroism

XMLD





XMLD enhanced by mulitplet

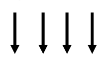
Enables to measure antiferromagnetic systems!

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

XMLD ~ <**M**²> cos²(**M**,**E**)

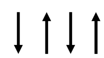
Ferromagnet (FM)

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)

Brief excursion
X-rays / Synchrotron generation

1895 Discovery of X-rays by Wilhelm Röntgen
1901 Nobel prize in physics

Image of hand of Albert von Kölliker
this is the second image, the first one, very similar is said to be the hand of his wife

Wilhelm Röntgen

27. März 1845 in Lennep geboren.

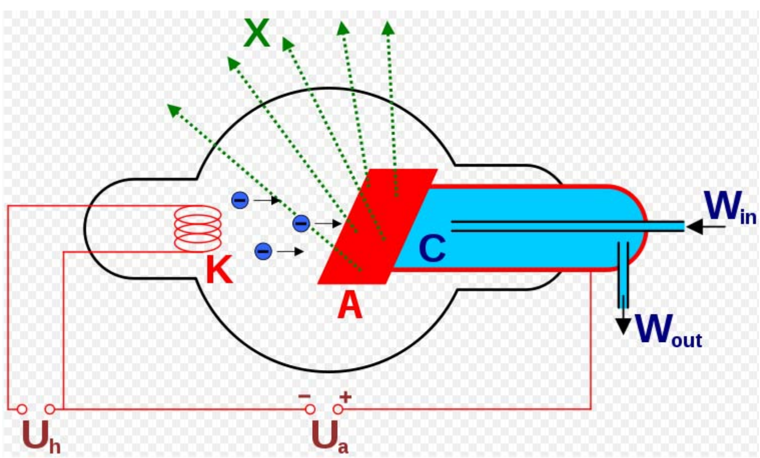
1861 bis 1863 Technische Schule in Utrecht. Aus disziplinarischen Gründen, weil er irrtümlich für den Urheber einer Karikatur seines Klassenlehrers gehalten wurde, verwies man ihn ohne Abitur von der Schule.

1864 - 1868 Eidgenössischen Technischen Hochschule Zürich (ETH Zürich)
Maschinenbauingenieur
1869 promovierte Röntgen an der Universität Zürich in Physik mit „Studien über Gase".

1870 begleitete er August Kundt als Assistent nach Würzburg.
1874 Habilitation Universität Straßburg die ihm die Universität Würzburg zuvor wegen seines fehlenden Abiturs verweigert hatte.

1875 außerordentlicher Professor für Physik und Mathematik an der Landwirtschaftlichen Akademie Hohenheim.
1876 eine Stelle als außerordentlicher Professor für Physik in Straßburg.
1879 ordentliche Professur in Gießen
1888 Professor der Experimentalphysik Würzburg.
1900 Professor an der Universität München
1923 verstorben

X-ray tube



Creation of electromagnetic radiation

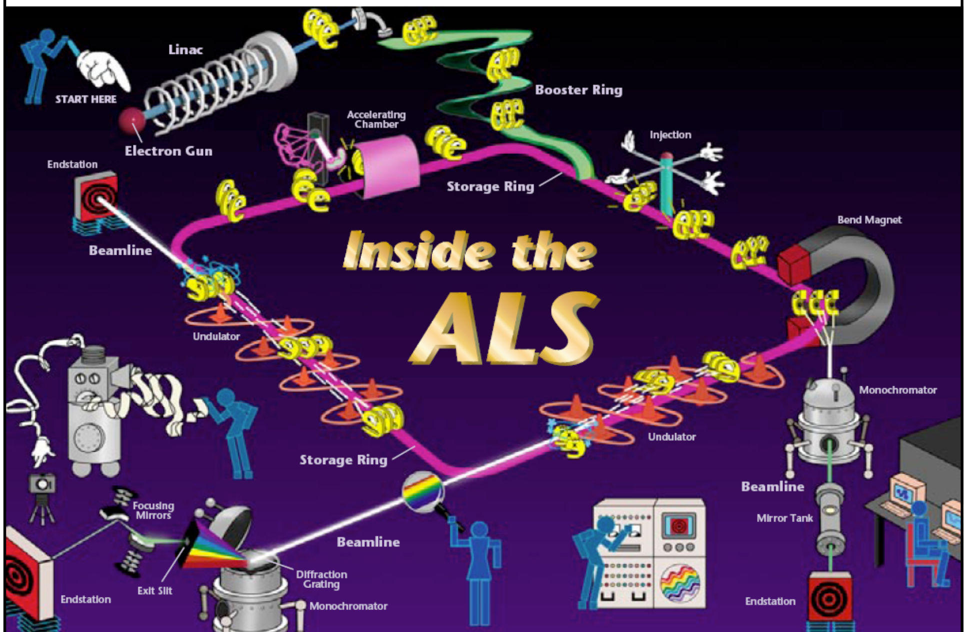
The Liénard–Wiechert field $\boldsymbol{E}(t)$ of a point charge q detected by an observer at a time t is determined by the distance r^*, the velocity v^*, and acceleration a^* of the charge at the emission or retarded time $t^* = t - r^*/c$. Defining $\boldsymbol{\beta}^* = \boldsymbol{v}^*/c$ we have

$$\boldsymbol{E}(t) = \frac{q}{4\pi\epsilon_0} \underbrace{\frac{1-(\beta^*)^2}{(r^*)^2\,(1-\boldsymbol{n}^*\cdot\boldsymbol{\beta}^*)^3}\,[\boldsymbol{n}^* - \boldsymbol{\beta}^*]}_{\text{velocity field}}$$

$$+ \frac{q}{4\pi\epsilon_0} \underbrace{\frac{1}{c^2\,r^*\,(1-\boldsymbol{n}^*\cdot\boldsymbol{\beta}^*)^3}\,\{\boldsymbol{n}^* \times ([\boldsymbol{n}^* - \boldsymbol{\beta}^*] \times \boldsymbol{a}^*)\}}_{\text{acceleration field}}\,. \quad (4.58)$$

We have indicated all retarded quantities by an asterisk.

Swiss Light Source



Taken from the Advanced Light Source, Berkeley USA

Speicherring

Quadrupol: magnetische Linse

Sextupol: Farbkorrektur

Bündelung und Speicherung der Elektronen über mehrere Stunden.

polarized X-rays!

$$l = m_e(r \times v) = m_e\, r^2 \omega$$

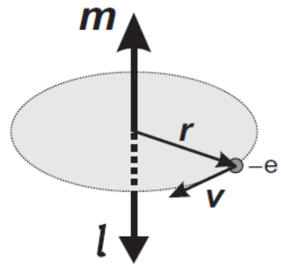
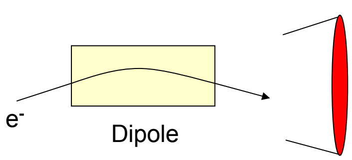
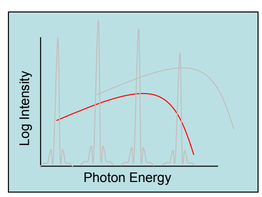


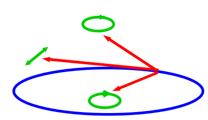
Fig. 3.5. Definition of the magnetic moment caused by an electron $q = -e$ that orbits around a center at a distance r with a tangential velocity v and angular velocity ω. The classical angular momentum l of the rotating electron with mass m_e is also shown

polarized X-rays!

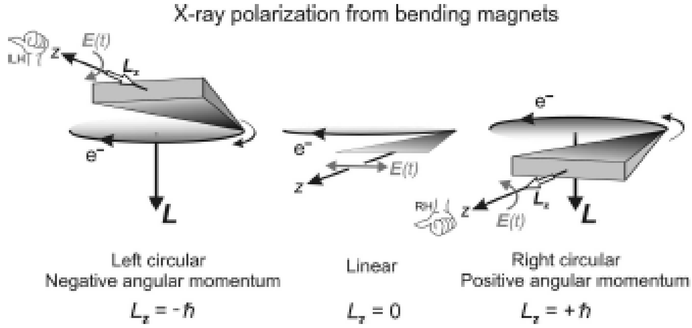
Slide Courtesy: Thomas Schmidt



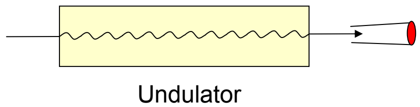


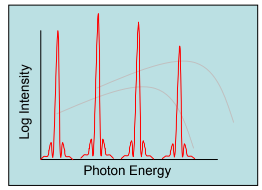


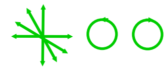
X-ray polarization from bending magnets

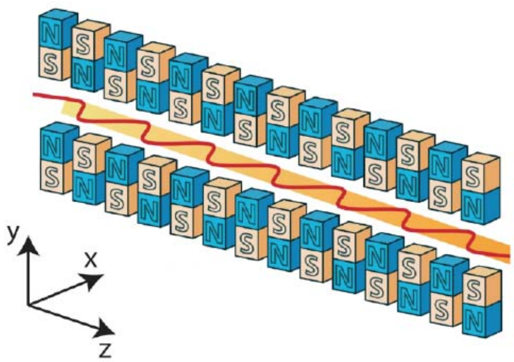


polarized X-rays!





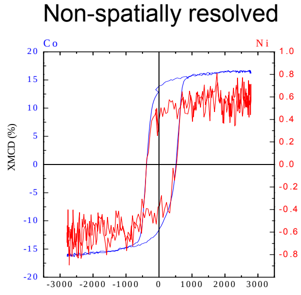




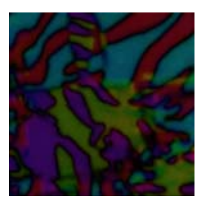
Conclusions

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
- …