XMCD ..... 

Outlook of the lecture

• Magnetism in nutshell
• X-ray absorption spectroscopy XAS
• Magnetic XAS = XMCD (X-ray Magnetic Circular Dichroism)

Eberhard Goering, MPI-IS, Stuttgart
Magnetism in a nutshell

• “Rotating“ charges produce magnetic field (angular momentum)
• There are two types spin (S) and orbital (L) magnetic moments

\[ |\vec{m}| = A \cdot I \]

macroscopic

Magnetism is related to angular momenta of charges L and S

L is often quenched (3d) = close to zero \( \Rightarrow \) super important, but hard to quantify!

\[
\langle m_L \rangle_z = \langle L_z \rangle \cdot \mu_B \quad \langle m_S \rangle_z = g \cdot \langle S_z \rangle \cdot \mu_B \approx 2 \cdot \langle S_z \rangle \cdot \mu_B \quad \mu_B = 9.274 \cdot 10^{-24} \text{ J/T}
\]

\( g = G \) – factor \( \mu_B = \) Bohr's Magneton
orbital moment

- orbital moment has preferred axis in anisotropic crystal field
  - LS-coupling in 3d-shell orients the spin
- The small L is important for almost all properties, especially for technology
  - remnant field, easy and hard axis, coercivity ....

Some examples for “modern” magnetism applications!

- Supermagnets

Low weight and high field = forces
Optimizing interaction strength between lattice and magnetic moments ➔ orbital moments

Important to know:
What is the magnetism of each element? Nd? Fe? Co? Sm?....
Some examples for “modern” magnetism applications!

- Data storage

Optimizing interaction strength between lattice and magnetic moments

→ orbital moments

permanent magnets, magnetostriction, spin wave damping, etc. etc.
Why X-rays and magnetism?

• It is important to know spin and orbital moments for each element in the system separately
• Contact areas are important → probing single atomic layers and separating them from others

• We know: X-rays provide significant spatial resolution on the atomic scale

• Your will see here how this is transferred to magnetism using X-ray Magnetic Circular Dichroism (XMCD)
• Or in other words: XMCD is able to transfer ANY X-ray technique in it’s magnetic counterpart!
Now XAS

• X-ray absorption spectroscopy XAS
  • Dipole selection rules provide “wanted projections”
    • symmetry selective
  • Electric field vector can provide orbital occupation and orientation

• Further Examples:
  • Gas on a surface ➔ Chemistry and binding orientation
  • Valence and Band structure determination (unoccupied of cause)
Why XAS!

One famous example (also for magnetism): $2p \rightarrow 3d$

- X-ray absorption spectroscopy (XAS)
  - dipole selection rules
    \[ m' = m + q \]
    \[ l' = l \pm 1 \]

- probing 3d magnetism
  $2p \rightarrow 3d$

- probing 4f magnetism
  $3d \rightarrow 4f$

Spin-Orbit-Splitting

\[
2p_{3/2} \quad 2p_{1/2}
\]

\[
2p_J = 2p_{3/2} \quad J = L + S = 1 + 1/2
\]

\[
2p_J = 2p_{1/2} \quad J = L - S = 1 - 1/2
\]
Spin-Orbit-Splitting

XAS: In resonance very strong effects

One famous example (also for magnetism): $2p \rightarrow 3d$

probes the **unoccupied** (here) 3d electrons $\rightarrow$ holes

energy position of the resonant spectra (binding energy) depends strongly on the nuclear charge $\rightarrow$ element specific!
All is based on Fermi’s Golden Rule!

- It provides the probability \( W_{ba} = \frac{d}{dt} |c_b^{(1)}(t)|^2 \) to excite an electron from the initial state \( |\psi_i\rangle \) to the final state \( |\psi_f\rangle \).

Fermi's Golden Rule: \[ W_{fi} = \frac{2\pi}{\hbar} \left| \langle \psi_f | H_{\text{phot}} | \psi_i \rangle \right|^2 \cdot \delta(E_f - E_i - \hbar \omega) \]

The total Hamiltonian is: \[ H_{\text{tot}} = H_0 + H_{\text{phot}}(t) \]

Based on time dependent perturbation theory

Time integral \( \Rightarrow \) “Energy-Conserving- Deltafunction”
What have we learned so far?
XAS because..

- it probes unoccupied states
- element specific due to energy position
- symmetry selective due to selection rules $p \rightarrow d$

What else?
Good for chemistry and band structure determination

- Example: Mn $L_{2,3}$ 2p $\rightarrow$ 3d
  - different oxidization states
  - shape provides important information about the unoccupied density of states
  - some less clear chemical shift observable
    - reason: also the initial (here 2p) and the final states (here 3d) are shifted
  - details often complicated, due to electron-electron-interaction and so called "multiplet effects"
    (not discussed here)

source: PHYSICAL REVIEW B Volume: 75 Issue: 4 Article Number: 045102
Hexadecane \( \text{C}_{16}\text{H}_{34} \) on a Cu surface

- Molecular orientation on the surface

Tilt angle determined by the angular dependency of the XAS spectra

This also works nicely in anisotropic single crystals

Source: D.A. Fischer Tribology Letter 3 (1997) 41
XAS: How to measure X-ray Absorption Spectroscopy

Lambert-Beer-Law:

\[ I(E_{\text{phot}}) = I_0 \cdot e^{-\mu(E)d} \]

\[ \Leftrightarrow \mu(E) = \frac{1}{d} \cdot \ln \frac{I_0}{I(E_{\text{phot}})} \]

\[ \xi = \frac{1}{\mu(E)} = \text{attenuation length,} \]

i.e. the length for 1/e intensity

Example: Fe metal
(calculation without resonances and spin–orbit-splitting)

Hard to measure below 3-5keV, due to the very short attenuation length

⇒ Other techniques to measure the absorption
The absorption coefficient is often measured indirectly

- Example: Soft X-rays $\sim$ 50-2000eV

**Idea:** Every additionally absorbed photon, for example due to the $2p \rightarrow 3d$ transition, produce additional electrons (Photo el., AUGER and *secondaries*) and **fluorescence photons**

- Higher absorption $\Rightarrow$ more electrons (fluorescence photons)

Typical sampling depth:
- Transmission: like $\xi$
- TEY: $\approx$0.5-3nm
- TFY: $\approx$30-200nm
Helical Undulator

$\Delta t \sim 2 \text{ ns}$

You need tunable polarized soft X-rays $\rightarrow$ Synchrotron radiation

Global Synchrotron Density

$10^8 \times$ more brilliance than x-ray tubes
For dynamic investigations ➔ time structure of synchrotron radiation

Single Bunch Mode

\[ I = \leq 25 \text{ mA} \]

\[ T = 800 \text{ ns} \]

available only for 2 x 2 weeks/a

Pulse width down to 10 psec

multi-bunch mode:
348 buckets (~ 0.75 mA)
+ “camshaft” (~ 10 mA)

\[ I = 200-300 \text{ mA} \]

standard operation mode
Now we go for Magnetism

- As magnetism is related to angular motion, why not using an “angular” probe?
- We will use circular polarized X-rays!
XMCD: X-ray Magnetic Circular Dichroism

• In other words: Sample magnetization changes the absorption of X-rays
  • Sometimes a rather dramatic effect

• Pathway
  • What is XMCD?
  • How does it look like? Example: Fe Metal
  • How is it used? Quantitative! \(\rightarrow\) sum rules
  • Can we understand this? Somehow!

Actually: First observed by Gisela Schütz in 1987
Director MPI for Intelligent Systems
Again: How to get polarized X-rays?

1. Bending magnet

2. Undulator

We also need „optical“ components
How does it look exactly for soft x-rays

- typical setup for soft x-rays (100-2000eV)

Planar grating (approx 1000 lines/mm) for about 0.5-10 nm wave length

Ultra-High-Vacuum! $\approx 10^{-10}$ mBar
Measurement of the absorption coefficient $\mu \Rightarrow$ now depending on the sample magnetization

\[ I_\pm(x) = I_0 \exp(-d \mu_\pm) \]

\[ \Delta \mu = \mu^+ - \mu^- \sim \Delta(P \cdot M) \]

Magnetic circular dichroism: XMCD
XMCD: element specific, as XAS is!

Element specific, due to the defined energy of the absorption edges!
Magnetism has a strong impact on the absorption coefficient!

XMCD strongly modifies the X-ray optical properties
Magneto-Optic-Effects: Origin (also for XMCD :=)

Start: Hunds rules  
Groundstate: Simplest example 3d¹  
L = 2 ; S = ½  and J = L - S = 3/2

For T→ 0 and B→ ∞ only m_J = -2 +1/2 = -3/2 is occupied (saturated)

Dipole-Selection-Rules: Δl = ±1 ⇒ circular Pol.: Δm_J = ±1

• This is a very general approach!
• Could be done in resonance or off resonance

Take home message:
For circular polarization absorption is modified by magnetism!
This is how the L2 and L3 edge excitations are using right circular polarized light!

• Schematics of the excitation:

Flipping the magnetization gives different excitation probabilities

\[ \Delta l = +1 \]
\[ \Delta j = 0, \pm 1 \]
\[ \Delta m = +1 \]


Flipping the magnetization gives different excitation probabilities
One example: SmCo$_5$ doped with some Fe

• The magnetic moment of each element could be extracted separately

• Good for the understanding of magnetism in complex systems

• Sample has been modified to change the coercive behavior ➔ Sm is responsible for that!

Schütz, Goering, Stoll, Int. J. Mat. Sci. 102 (2011) 773
XMCD in 3d Transition Elements

Spin orbit splitting of 2p shell decreases from Cu to Ti
Width increase ➞ more unoccupied electrons
Now it happens: Sum rules

Orbital L and Spin S XMCD

„Real“ Spectra (Fe)

\[ \text{Real XMCD Spektrum} \]

\[ \text{Photonenergie [eV]} \]

\[ \text{Reales XMCD Spektrum} \]

\[ \text{XMCD} \]

\[ \text{XAS} \]

\[ \Delta E_{\text{s.o.}} \]

\[ \frac{(\mu^+ + \mu^-)}{2} \]

\[ A(L_2) \]

\[ A(L_3) \]

\[ \mu^+ - \mu^- \]

pure S

pure L

\[ \text{Röntgenenergie } E_\gamma \]
XMCD is famous because its quantitative: Sum-Rules

- Quantitative determination of projected magnetic moments
  - S, L and T_z separable
  - in projected Bohr-magnetons!
- One needs the “areas” and the number of holes
  - \((10-n_{3d})\)

We will see T_z later more!


Exp. verification and rough procedure: C.T. Chen et al, PRL 75 (1995) 152
Data measurement and analysis: Co thin film!

Measure sample current $I_1$ and incoming intensity $I_0$ for north and south field

**Step 1:** Divide them $I_1/I_0$

north and south means field orientation with respect to the photon beam!
Data measurement and analysis

**Step 2:** Remove „offset“ by a simple factor

Important: Make sure that pre- and Post-Edge region (without XMCD) are equal

Here the factor is 1.04
Data measurement and analysis

**Step 3:** Subtract background by a linear approximation

Important: Exactly the same for north and south spectra

![Graph showing Co 2p > 3d transition and L2,3 subtractions for South and North spectra.](image)
Data measurement and analysis

**Step 4:** Divide by post edge value to normalize

Important: Exactly the same value for north and south spectra

Now the data is so called edge normalized!

Here 0.425
Data measurement and analysis

**Step 5:** Plot together with difference XMCD = North-South

![Graph showing Co 2p > 3d L2,3](image)
Data measurement and analysis

**Step 6:** For **sum rule** analysis remove non resonant background and calculate the “non magnetic” average. This does not change XMCD signal.
Data measurement and analysis

Step 7: Calculate the integrals for XAS (= nonmagnetic) and XMCD

\[ \text{XAS Integral} \]

\[ \text{XMCD (L}_2\text{)} = -1.169 \]

\[ = -3.684 \]

\[ = 2.515 \]

\[ \text{XAS} = 13.77 \]
Data measurement and analysis

Step 8: Sum Rules Calculation: Use values in formula

\[ \langle L_z \rangle = \frac{4}{3} \cdot \frac{+}{2} \cdot (10 - n_{3d}) \]

\[ \langle S_z \rangle + 7 \cdot \langle T_z \rangle = -\frac{-2}{2} \cdot (10 - n_{3d}) \]

\[ XAS = 13.77 \]
\[ XMCD (L_3) = -3.684 \]
\[ XMCD (L_2) = 2.515 \]
\[ 1 - n_{3d} (Co) = 2.49 \]

\[ \langle L_z \rangle = -\frac{4}{3} \cdot \frac{-3.64 + 2.515}{2 \cdot 13.77} \cdot 2.49 = 0.14 \]

\[ \langle S_z \rangle + 7 \cdot \langle T_z \rangle = -\frac{-3.64 - 2 \cdot 2.515}{2 \cdot 13.77} \cdot 2.49 = 0.785 \]
Data measurement and analysis

**Step 9:** Correct for finite degree of circular polarization

Depends on Energy, setup, beamline, source as bending or undulator etc. etc. ➔ usually ask the beamline responsible

In our case here 84%!

Using the g-factor of 2 for the spin and transfer from angular momenta to magnetic moments

\[
\langle m_L^z \rangle = \frac{\langle L_z \rangle}{0.84} \cdot \mu_B = \frac{0.14}{0.84} \cdot \mu_B = 0.17 \mu_B
\]

\[
\langle m_S^z \rangle = 2 \cdot \frac{\langle S_z \rangle}{0.84} \cdot \mu_B = 2 \cdot \frac{0.785}{0.84} \cdot \mu_B = 1.87 \mu_B
\]

The deviation here is because of Tz!

<table>
<thead>
<tr>
<th>Element</th>
<th>exp. (XMCD)</th>
<th>theo.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m_s (\mu_B)</td>
<td>m_l (\mu_B)</td>
</tr>
<tr>
<td>Fe</td>
<td>1.98</td>
<td>0.085</td>
</tr>
<tr>
<td>Co</td>
<td>1.55</td>
<td>0.153</td>
</tr>
<tr>
<td>Ni</td>
<td>0.58</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Chen PRL 75

Dhesi PRB 60
Sum-Rules Hands On

- Try to estimate the areas using a rule and a pen.

Co 2p > 3d

\[ \langle I_z \rangle = \frac{4}{3} \cdot \frac{\sqrt{2}}{} + \cdot (10-n_{3d}) \cdot \mu_B \]

\[ \langle S_z \rangle + 7 \cdot (I_z) = -2 \cdot \frac{\sqrt{2}}{} \cdot (10-n_{3d}) \cdot \mu_B \]
Estimating area by FWHM x Height or as you want

\[ \text{Co } 2p > 3d \]

\[ L_{2,3} \]

\[ \frac{L_i}{L_0} \text{ (edge norm)} \]

\[ \langle L_z \rangle = 0.14 \mu_B \]

\[ \langle S_z \rangle + 7 \cdot \langle T_z \rangle = 1.57 \mu_B \]
Data measurement and analysis

Typical pitfall: Offset corrected with wrong factor

Best visible in a finite slope in the XMCD integral
If present ➔ better factor
Why using a single factor for Offset correction?

Electron current depends on B-field dependent proportionality.

Could be asymmetric

\[ I(E_{\text{phot}}, B) = f(B) \cdot \mu(E_{\text{phot}}, B) \]

\[ \mu(E_{\text{phot}}, B^+) = \mu_0(E_{\text{phot}}) + \mu_c(E_{\text{phot}}|B|) \]

\[ \mu(E_{\text{phot}}, B^-) = \mu_0(E_{\text{phot}}) - \mu_c(E_{\text{phot}}|B|) \]

\[ \Delta I(E_{\text{phot}}, B) = f(B^+) \cdot \left[ \mu_0(E_{\text{phot}}) + \mu_c(E_{\text{phot}}|B|) \right] - f(B^-) \cdot \left[ \mu_0(E_{\text{phot}}) - \mu_c(E_{\text{phot}}|B|) \right] \]

\[ = \left[ f(B^+) - f(B^-) \right] \cdot \mu_0(E_{\text{phot}}) + \left[ f(B^+) + f(B^-) \right] \cdot \mu_c(E_{\text{phot}}|B|) \]

if \( f(B^+) = f(B^-) = f(B) \):
\[ \Delta I(E_{\text{phot}}, B) = 2 \cdot f(B) \cdot \mu_c(E_{\text{phot}}|B|) \]

\[ \Delta I(E_{\text{phot}}, B) \]

if \( f(B^+) \neq f(B^-) \) choose \( k \) as \( f(B^+) = k \cdot f(B^-) \)

As \( \mu_0 \) is not a straight line, a line offset subtraction is wrong!

Sum Rules: In general for all edges!

\[ \frac{-\int_{j_+ + j_-} (\mu^+(E) - \mu^-(E)) \cdot dE}{\int_{j_+ + j_-} (\mu^+(E) + \mu^-(E) + \mu^0(E)) \cdot dE} = a \cdot \frac{\langle L_z \rangle}{n_h} \]

\[ -\left( \int_{j_+} (\mu^+(E) - \mu^-(E)) \cdot dE \right) - b \cdot \int_{j_-} (\mu^+(E) - \mu^-(E)) \cdot dE \]

\[ \frac{\int_{j_+ + j_-} (\mu^+(E) + \mu^-(E) + \mu^0(E)) \cdot dE}{n_h} = c \cdot \langle S_z \rangle + d \cdot \langle T_z \rangle \]

This is the absorption sum for all absorption channels: \( \mu = \text{left}, \) \( \mu = \text{right}, \) and \( \mu^0 = \text{z-polarized light} \)

Angular momenta for the \( i = \text{initial} \) and \( f = \text{final states} \)

From Schütz, Stoll, and Goering Handbook of Magnetism (Wiley)
What is this $T_z$?

perturbation theory provides: $T_z \approx -\frac{2}{7} \cdot Q \cdot \hat{S}$

$Q$: quadrupolar charge distribution
traceless tensor 2$^{\text{nd}}$ order

$T_z = 0$

$T_z \neq 0$

Is important in less than cubic systems, with oriented crystals, in 4f metals, and in ultra thin films and interfaces

Something more about $T_z$: König and Stöhr, PRL 75 (1995) 3748; Buck and Fähnle, JMMM 166 (1997) 297
Further “Problems”

- For the light 3d transition metals, it’s hard to separate $P_{3/2}$ and $P_{1/2}$ excitations $\Rightarrow$ excitations “mix”

  see: E. Goering, Phil. Mag. 85 (2005) 2897-2911 and references therein

- In 4f systems, as supermagnets, the spin-sum-rule is not „simply“ valid anymore (orbital works fine)


- Actually, we are working on this at the moment, and it looks to be solvable, at least in a practical way.
2013 we could inaugurate our “new” 7T XMCD system!

- ANKA-Karlsruhe
  @ WERA-Beamline

- Unique superconducting magnet system
- 7T ramped with 1.5T/s! (-5T → +5T in 6.6s)
  - low temperatures, portable, “load lock”
  - TEY, FY, Transmission → parallel
  - No L-He refill → two “cryo-coolers”
  - Gives enough signal to detect paramagnetism of diluted systems → now 0.0002µ₀ sensitivity
  - Fast XMCD measurements with highest quality → 2-5 min/spectra
XMCD at the „recent“ limit: 0.2ML paramagnetic Ni on Graphen

In-situ prepared Ni nanostructures (3nm height):
0.2 ML nominal (@ 200 K) on Graphen/Ir Moiré-template

Cooperation with group of M. Fonin, Univ.-Konstanz

The oscillations are the so called EXAFS, which are usually not recognized, because they are so tiny! (for those who are interested)

Sicot et. al.: APPLIED PHYSICS LETTERS 96, 093115 2010
Questions:

1: Can we distinguish between pinned and rotatable moments?

2: Do we get a XMCD signal for a sample with permanent magnetic moments but disordered?

3: What do we get, if we have the same magnetic atoms, but half the amount? As Fe-XMCD for Fe \(\rightarrow\) FeCo alloy

Remember:

\[ \Delta \mu = \mu^+ - \mu^- \sim \Delta (P \cdot M) \]

**X-ray magnetic circular dichroism: XMCD**