Using x-ray absorption spectroscopy for studying magnetism

Some risks and opportunities

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Outline

Influence of the magnetic dipole T_z term on the XMCD spectra

Effect of spin-orbit coupling on T_z

Local structure and magnetism of Cu-doped ZnO

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Influence of the magnetic dipole T_z term on the XMCD spectra of clusters

When T_z really messes things up.

with Ján Minár, Sven Bornemann, Hubert Ebert, Jiří Vackář, Sergey Mankovskyy

Clusters and magnetism: Why people like them ?

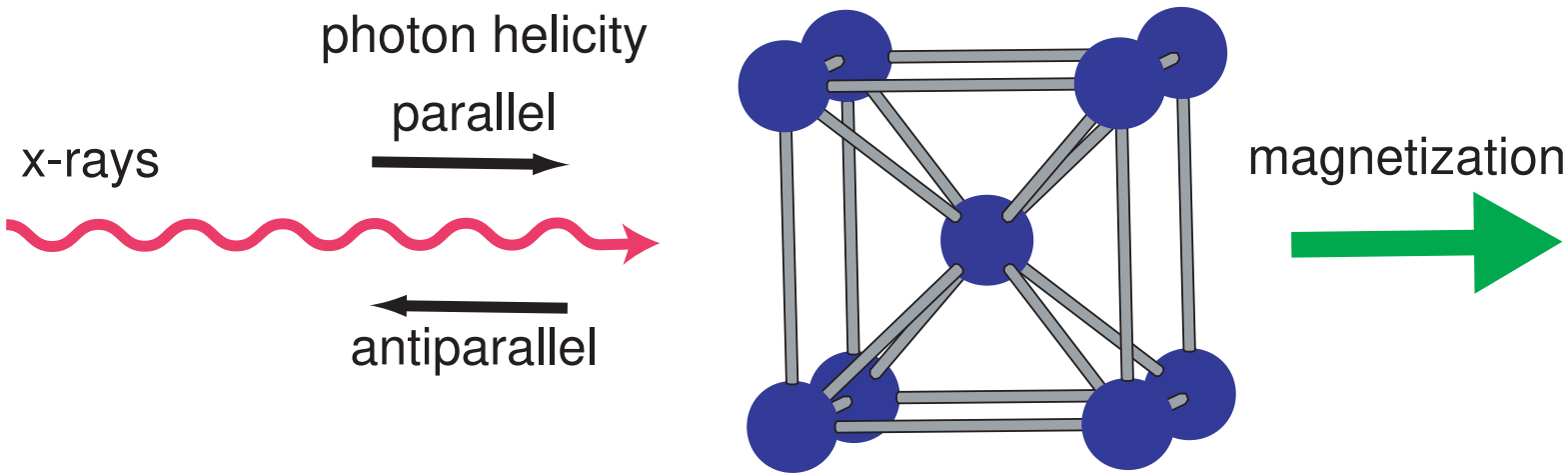
- Clusters have a *high portion of surface atoms* $\Rightarrow$ average coordination number is smaller than in bulk.
- Rule of thumb: The lower the coordination number, the larger the magnetic moment per atom.
- Thin films and clusters have large magnetocrystalline anisotropy per atom (that's what you want for magnetic recording).

XMCD = XAS − XAS + magnetization + SOC

X-ray **M**agnetic **C**ircular **D**ichroism

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

$$\mu_{\mathrm{XMCD}} = \mu^{(+)}_{\mathrm{XAS}} - \mu^{(-)}_{\mathrm{XAS}}$$



Two ways of moving an electron

(A quick and dirty introduction to magnetism)

- Spinning:

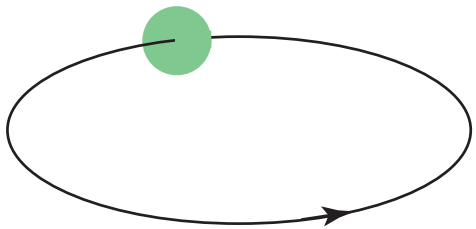
  μ_{spin}

  usually large, $\sim$2.2 μ_B for Fe

- Orbiting:

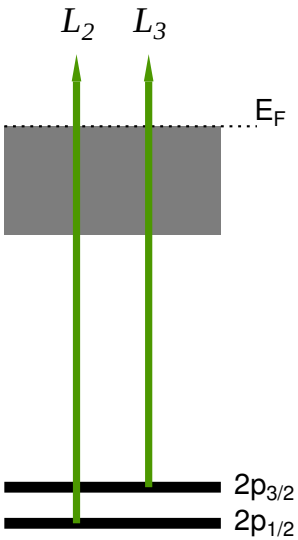
  μ_{orb}

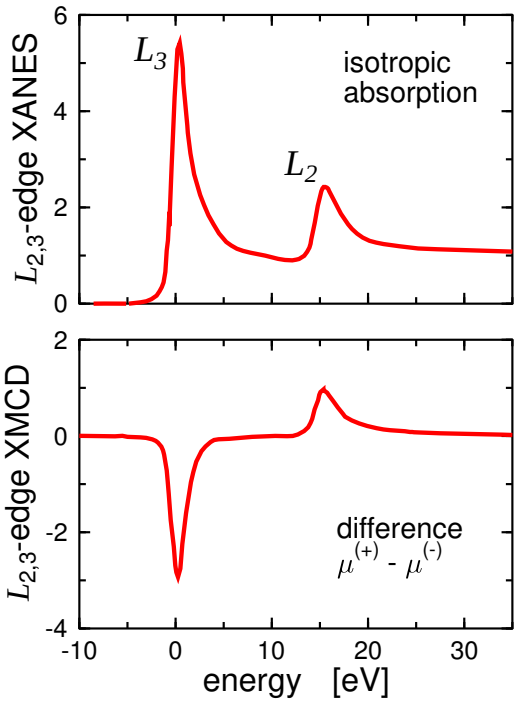
  usually small, $\sim$0.1 μ_B for Fe



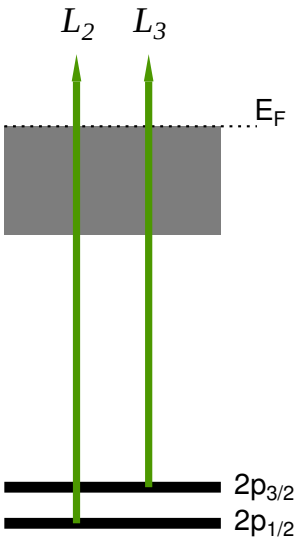
important for links to magnetocrystalline anisotropy

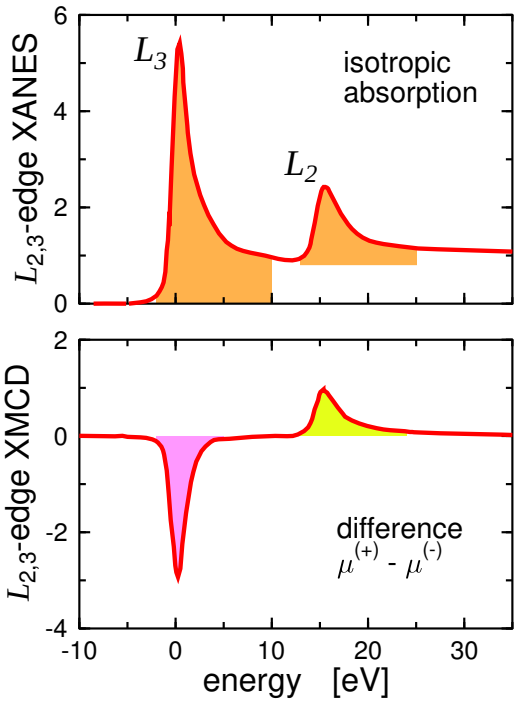
$L_{2,3}$ edge of magnetic TM systems





$L_{2,3}$ edge of magnetic TM systems





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 spin asphericity.
  If the SOC is neglected, one can decouple $Q_{\alpha\beta}$ from S_β to get

$$T_\alpha = \sum_m \frac{1}{2} \langle Y_{2m} | \hat{Q}_{\alpha\alpha} | Y_{2m} \rangle \, \mu_{\text{spin}}^{(m)}$$

  (Components of μ_{spin} resolved according to the magnetic quantum number m are not the same.)

- For bulk systems T_α is usually negligible.

- For surfaces, monolayers or wires, absolute value of $7T_\alpha$ is about 20 % of μ_{spin} [Wu & Freeman PRL **73** 1994 (1994); Komelj *et al.* PRB **66** 140407(R) (2002)]
  $\Rightarrow$ T_α matters for low-dimensional systems!

Do we really need to care about T_z?

- For investigating trends of μ_{spin} within a series of systems, what matters is how T_z varies from one system to another.
  - If variations in T_z are small, neglect of T_z causes just an overall shift of the deduced 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 ?
- Common experience: Variations in the number of holes n_h in the d band do not really matter, their effect is more-or-less negligible.

Investigate a series of clusters

- Take a series of supported clusters.
- For each cluster size, evaluate average of d components of μ_{spin}

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

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

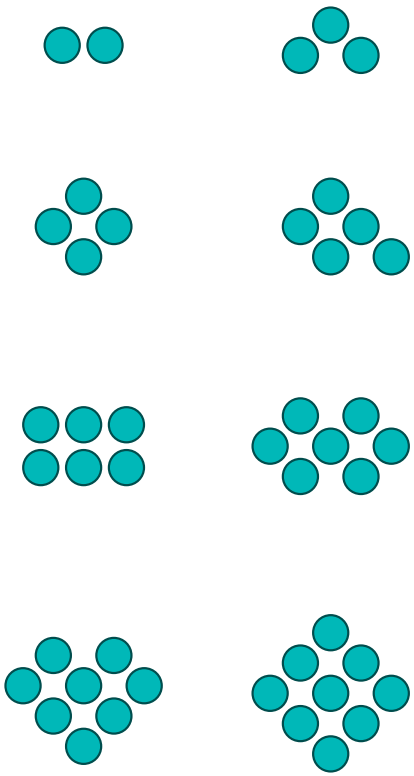
$$\frac{1}{N}\sum_{j=1}^{N}\frac{\mu_{\mathrm{spin}}^{(j)}+7T_z^{(j)}}{n_h^{(j)}} \quad .$$

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

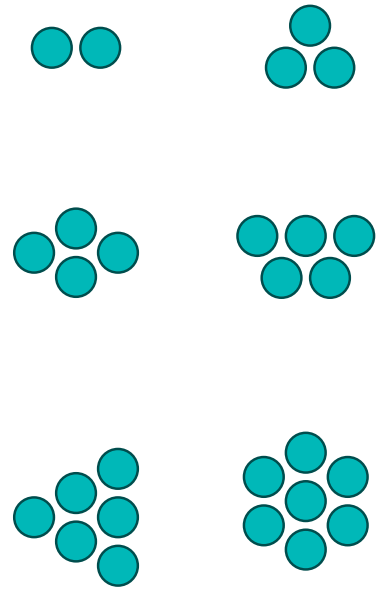
Systems: compact clusters on metalic surfaces

Clusters: Fe_N, Co_N

Substrates: Ni(001), Au(111)



Clusters on Ni(001)
N=1–9



Clusters on Au(111)
N=1–7

Calculational procedure

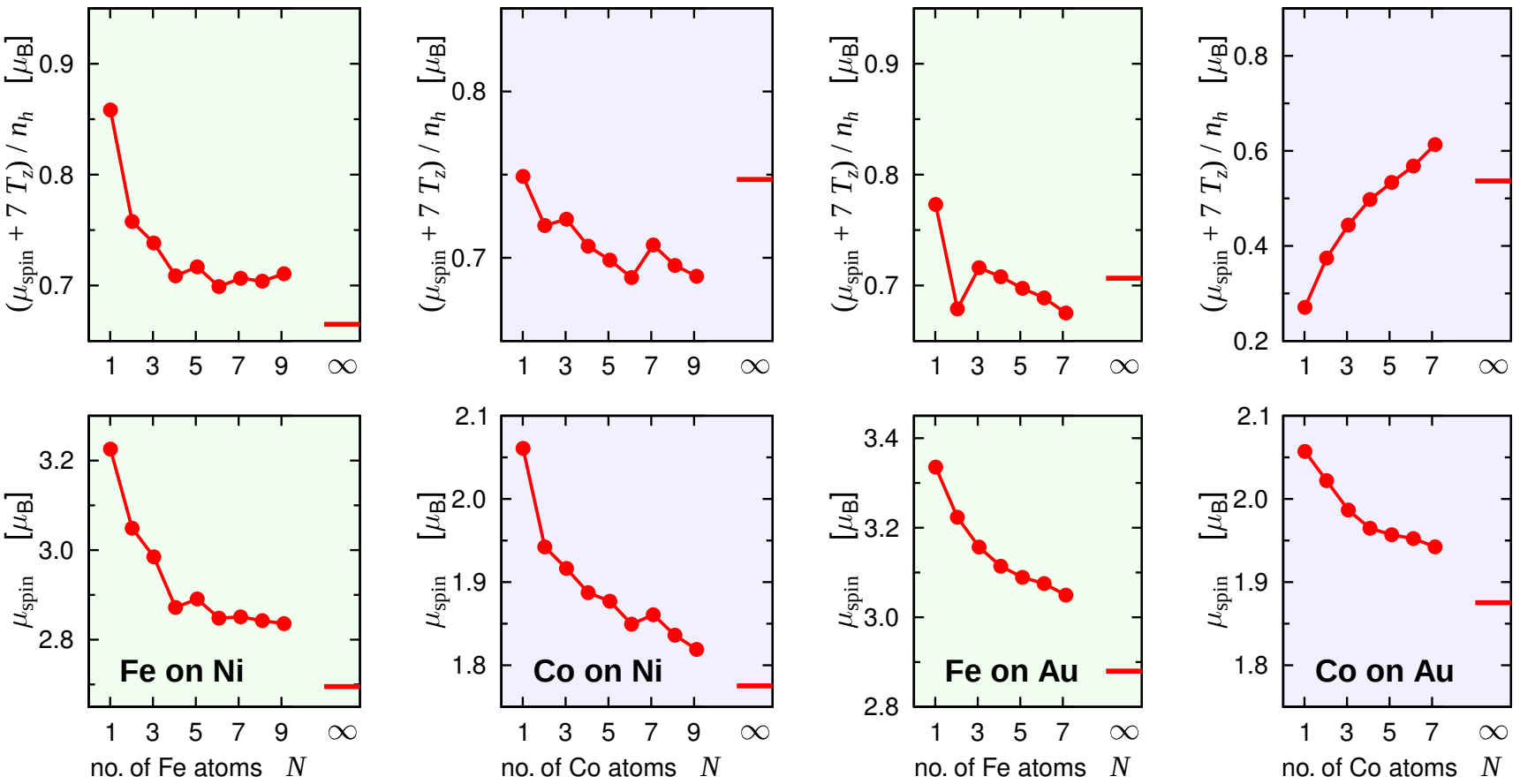
- Ab-initio, fully relativistic, LDA, SPRKKR code

  `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.
  - Calculate electronic structure of the "host" system (clean surface).
    Tight-binding or screened KKR [Zeller *et al.* PRB **52** 8807].
- Supported cluster treated as a perturbation: Green's function of the new system (cluster plus substrate) is obtained by solving the Dyson equation.

  [Minár *et al.* Appl. Physics A **82** 139 (2006)].
- Atomic sphere approximation (ASA).
- Structural relaxation partly accounted for (distances between cluster atoms and the substrate taken from other works).

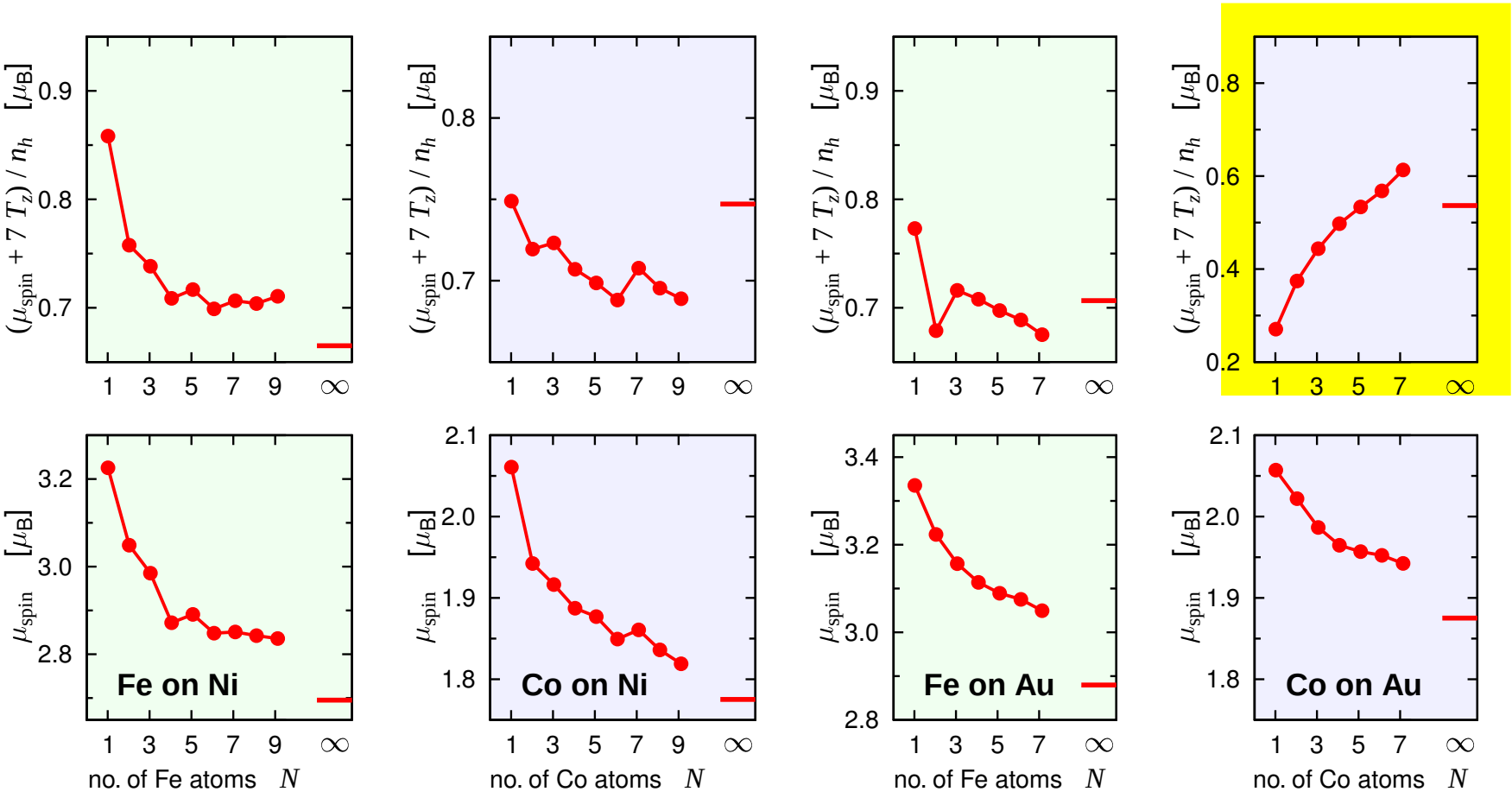
Results: μ_{spin} and $[\mu_{\mathrm{spin}} + 7\,T_z]/n_h$ for compact clusters



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

O. Šipr *et al.* EPL **87**, 67007 (2009)

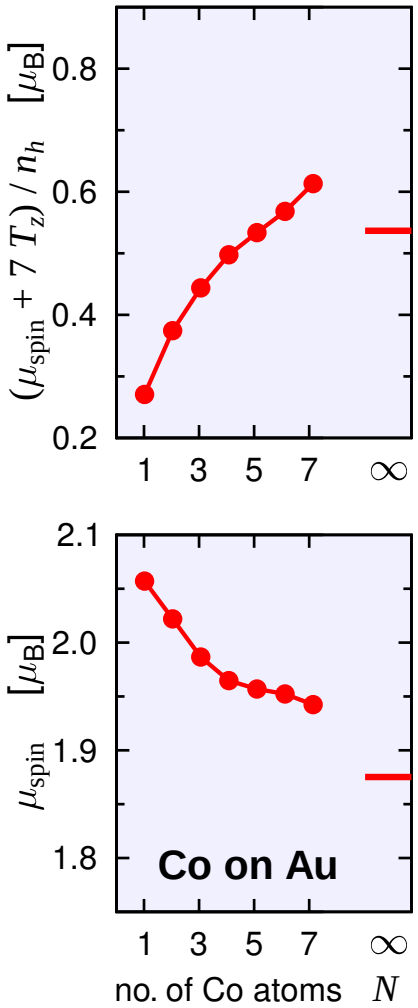
Results: μ_{spin} and $[\mu_{\mathrm{spin}} + 7\,T_z]/n_h$ for compact clusters



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

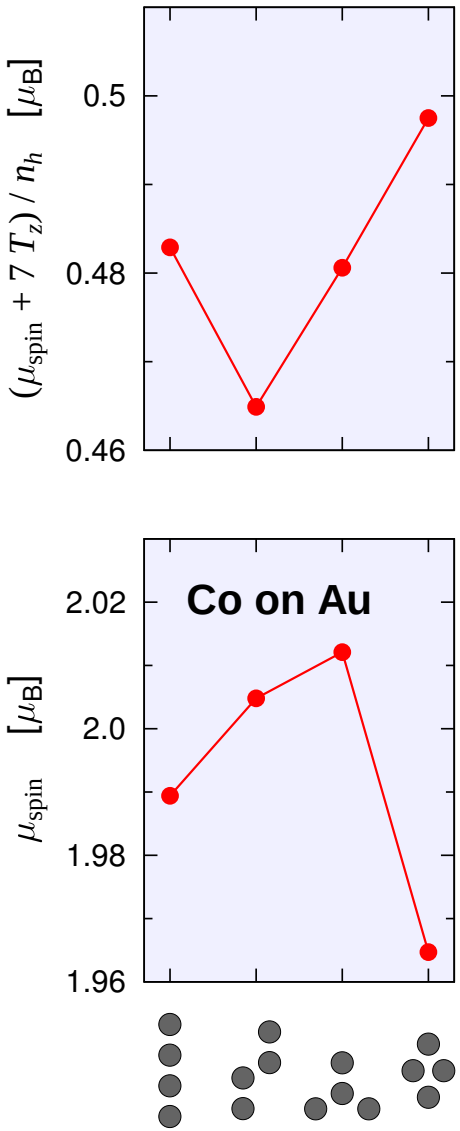
O. Šipr *et al.* EPL **87**, 67007 (2009)

$Co_N/Au(111)$: 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.

Results: Clusters of the same size but different shapes



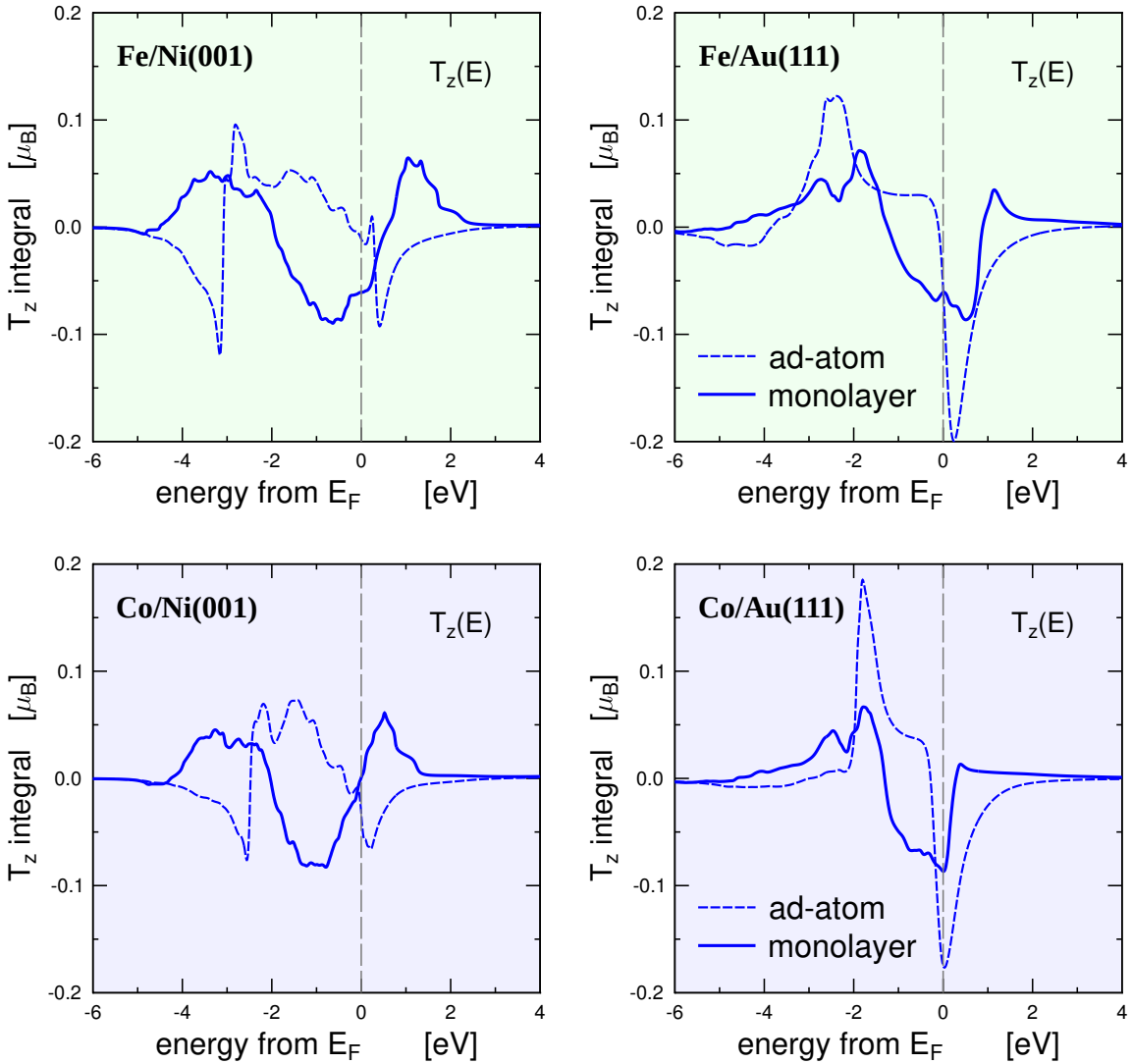
Dependence of μ_{spin} (lower panel) and $(\mu_{\mathrm{spin}} + 7\,T_z)/n_h$ (upper panel) per atom on the shapes of Co_4 clusters on Au(111).

The cluster shapes are depicted below the horizontal axis.

The trends for μ_{spin} and for $[\mu_{\mathrm{spin}} + 7\,T_z]/n_h$ differ.

O. Šipr *et al.* EPL **87**, 67007 (2009)

Have a closer look: effect of E_F (1)

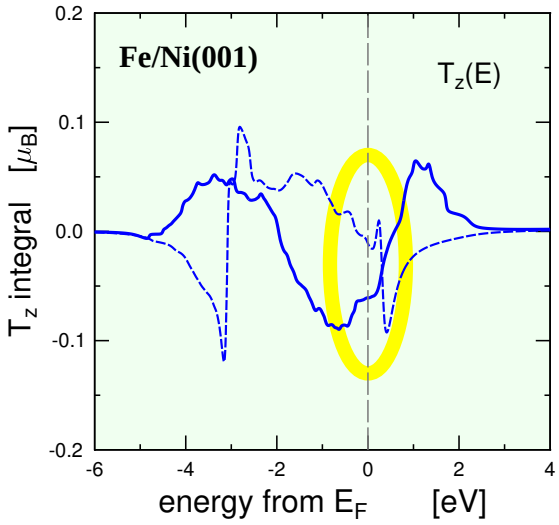


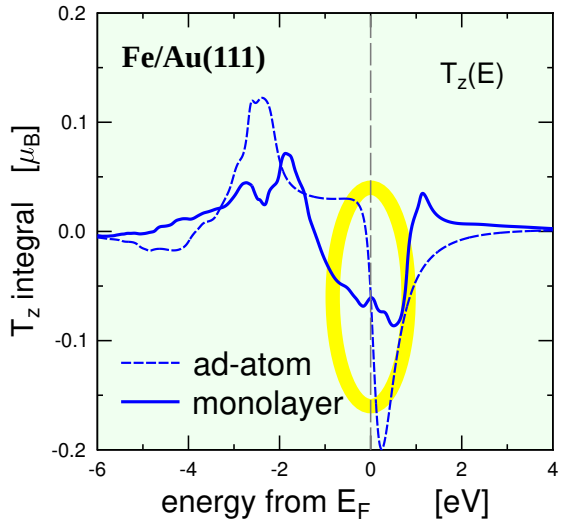
T_z seen as an integral of "magnetic dipole polarization:"

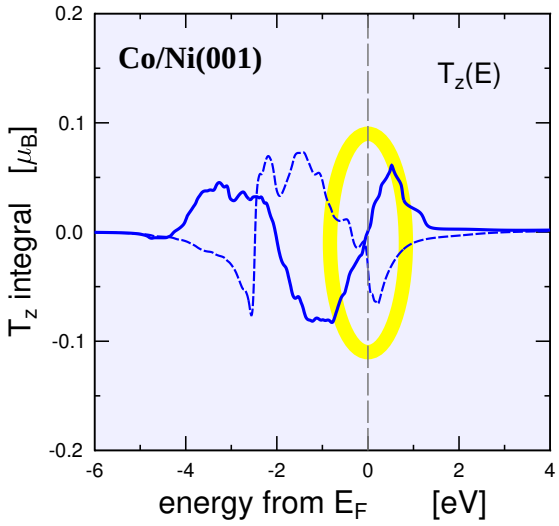
$$T_z(E_F) = \int_{-\infty}^{E_F} \frac{\mathrm{d}\,T_z(E)}{\mathrm{d}E}\,\mathrm{d}E$$

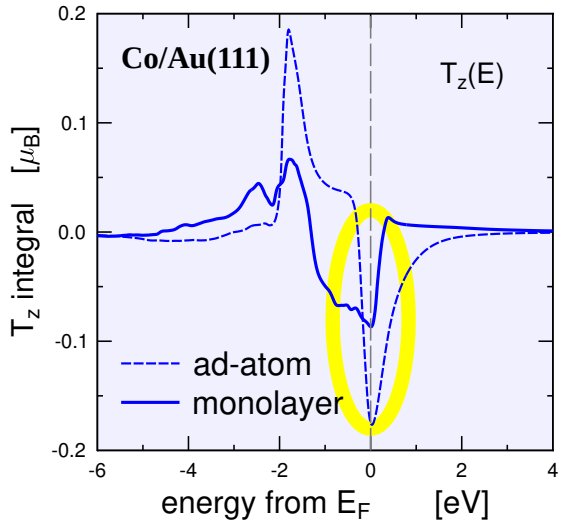
Monitor how T_z evolves if E_F changes.

Have a closer look: effect of E_F (2)









- Different slopes for *ad-atoms* and for *monolayer.*
- T_z is very sensitive to position of E_F.
- Whether T_z will be larger for an ad-atom or for a monolayer depends both on cluster and on substrate.

Intuition does not help, one *has* to calculate it!

T_α depends on the orientation of the magnetization

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

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

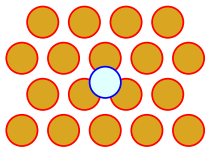
$$T_z = \left\langle \hat{T}_z \right\rangle = \left\langle \tfrac{1}{2}\left[\boldsymbol{\sigma} - 3\hat{\mathbf{r}}(\hat{\mathbf{r}}\cdot\boldsymbol{\sigma})\right]_z \right\rangle$$

Consequently, even though μ_{spin} does not depend on the orientation of the magnetization, the "XMCD sum rules-related combination" $\mu_{\mathrm{spin}} + 7T_z$ does.

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

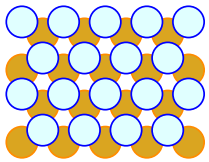
Co adatom and Co monolayer on Pd(111),
varying the direction of the magnetization.

adatom



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

monolayer



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

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

Can the results be trusted?

- Dealing not with isolated systems but with whole series of clusters, spanning from single ad-atoms to complete monolayers.
- All the systems treated in the same manner.
- Conclusions are not crucially sensitive to the accuracy of the calculations.
- The fact that μ_{spin} and $[\mu_{\mathrm{spin}} + 7T_z]/n_h$ may have opposite trends has thus been established quite reliably.

Summarizing notes on the T_α trends' stuff

- Magnetic dipole term T_z is not just a minor pseudo-additive factor that affects the analysis.
- Knowing how T_z varies with cluster size is essential for applying XMCD spin sum rule in clusters.
- Whether the size-dependence of μ_{spin} and of $[\mu_{\mathrm{spin}} + 7T_z]/n_h$ will be opposite or not depends both on the clusters and on the substrate.

Effect of spin-orbit coupling on the magnetic dipole T_z

When T_z can be by-passed and when it cannot.

with Ján Minár and Hubert Ebert

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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,

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

Some useful properties of T_α can then be deduced.

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

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Quest for a T_α-free XMCD measurement (2)

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

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

- If the SOC is neglected, the dependence of magnetic dipole term on the magnetization direction goes as

$$T(\theta) \sim 3\cos^2\theta - 1 \ ,$$

where θ is the angle between the magnetization and the symmetry axis.

- If the SOC is neglected, T_α vanishes at the magic angle $\theta = 54°$.

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

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Can the effect of SOC on T_α be always neglected?

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

Can the effect of SOC on T_α be always neglected?

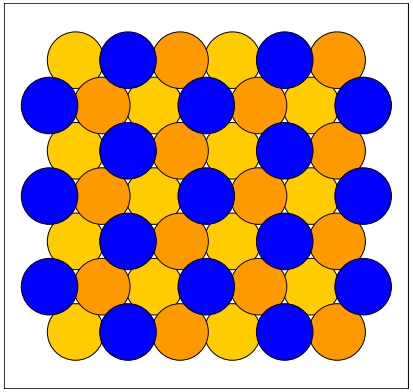
A tell-tale sign that the SOC cannot be neglected is breakdown of the $T_x + T_y + T_z = 0$ equation.

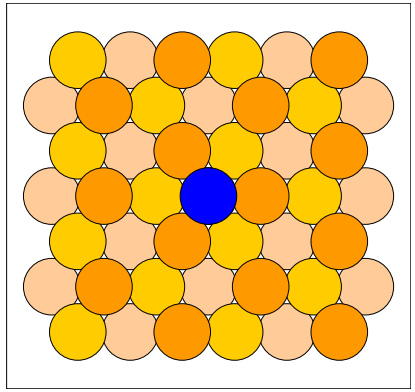
- Many-body effects beyond the LDA violate the $T_x + T_y + T_z = 0$ condition for low-dimensional systems such as *free-standing* $3d$ wires.
  [Ederer *et al.* JESRP **130**, 97 (2003)]

- 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)]

The playground

Scan a series of Co monolayers and adatoms
on Cu, Pd, Ag, Pt, Au (111) surfaces:





Different substrate properties:

Low polarizability:
Cu, Ag, Au

High polarizability:
Pd, Pt

Small SOC:
Cu

Large SOC:
Pt, Au

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Results: the $T_x + T_y + T_z = 0$ criterion

Compare $\frac{\sum_\alpha 7T_\alpha}{\mu_{\mathrm{spin}}}$ 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

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Results: the $T_x + T_y + T_z = 0$ criterion

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SOC is *nominally* small yet. . .

Dimensionality seems to be more important than the SOC for the substrate.

SOC strength ξ is to be compared to the bandwidth.

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Results: Focus on the dimensionality

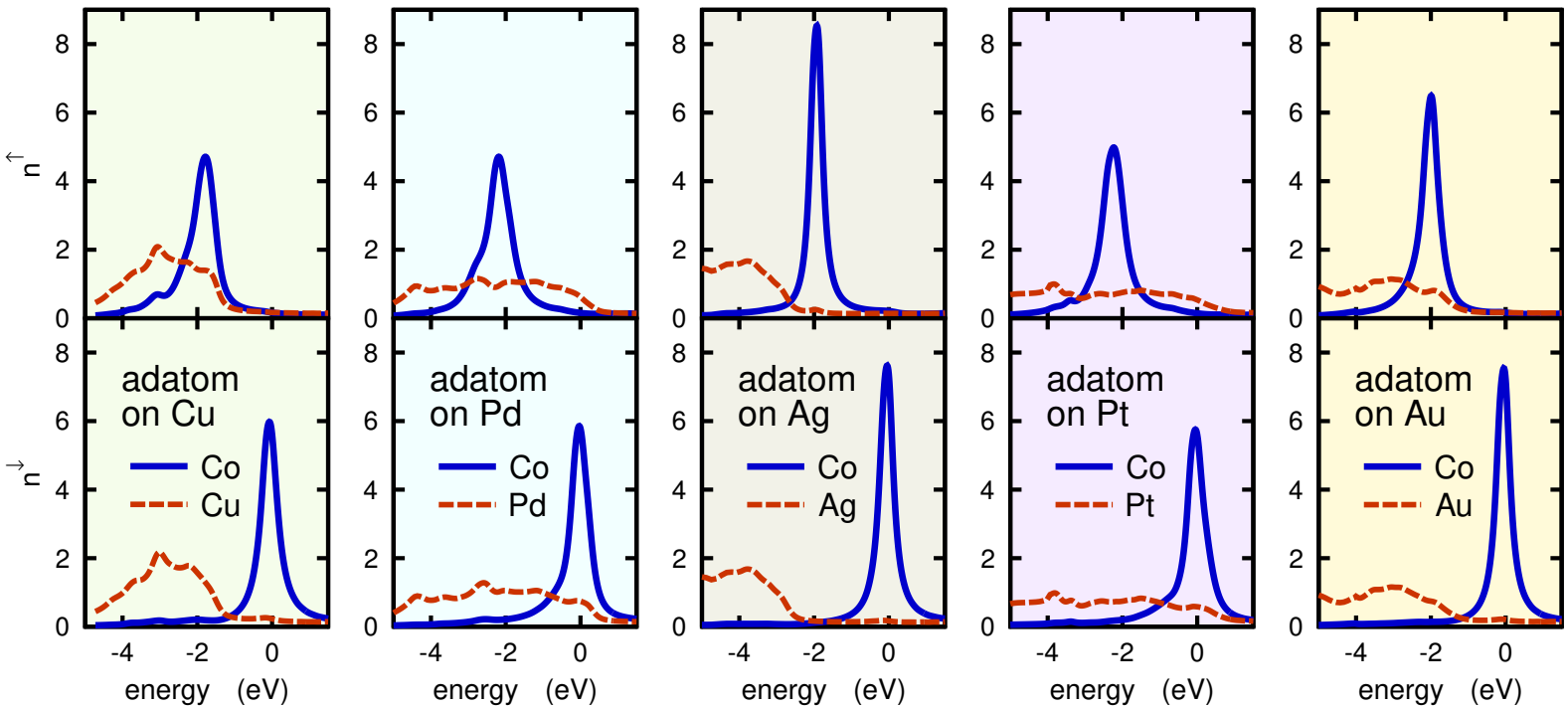
Monitor how $\frac{\sum_\alpha 7T_\alpha}{\mu_{\mathrm{spin}}}$ varies with effective dimensionality for a series of Co systems supported by Au(111):

	$\frac{\sum_\alpha 7T_\alpha}{\mu_{\mathrm{spin}}}$	
Co adatom	0.284	
Co wire	0.058	
Co biwire	0.020 / 0.009	(two inequivalent Co atoms)
Co monolayer	0.009	

Effect of SOC on T_α can be neglected for two-dimensional systems but it cannot be neglected for clusters.

Why SOC sometimes matters and sometimes not?

Effective dimensionality is determined by hybridization — overlap between the DOS of the adsorbate and the DOS of the substrate.



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Majority-spin states mostly occupied, therefore it is the incomplete occupancy of minority-spin states which matters.

SOC strength compared to the bandwidth

The SOC strength ξ in metals should be compared to the bandwidth.

The bandwidth depends on the hybridization, i.e., on how electronic states around the $3d$ atom are affected by its neighbors.

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.

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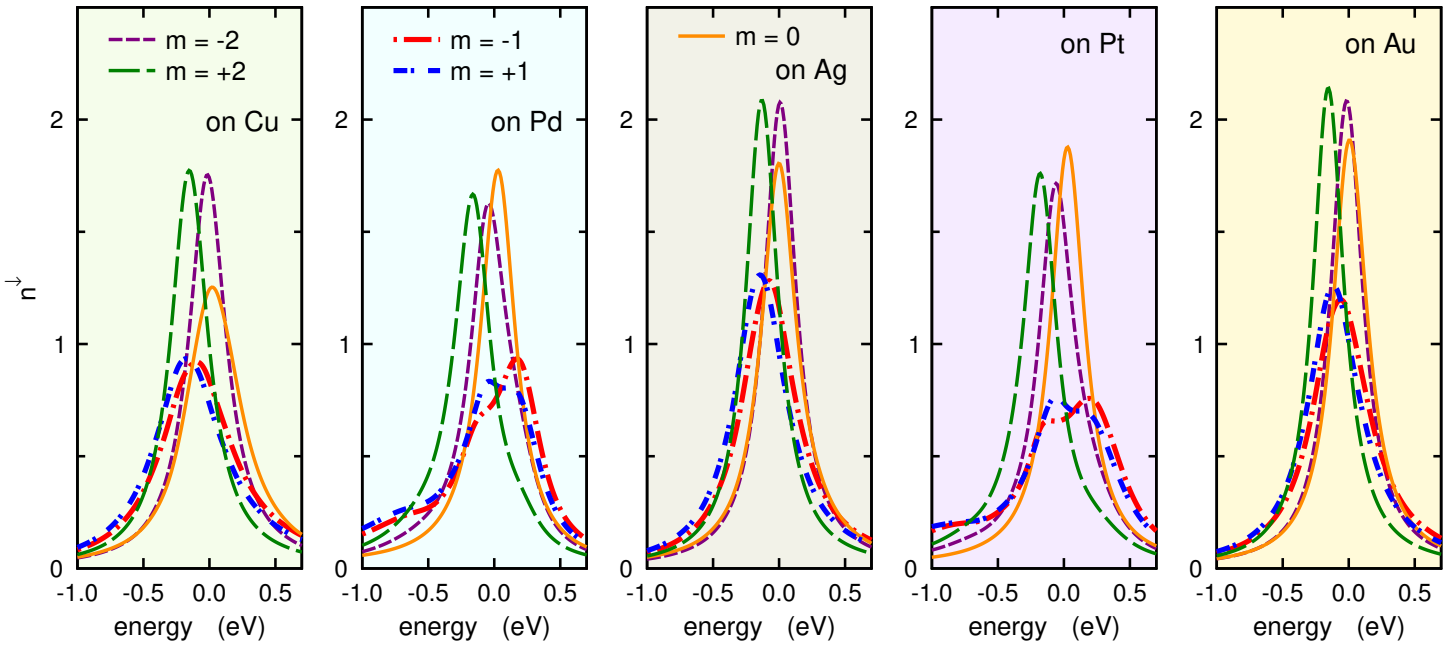
Orbitally-resolved DOS for Co adatoms



Minority-spin orbitally-resolved *d* states of Co ad-atoms on Cu, Pd, Ag, Pt, and Au (111) surfaces.

Lobes of the $m = \pm 1$ orbitals are directed toward neighboring atoms.

One single peak for each of the $m = \pm 1$ components for the Cu, Ag, and Au substrates, two peaks for the Pd and Pt substrates.

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

Summarizing notes on the influence of SOC on T_z

- For small supported systems such as adatoms and clusters, the T_α-eliminating relation

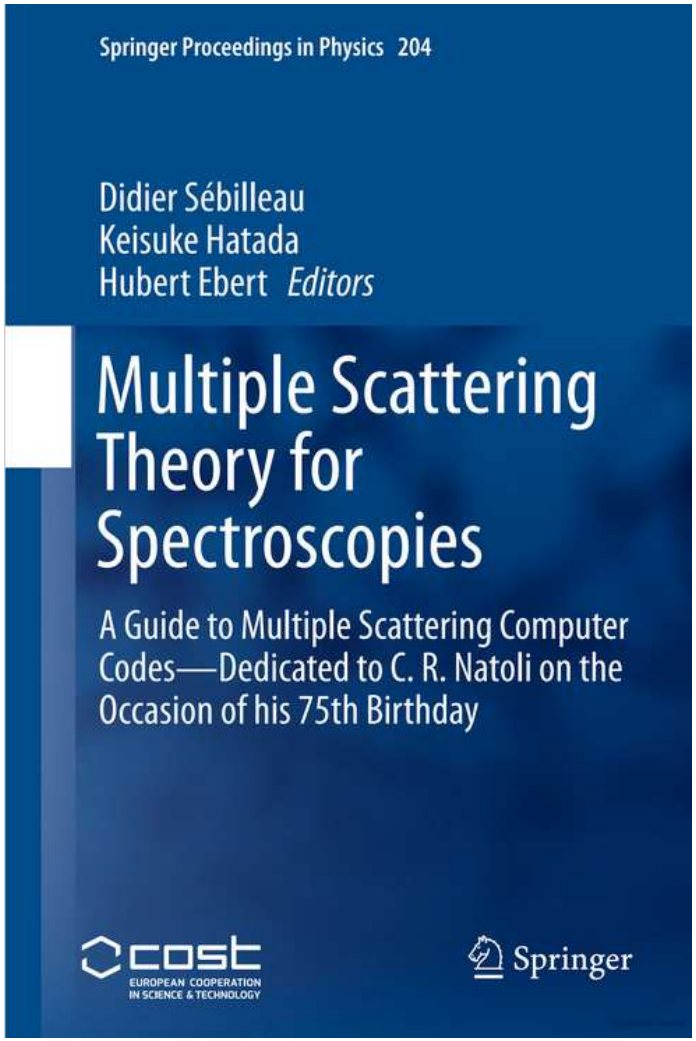
$$T_x + T_y + T_z = 0$$

  cannot be relied on.

- For adatoms and clusters one cannot benefit from effectively T_z-free XMCD measurements (which can be achieved for other systems by means of the magic angle $\theta = 54^\circ$).

- Bad luck: Adatoms and clusters are systems where the XMCD is especially useful, yet these are the systems where the influence of the SOC on T_α cannot be neglected.

Further reading



Chapter 4
KKR Green's Function Method in Reciprocal and Real Space

Ján Minár, Ondřej Šipr, Jürgen Braun and Hubert Ebert

Abstract The Korringa–Kohn–Rostoker (KKR) method is a very flexible band structure technique which is based on the multiple scattering formalism. In contrast to many other band structure methods, which are based on a representation of the electronic structure in terms of Bloch wave functions, the KKR method represents the properties of solids in terms of Green's functions. In this chapter we demonstrate the flexibility of the KKR method as a tool to describe spectroscopic aspects such as x-ray absorption spectra theory and one-step model of photoemission.

Chapter 29
Magnetic Dipole Term T_z and its Importance for Analysing XMCD Spectra

Ondřej Šipr

Abstract Magnetism of nanostructures is often studied by means of x-ray magnetic circular dichroism (XMCD). The XMCD sum rules are a very powerful tool but they allow for the spin magnetic moment μ_{spin} to be determined only in combination with the magnetic dipole term T_z. This chapter presents few examples demonstrating that neglecting T_z could in some cases lead to completely wrong conclusions about the trends of μ_{spin} with the size of the system or with the magnetisation direction. Further, we inspect conditions that have to be met so that eliminating of T_z from the XMCD sum rules is possible.

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Local structure and magnetism of Cu-doped ZnO via Cu *K*-edge XAS and XMCD

Theory and experiment.

with Prashant Vachhani, Francesco Rocca, Anil Bhatnagar, Giuseppe Dalba, Jiří Vackář, ...

Doped ZnO: para-, ferro-, non-magnetic material?

- World-wide project: Induce ferromagnetism in the otherwise non-magnetic semiconductors by doping them with (magnetic) atoms.

- ZnO is a prominent representative of diluted magnetic semiconducting oxides (attractive optical properties).
  - Often doped with magnetic atoms such as Co or Mn.
  - However, ferromagnetism observed also if doped with non-magnetic Cu atoms.

- Results highly interesting but also highly controversial.

  Keavney *et al.* Appl. Physics Lett. **92**, 012501 (2007); Ma *et al.* PRB **78**, 214429 (2008); Herng *et al.* PRL **105**, 207201 (2010); Ogale *et al.* Adv. Mater. **22**, 3125 (2010).

What's wrong with magnetism of doped ZnO?

- Doped ZnO is not a well-defined material.
  (Two doped ZnO's may be quite different materials.)

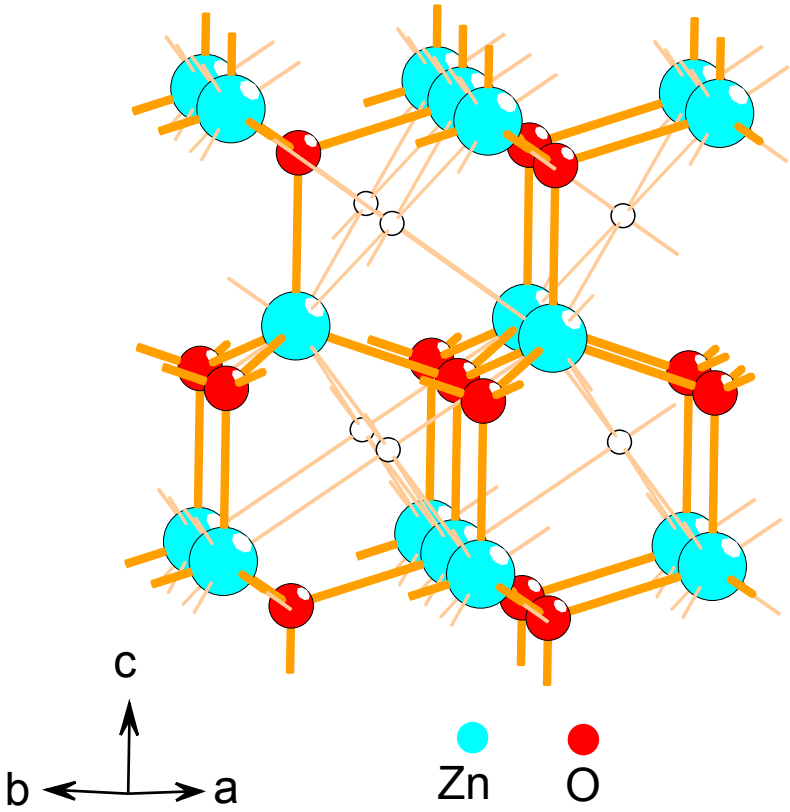
- Depending on (at least) the method of preparation,
  - different magnetic properties were observed,
  - different structures were determined.

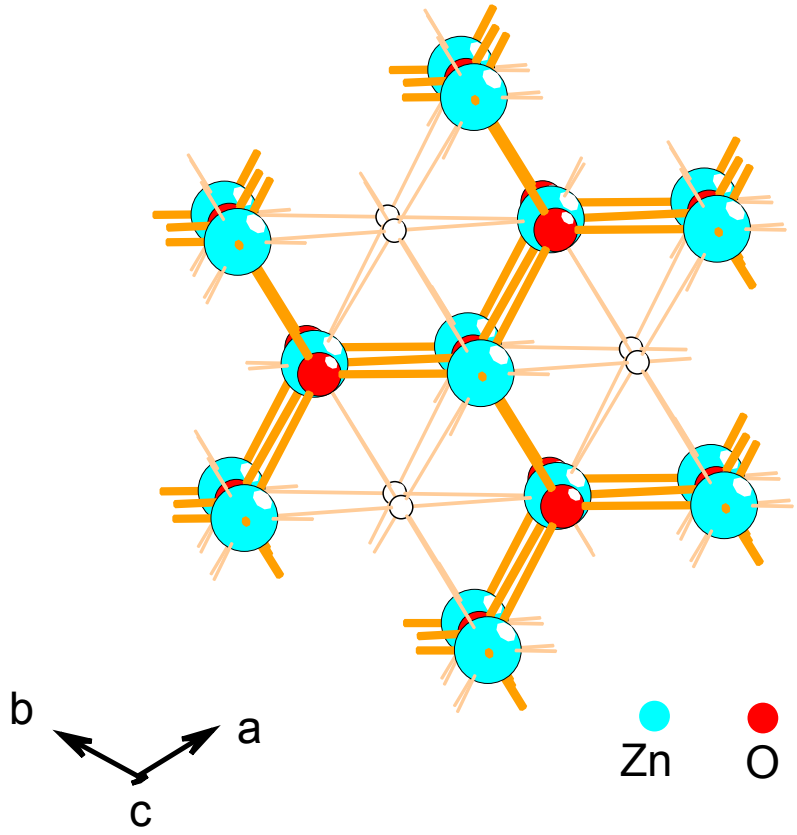
- To make head and tail of it, one should not deal with separate entities [structure] and [magnetism] but rarther with pairs [structure,magnetism] instead.

Study structure and magnetism on the same footing

- XAS provide information about local structure around chemically specific atoms.
- XMCD provides information about the magnetic status of these atoms.
- *Edge problem:* For $3d$ transition metals, the K-edge spectra are better for studying structure while $L_{2,3}$-edge spectra are better for studying magnetism.
  - Here, we focus on the K-edge: EXAFS analysis is at our disposal and element-specific magnetism still can be investigated.

Structure of wurtzite ZnO





Zn and O atom form *ab* planes. Spectra will be anisotropic.

Interstitial sites — possible locations of doped atoms?

Experiment

- Two classes of material:
  1. polycrystalline $Zn_{1-x}Cu_xO$ pellets,
  2. oriented $Zn_{1-x}Cu_xO$ thin films

  (x=2%, 4%, 7%, 10%).
- XANES and EXAFS measured at ESRF BM08-Gilda.
- XMCD recorded at ESRF ID12 beamline.
- X-ray linear dichroism (XLD): Difference between XAS for two perpendicular linear polarizations of incoming x-rays ($\varepsilon \| c$, $\varepsilon \perp c$).
- Bulk magnetization measurement by SQUID.
  - $Zn_{1-x}Cu_xO$ pellets are paramagnetic,
  - $Zn_{1-x}Cu_xO$ thin films pellets are ferromagnetic.

Vachhani *et al.*, J. Phys.: Condens. Matter, **24**, 506001 (2012)
Šipr *et al.* J. Phys.: Conf. Ser., **430**, 012128 (2013)
Vachhani *et al.*, J. Alloys and Compd. **678**, 304 (2016)

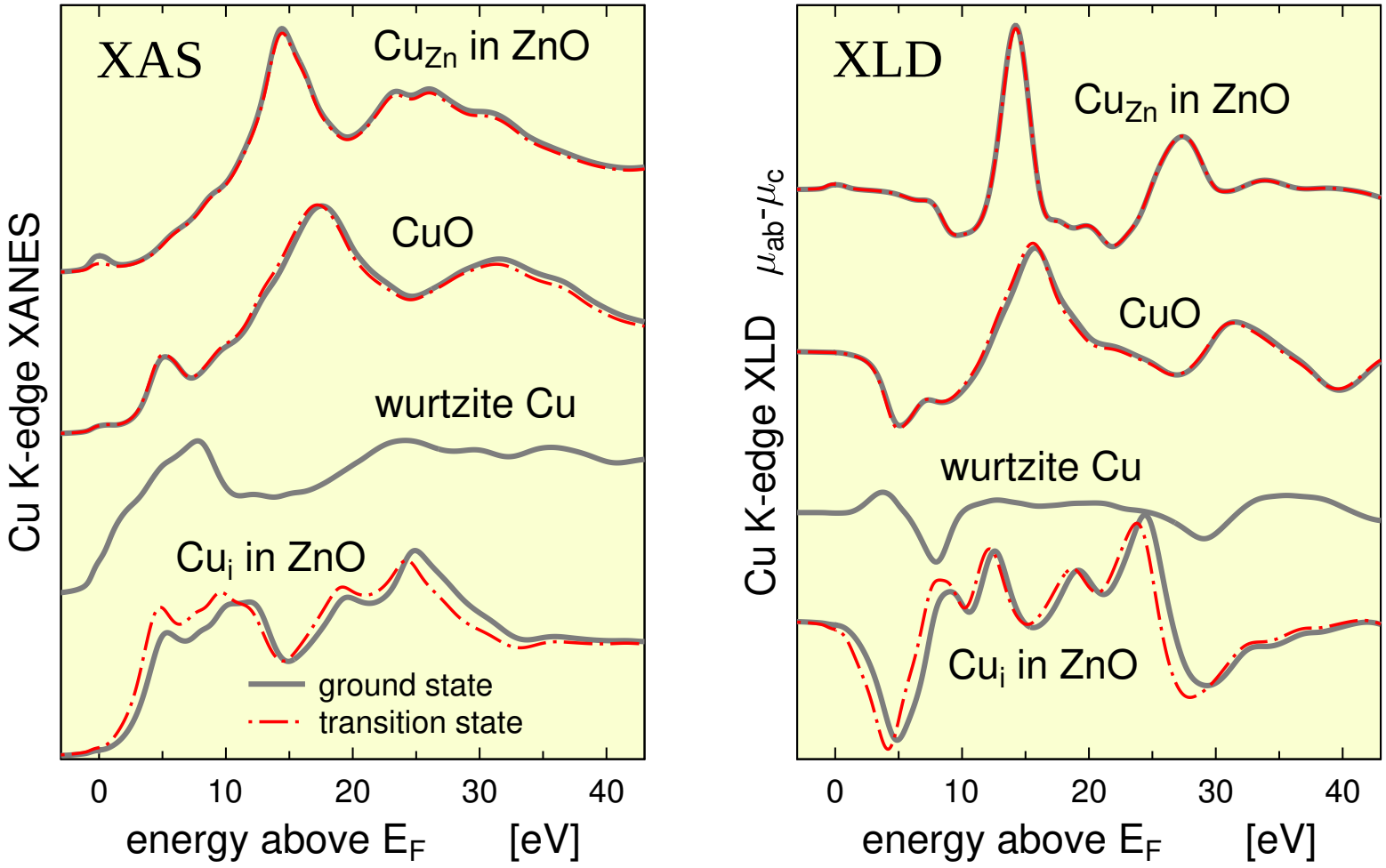
Role of theory

Check sensitivity of XAS and XMCD to relevant structural variations.

- Geometry of the nearest neighborhood of Cu atoms: Zn-substitutional, interstitial, Cu-precipitate, CuO-like?
- Are there oxygen vacancies around?

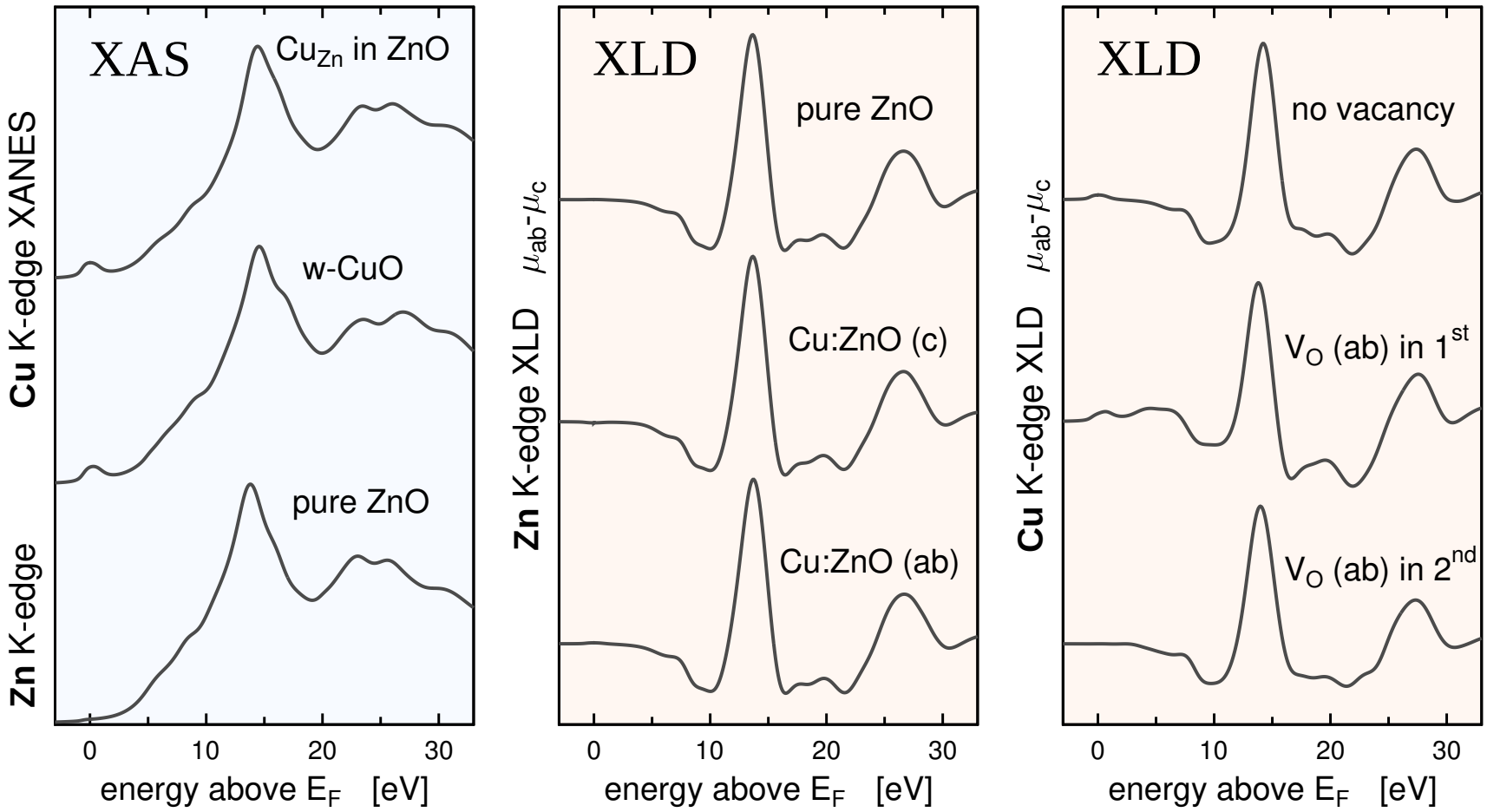
Structural sensitivity of Cu *K*-edge XANES and XLD

Models: Cu_{Zn} in ZnO, CuO, hypothetic w-Cu metal and Cu_i in ZnO.



Conclusion: XAS together with XLD is able to distinguish between various Cu positions reliably.

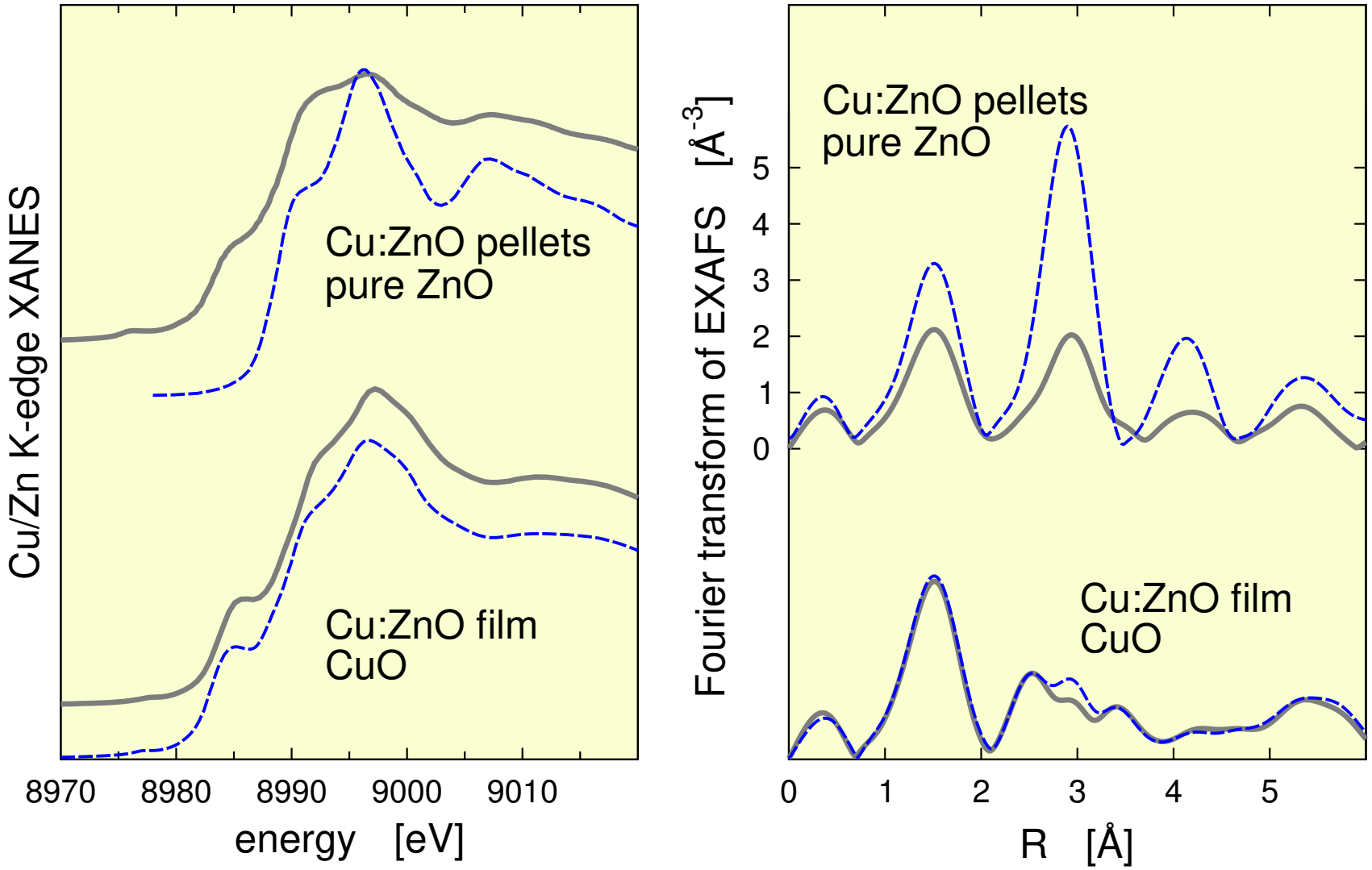
"Non-sensitivity:" Zn–Cu replacement, V_O in the *ab* plane



Left & middle: Zn and Cu neighbors cannot be distinguished from each other.

Right: Oxygen vacancies in the *ab* plane do not affect XAS or XLD.

Experimental XANES and EXAFS for Cu:ZnO



XANES and FT-EXAFS of Cu:ZnO films and pellets (grey lines) compared to CuO and pure ZnO (blue lines). Cu concentration x=7%.

Verdict on the structure

- XANES and XLD can serve as markers of local structures conceivable in Cu:ZnO.
  - XAS cannot distinguish between Zn and Cu in neighboring shells, cannot see oxygen vacancies in the *ab* plane.

- Local environment of Cu in Cu:ZnO pellets: substitutional Zn-site.
- Local environment of Cu in Cu:ZnO thin films: CuO-like (however, long-range order is still wurtzite).

- *Pellets and thin films have different local structures, therefore no wonder than they have different global magnetic properties (paramagnetic and ferromagnetic, respectively).*

Effect of oxygen vacancies on magnetism

Embedded impurity calculation:

	$\mu_{\mathrm{spin}}(\mathrm{tot})$	$\mu_{\mathrm{spin}}(\mathrm{Cu})$	$\mu_{\mathrm{orb}}(\mathrm{Cu})$	$\mu_{\mathrm{orb}}^{(p)}(\mathrm{Cu})$
no vacancy	1.70	0.59	0.14	−0.0016
vacancy in 1^{st} shell	0.54	0.18	0.06	−0.0005
vacancy in 2^{nd} shell	1.18	0.52	0.30	−0.0096

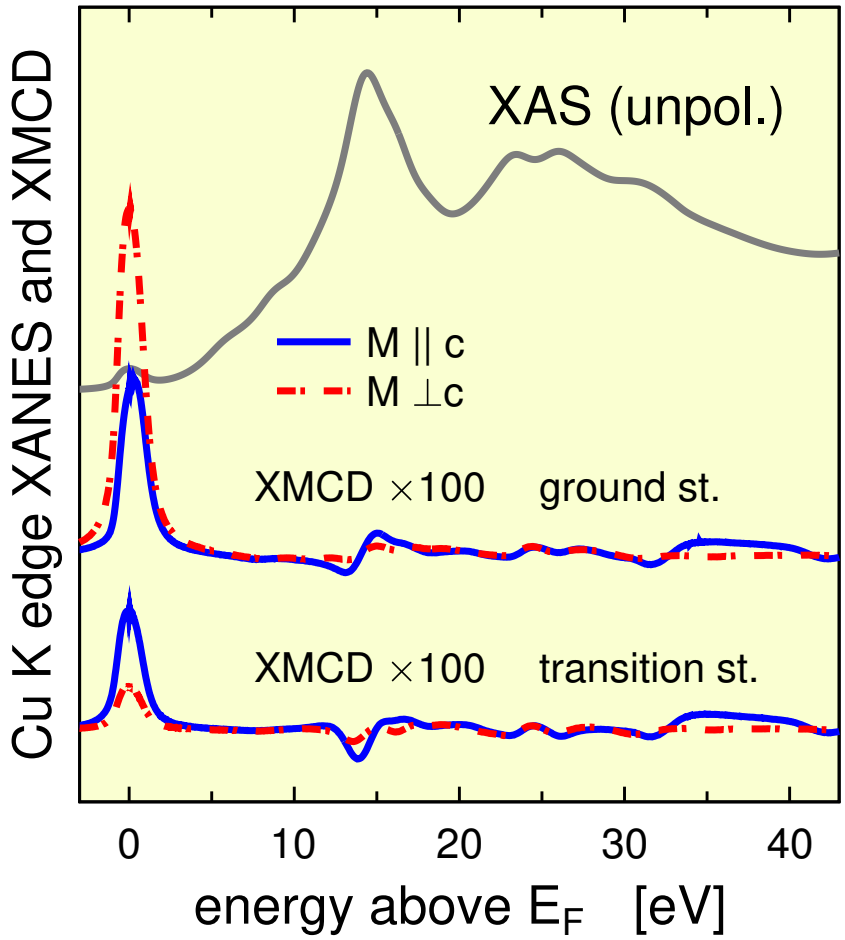
Magnetic moments for $\mathrm{Cu_{Zn}}$ in ZnO with no vacancies and with $\mathrm{V_O}$ in the *ab* plane (in the 1^{st} or in the 2^{nd} shell of O atoms).

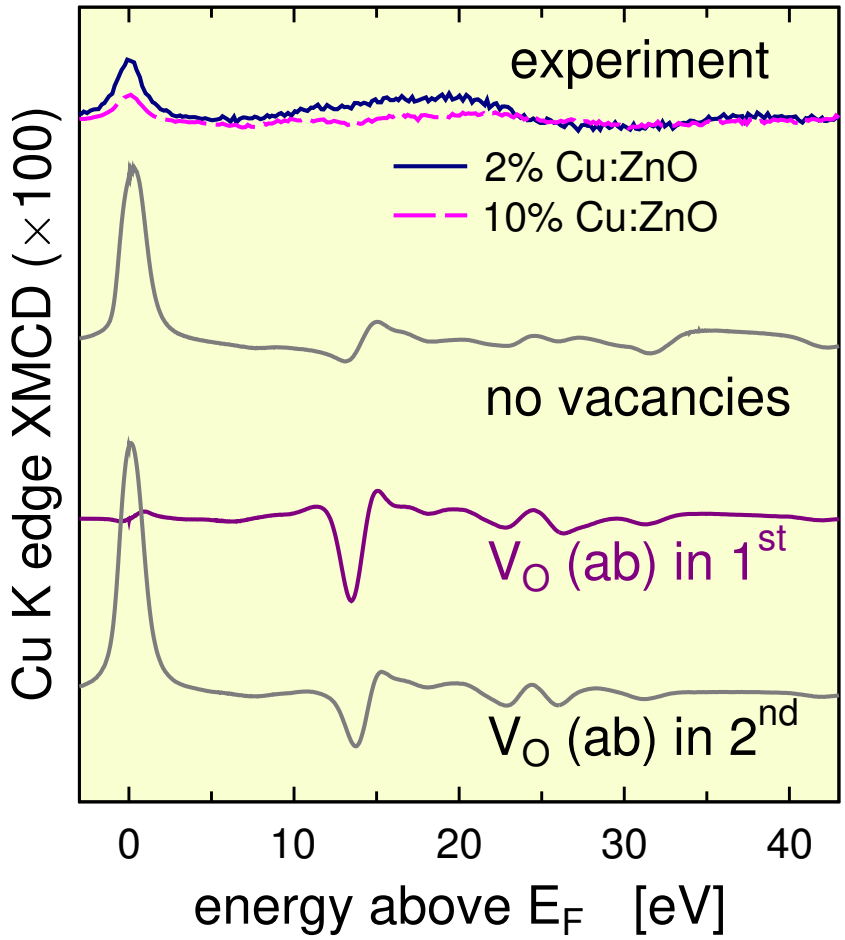
Interstitial impurity $\mathrm{Cu_i}$ is non-magnetic.

Experiment: $\mu_{\mathrm{eff}} = 0.8 - 1.5\ \mu_B$ per Cu atom for Cu concentrations 2–10 %.
(Based on fitting the temperature-dependence of the magnetization.)

Vachhani *et al.* JPCM **24**, 506001 (2012)

Cu K-edge XMCD spectra of Cu:ZnO pellets (1)





Left: Calculated Cu K-edge XMCD for Cu_{Zn} in ZnO.

Right: Calculated Cu K-edge XMCD for Cu_{Zn} without or with V_O in the ab plane, together with experimental XMCD for Cu:ZnO pellets.

Cu K-edge XMCD spectra of Cu:ZnO pellets (2)

- By measuring XAS and XMCD at the same edge we can connect local geometric and local magnetic structure.
  - Experiment and theory agree $\Rightarrow$ Cu K-edge XMCD signal recorded for pellets is really linked to magnetic $\mathrm{Cu_{Zn}}$.

- Oxygen vacancies do not suppress magnetism of substitutional Cu, even though they affect it significantly. Cu K-edge XMCD is strongly modified by them.

  Comparison between theoretical and experimental XMCD suggests that occurence of oxygen vacancies is not probable.

  Note: XAS and XLD alone would not be able to claim this.

Vachhani *et al.* JPCM **24**, 506001 (2012)

Cu K-edge XMCD spectra of Cu:ZnO thin films

Experiment:
No Cu K edge XMCD signal detected for ferromagnetic Cu:ZnO thin films!

- Cu atoms in ferromagnetic Cu:ZnO films are not magnetic.
- $\Rightarrow$ Another argument that ferromagnetism of doped ZnO is not directly connected to the magnetism of dopant atoms.

Vachhani *et al.*, J. Alloys and Compd. **678**, 304 (2016)

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Summarizing notes on Cu-doped ZnO

- Cu *K*-edge XANES and XLD is able to distinguish different geometries conceivable for Cu:ZnO.
  - Unfortunately, there is no way to distinguish Zn and Cu neighbors in further coordination shells.
- Different local geometry and local magnetism for Cu in paramagnetic Cu:ZnO pellets and in ferromagnetic Cu:ZnO thin films:
  - for the pellets, Cu is in Zn-substitutional sites and Cu atoms are magnetic,
  - for the films, Cu is in CuO-like environment and Cu atoms are non-magnetic.
- Ferromagnetism of transition metal doped ZnO is not directly linked to magnetism of the dopant but rather is connected with structural changes induced by these dopants.

Message to the mankind

- Intuition may not be enough when analyzing XMCD spectra of nanosystems.
- 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 this is most needed.
- Combining XAS and XMCD may be the right way to investigate magnetism of doped semiconductors.

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