

# Magnetic and spectroscopic properties of free iron clusters

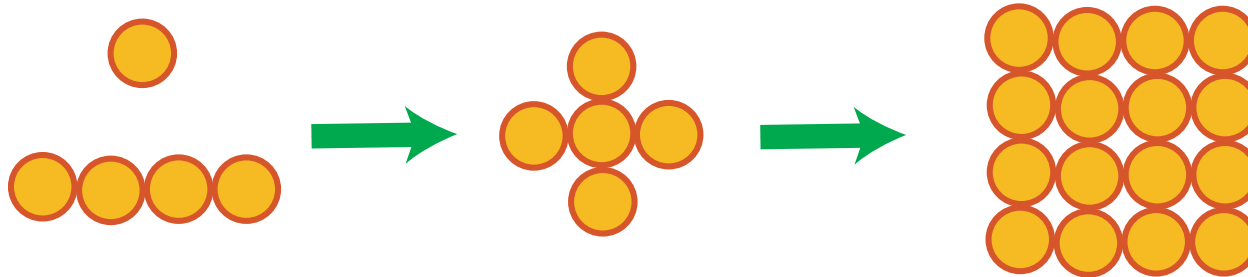
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162 53 Prague, Czech Republic

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Germany

# 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

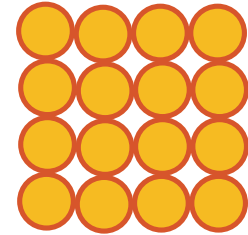
# Magnetic properties of iron



atom



surface



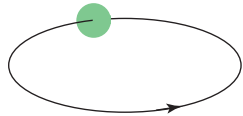
bulk



$$\mu_{\text{spin}} = 4 \mu_B$$

$$\mu_{\text{spin}} = 2.5\text{--}3.0 \mu_B$$

$$\mu_{\text{spin}} = 2.2 \mu_B$$



$$\mu_{\text{orb}} = 2 \mu_B$$

$$\mu_{\text{orb}} = 0.07\text{--}0.12 \mu_B$$

$$\mu_{\text{orb}} = 0.05 \mu_B$$

(clusters go in between)

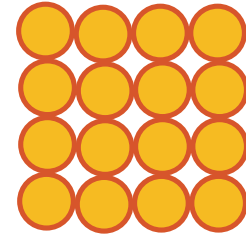
# Magnetic properties of iron



atom



surface



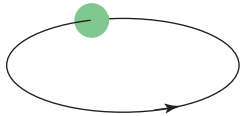
bulk



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(clusters go in between)

Clusters contain a high portion of surface atoms

⇒ ought to have larger magnetic moments

their properties should display traces of surface and bulk trends

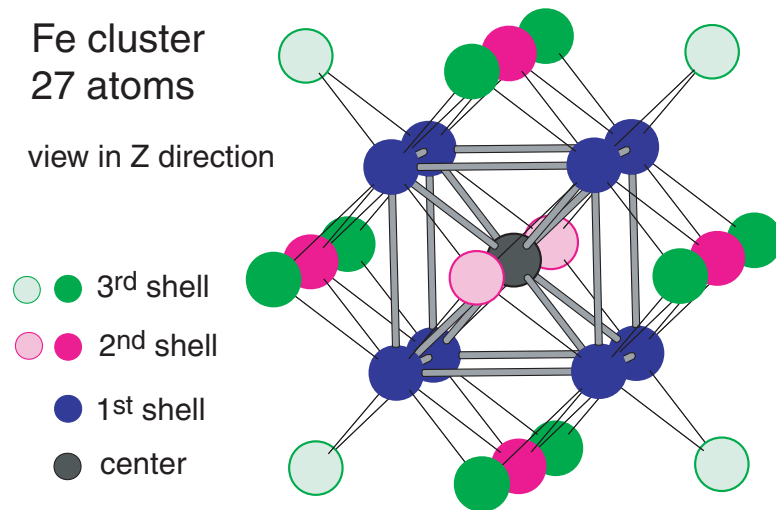
# Our aim

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)

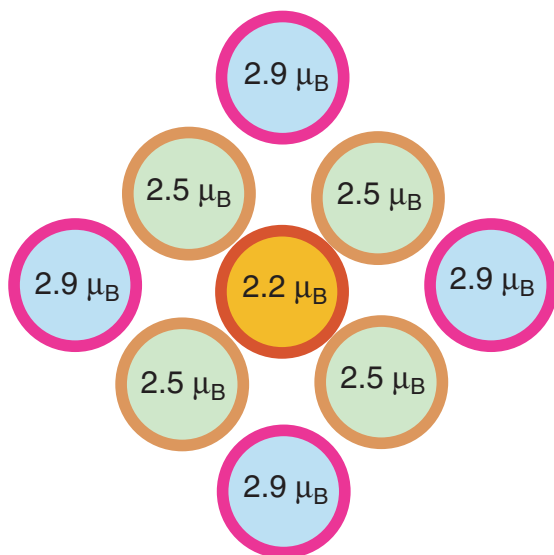


shells	atoms	radius [Å]
1	9	2.49
2	15	2.87
3	27	4.06
4	51	4.76
5	59	4.97
6	65	5.74
7	89	6.25

# Theoretical formalism

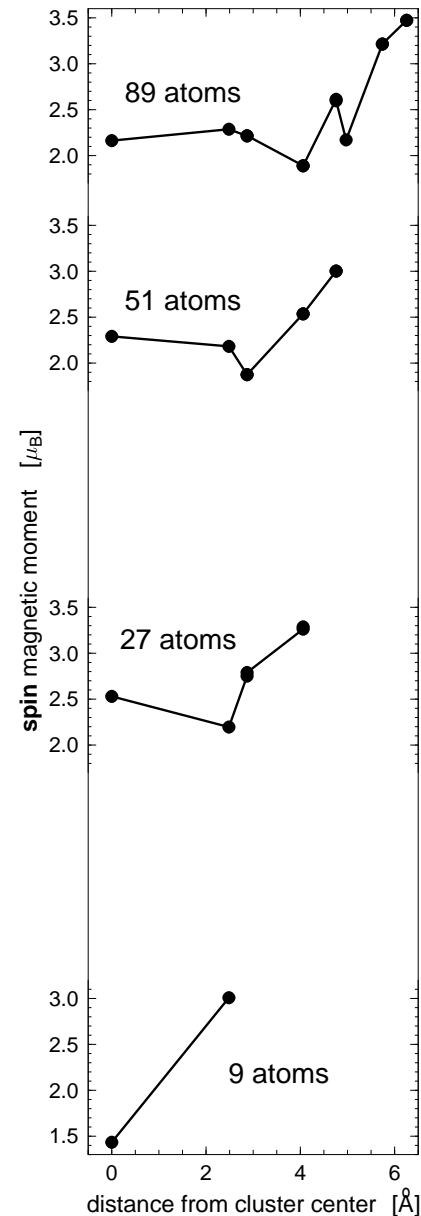
- local density approximation scheme, Vosko, Wilk and Nusair parametrization of the exchange-correlation potential
- electronic structure and XMCD spectra of free clusters calculated in real space via a fully-relativistic spin-polarized multiple-scattering technique as implemented in the `SPRKKR` code
- scattering potential obtained from scalar-relativistic SCF ( $X_\alpha$ -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



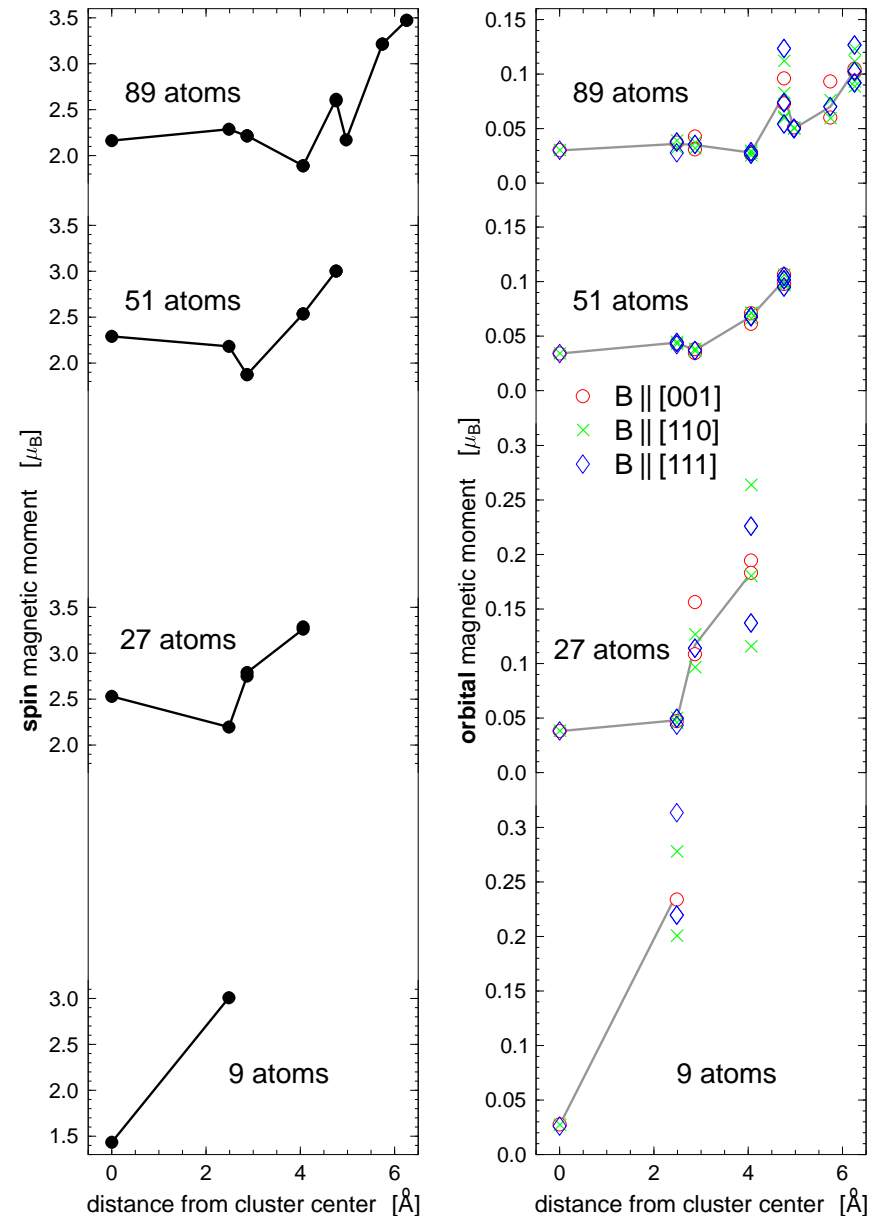
# Magnetic profiles of free iron clusters

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

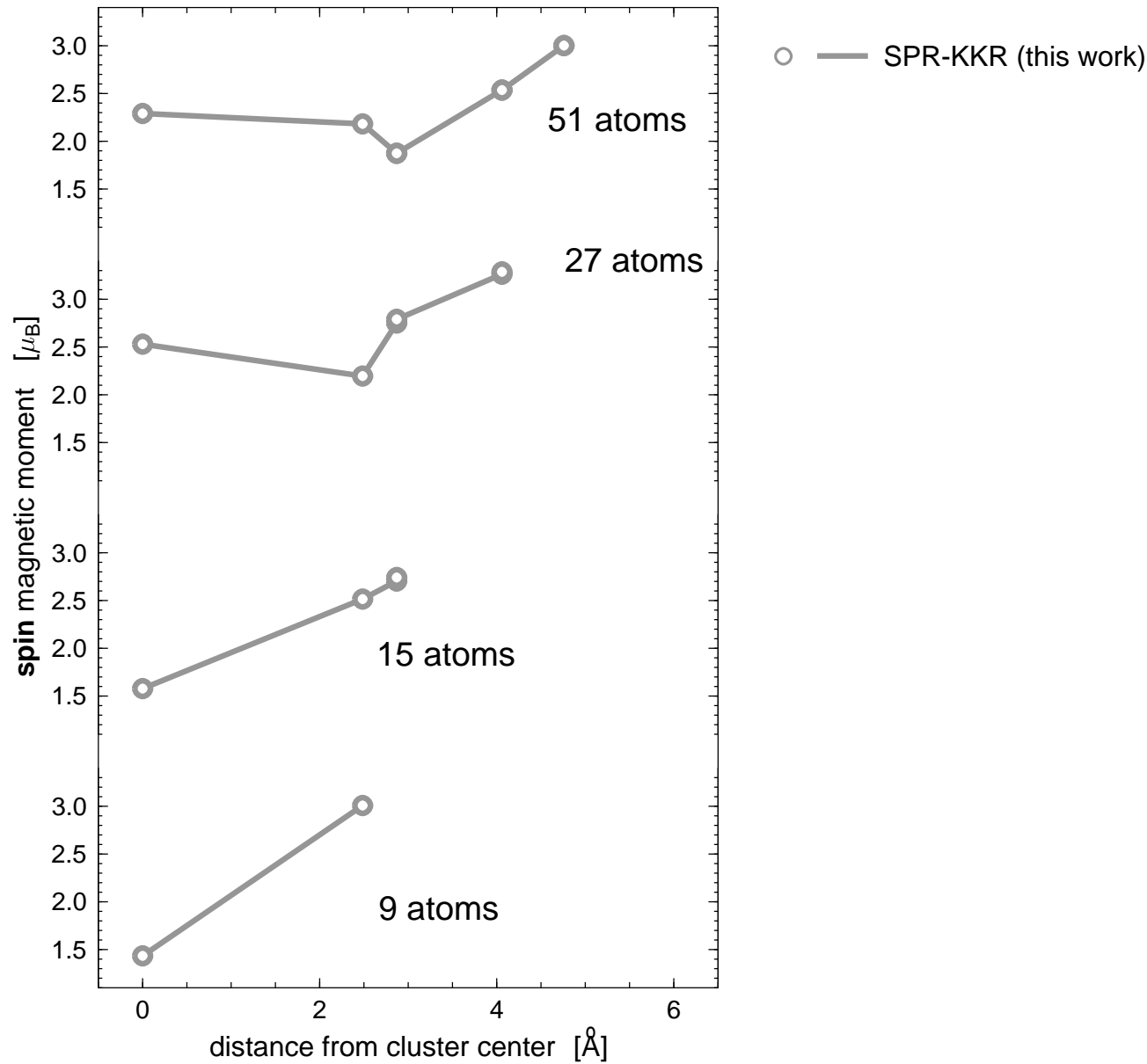


# Magnetic profiles of free iron clusters

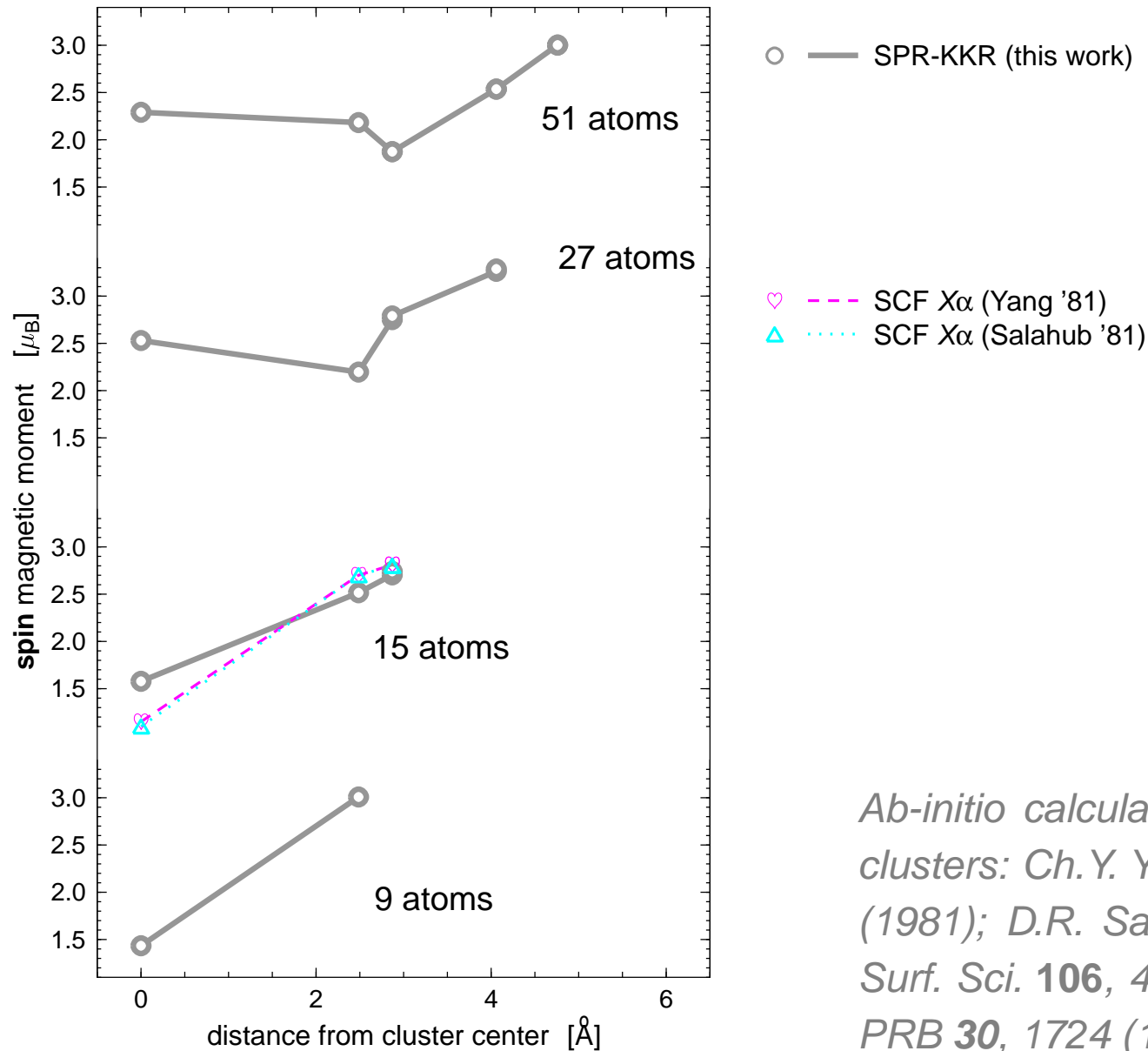
- $\mu_{\text{spin}}$  does not depend on the direction of  $B$ ,  $\mu_{\text{spin}}$  for inequivalent atoms of the same coordination sphere are the same
- $\mu_{\text{orb}}$  depends on the direction of  $B$ ,  $\mu_{\text{orb}}$  for symmetry-inequivalent atoms of the same coordination sphere differ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



# Comparing with other works (1)

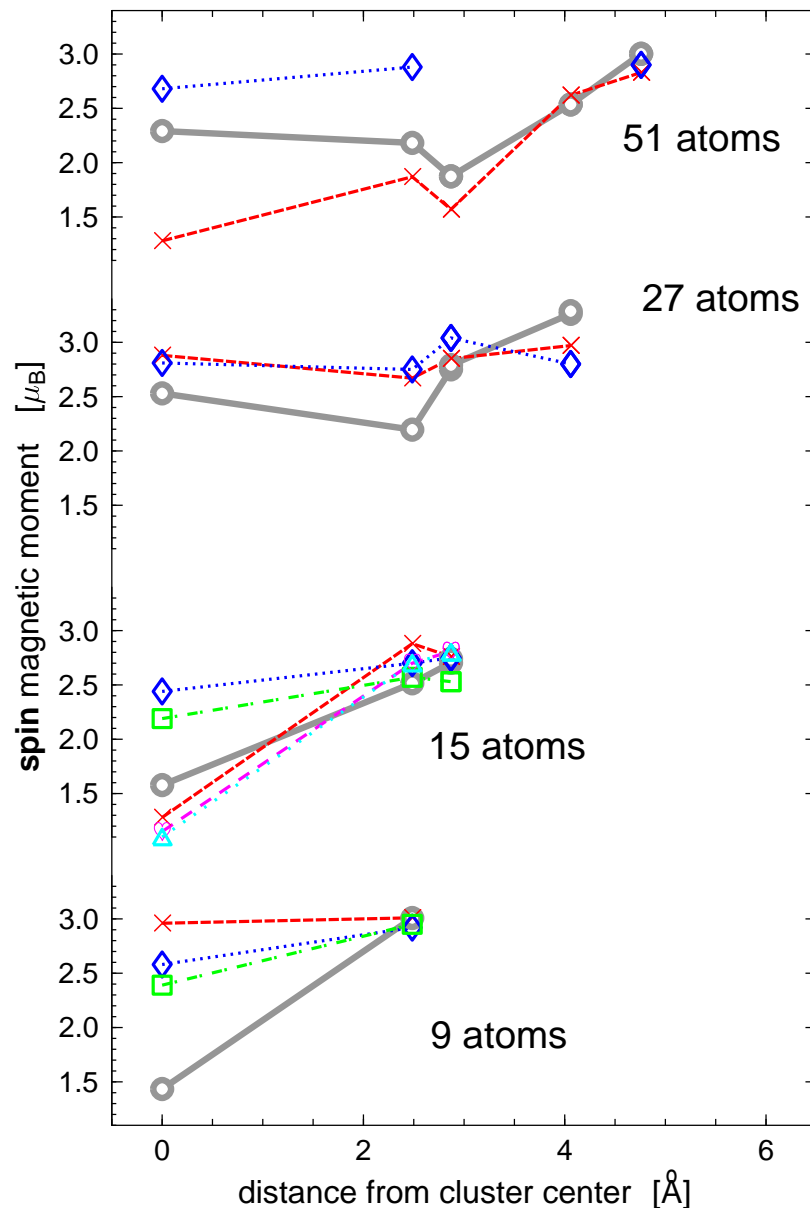


# Comparing with other works (1)



*Ab-initio calculations for bulk-geometry clusters: Ch. Y. Yang et al. PRB **24**, 5673 (1981); D.R. Salahub & R.P. Messmer, Surf. Sci. **106**, 415 (1981); K. Lee et al. PRB **30**, 1724 (1984)*

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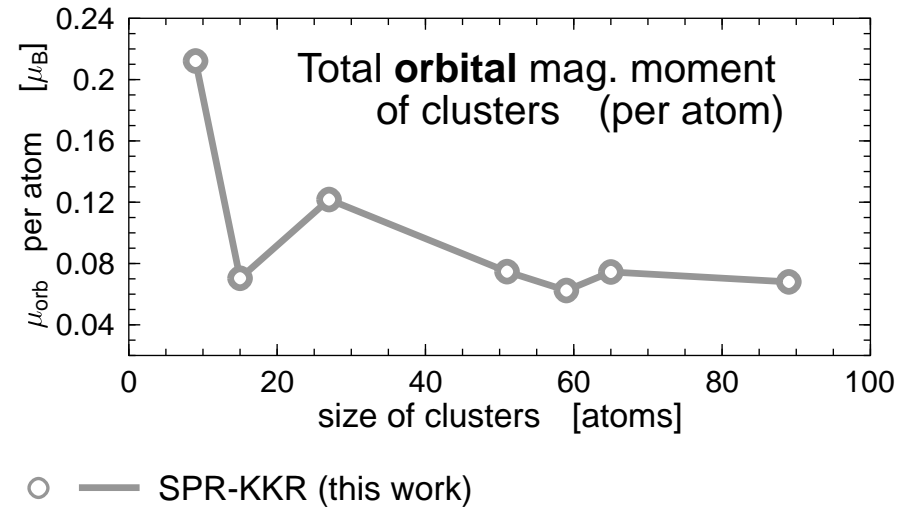
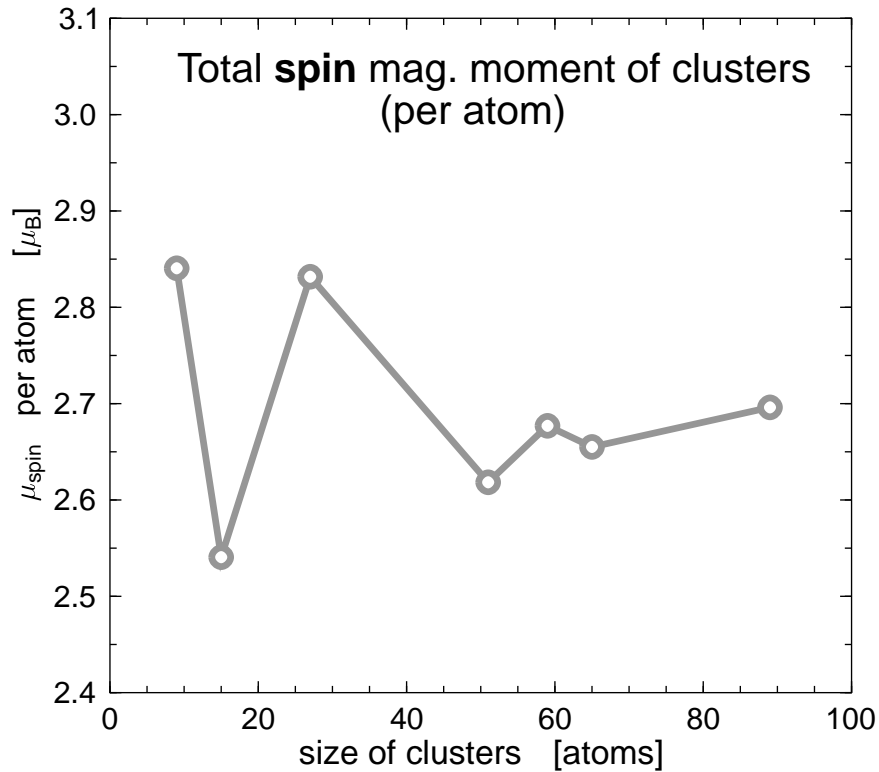


- — SPR-KKR (this work)
- × —  $d$ -band model (Pastor '89)
- —  $spd$ -band model (Vega '93)
- ◇ —  $spd$ -band model (Franco '99)
- ♡ — SCF  $X\alpha$  (Yang '81)
- △ — SCF  $X\alpha$  (Salahub '81)

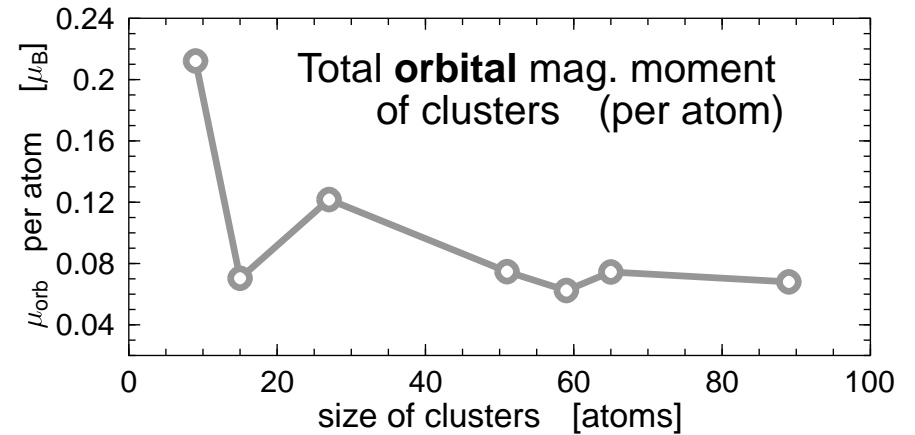
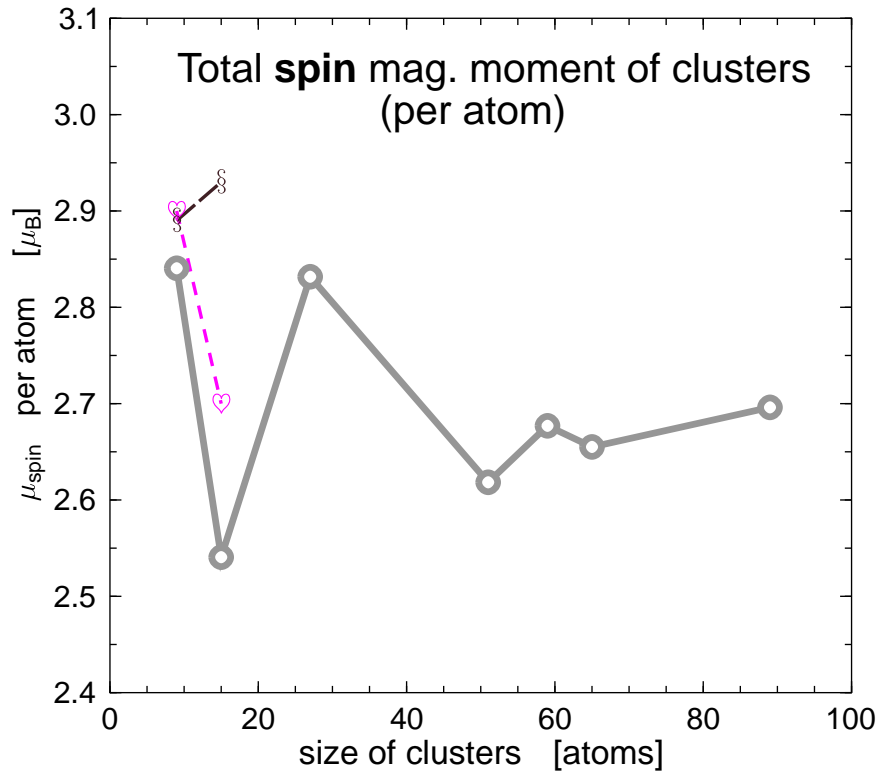
*Model Hamiltonian calculations for bulk-geometry clusters: G.M. Pastor et al. PRB **40**, 7642 (1989); A. Vega et al. PRB **47**, 4742 (1993); J. Guevara et al. PRB **55**, 13283 (1997); J.A. Franco et al. PRB **60**, 434 (1999)*

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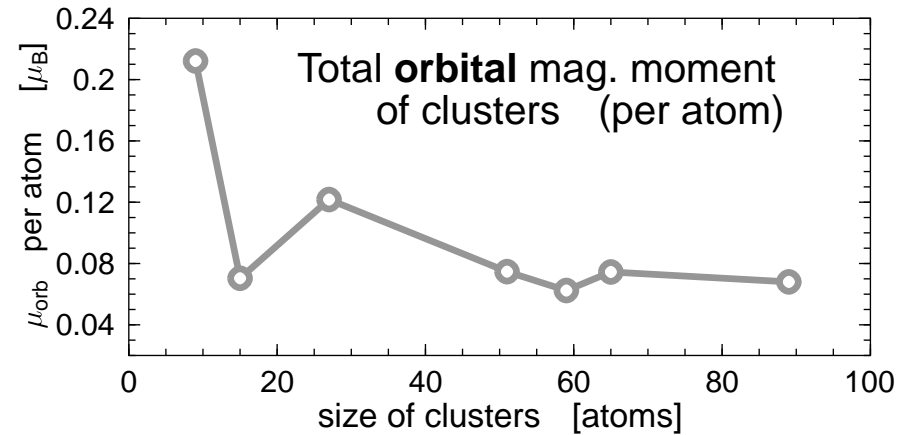
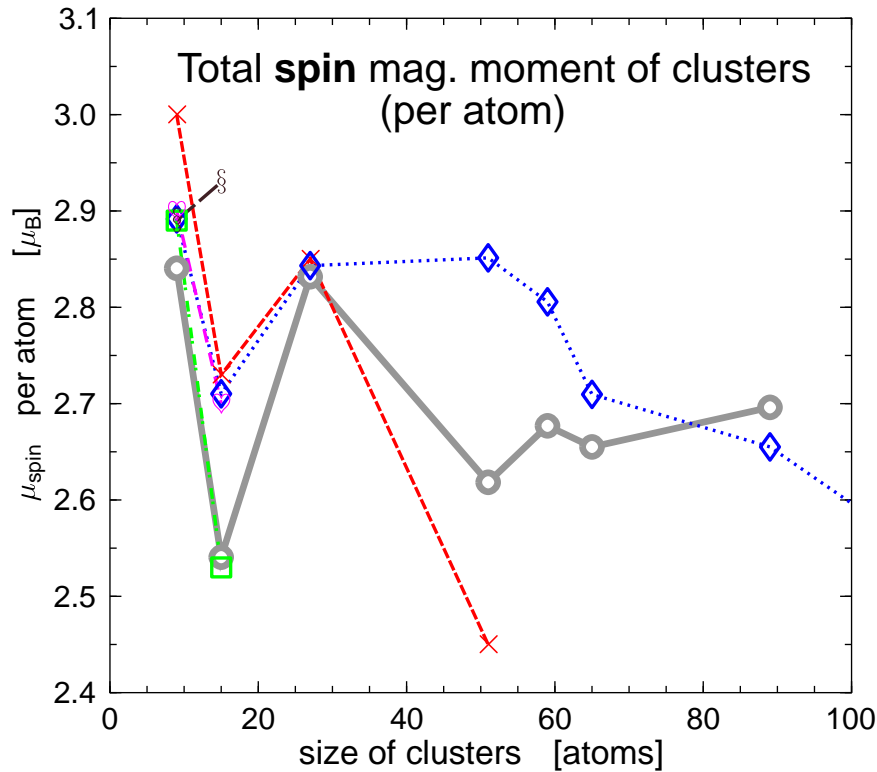


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♡ --- SCF  $X\alpha$  (Yang '81)

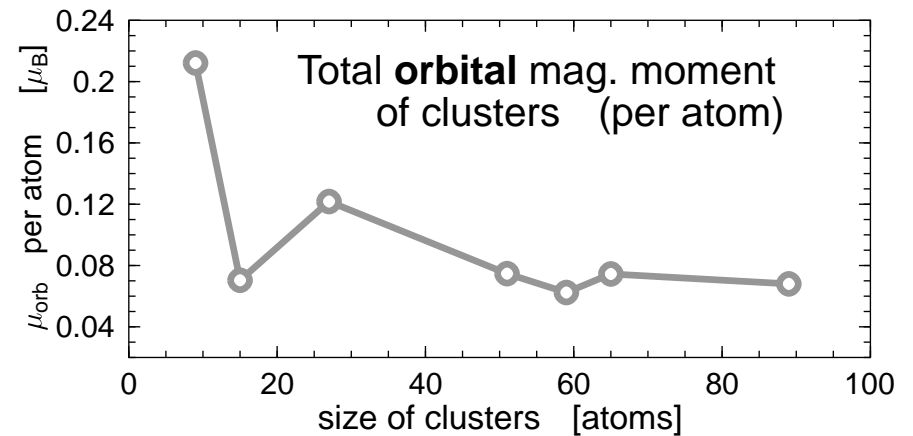
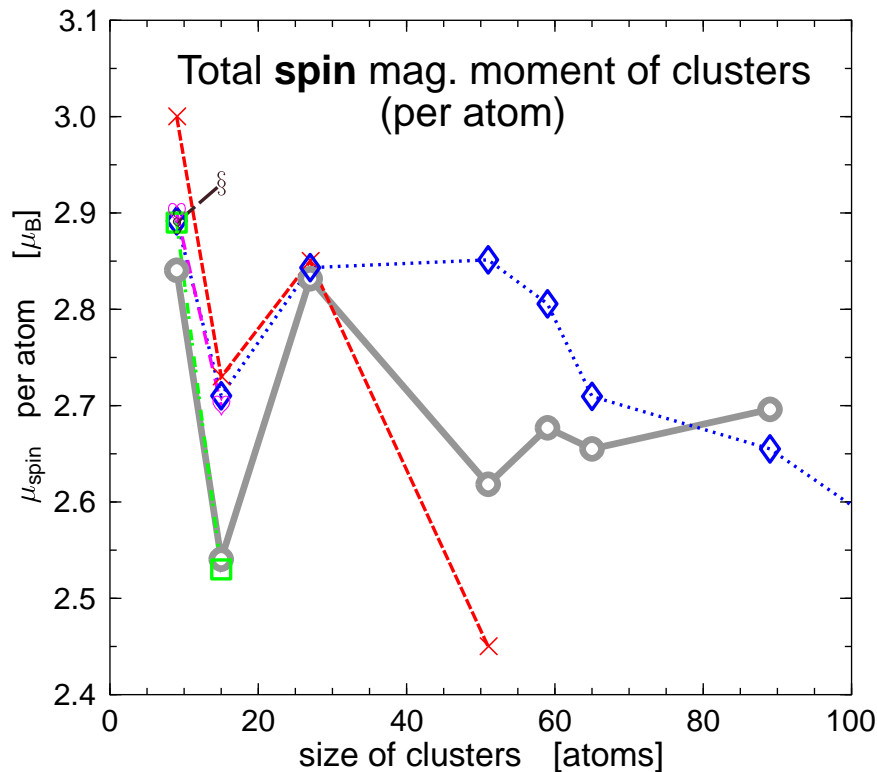
§ --- LCGO (Lee '84)

# Comparing with other works (2)



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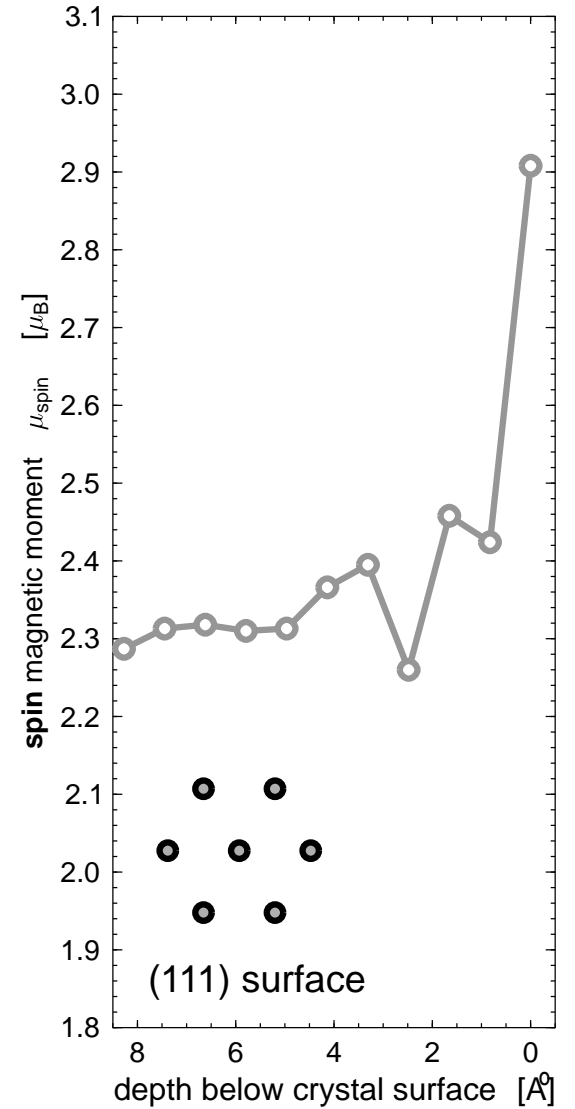
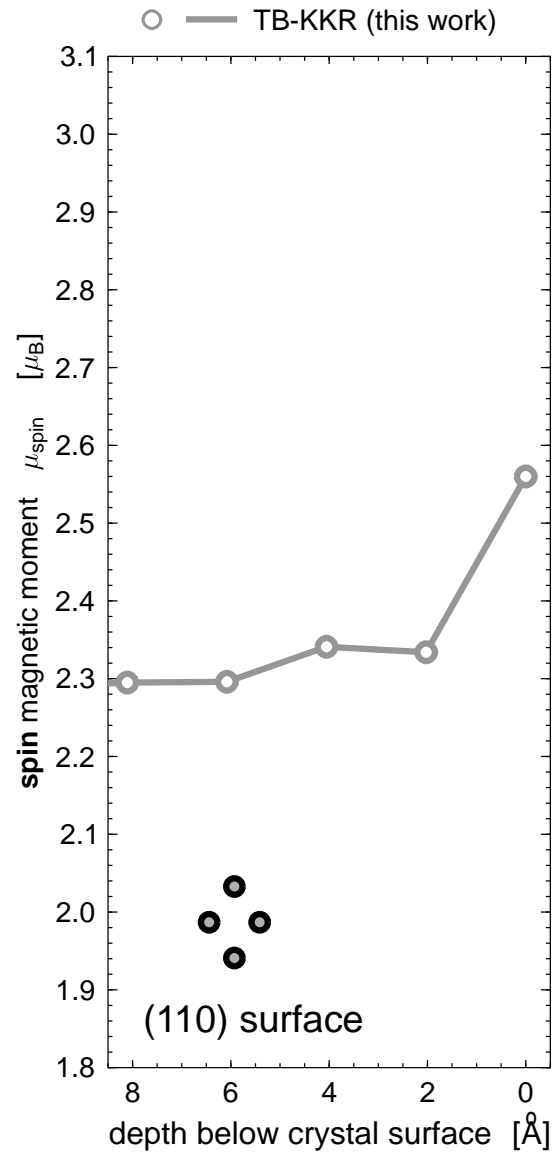
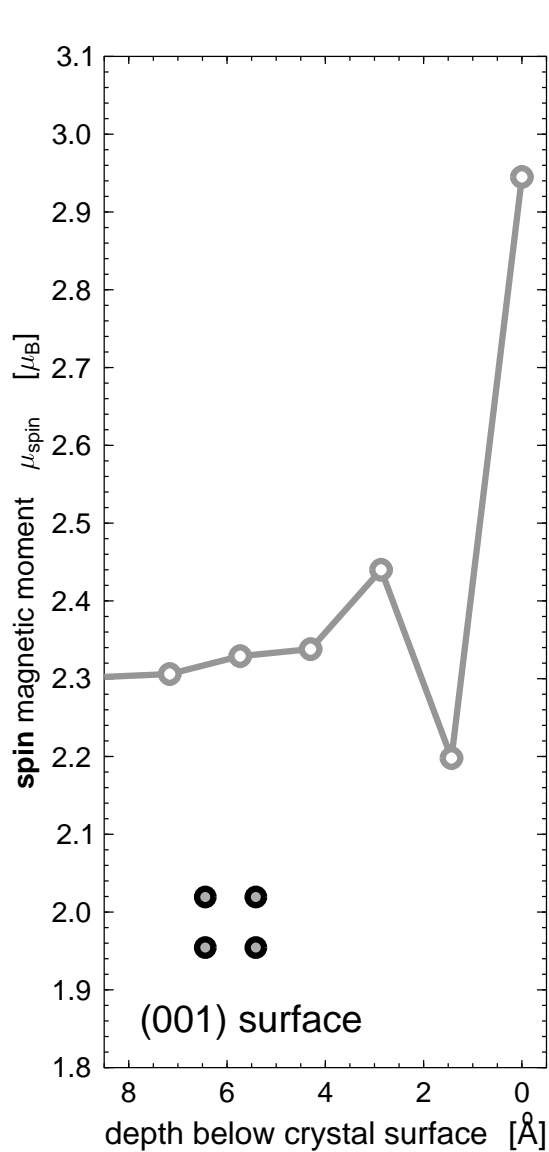


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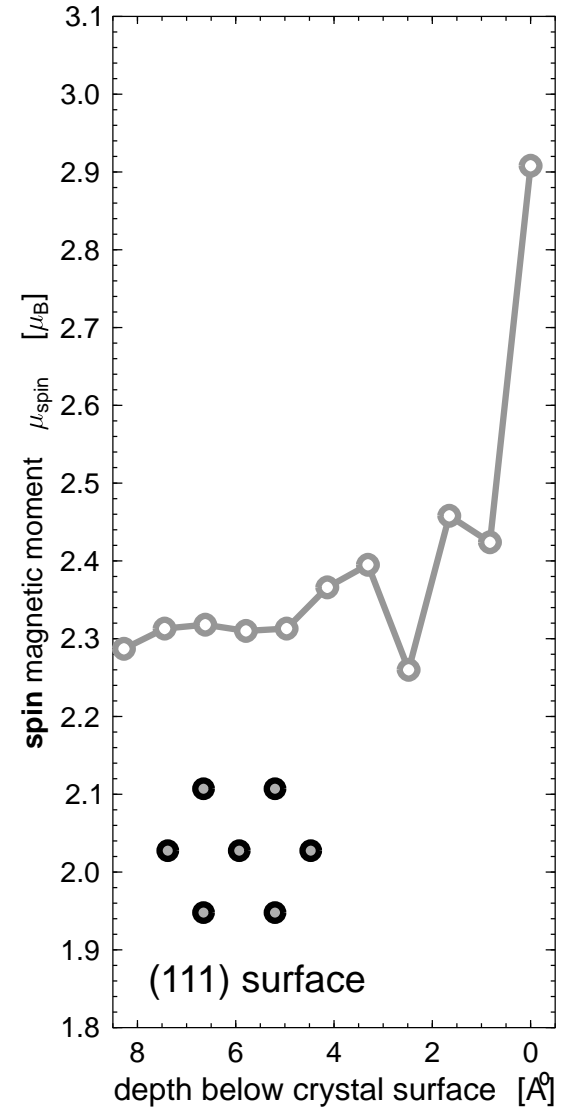
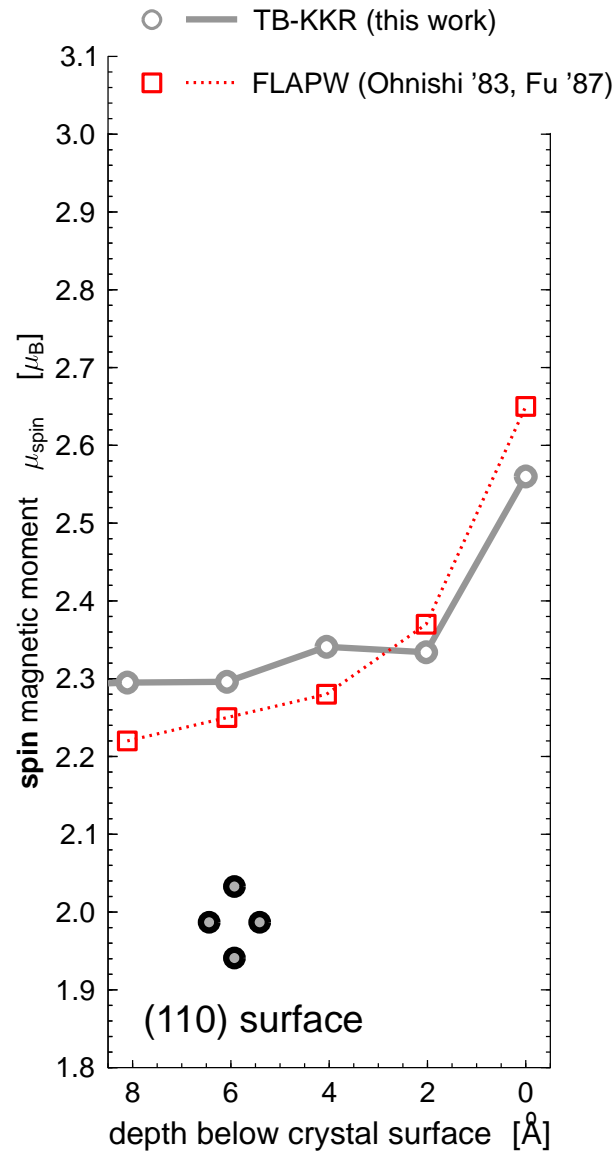
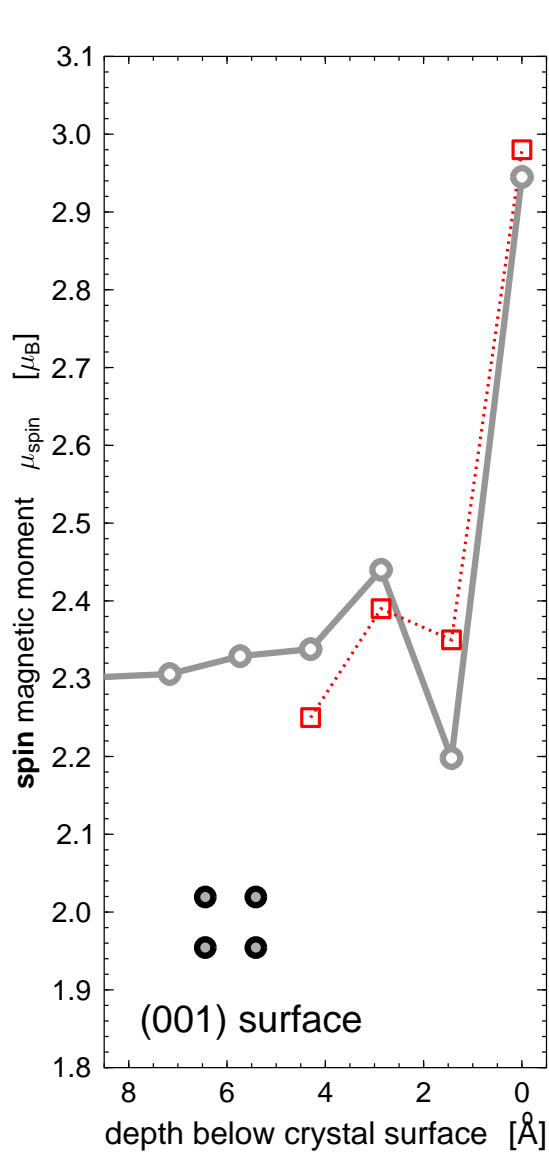


Even the “simple” task of calculating magnetic properties of free iron clusters with **fixed bulk-like geometry** appears to be beyond current abilities of mankind... (?)

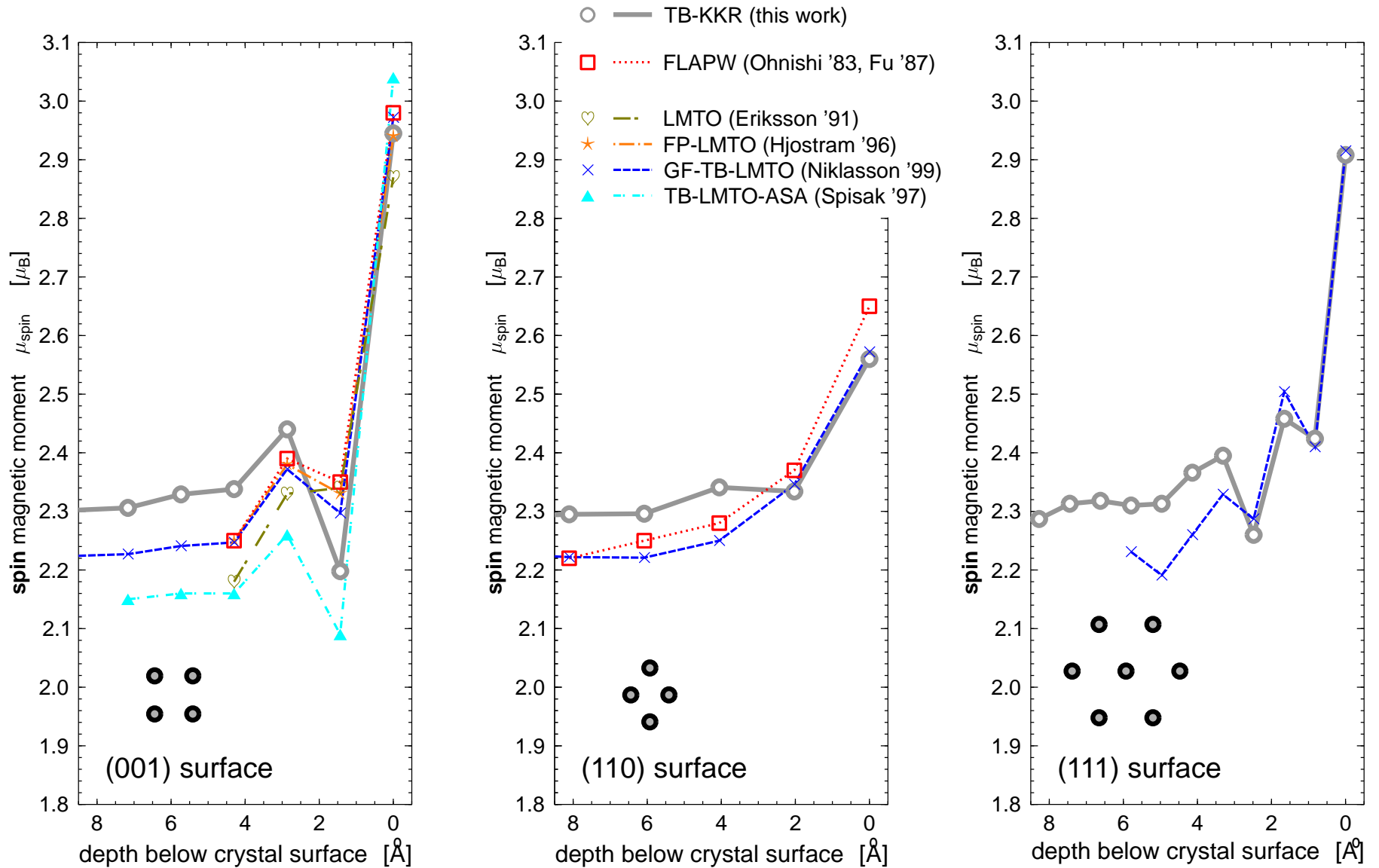
# Magnetic profiles of crystal surfaces (1)



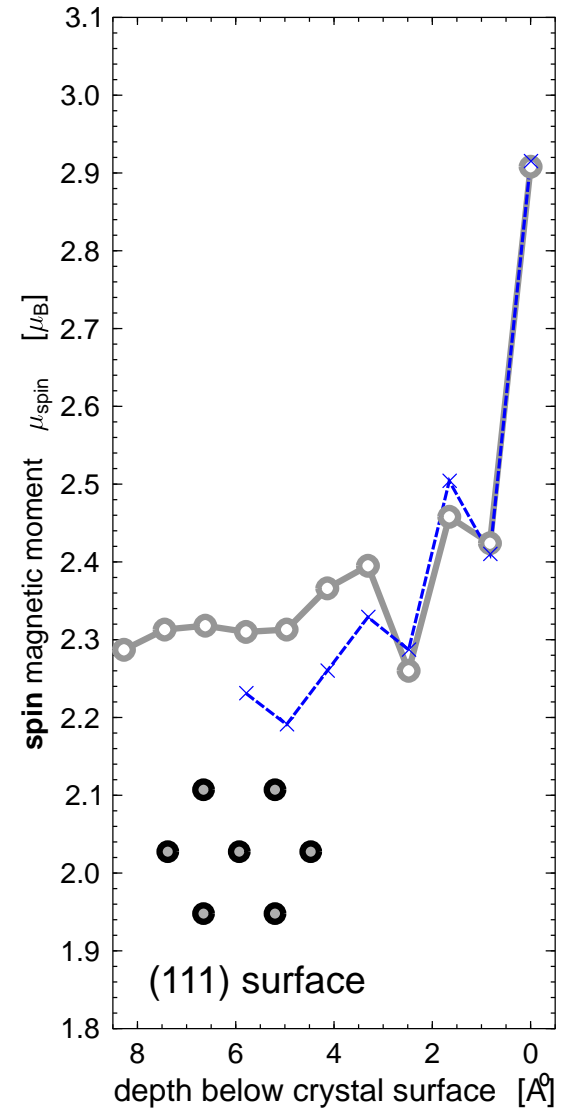
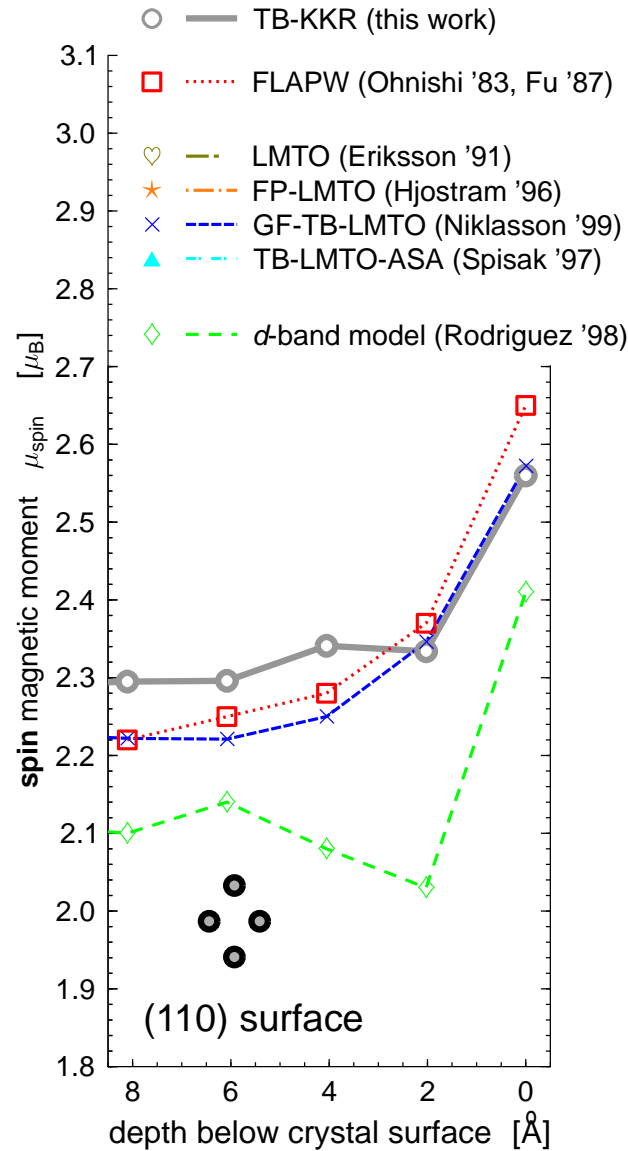
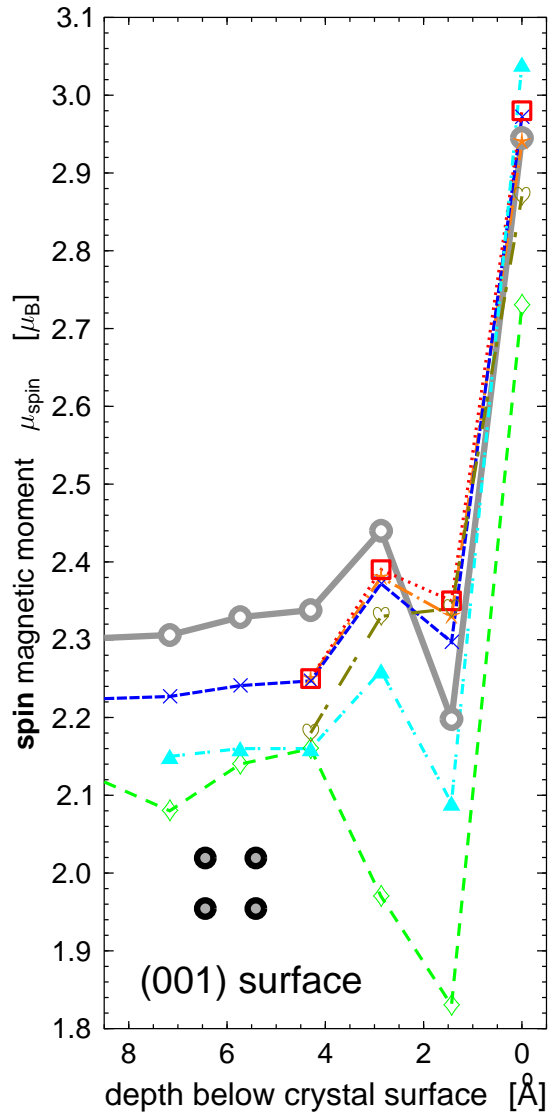
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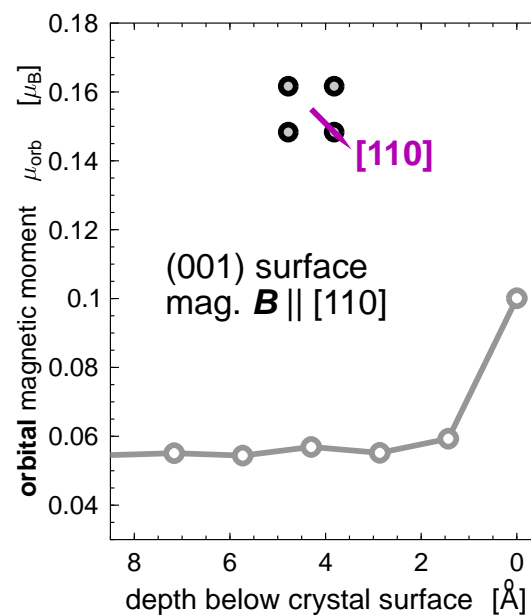
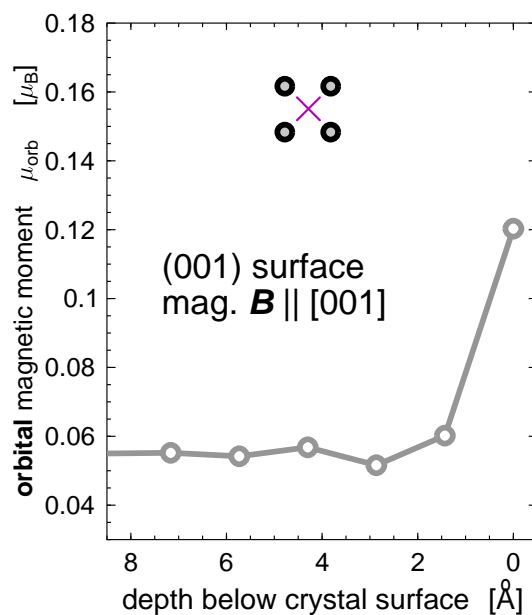


# Magnetic profiles of crystal surfaces (1)



# Magnetic profiles of crystal surfaces (2)

○ — TB-KKR (this work)



# Magnetic profiles of crystal surfaces (2)

Orbital polarization:

SPRKKR estimate  
of bulk iron:

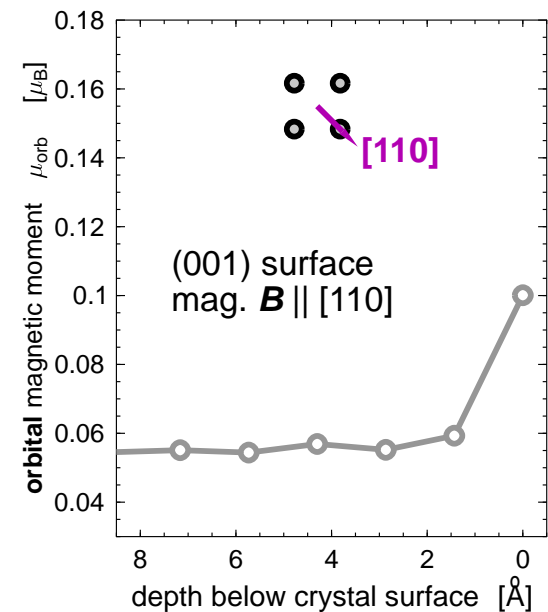
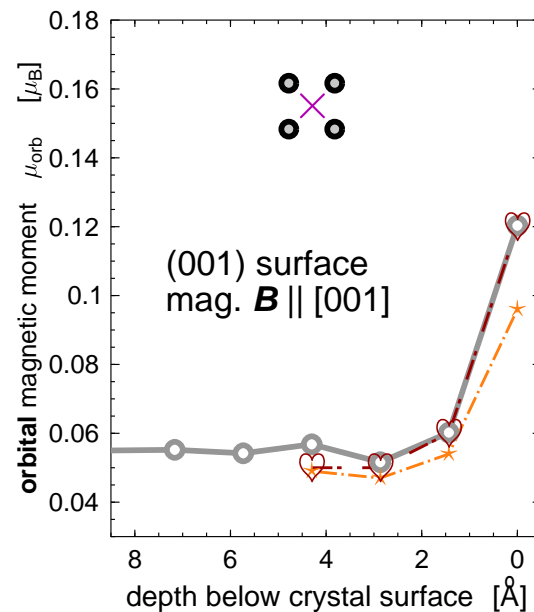
without OP:

$$\mu_{\text{orb}} = 0.054$$

with OP:

$$\mu_{\text{orb}} = 0.086$$

- — TB-KKR (this work)
- ♡ — LMTO (Eriksson '91)
- ★ — FP-LMTO (Hjostrom '96, without OP)



# Magnetic profiles of crystal surfaces (2)

Orbital polarization:

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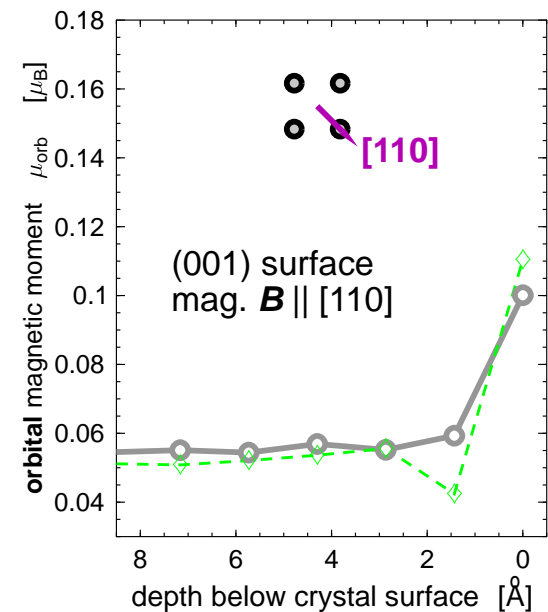
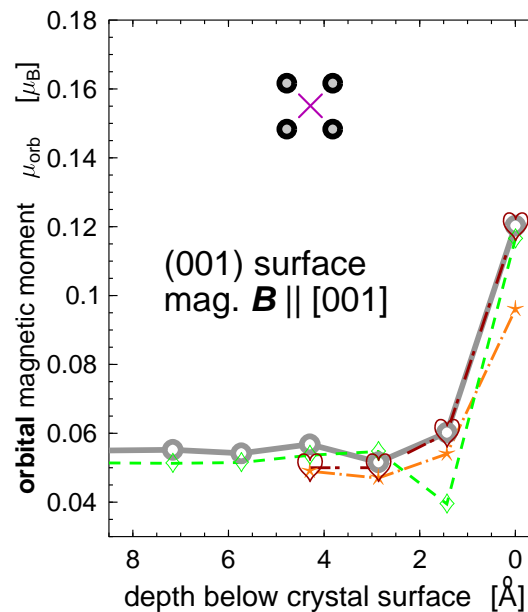
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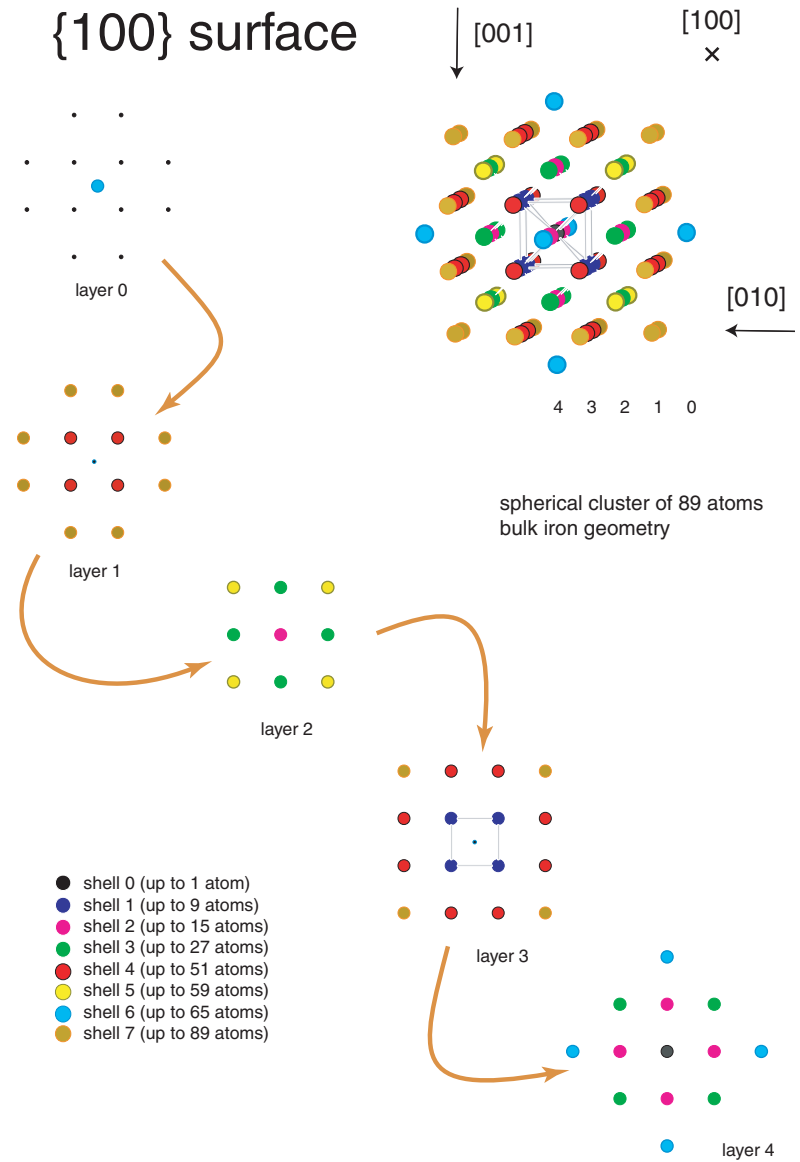
- — TB-KKR (this work)
- ♡ — LMTO (Eriksson '91)
- ★ — FP-LMTO (Hjostrom '96, without OP)
- ◇ — *d*-band model (Rodriguez '98, OP contribution scaled down)



# Clusters vers. surfaces: HOWTO

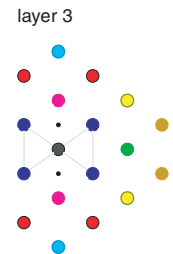
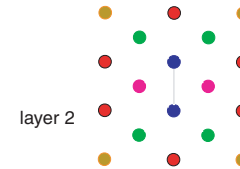
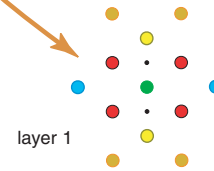
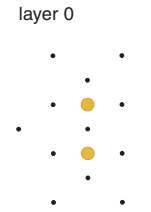
- take free iron clusters of 89 atoms
- drill into the cluster a hole (starting from outside towards the center)
- look around for the magnetic moments and compare them with what you see if you drill a hole beneath a crystal surface
- explore various “crystallographic directions”

# Clusters vers. surfaces: HOWTO

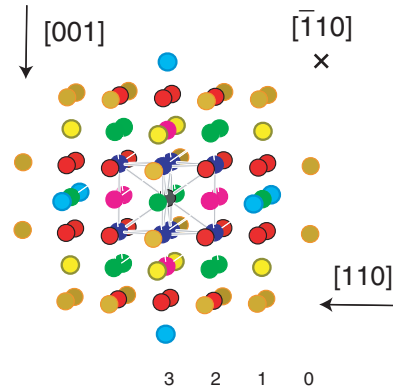


# Clusters vers. surfaces: HOWTO

{110} surface



- shell 0 (up to 1 atom)
- shell 1 (up to 9 atoms)
- shell 2 (up to 15 atoms)
- shell 3 (up to 27 atoms)
- shell 4 (up to 51 atoms)
- shell 5 (up to 59 atoms)
- shell 6 (up to 65 atoms)
- shell 7 (up to 89 atoms)

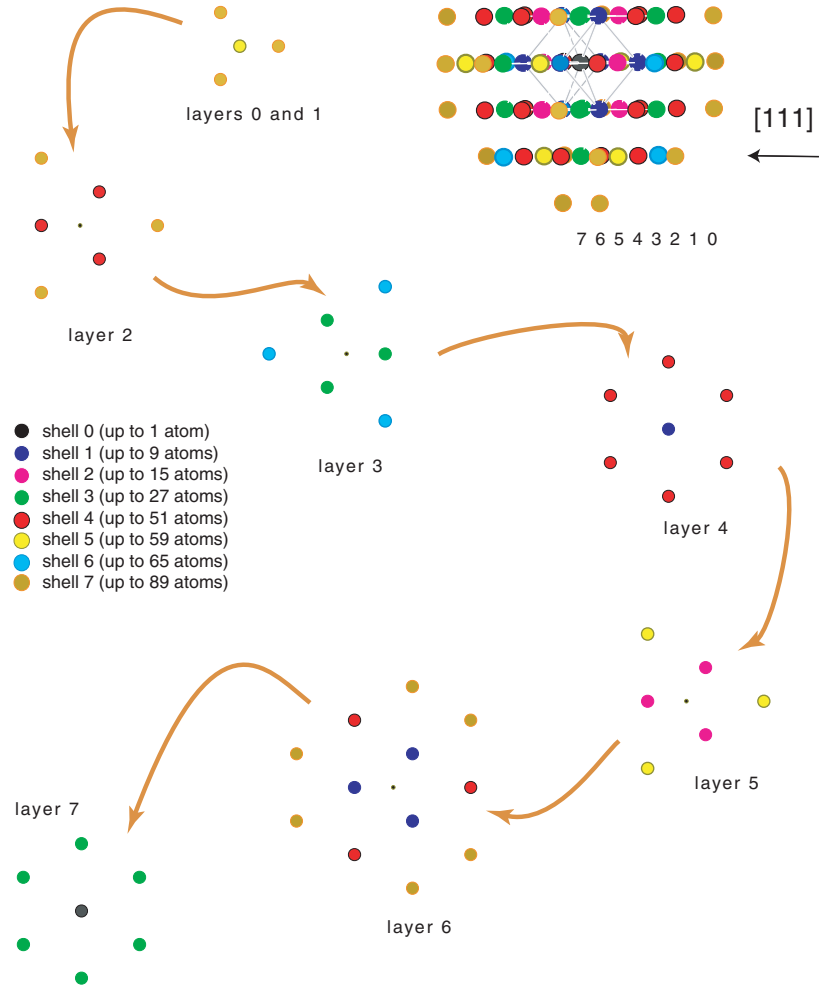


spherical cluster of 89 atoms  
bulk iron geometry

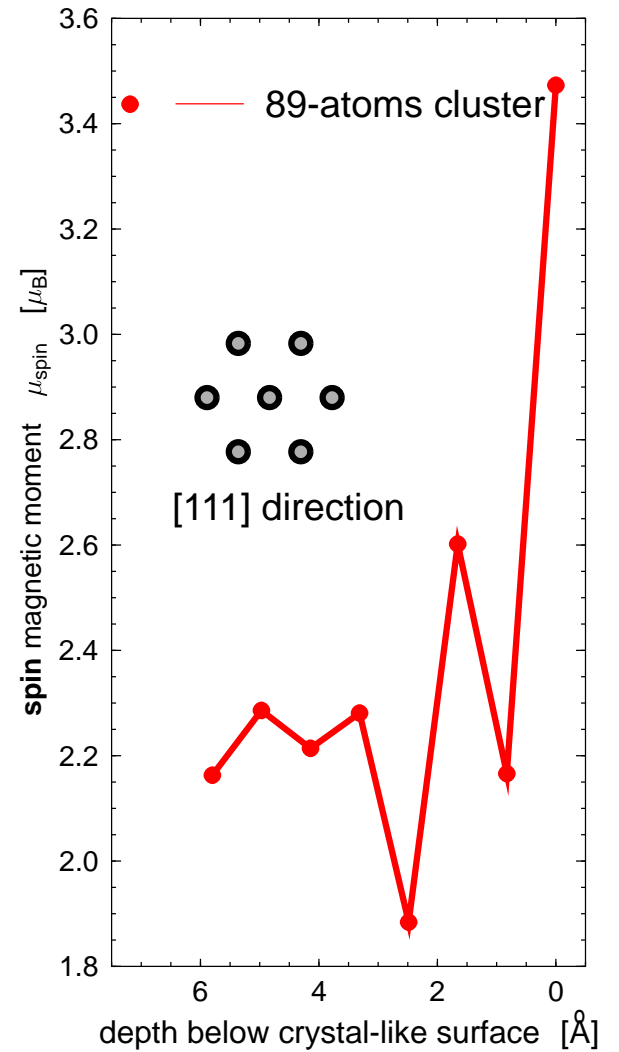
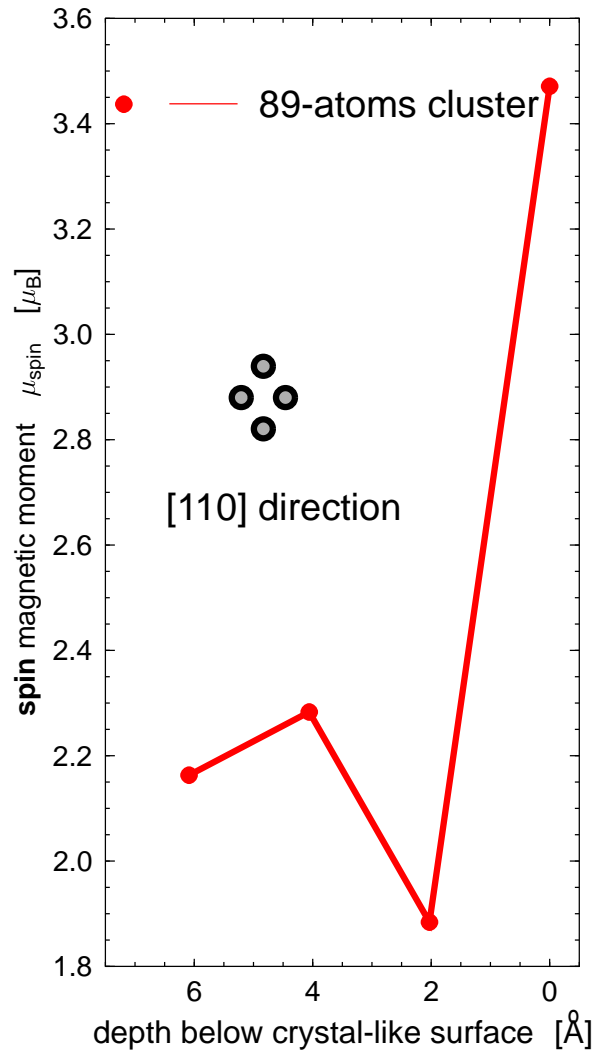
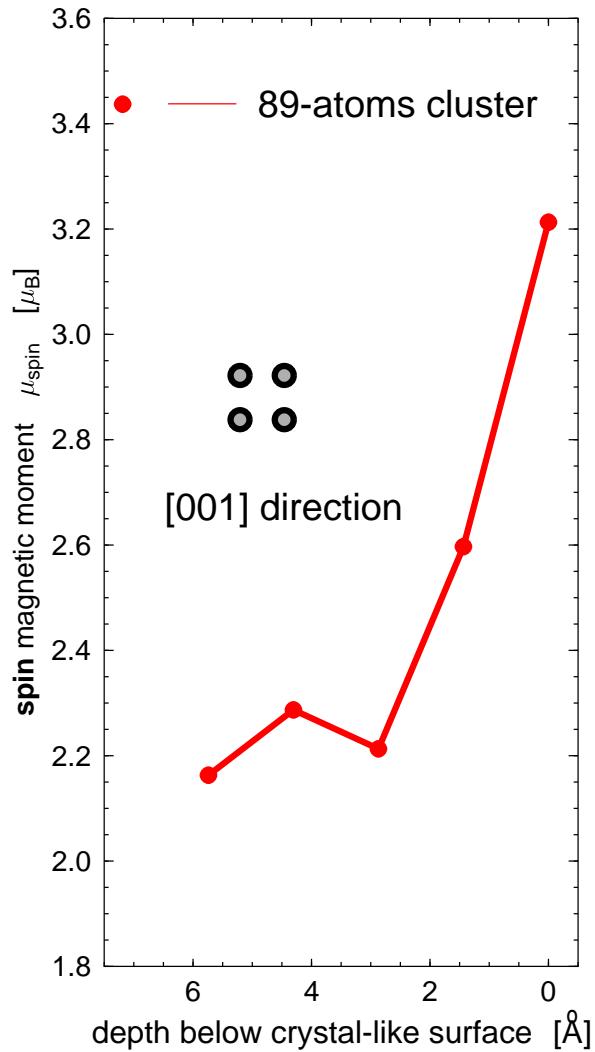
# Clusters vers. surfaces: HOWTO

{111} surface

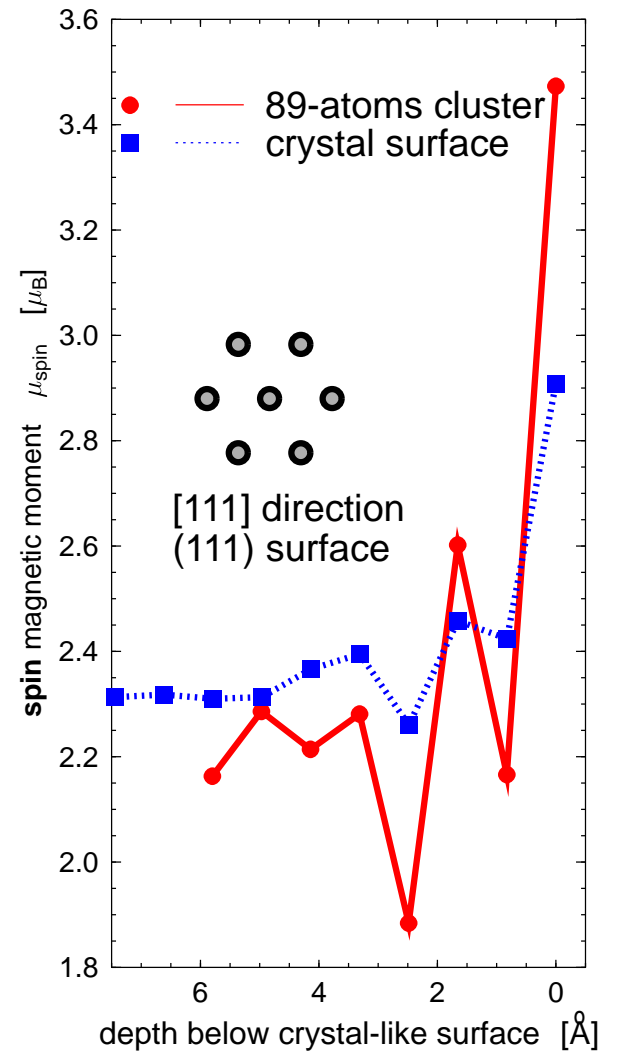
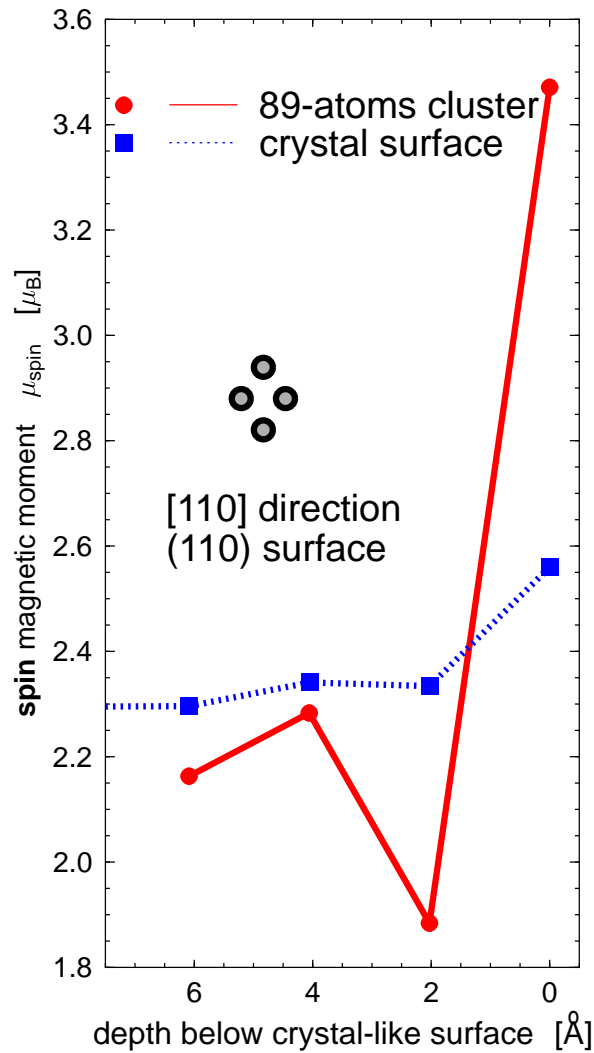
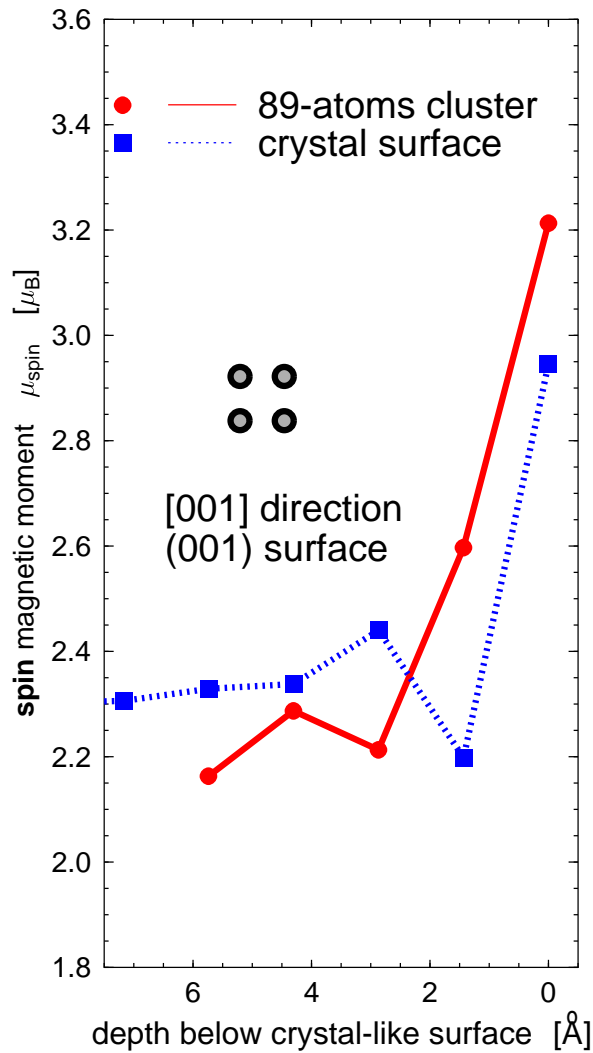
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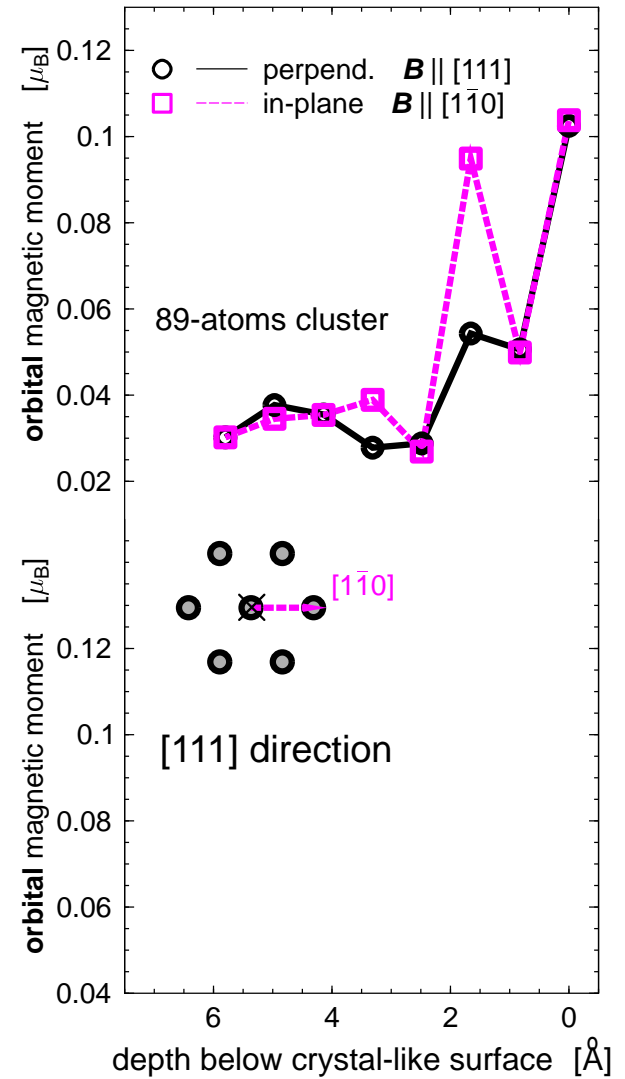
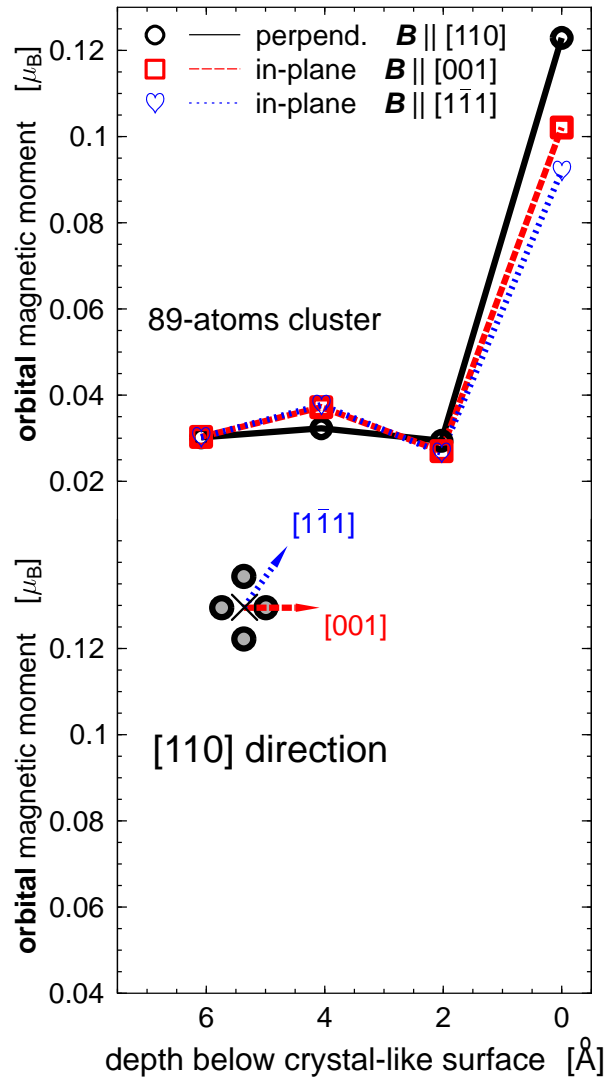
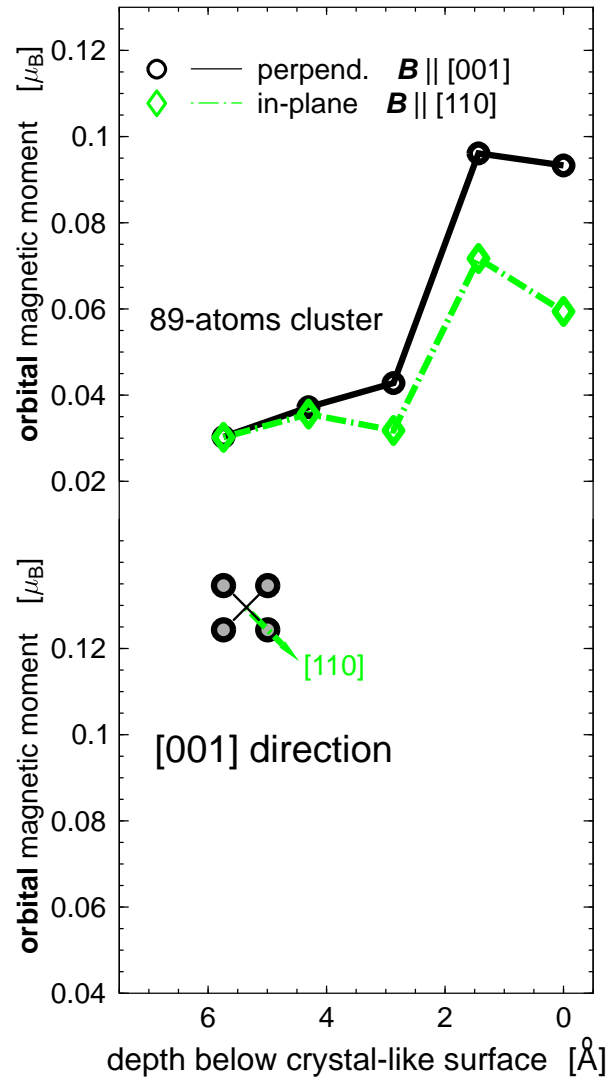
# Clusters vers. surfaces: $\mu_{\text{spin}}$



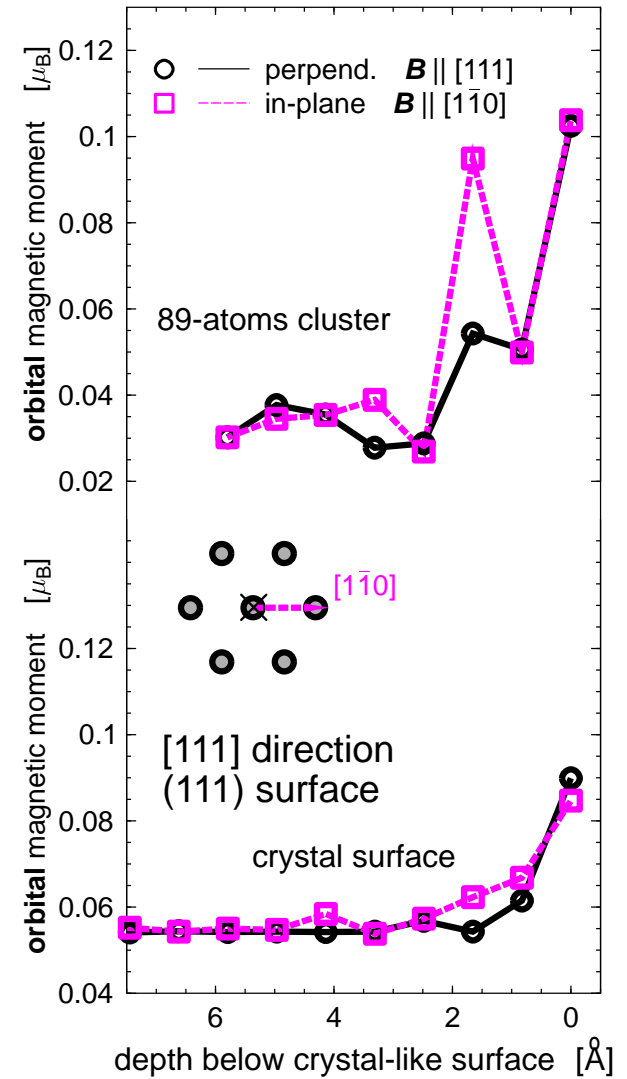
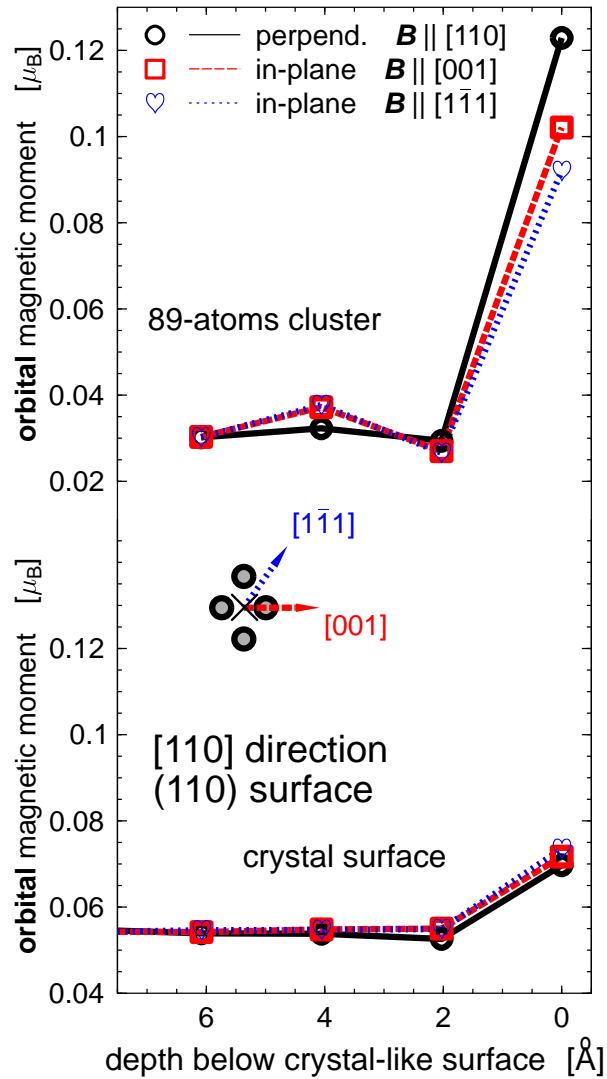
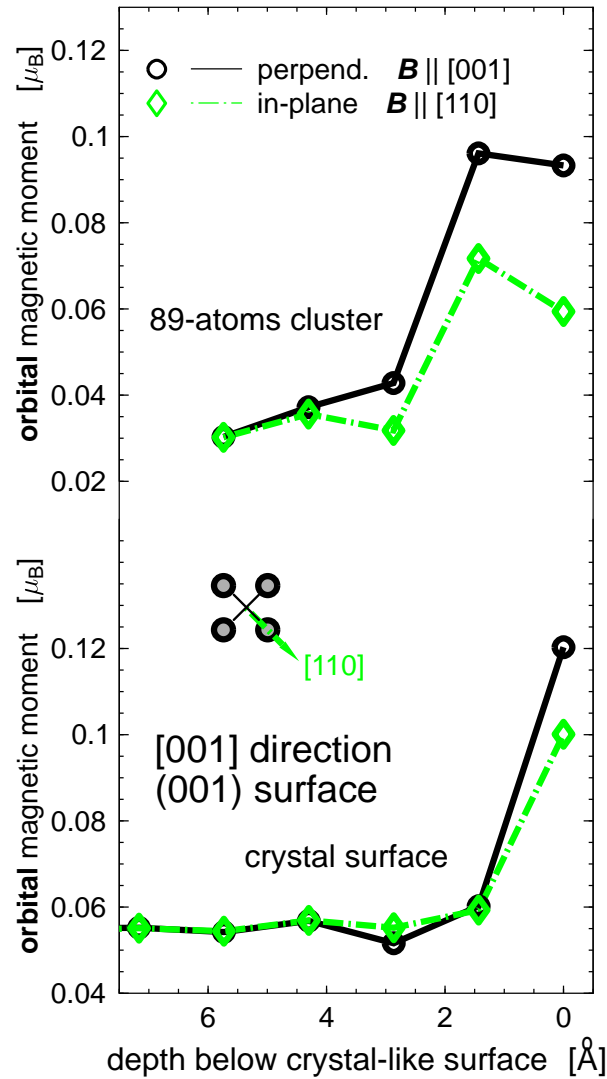
# Clusters vers. surfaces: $\mu_{\text{spin}}$



# Clusters vers. surfaces: $\mu_{\text{orb}}$



# Clusters vers. surfaces: $\mu_{\text{orb}}$



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

*Is there a way out?*

# Dependence of $\mu_{\text{spin}}$ on $N_{\text{eff}}$

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

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

where  $N_1$  is number of 1<sup>st</sup>  
neighbors and  $N_2$  is number of  
2<sup>nd</sup> neighbors.

[D. Tománek *et al.* PRB **28**, 665  
(1983); J. Zhao *et al.* Physics  
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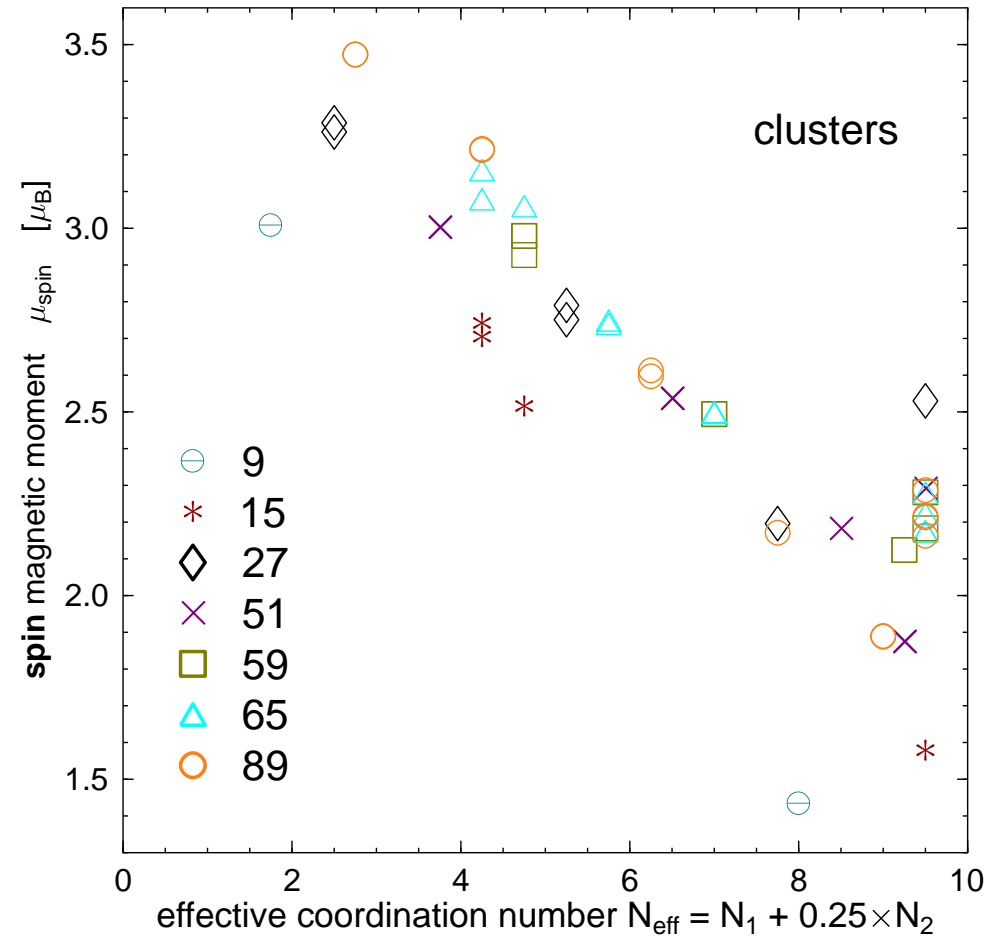
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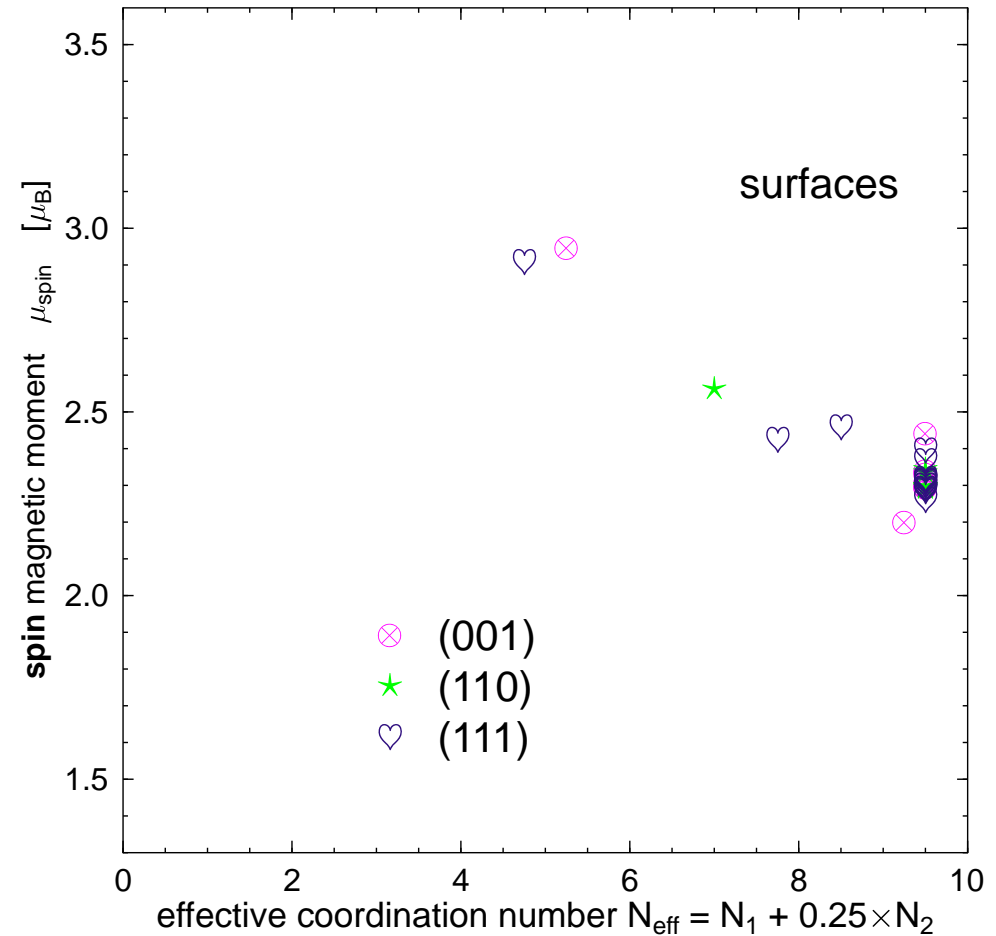
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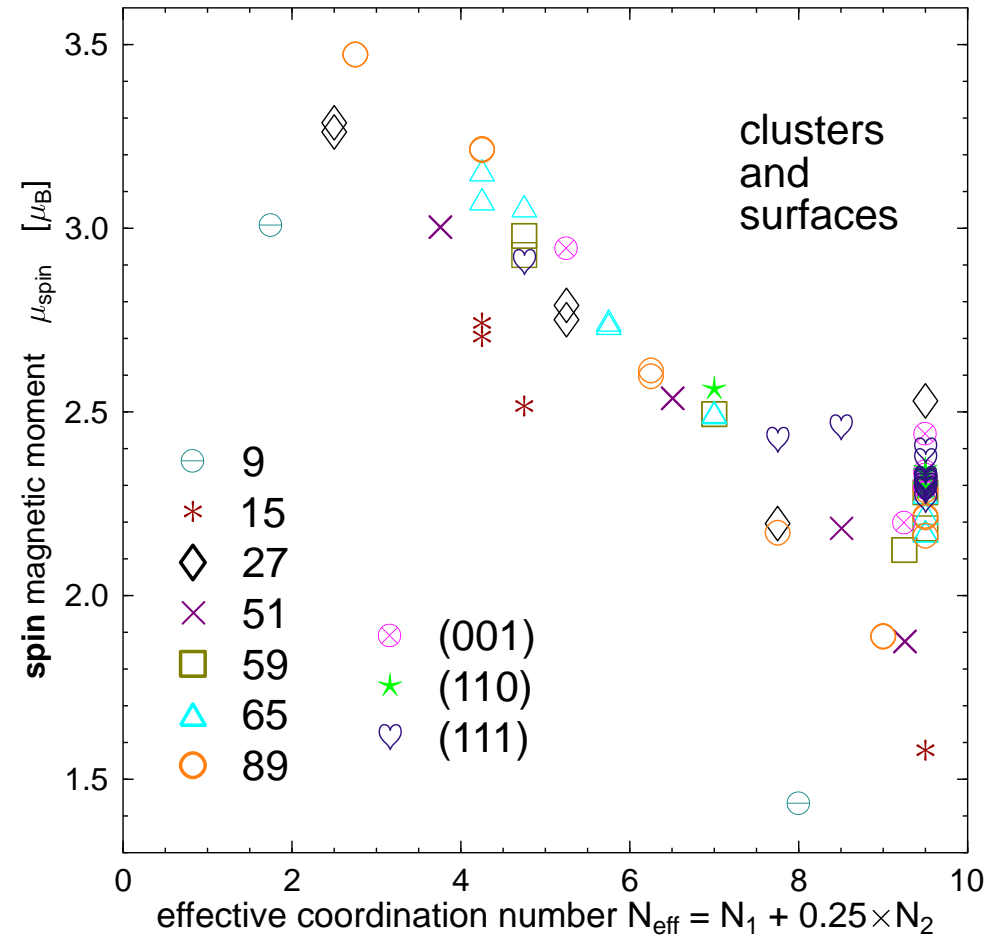
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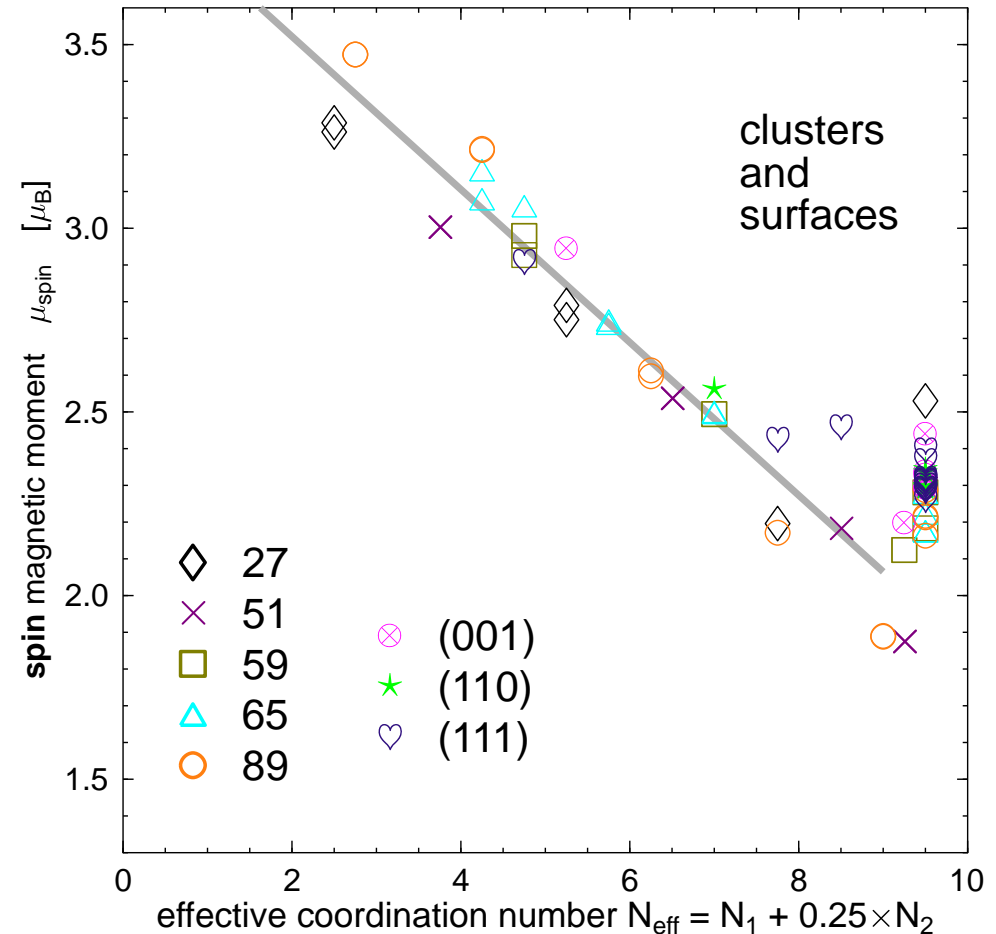
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neighbors and  $N_2$  is number of  
2<sup>nd</sup> neighbors.

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

Empirical model dependence:

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



# Dependence of $\mu_{\text{spin}}$ on $N_{\text{eff}}$

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

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

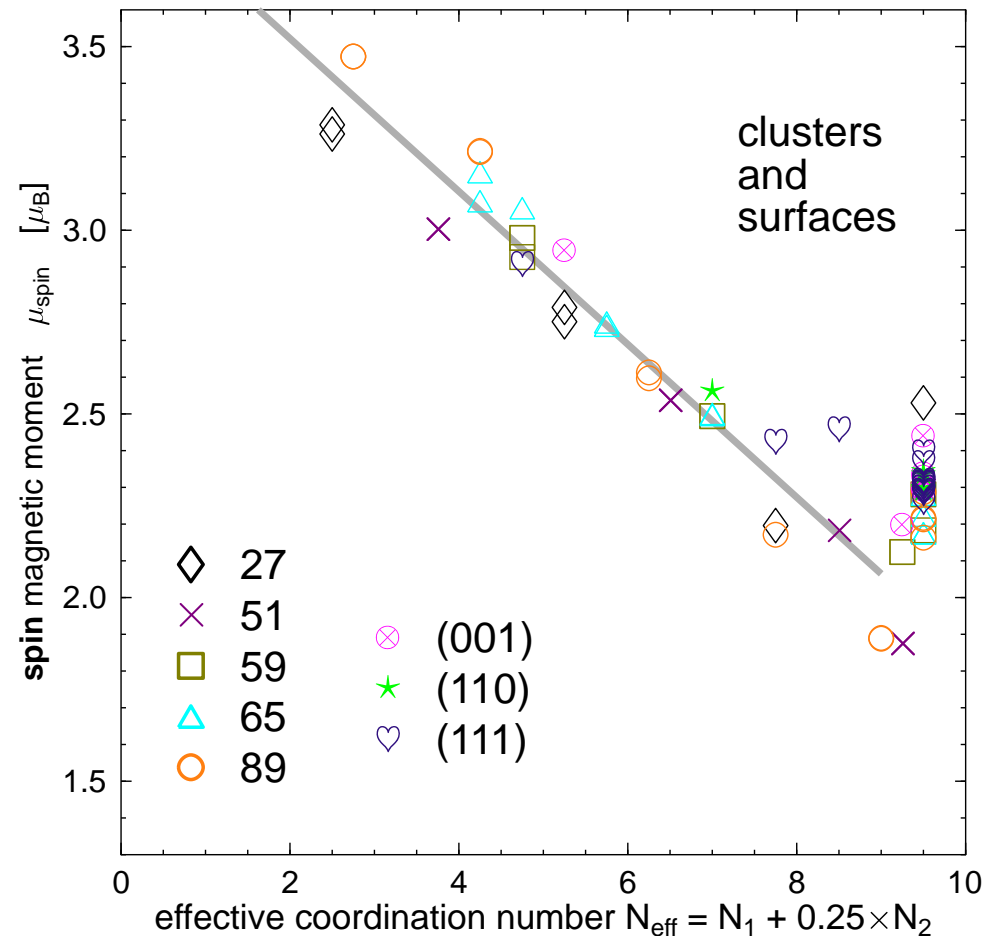
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[D. Tománek *et al.* PRB **28**, 665  
(1983); J. Zhao *et al.* Physics  
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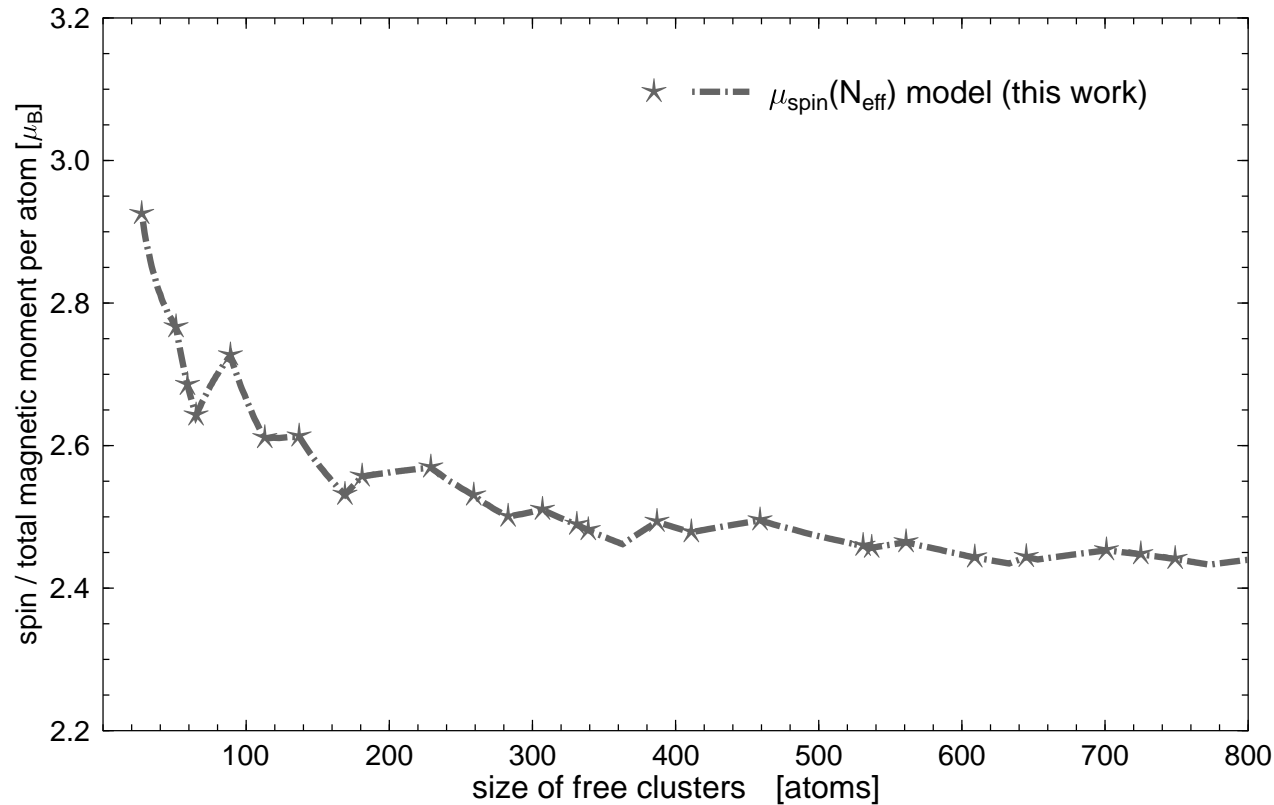
Empirical model dependence:

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

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

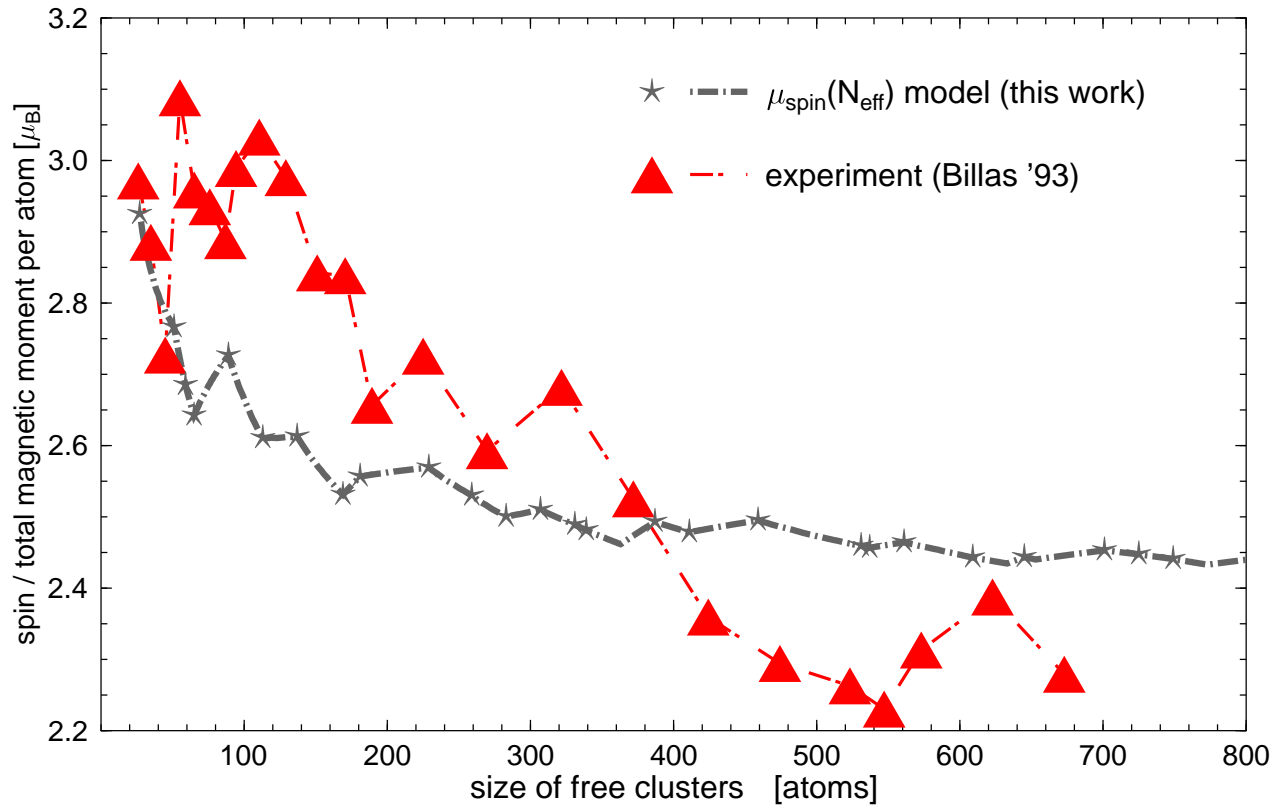


# Large clusters via $\mu_{\text{spin}}(N_{\text{eff}})$



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

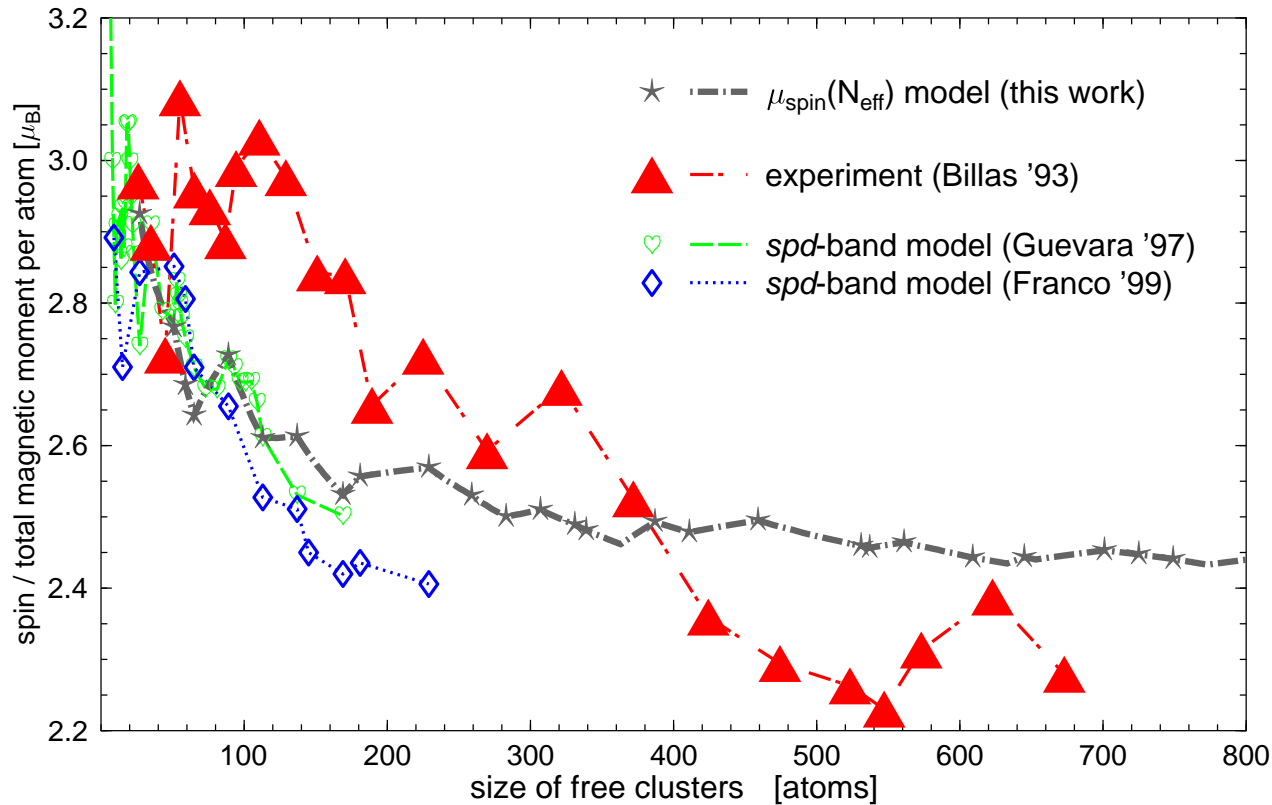
# Comparing model with experiment



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

Magnetic moment of whole clusters (per atom) can be compared with experiment [I.M.L. Billas *et al.* PRL **71**, 4067 (1993)].

# Comparing model with experiment

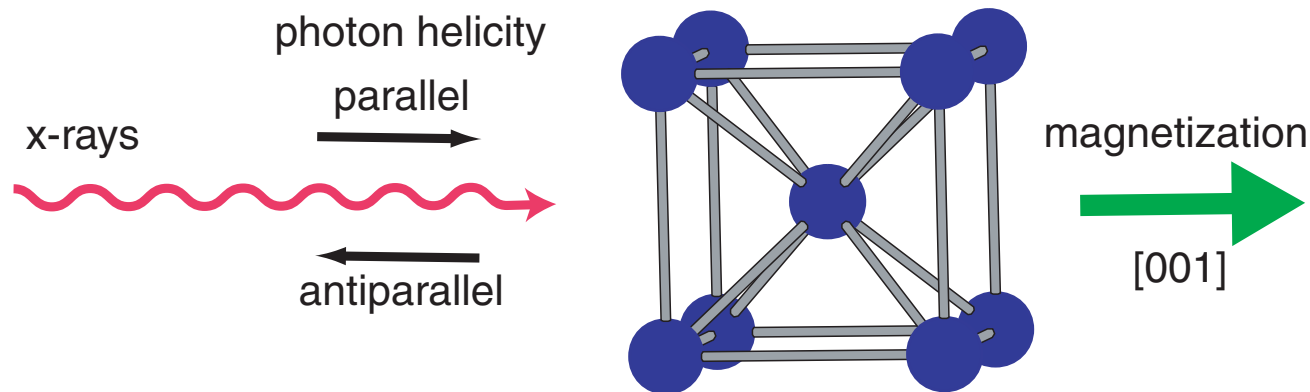


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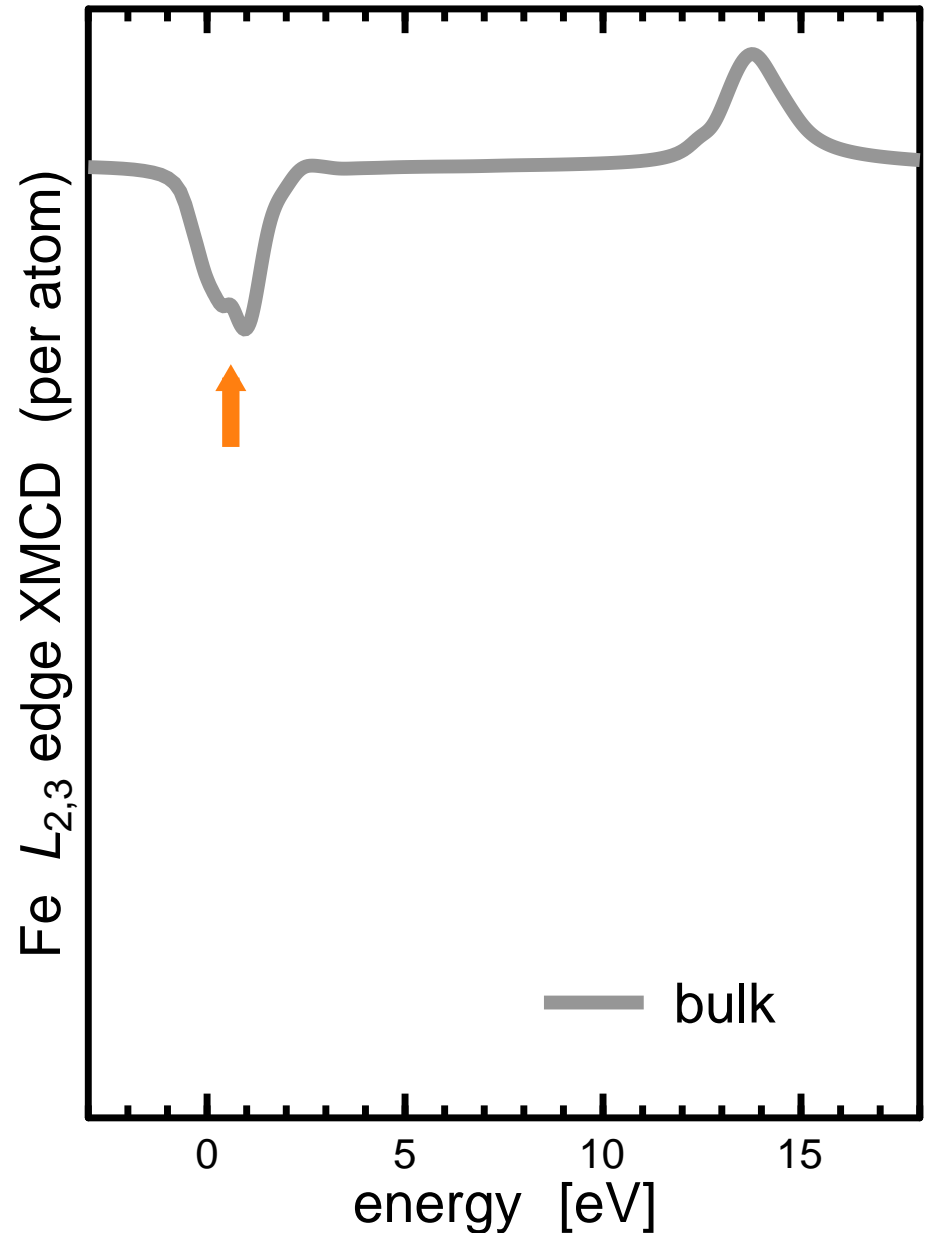
# What can XMCD do for us?

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



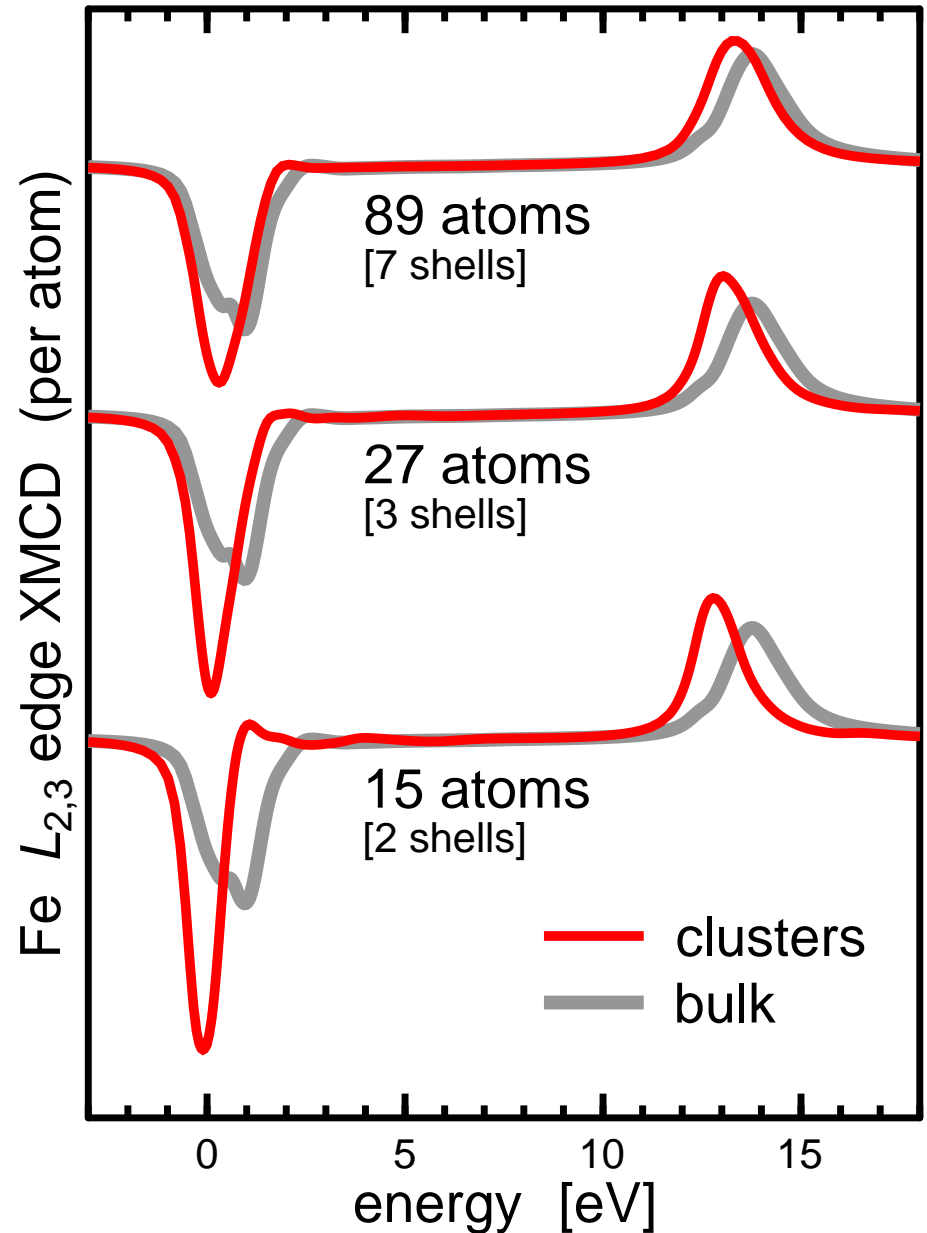
# XMCD of iron clusters

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



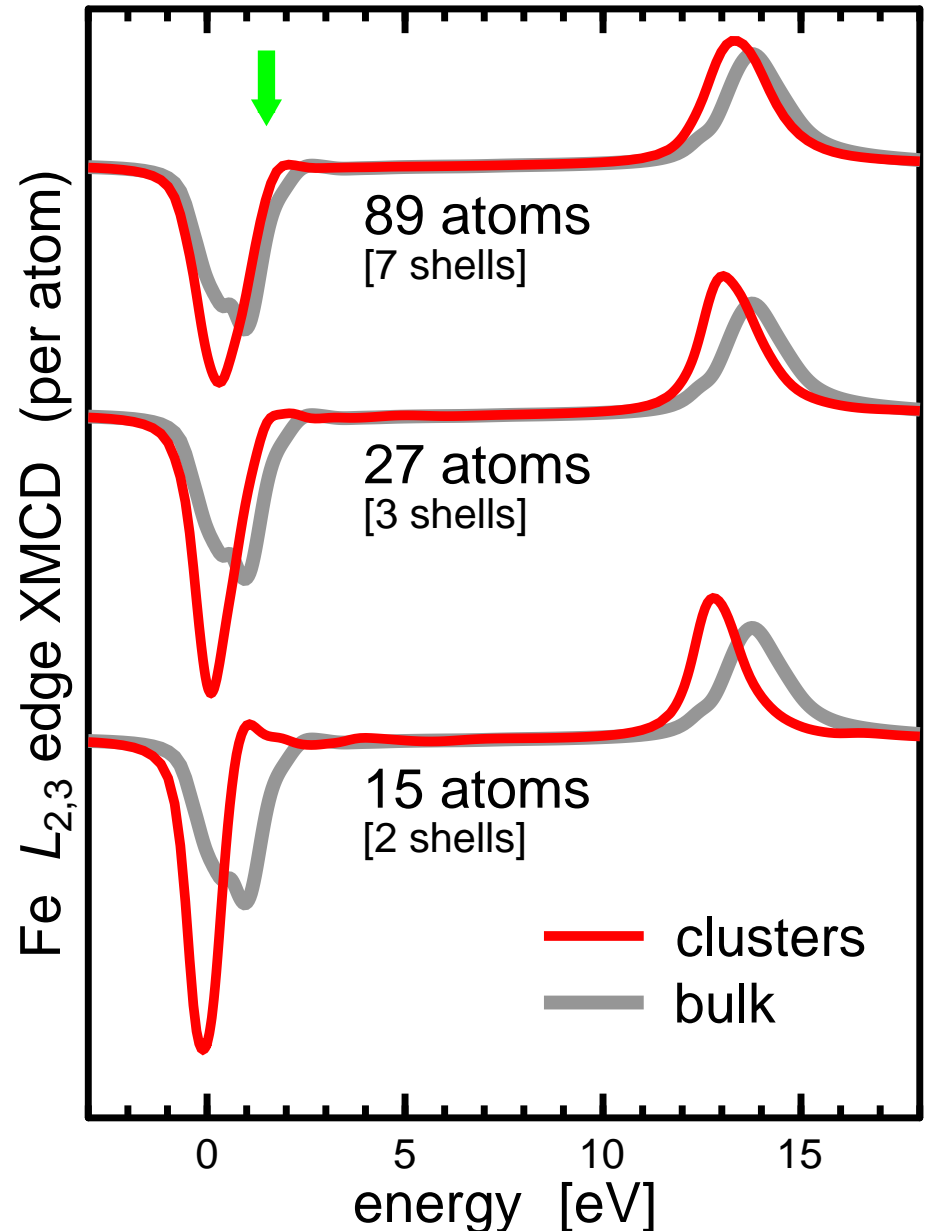
# XMCD of iron clusters

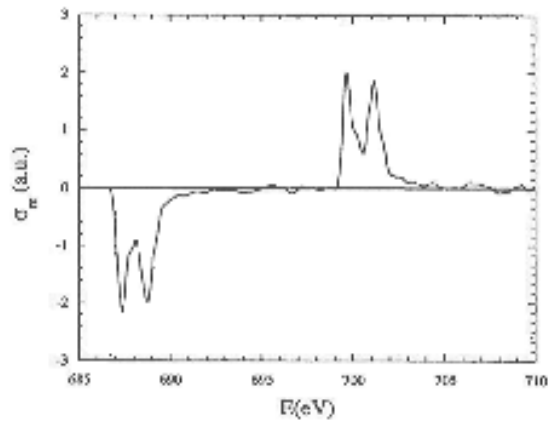
- Splitting of the bulk  $L_3$  peak not seen in experiment (but present in full-potential calculations). Energy resolution?
- Narrowing and enhancement of main peaks (more apparent at  $L_3$  than at  $L_2$ ).
- Peaks tilted towards the low-energy side.



# XMCD of iron clusters

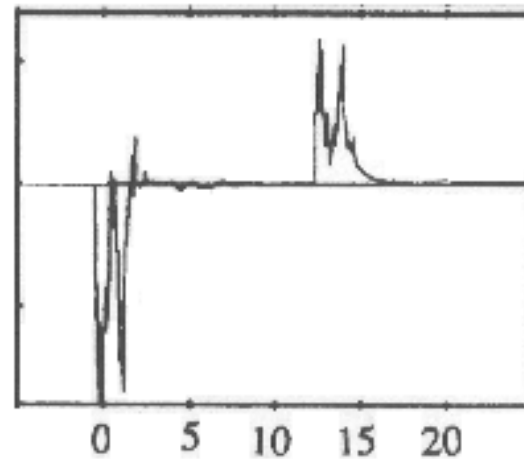
- Splitting of the bulk  $L_3$  peak not seen in experiment (but present in full-potential calculations). Energy resolution?
- Narrowing and enhancement of main peaks (more apparent at  $L_3$  than at  $L_2$ ).
- Peaks tilted towards the low-energy side.
- Small positive peak just after the main  $L_3$  minimum.





Fe(001) surface

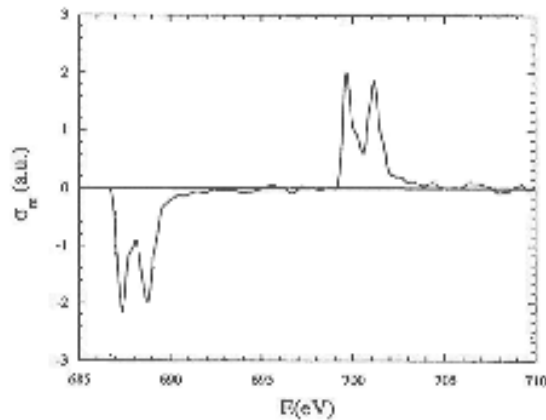
[Wu et al. PRL 71, 3581 (1993)]



Fe<sub>2</sub>Cu<sub>6</sub> (001) multilayer

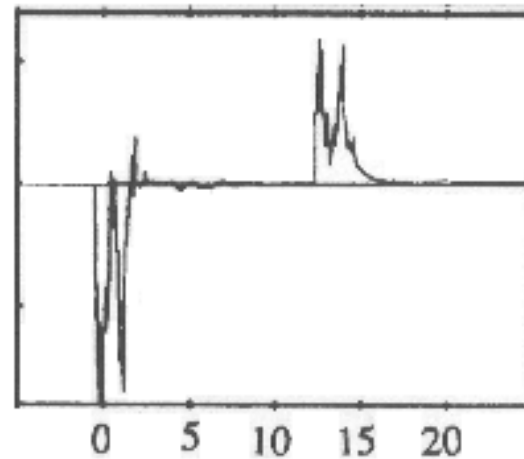
[Guo et al PRB 50, 3861 (1994)]

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



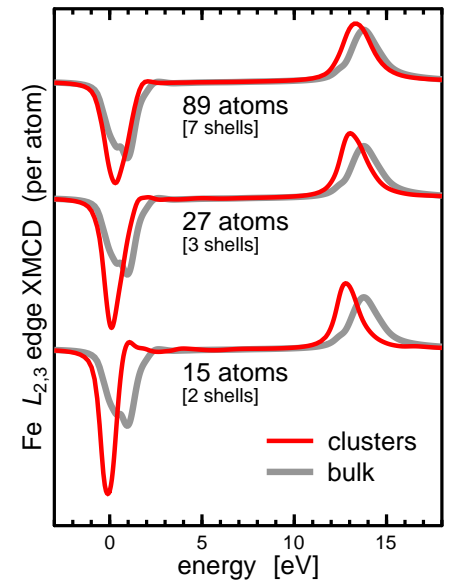
Fe(001) surface

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



Fe<sub>2</sub>Cu<sub>6</sub> (001) multilayer

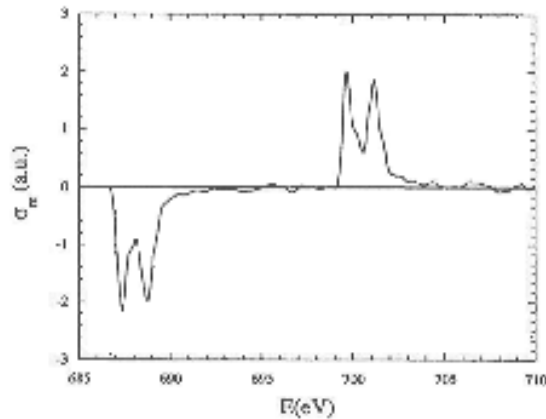
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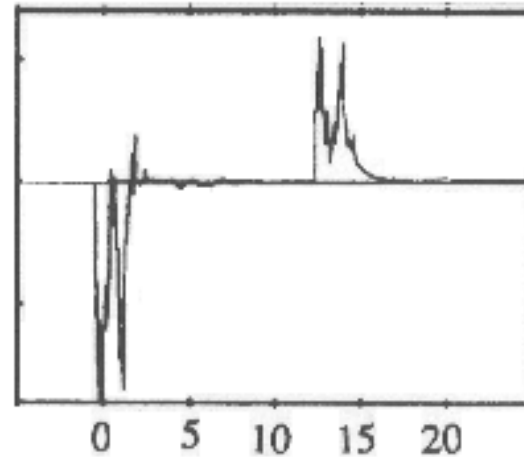
Calculated XMCD of clusters display no such fine structure.

# Where have all the structures gone?



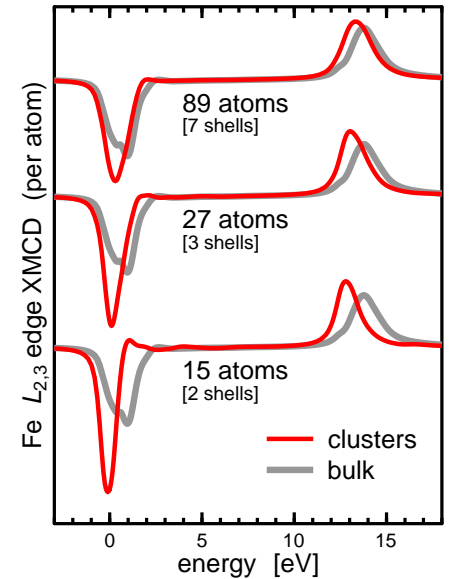
Fe(001) surface

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



Fe<sub>2</sub>Cu<sub>6</sub> (001) multilayer

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



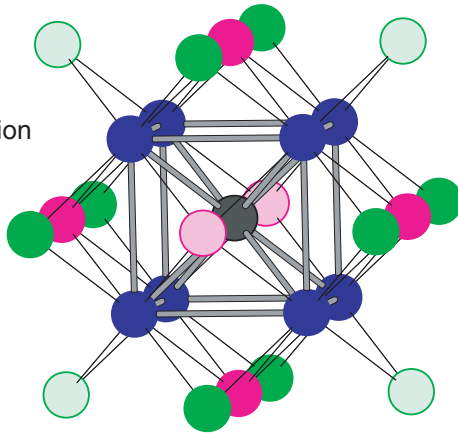
Calculated XMCD of surface or multilayers exhibit quite a **pronounced fine structure** at the Fe  $L_3$  and  $L_2$  edges.

Calculated XMCD of clusters display no such fine structure.

Fe cluster  
27 atoms

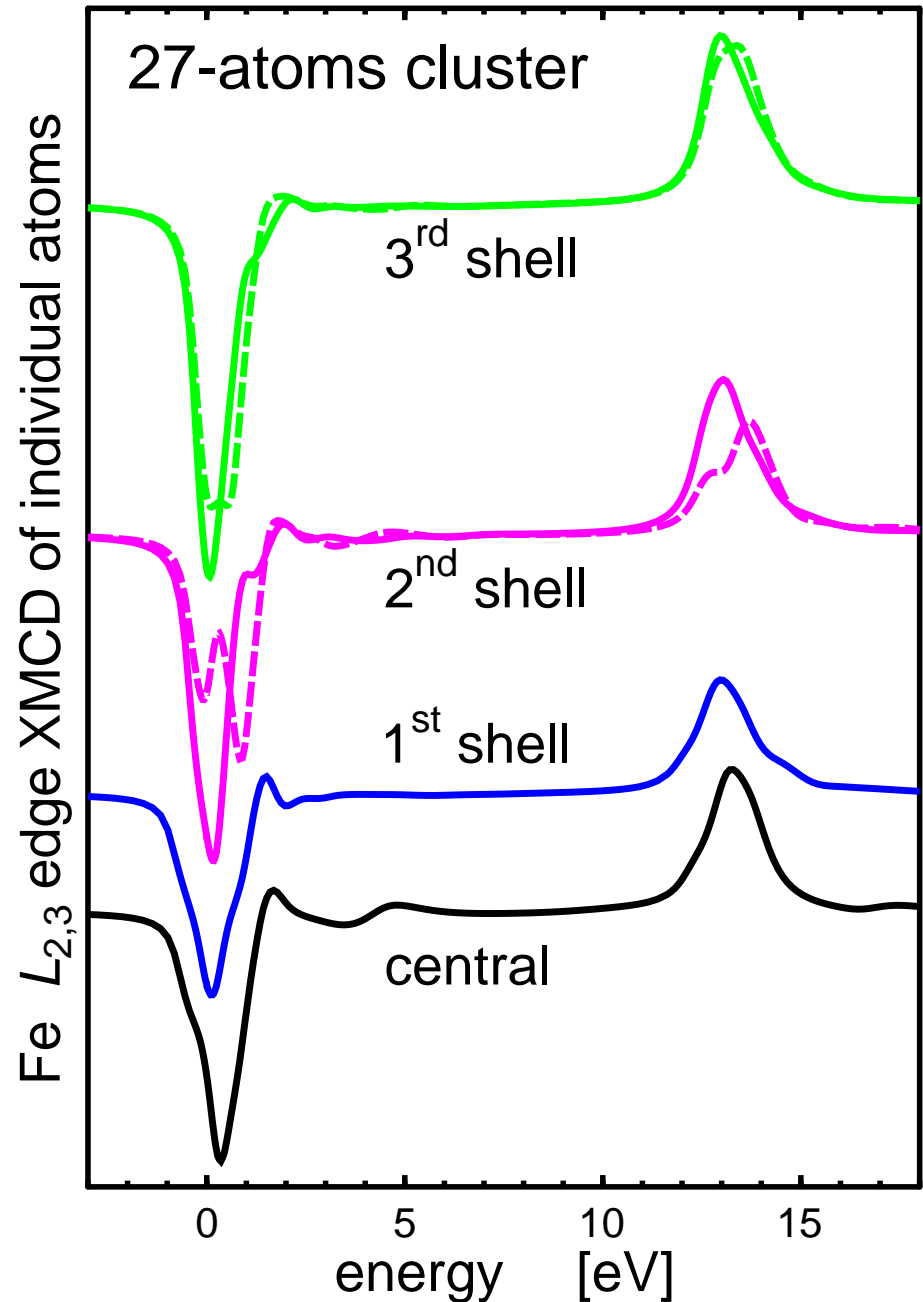
view in Z direction

- 3<sup>rd</sup> shell
- 2<sup>nd</sup> shell
- 1<sup>st</sup> shell
- center



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*

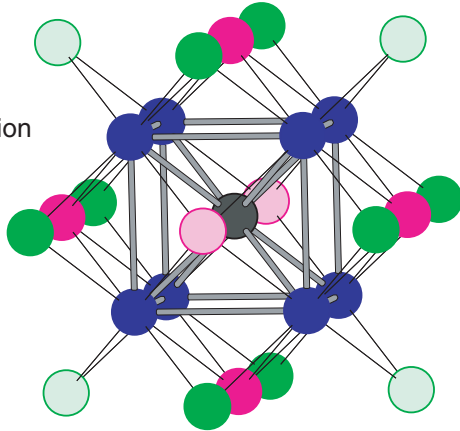


# The wiggles in XMCD mutually cancel!

Fe cluster  
27 atoms

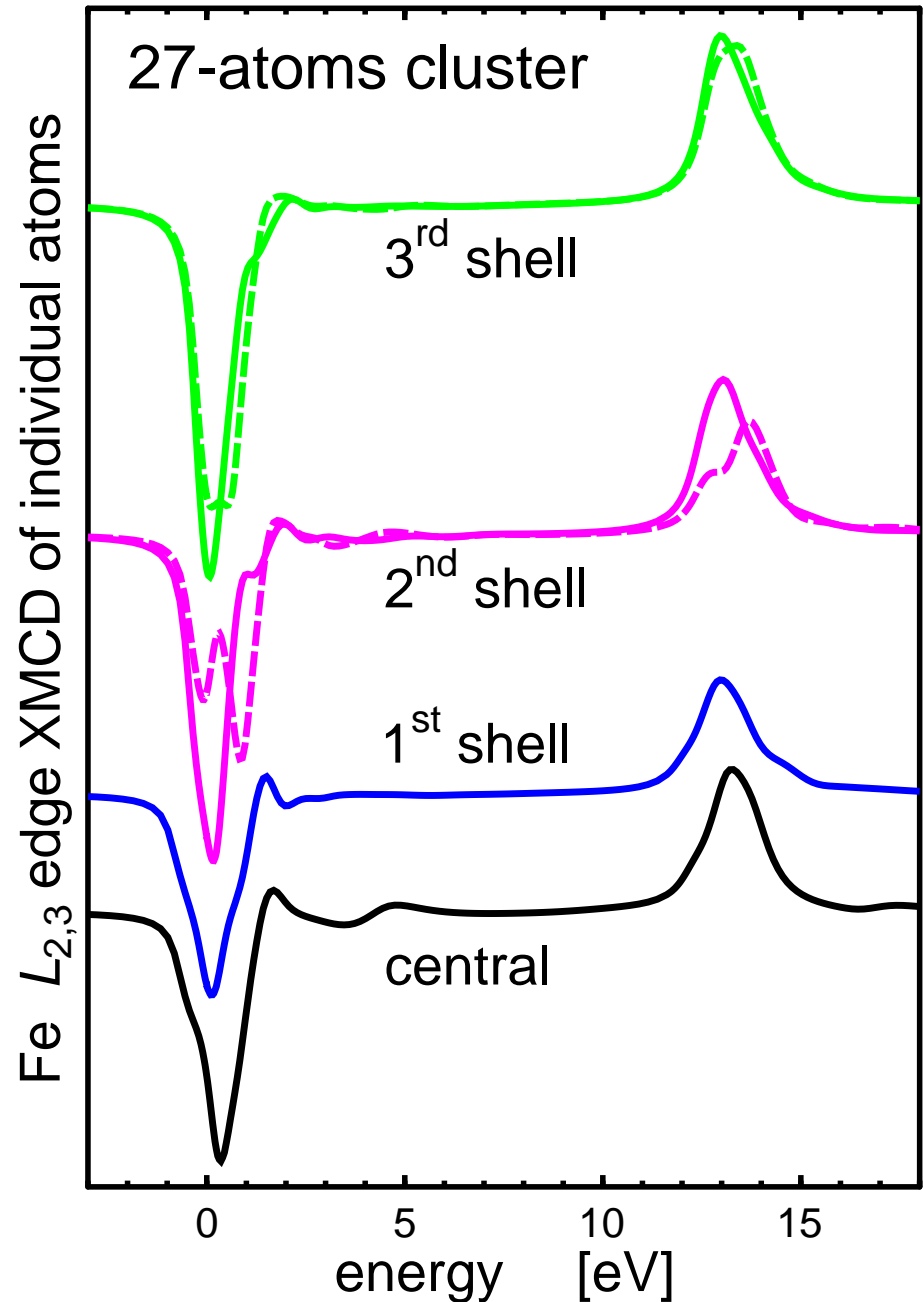
view in Z direction

- 3<sup>rd</sup> shell
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- 1<sup>st</sup> shell
- center



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*



# Conclusions

- In free clusters,  $\mu_{\text{spin}}$  and  $\mu_{\text{orb}}$  are enhanced at atoms close to the cluster surface.
- $\mu_{\text{orb}}$  at individual atoms strongly depends on the direction of the magnetic field. However, the anisotropy in  $\mu_{\text{orb}}$  averaged over whole coordination spheres is very small.
- Friedel-like oscillations both in  $\mu_{\text{spin}}$  and in  $\mu_{\text{orb}}$  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.
- $\mu_{\text{spin}}$  in clusters and at crystal surfaces depends linearly on  $N_{\text{eff}}$ .
- 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?