

Dichroism in x-ray spectra

XLD, XMCD, XMLD, and all that jazz

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Outline

X-ray absorption spectroscopy: recalling the basic facts

Polarization of x-rays

X-ray linear dichroism: what it can be good for

X-ray magnetic circular dichroism: benefits and risks

X-ray magnetic linear dichroism: not so common but useful

Non-collinear systems: tasting via a case study

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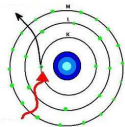
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X-ray absorption spectroscopy

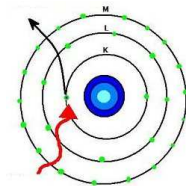
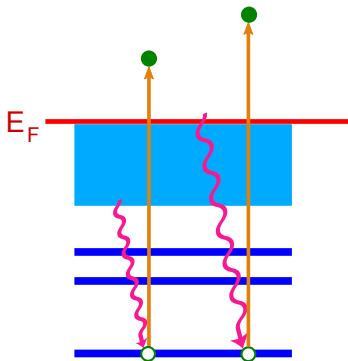
- ▶ X-rays go in, x-rays go out, absorption coefficient is measured as a function the energy of incoming x-rays.



- ▶ Focusing on energies where most of the absorption (or rather most of its variation with the energy) goes on account of the photoelectric effect on core electrons.

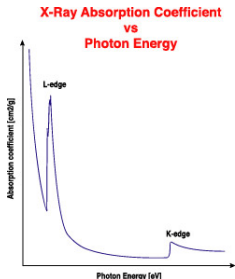
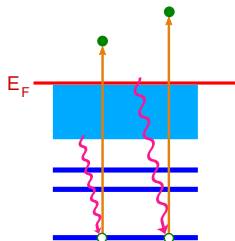


Absorption via core electron excitation



X-ray absorption spectrum (XAS) probes the unoccupied states as seen from a certain well-defined location.

Chemical selectivity



absorption edge	core level
K	1s
L ₁	2s
L ₂	2p _{1/2}
L ₃	2p _{3/2}

If the energy of incoming x-rays is large enough to excite another core electron, the absorption coefficient suddenly increases.

- ▶ Close to this jump, photoelectric effect on electrons arising from **just one core level** will dominate.
- ▶ Chemical sensitivity of XAS originates from the same mechanism as the characteristic spectrum.

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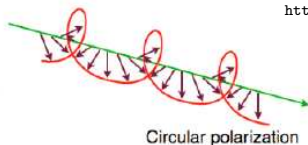
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X-ray polarization vectors

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 e^{i(\mathbf{q}\mathbf{r} - \omega t)} \quad \mathbf{A}_0 \perp \mathbf{q}$$

- \mathbf{q} x-rays wave vector ("the direction where the light comes from")
 \mathbf{A}_0 amplitude of the x-rays (specifies the polarization vector ϵ)
 ω frequency of the x-ray wave ($E = \hbar\omega$, $cq = \hbar\omega$)



<http://www.spring8.or.jp>

$$\mathbf{A} = \hat{\epsilon} A_0 e^{i(\mathbf{q}\mathbf{r} - \omega t)}$$

$$\mathbf{A} = \frac{1}{\sqrt{2}} (\hat{\epsilon}_x \pm i \hat{\epsilon}_y) A_0 e^{i(\mathbf{q}\mathbf{r} - \omega t)}$$

(in case that $\mathbf{q} \parallel \hat{z}$)

Interaction of radiation with electrons

relativistic: $H_{\text{int}} = -e \boldsymbol{\alpha} \cdot \mathbf{A}$
($\boldsymbol{\alpha}$ is the Dirac α -matrix)

nonrelativistic: $H_{\text{int}} = -\frac{e}{m c} \mathbf{p} \cdot \mathbf{A}$

\mathbf{A} contains the polarization vector $\boldsymbol{\epsilon}$ of the incoming x-rays.

$$A_0 \left\{ \frac{1}{\sqrt{2}} (\hat{\boldsymbol{\epsilon}}_x \pm i \hat{\boldsymbol{\epsilon}}_y) \right\} e^{i \mathbf{q} \cdot \mathbf{r}} e^{-i \omega t} \quad \begin{array}{l} \text{linearly polarized} \\ \text{circularly polarized } \mathbf{q} \parallel \hat{\mathbf{z}} \end{array}$$

Taylor expansion: $e^{i \mathbf{q} \cdot \mathbf{r}} = 1 + i \mathbf{q} \cdot \mathbf{r} + \frac{1}{2} (i \mathbf{q} \cdot \mathbf{r})^2 + \dots$

Dipole and quadrupole transitions

Taylor expansion: $e^{i\mathbf{q}\cdot\mathbf{r}} = 1 + i\mathbf{q}\cdot\mathbf{r} + \frac{1}{2}(i\mathbf{q}\cdot\mathbf{r})^2 + \dots$

Dipole term (nonrelativistic):

$$e^{i\mathbf{q}\cdot\mathbf{r}} = 1$$

$$M_{fi} \approx \langle \psi_f | \boldsymbol{\epsilon} \cdot \mathbf{r} | \psi_i \rangle$$

Intensity of dipole transitions depends on the direction of the polarization vector $\boldsymbol{\epsilon}$, **not** on the direction of the incoming x-rays.

Quadrupole term (nonrelativistic):

$$\dots + i\mathbf{q}\cdot\mathbf{r}$$

$$M_{fi} \approx \langle \psi_f | \boldsymbol{\epsilon} \cdot \mathbf{r} \mathbf{q} \cdot \mathbf{r} | \psi_i \rangle$$

Intensity of quadrupole transitions depends on the direction of the polarization vector $\boldsymbol{\epsilon}$ **and** on the direction of the incoming x-rays \mathbf{q} .

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Linearly polarized x-rays



drawing G. Waychunas

- ▶ By varying the direction of the x-rays' polarization vector ϵ , one probes the **local environment in different directions**.
- ▶ **X**-ray **l**inear **d**ichroism (XLD):

$$\text{XLD} = \sigma(\epsilon_1) - \sigma(\epsilon_2)$$

$\sigma(\epsilon)$ is the absorption coefficient for photon polarization ϵ .
Usually $\epsilon_1 \perp \epsilon_2$.

- ▶ The dichroism may have a **geometric** as well as a magnetic component.
Focus on the geometry for now.

General relation for linearly polarised spectra

Spherical tensor formalism can be used to get the explicit form of the angular dependence [Brouder, JPCM 2, 701 (1990)]

$$\sigma = \sum_{ij} \hat{\epsilon}_i \hat{\epsilon}_j X_{ij}^{(\text{dip})} + \sum_{ijmn} \hat{\epsilon}_i \hat{\epsilon}_j \hat{q}_m \hat{q}_n X_{ijmn}^{(\text{qdr})} .$$

The components of the cartesian tensors $X_{ij}^{(\text{dip})}$, $X_{ijmn}^{(\text{qdr})}$ are not independent of each other. Number of **independent spectral components** depends on the **symmetry**.

For systems which have a rotation axis of order greater than two, we have a pure **dichroism** for dipole transitions, i.e., there are **two** independent spectral components. The dependence of the cross-section on the angle θ between the rotation axis and the polarisation vector can be described as

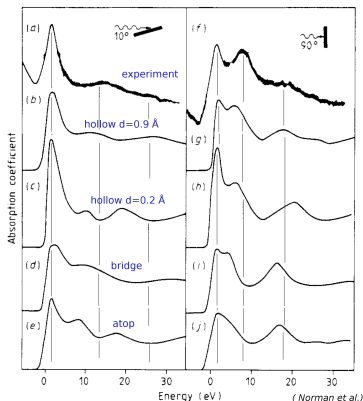
$$\sigma^{(\text{dip})} = \sigma_{\parallel}^{(\text{dip})} \cos^2 \theta + \sigma_{\perp}^{(\text{dip})} \sin^2 \theta .$$

Benefits of x-ray linear dichroism (XLD)

- ▶ **More data** means **more information**.
- ▶ Dealing with polarized spectra (i.e., with both XAS and XLD) means that we have got more data.
- ▶ Best-fitting polarized spectra leads to **more reliable** results.
- ▶ Polarized spectra present **more stringent** test to the theory.
 - ▶ If you want to show that your theory works, stay away from polarized spectra! 😊
- ▶ Dipole and quadrupole transitions exhibit different polarization dependence \Rightarrow inspecting the polarization dependence (a.k.a. the angular dependence) of the spectra can **distinguish between dipole and quadrupole** transitions.

Using XANES simulation to find the adsorption site

Having more spectra means having more data, diminishing thus the ambiguity in structural fitting.



Adsorption
of O on Ni(100)

Polarized spectra calculated by
assuming that the O atom is sitting
in various adsorption sites.

The winner is the hollow site
with vertical distance $d=0.9 \text{ \AA}$.

Vvedensky *et al.* J. Phys. C: Solid State Phys. **19** 3273 (1986)

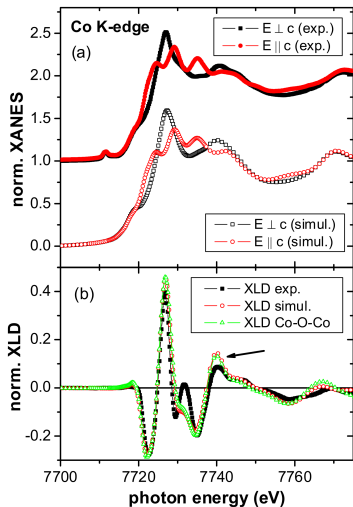
Localization of impurities in the bulk

ZnO doped by Co atoms.

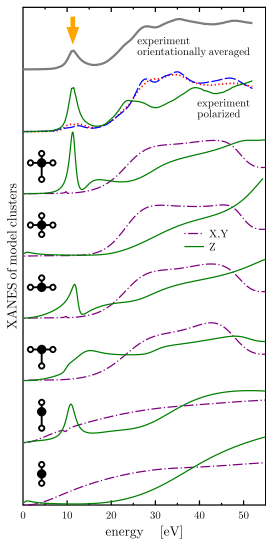
Are the Co atoms sitting in a substitutional or an interstitial position?

Comparison of experimental and theoretical Co *K* edge XLD provides a convincing proof that **Co atoms** are located in **Zn-substitutional sites**.

Ney *et al.* PRL 100, 157201 (2008)



Links between structural units and XAS features

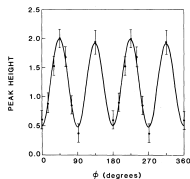
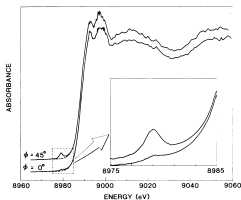


V K-edge of V_2O_5

The dominant sharp peak at the onset of the spectrum is formed only if the nearest neighbourhood of the V atom is asymmetric and a very short V-O bond parallel to the \hat{z} direction is present.

Šipr *et al.* PRB **60** 14115 (1999)

Identifying the quadrupole transitions



Hahn *et al.* CPL **88**, 595 (1982)



CuCl4

The angular (or, equivalently, polarization) dependence of the spectrum is different for dipole and quadrupole transitions:

$$\sigma(\phi) = \sigma_0^{(\text{dip})} + \sigma_0^{(\text{qdr})} + \sigma_1^{(\text{qdr})} \cos 4\phi .$$

The CuCl4 complex has a D_{4h} symmetry \Rightarrow the dipole transitions do not depend on the azimuthal angle ϕ .

The height of the pre-peak oscillates with a **four-fold** periodicity, consistently with the angular dependence of the **quadrupole** transition for the respective symmetry.

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Circularly polarized light: conventions

Ambiguity in conventions: **left-** and **right-**circularly polarized light.

In optics, the prevailing convention is:

$$\begin{aligned} \frac{1}{\sqrt{2}} (\hat{\epsilon}_x + i \hat{\epsilon}_y) & \quad \text{left circularly polarized photon} \\ \frac{1}{\sqrt{2}} (\hat{\epsilon}_x - i \hat{\epsilon}_y) & \quad \text{right circularly polarized photon} \end{aligned}$$

To by-pass the conventions ambiguity, use helicity instead.

The helicity is the projection of the particle spin along the direction of its motion.

In optics, the prevailing convention is:

$$\begin{aligned} \text{positive helicity } (+\hbar) & \quad \text{left circularly polarized photon} \\ \text{negative helicity } (-\hbar) & \quad \text{right circularly polarized photon} \end{aligned}$$

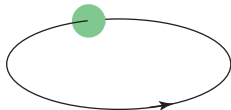
It is enough to remember that there is ambiguity in definitions.

Spin and orbital magnetic moments of electron

- ▶ Spinning: μ_{spin}
usually large, $\sim 2.2 \mu_B$ for Fe
its magnitude does not depend on the direction



- ▶ Orbiting: μ_{orb}
usually small, $\sim 0.1 \mu_B$ for Fe
its magnitude depends on the direction



μ_{orb} is small but important, among others, because of its links to magnetocrystalline anisotropy.

Recall the Bruno formula: $E_{\text{MCA}} \sim \mu_{\text{orb}}^{\parallel} - \mu_{\text{orb}}^{\perp}$.

Spin-orbit coupling

Spin-orbit interaction (SOC) is a **relativistic effect**, it follows from the Dirac equation.

Schrödinger equation: SOC can be incorporated as a perturbation,

$$V_{\text{SO}} \approx \frac{1}{r} \frac{dV(r)}{dr} (\mathbf{L} \cdot \mathbf{S}) .$$

- ▶ Spin-orbit interaction is large for **core electrons**.
- ▶ Spin-orbit interaction is large for **heavy elements**.

SOC is the only way the magnetic moment direction is **coupled to the crystal lattice**.

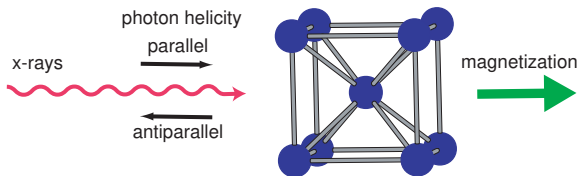
Low-dimensional systems and magnetism

- ▶ Low-dimensional systems have on average smaller coordination number than bulk systems.
 - ▶ Lower coordination number means **larger magnetic moment** per atom.
- ▶ Low-dimensional systems have **large magnetocrystalline anisotropy** per atom.
- ▶ Investigating magnetism of clusters is **difficult** because of **small amount of material**.
 - ⇒ Chemically-specific spectroscopic methods such as XAS are in high demand.

$$\text{XMCD} = \text{XAS} - \text{XAS} + \text{magnetization} + \text{SOC}$$

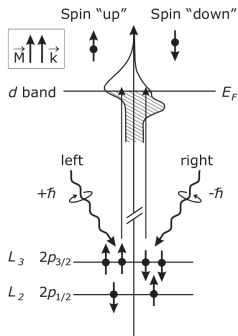
X-ray **M**agnetic **C**ircular **D**ichroism: $\sigma_{\text{XMCD}} = \sigma_{\text{XAS}}^{(+)} - \sigma_{\text{XAS}}^{(-)}$

Difference between absorption of left- and right-circularly polarized x-rays in a magnetic sample.



Spin-orbit coupling (SOC) is **necessary** for XMCD.

Origin of XMCD: quick and dirty

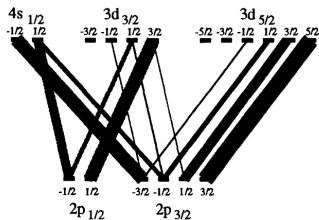


Sorg, PhD thesis (2005)

1. Angular momentum of the photon interacts with the spin of the electron by means of the SOC (Fano effect).
 - ▶ Right- and left-circularly polarized photons carry opposite momentum \Rightarrow there is a **spin imbalance** in the photocurrent produced by the right- and left-circularly polarized x-rays.
2. Valence band acts as a **spin detector** for the (spin-imbalanced) photocurrent.

To get XMCD, you need **SOC** and **magnetism**.

Origin of XMCD: a bit more formal



Line thickness represents the matrix elements for transitions from L_2 and L_3 edges for the left circularly polarized light.

Ebert: Spin-Orbit-Influences Spectroscopies (1996)

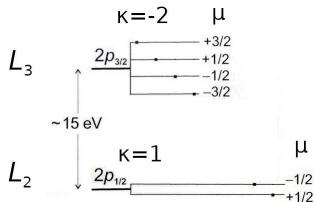
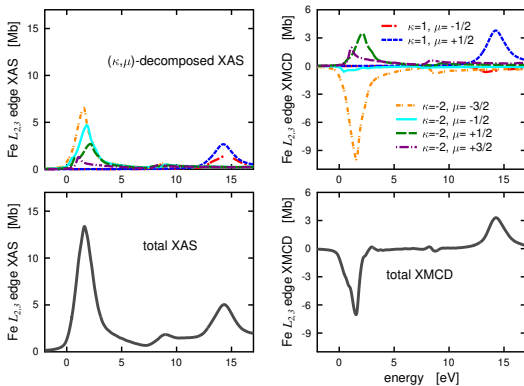
SOC makes radial wave functions dependent on the relativistic magnetic quantum number $\mu \Rightarrow$ transition probabilities depend on μ of initial and final states.

Magnetic order makes the numbers of available final states for (κ, μ) and $(\kappa, -\mu)$ different.

For transitions from the s states, XMCD is due to the SOC among the final p states.

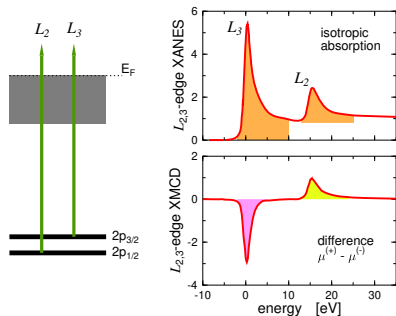
XMCD for K levels is by order of magnitude smaller than for the $L_{2,3}$ levels.

Anatomy of an XMCD spectrum



- ▶ SOC splitting is between states with different κ (L_2 and L_3 edges).
- ▶ Exchange splitting is between states with same κ but different μ .

XMCD sum rules: the basics



XMCD sum rules:

By adding, subtracting and dividing the peak areas, **chemically-specific** μ_{spin} , μ_{orb} , and $\mu_{\text{orb}}/\mu_{\text{spin}}$ can be obtained

$$\int (\Delta\sigma_{L_3} - 2\Delta\sigma_{L_2}) dE \sim \frac{\mu_{\text{spin}}^{(d)} + 7T_z^{(d)}}{3n_h^{(d)}}$$

$$\int (\Delta\sigma_{L_3} + \Delta\sigma_{L_2}) dE \sim \frac{\mu_{\text{orb}}^{(d)}}{2n_h^{(d)}}$$

$n_h^{(d)}$ number of holes in the d band

T_z magnetic dipole term (see below)

More on the XMCD sum rules

Derived assuming:

- ▶ One can isolate the transitions to the $3d$ shell (as in the atom).
- ▶ Only dipole transitions are important.
- ▶ Transitions from the $2p$ states to the s states can be ignored.
- ▶ The energy of core levels does not depend on μ .
- ▶ Radial parts of the $2p_{1/2}$ and $2p_{3/2}$ wave functions are identical.
- ▶ ...

For practical applications, the ultimate problem is the requirement to focus just on transitions to the $3d$ shell (or to another **isolated** shell).

Core hole: the influence of the core hole is “integrated out”. Integrated quantities probe the initial states, **without** the core hole.

Sum rules and the geometric approach to μ_{orb}

Intuitive definition of orbital magnetization as

$$\mathbf{M}_{\text{orb}} = -\frac{e}{2cV} \sum_n f_n \langle \psi_n | \mathbf{r} \times \mathbf{v} | \psi_n \rangle$$

is formally consistent only for finite systems.

Geometric approach to orbital magnetization exploits concepts such as the **Berry phase**.

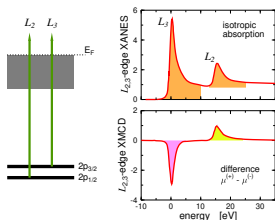
$$\mathbf{M}_{\text{orb}} = -\frac{e}{2\hbar c} \text{Im} \sum_n \int \frac{d\mathbf{k}}{(2\pi)^3} f_{nk} \langle \frac{\partial u_{nk}}{\partial \mathbf{k}} | \times (e^{-i\mathbf{k}\cdot\mathbf{r}} H e^{-i\mathbf{k}\cdot\mathbf{r}} + E_{nk} - 2\mu) | \frac{\partial u_{nk}}{\partial \mathbf{k}} \rangle$$

$\psi_{nk} = \exp(i\mathbf{k}\cdot\mathbf{r})u_{nk}$; f_{nk} = occupation number; μ = chemical potential.

Using these concepts, ~~x-ray~~ magneto-optical sum rules can be derived connecting integrals of ~~x-ray~~ magneto-optical dichroism spectra with quantities derived from the electronic structure [Kuneš & Oppeneer PRB **61**, 15774 (2000), Resta PRRResearch **2**, 023139 (2020)].

Interesting and revealing from a fundamental points of view but *no practical implications* (yet?).

Validity of sum rules: theory against theory

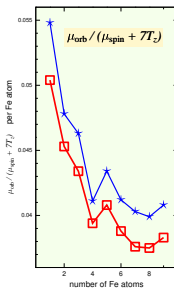
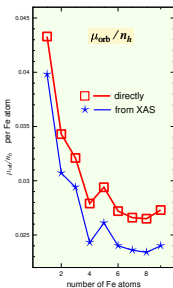
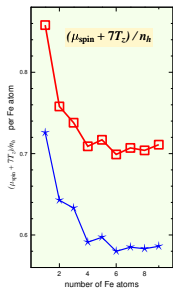


$$\int (\Delta\sigma_{L_3} - 2\Delta\sigma_{L_2}) dE \sim \frac{\mu_{\text{spin}}^{(d)} + 7T_z^{(d)}}{3n_h^{(d)}}$$

$$\int (\Delta\sigma_{L_3} + \Delta\sigma_{L_2}) dE \sim \frac{\mu_{\text{orb}}^{(d)}}{2n_h^{(d)}}$$

- ▶ Calculate the XAS and XMCD spectra
- ▶ Evaluate the integrals of the theoretical spectra
- ▶ Compare the results with magnetic moments obtained directly from electronic structure calculations.

Validity of sum rules: the trends



$\text{Fe}_N/\text{Ni}(001)$

Šipr *et al.* EPL 87, 67007 (2009)

- ▶ **Trends** of the “effective moments” $(\mu_{\text{spin}} + 7T_z)/n_h$ and μ_{orb}/n_h are reproduced well.
- ▶ Particular values of μ_{spin} and μ_{orb} are less reliable.
- ▶ Applying sum rules to a series of related systems (such as supported clusters) makes sense.

μ_{spin} comes only in combination with $7T_z$ 😞

XMCD sum rule for the $L_{2,3}$ -edge spectra:

$$\frac{\mu_{\text{spin}} + 7T_z}{n_h} \sim \int (\Delta\sigma_{L_3} - 2\Delta\sigma_{L_2}) dE$$

Magnetic dipole term: $T_z = \langle \hat{T}_z \rangle = \langle \frac{1}{2} [\boldsymbol{\sigma} - 3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \boldsymbol{\sigma})]_z \rangle$

Magnetic dipole term **depends on the orientation of the magnetization** (therefore " T_α "):

If magnetic field is oriented
along the x axis or the y axis:

$$T_x = \langle \hat{T}_x \rangle = \langle \frac{1}{2} [\boldsymbol{\sigma} - 3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \boldsymbol{\sigma})]_x \rangle$$

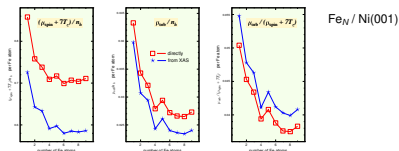
$$T_y = \langle \hat{T}_y \rangle = \langle \frac{1}{2} [\boldsymbol{\sigma} - 3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \boldsymbol{\sigma})]_y \rangle$$

What to think about magnetic dipole T_α term?

- ▶ T_α is a measure of the intra-atomic **spin asphericity** (components of μ_{spin} resolved according to the magnetic quantum number m are not the same).
- ▶ For bulk systems T_α is usually negligible (unless you deal with actinides with huge SOC. . .).
- ▶ For surfaces, monolayers or wires, $7T_\alpha$ can easily amount to about 20 % of μ_{spin} .
 $\Rightarrow T_\alpha$ matters for low-dimensional systems!

Do we really need to care about T_z ?

- ▶ For investigating **trends** of magnetism for a series of systems, what matters is how T_z varies from one system to another.
 - ▶ If **variations** in T_z are small, T_z can be neglected (it would cause just an overall shift of the deduced values of μ_{spin}).
 - ▶ Can T_z vary in such a way that the **overall trends** of $\mu_{\text{spin}} + 7T_z$ and μ_{spin} would be quite **different** ?



Things were good for Fe_N clusters on Ni(001) but will it be always like this?

Case study: several sets of supported clusters

- ▶ For each cluster, evaluate average μ_{spin}

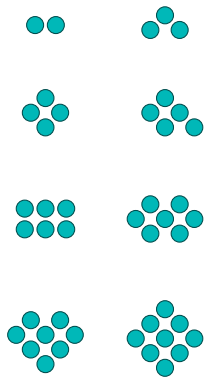
$$\frac{1}{N} \sum_{j=1}^N \mu_{\text{spin}}^{(j)}$$

and average XMCD-rules-related-quantity $[\mu_{\text{spin}} + 7T_z]/n_h$

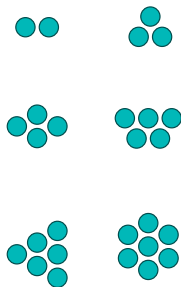
$$\frac{1}{N} \sum_{j=1}^N \frac{\mu_{\text{spin}}^{(j)} + 7T_z^{(j)}}{n_h^{(j)}} .$$

- ▶ Compare **how** μ_{spin} and $[\mu_{\text{spin}} + 7T_z]/n_h$ **depend on the cluster size.**

Compact Fe_N and Co_N clusters on metal surfaces

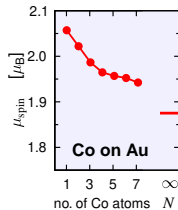
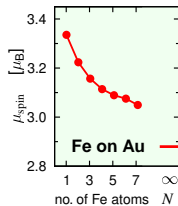
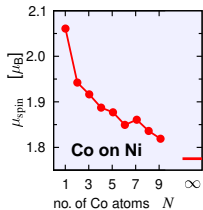
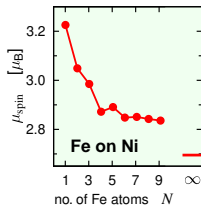
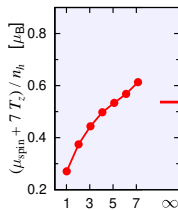
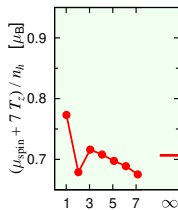
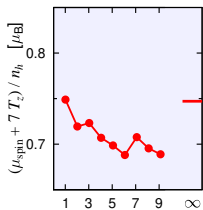
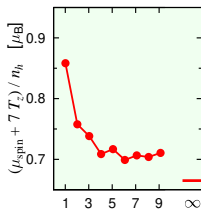


Clusters on Ni(001)
 $N=1-9$



Clusters on Au(111)
 $N=1-7$

Results: μ_{spin} and $[\mu_{\text{spin}} + 7T_z]/n_h$ for compact clusters



Fe_N/Ni(001)

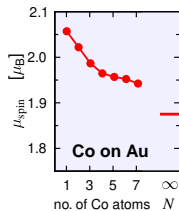
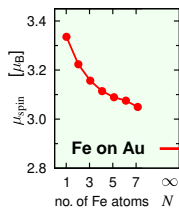
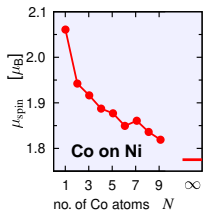
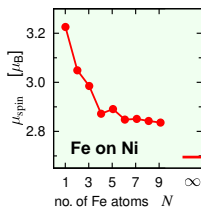
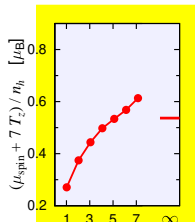
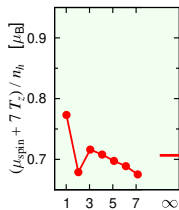
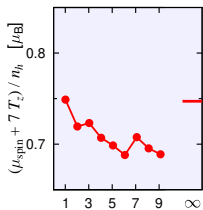
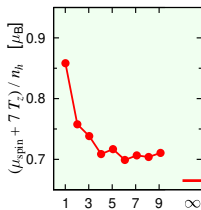
Co_N/Ni(001)

Fe_N/Au(111)

Co_N/Au(111)

Šipr *et al.* EPL 87, 67007 (2009)

Results: μ_{spin} and $[\mu_{\text{spin}} + 7T_z]/n_h$ for compact clusters



Fe_N/Ni(001)

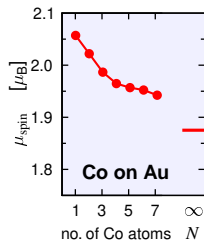
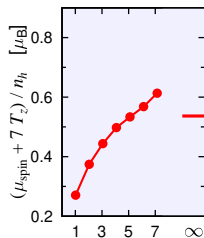
Co_N/Ni(001)

Fe_N/Au(111)

Co_N/Au(111)

Šipr *et al.* EPL 87, 67007 (2009)

Oops: T_z changes the picture for $\text{Co}_N/\text{Au}(111)$!

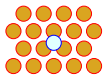


- ▶ For Co_N clusters on $\text{Au}(111)$, the trends of μ_{spin} and of $(\mu_{\text{spin}} + 7T_z) / n_h$ are opposite.
- ▶ Ignoring variations in T_z would lead to a false estimate of how μ_{spin} per atom depends on the cluster size.

T_α can falsely make μ_{spin} to look anisotropic

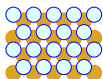
Co adatom and Co monolayer on Pd(111),
varying the direction of the magnetization.

adatom



	$\mu_{\text{spin}} [\mu_B]$	$\mu_{\text{spin}} + 7T_\alpha [\mu_B]$
$\mathbf{M} \parallel xy$	2.47	2.65
$\mathbf{M} \parallel z$	2.47	2.11

monolayer



	$\mu_{\text{spin}} [\mu_B]$	$\mu_{\text{spin}} + 7T_\alpha [\mu_B]$
$\mathbf{M} \parallel xy$	2.02	2.26
$\mathbf{M} \parallel z$	2.02	1.56

Šipr *et al.* PRB **88**, 064411 (2013)

One can get rid of T_α (or not?)

If the influence of SOC on T_α can be neglected, the T_α term can be eliminated from the spin moment sum rule

$$\int (\Delta\sigma_{L_3} - 2\Delta\sigma_{L_2}) dE \sim \frac{\mu_{\text{spin}}^{(d)} + 7T_z^{(d)}}{3n_h^{(d)}}$$

via a clever choice of the directions of the incoming light, either

- ▶ by measuring the XMCD for three directions of the incoming light, making use of the $T_x + T_y + T_z = 0$ relation (because μ_{spin} is nearly independent on the magnetization direction),

or

- ▶ by measuring the XMCD for the magic angle $\theta = 54^\circ$ (θ is the angle between the incoming light direction and the high-symmetry axis of the system).

[Stöhr & König PRL **75**, 3748 (1995), Crocombette *et al.* JPCM **8**, 4095 (1995), Stöhr JMMM **200**, 470 (1999), Šipr *et al.* PRB **88**, 064411 (2013)]

T_α and SOC: Case study for Co monolayers and adatoms

Verify whether the $T_x + T_y + T_z = 0$ relation holds.

Compare the $\frac{\sum_\alpha T_\alpha}{\mu_{\text{spin}}}$ quantity for different systems:

	monolayer	ad-atom
Co/Cu(111)	0.011	0.206
Co/Pd(111)	0.015	0.072
Co/Ag(111)	0.021	0.372
Co/Pt(111)	0.008	0.098
Co/Au(111)	0.009	0.284

SOC is *nominally* small but...

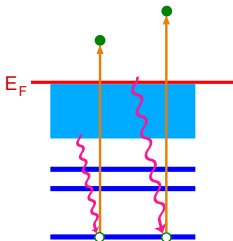
Šipr *et al.* PRB **94**, 144406 (2016)

What matters is not the absolute magnitude of the SOC strength ξ but how it compares to the crystal field splitting Δ_{CF} .

The verdict on T_α and the sum rules

- ▶ The T_α (a.k.a. T_z) term can alter the apparent dependence of μ_{spin} on the cluster size or cause that μ_{spin} falsely looks anisotropic.
- ▶ For small supported systems such as **ad-atoms and clusters**, the effect of SOC on T_α cannot be neglected.
 - ▶ The effect of T_z in the spin moment sum rule cannot be eliminated by using $T_x + T_y + T_z = 0$.
 - ▶ T_z -free XMCD measurement by means of exploiting the magic angle $\theta = 54^\circ$ cannot be employed.
- ▶ The T_α term is doomed to mess with the spin sum rule for low-dimensional systems.

Finite core hole lifetime



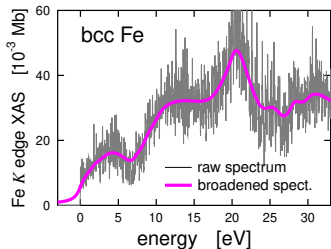
A hole in the core level is left by the ejected photoelectron.

The core hole will be eventually filled \Rightarrow its lifetime is not infinite.

Time-energy uncertainly relations:
 $\Delta E \cdot \Delta t > \hbar/2$

[For a formal derivation see, e.g., Messiah:
Quantum Mechics.]

Finite lifetime of the core hole means that the experimental spectra are broadened as if the core level had a finite width.



Broadening the calculated spectrum

Convoluting with a Lorentzian: $L(E) = \frac{1}{\pi} \frac{\Gamma/2}{E^2 + (\Gamma/2)^2}$ (Γ is FWHM).

XAS with the influence of the finite core hole lifetime included:

$$\sigma_{\text{broaden}}(E) = \int_{E_F}^{\infty} dE' \sigma_{\text{raw}}(E') L(E - E') .$$

If the **cut-off below E_F** is ignored, **convolution with a Lorentzian** is equivalent to calculating the spectrum for **energies with an added imaginary component**:

$$\int_{-\infty}^{\infty} dE' \sigma_{\text{raw}}(E') L(E - E') = \sigma_{\text{raw}}(E + i\Gamma/2) .$$

Problem with the Fermi energy cut-off

- ▶ Calculating XAS for energies with a small imaginary components has merits: the energy mesh does not have to be so dense.
- ▶ Calculating x-ray absorption spectra for energies with an added imaginary component is strictly **equivalent** to a convolution with a Lorentzian **only if there is no cut-off** of the spectra **below the Fermi level E_F** , i.e., in the limit $E_F \rightarrow -\infty$ [Vedrinskii *et al.* pssb 111, 433 (1982); Brouder *et al.* PRB 54, 7334 (1996)].
- ▶ Can employing an **imaginary energy** component to calculate the broadened spectrum introduce significant **artefacts**?

Shifting the emphasis between $\text{Im}E$ and Γ

Convoluting the spectrum by a Lorentzian with FWHM of Γ is equivalent^(*) to adding imaginary part $\text{Im}E = \Gamma/2$ to the photoelectron energy.

Convolution of two Lorentzians is again a Lorentzian, with FWHM

$$\Gamma = \Gamma_1 + \Gamma_2 .$$

⇒ One can **shift the weight of the broadening** between

1. adding an imaginary part $\text{Im}E$ to the energy and
 2. convoluting the raw spectrum with a Lorentzian of width Γ ,
- while keeping **total effective broadening** unchanged:

$$2\text{Im}E + \Gamma = \Gamma_{\text{total}} .$$

^(*) Apart from the E_F cut-off.

Fe $L_{2,3}$ -edge XAS and XMCD: the objective

$$2\text{Im}E + \Gamma = \Gamma_{\text{core}}$$

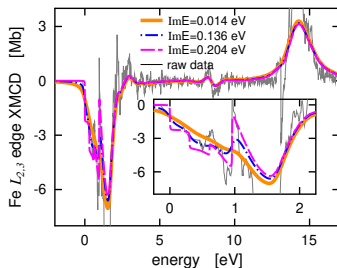
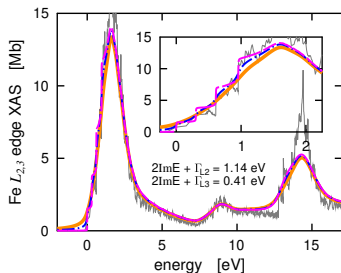
Check how shifting the burden of broadening from $\text{Im}E$ to Γ affects the final spectrum.

$\text{Im}E$	Γ_{L_2}	Γ_{L_3}	$2\text{Im}E + \Gamma_{L_2}$	$2\text{Im}E + \Gamma_{L_3}$
0.014	1.113	0.383	1.140	0.410
0.136	0.868	0.138	1.140	0.410
0.204	0.732	0.002	1.140	0.410

The total broadening corresponds to $\Gamma_{\text{core}} = 1.14$ eV for the L_2 edge and to $\Gamma_{\text{core}} = 0.41$ eV for the L_3 edge.

[Campbell & Papp At. Data Nucl. Data Tables 7, 1 (2001)]

Fe $L_{2,3}$ -edge XAS and XMCD: the results



Šipr *et al.* PRB **72**, 134406 (2005); J. Synch. Rad. **25**, 523 (2018)

[The *total* broadening is identical for all curves: $2\text{Im}E + \Gamma = \text{const.}$]

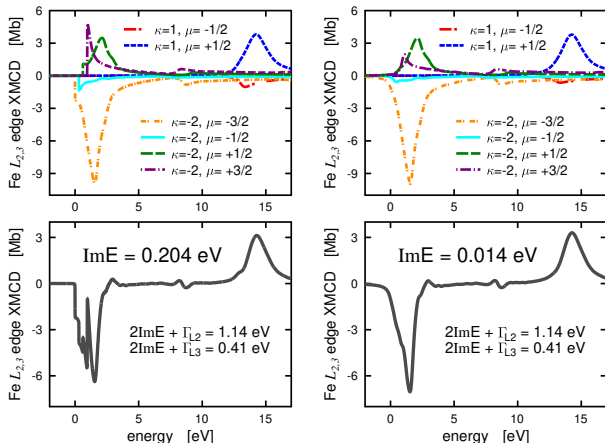
If substantial part of the broadening is done by adding an **imaginary** part to the energy, a **spurious doublet** appears at the L_3 edge XMCD peak.

The L_3 XMCD appears to be **hypersensitive** to the way the broadening is split between $\text{Im}E$ and Γ .

Resolving XMCD according to the (κ, μ) components

Relativistic
exchange splitting
of the core levels:

For the L_2 and
 L_3 edges, core levels
are split by 0.3 eV.



Šipr *et al.* J. Synch. Rad. **25**, 523 (2018)

If individual (κ, μ) -components are smoothed *before* the summation, the resulting spectrum is smooth, without the quasi-doublet at L_3 XMCD.

The verdict on broadening the calculated spectra

- ▶ Simulating the finite core hole lifetime by means of an imaginary energy component and by means of convoluting with a Lorentzian is equivalent **only for energies well above the absorption edge.**
- ▶ If too much weight is put on **broadening via an imaginary energy** component, spurious features may appear at the edge, especially for the dichroic spectra.
- ▶ Special care needed for XMCD spectra: $\text{Im}E$ should be about **ten times smaller** than the FWHM of the Lorentzian which represents the natural core level broadening.

Outline

X-ray absorption spectroscopy: recalling the basic facts

Polarization of x-rays

X-ray linear dichroism: what it can be good for

X-ray magnetic circular dichroism: benefits and risks

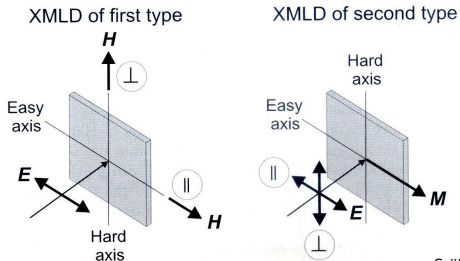
X-ray magnetic linear dichroism: not so common but useful

Non-collinear systems: tasting via a case study

X-ray magnetic linear dichroism (XMLD)

Linearly polarized light, magnetic sample.

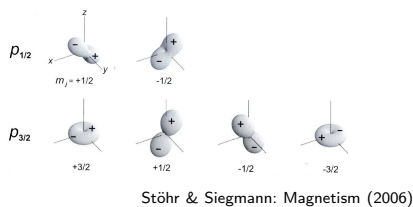
You may rotate the magnetization or the polarization vector.



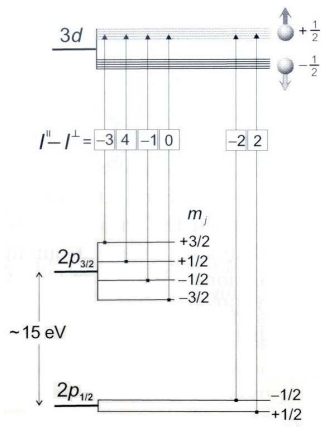
Stöhr & Siegmann: Magnetism (2006)

Focus on systems where the linear dichroism due to magnetism, not due to geometry.
(Typically: cubic systems.)

XMLD: a closer look on the mechanism

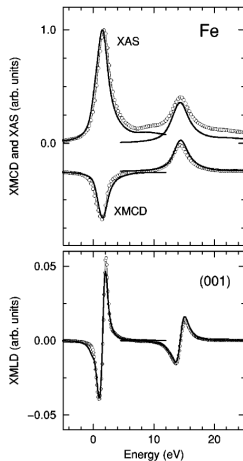


- ▶ Individual core orbitals are not spherically symmetric (just their *sum* is).
- ▶ Transitions from states with different μ have different probabilities.



Exchange splitting between levels with different quantum number μ means that the individual differences $I_{\parallel} - I_{\perp}$ do not compensate.

XAS, XMCD and XMLD: what to expect



For 3d transition metals, XMLD intensity is by order of magnitude smaller than XMCD.

$$\text{XMCD} \sim \langle M \rangle \quad M = 0 \Rightarrow \text{XMCD} = 0$$

$$\text{XMLD} \sim \langle M^2 \rangle \quad M = 0 \not\Rightarrow \text{XMLD} = 0$$

For antiferromagnetic systems, XMCD will be zero but XMLD will be non-zero.

Kuneš & Oppeneer, PRB **67**, 024431 (2003)

Magnetism-generated XMLD and geometry-generated XLD often interpenetrate. See below...

Outline

X-ray absorption spectroscopy: recalling the basic facts

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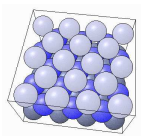
X-ray magnetic circular dichroism: benefits and risks

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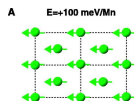
Non-collinear systems: tasting via a case study

Magnetic structure of a Mn monolayer on W(110)

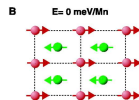
atomic structure of bcc(110):



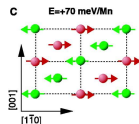
magnetic structures:



ferromagnetic
(FM)



antiferromagnetic
(AFM) $c(2 \times 2)$

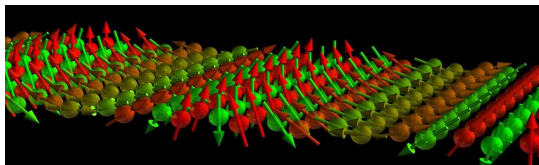
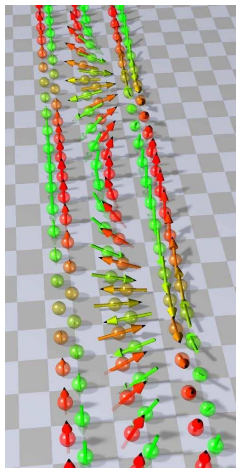


AFM $p(2 \times 1)$

- ▶ Early STM and ab-initio theoretical studies suggested antiferromagnetic (AFM) order

[Heinze *et al.* Science 2000, Denzler & Hafner PRB 2005].

Antiferromagnetic cycloidal spin spiral



- ▶ Later studies: a more complicated magnetic structure.
- ▶ Options: spin density wave (SDW), helical spin spiral (hSS), cycloidal spin spiral (cSS).
- ▶ Experiment and model calculations suggested that the most probable option is a **cycloidal spin spiral** [Bode *et al.* Nature 2007, Haze *et al.* Sci. Rep. 2017].

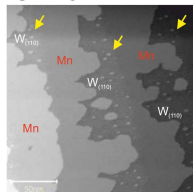
SDW hSS cSS

STM may not provide the whole story

- ▶ STM probes a **small part of the sample**, it may not be quite representative [especially when dealing with terraced surfaces such as $W(110)$].
- ▶ STM informs about **projections** of magnetic moments, not about their more complex structure.
 - ▶ Spin density wave?
 - ▶ Helical spin spiral?
 - ▶ Cycloidal spin spiral?
- ▶ Performing an STM measurement takes time, the system may change in between: **thermal depinning of spin spirals**.

Mn monolayer on W(110)

(a) Step-flow growth of Mn on W(110)

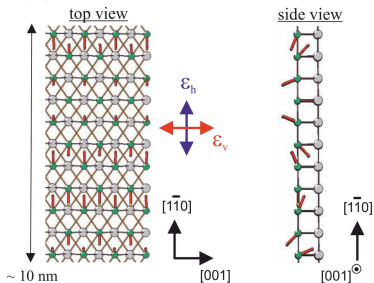


LEED orientation:
W(110) substrate

$\phi = 0^\circ$

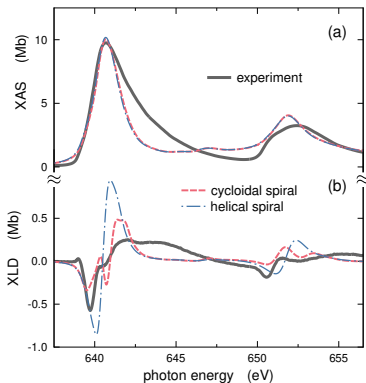


(b) Mn / W(110) surface



- (a) STM image of the Mn/W(110) surface with a Mn coverage of about 80% of a monolayer.
- (b) Schematic depiction of the surface atomic configuration and respective orientation of ϵ_h and ϵ_v photon polarization vectors. **Magnetic moments** are represented by red rods.

Mn/W(110): Comparing experiment and theory

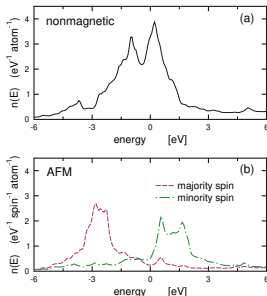
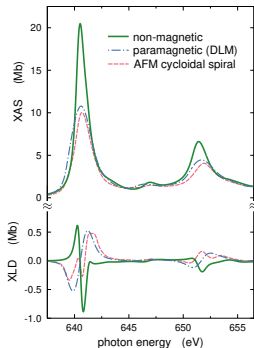


Honolka *et al.* PRB **103**, 174419 (2021)

- ▶ Experimental and theoretical Mn $L_{2,3}$ -edge spectra:
 - (a) X-ray absorption (XAS)
 - (b) X-ray linear dichroism
$$\text{XLD} = \sigma(\epsilon_v) - \sigma(\epsilon_h)$$
- ▶ Theory: **Cycloidal** and **helical** spin spirals give rise to significantly **different** XLD signals.
- ▶ X-ray absorption spectroscopy confirms that the magnetic ground state of Mn/W(110) is an AFM cycloidal spin spiral.

XLD in the presence of **magnetism**.

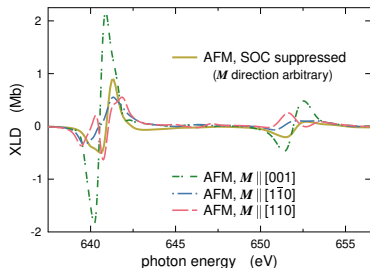
Magnetism is not a mere “perturbation”



Honolka et al. PRB 103, 174419 (2021)

- ▶ XAS and XLD for the same structure in a *non-magnetic* state and in a *paramagnetic* state **differ a lot**.
- ▶ DOS for the same structure in a *non-magnetic* state and in an *antiferromagnetic* state **differ a lot**.
- ▶ Changing the magnetic state is like **taking a different element from the periodic table**.

Spin-orbit coupling (SOC) matters



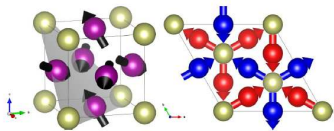
The direction of the magnetic moments (linked to the structure via SOC) has a significant impact on Mn $L_{2,3}$ -edge XLD of a Mn monolayer on W(110).

Honolka *et al.* PRB **103**, 174419 (2021)

Mn $L_{2,3}$ -edge XLD spectra for Mn/W(110) calculated for collinear AFM configurations, assuming that the direction of the magnetic moments is parallel to one of three mutually perpendicular directions.

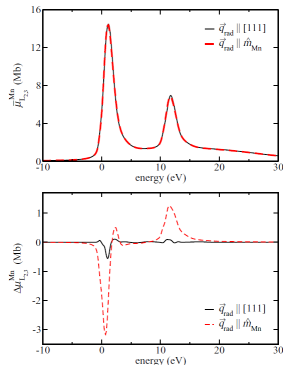
Technical note: Non-relativistic mode simulated by (i) suppressing the SOC in the valence band and (ii) suppressing the relativistic exchange splitting of the $2p$ core levels pertaining to the same relativistic quantum number κ .

Non-zero XMCD with zero magnetization



Mn₃Ir has got a cubic structure.

- ▶ Non-collinear AFM magnetic order, zero total magnetization.
- ▶ XMCD generated at all the Mn_{*i*} atoms with x-rays direction varied so that $\mathbf{q} \parallel \mu_{\text{Mn}_i}$ would compensate each other (the sum would be zero).
- ▶ XMCD spectra for a fixed incoming x-rays direction $\mathbf{q} \parallel [111]$ do not compensate.



Wimmer *et al.* PRB **100**, 214429 (2019)

"It's the magnetic symmetry, stupid!"

Conclusions

- ▶ You can get much further with XAS and XLD than you can with XAS alone.
- ▶ XMCD sum rules are your friend but beware of the bad guy T_z .
- ▶ Employing $\text{Im}E$ to coarsen the energy grid is useful but if you are concerned with XMCD, most of the broadening has to be done by convoluting the spectrum with a Lorentzian.
- ▶ Dichroic spectra can be useful also when dealing with AFM and/or non-collinear magnetic states.

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