Impact of the magnetic dipole term T_z on x-ray magnetic circular dichroism spectra of low-dimensional systems

When you can get rid of it and when you cannot

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Outline

- What is it the T_z term and why to care about it?
- What kind of mess can the T_z term cause?
- When you can get rid of the T_z term and when you cannot.

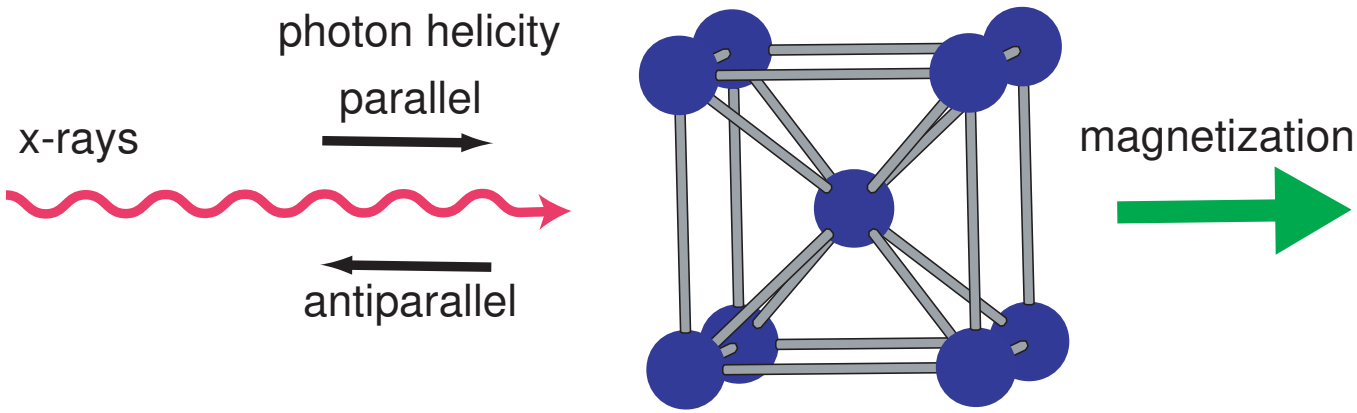
Low-dimensional systems and magnetism

- 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.
  - $\Rightarrow$ Chemically-specific spectroscopic methods are in high demand.

XMCD = XAS − XAS + magnetization + SOC

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

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



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

Spin and orbital magnetic moments

(A quick and dirty introduction to magnetism.)

- Spinning:

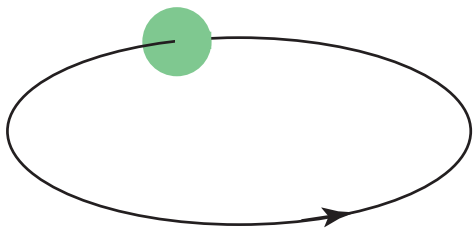
  μ_{spin}

  usually large, $\sim$2.2 μ_B for Fe

- Orbiting:

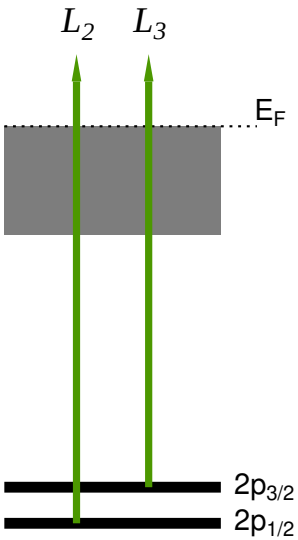
  μ_{orb}

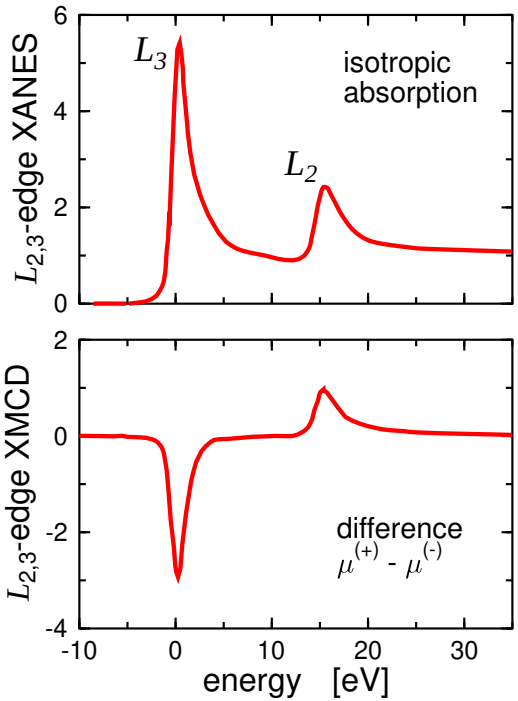
  usually small, $\sim$0.1 μ_B for Fe



Important for links to magnetocrystalline anisotropy.

Typical $L_{2,3}$ edge XAS and XMCD for transition metals





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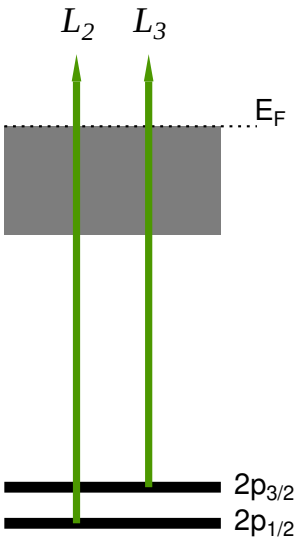
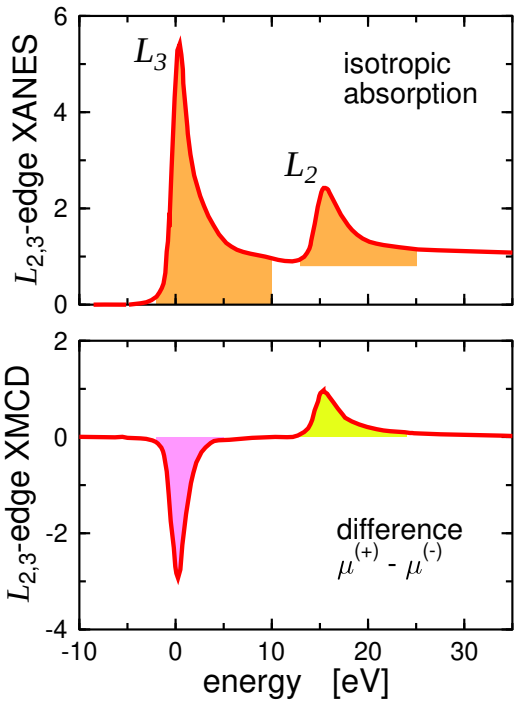




XMCD sum rules:

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

$$\int (\Delta\mu_{L_3} - 2\Delta\mu_{L_2})\,\mathrm{d}E \sim \frac{\mu_{\mathrm{spin}}^{(d)} + 7T_z^{(d)}}{3n_h^{(d)}}$$

$$\int (\Delta\mu_{L_3} + \Delta\mu_{L_2})\,\mathrm{d}E \sim \frac{\mu_{\mathrm{orb}}^{(d)}}{2n_h^{(d)}}$$

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

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

$$\frac{\mu_{\mathrm{spin}} + 7T_z}{n_h} \sim \int (\Delta\mu_{L_3} - 2\Delta\mu_{L_2})\,\mathrm{d}E$$

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

Magnetic dipole term depends on the orientation of the magnetization, better to speak about "T_α term."

What to think about magnetic dipole T_α term?

- T_α is a measure of the intra-atomic asphericity of the spin moment.
- For bulk systems T_α is usually negligible.
- For surfaces, monolayers or wires, $7T_\alpha$ is about 20 % of μ_{spin} $\Rightarrow$ T_α 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 $\mu_{\mathrm{spin}}+7\,T_z$ and μ_{spin} would be quite different ?

Calculational procedure

- Ab-initio, fully relativistic, LDA, SPRKKR code
  `http://olymp.phys.chemie.uni-muenchen.de/ak/ebert/SPRKKR`
  [Ebert *et al.* Rep. Prog. Phys. 2011].

- Embedded impurity Green's function formalism:
  no need for supercells.

Series of supported clusters

- For each cluster, evaluate average μ_{spin}

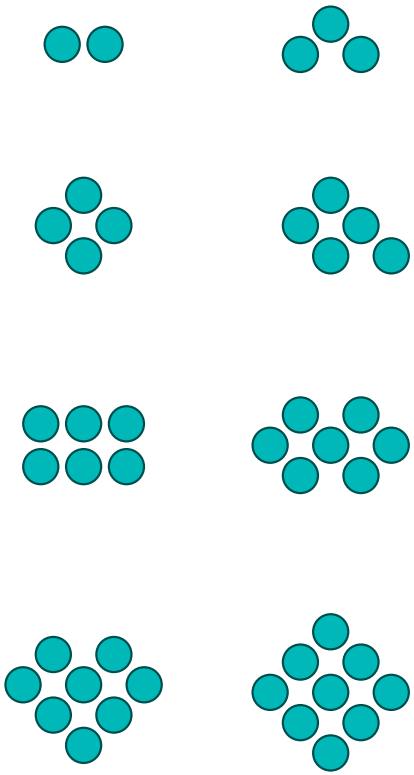
$$\frac{1}{N}\sum_{j=1}^{N}\mu_{\mathrm{spin}}^{(j)}$$

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

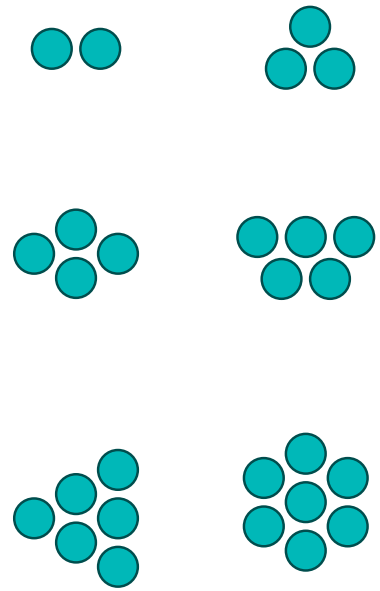
$$\frac{1}{N}\sum_{j=1}^{N}\frac{\mu_{\mathrm{spin}}^{(j)}+7T_z^{(j)}}{n_h^{(j)}} \quad .$$

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

Compact Fe_N and Co_N clusters on metal surfaces

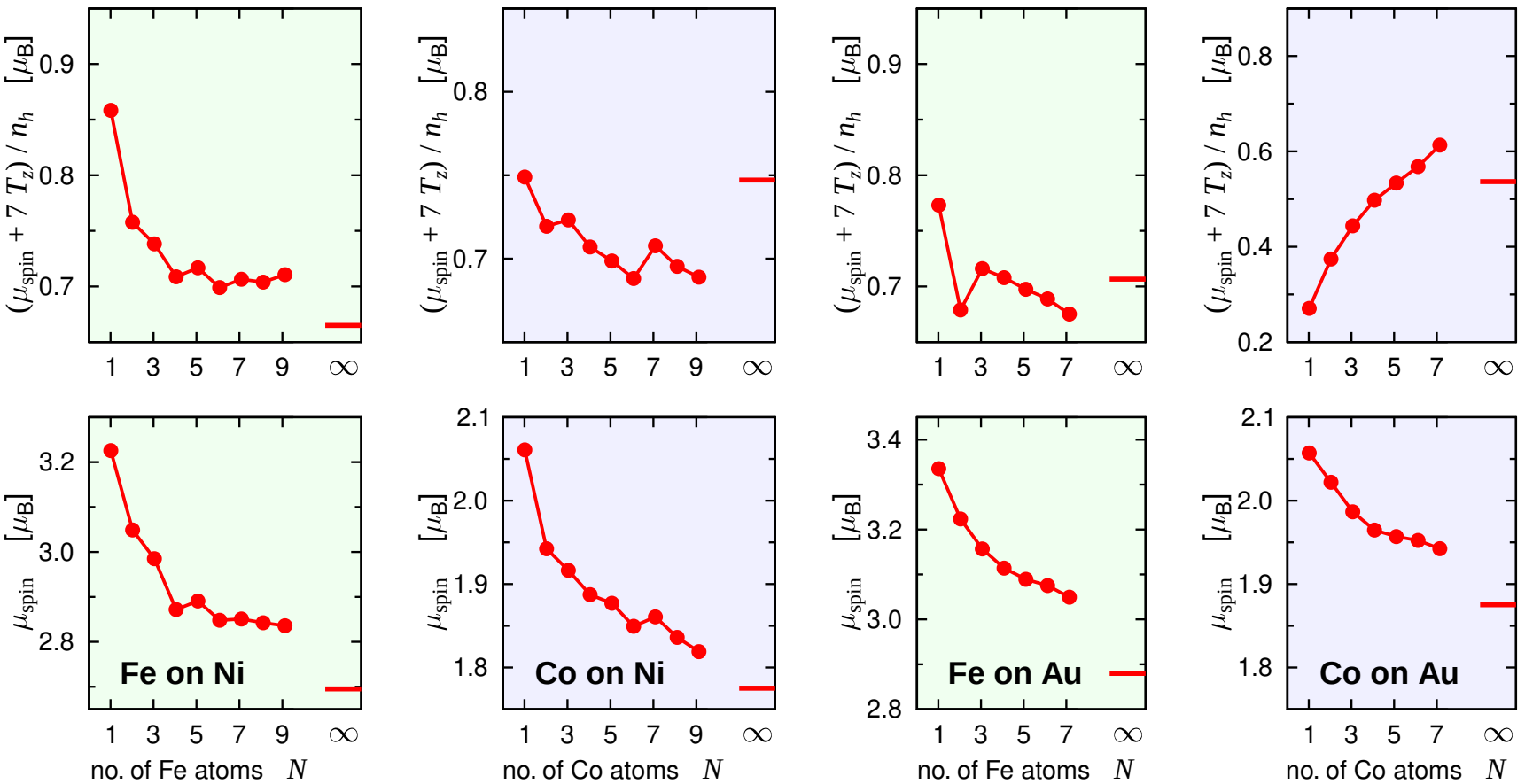


Clusters on Ni(001)
N=1–9



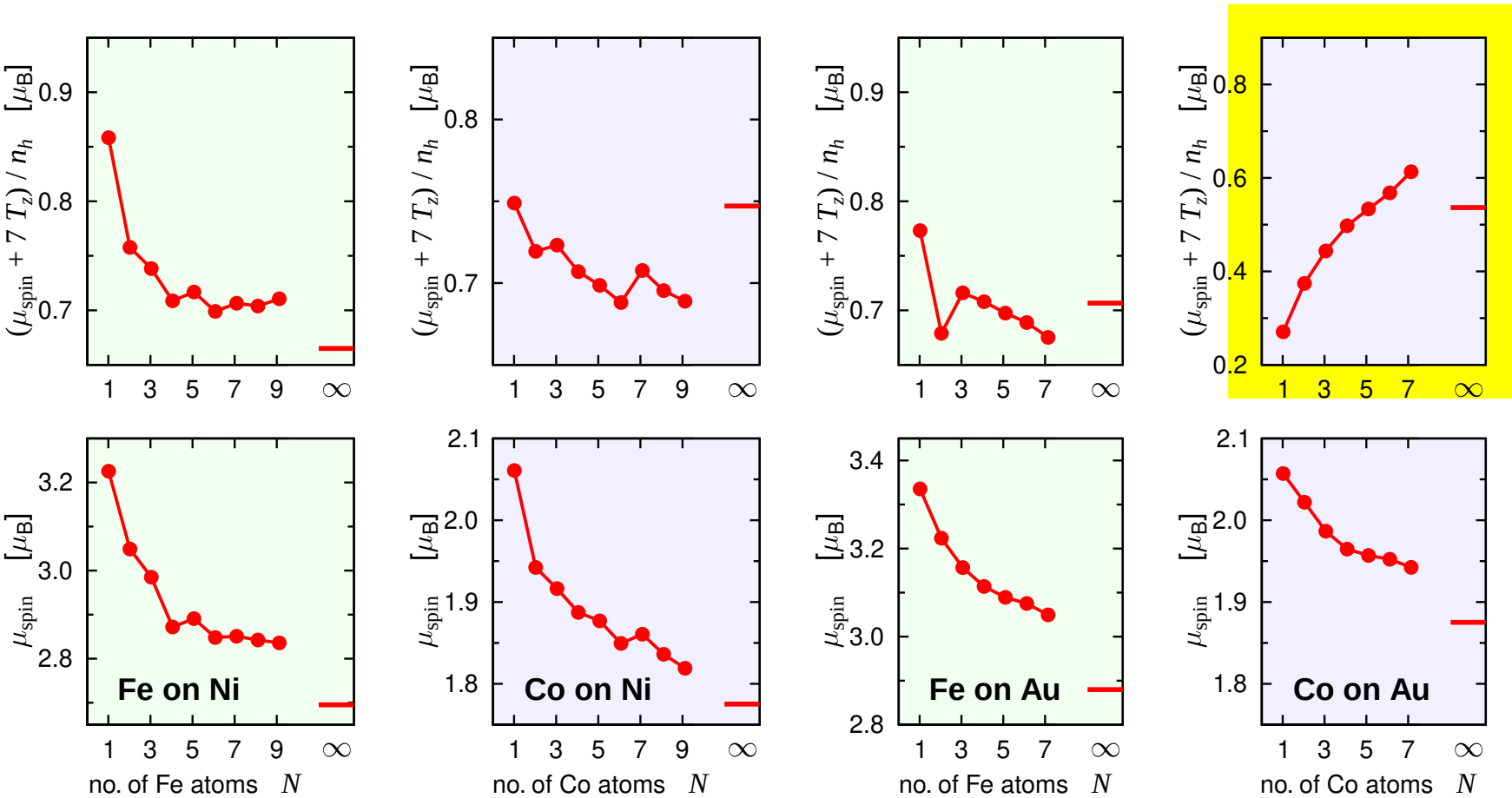
Clusters on Au(111)
N=1–7

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



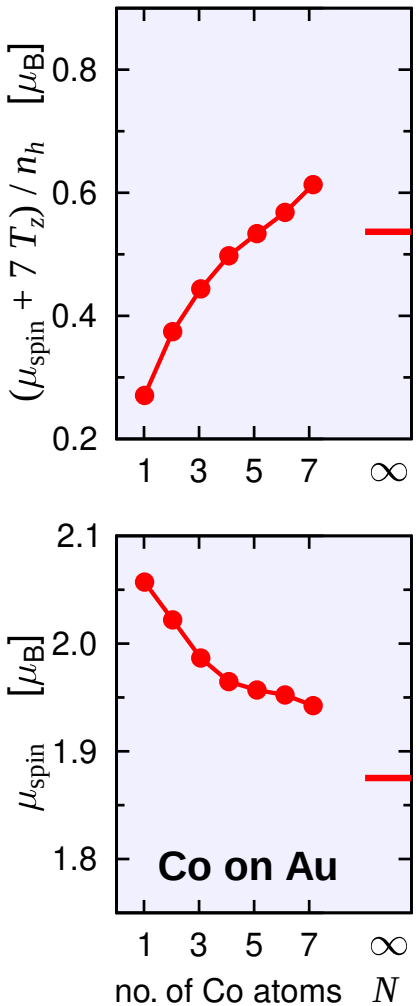
$Fe_N/Ni(001)$ $Co_N/Ni(001)$ $Fe_N/Au(111)$ $Co_N/Au(111)$

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



$\mathrm{Fe}_N/\mathrm{Ni}(001)$ $\mathrm{Co}_N/\mathrm{Ni}(001)$ $\mathrm{Fe}_N/\mathrm{Au}(111)$ $\mathrm{Co}_N/\mathrm{Au}(111)$

Co_N/Au(111): T_z changes the picture completely!

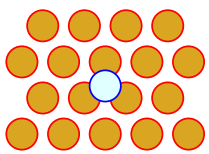


- For Co_N clusters on Au(111), the trends of μ_{spin} and of $[\mu_{spin} + 7\,T_z]/n_h$ are exactly opposite.
- Ignoring variations in T_z would lead to a false estimate of how μ_{spin} per atom depends on the cluster size.

T_α can (falsely) make μ_{spin} to look anisotropic

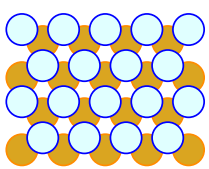
Co adatom and Co monolayer on Pd(111),
varying the direction of the magnetization.

adatom



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

monolayer



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

Quest for a T_α-free XMCD measurement (1)

T_α-free measurement is feasible for systems where the effect of SOC on T_α can be neglected.

$$T_\alpha = -\frac{\mu_B}{\hbar} \left\langle \sum_\beta Q_{\alpha\beta} S_\beta \right\rangle$$

$Q_{\alpha\beta} = \delta_{\alpha\beta} - 3 r^0_\alpha r^0_\beta$ is the quadrupole moment,
S_α is the spin.

If the SOC is neglected, one can decouple $Q_{\alpha\beta}$ from S_β,

$$T_\alpha = -\frac{\mu_B}{\hbar} \sum_\beta \langle Q_{\alpha\beta} \rangle \langle S_\beta \rangle \quad .$$

[Stöhr & König PRL**75**, 3748 (1995), Stöhr JMMM **200**, 470 (1999)]

Quest for a T_α-free XMCD measurement (2)

- If the SOC is neglected, average of T_α is zero:

$$T_x + T_y + T_z = 0 \ .$$

  - One can get rid of T_z by doing three XMCD measurements for perpendicular magnetization directions and taking the average.

- If the SOC is neglected, T_α vanishes at the magic angle $\theta = 54^\circ$ between the magnetization and the symmetry axis.

[König & Stöhr PRL **75**, 3748 (1995), Stöhr JMMM **200**, 470 (1999), Ederer *et al.* JESRP **130**, 97 (2003)]

Can the effect of SOC on T_α be neglected?

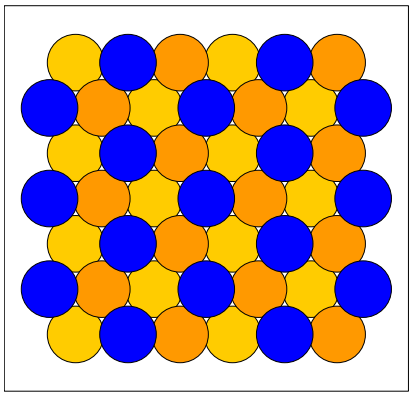
A tell-tale sign that the SOC cannot be neglected is breakdown of the $T_x + T_y + T_z = 0$ equation.

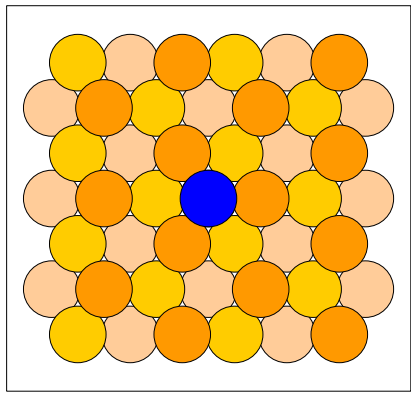
- Experimental evidence that SOC matters: deviations from the $T_x + T_y + T_z = 0$ rule observed for magnetite nanoparticles in the monoclinic low-temperature phase.

  [Schmitz *et al.* Sci. Rep. **4**, 5760 (2014)]

Series of Co monolayers and adatoms

Substate: Cu, Pd, Ag, Pt, and Au (111) surfaces.





Different substrate properties:

Low polarizability:
Cu, Ag, Au

High polarizability:
Pd, Pt

Small SOC:
Cu

Large SOC:
Pt, Au

The $T_x + T_y + T_z = 0$ criterion

Compare $\frac{\sum_\alpha 7 T_\alpha}{\mu_{\mathrm{spin}}}$ for different systems: the smaller, the better.

	monolayer	adatom
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

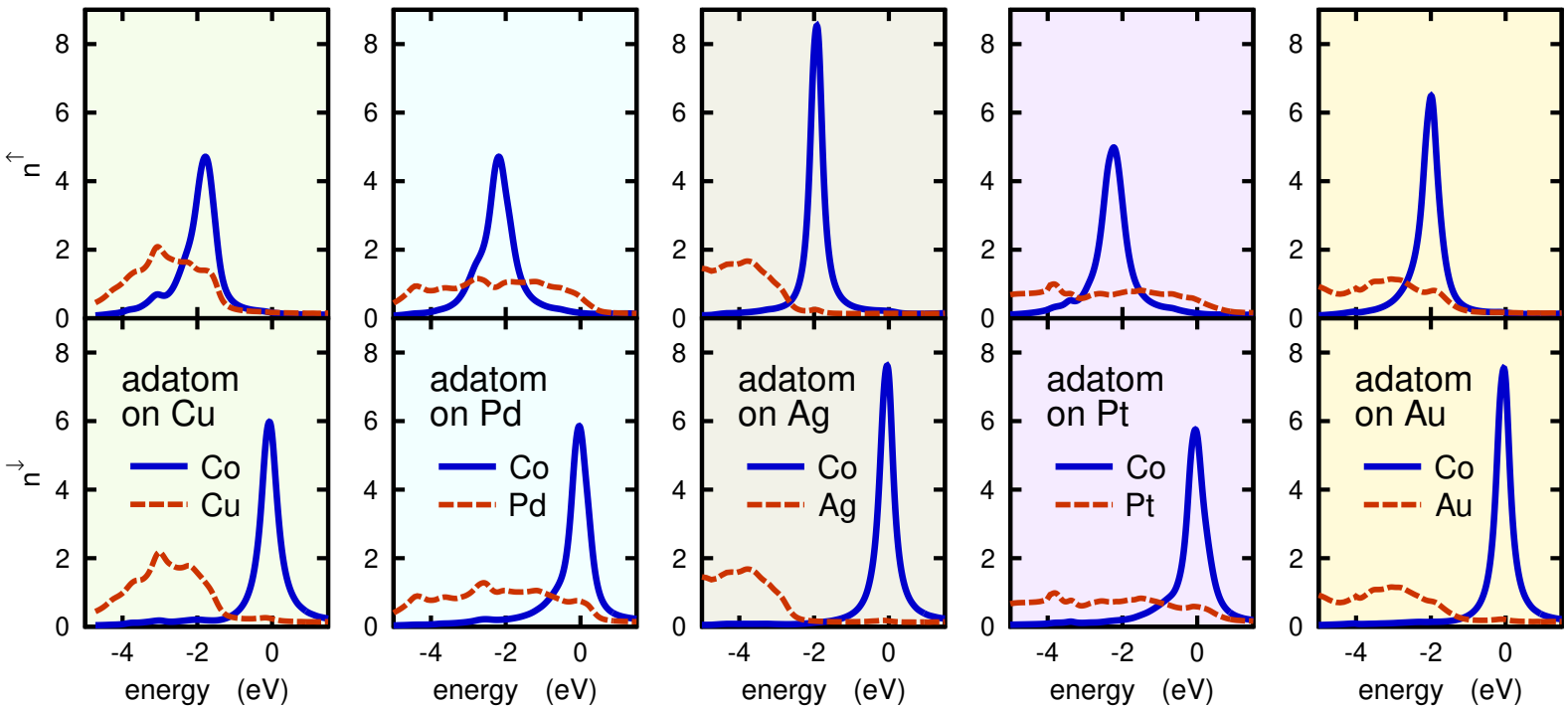
SOC is *nominally* small yet. . .

Dimensionality is more important than the SOC in the substrate.

SOC strength ξ is to be compared to the bandwidth.

Why SOC sometimes matters and sometimes not?

Bandwidth is determined by hybridization, i.e., by overlap between DOS of the adsorbate and DOS of the substrate.



Majority-spin states mostly occupied, therefore it is the incompletely occupied minority-spin states which matter.

SOC strength compared to the bandwidth

DOS overlap integral: $h^{(s)} \equiv \int \mathrm{d}E\, n^{(s)}_{\mathrm{Co}}(E)\, n^{(s)}_{\mathrm{subs}}(E)$

Co adatom on (111) surfaces:

substrate	relative weight of $\sum_\alpha 7T_\alpha/\mu_{\mathrm{spin}}$	relative weight of $1/\int \mathrm{d}E\, n^{\downarrow}_{\mathrm{Co}}(E)\, n^{\downarrow}_{\mathrm{subs}}(E)$
Cu(111)	0.181	0.197
Pd(111)	0.061	0.091
Ag(111)	0.390	0.324
Pt(111)	0.092	0.117
Au(111)	0.276	0.269

Importance of SOC increases if the bandwidth decreases.

Small hybridization between adatom and substrate means that the effect of SOC on T_z cannot be neglected.

Message to the mankind

- Magnetic dipole term T_z is not just a minor pseudo-additive factor that affects the XMCD.
  - Intuition may not be enough when analyzing XMCD spectra of low-dimensional systems.
  - Knowing how T_z varies with cluster size is essential for applying XMCD spin sum rule.
- For small supported systems such as adatoms and clusters, the T_α-eliminating relation
$$T_x + T_y + T_z = 0$$
cannot be relied on.
  - *The nasty T_z term cannot be eliminated* via the magic angle or the $T_x + T_y + T_z = 0$ relation in situations *when it would be mostly needed.* 😕

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