Magnetic and spectroscopic properties of free iron clusters

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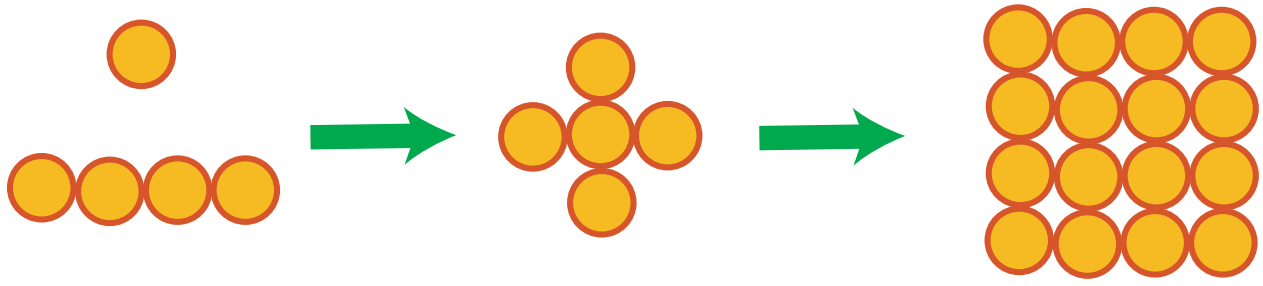
What are the clusters about?

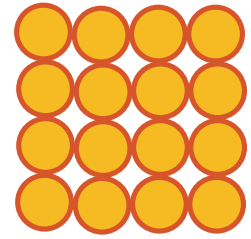
- Clusters mark the transition between atoms, surfaces and bulk systems



- Interesting phenomena (and a lot of fun) can be expected
- We concentrate on their magnetic properties

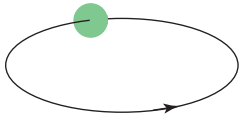
Magnetic properties of iron





atom | surface | bulk

$\mu_{\text{spin}} = 4\ \mu_B$ | $\mu_{\text{spin}} = 2.5\text{–}3.0\ \mu_B$ | $\mu_{\text{spin}} = 2.2\ \mu_B$

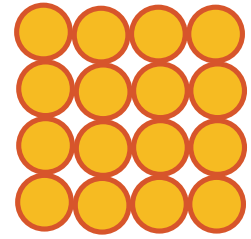


$\mu_{\text{orb}} = 2\ \mu_B$ | $\mu_{\text{orb}} = 0.07\text{–}0.12\ \mu_B$ | $\mu_{\text{orb}} = 0.05\ \mu_B$

(clusters go in between)

Magnetic properties of iron





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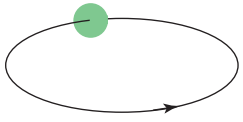	$\mu_{\text{orb}} = 2\ \mu_B$	$\mu_{\text{orb}} = 0.07\text{–}0.12\ \mu_B$	$\mu_{\text{orb}} = 0.05\ \mu_B$

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Clusters contain a high portion of surface atoms

$\Rightarrow$ ought to have larger magnetic moments

their properties should display traces of surface and bulk trends

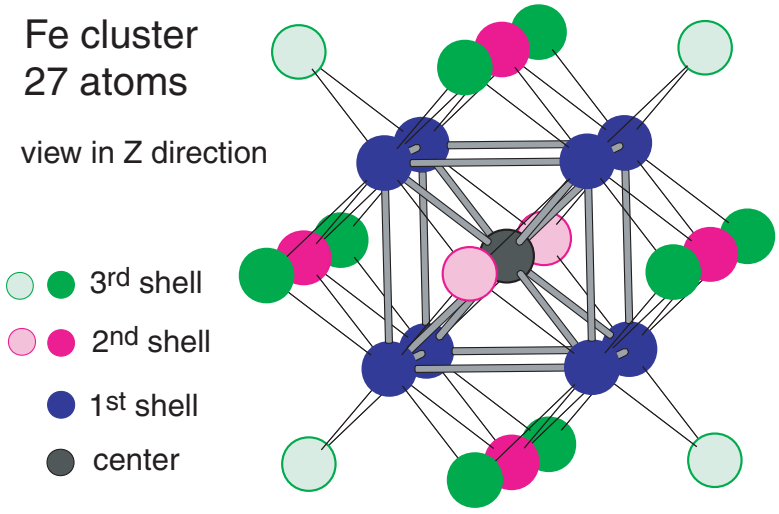
Our aim

The task we subscribed to:

- Explore theoretically magnetic properties of free iron clusters
- Compare properties of clusters with properties of crystal surfaces
- Look for some systematic trends (if any. . .)
- Find out how the magnetic properties of clusters get revealed through XMCD

System we study

- free spherical-like clusters with geometry taken as if they were cut from a bulk *bcc* Fe crystal
- cluster size range between 9 atoms (one coordination shell) and 89 atoms (seven coordinations shells)

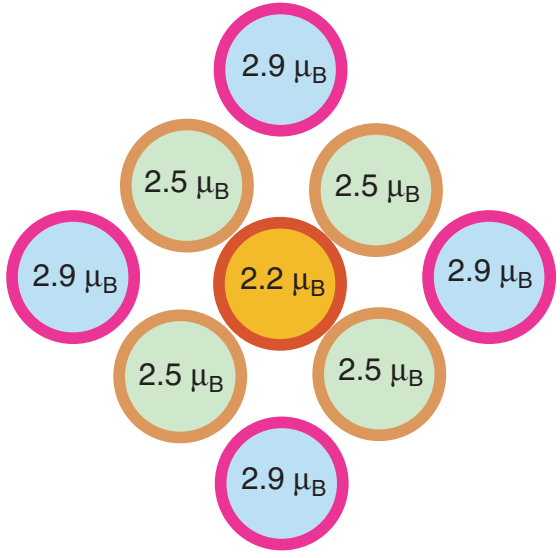


shells	atoms	radius [Å]
1	9	2.49
2	15	2.87
3	27	4.06
4	51	4.76
5	59	4.97
6	65	5.74
7	89	6.25

Theoretical formalism

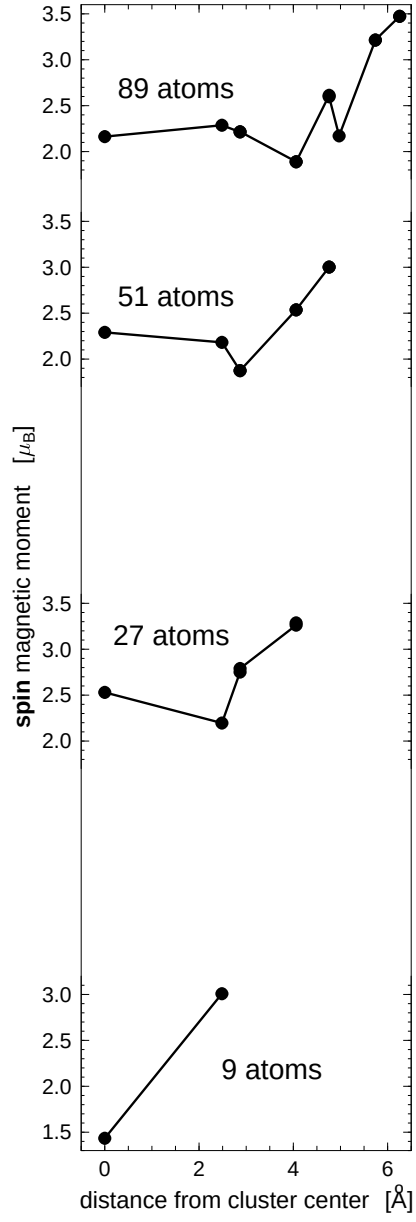
- local density approximation scheme, Vosko, Wilk and Nusair parametrization of the exchange-correlation potential
- electronic structure and XMCD spectra of free clusters calculated in real space via a fully-relativistic spin-polarized multiple-scattering technique as implemented in the SPRKKR code
- scattering potential obtained from scalar-relativistic SCF (Xα-like) calculations applied to molecular clusters
- surfaces treated as 2D finite slabs, their electronic structure calculated by a fully-relativistic spin-polarized TB-KKR method
- spherical ASA approximation used both for clusters and for surfaces
- vacuum spheres used in order to account for spilling of the electron charge into vacuum

Magnetic profiles of free iron clusters



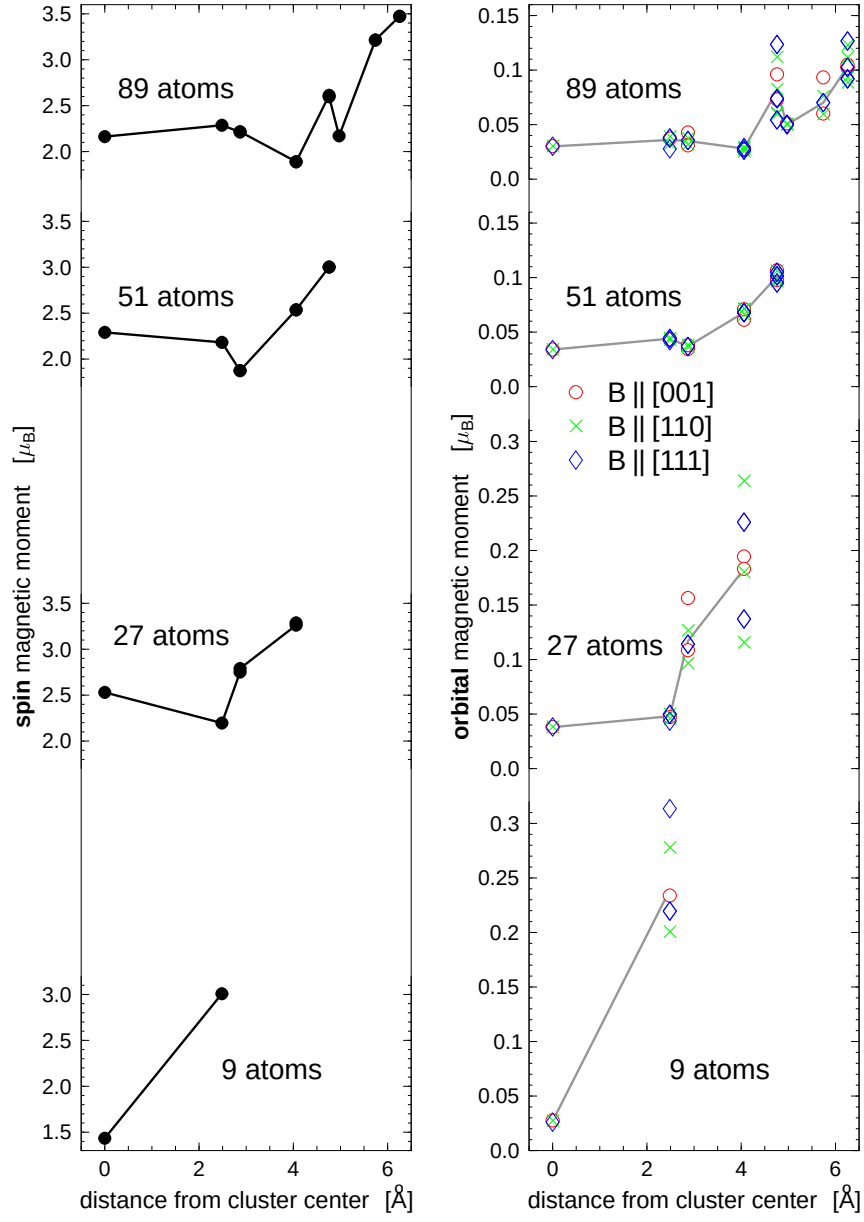
Magnetic profiles of free iron clusters

- μ_{spin} does not depend on the direction of $\boldsymbol{B}$, μ_{spin} for inequivalent atoms of the same coordination sphere are the same

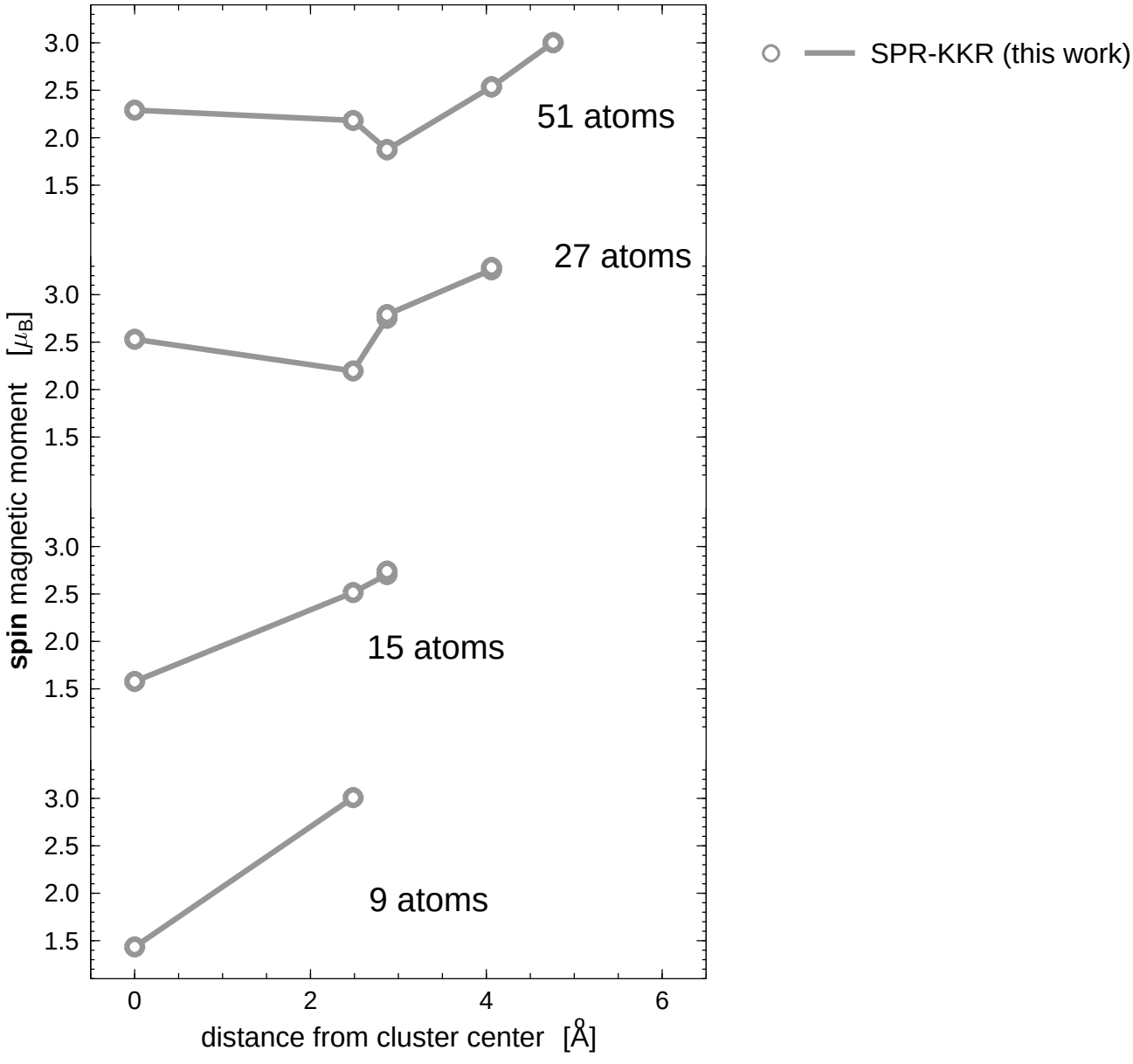


Magnetic profiles of free iron clusters

- μ_{spin} does not depend on the direction of $\boldsymbol{B}$, μ_{spin} for inequivalent atoms of the same coordination sphere are the same
- μ_{orb} depends on the direction of $\boldsymbol{B}$, μ_{orb} for symmetry-inequivalent atoms of the same coordination sphere differ
- μ_{orb} averaged over coordination spheres does not depend on the direction of $\boldsymbol{B}$



Comparing with other works (1)



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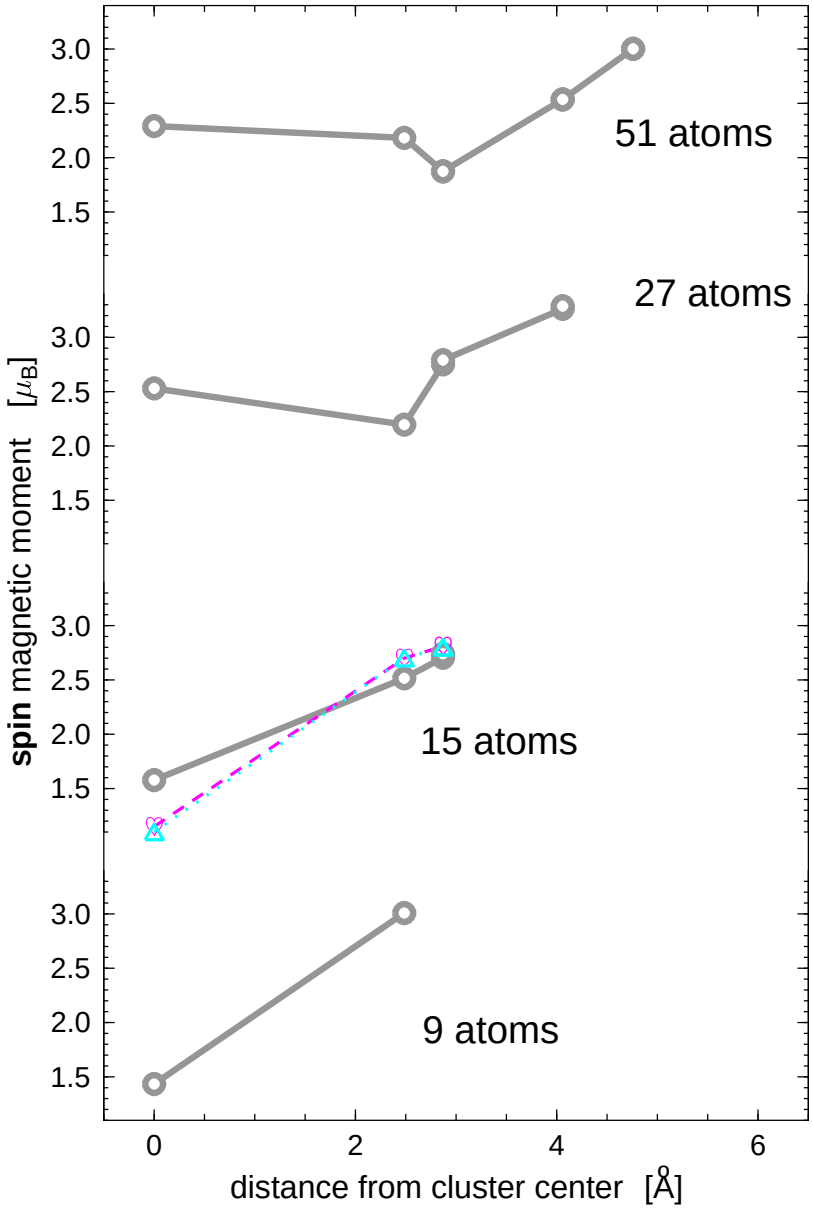

SPR-KKR (this work)

SCF $X\alpha$ (Yang '81)

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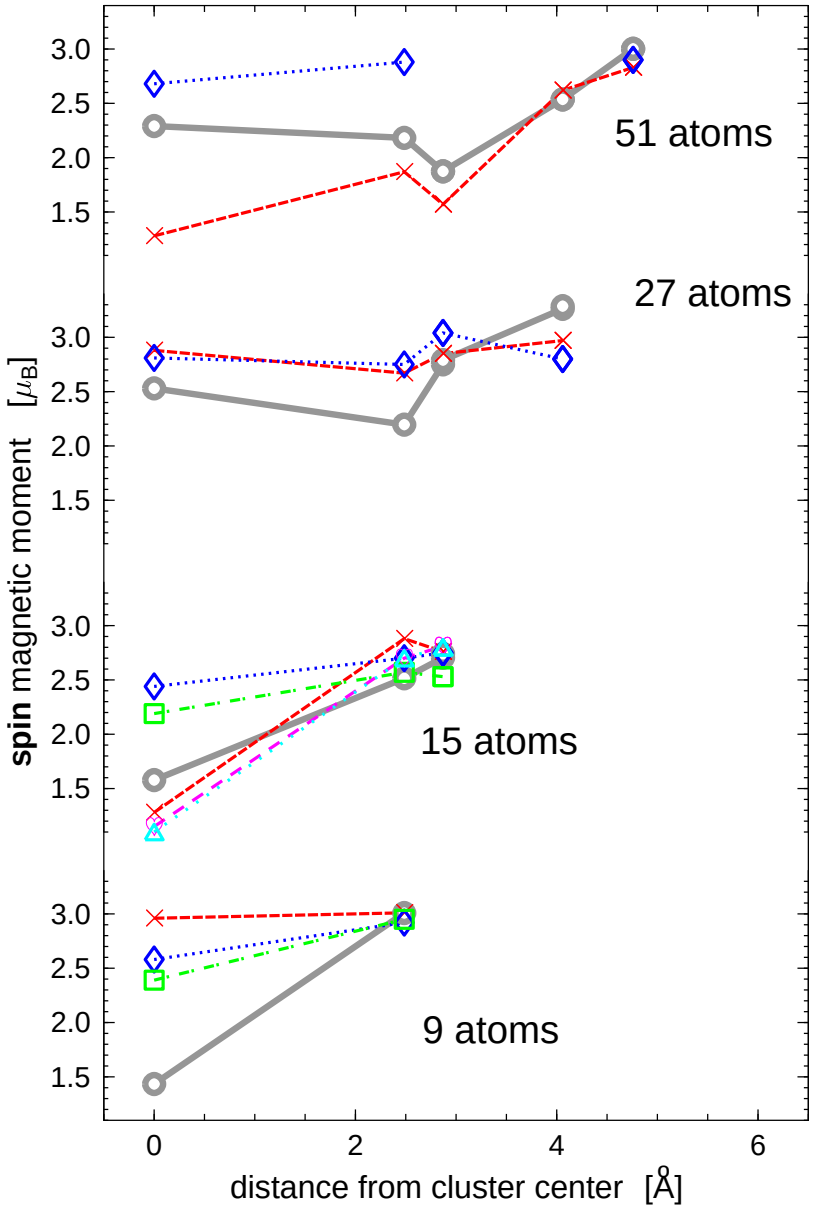

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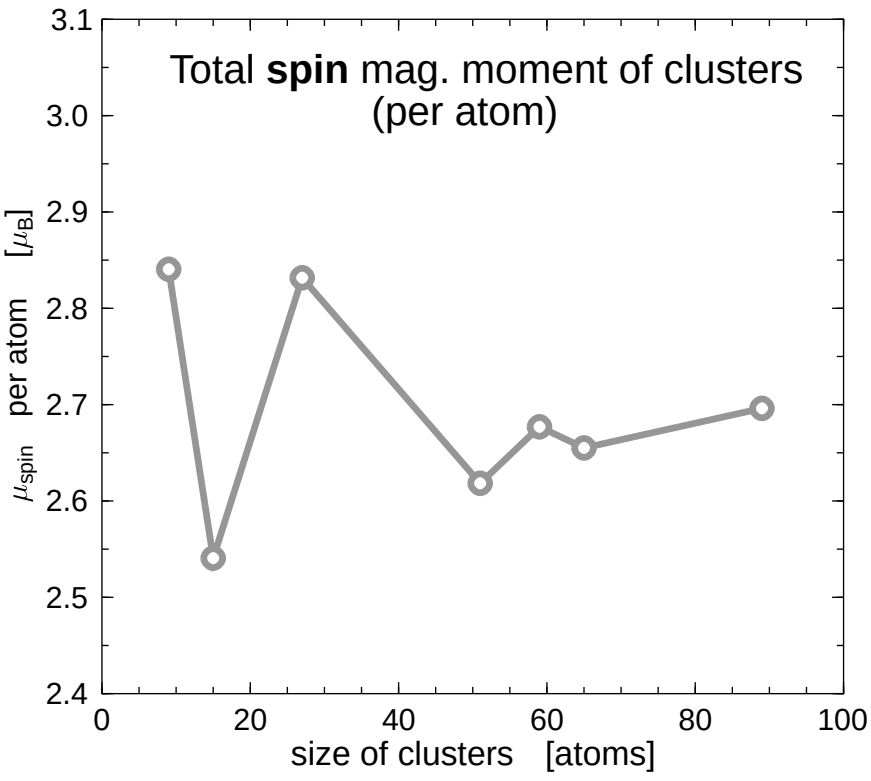

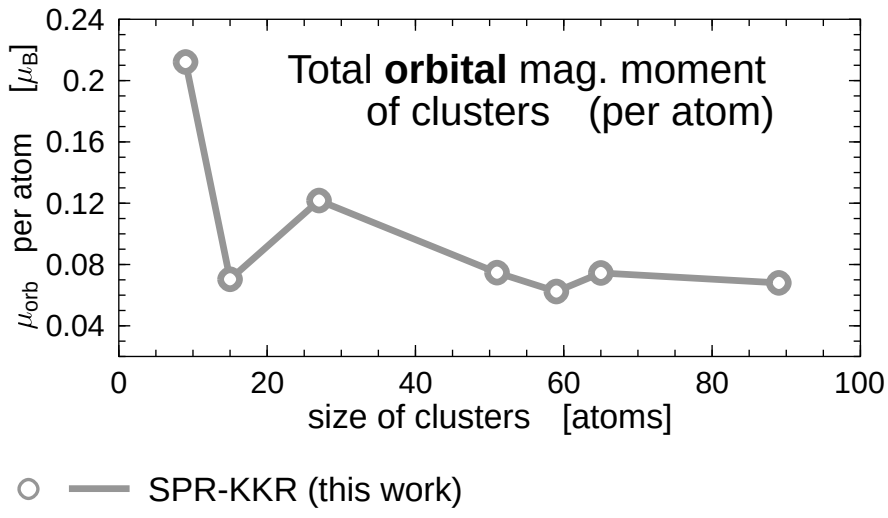

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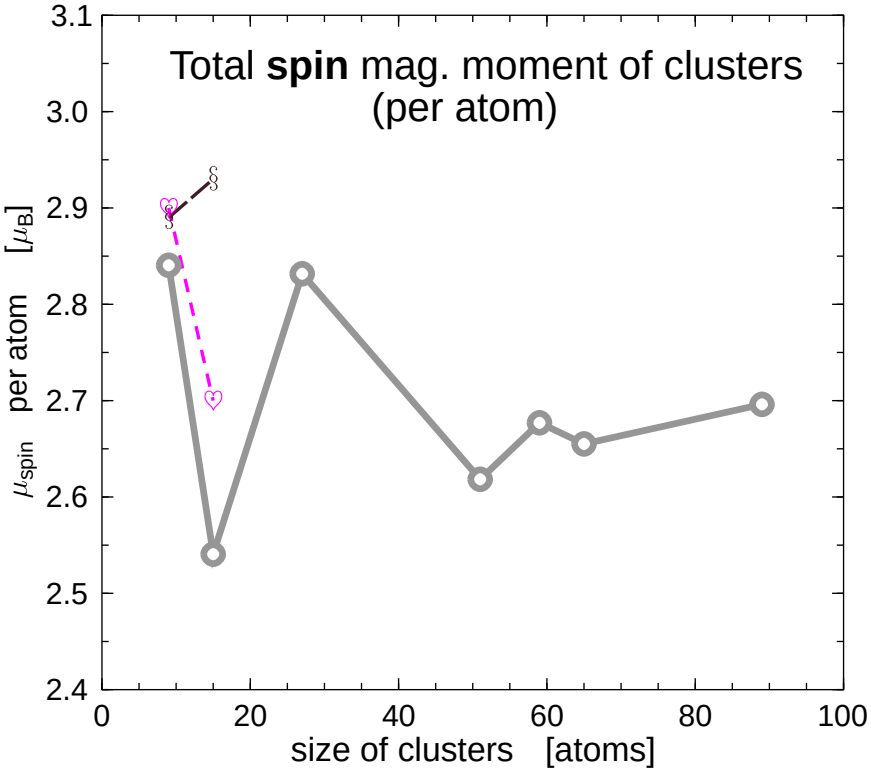

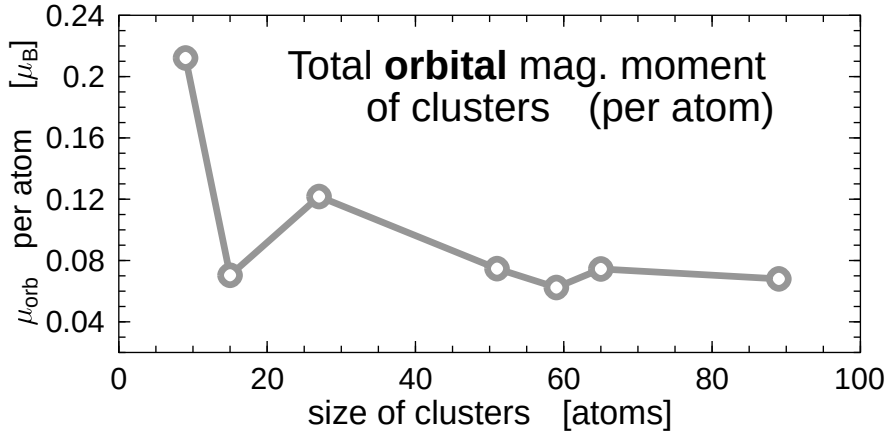

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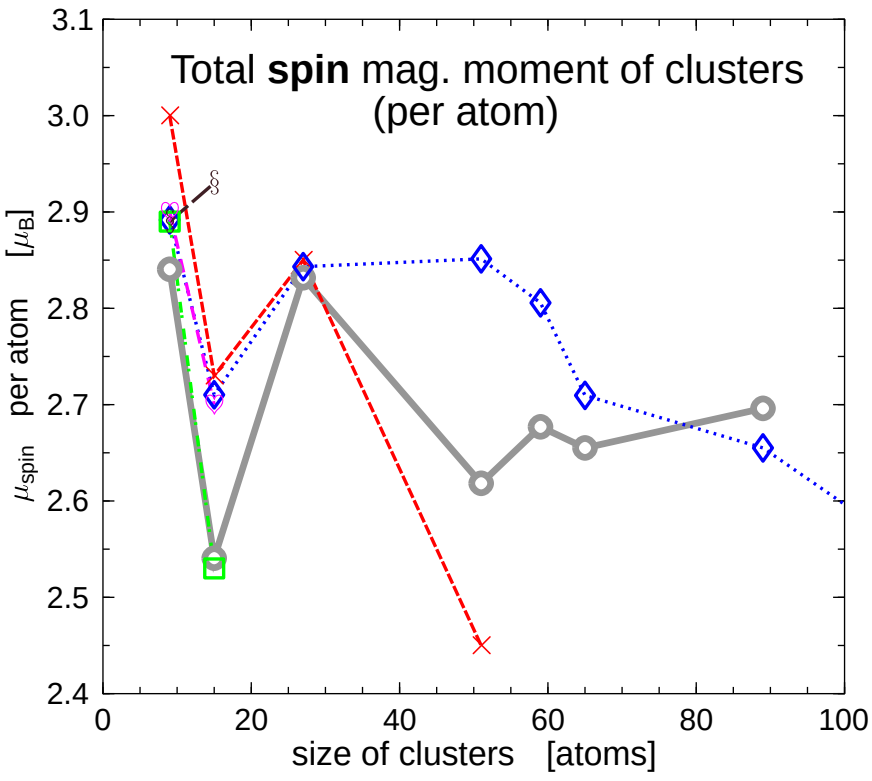

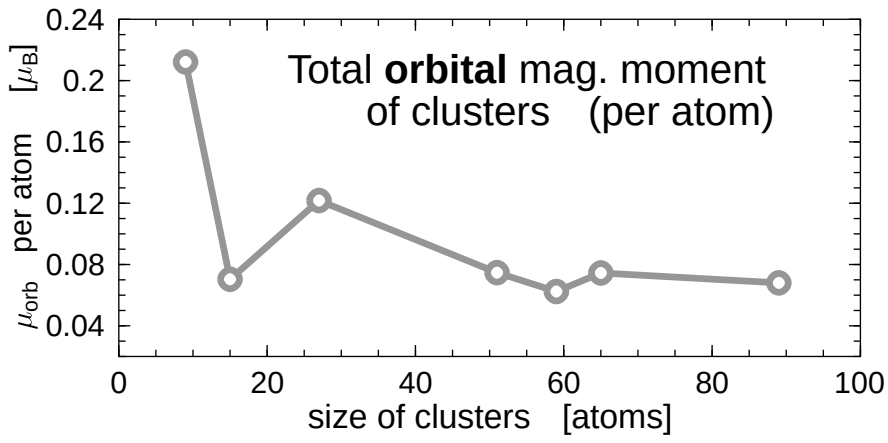

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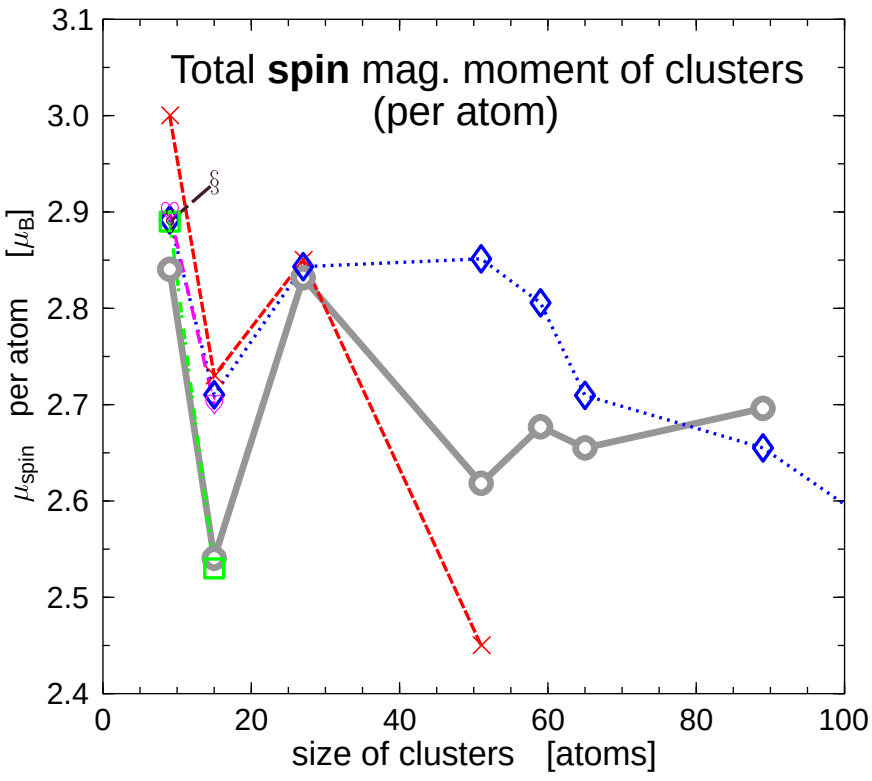

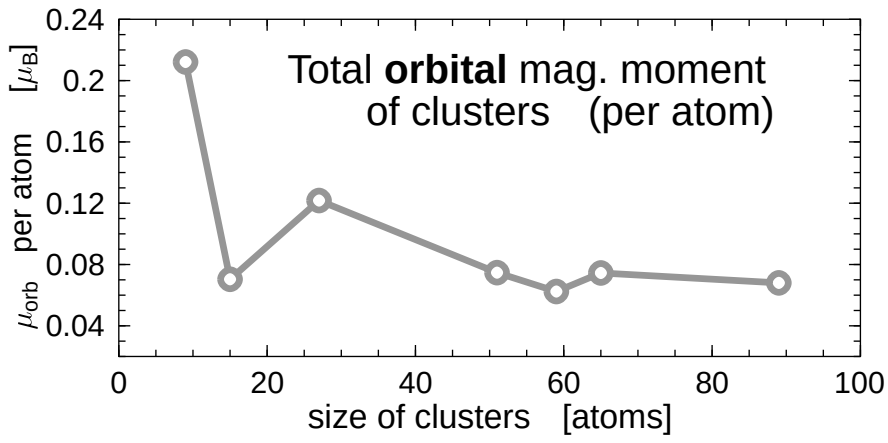

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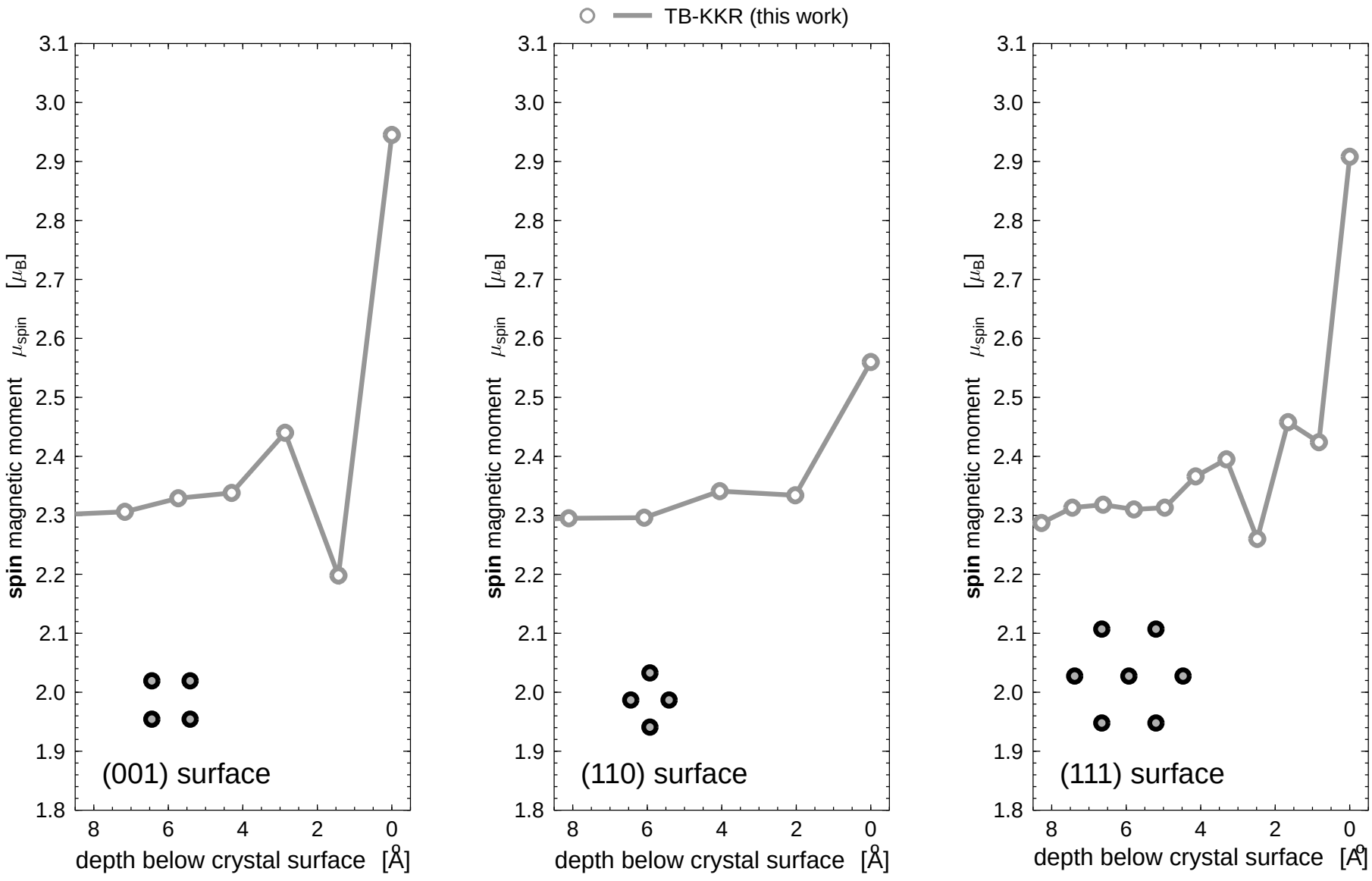
$\Rightarrow$

Even the "simple" task of calculating magnetic properties of free iron clusters with fixed bulk-like geometry appears to be beyond current abilities of mankind. . . (?)

Magnetic profiles of crystal surfaces (1)



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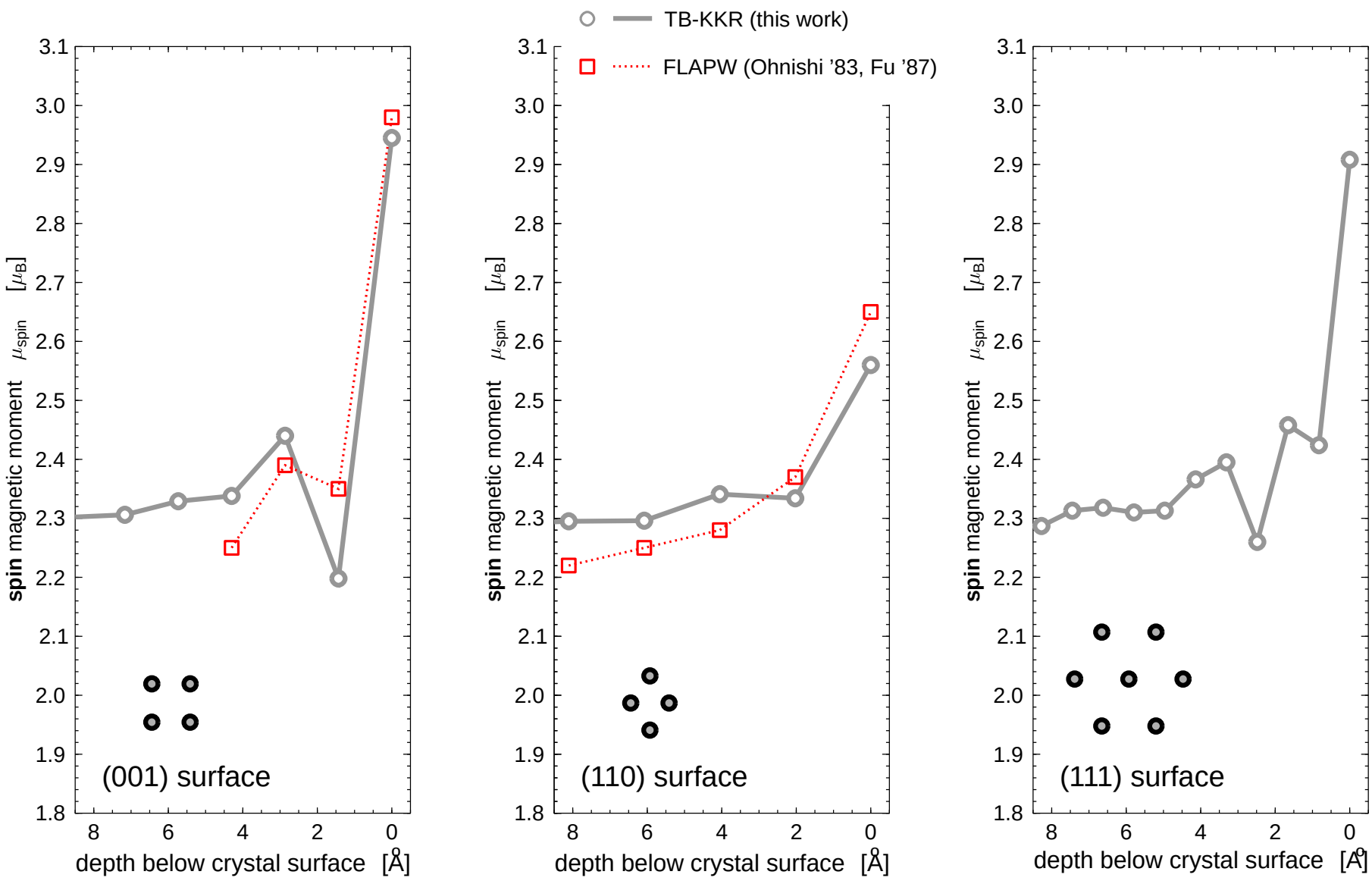

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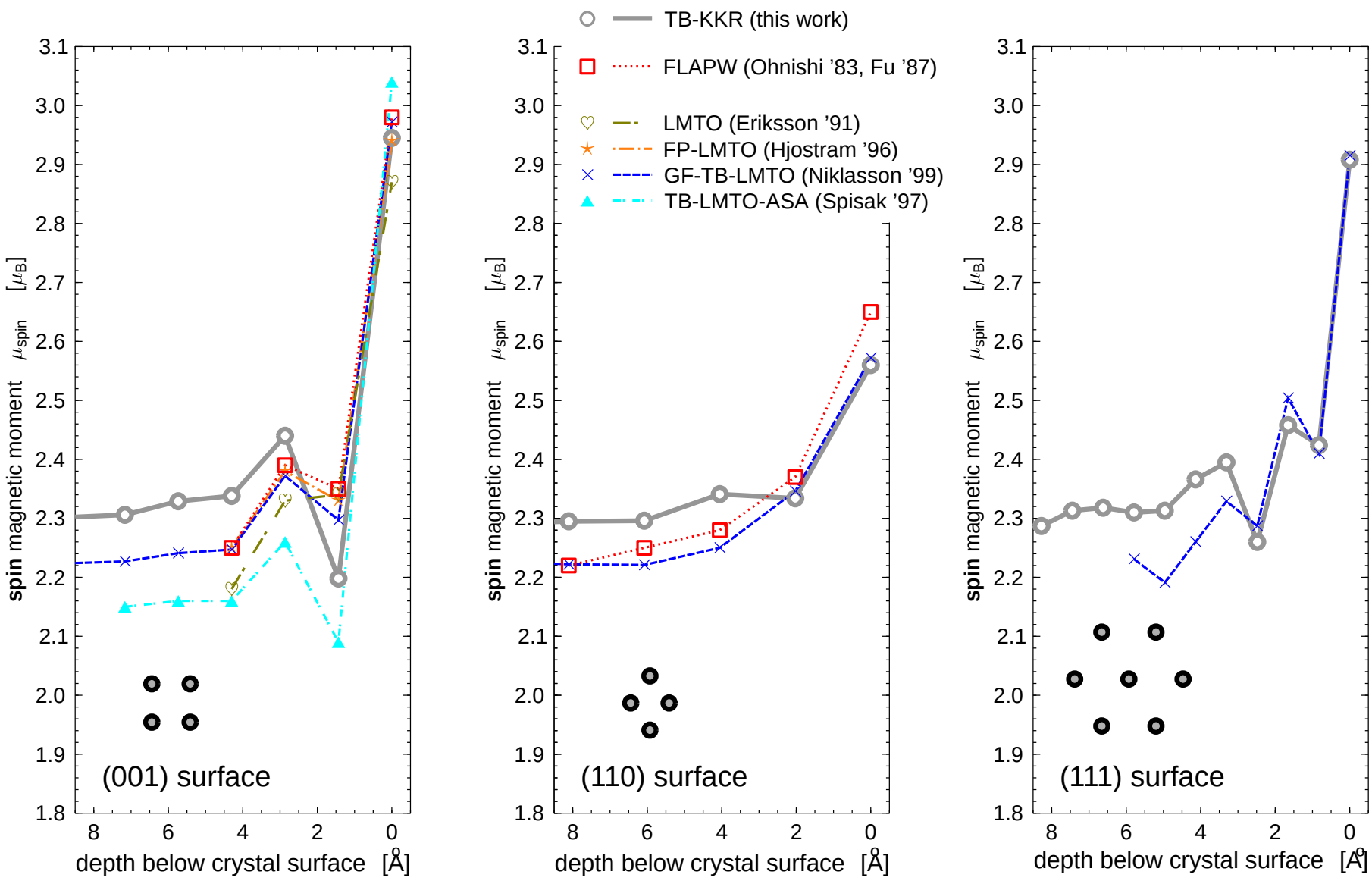

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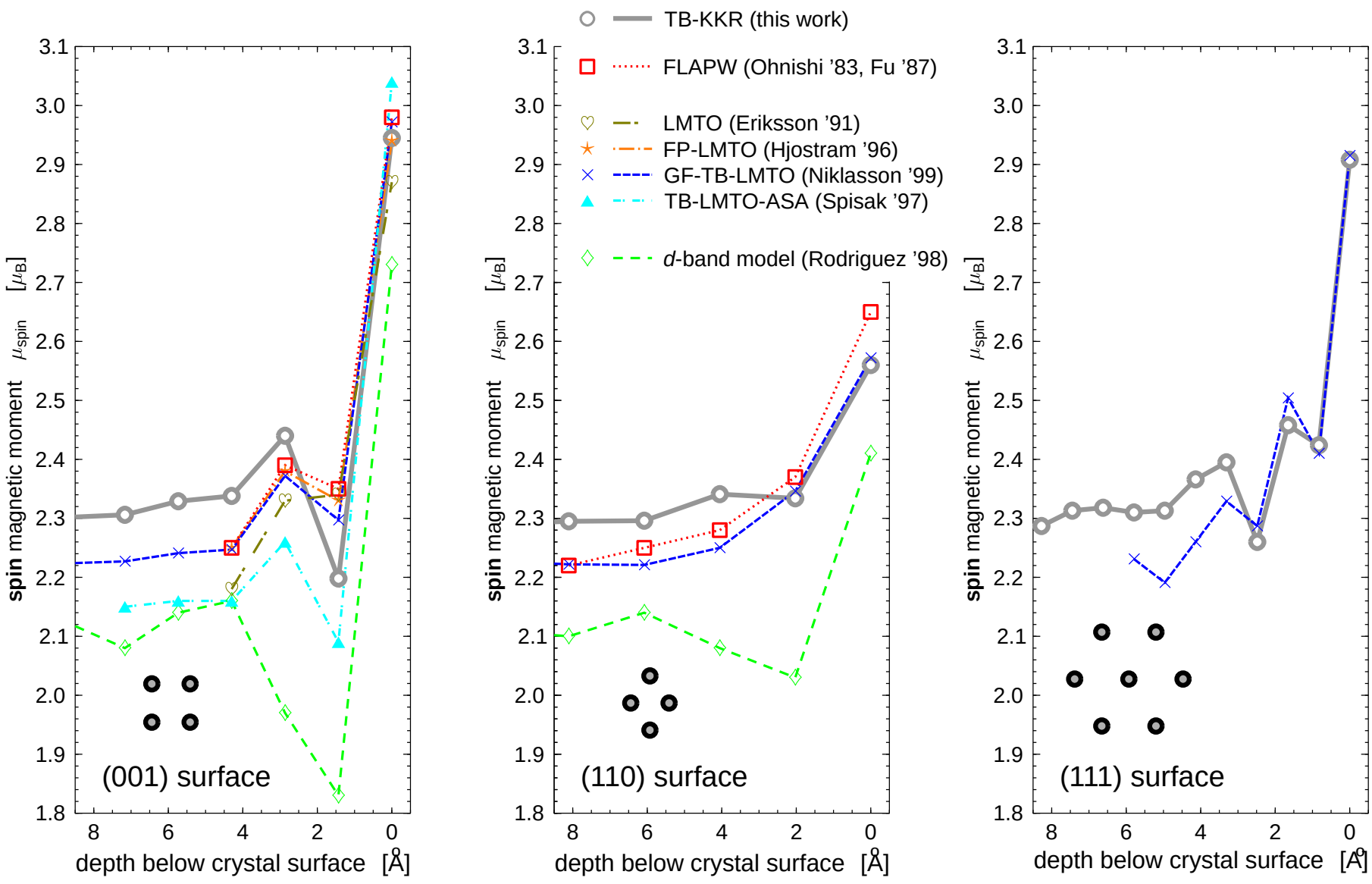
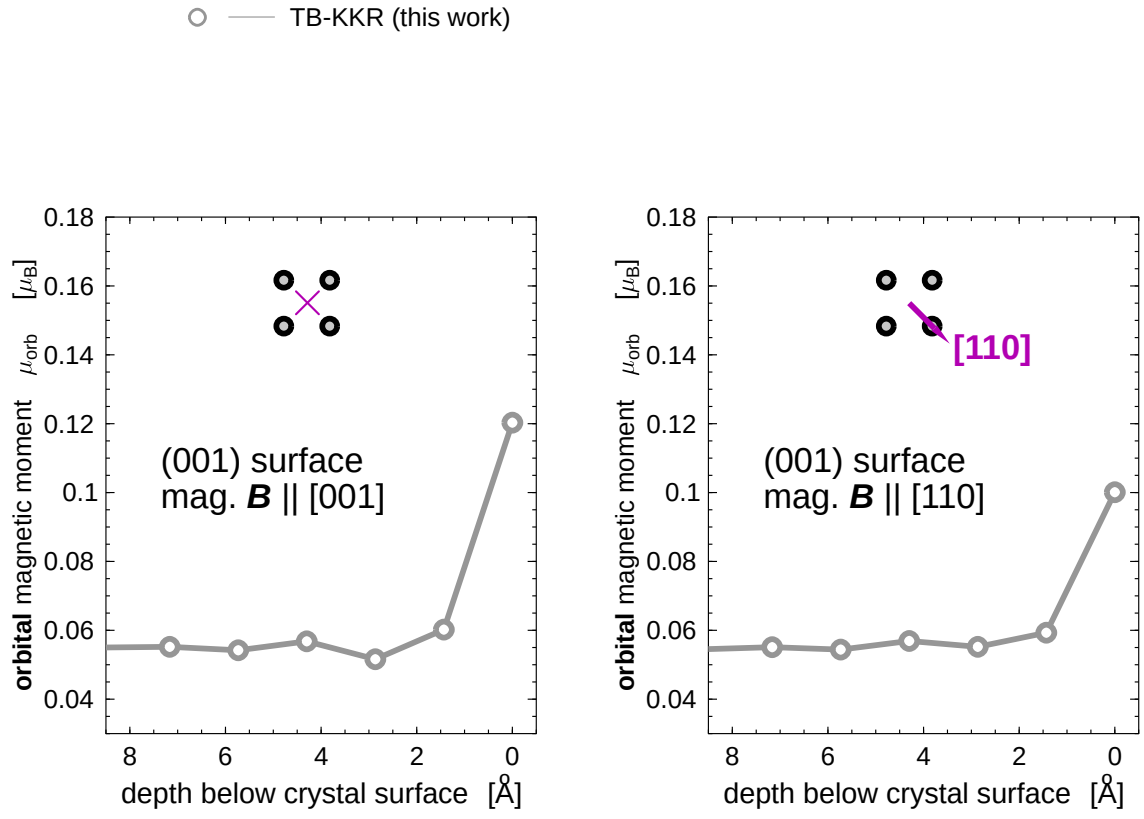


Magnetic profiles of crystal surfaces (2)



Magnetic profiles of crystal surfaces (2)

Orbital polarization:

SPRKKR estimate of bulk iron:

without OP:
$\mu_{\mathrm{orb}} = 0.054$

with OP:
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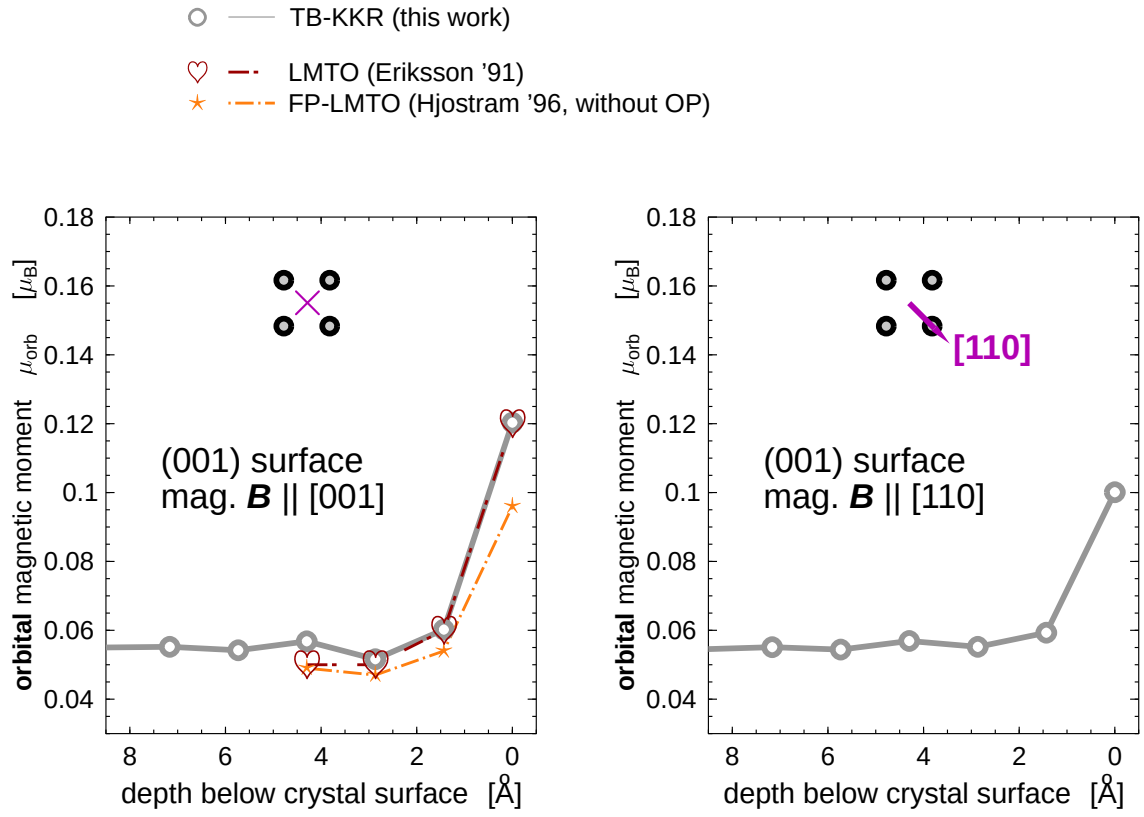

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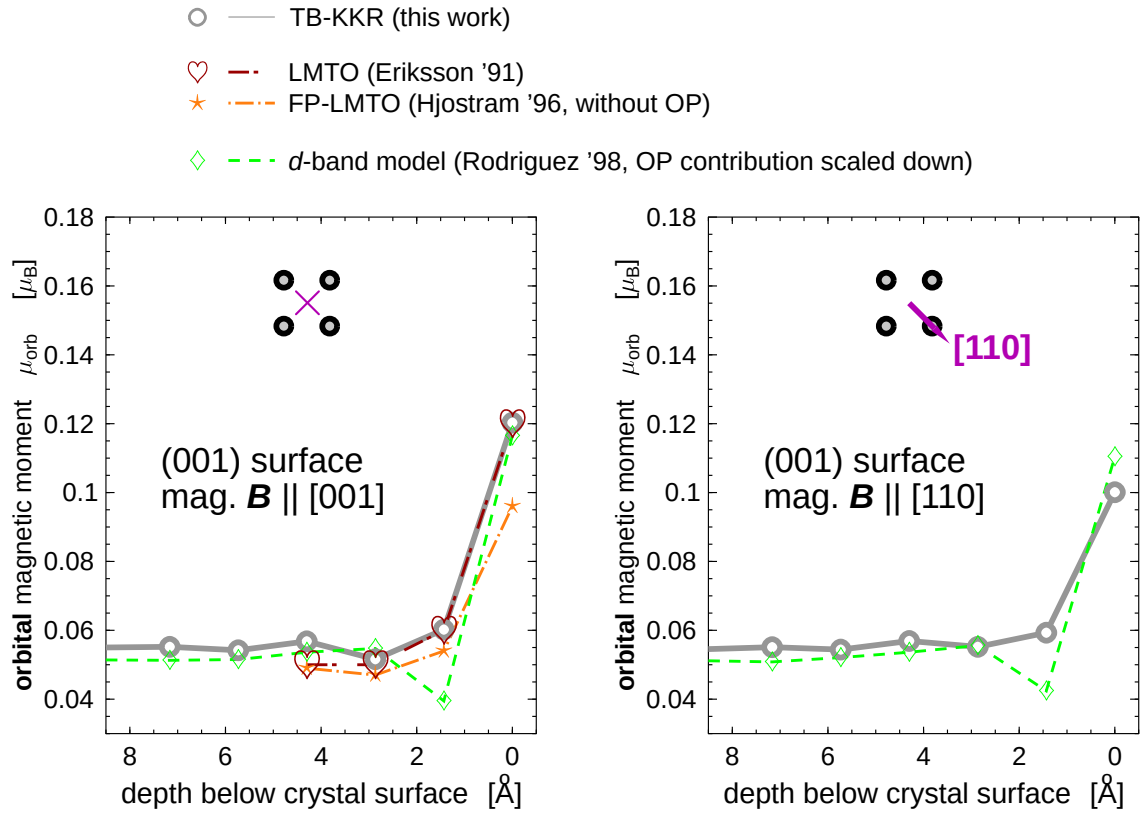
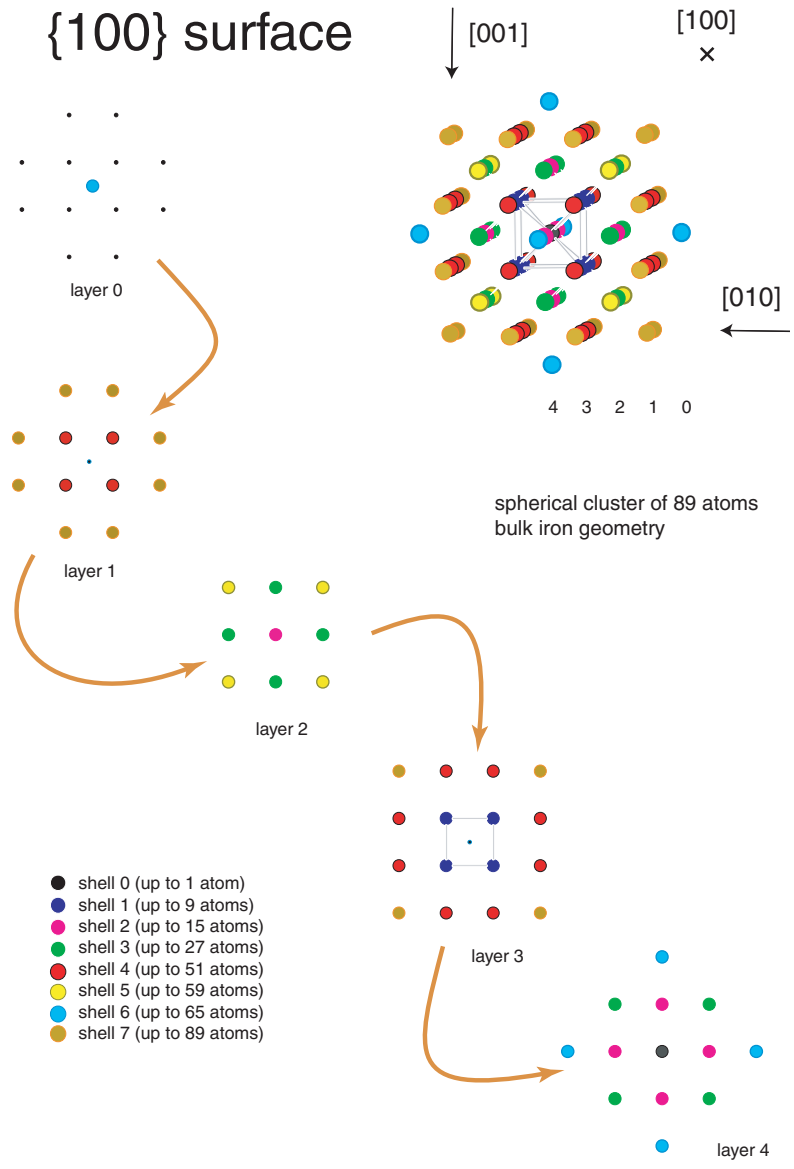


Clusters vers. surfaces: HOWTO

- take free iron clusters of 89 atoms
- drill into the cluster a hole (starting from outside towards the center)
- look around for the magnetic moments and compare them with what you see if you drill a hole beneath a crystal surface
- explore various “crystallo-graphic directions”

Clusters vers. surfaces: HOWTO



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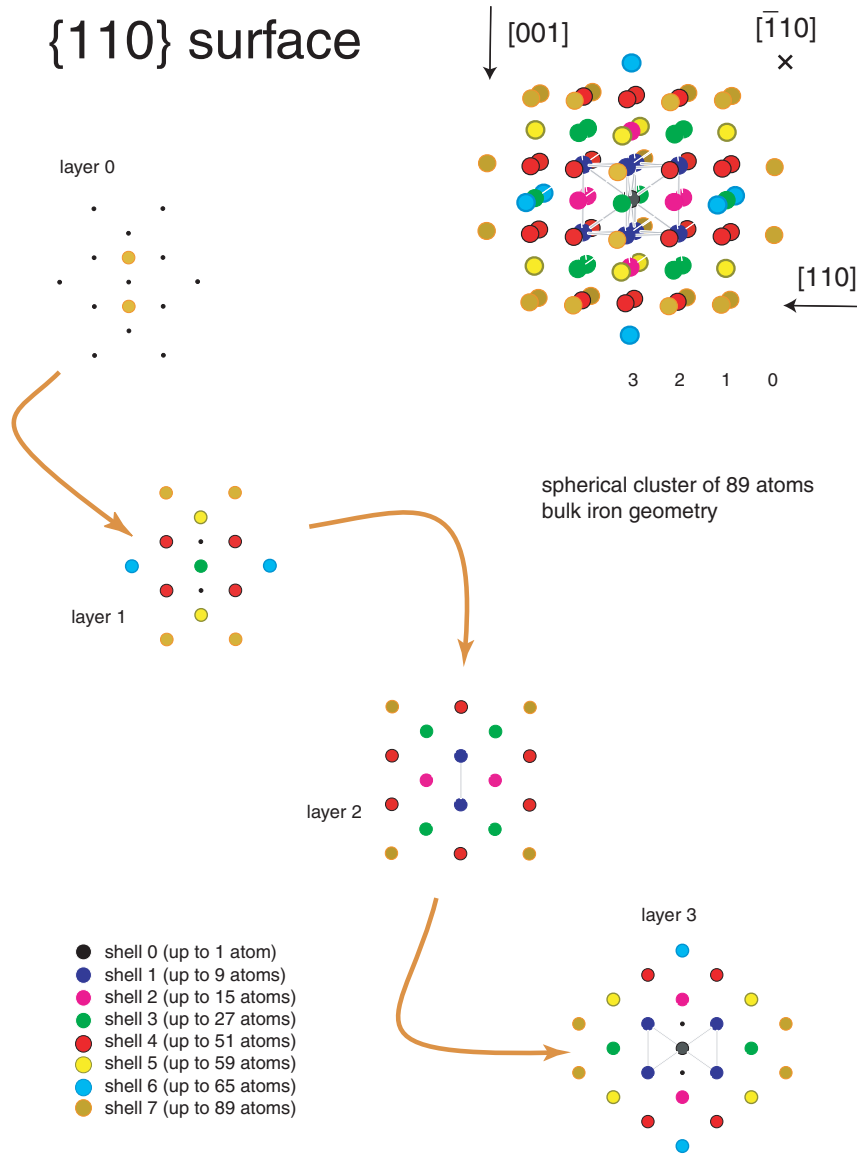

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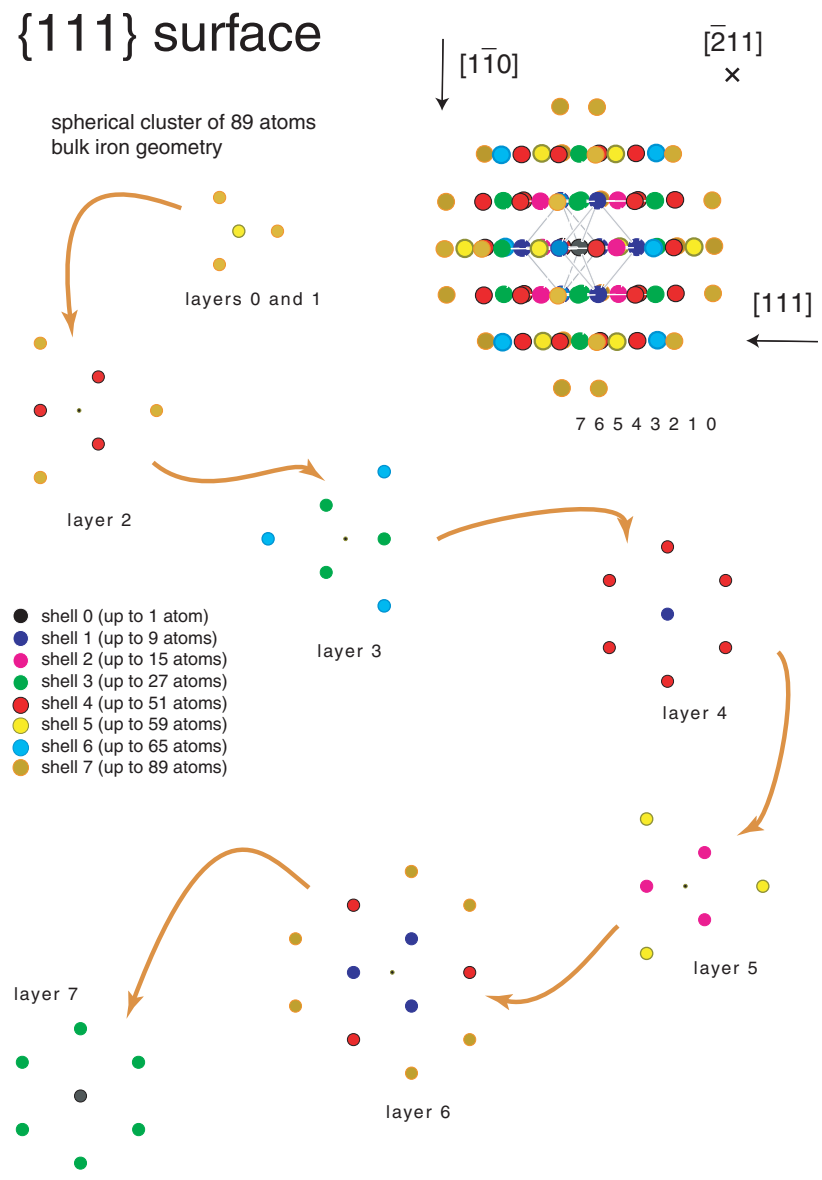
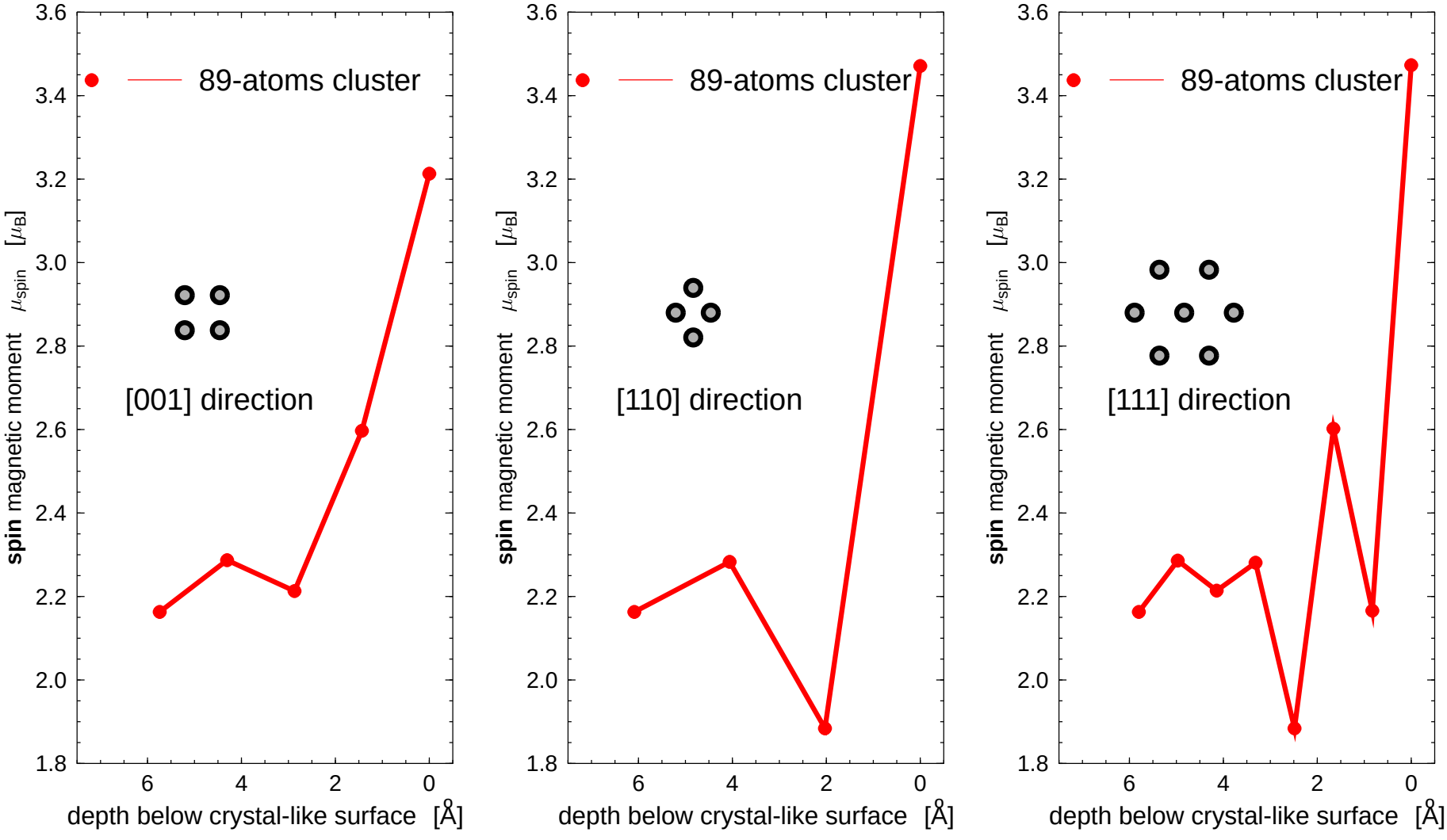


Clusters vers. surfaces: μ_{spin}



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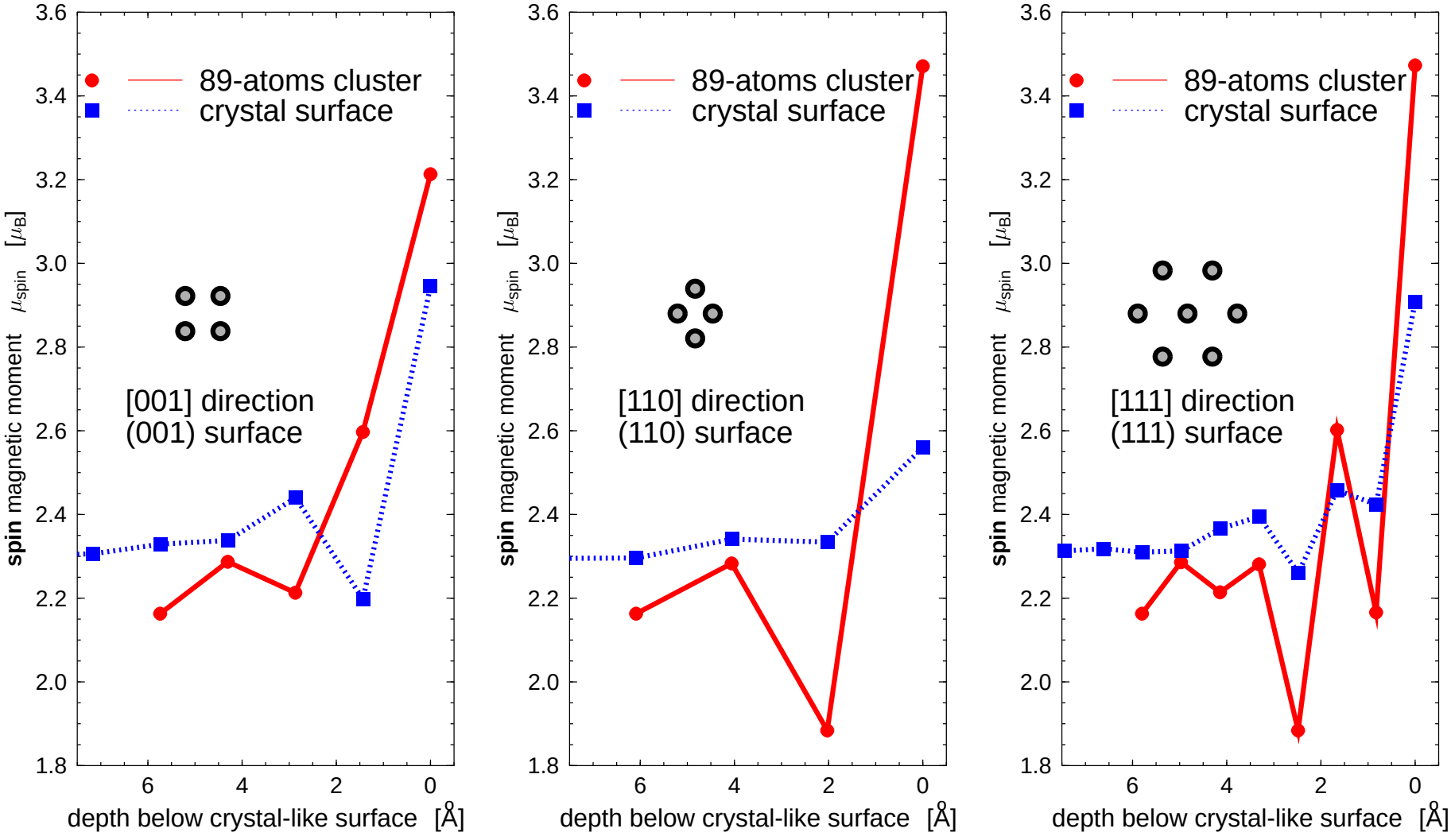
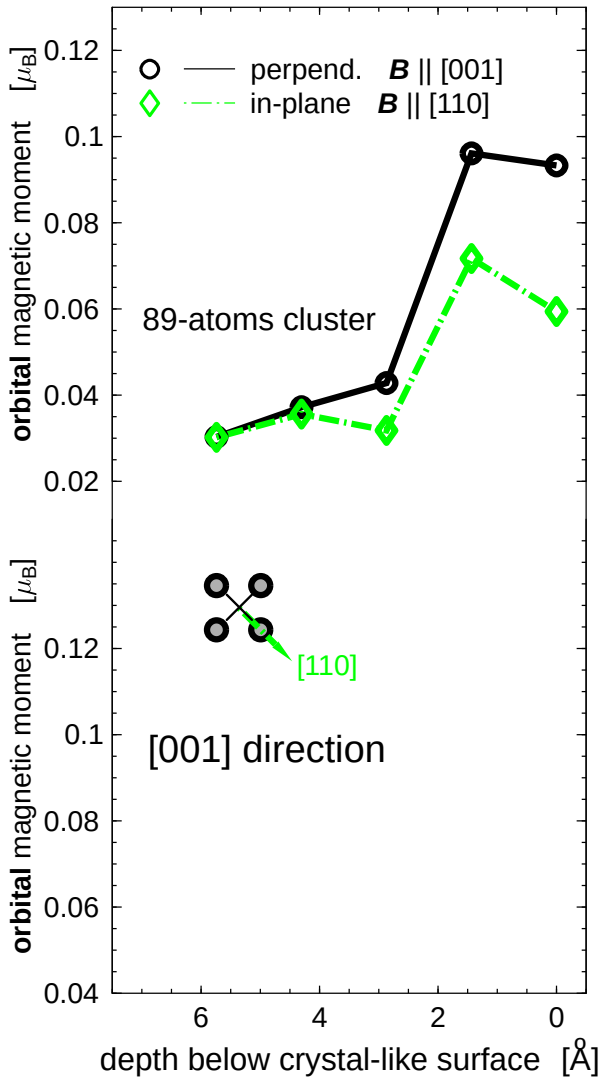
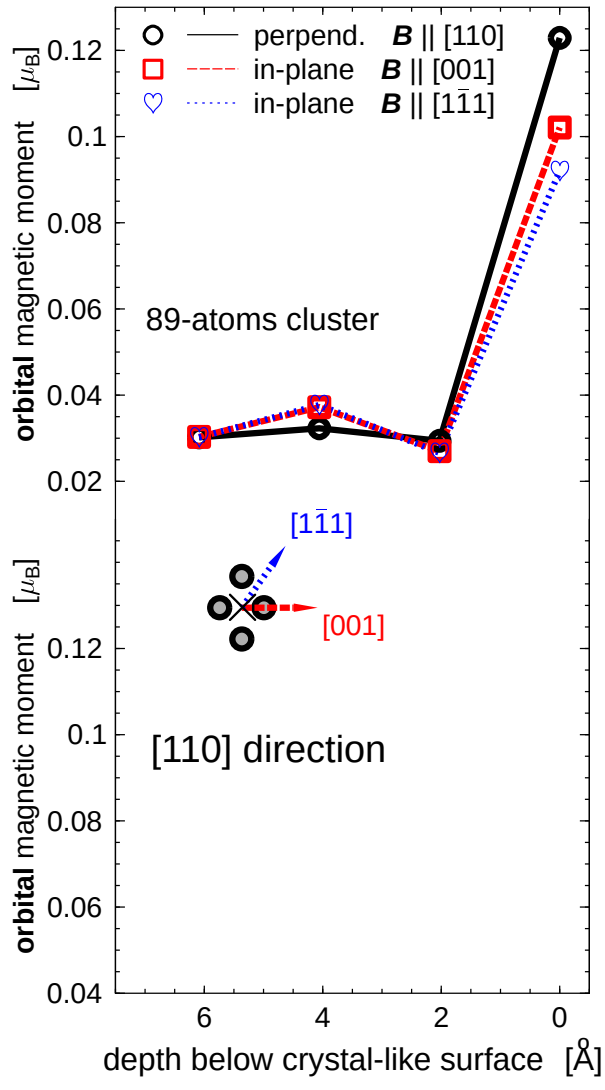
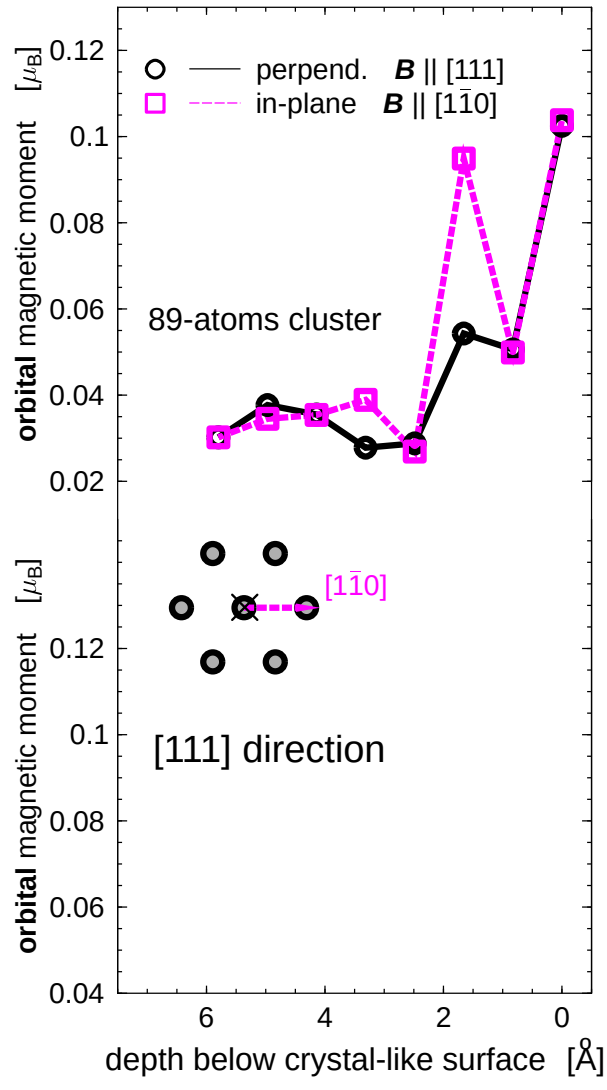


Clusters vers. surfaces: μ_{orb}







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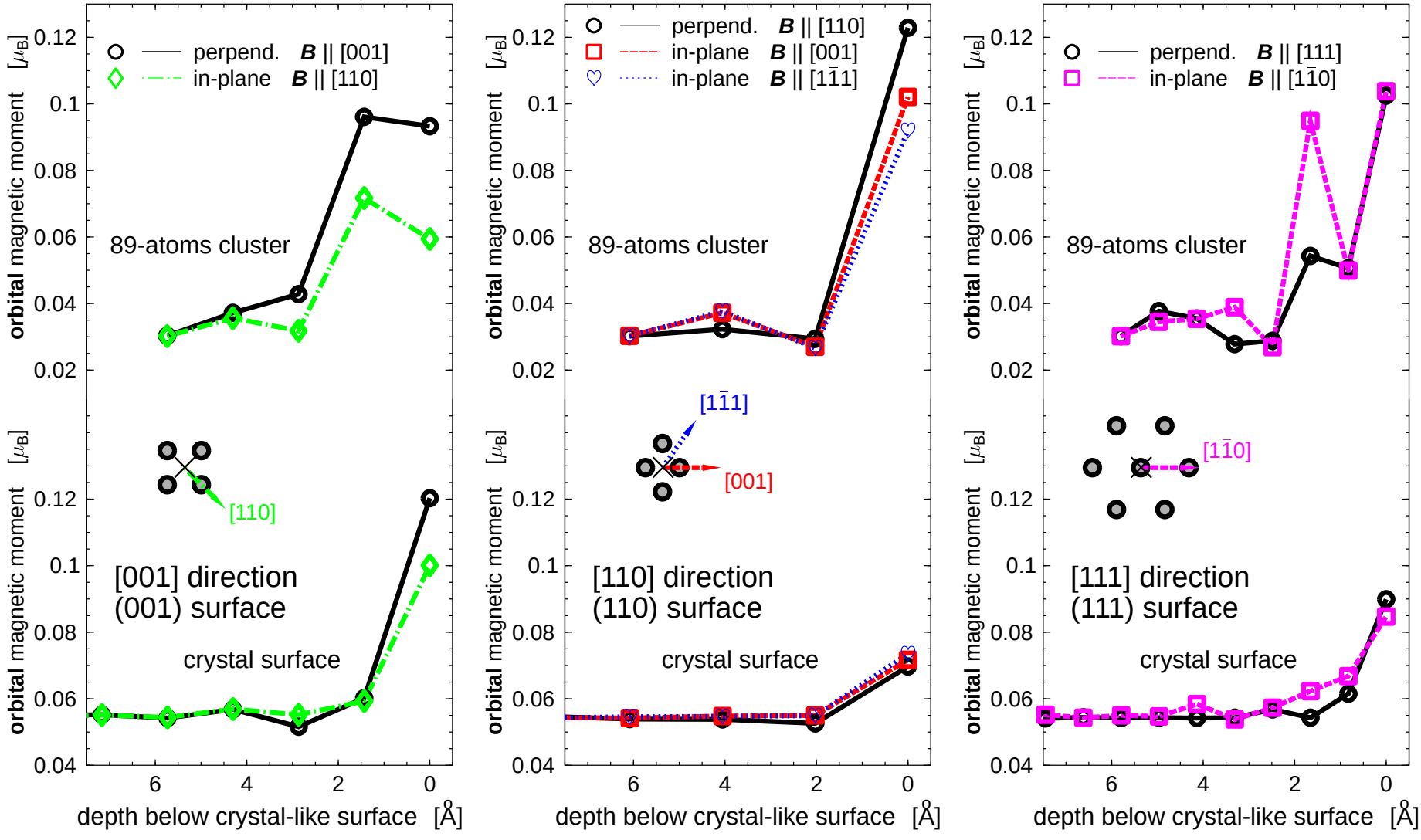

A lot of profiles, a lot of data $\Rightarrow$ a lot of chaos. . .

Is there a way out?

Dependence of $\mu_{\rm spin}$ on $N_{\rm eff}$

Effective coordination number: for a *bcc* crystal one defines

$$N_{\rm eff} = N_1 + 0.25 \times N_2,$$

where N_1 is number of 1^{st} neighbors and N_2 is number of 2^{nd} neighbors.

[D. Tománek *et al.* PRB **28**, 665 (1983); J. Zhao *et al.* Physics Letters A **205**, 308 (1995)]

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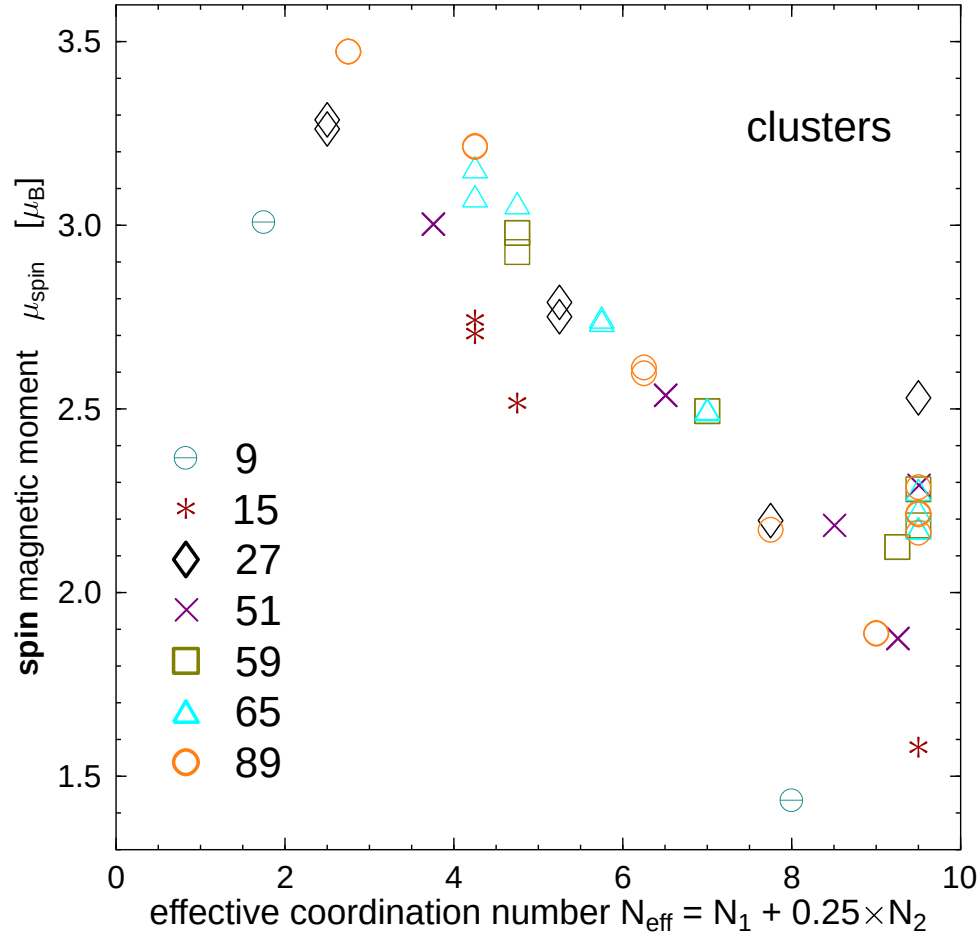

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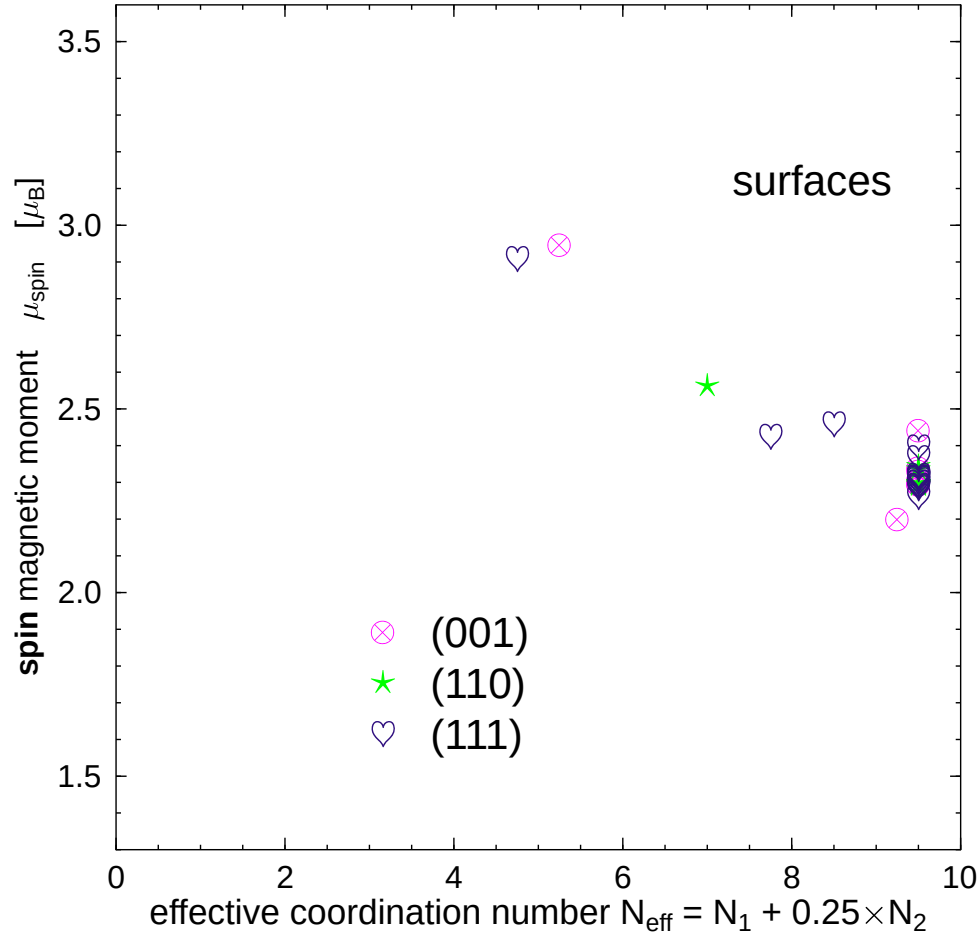

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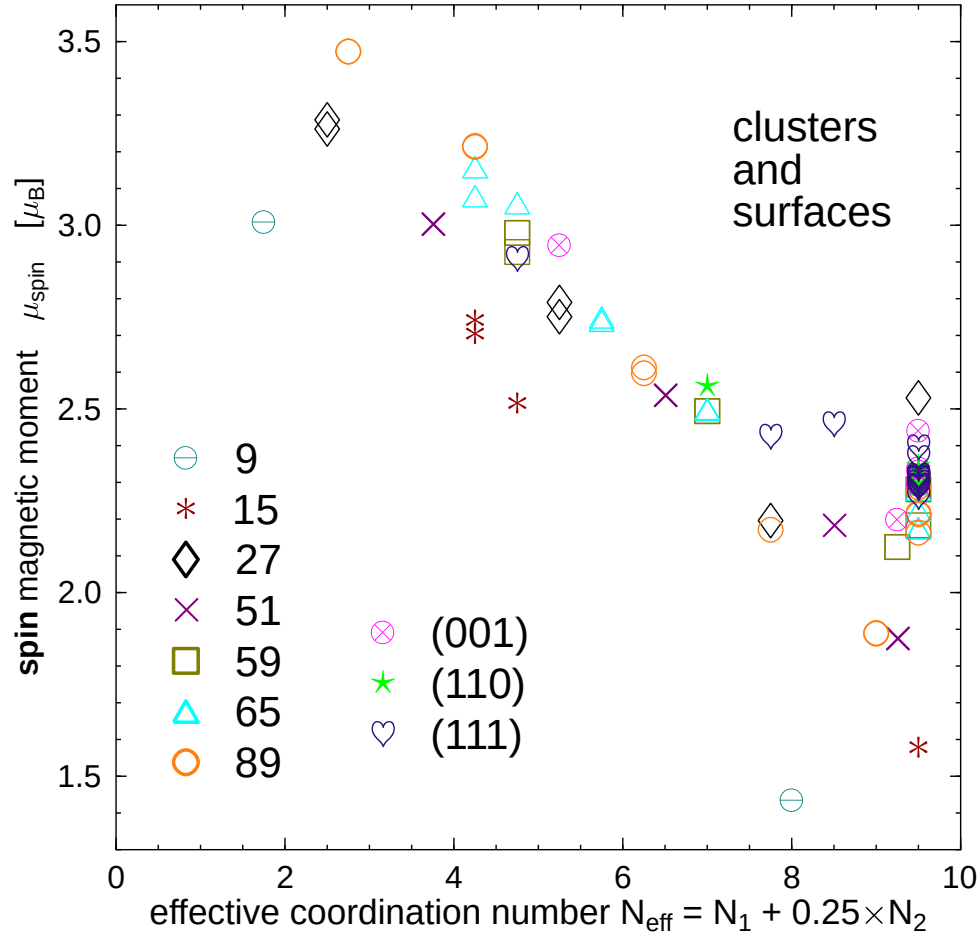

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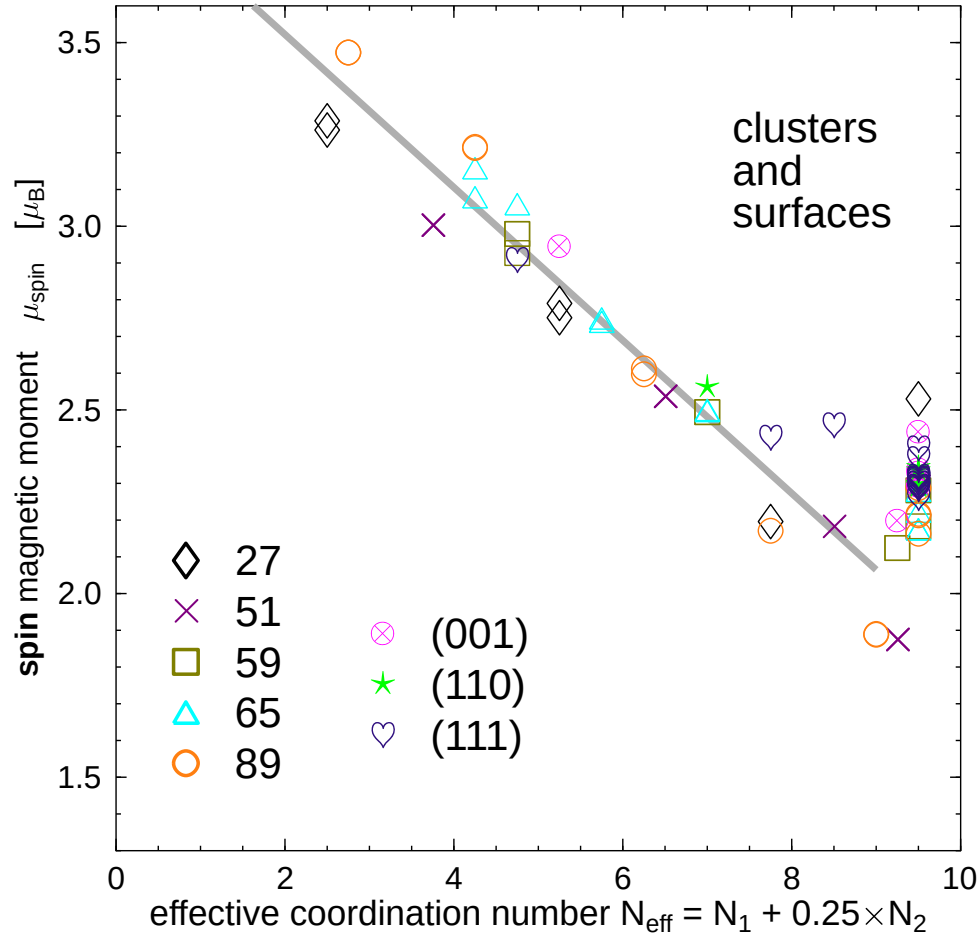
Empirical model dependence:

$$\mu_{\rm spin} = -0.21 \times N_{\rm eff} + 3.94$$



Dependence of $\mu_{\rm spin}$ on $N_{\rm eff}$

Effective coordination number: for a *bcc* crystal one defines

$$N_{\rm eff} = N_1 + 0.25 \times N_2,$$

where N_1 is number of 1^{st} neighbors and N_2 is number of 2^{nd} neighbors.

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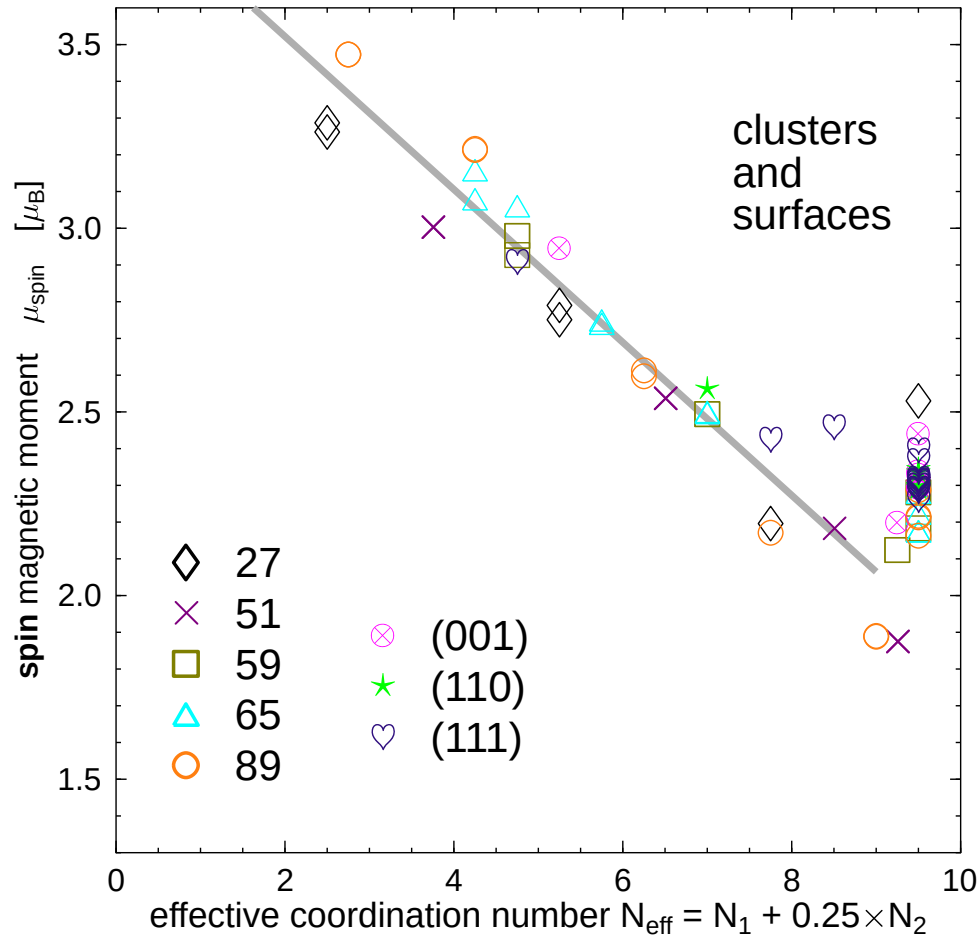
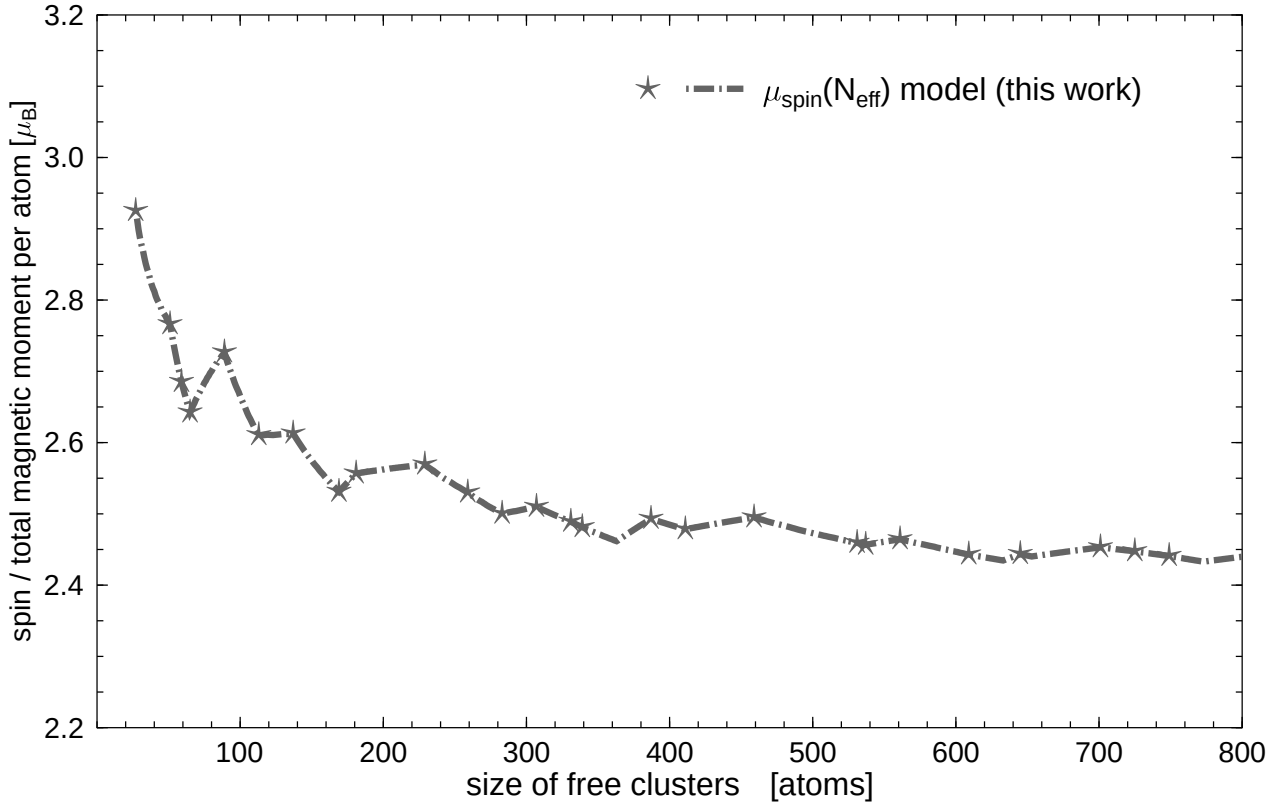


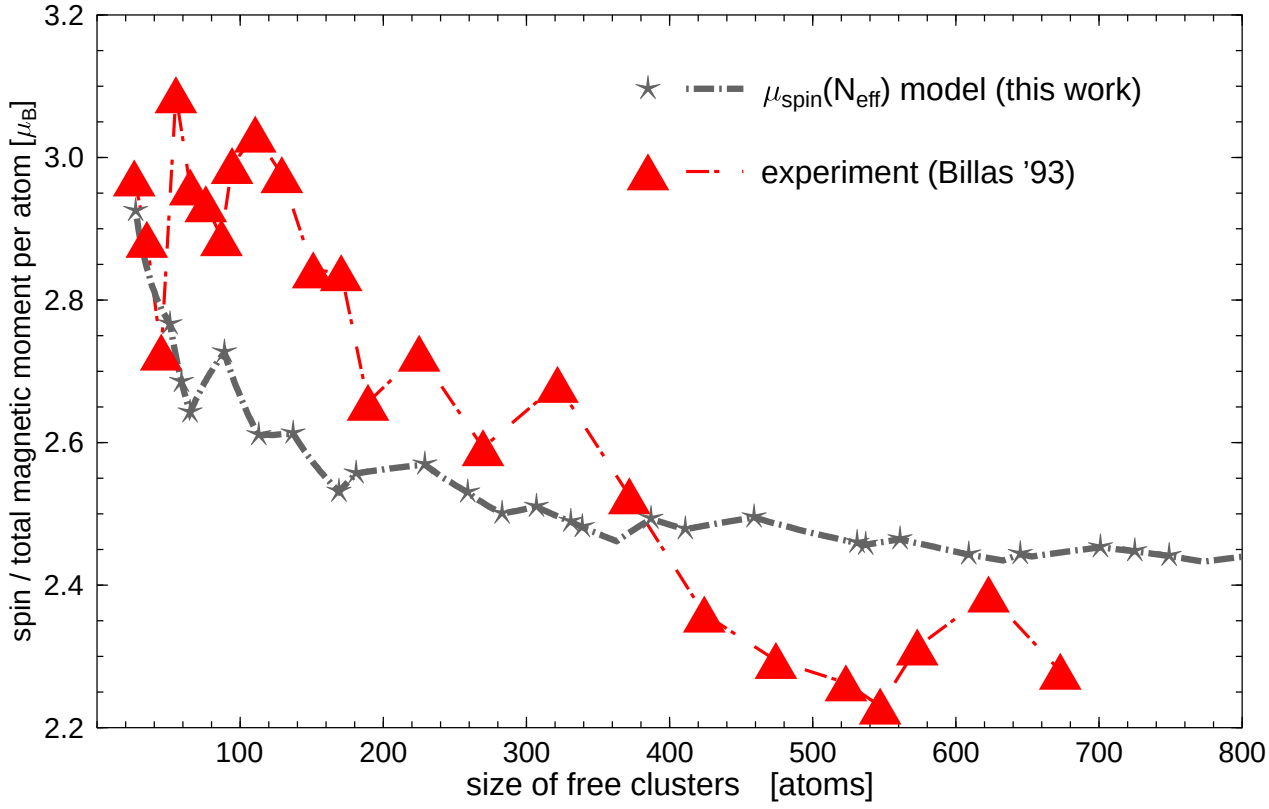
No simple dependence works for the orbital moment $\mu_{\rm orb}$.

Large clusters via $\mu_{\mathrm{spin}}(N_{\mathrm{eff}})$



Assumption: clusters grow by filling successive coordination spheres; within a sphere, atoms adsorb so that they have max. coordination.

Comparing model with experiment



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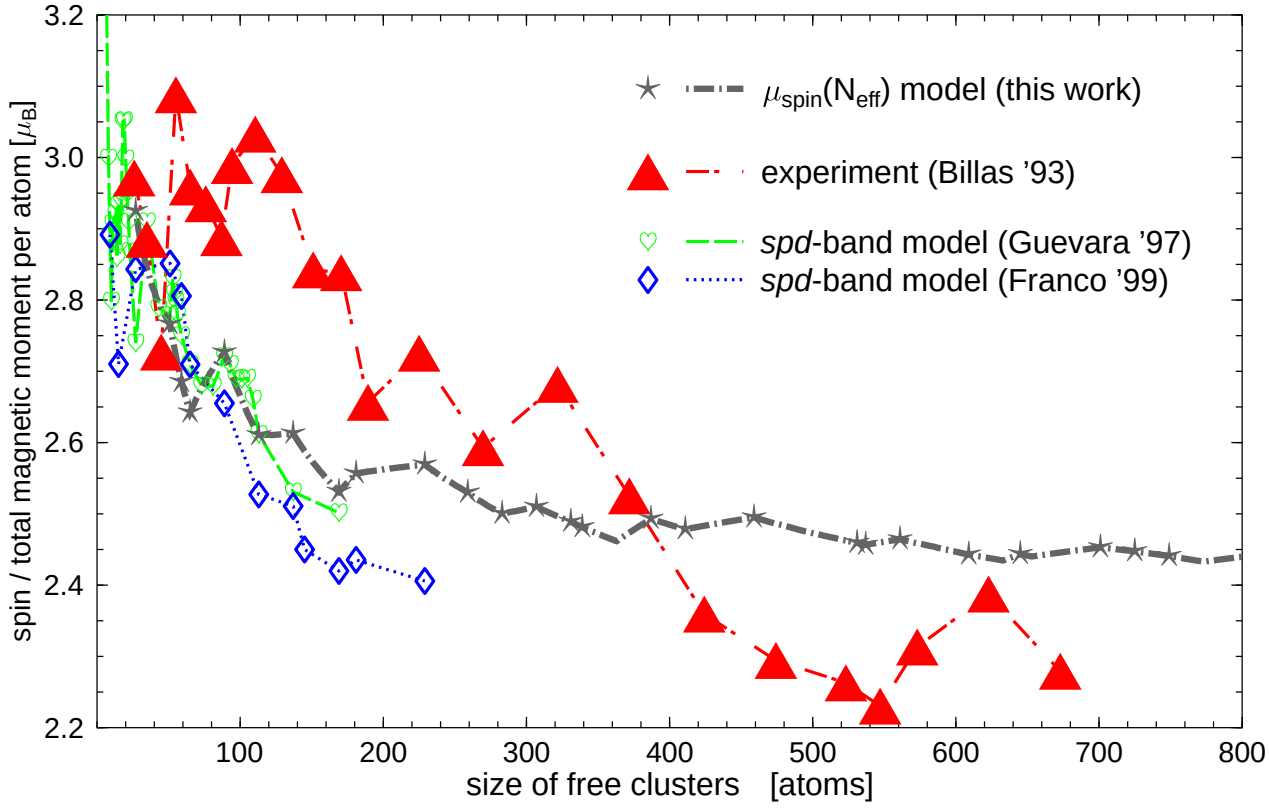

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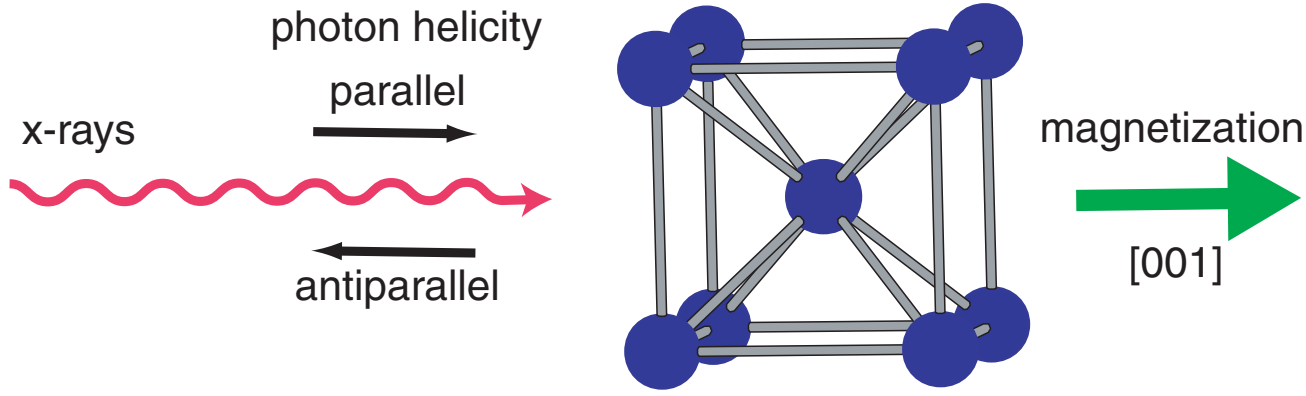
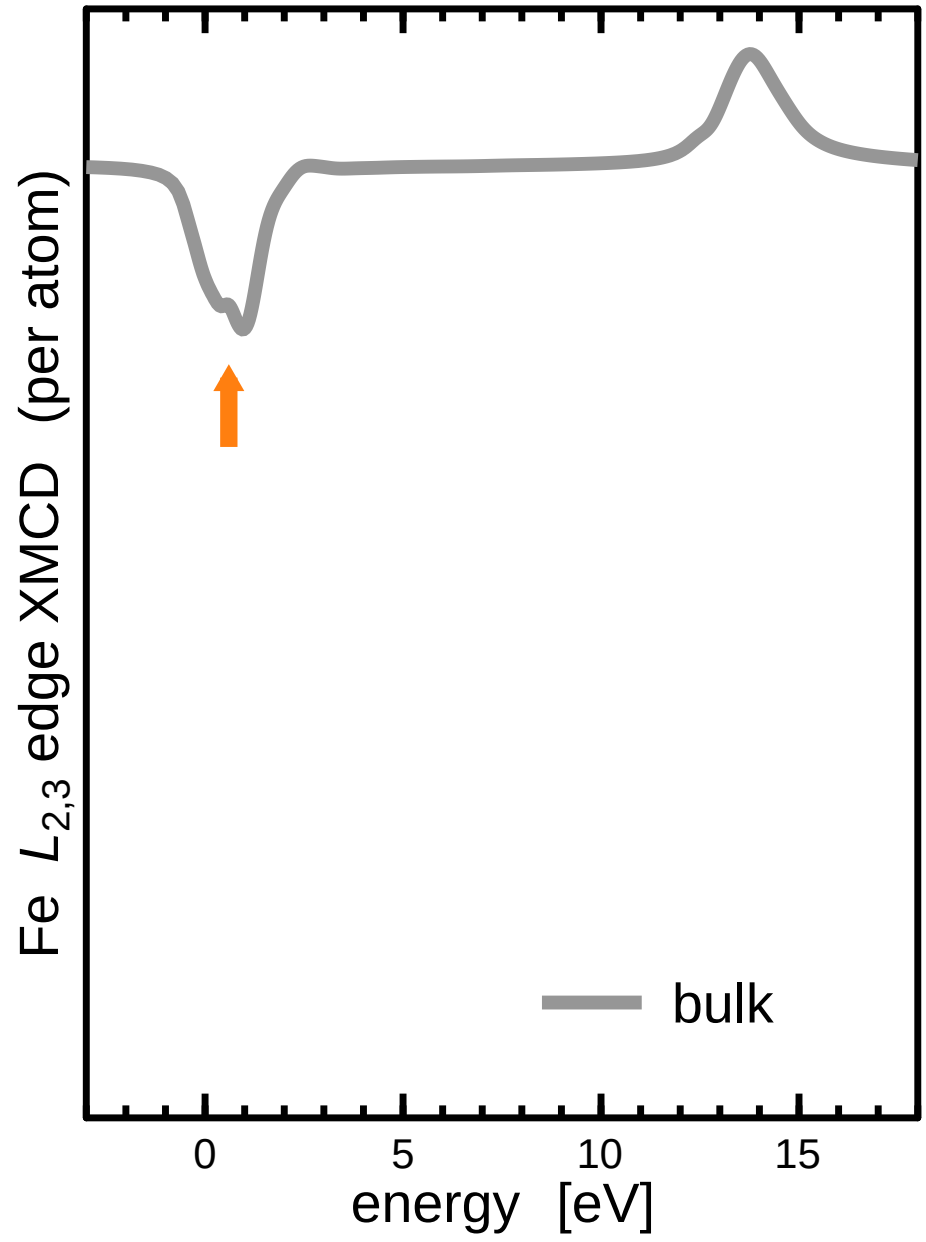
What can XMCD do for us?

- X-ray magnetic circular dichroism (XMCD) spectroscopy probes the magnetic properties of materials.
- Through the sum rules, XMCD can inform about μ_{spin} and μ_{orb} separately.
- Our setup: helicity of the incoming photons parallel or antiparallel with the cluster magnetization (coincides with the [001] direction in the parental crystal)



XMCD of iron clusters

- Splitting of the bulk L_3 peak not seen in experiment (but present in full-potential calculations). Energy resolution?



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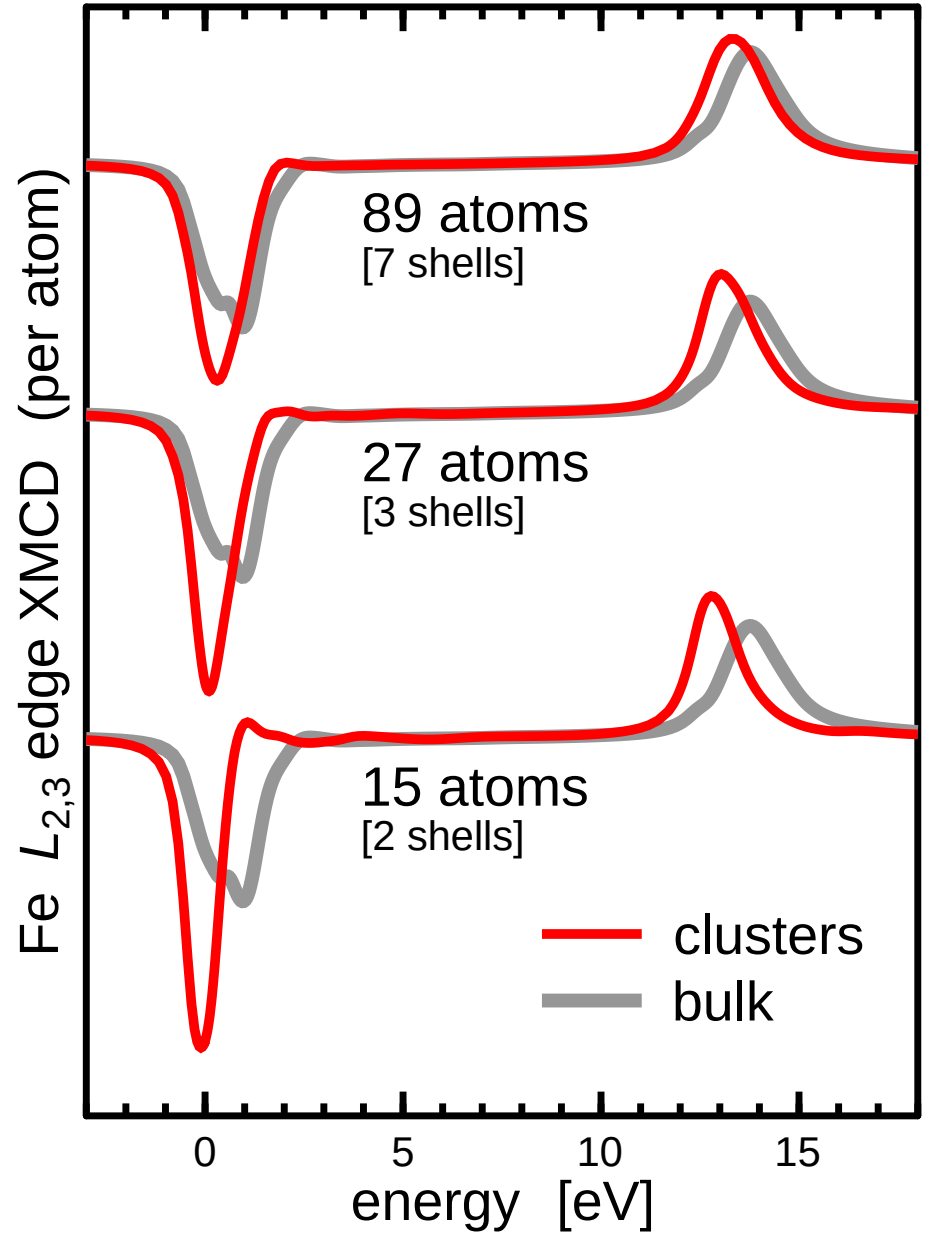

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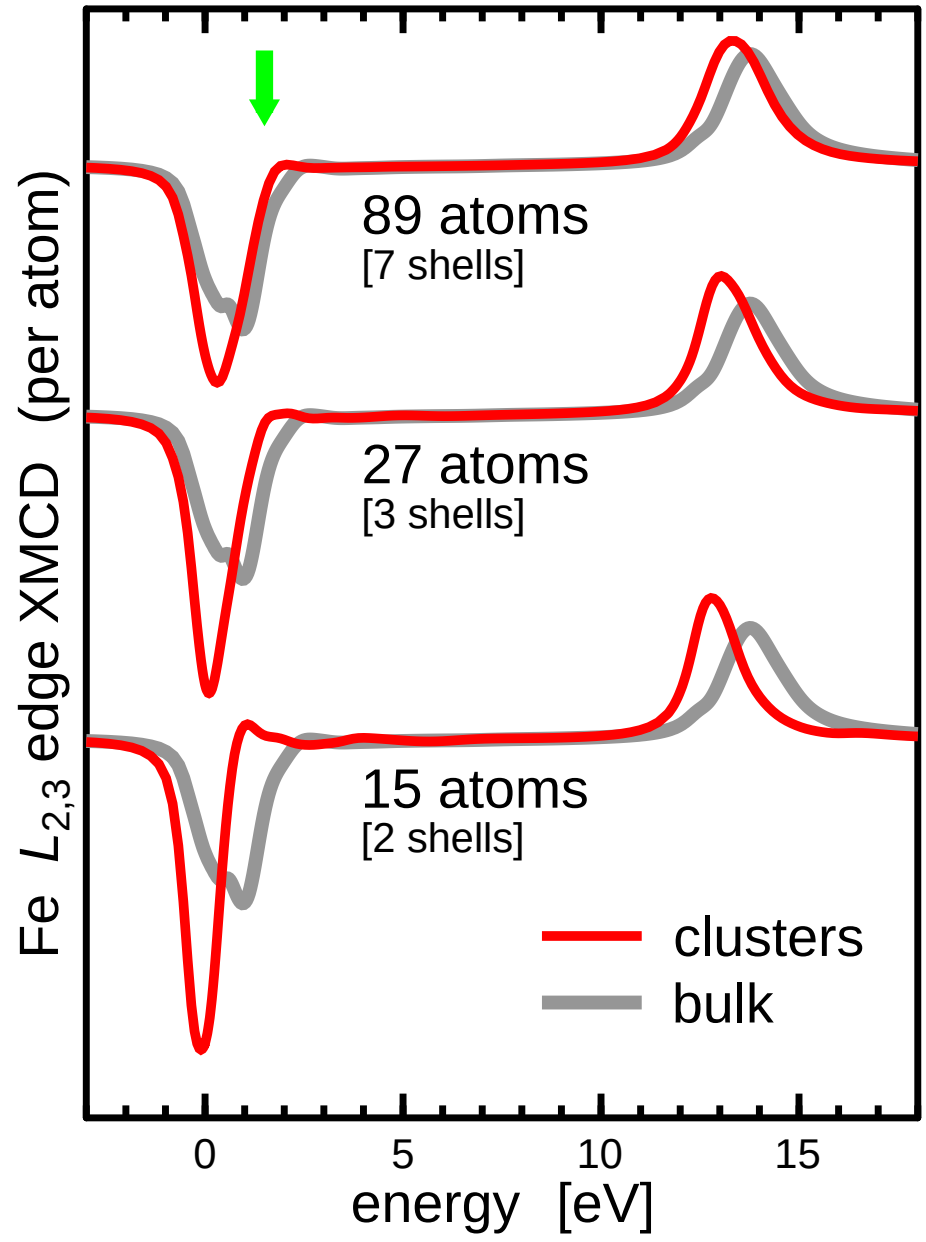
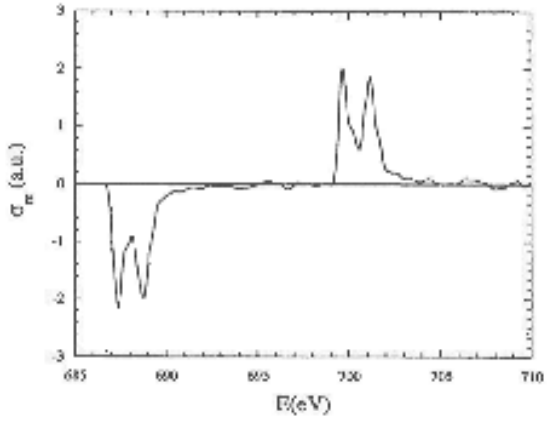
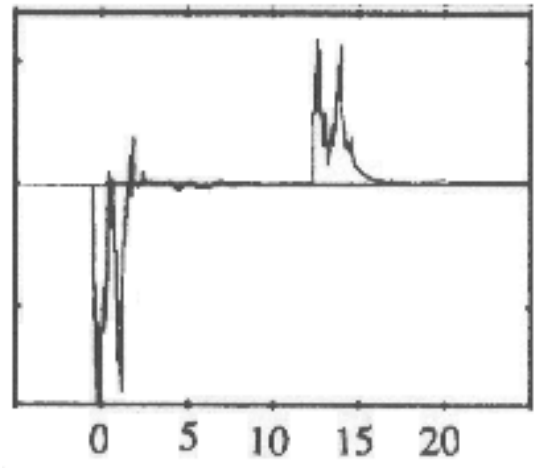
- Small positive peak just after the main L_3 minimum.





Fe(001) surface

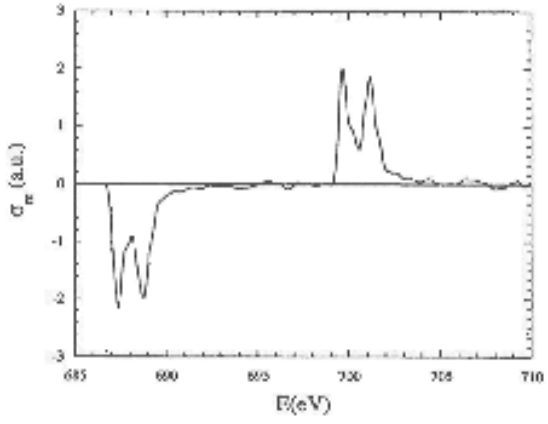
[Wu et al. PRL 71, 3581 (1993)]



Fe_2Cu_6 (001) multilayer

[Guo et al PRB 50, 3861 (1994)]

Calculated XMCD of surface or multilayers exhibit quite a pronounced fine structure at the Fe L_3 and L_2 edges.



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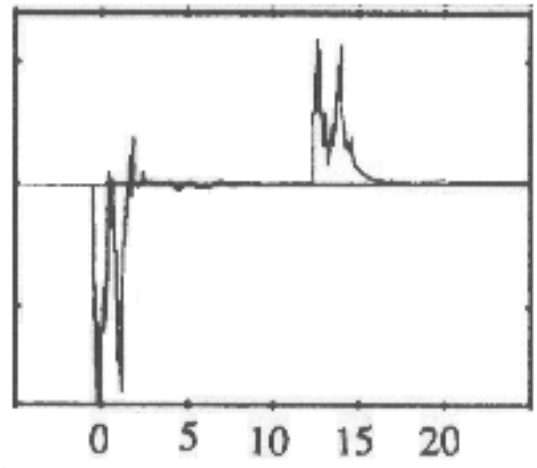

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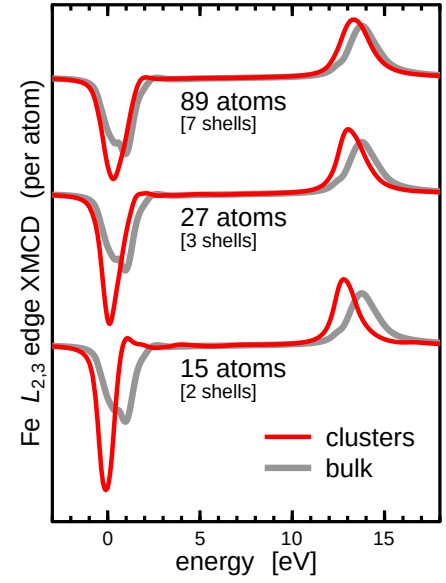

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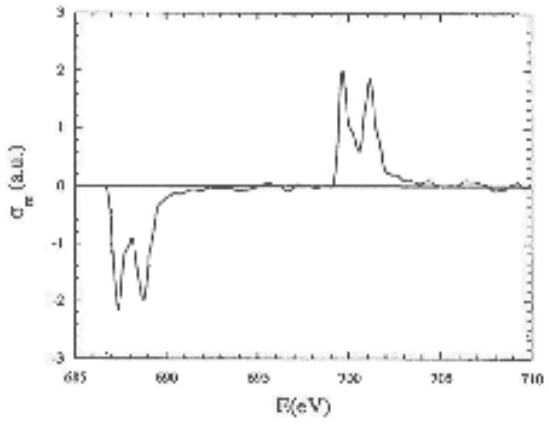
Calculated XMCD of clusters display no such fine structure.

Where have all the structures gone?



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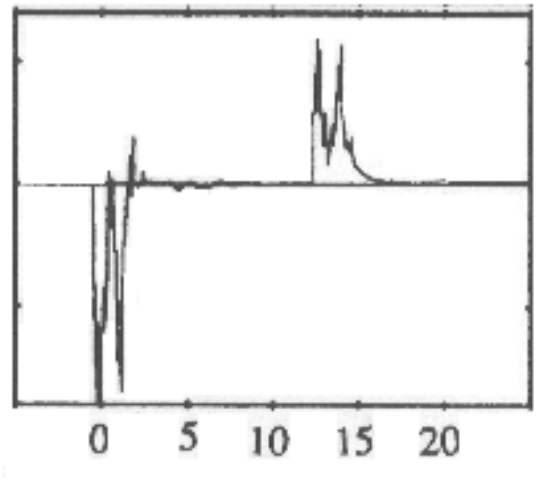

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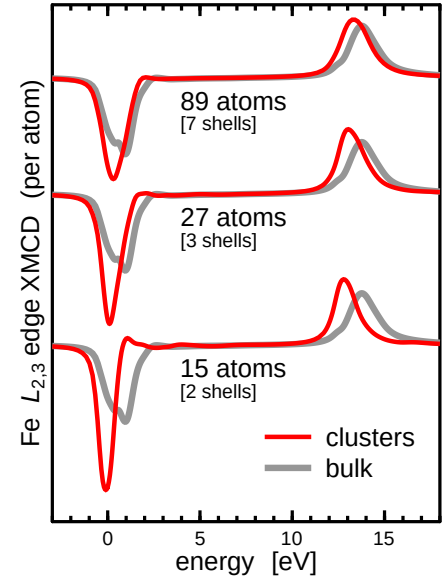

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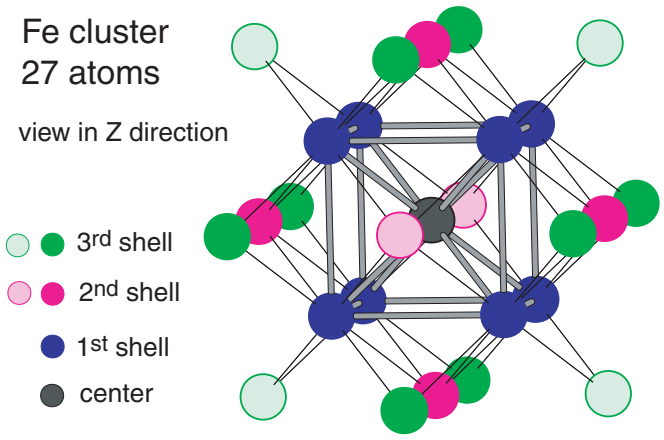
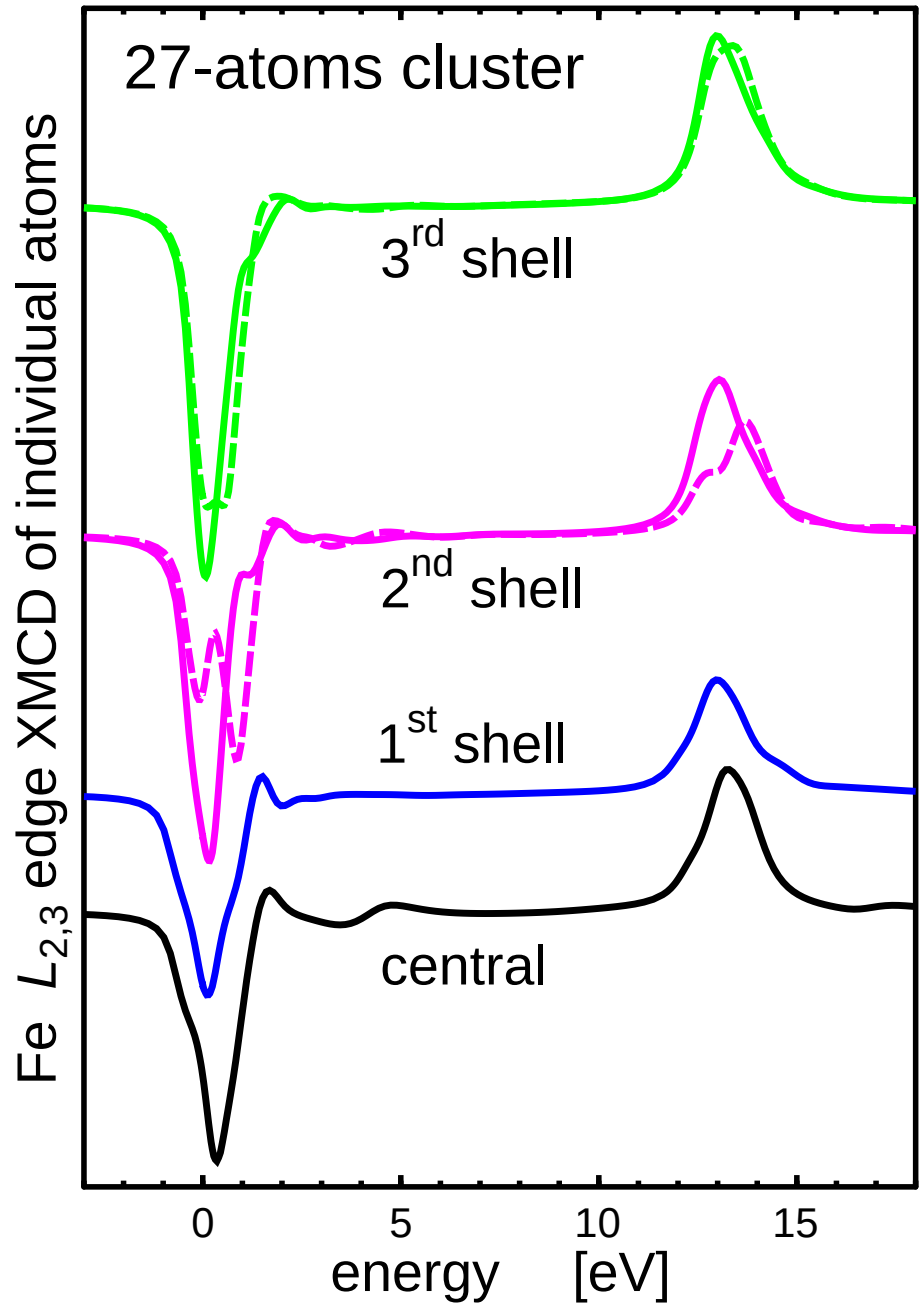
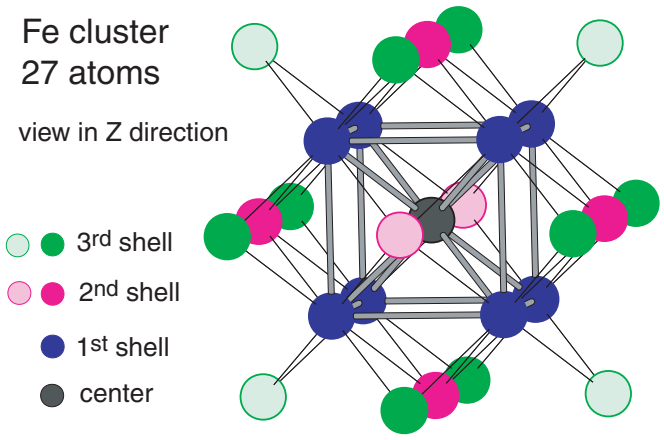


Spectrum of the whole cluster is a superposition of signals from all individual atoms

Magnetization decreases the symmetry → more inequivalent atomic sites in a single shell



The wiggles in XMCD mutually cancel!



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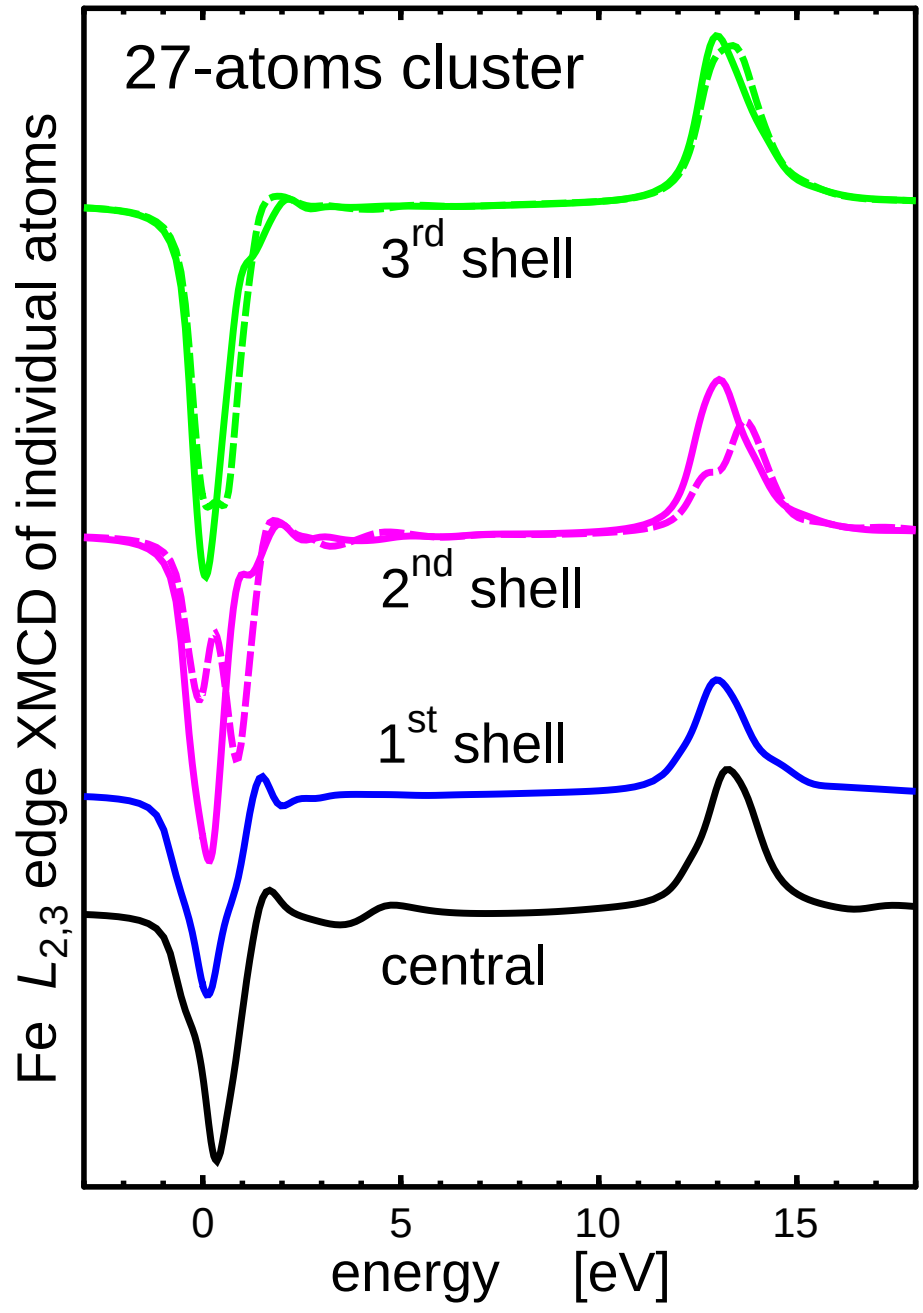

Conclusions

- In free clusters, $\mu_{\rm spin}$ and $\mu_{\rm orb}$ are enhanced at atoms close to the cluster surface.
- $\mu_{\rm orb}$ at individual atoms strongly depends on the direction of the magnetic field. However, the anisotropy in $\mu_{\rm orb}$ averaged over whole coordination spheres is very small.
- Friedel-like oscillations both in $\mu_{\rm spin}$ and in $\mu_{\rm orb}$ are a general feature of magnetic profiles in clusters as well as at crystal surfaces. These oscillations are more pronounced in clusters than at crystal surfaces.
- $\mu_{\rm spin}$ in clusters and at crystal surfaces depends linearly on $N_{\rm eff}$.
- XMCD spectra of clusters distinguish from XMCD of bulk through leaner and enhanced peaks.
- Small yet distinct positive hump just after the L_3 peak — a general marker of clusterization in XMCD spectra?