Using X-rays

Instrumentation for Spectroscopy

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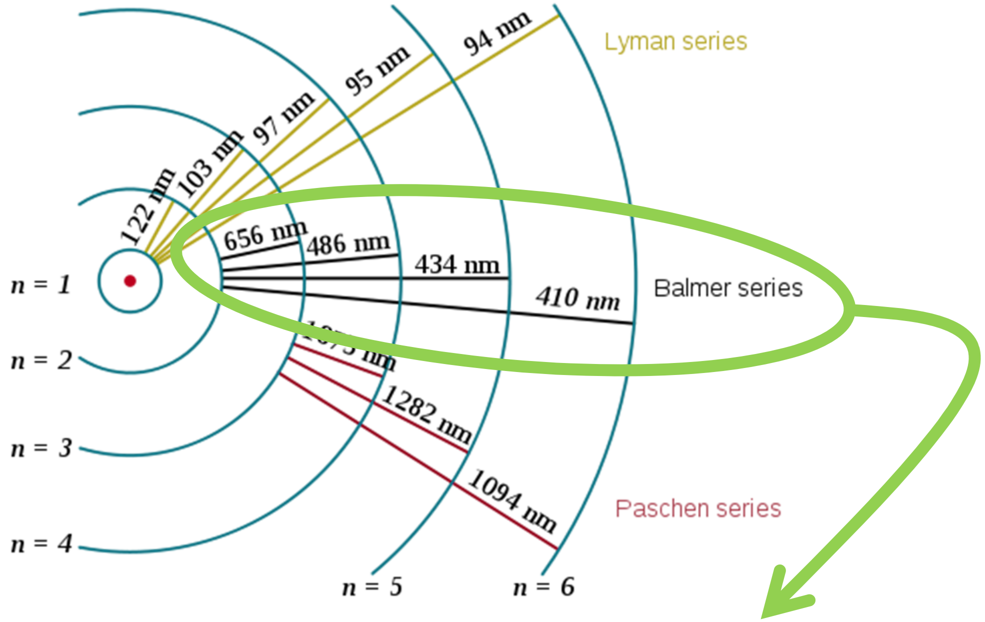
What is Spectroscopy?

- Study of interaction of light (or: e.m. radiation) with matter
- Measure intensity as a function of wavelength λ or energy $E = \frac{hc}{\lambda}$

hydrogen
atom



Picture source: Wikipedia

Here: Measure X-ray absorption as a function of photon energy

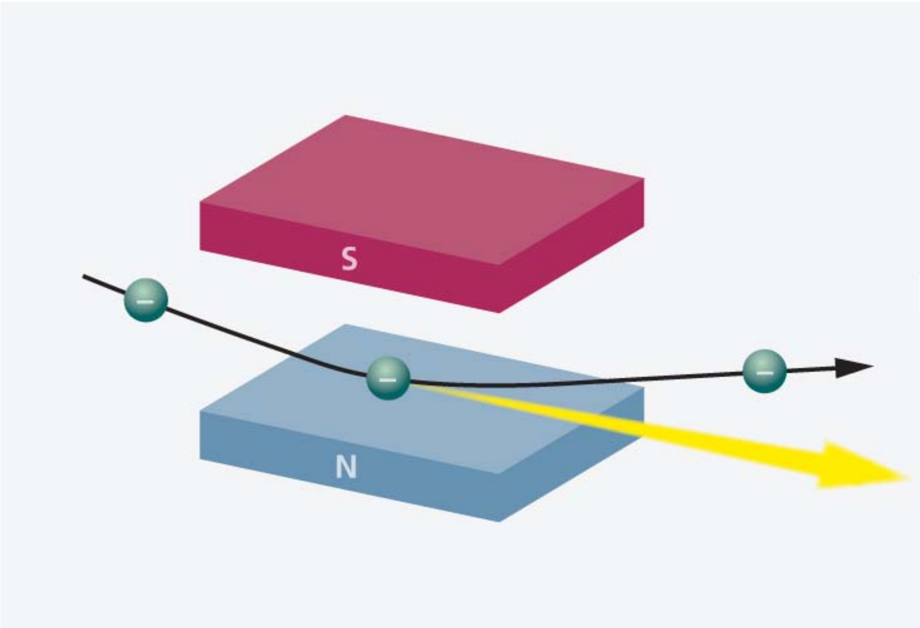
$$\mu(E) = \rho_a \cdot \sigma(E)$$

Absorption coefficient [cm^{-1}]

Atomic number density [cm^{-3}]

Absorption cross section [cm^2]

Why Not Use an X-ray Tube?



Synchrotron

- Monochromatic
- Tunable wavelength
- Well-defined polarization
- High intensity

SLS (Villigen, Switzerland)

ESRF (Grenoble, France)

Diamond (Oxford, GB)

BESSY (Berlin, Germany)

MAXLAB (Lund, Sweden)

…

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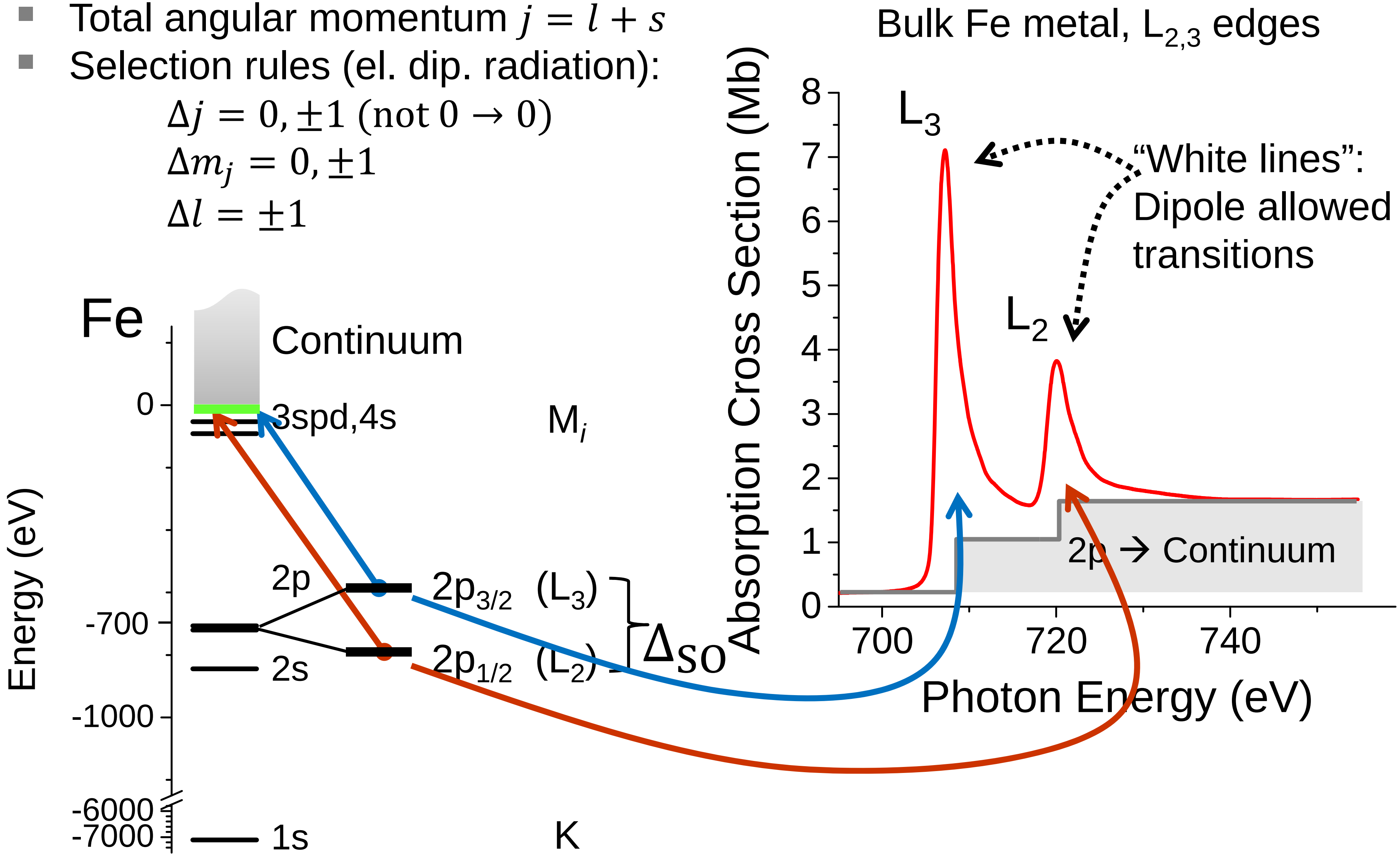
4. X-ray linear dichroism and circular dichroism
5. Origin of X-ray magnetic circular dichroism effect, sum rules
6. Science examples

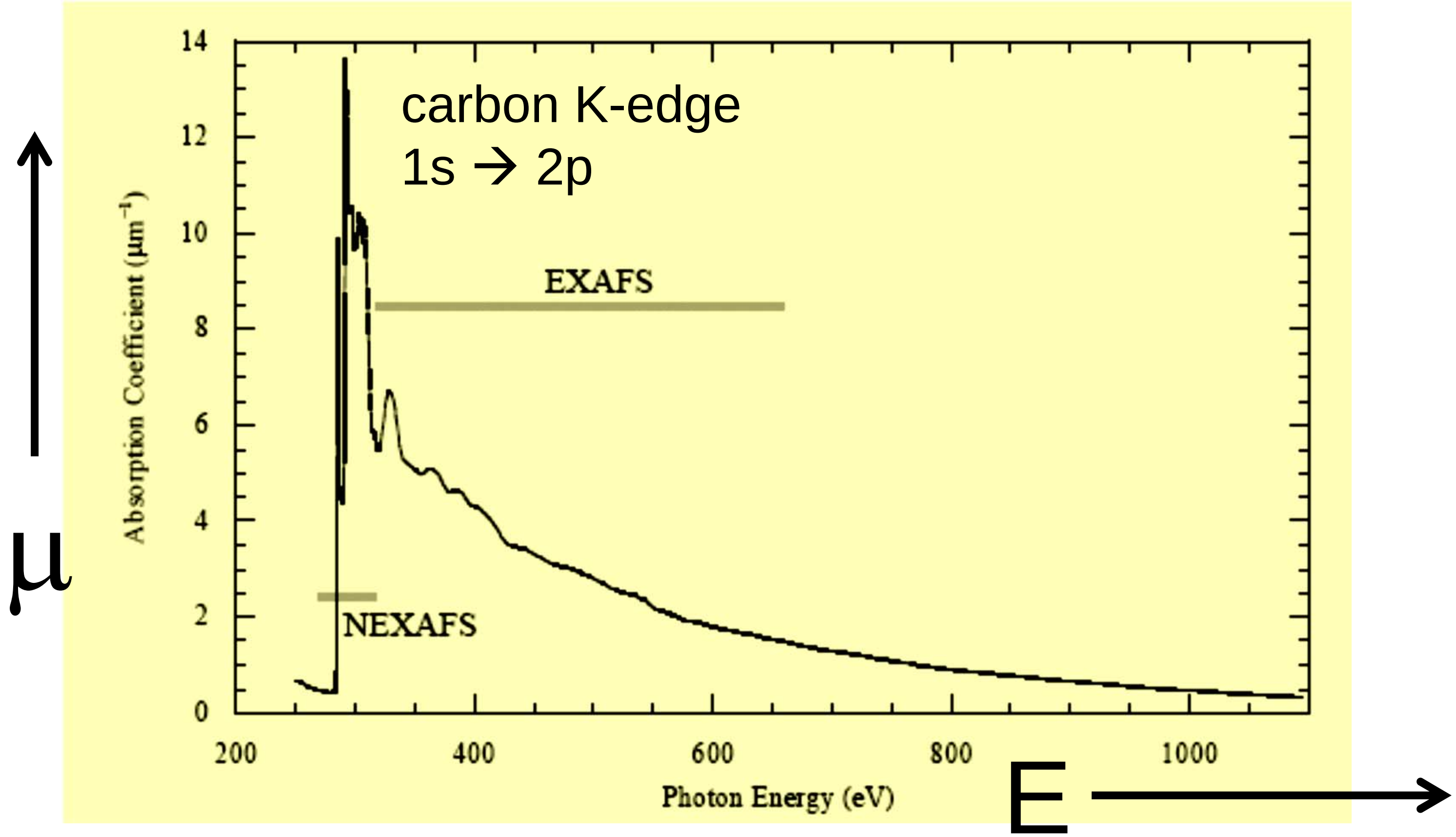
An Example

- Quantum numbers n, l, m_l, s, m_s
- Total angular momentum $j = l + s$
- Selection rules (el. dip. radiation):

$$\Delta j = 0, \pm 1 \text{ (not } 0 \rightarrow 0)$$
$$\Delta m_j = 0, \pm 1$$
$$\Delta l = \pm 1$$



Electromagnetic Radiation



Near Edge X-ray Absorption Fine Structure (NEXAFS)

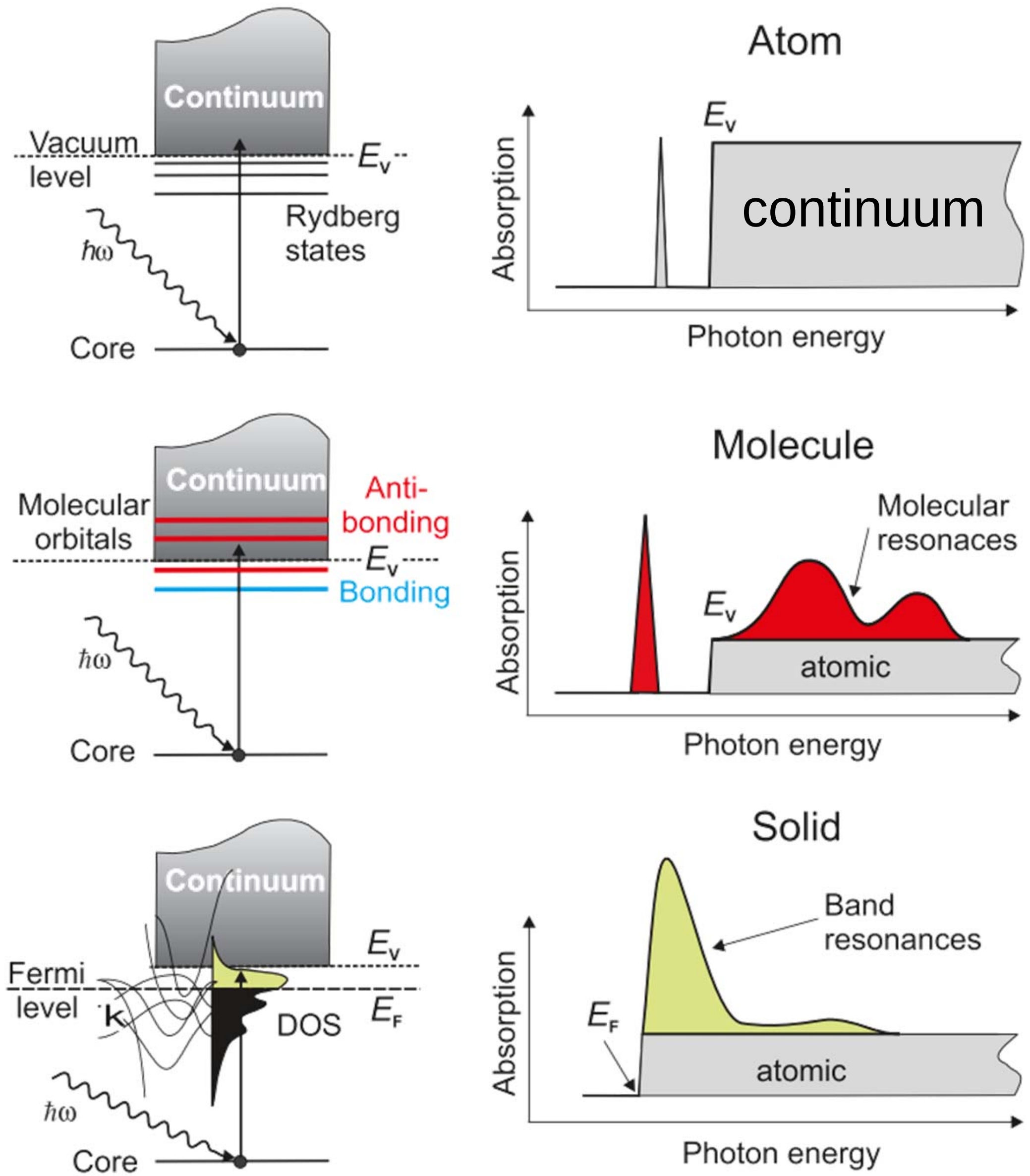
reflects density of unoccupied states

Also called XANES

Extended X-ray Absorption Fine Structure

reflects spatial location of neighboring atoms

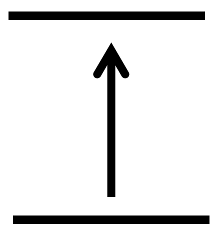
X-ray Absorption



From Stöhr & Siegmann: Magnetism

Quantum Theory of Light-Matter Interaction

Classical (n,k) $\leftrightarrow$ phenomenological
Quantum $\leftrightarrow$ direct calculation of transitions between quantum states



$$|f\rangle = |e\rangle|n_p - 1\rangle$$

$$|i\rangle = |g\rangle|n_p\rangle$$

$$T_{if} = \frac{2\pi}{\hbar} |\langle f|\mathcal{H}_{int}|i\rangle|^2 \, \delta(\varepsilon_i - \varepsilon_f)\rho(\varepsilon_f)$$

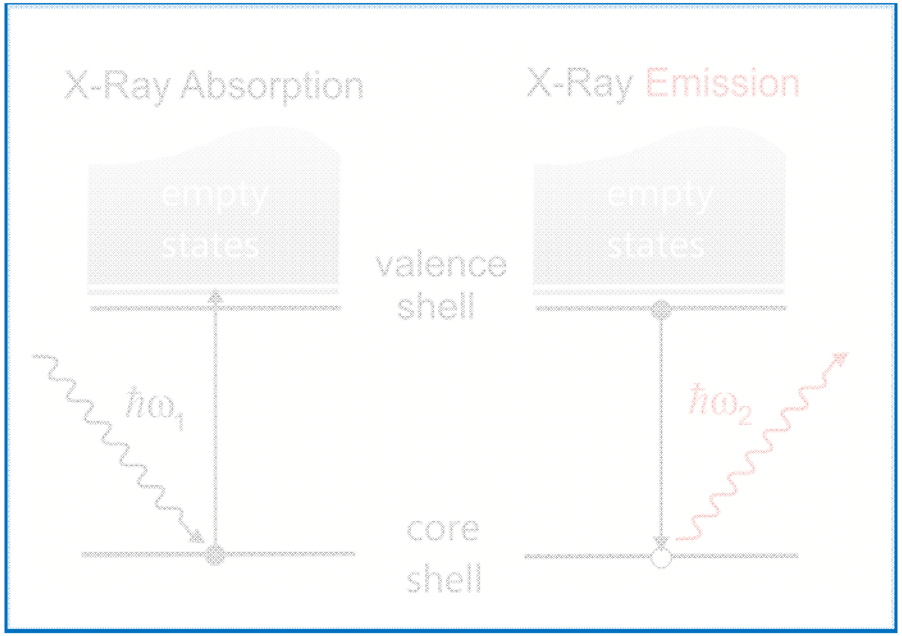
- Interaction Hamiltonian $\mathcal{H}_{\text{int}}$
- Facilitates comparison between theory and experiment

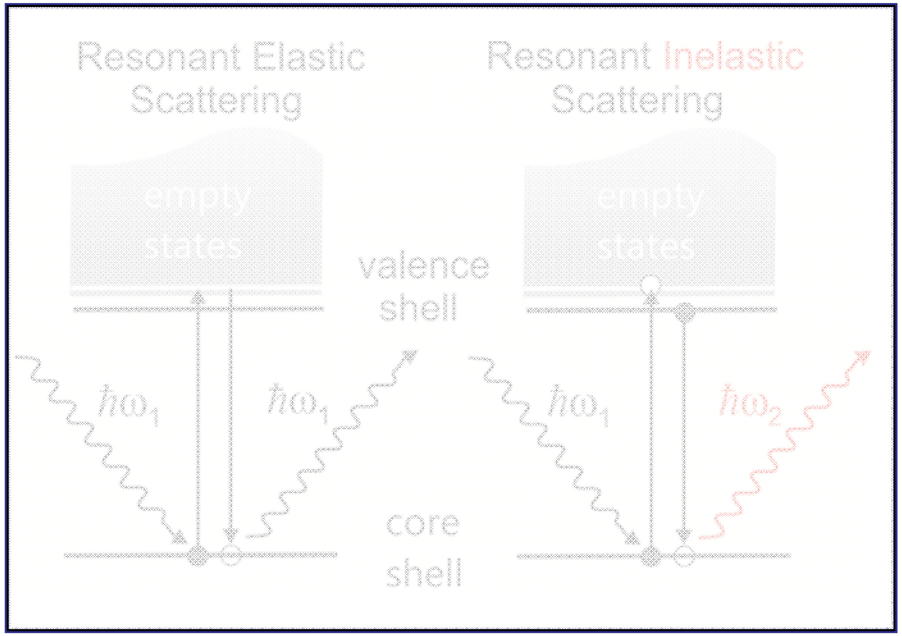
Kramers-Heisenberg theory: up to second order

- interaction is assumed to be weak and treated by perturbation theory
- interaction is time-independent
- K-H theory very powerful - describes all synchrotron radiation experiments
- It breaks down for high intensity X-FEL interactions

Adapted from J. Stohr

The Four Basic Resonant X-Ray Processes





First order: "Fermi's golden rule"

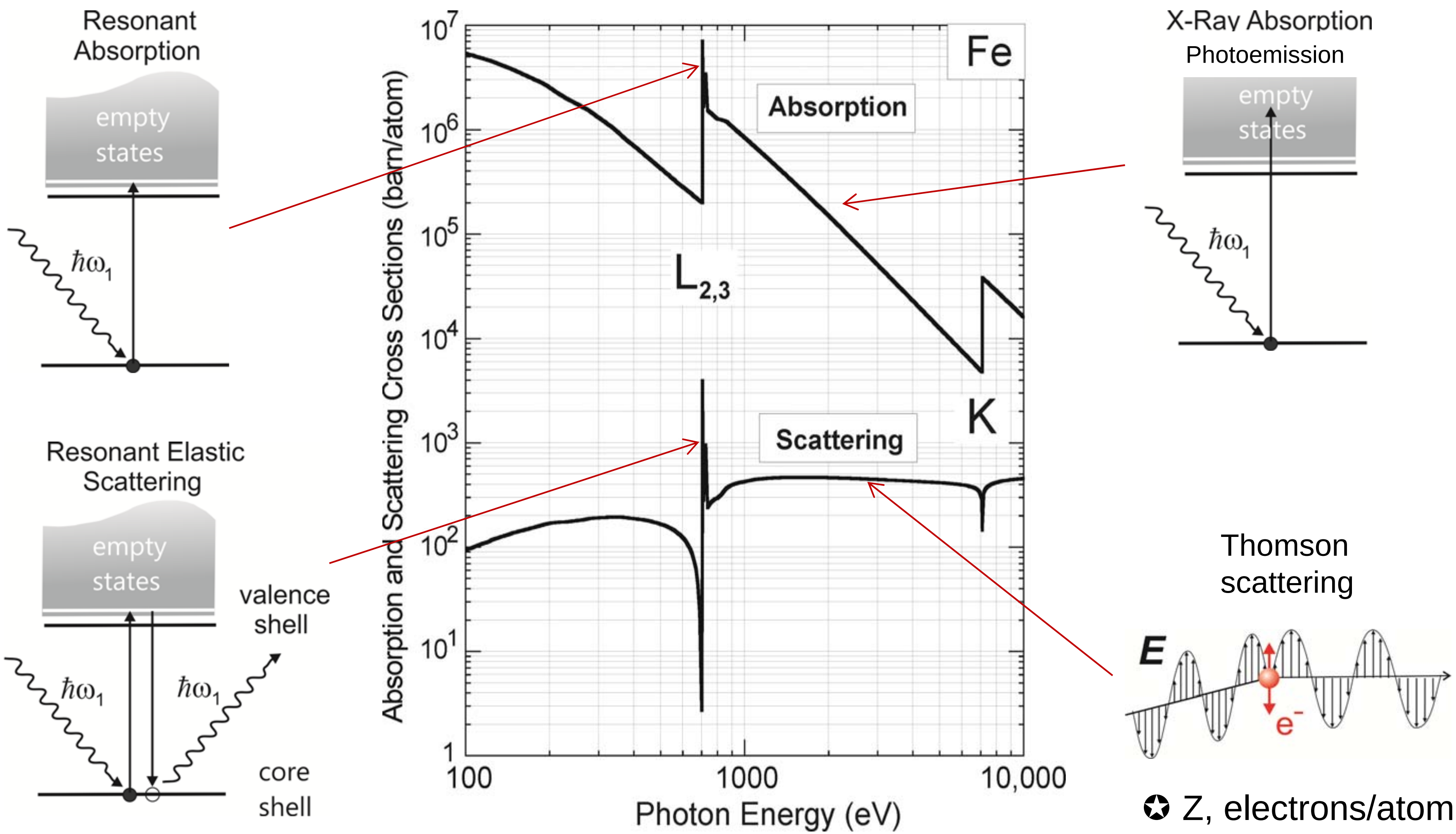
Second order: "Kramers-Heisenberg"

$$T_{if} = \frac{2\pi}{\hbar} \left| \langle f|\mathcal{H}_{int}|i\rangle + \sum_j \frac{\langle f|\mathcal{H}_{int}|j\rangle\langle j|\mathcal{H}_{int}|i\rangle}{\varepsilon_i - \varepsilon_j} \right|^2 \delta(\varepsilon_i - \varepsilon_f)\ \rho(\varepsilon_f)$$

$$\mathcal{H}_{\rm int} = \frac{e}{m_{\rm e}} \boldsymbol{p} \cdot \boldsymbol{A}(\boldsymbol{r}, t) = -e\,\boldsymbol{r} \cdot \boldsymbol{E}(\boldsymbol{r}, t)$$

Adapted from J. Stohr

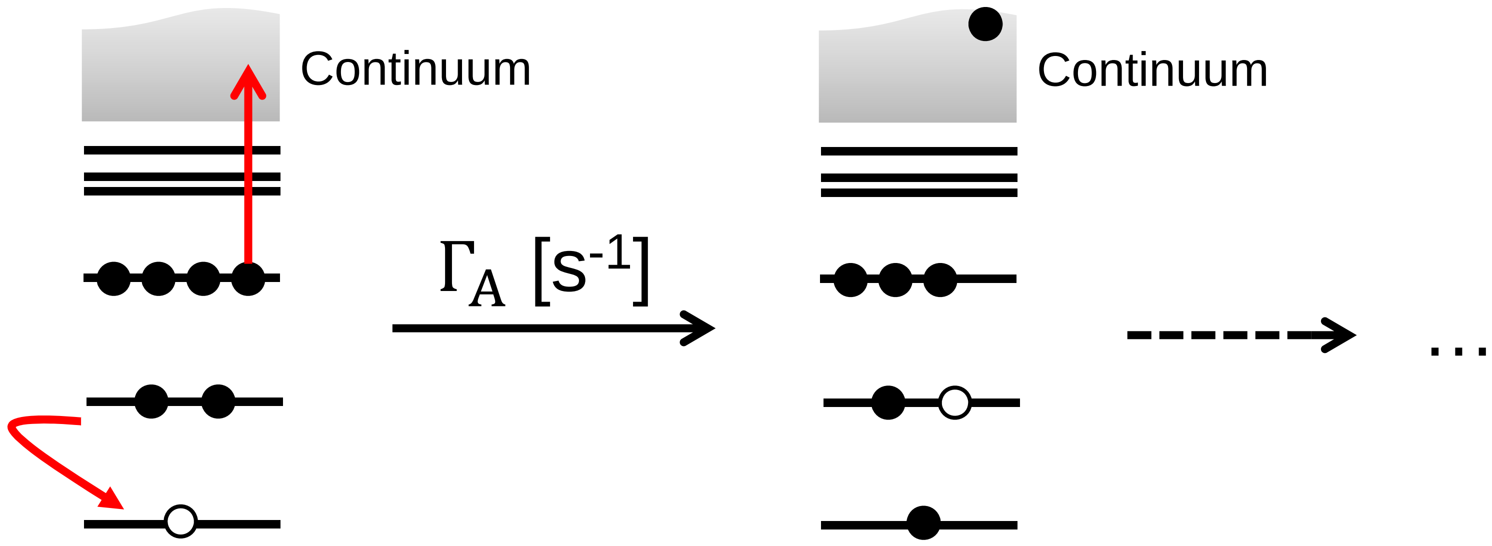
Photon Energy Dependence of Cross Sections



Resonant processes give orders of magnitude signal enhancements

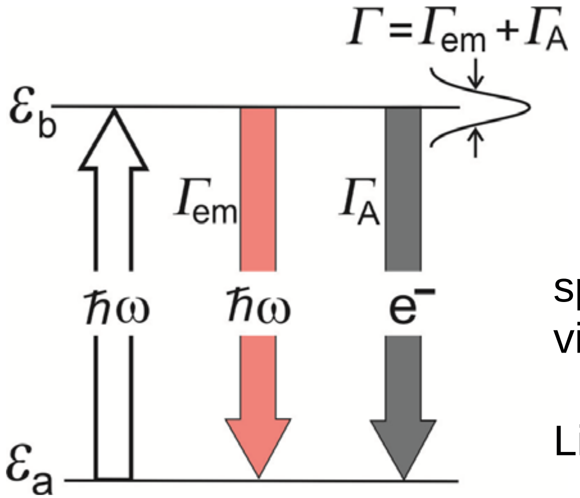
Adapted from J. Stohr

Auger Processes



- Most important process de-exciting the core hole in the soft x-ray range
- Followed by a cascade of secondary electrons
- Competition with X-ray emission (fluorescence) at rate Γ_{em}

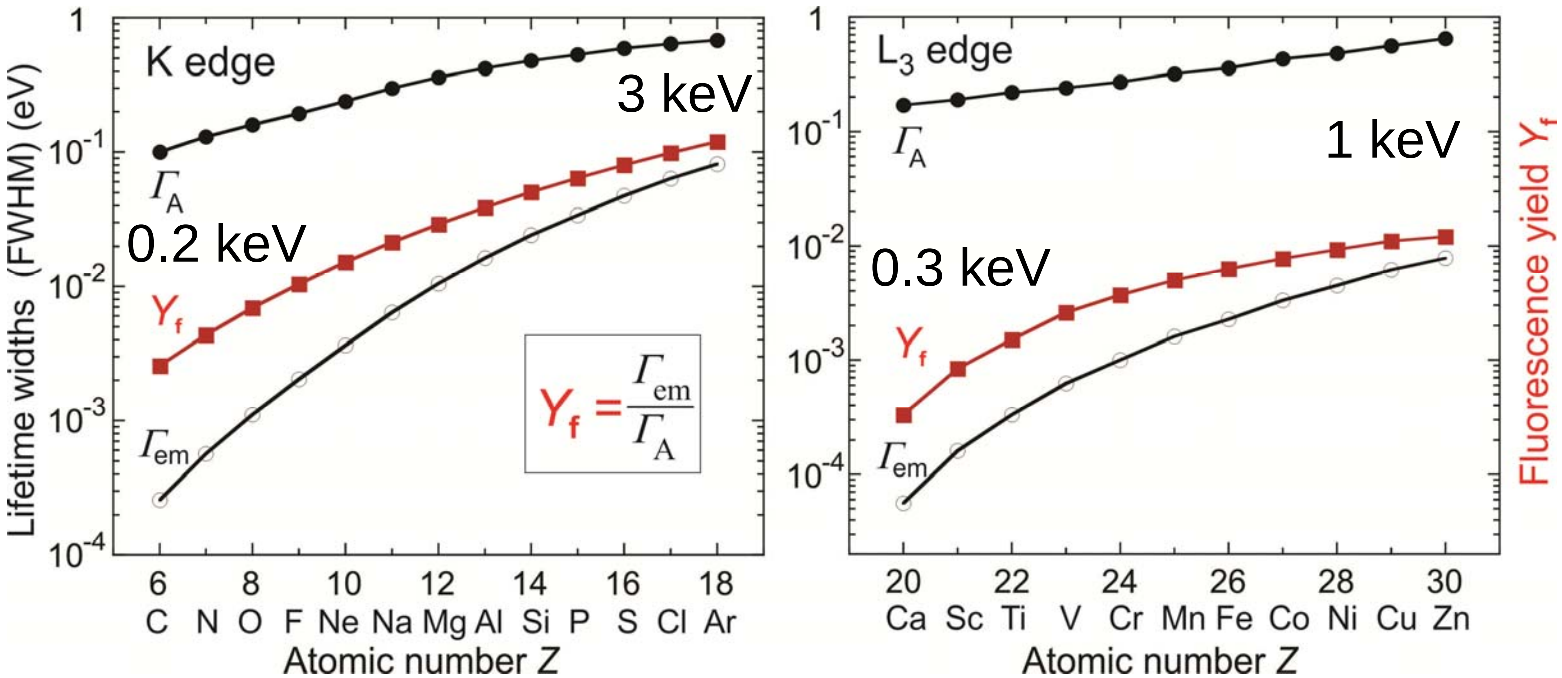
The Soft X-ray Fluorescence Yield



Soft X-rays: ~100 eV … ~2 keV

spontaneous decay
via Auger or x-ray emission

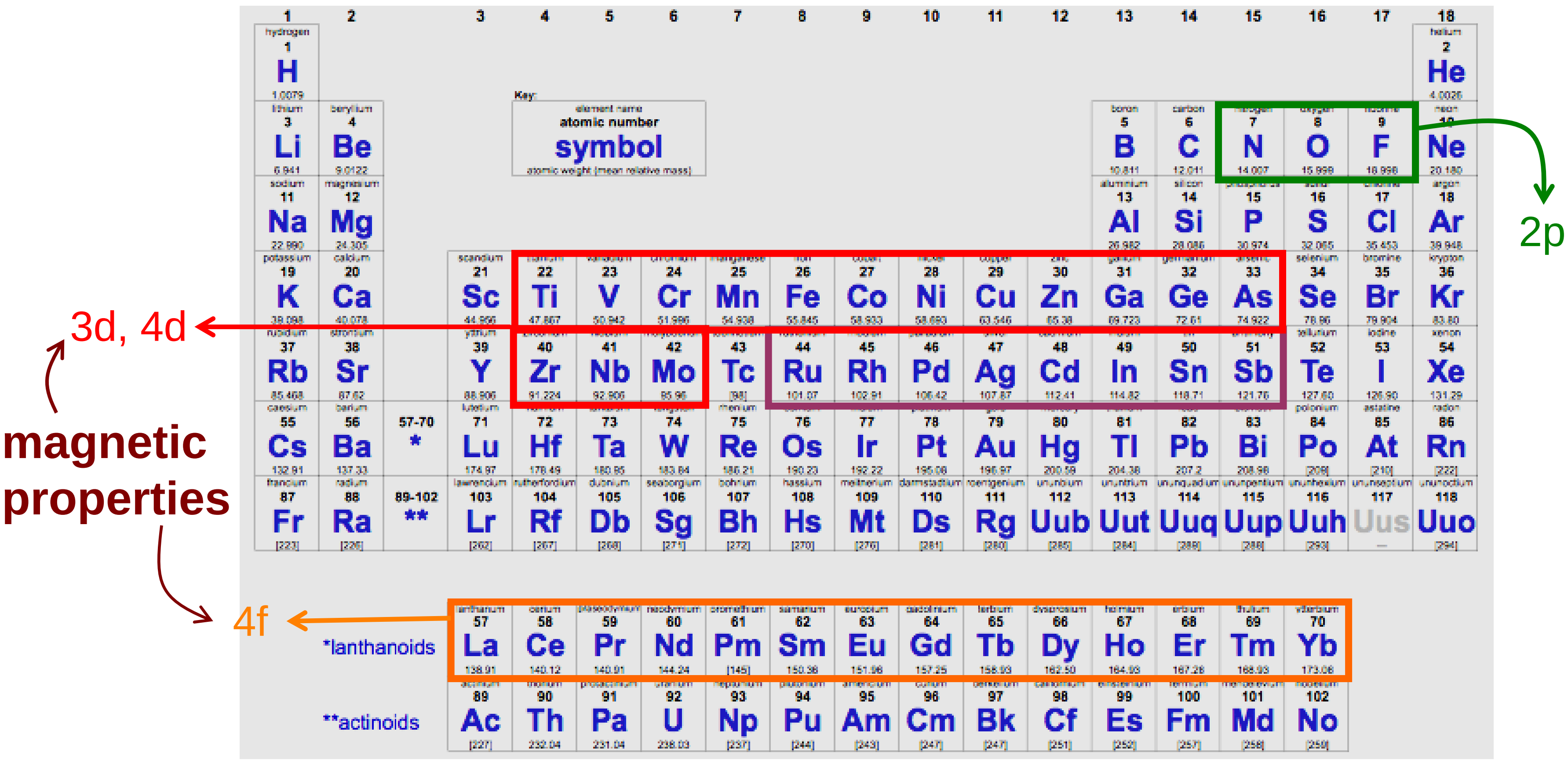
Lifetime width [eV] = $\hbar\Gamma$



Adapted from J. Stohr

Soft X-rays: Accessibe Elements

- K-edges: 1s $\rightarrow$*n***p**
- $L_{2,3}$-edges: 2p $\rightarrow$*n***d**
- $M_{2,3}$-edges: 3p $\rightarrow$*n***d**
- $M_{4,5}$-edges: 3d $\rightarrow$ *n***f**



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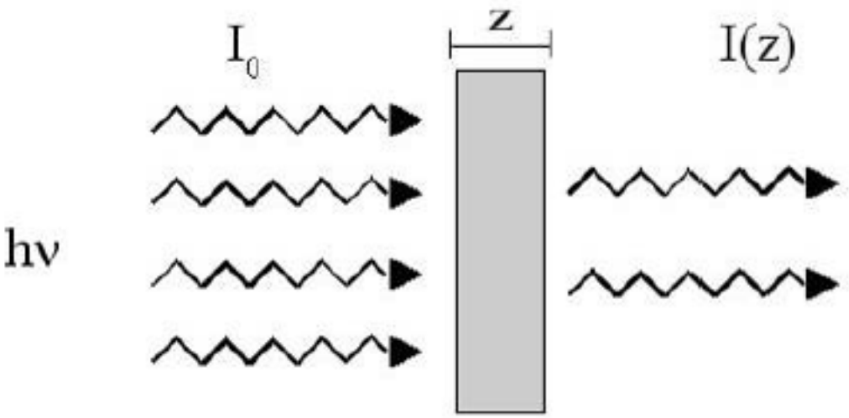
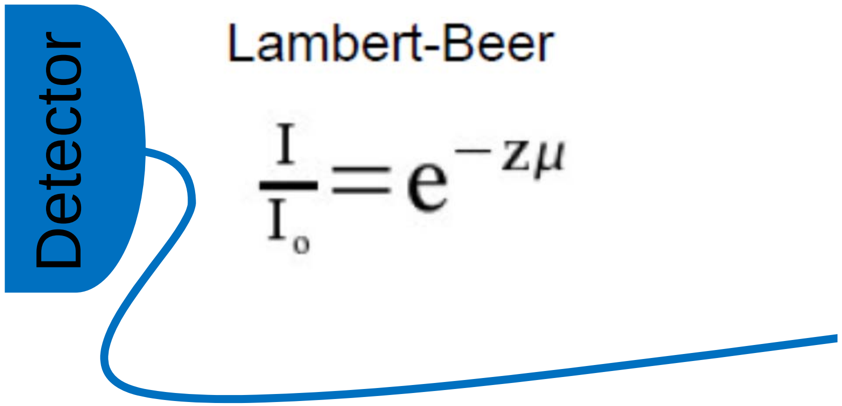
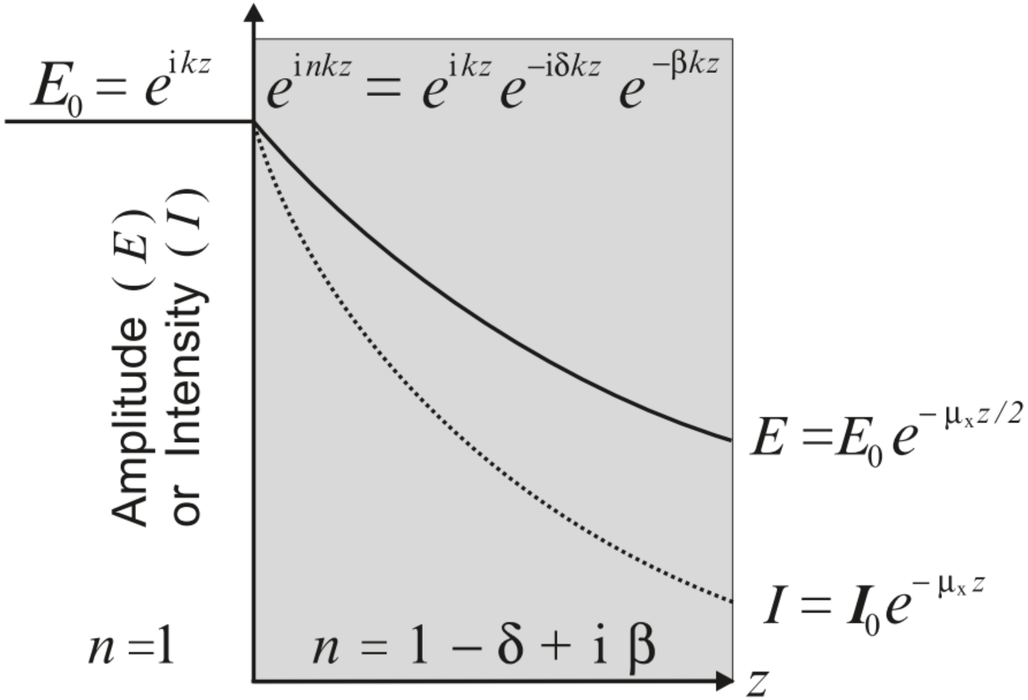
An Optical Transmission Experiment





Lambert-Beer

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



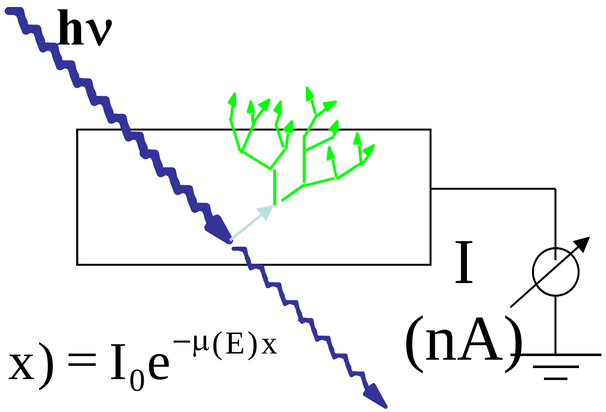
$$I(z) = I_0 e^{-\mu_x z}$$

Soft X-rays:

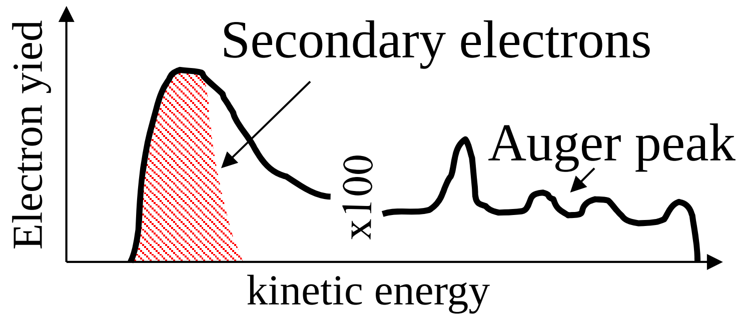
z must be $\lesssim$ 1 μm

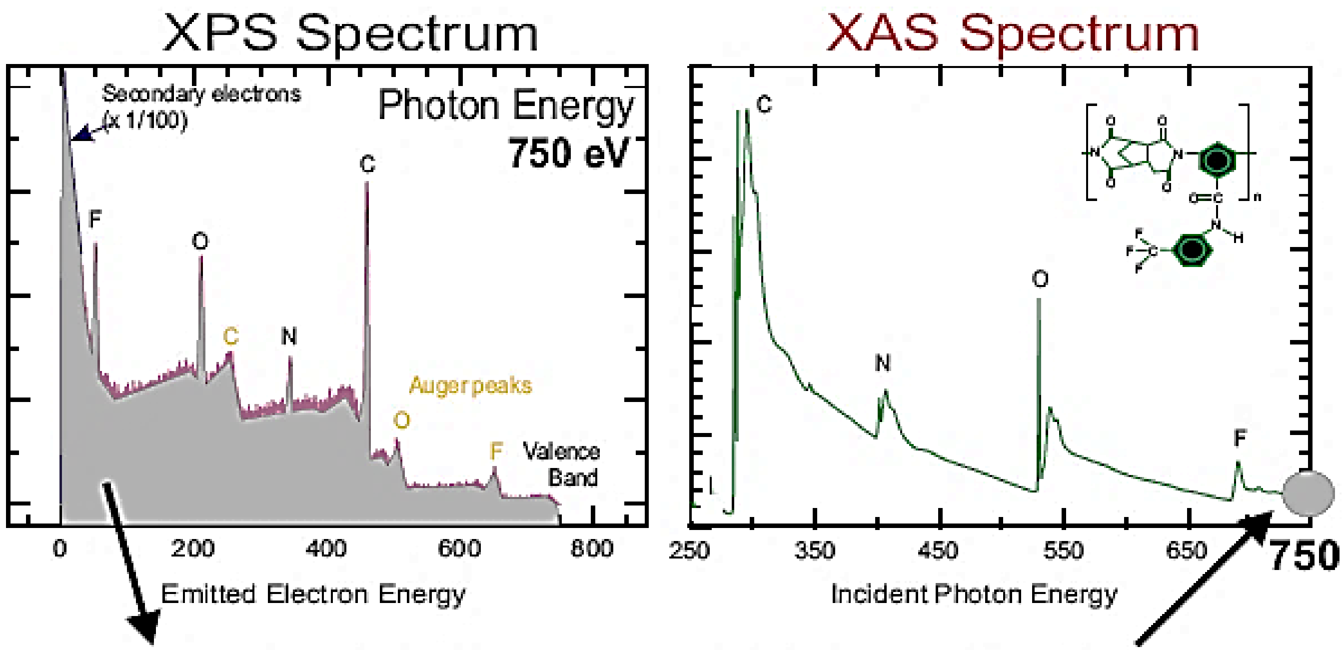
→ Total electron yield

Total Electron Yield (TEY)



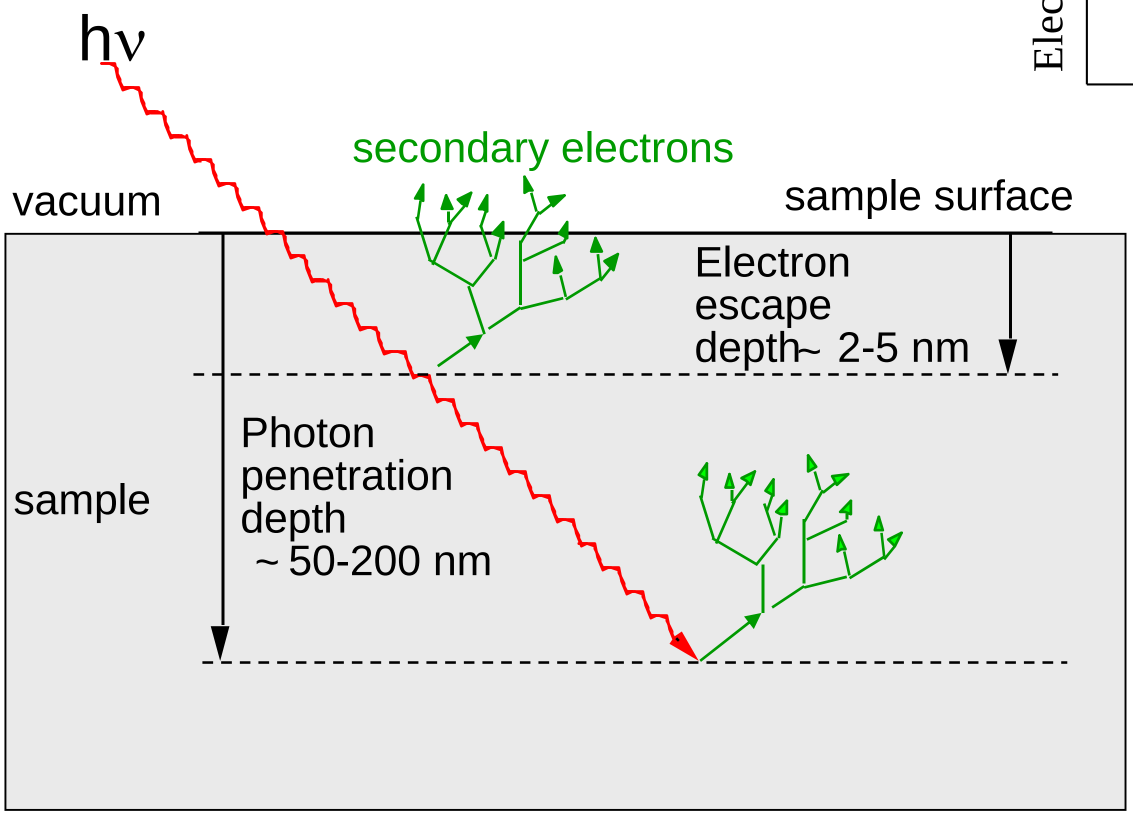
$$I(E,x) = I_0 e^{-\mu(E)x}$$

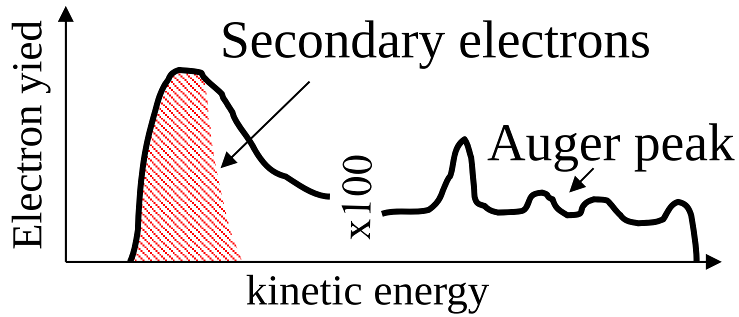




Add all emitted electrons... ...to get one point of XAS spectrum

Sampling Depth in TEY





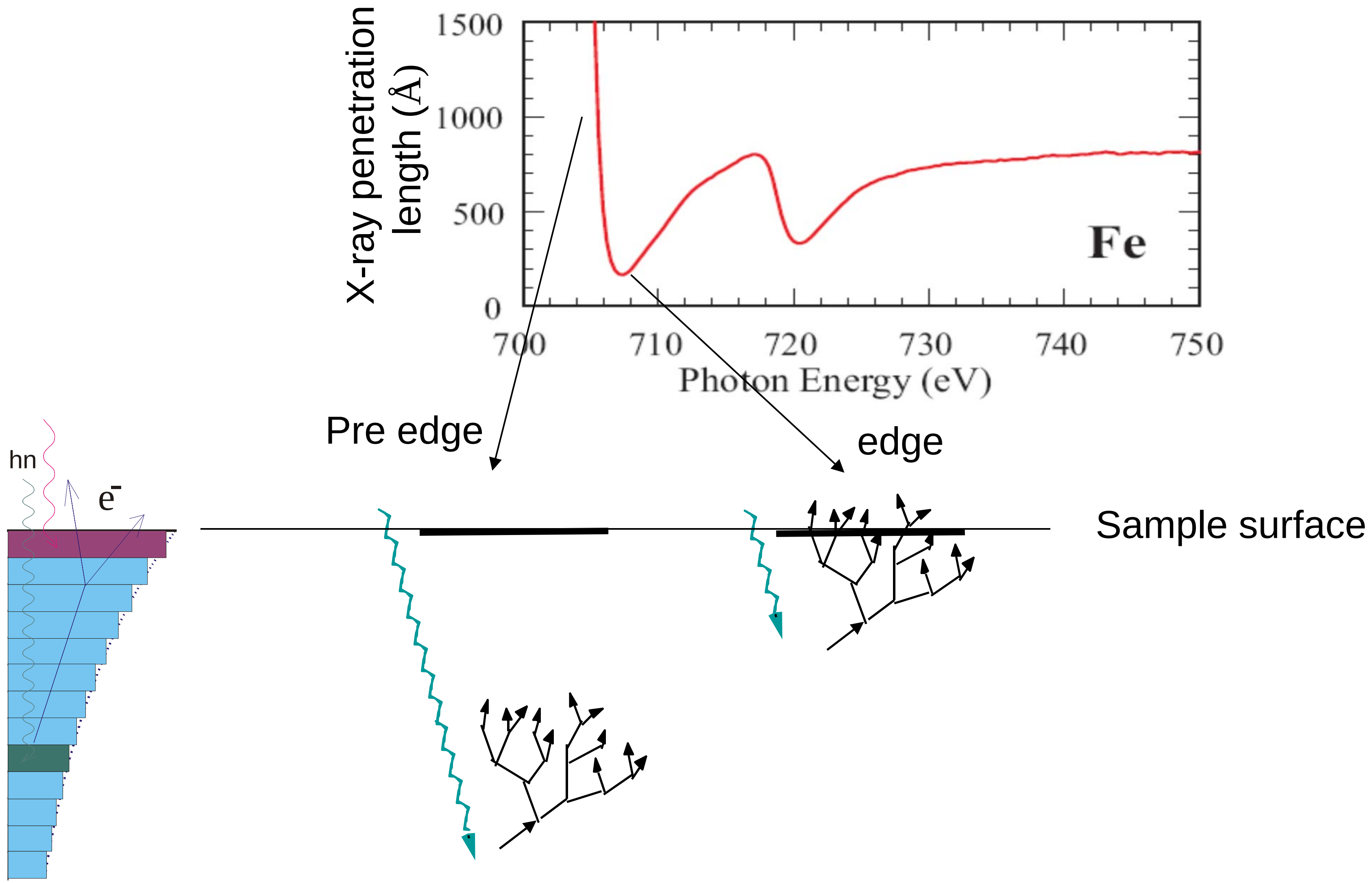
$\text{TEY} \propto \mu$

(with some approximations)

TEY probes the surface/interface

Slide courtesy of F. Nolting

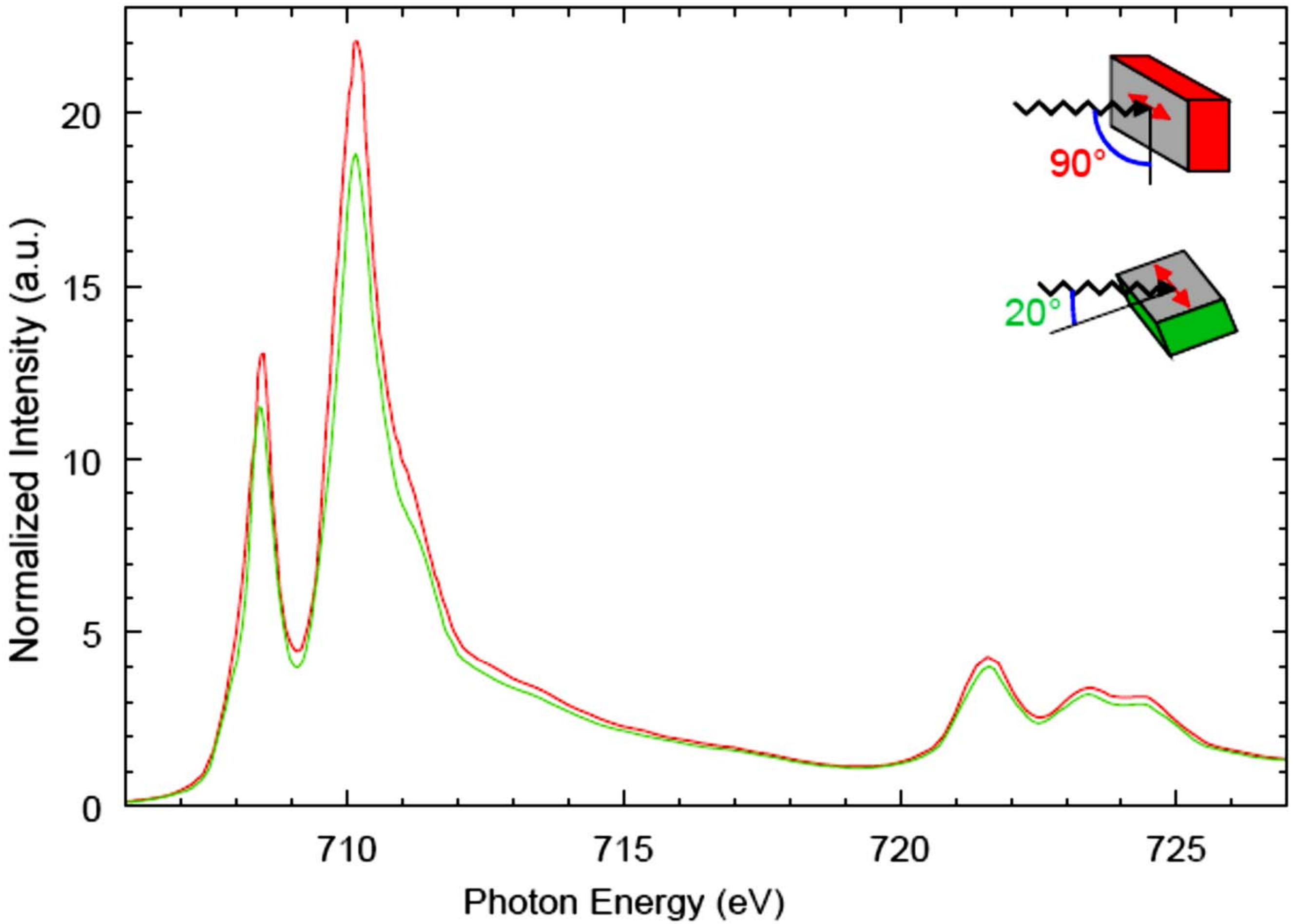
Why is TEY Proportional to Absorption Coefficient?

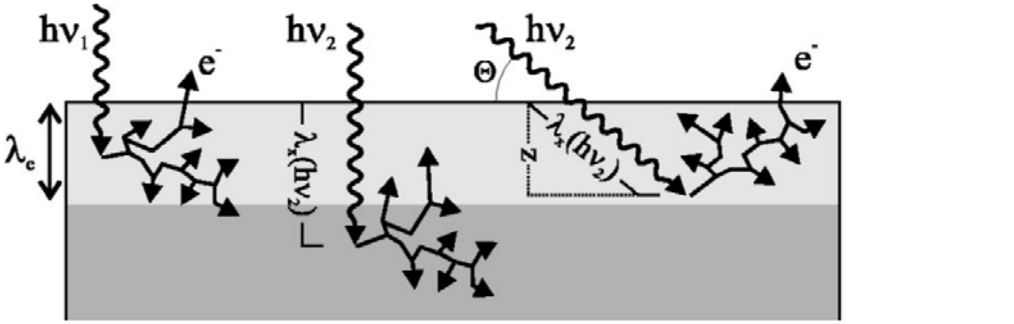


Probability that electron escapes

→ Penetration depth depends on the angle of incidence

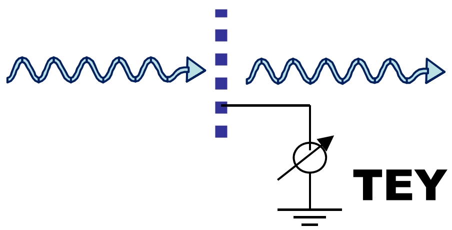
Saturation Effects in TEY Detection



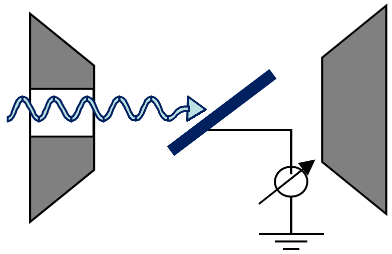


J. Lüning *et al.*, PRB 67, 214433 (2003)

How Do We Measure?

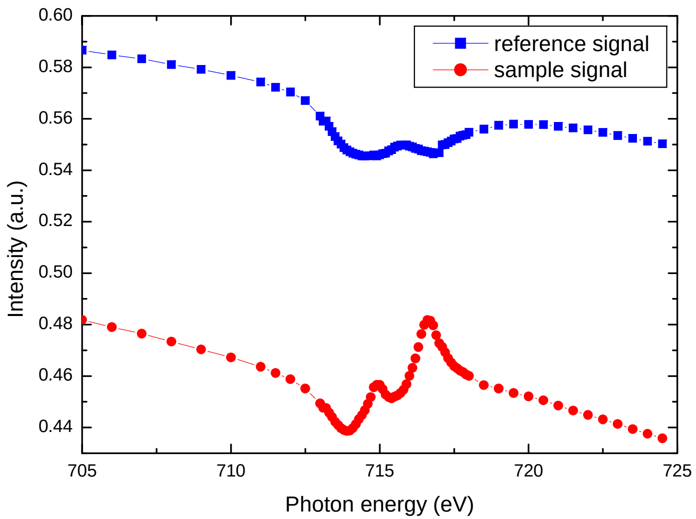


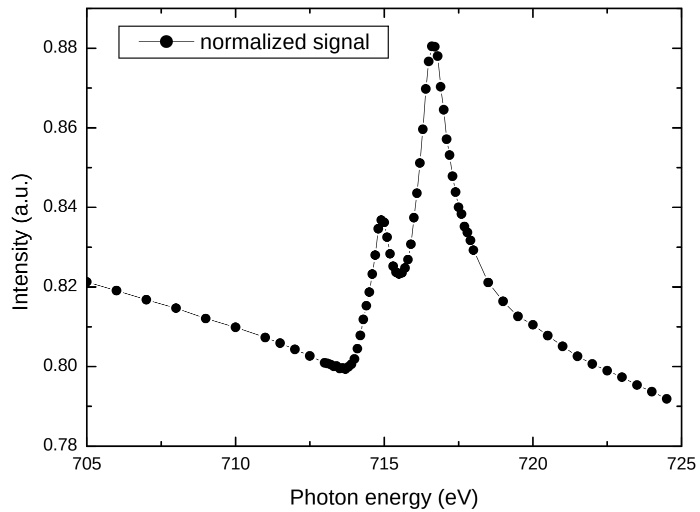
Reference signal



Sample signal

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





Slide courtesy of F. Nolting

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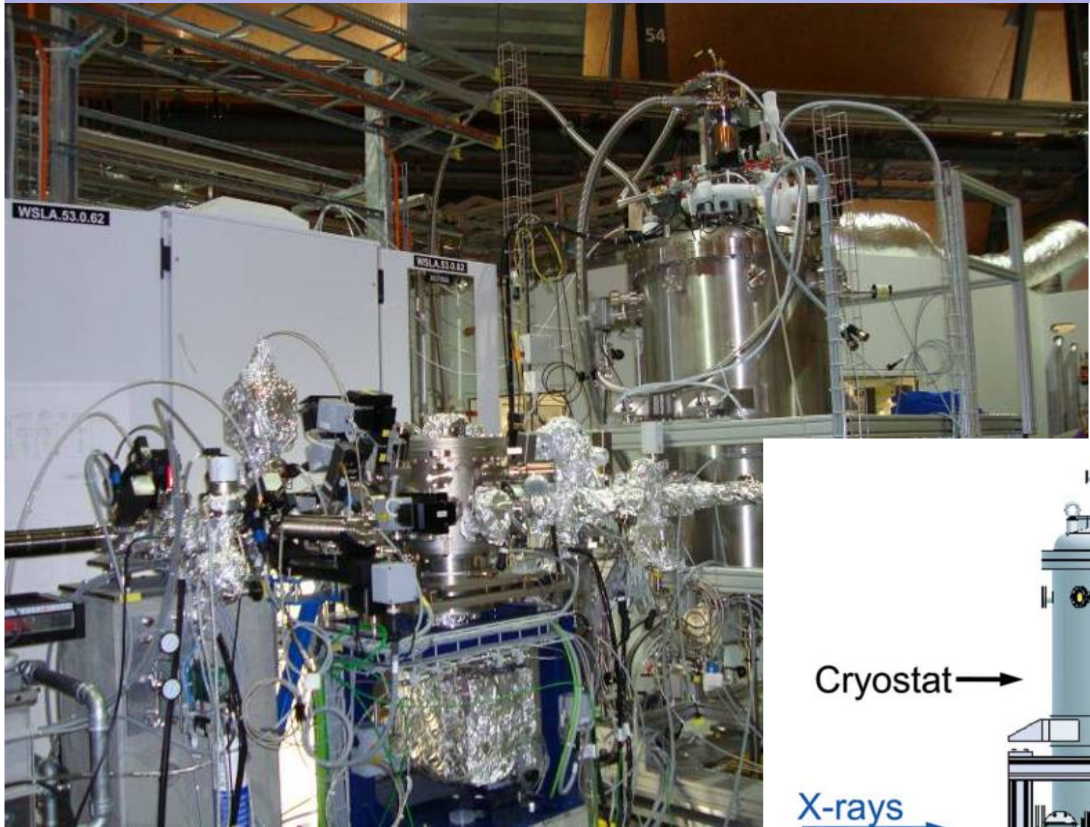
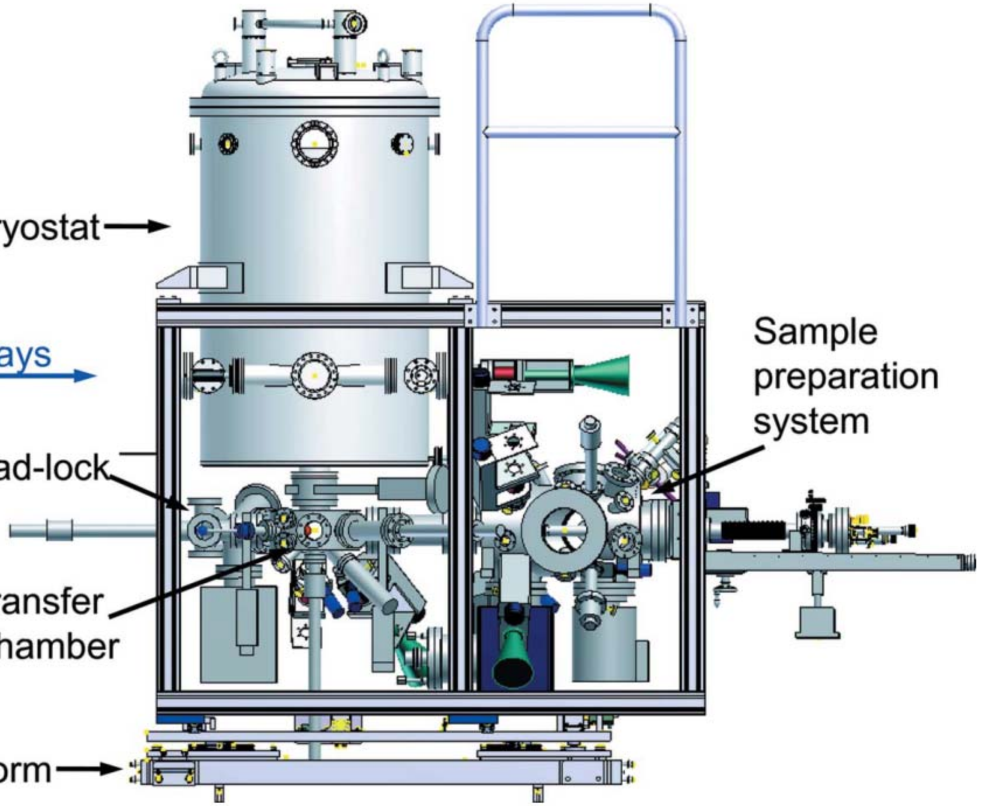
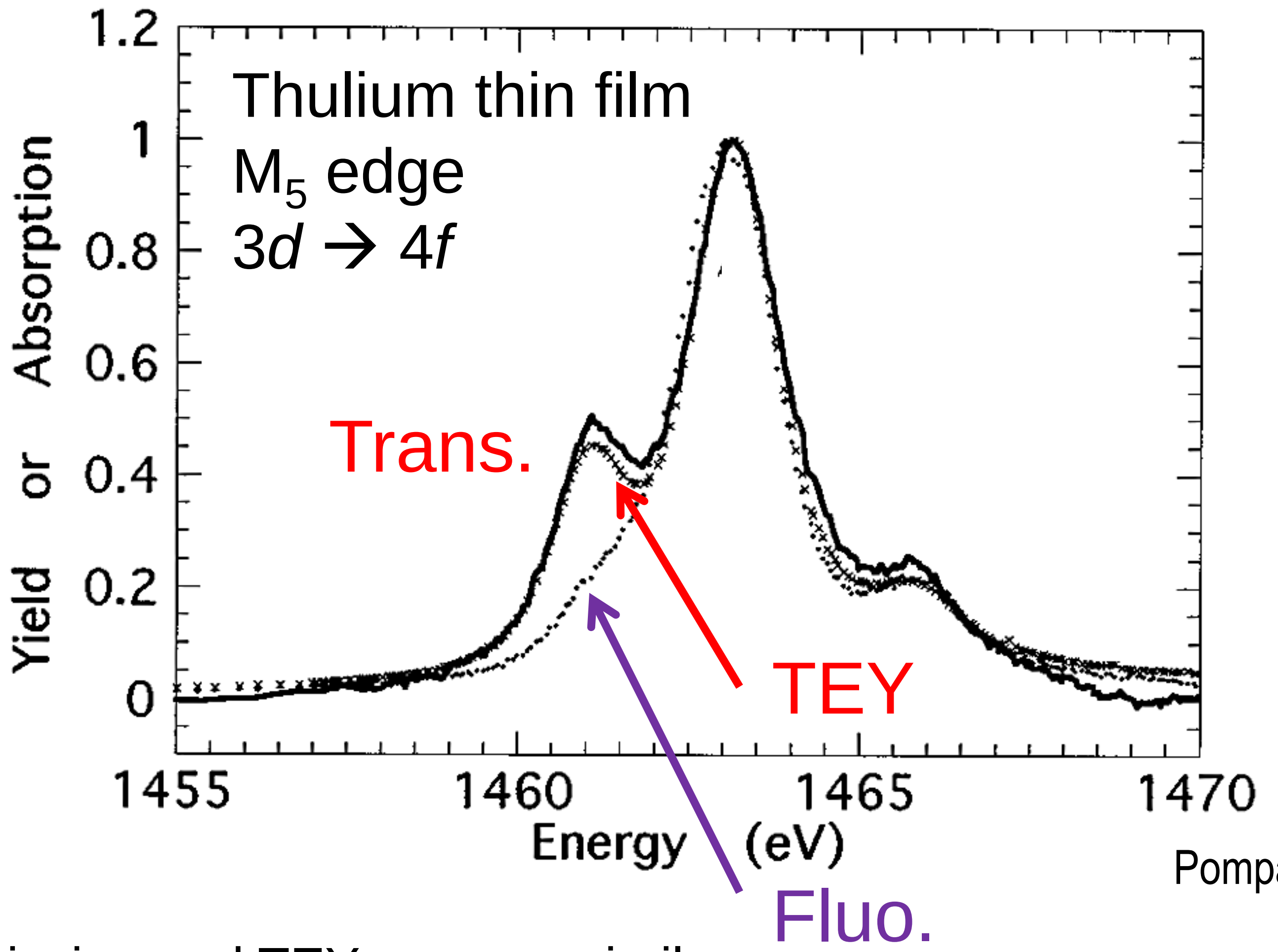




$T = 3$ K
$B = 7$ T
p ~ 2 × 10^{-11} mbar

X-Treme Endstation at SLS

Fluorescence Detection



Pompa *et al.*, PRB 1997

- Transmission and TEY are very similar
- Strong deviation in fluorescence measurement
- Reason: state (and energy) dependent fluorescence yield!

$$Y_f = \Gamma_{\mathrm{em}}/\Gamma_{\mathrm{a}} = \boldsymbol{Y_f(E)}$$

- Another issue that can occur in fluorescence detection is self absorption

Comparison of Detection Schemes

Fluorescence	Electron yield	Transmission
+ Probing depth larger than in TEY + Insensitive to electric / magnetic fields	+ Highly surface sensitive + XMCD sum rules applicable	+ True bulk measurement + Insensitive to electric / magnetic fields + Direct measurement of abs. cross section **σ**
- Not always proportional to the abs. cross section **σ** - Limited applicability of XMCD sum rules	- Saturation effects - Highly surface sensitive - Sensitive to electric / magnetic fields	- Very thin sample needed (< 1μm thickness)

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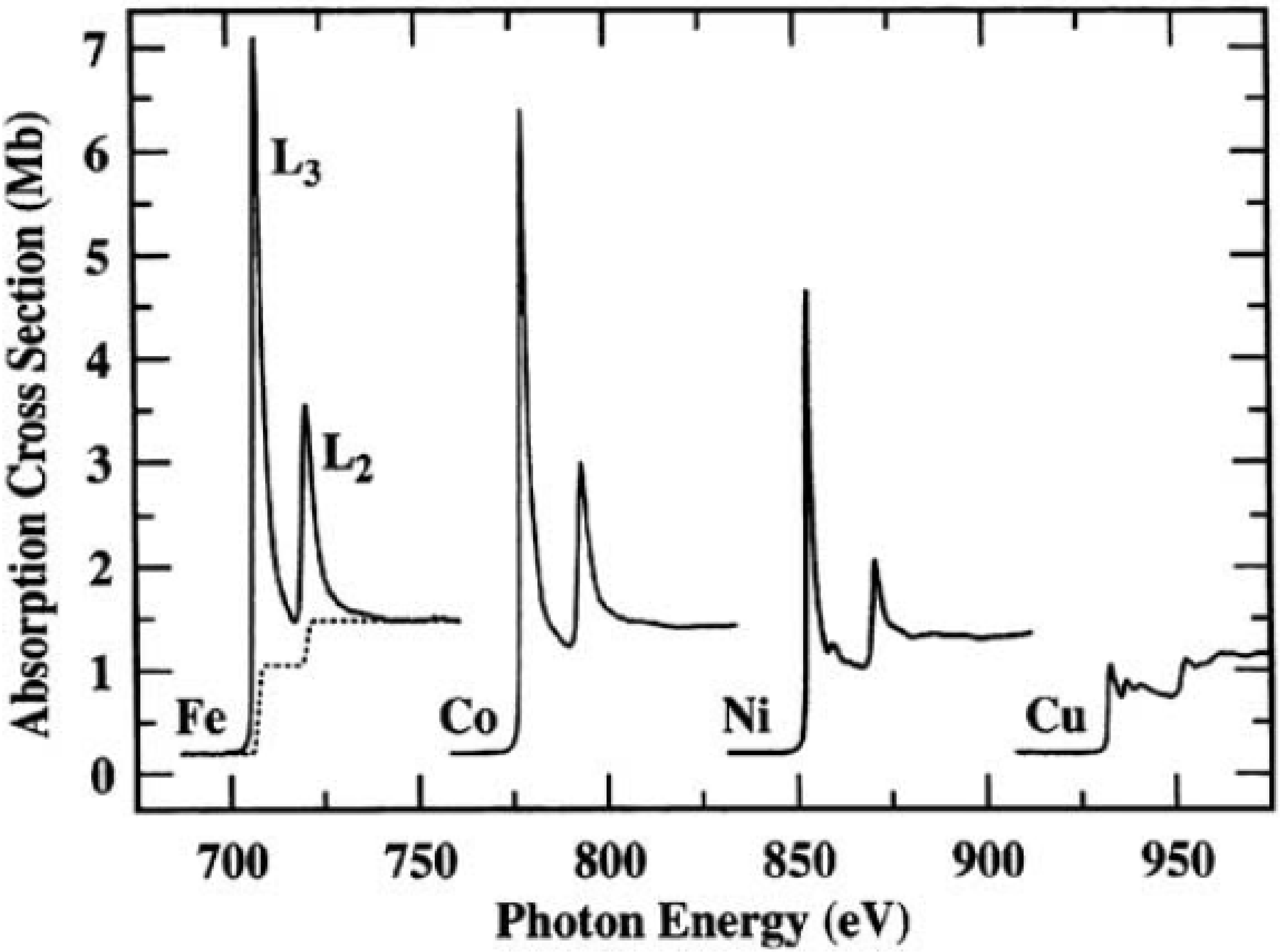
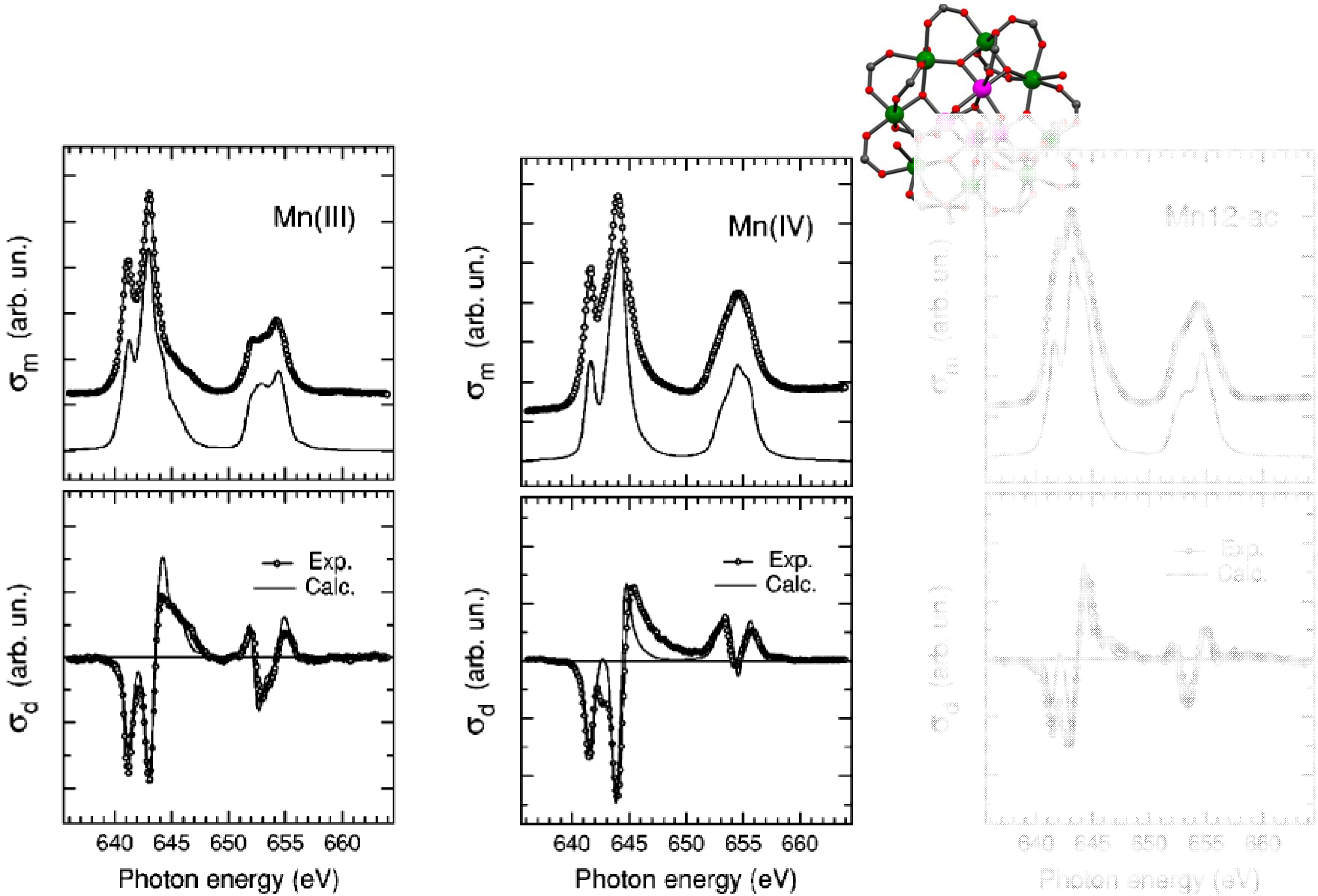
Chemical Sensitivity



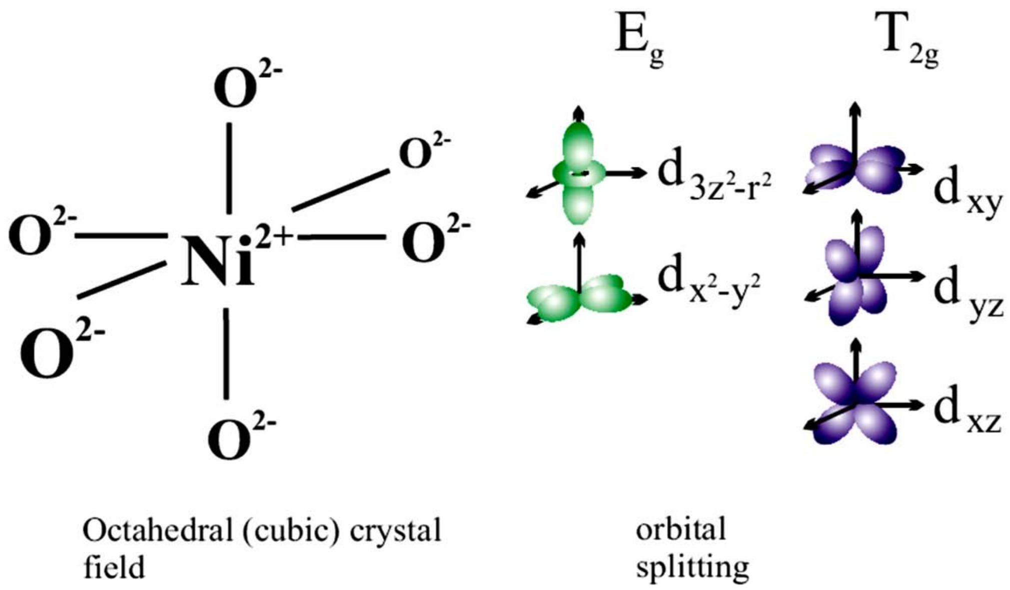
T. Funk *et al.*, *Coord. Chem. Rev*. 2005

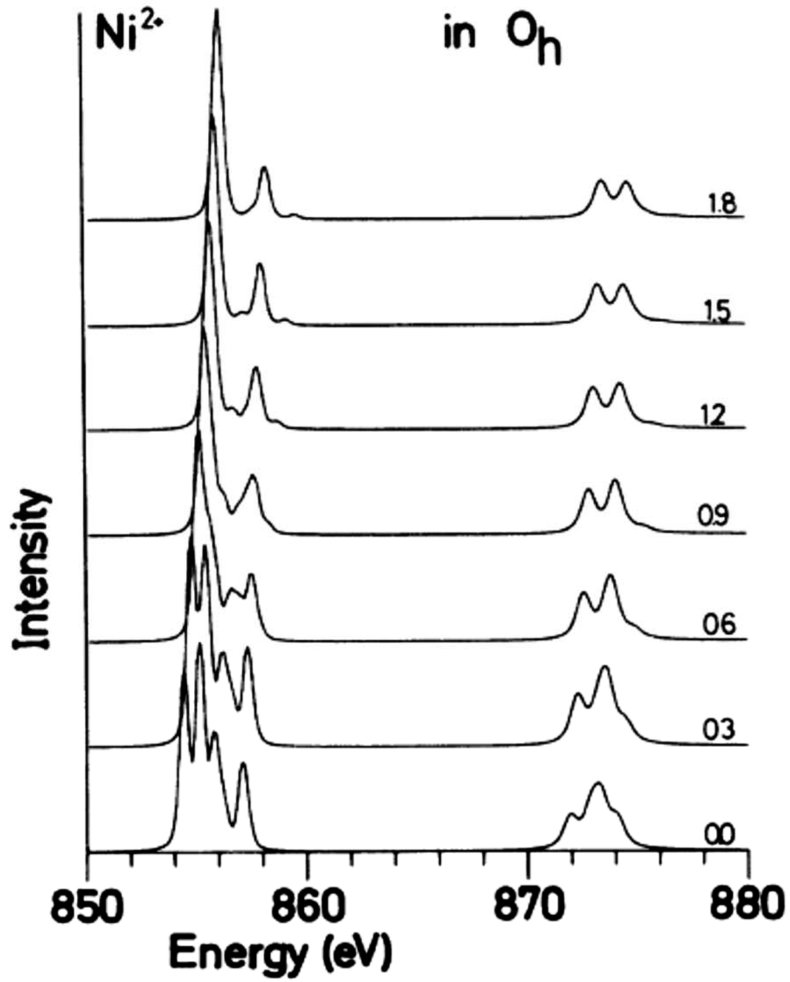
Valence Sensitivity



R. Moroni *et al.*, *Phys. Rev. B* 2002

Crystal Field Sensitivity





Further parameter is charge transfer

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

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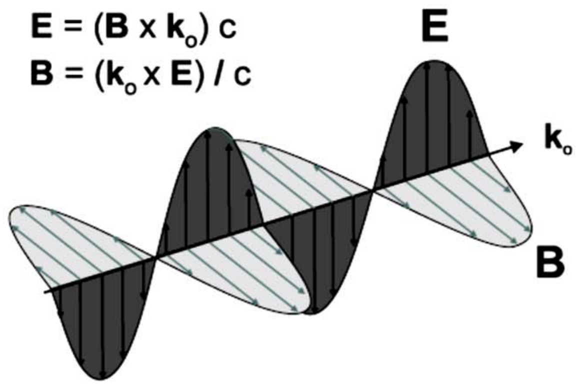
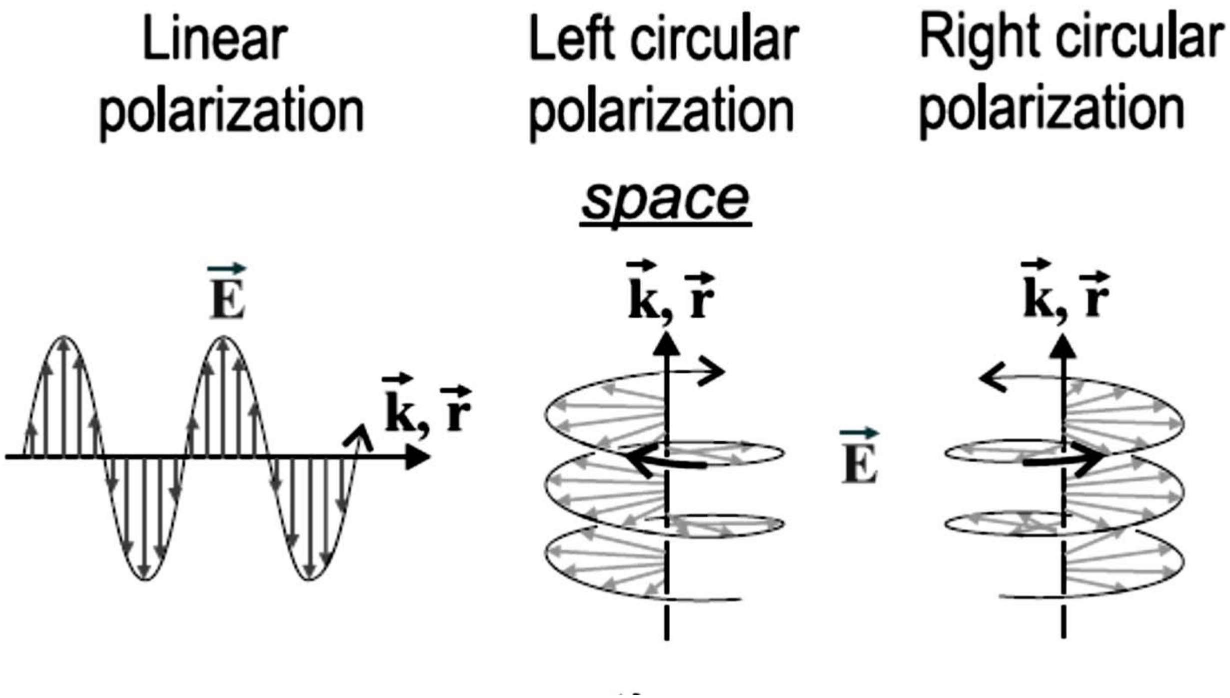
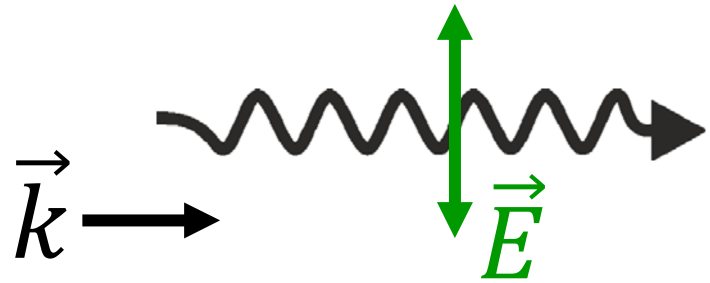
Polarized Photons

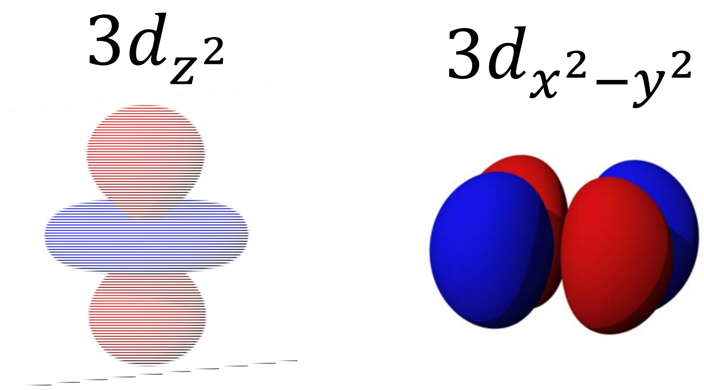




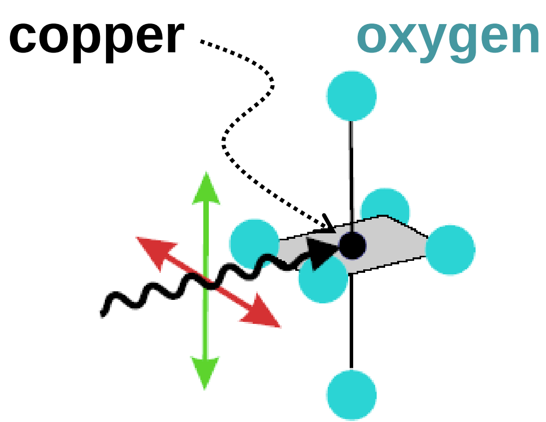
Interaction with Linear Light - Charge

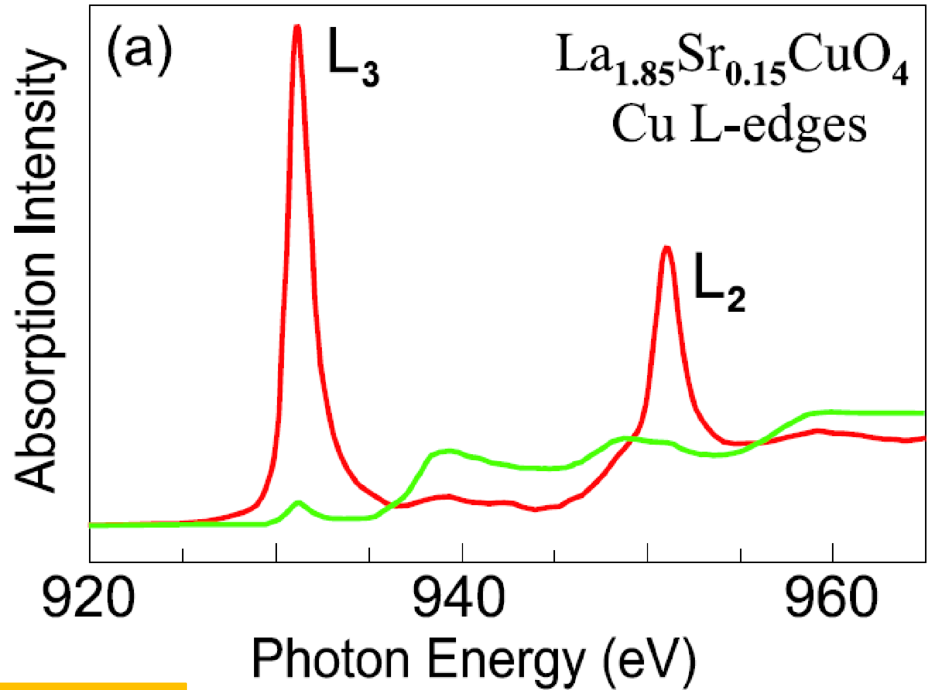
Excitation into 3*d* band
Linearly polarized X-rays





for empty orbitals!





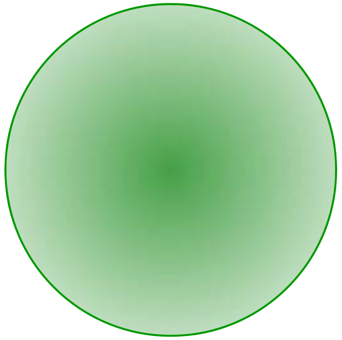
XNLD $[\mu_v(E) - \mu_h(E)]$

X-ray Natural Linear Dichroism

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

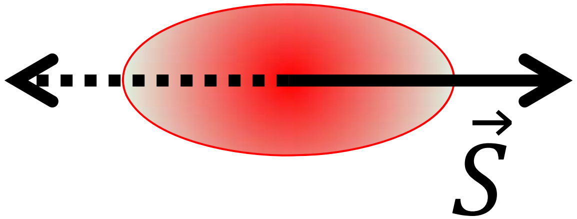
Interaction with Linear Light - Spin

Paramagnetic state



- No preferred orientation of spins
- Isotropic charge (electron) density
- → No linear dichroism

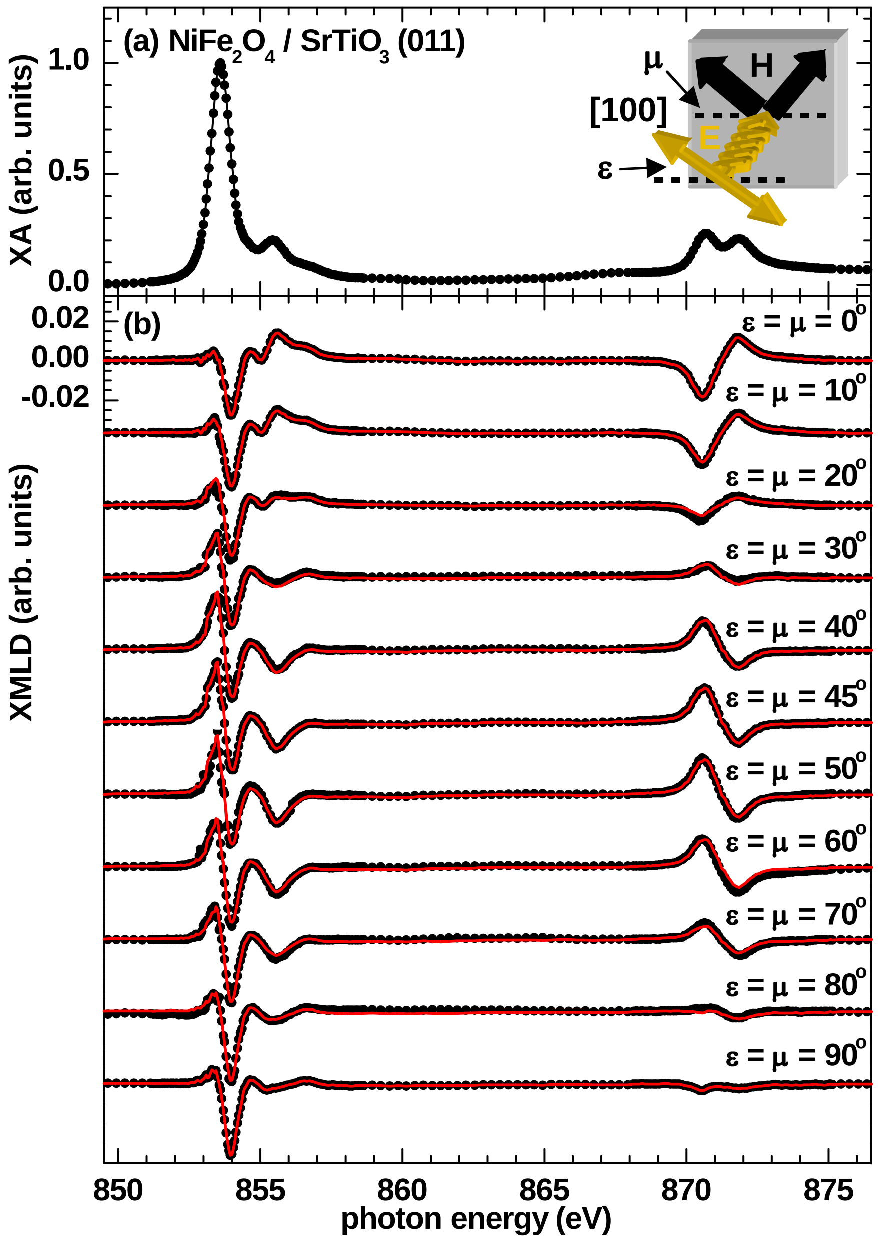
Ordered state (FM, AFM)



- Preferred orientation of spins
- Spin orbit coupling $\mathcal{H}_{\mathrm{SOC}} = \zeta \vec{L} \cdot \vec{S}$ breaks spherical symmetry of the charge density
- → Linear dichroism
- XMLD intensity $I_{\mathrm{XMLD}} \propto \langle M^2 \rangle$

XMLD **X-ray Magnetic Linear Dichroism**

Line Shape of XMLD at L_3 and L_2 Edges

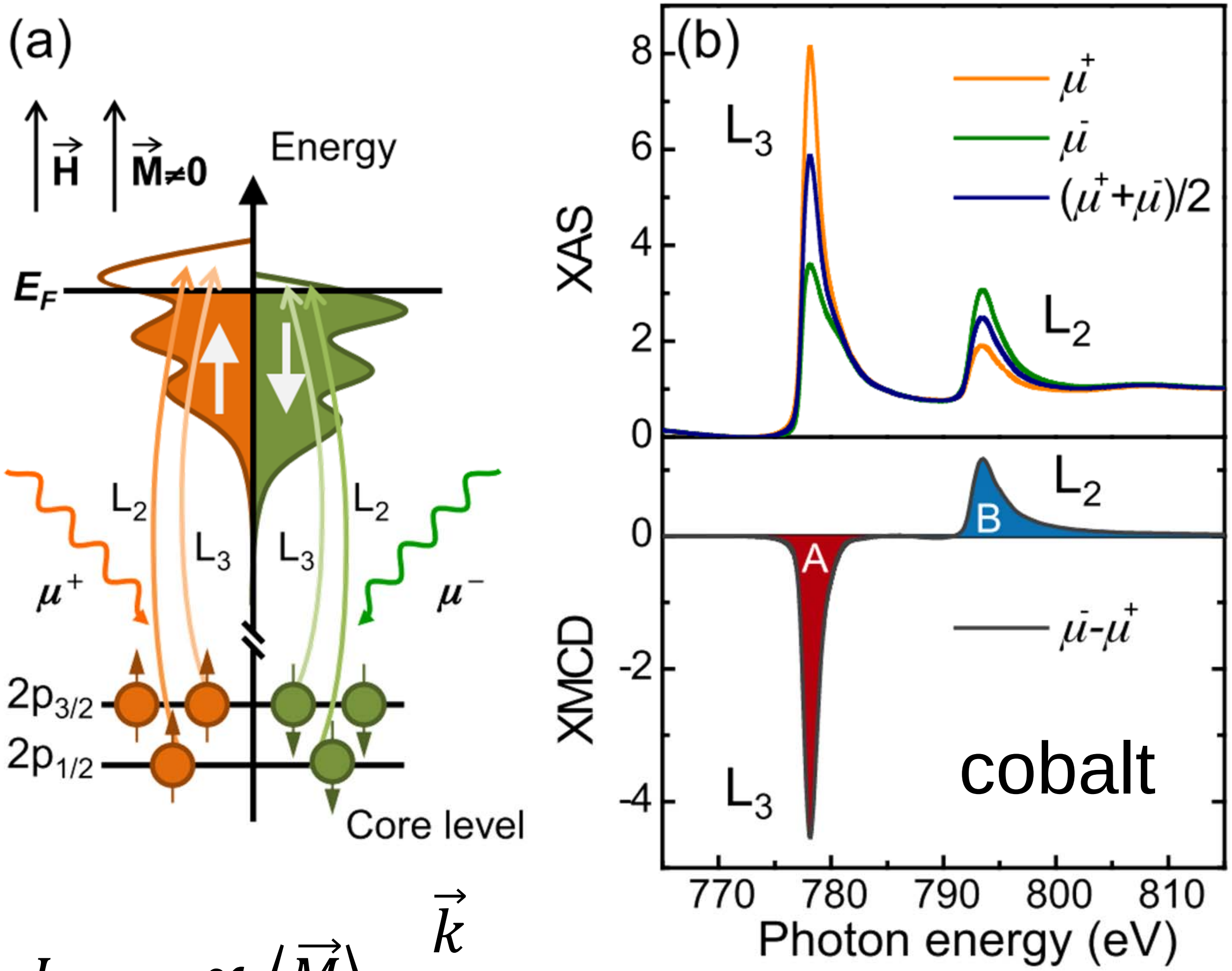


E. Arenholz, G. van der Laan et al
PRL 98, 197201 (2007).

L_2 sign reversal
L_3 unique fingerprint

XMLD depends on the relative orientation of crystal axis and AFM axis

Interaction with Circularly Polarized X-rays



$$I_{\mathrm{XMCD}} \propto \langle \vec{M} \rangle \cdot \frac{\vec{k}}{|\vec{k}|}$$

X-ray Magnetic Circular Dichroism

$$I_{\mathrm{XMCD}} = \mu_{-}(E) - \mu_{+}(E)$$

Picture from van der Laan & Figueroa, Coord. Chem. Rev. (2014)

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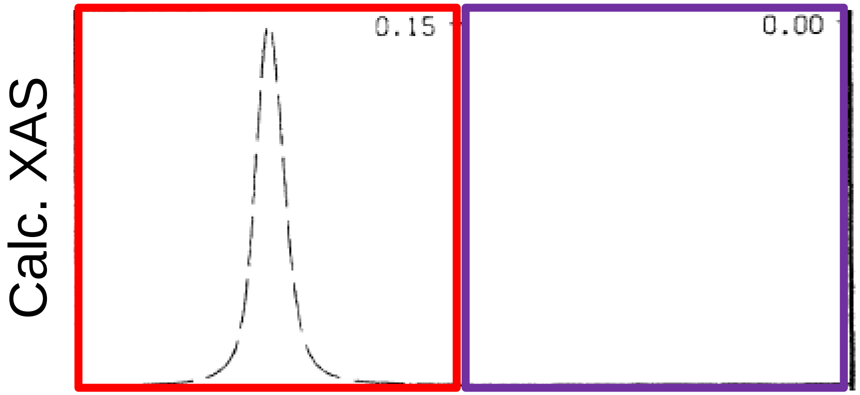
Origin of XMCD – 4*f*

Example Yb^{3+}

- M_5 edge ~ 1500 eV
- Excitation: $3d^{10}\,4f^{13} \rightarrow 3d^{9}\,4f^{14}$
- Hund's rules: $^2F_{7/2} \rightarrow {}^2D_{5/2}$



Absorption

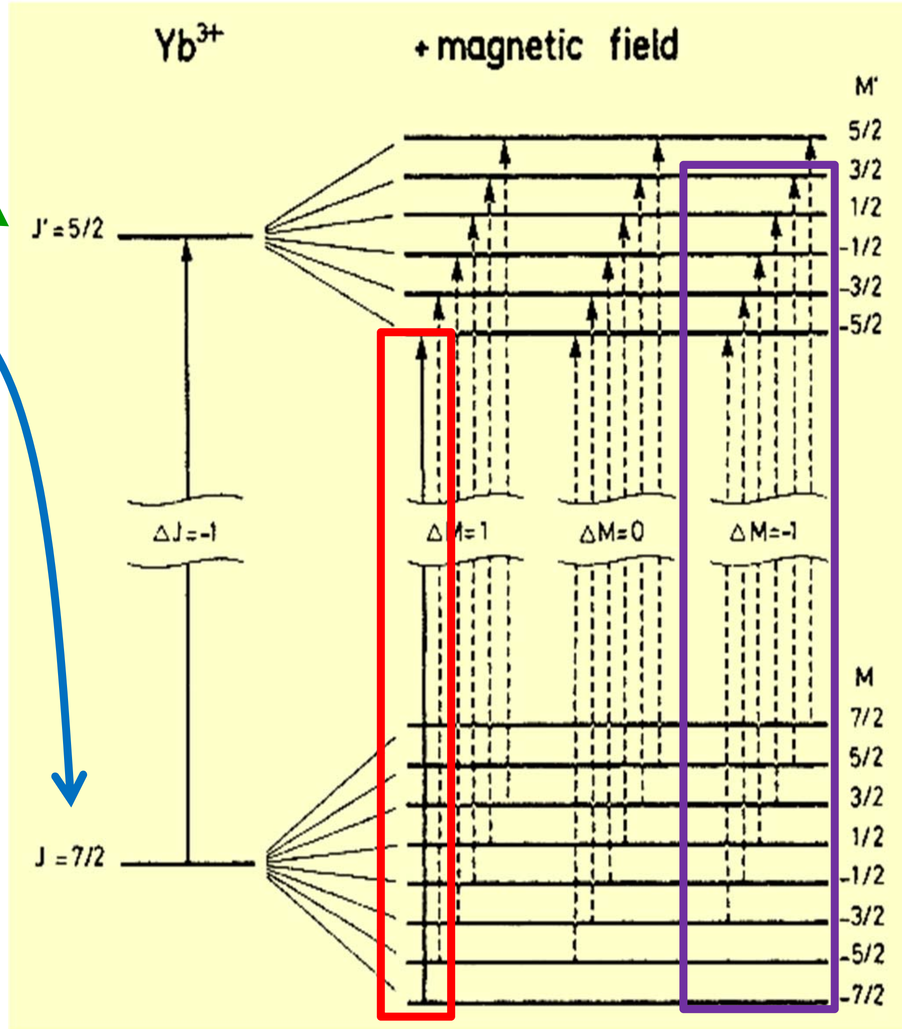
$\Delta M = +1$

No absorption

$\Delta M = -1$

Wigner 3-*j*-symbol

$$\mu_i \propto \begin{pmatrix} J & 1 & J' \\ M & \Delta M & -M' \end{pmatrix}^2$$

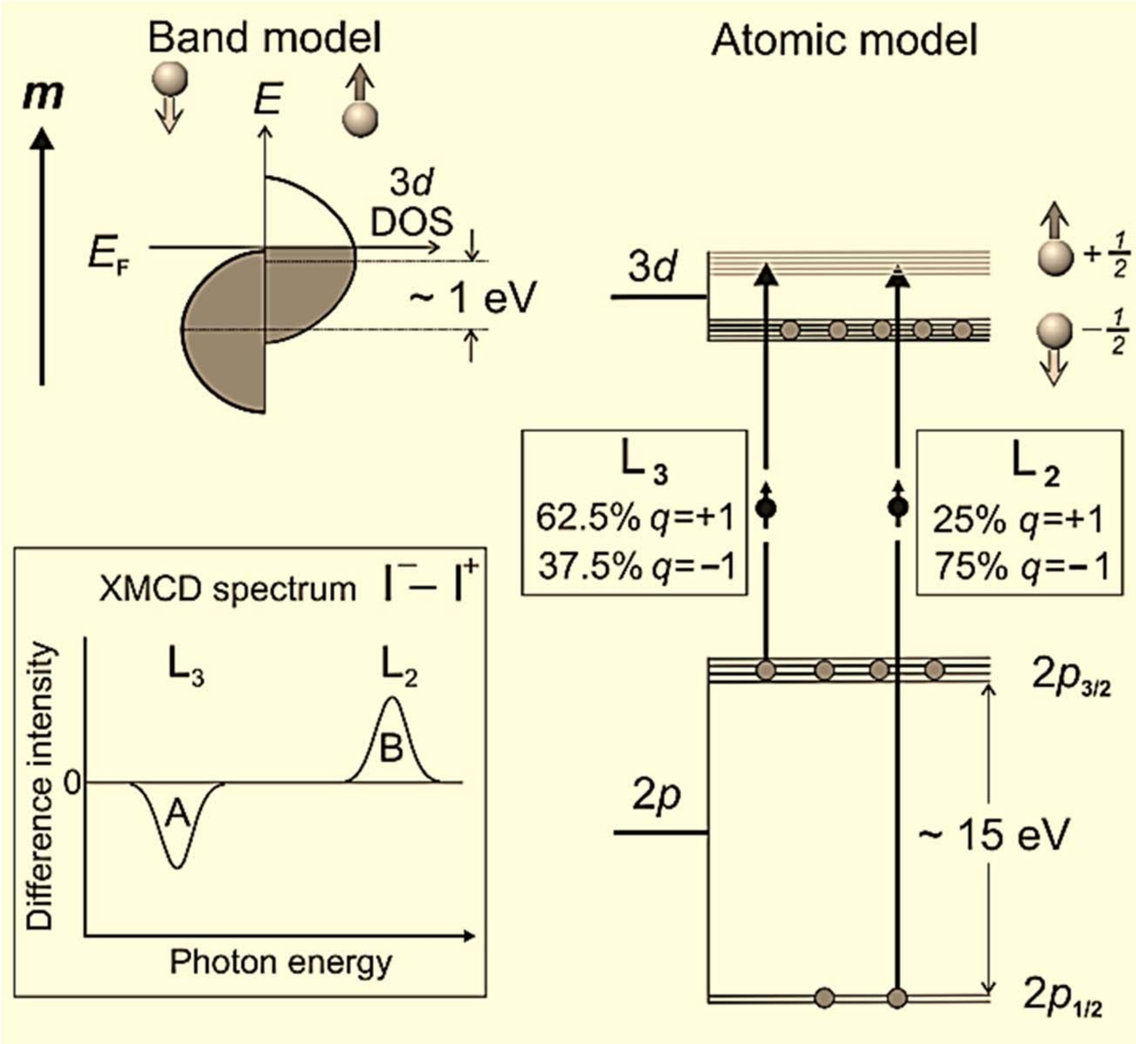


Goedkoop, *et al.* Phys. Rev. B (1988)

Origin of XMCD – 3*d*

Magnetism 3d metals
small orbital moment
large spin moment

Photons
angular momentum

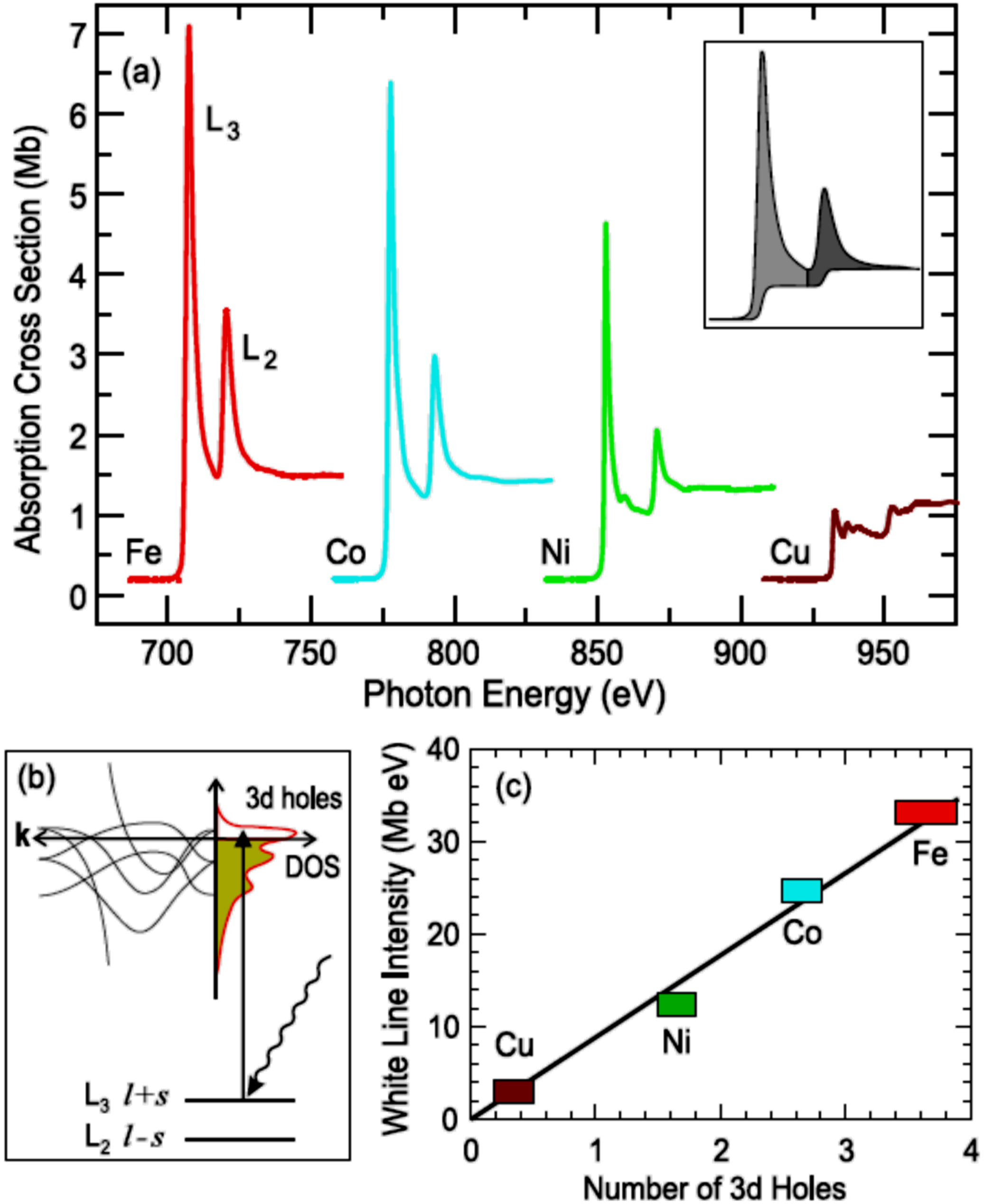


From Stöhr & Siegmann: Magnetism

Determine Number of 3d Holes

Charge sum rule

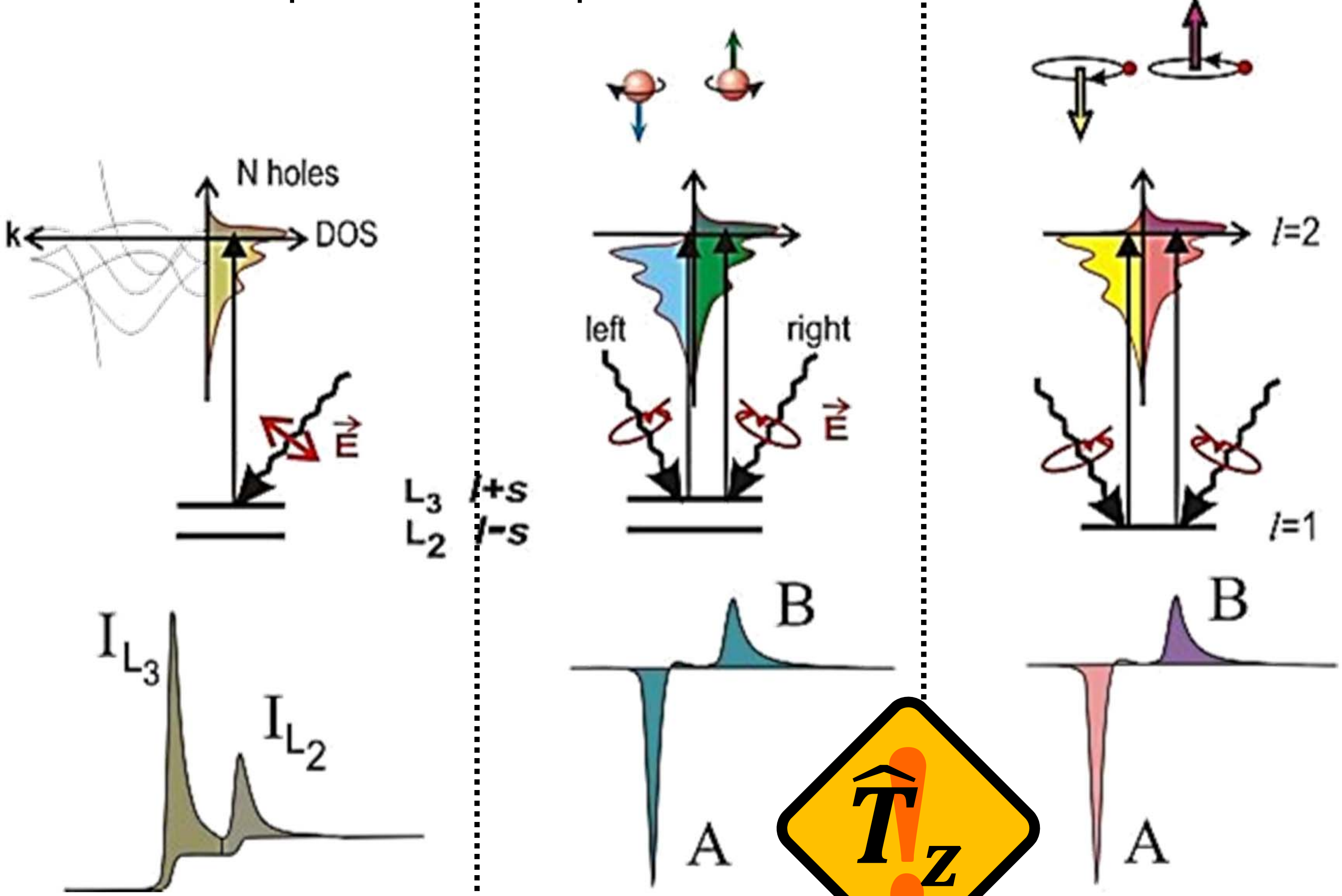
Integrated intensity is proportional to number of empty valence states



Courtesy J. Stöhr

Absolute Values of Magnetic Moments: Sum Rules

d-Orbital Occupation | Spin Moment | Orbital Moment



$N_h = (I_{L3} + I_{L2})/C$

$\langle m_{s,\text{eff}} \rangle = \mu_B(|A| + 2|B|)/C$

$\langle m_{\text{orb}} \rangle = 2\mu_B(|A| - |B|)/3C$

from http://ssrl.slac.stanford.edu/stohr/

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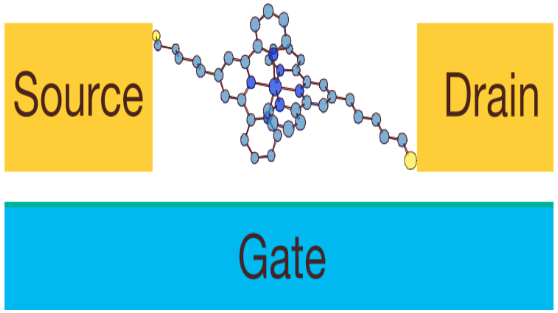
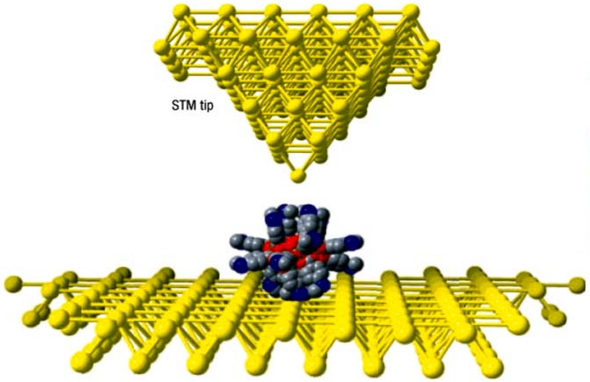
6. Science examples

(Magnetic) Molecules – Why Are They Interesting?

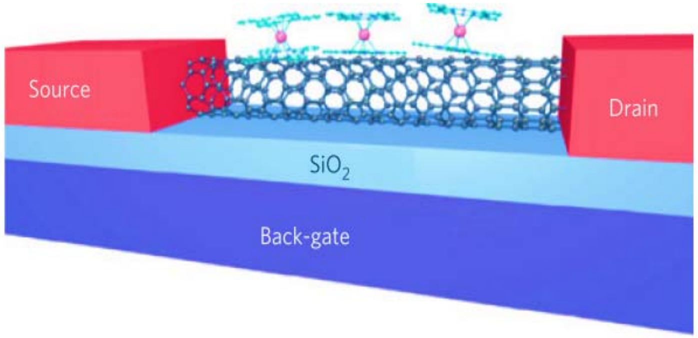
Molecular Spintronics



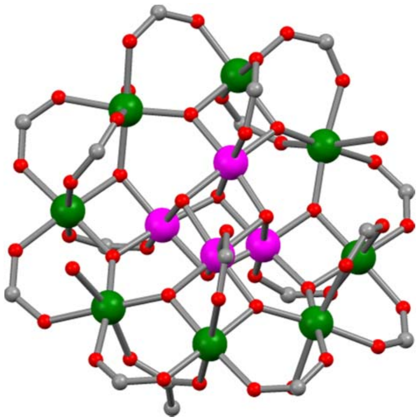
J. Park *et al.*,
Nature 2002



L. Bogani, W. Wernsdorfer,
Nature Materials, 2008



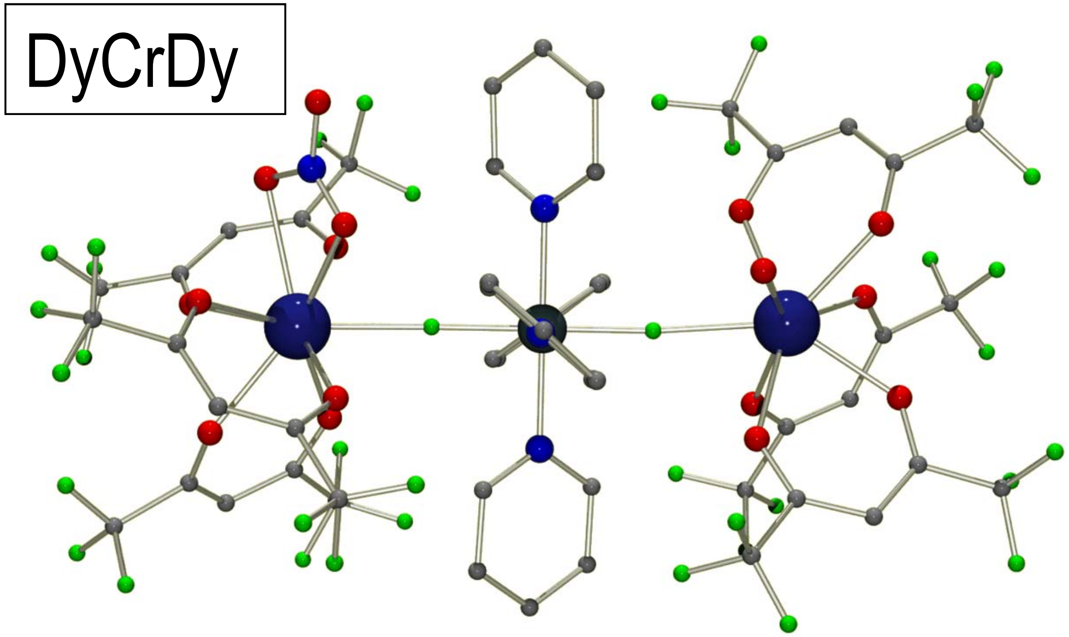
M. Urdampilleta *et al.*,
Nature Materials, 2011



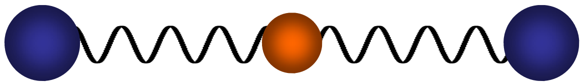
Why (Magnetic) Molecules?

- Multifunctional (e.g. spin crossover, optical fluorescence…)
- Chemical engineering possible
- Self assembly on surfaces

Lanthanide (4*f*) Ions in Molecular Nanomagnets



$[Dy(hfac)_3(NO_3)$ -$Cr(py)_4F_2$-$Dy(hfac)_3(H_2O)]$



Dy^{3+} has $L=5$ and $S=5/2$ → $^6H_{15/2}$ (free ion)

Typical ground state with crystal field

$$J = 15/2 \quad m_J = \pm 15/2$$

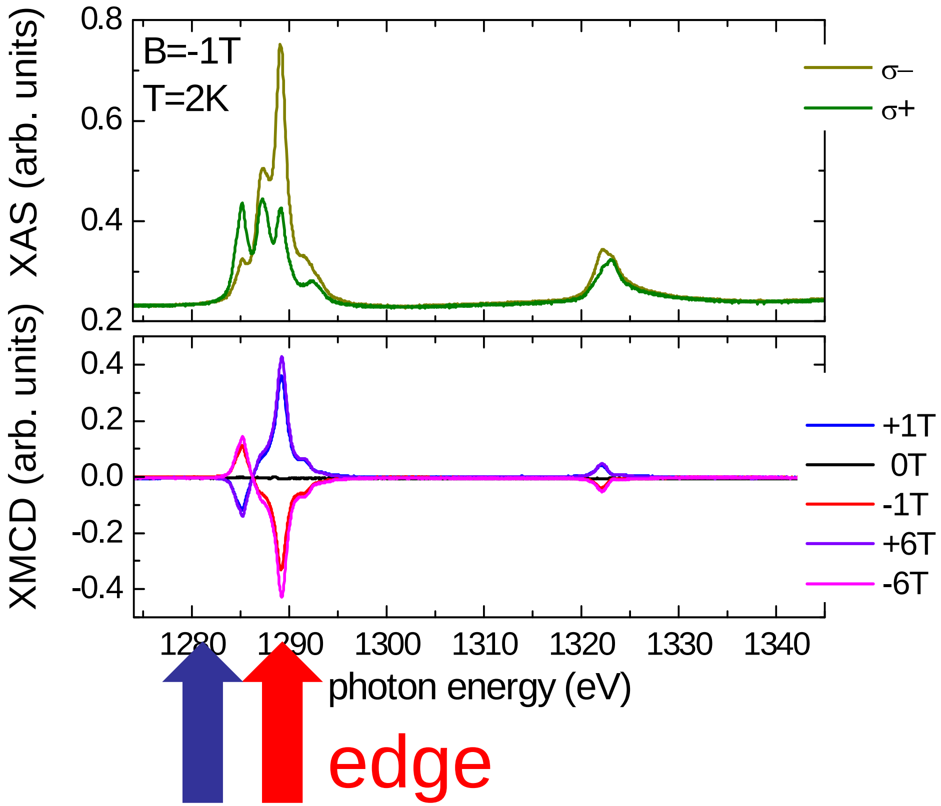
Synthesis: K. S. Pedersen, J. Bendix

- Unquenched orbital momentum
- Strong spin-orbit coupling
- Large magnetic anisotropies

- Magnetic coupling often weak as 4*f* shell is strongly localized

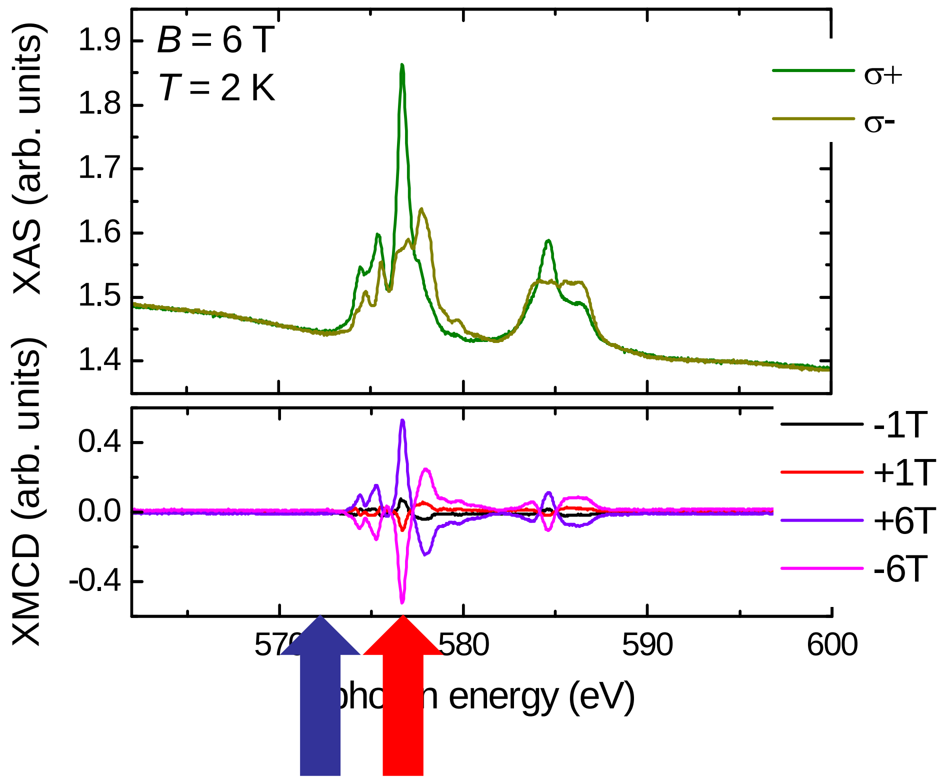
XAS / XMCD on DyCrDy Powder

Dy $M_{4,5}$



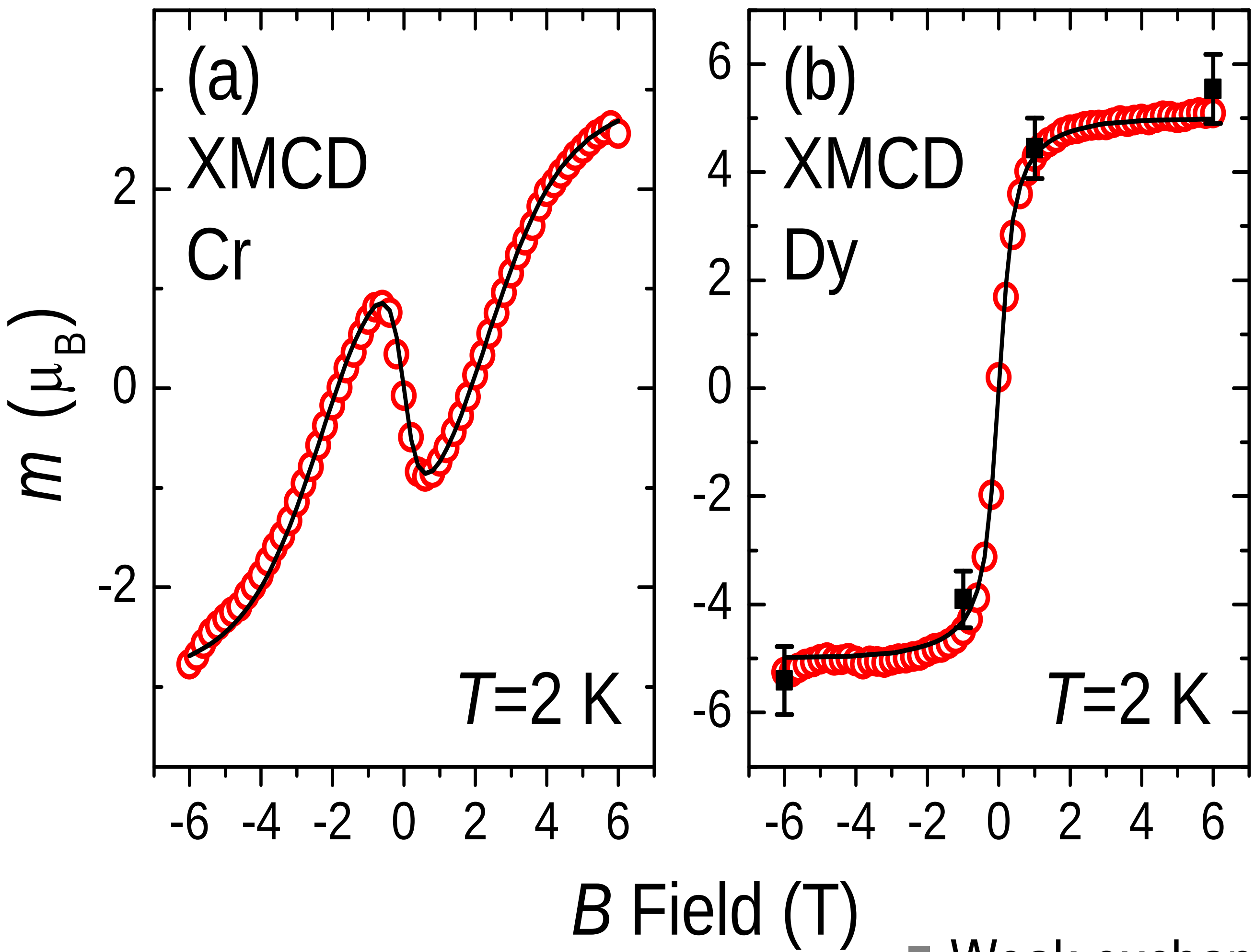
pre-edge

Cr $L_{2,3}$



→ Obtain $M(H)$

Mixed 3d-4f Compounds

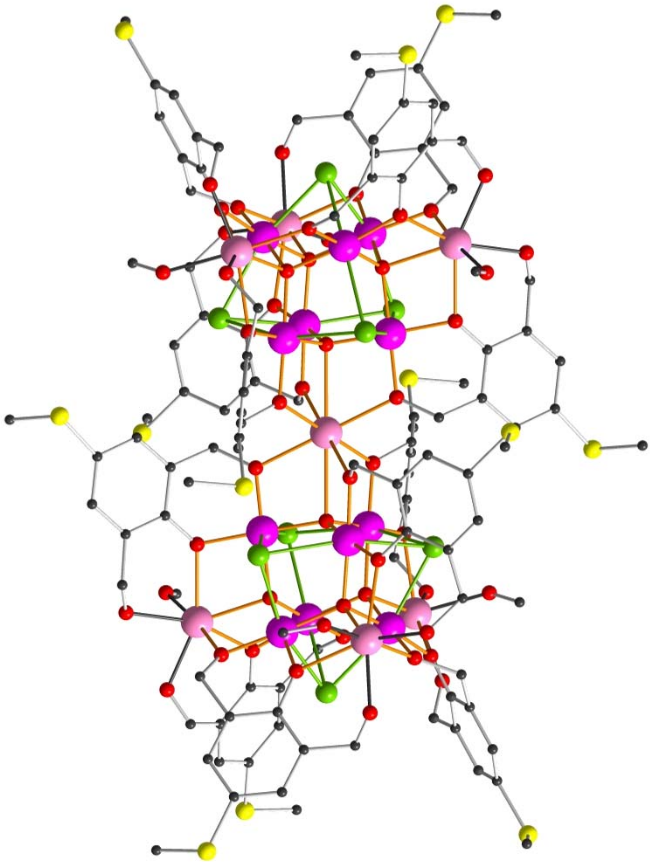


- Weak exchange coupling
- Coupling strength can be measured by XMCD

JD *et al.*, *Chemical Science*, 3, *1024* (2012)

The Example of Mn_{19} Coordination Clusters

S = 83/2



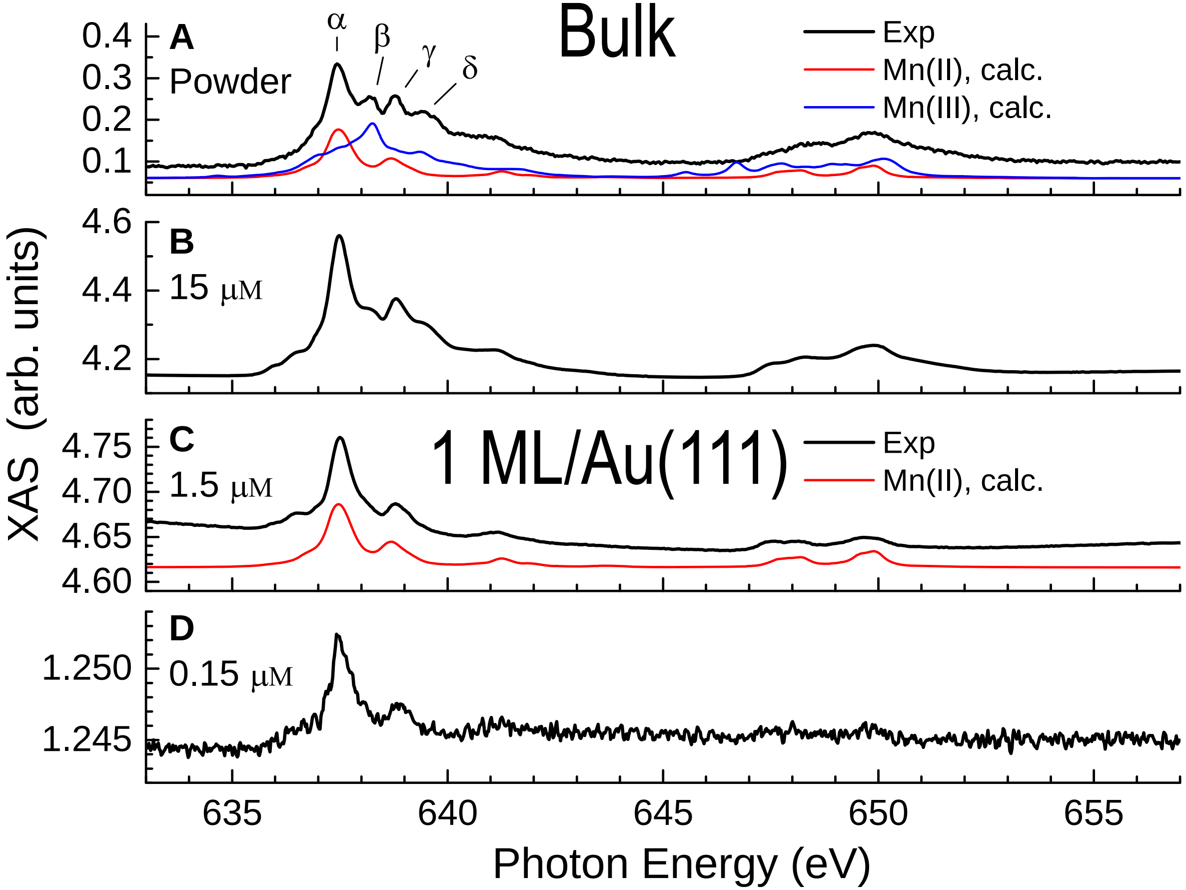
"Mn_{19}(SMe)"

Mn(II)

Mn(III)

JD et al., *J. Phys. Chem. C* 2015

→ Exploit surface sensitivity of soft-XAS !



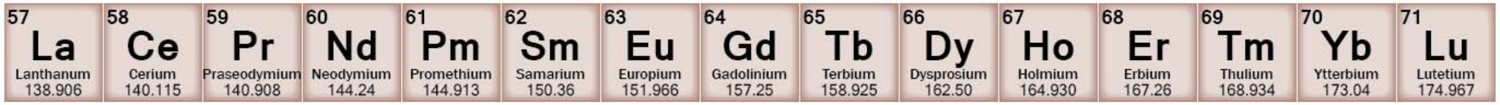
Mn12:

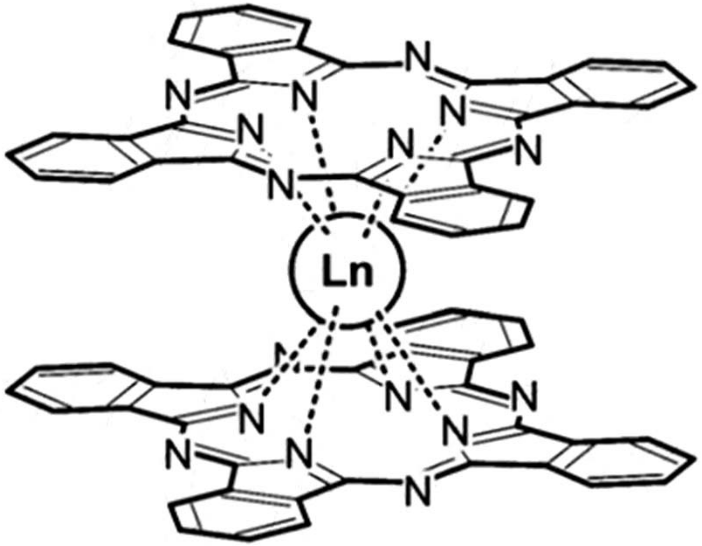
Voss et al., *Phys Rev. B* 2007

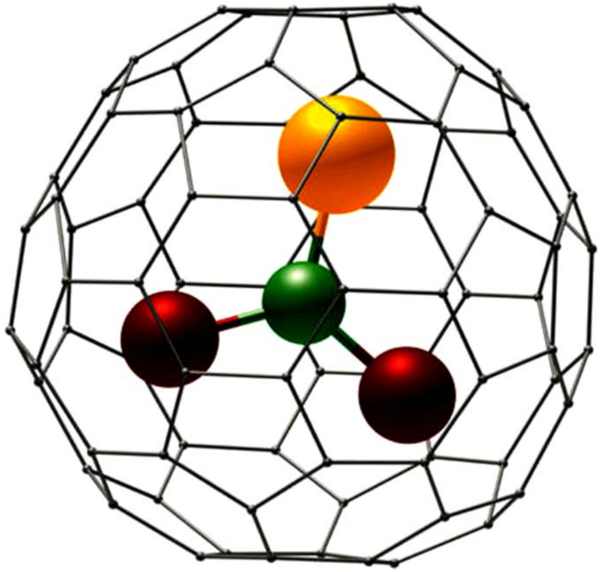
Mannini et al., *Chem. Eur. J.* 2008

Saywell et al., *Nanotechnology* 2011

Lanthanide Molecular Single-Ion Magnets







Coordination Complex $[LnPc_2]^-$

Ishikawa *et al*., JACS 2003

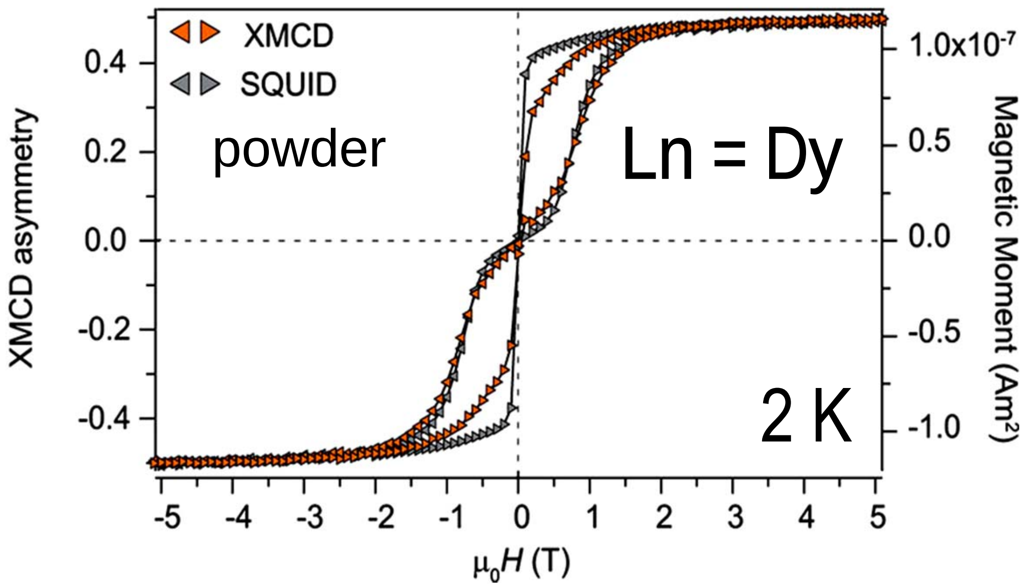
Endohedral Metallofullerene $LnSc_2N@C_{80}$

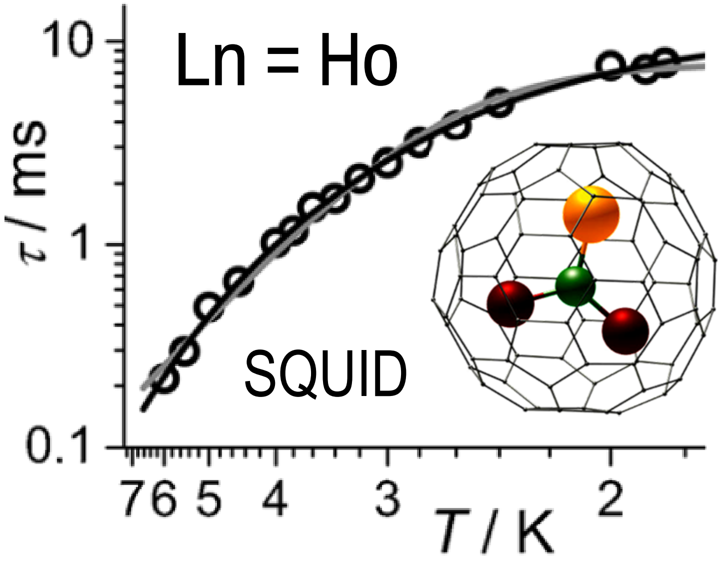
Stevenson *et al*., Nature 1999

- Large magnetic anisotropies → Magnetic bistability
- Single-molecule magnets (SMMs) or: single-ion magnets (slow relaxation in a single ion)

Reviews: Jiang *et al*., *Struct. and Bond.* 2014; JD, *J. Phys: Cond. Mat*. 2015

Endohedral Single-Ion Magnets

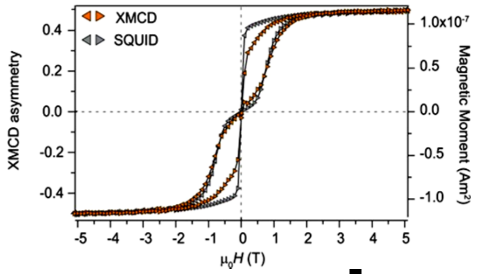


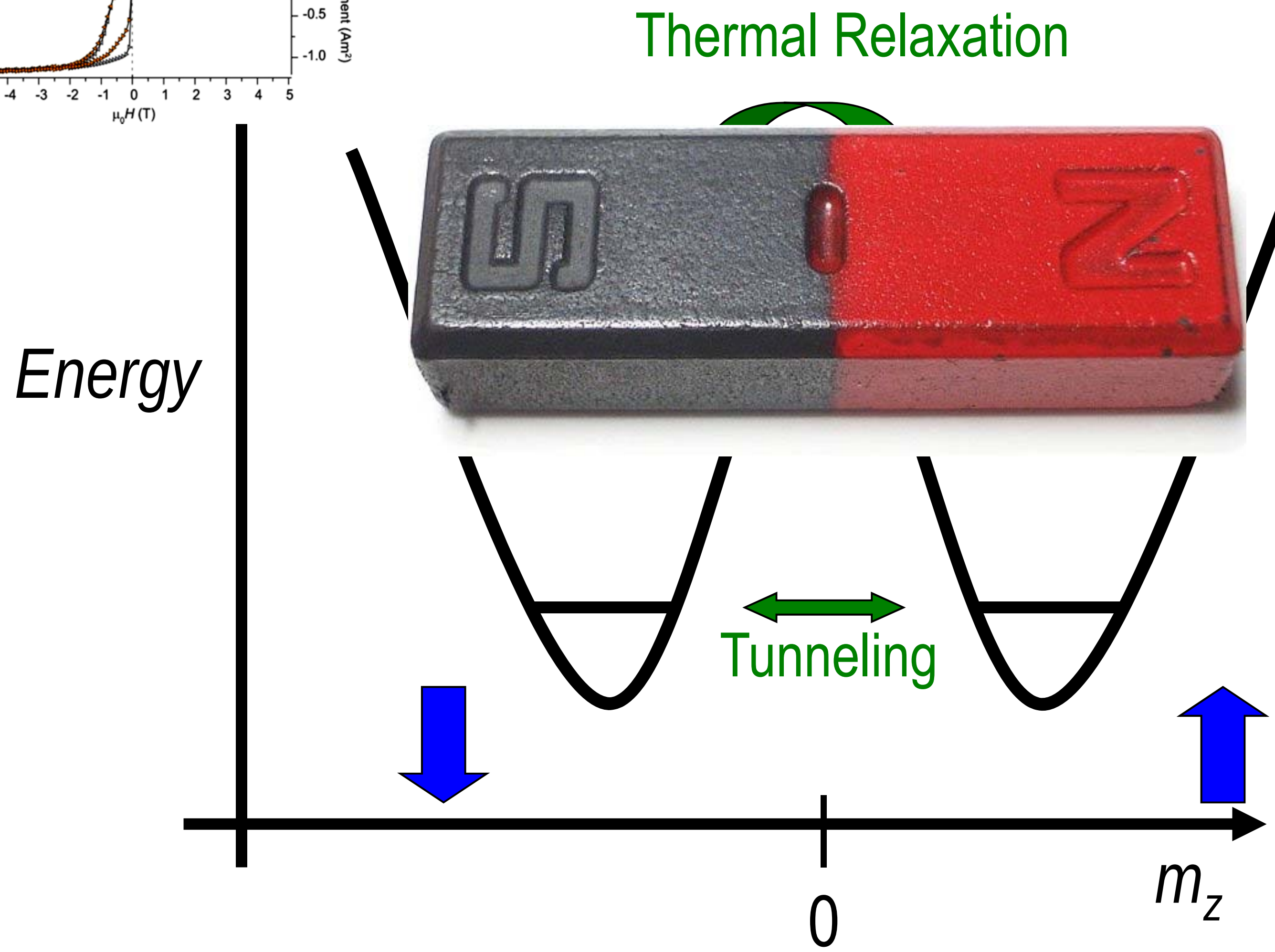


- Strong uniaxial magnetic anisotropy on Dy^{III} and Ho^{III} ions
- Magnetization relaxation times of up to hours at 2 K with Ln = Dy
- Shorter relaxation times with Ln = Ho

Westerström *et al*., *J. Am. Chem. Soc.* 2012
Westerström *et al*., *Phys. Rev. B* 2014
Dreiser *et al.*, *Chem. Eur. J.* 2014

Blocking of Magnetization Relaxation

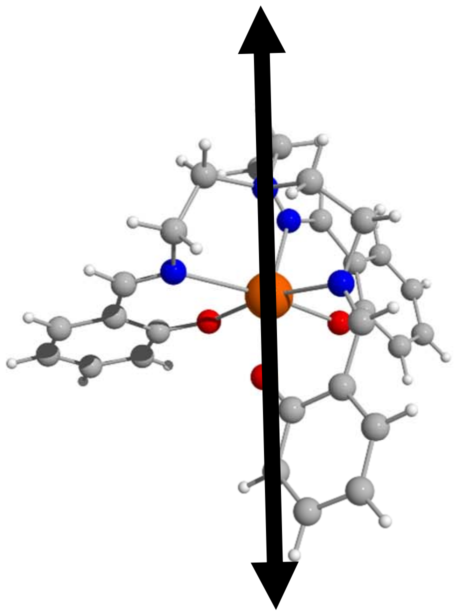




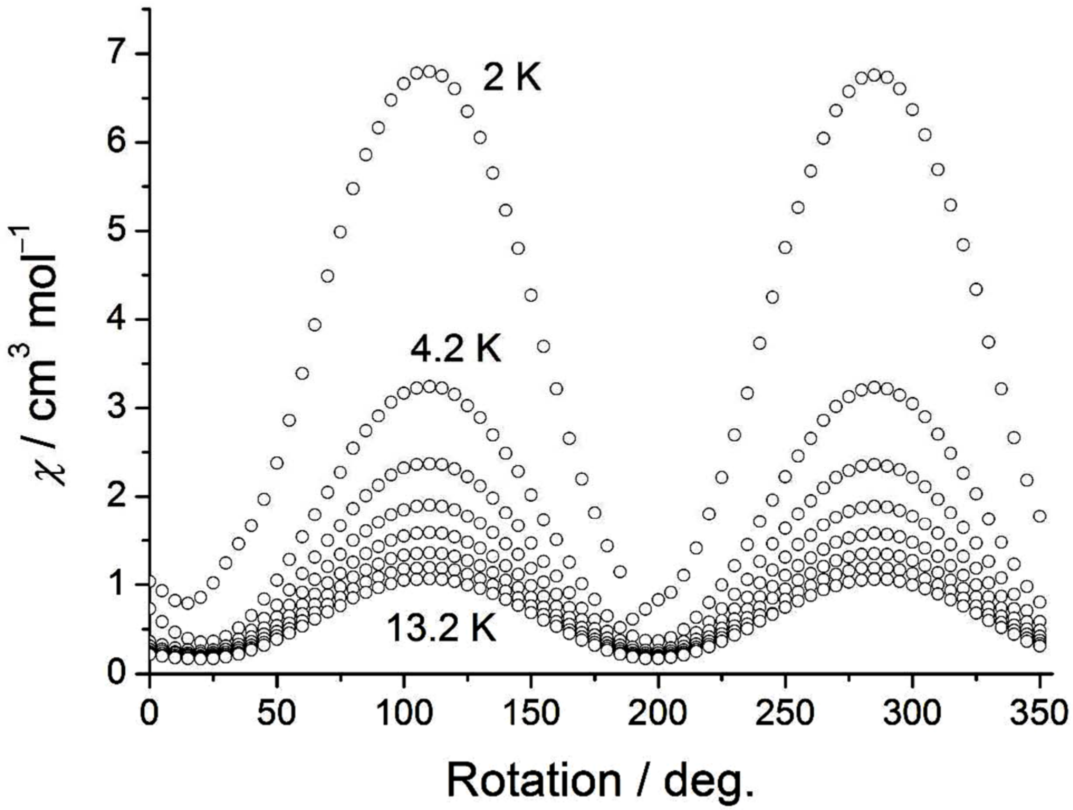
Magnetic Anisotropy

Magnetic Anisotropy

„Easy axis“

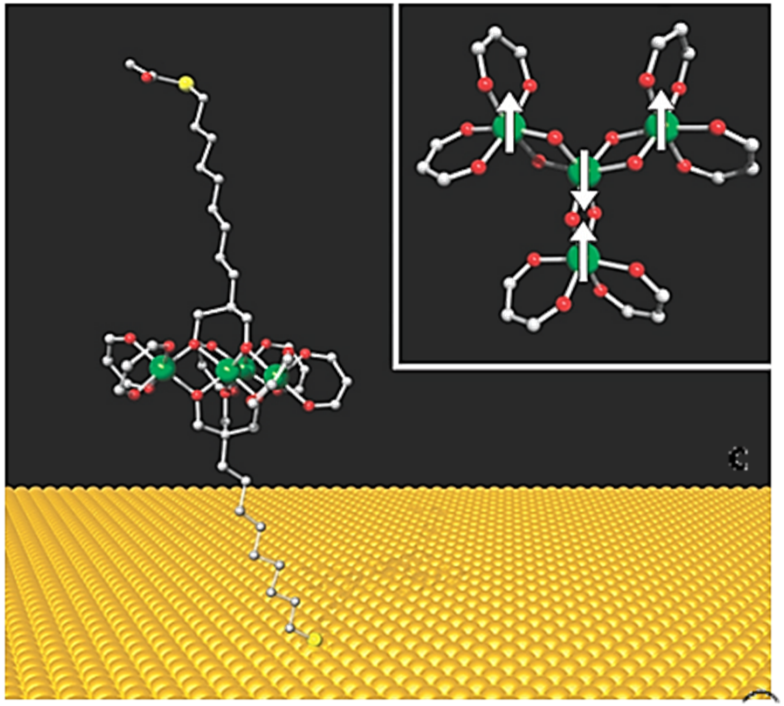


SQUID (Single crystal measurement)

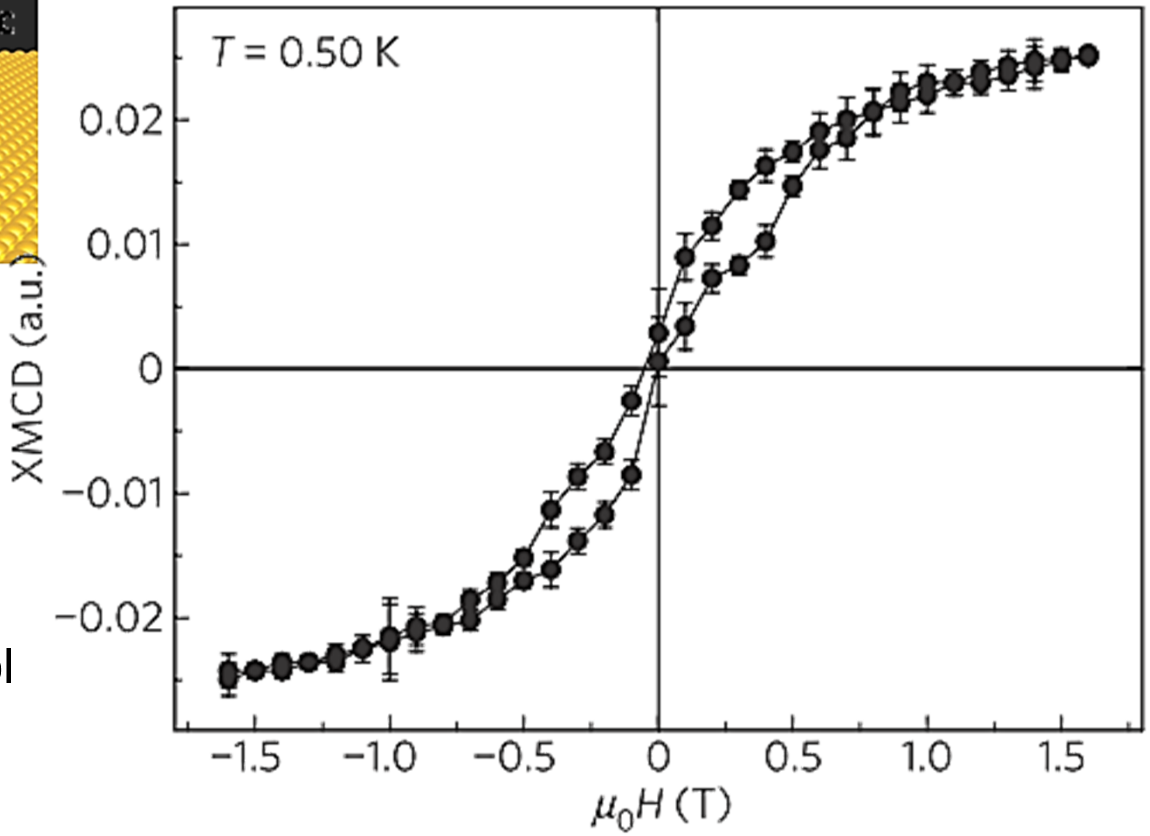


K. S. Pedersen *et al.*, *Chemical Science* 2014

Fe_4 : Slow Relaxation on Surface-Deposited SMMs



Magnetic hysteresis from a **submonolayer** of surface-deposited single-molecule magnets for the first time!



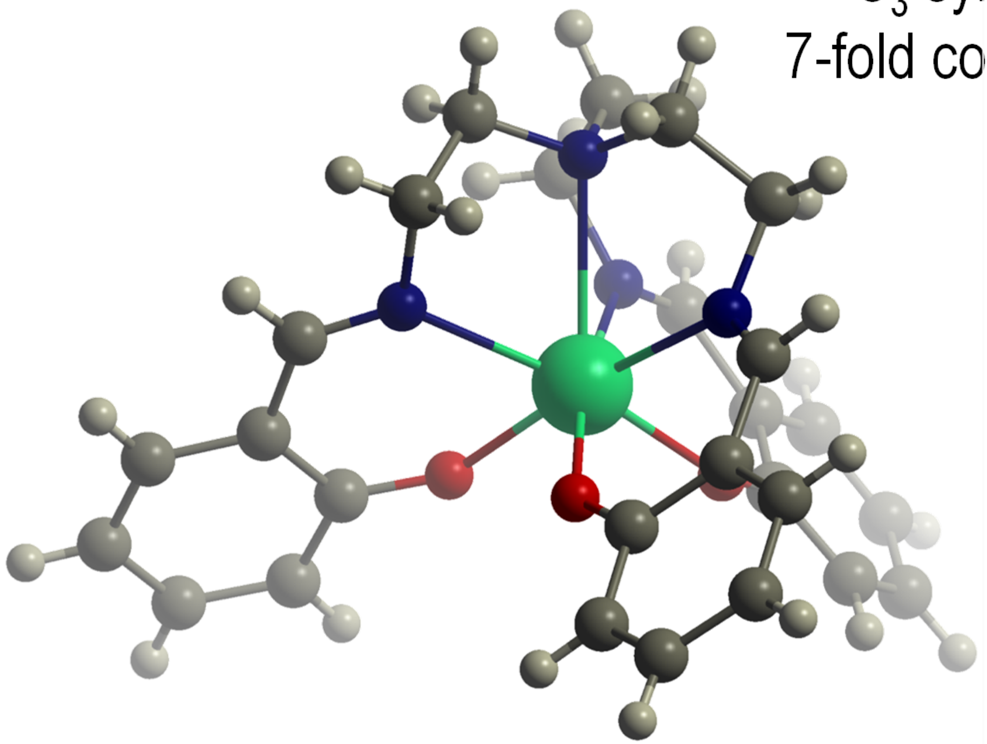
$[Fe_4(L)_2(dpm)_6]$

With: H_3L = 11-(acetylthio)-2,2-bis (hydroxymethyl)undecan-1-ol and Hdpm = dipivaloylmethane

M. Mannini *et al*., *Nature Materials* 2009

The Er(trensal) Single-Ion Magnet, Bulk Properties

C_3 symmetry
7-fold coordination

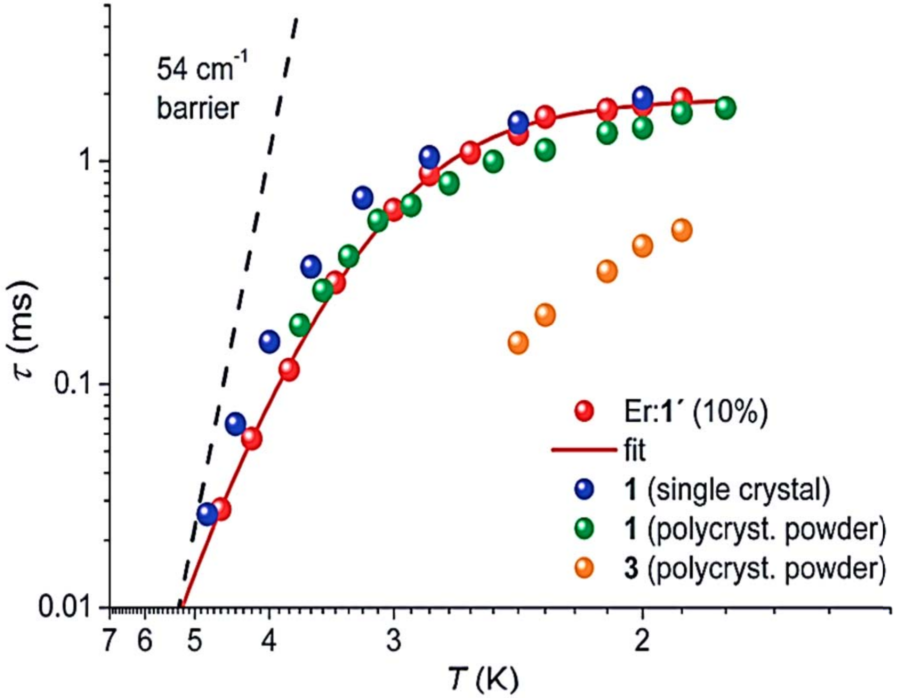


Structure from X-ray diffraction

Flanagan et al., *Inorg. Chem.*, 2002
Synthesis and SQUID measurements: K. S. Pedersen, J. Bendix

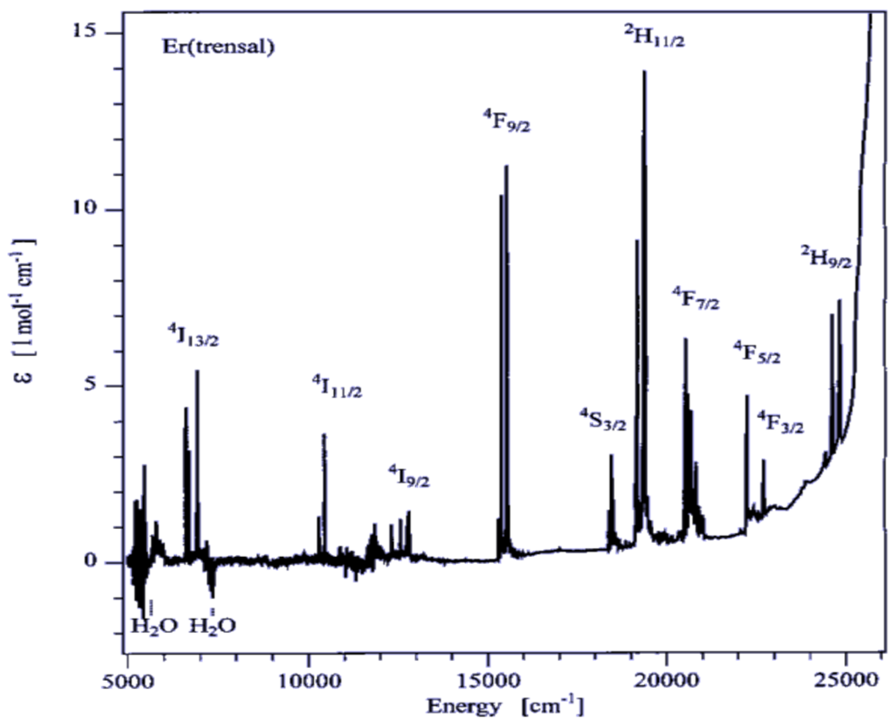
The Er(trensal) Single-Ion Magnet, Bulk Properties

SQUID, ac susceptibility



K. S. Pedersen *et al.*, *Chem. Sci.,* 2014
Lucacchini *et al.*, *Chem. Commun.*, 2014

Optical Absorption UV-vis-NIR



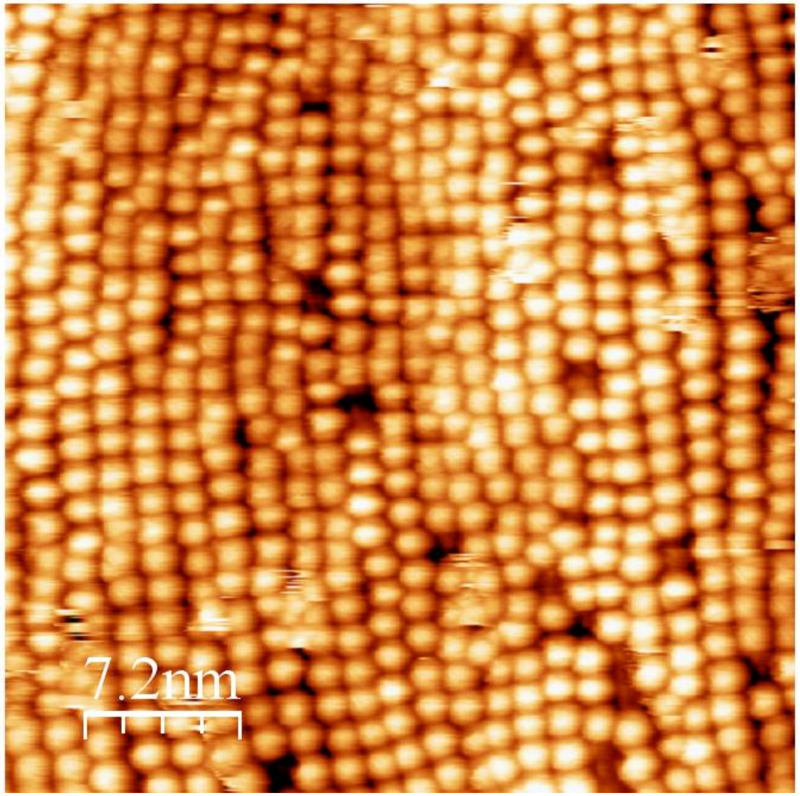
2000 nm 400 nm

Flanagan *et al*., *Inorg. Chem*., 2002

Er(trensal) on Au(111)

- Sublime molecules in ultrahigh vacuum
- Deposit onto single-crystalline, clean metal substrates

- Molecules are intact
- At room temperature molecules are mobile
- At low temperatures formation of a quasi-regular pattern



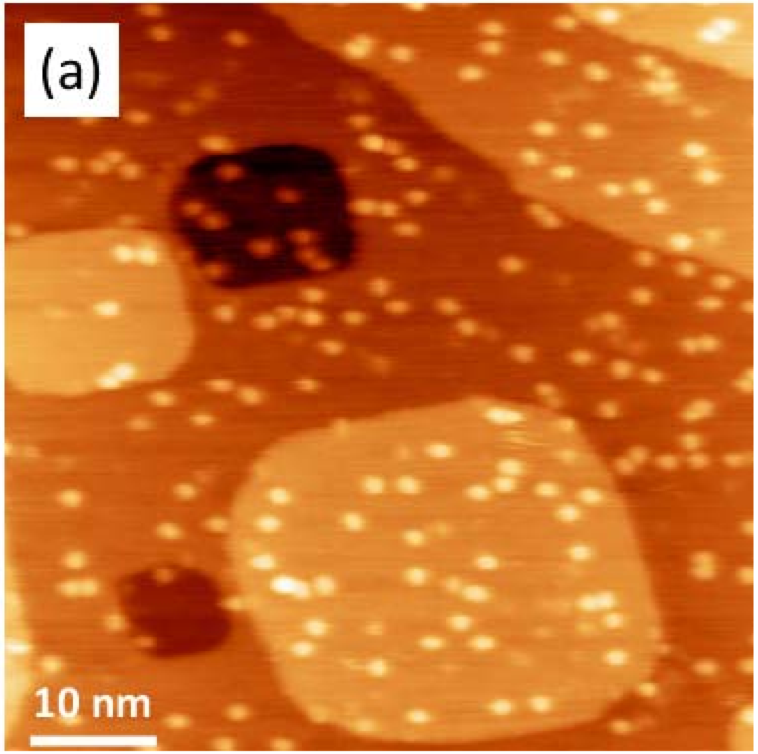
-1.6V, 10pA   *T* = 130 K

STM: C. Wäckerlin

JD *et al.*, *ACS Nano* 2014

Er(trensal) on Ni/Cu(100)

- Molecules are intact
- Molecules are immobile at room temperature
- Random distribution of molecules
- Indicates strong interaction with the Ni surface (chemisorption)

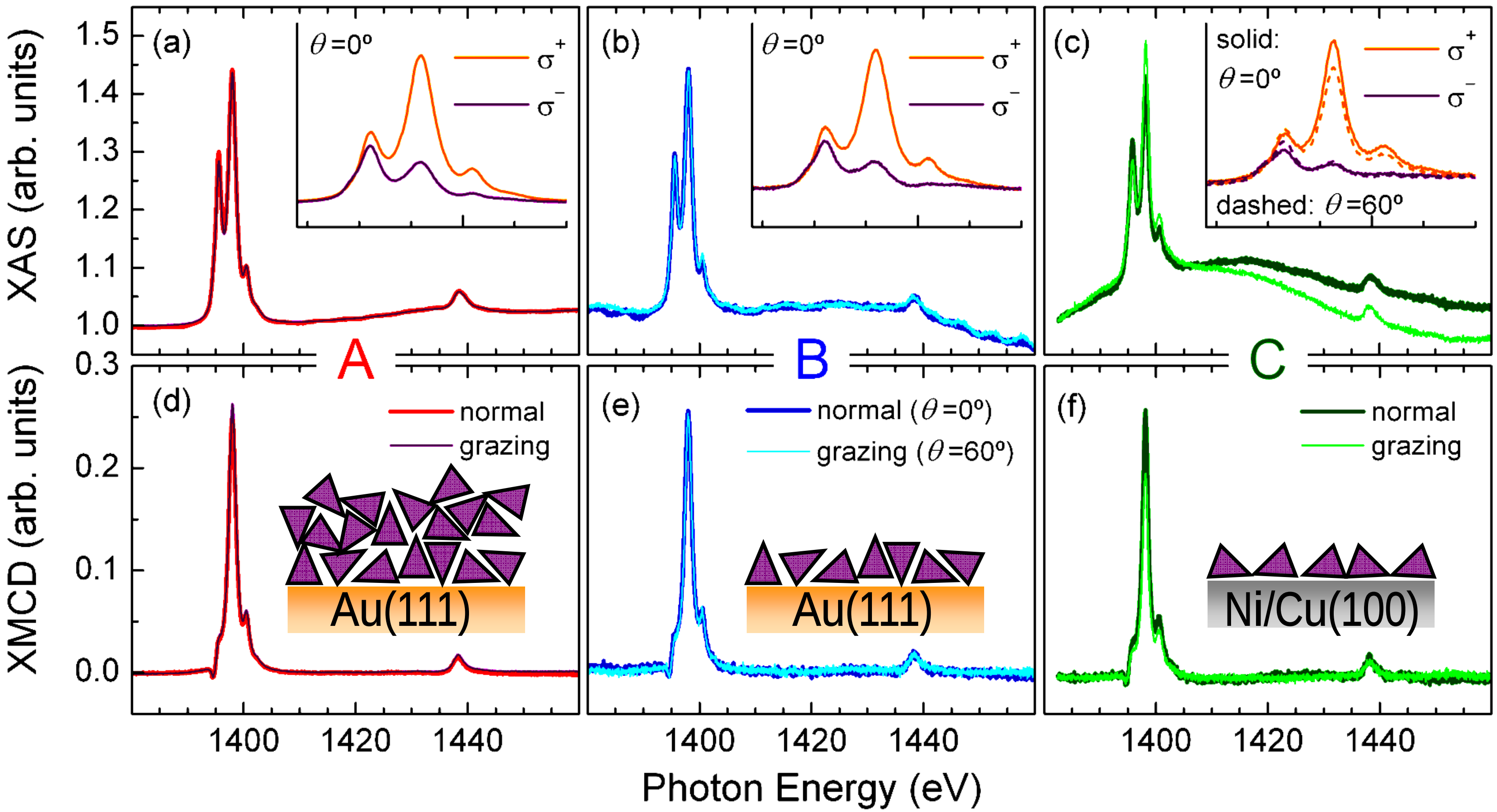


-1.05 V, 80pA   *T* = 300 K

STM: C. Wäckerlin

JD *et al.*, *ACS Nano* 2014

X-ray Absorption of Surface-Deposited Molecules



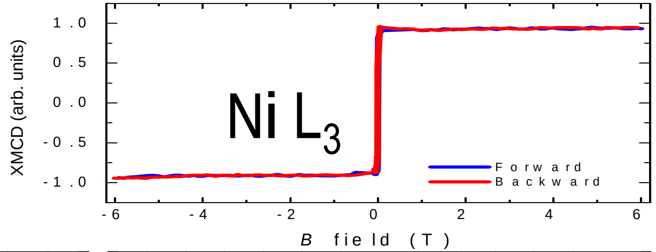
Results from X-Treme beam line (Swiss Light Source)

- On Au(111): No angle dependence
- On Ni/Cu(100): Preferred orientation

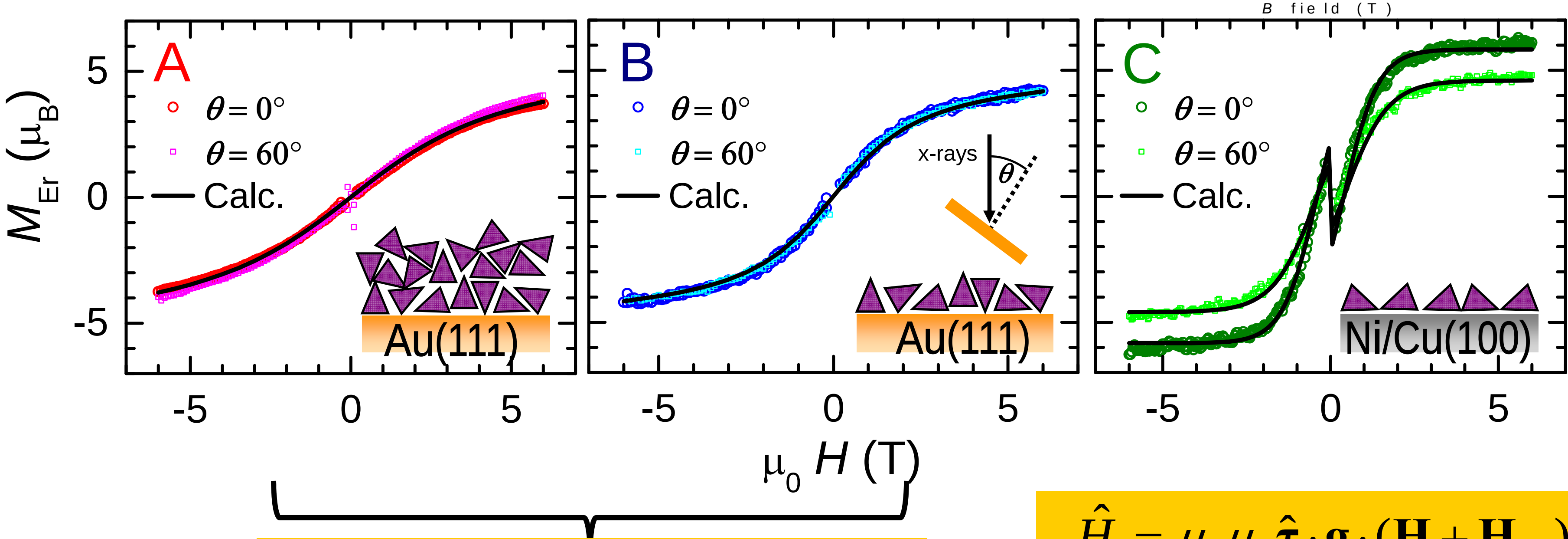
JD *et al.*, *ACS Nano* 2014

XMCD Reveals Molecule-Surface Exchange Coupling

Data recorded at X-Treme beam line (Swiss Light Source)



Er M_5



$$\hat{H} = \sum_{k,-k\le q\le k} B_k^q \hat{O}_k^q(\mathbf{J}) + \mu_0\mu_B g_J \mathbf{J}\cdot\mathbf{H}$$

$$\hat{H} = \mu_0\mu_B \hat{\boldsymbol{\tau}}\cdot\mathbf{g}\cdot(\mathbf{H}+\mathbf{H}_{ex})$$
$$\mathbf{H}_{ex} = H_{0,ex}\cdot \mathrm{sgn}(\mathbf{H}\cdot\mathbf{e}_\theta)\cdot\mathbf{e}_\theta$$

- On Au: Bulk mag. anisotropy & random orientation
- On Ni: Different anisotropy & preferred orientation

$\mu_0 H_{ex}$ = –0.4(1) T

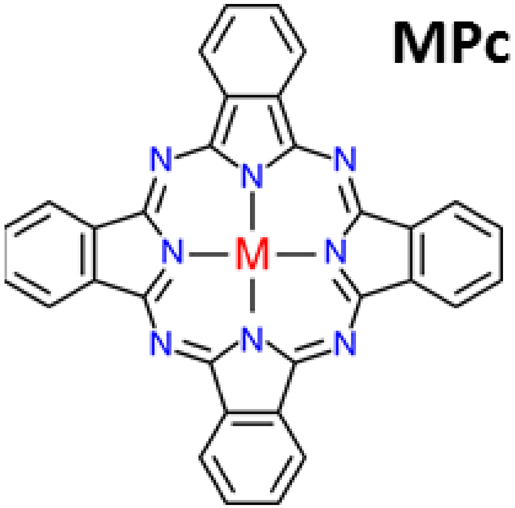
$g_x = g_y$ = 8(1)

g_z =11.7(8)

JD *et al.*, *ACS Nano* 2014

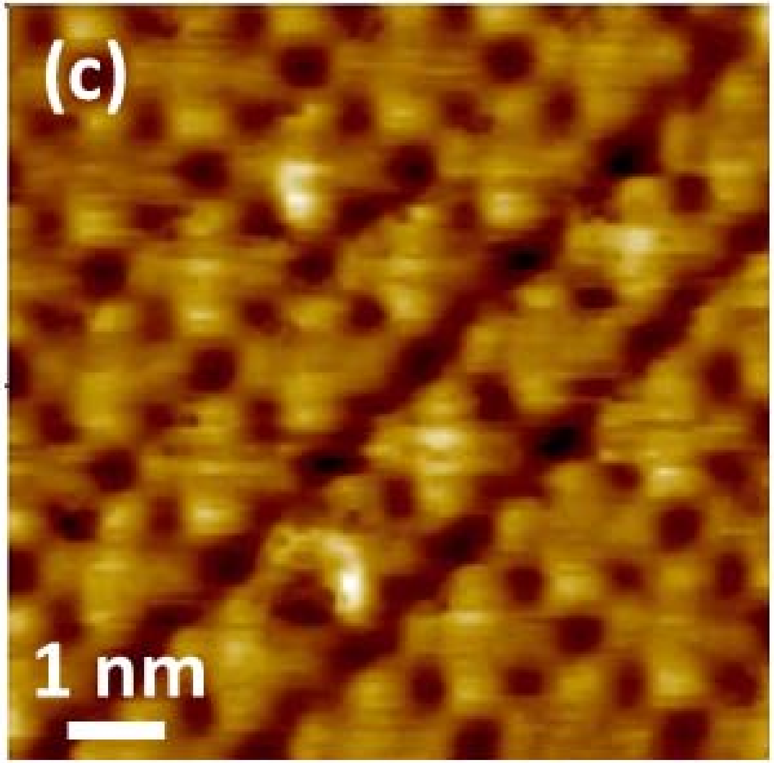
Metal(II)-Porphyrins and Pthalocyanines on Surfaces

Pc = phthalocyanine



M = Mn / Fe / Co

M-TPPCl TPP = tetraphenylporphyrin

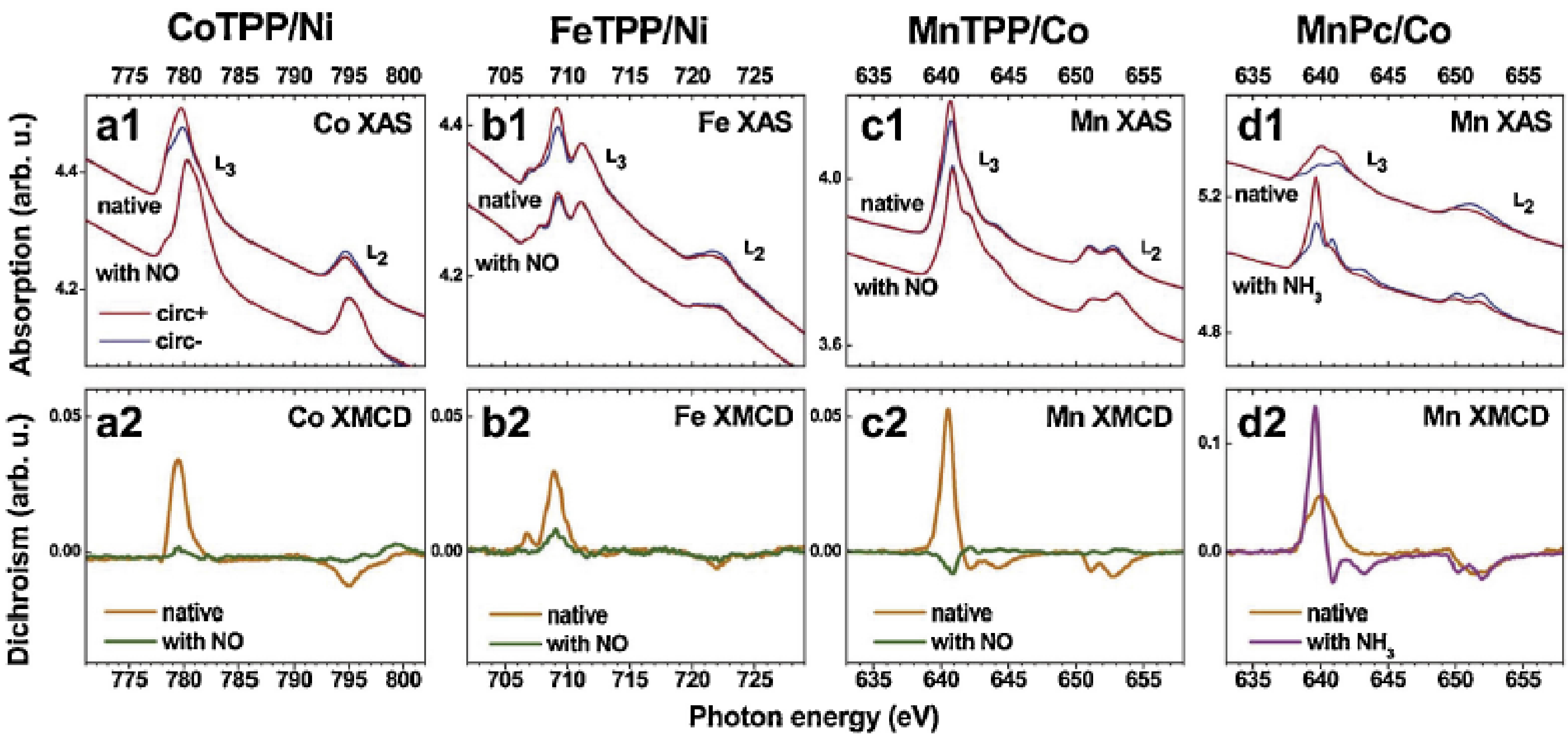


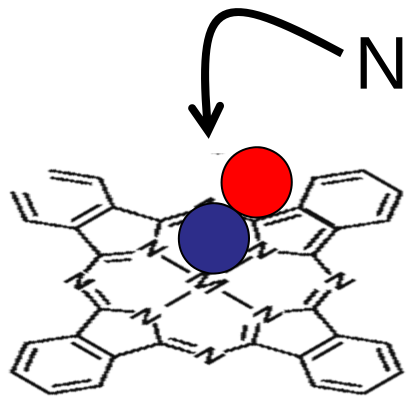
Mn-TPPCl on Cu(100)

Challenges

- In-situ experiments (ultrahigh vacuum)
- Requires sublimation of molecules

Spin-State Switching Upon Gas Adsorption



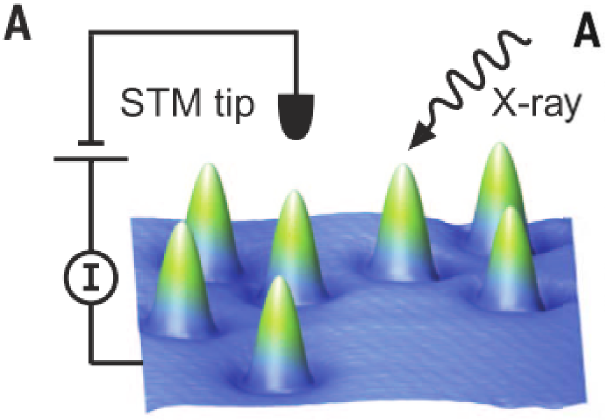


NO molecule

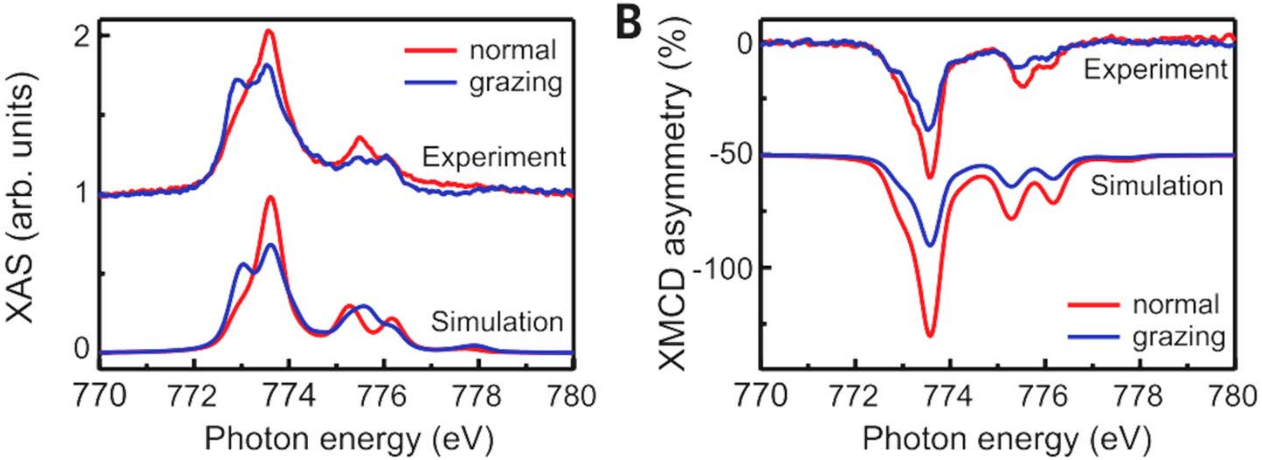
(*in situ* gas dosing)

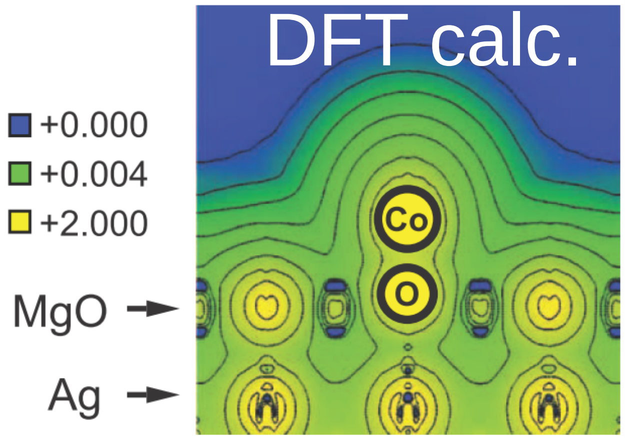
Ch. Wäckerlin *et al.*, *Chemical Science* 2012

Giant Magnetic Anisotropy of Single Co Atoms on MgO



XAS T = 3.5 K, 6.8 T XMCD





- Co Coverage: 0.03 monolayers !
- Uniaxial magnetic anisotropy from crystal field imposed by MgO
- M.A. energy: bulk Co 0.01 meV/atom, thin films 1 meV/atom, here: 58 meV/atom

Rau *et al.*, Science 2014

Conclusions

- Soft X-ray absorption spectroscopy is a very powerful technique

- Working with X-ray absorption spectroscopy is fun!

- If you have further questions and/or you are interested in doing XMCD at 3 K and 7 T:
  → please contact me: jan.dreiser@psi.ch