

# Electronic, magnetic and spectroscopic properties of free Fe clusters

O. Šipr<sup>1</sup>,

M. Košuth<sup>2</sup>, J. Minár<sup>2</sup>, S. Polesya<sup>2</sup> and H. Ebert<sup>2</sup>

<sup>1</sup> Institute of Physics, Academy of Sciences of the Czech Republic,  
Cukrovarnická 10, 162 53 Prague, Czech Republic

<sup>2</sup> Universität München, Department Chemie,  
Butenandtstr. 5-13, D-81377 München, Germany

## References:

O. Šipr and H. Ebert, Physica Scripta **T115**, 110–112 (2005)

O. Šipr, M. Košuth and H. Ebert, Phys. Rev. B **70**, 174423 (2004)  
(13 pages)

O. Šipr, M. Košuth and H. Ebert, Surf. Sci. **566-568** Part 1, pp.  
268–271 (2004)

O. Šipr and H. Ebert, Czech. J. Phys. **53**, 55–63 (2003)

## Websites:

<http://www.fzu.cz/~sipr>

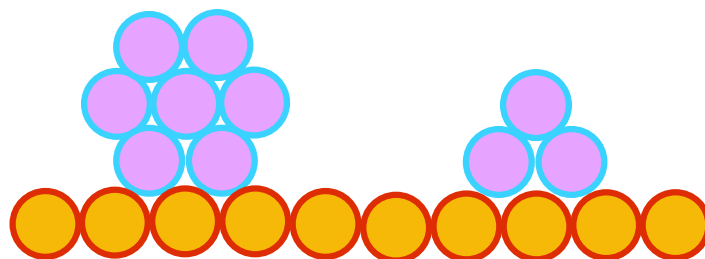
[http://olymp.phys.chemie.uni-muenchen.de/ak/ebert/index\\_eng.html](http://olymp.phys.chemie.uni-muenchen.de/ak/ebert/index_eng.html)

# Outline

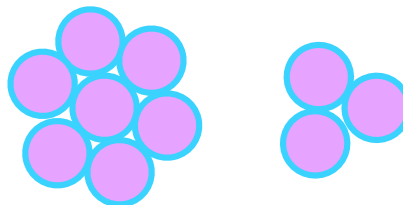
- Introducing clusters, magnetism and cluster magnetism
- Electronic properties and magnetism of clusters (at  $T=0$ )
- Magnetism of clusters and of crystal surfaces
- Exploring magnetism through spectroscopy (XMCD)
- Finite temperature magnetism of clusters

# Nomenclature

- Clusters = systems of **tens to hundreds** of atoms
- Radii from  $\sim 6$  Å for a 100-atom cluster to  $\sim 15$  Å for a 1000-atom cluster
- **Supported** clusters — adsorbed on a surface

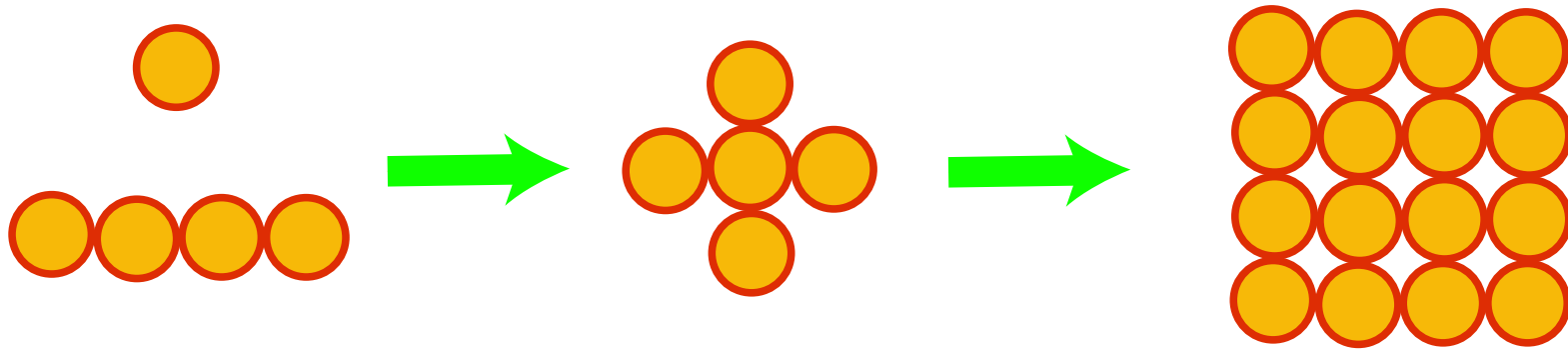


- **Free** clusters — giant molecules, surrounded by vacuum



# What can we expect?

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



- Interesting phenomena (and a lot of fun) can be anticipated
- Our main focus will be on their *magnetic* properties

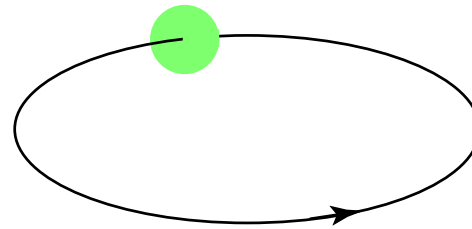
# Where does magnetism come from?

- Classically: Magnetic field is *something* produced by **moving** electric charges that affects other **moving** charges
- **Special relativity**: Magnetism is a *fictitious force* needed to guarantee **Lorentz invariance** when charges move  
[It's Einstein year!]
- There is nothing like “magnetic force”; electrical Coulomb interaction is enough.  
One observer may perceive a magnetic force where a moving observer perceives only an electrostatic force.
- Dealing with magnetism in the framework of **Dirac equation** is ideologically **simple** — no need for magnetism to be introduced by God (as it is the case with Schrödinger equation).

# Two ways of moving an electron

(A quick and dirty introduction to magnetism)

● Orbiting:



● Spinning:



# Orbital magnetic moment (1)

Classical expression for magnetic moment:

$$\boldsymbol{\mu}_{\text{orb}} = I \mathbf{S} \quad \Longrightarrow \quad \boldsymbol{\mu}_{\text{orb}} = -\mu_B \mathbf{L}$$

where  $\mu_B$  is Bohr magneton

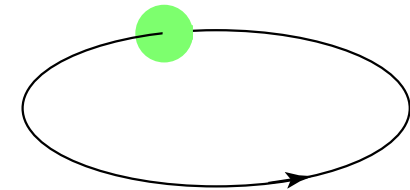
$$\mu_B \equiv \frac{e}{2m_e} \hbar$$

and  $\mathbf{L}$  is angular momentum divided by  $\hbar$ .

For **electron** orbiting **around an atom**, the  $z$ -component of orbital magnetic moment is thus

$$\mu_{\text{orb}}^{(z)} = -m_\ell \mu_B ,$$

where  $m_\ell$  is the magnetic quantum number.

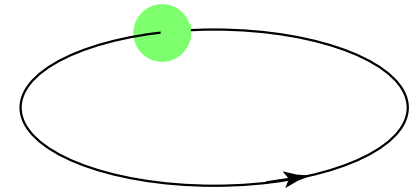




# Orbital magnetic moment (2)

Practical **evaluation** of orbital magnetic moment of electrons in a solid:

$$\mu_{\text{orb}}^{(z)} = -\frac{\mu_B}{\pi} \text{Im Tr} \int_{-\infty}^{E_F} dE \int d^3r \beta L_z G(\mathbf{r}, \mathbf{r}; E) ,$$



$\beta$  is Dirac matrix

$L_z$  is the  $z$ -component of a  $4 \times 4$  matrix vector  $I_4 \otimes \mathbf{L}$

$G(\mathbf{r}, \mathbf{r}; E)$  is a  $4 \times 4$  Green function matrix.

Even *more practical* evaluation of  $\mu_{\text{orb}}$ :

Find it in the output of the SPRKKR program.

# Spin magnetic moment (1)

Electron spin: Picture of a rotating charged sphere fails (again ...)

$$\mu_{\text{orb}} = -\mu_B \mathbf{L} \quad \text{vers.} \quad \mu_{\text{spin}} = -2\mu_B \mathbf{S}$$

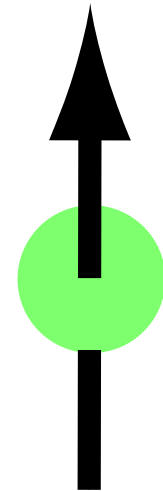
( $\mathbf{L}$  is angular momentum connected with *orbital* motion and  $\mathbf{S}$  is angular momentum connected with the “*spin* motion”).

For **electron around an atom**, the  $z$ -component of spin-related angular momentum is

$$S^{(z)} = \pm \frac{1}{2} \hbar ,$$

hence we get for a  $z$ -component of spin-related magnetic moment

$$\mu_{\text{spin}}^{(z)} = \pm \mu_B .$$

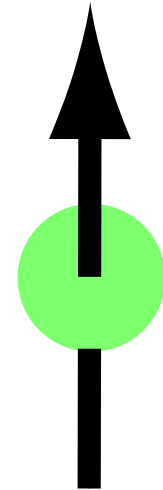


# Spin magnetic moment (2)

Practical **evaluation** of spin magnetic moment of electrons in a solid:

$$\mu_{\text{spin}}^{(z)} = -\frac{\mu_B}{\pi} \text{Im Tr} \int_{-\infty}^{E_F} dE \int d^3r \beta \sigma_z G(\mathbf{r}, \mathbf{r}, E) ,$$

$\sigma_z$  is the  $z$ -component of a  $4 \times 4$  matrix vector  $I_2 \otimes \sigma$



# Magnetism of Fe atom

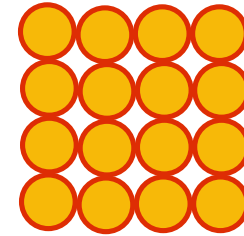
Magnetic properties of atoms are governed by Hund rules

Electron configuration:  $3d^6 4s^2$

- Spin magnetic moment:  $\mu_{\text{spin}} = 4 \mu_B$ 
  - First Hund rule: Total atomic spin quantum number  $S = \sum m_s$  is maximum (as long as it is compatible with Pauli exclusion principle)
- Orbital magnetic moment:  $\mu_{\text{orb}} = 2 \mu_B$ 
  - Second Hund rule: Total atomic orbital quantum number  $L = \sum m_\ell$  is maximum (as long as it is compatible with Pauli exclusion principle and first Hund rule)

# Bulk Fe

- Generally: Magnetism is **suppressed** in the bulk (with respect to atomic case)




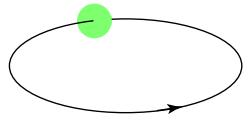
- Spin magnetic moment is  $\mu_{\text{spin}} \approx 2.2 \mu_B$  per atom
- The *orbital* magnetic moment is quenched (outright zero in non-relativistic case)
  - Intuitively: Electron are not free to orbit around atoms
  - **Relativistic** effect: The quenched orbital moment is partially restored by *LS* coupling ( $\mu_{\text{orb}} \approx 0.05 \mu_B$  per atom)

# Surfaces are magnetism-friendly

- Atoms at surfaces exhibit some atomic-like characteristics
- Spin magnetic moment is larger than in bulk; for Fe it is  $\mu_{\text{spin}} \approx 2.5\text{--}3.0 \mu_B$  per atom
- The orbital magnetic moment is increased by an even larger percentage,  $\mu_{\text{orb}} \approx 0.07\text{--}0.12 \mu_B$  per atom



# Magnetism of iron: summary

	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)

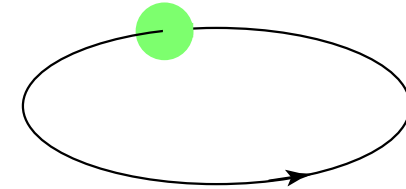
Clusters contain a high portion of surface atoms

⇒ ought to have larger magnetic moments

their properties should display traces of surface and bulk trends

# Why all the fuss with $\mu_{\text{orb}}$ ?

- $\mu_{\text{orb}}$  is small *but important* !



- It is a manifestation of spin-orbit coupling, which is the mechanism behind the **magnetocrystalline anisotropy**
- Under certain assumptions, magnetocrystalline anisotropy energy (MAE) can be estimated as

$$\Delta E_{\text{MAE}} = \text{const} \times \left( \mu_{\text{orb}}^{\parallel} - \mu_{\text{orb}}^{\perp} \right)$$

where  $\mu_{\text{orb}}^{\parallel}$  and  $\mu_{\text{orb}}^{\perp}$  are orbital magnetic moments for two perpendicular directions of the magnetization  $M$



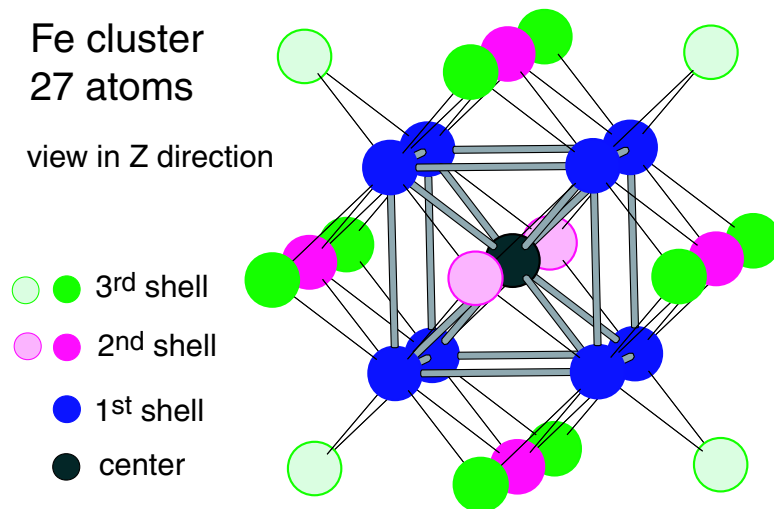
# Ground-state magnetic properties of clusters

# System we study

- free spherical-like Fe clusters with geometry taken as if cut from a bulk *bcc* Fe crystal
- cluster size between 9 atoms (1 coordination shell) and 89 atoms (7 coordinations shells)

Fe cluster  
27 atoms

view in Z direction

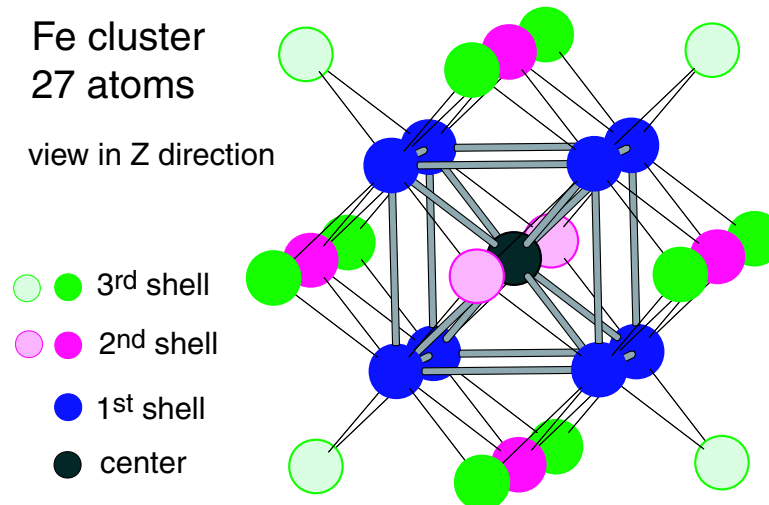


shells	atoms	radius [Å]
--------	-------	------------

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

# Lowering of symmetry

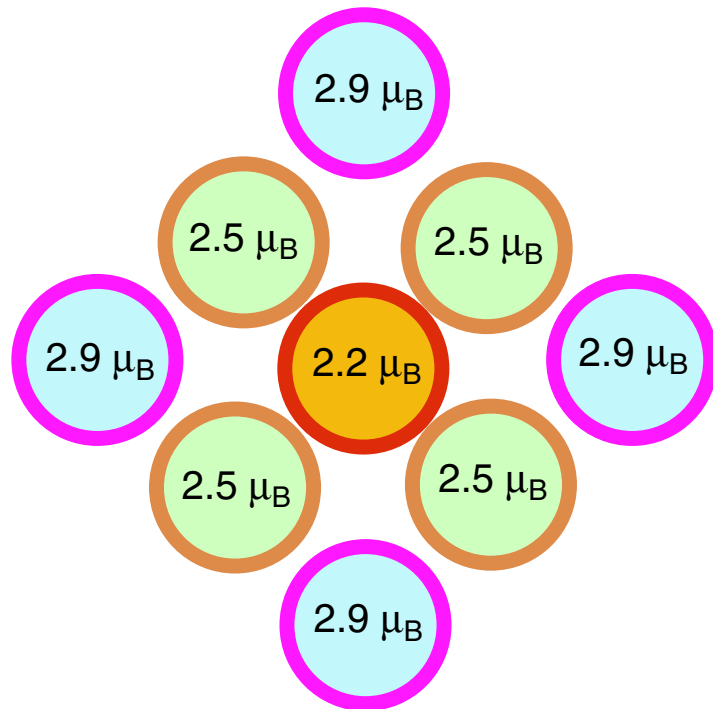
- Magnetization and spin-orbit coupling lowers the symmetry of our systems
- Atoms belonging to the same coordination shell may be inequivalent
- Classes of equivalent atoms depend on the direction of magnetization  $M$



# Theoretical formalism

- LDA scheme
- cluster calculations done in real space via a fully-relativistic spin-polarized multiple-scattering technique as implemented in the `SPRKKR` code
- crystal surfaces treated as 2D finite slabs (fully-relativistic spin-polarized TB-KKR method)
- spherical ASA approximation
- empty spheres put around the clusters in order to account for spilling of the electron charge into vacuum

# Magnetic profiles of clusters



Local magnetic moments:

$\mu_{\text{spin}}$  and  $\mu_{\text{orb}}$  can be attributed to **individual sites** by performing the integrations

$$\mu_{\text{spin}} \sim \int d^3r \beta \sigma_z G(\mathbf{r}, \mathbf{r}, E)$$

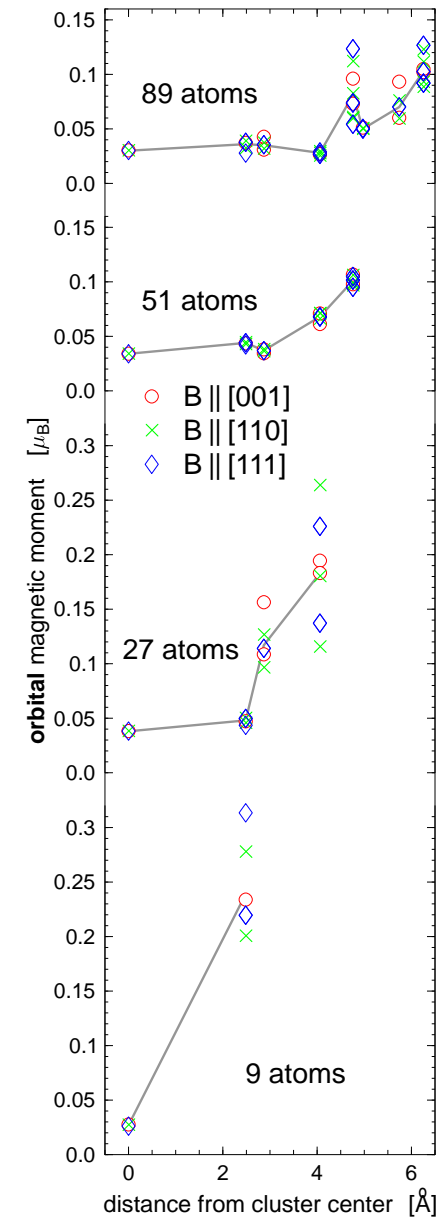
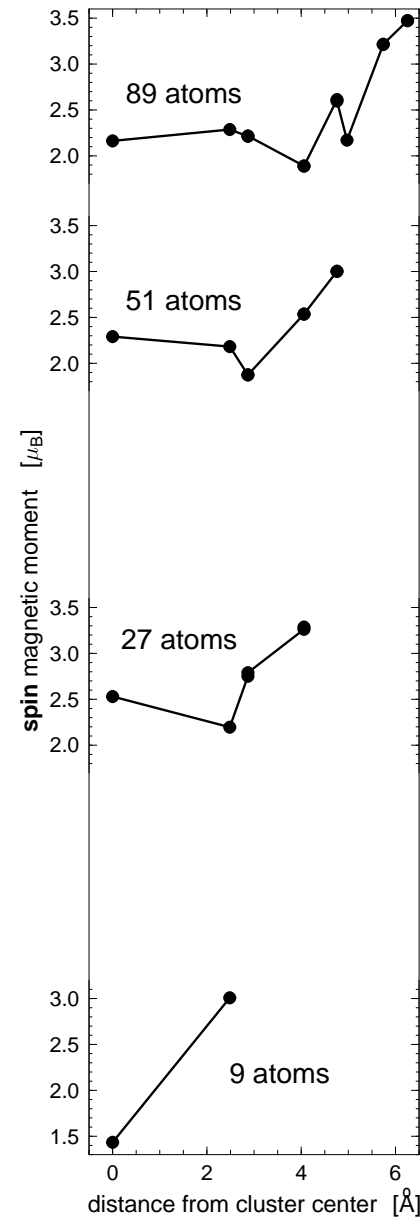
and

$$\mu_{\text{orb}} \sim \int d^3r \beta L_z G(\mathbf{r}, \mathbf{r}, E)$$

over atomic spheres

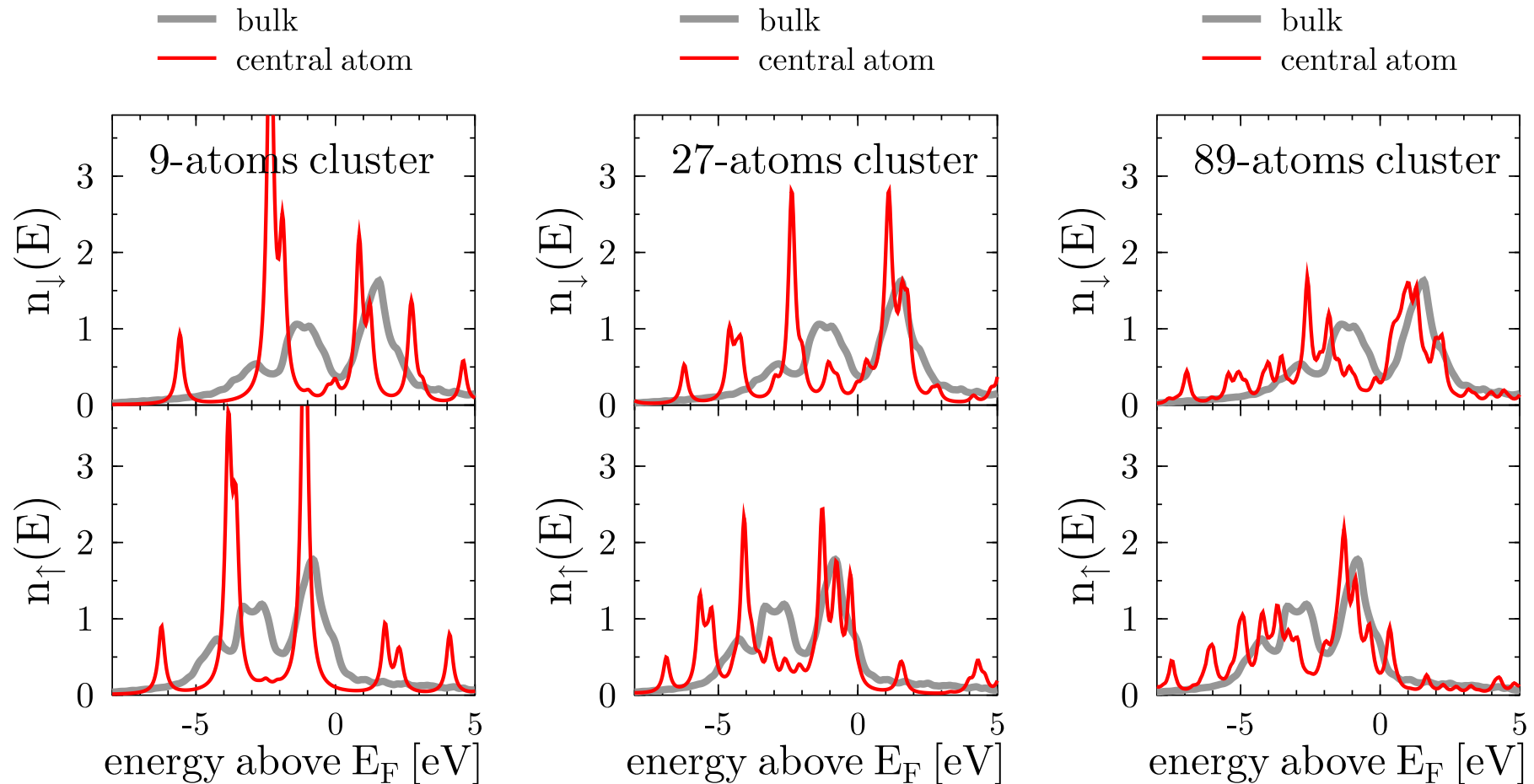
# Free Fe clusters — the results

- $\mu_{\text{spin}}$  does not depend on the direction of  $M$ 
  - for inequivalent atoms of the same coordination sphere  $\mu_{\text{spin}}$  is the same
- $\mu_{\text{orb}}$  depends on the direction of  $M$ 
  - for inequivalent atoms of the same coordination sphere  $\mu_{\text{orb}}$  differs
- $\mu_{\text{orb}}$  averaged over coordination spheres does not depend on the direction of  $M$



# DOS in clusters and in bulk

- Atomic-like features present in DOS of clusters
- DOS in the center of clusters approaches the bulk quite slowly

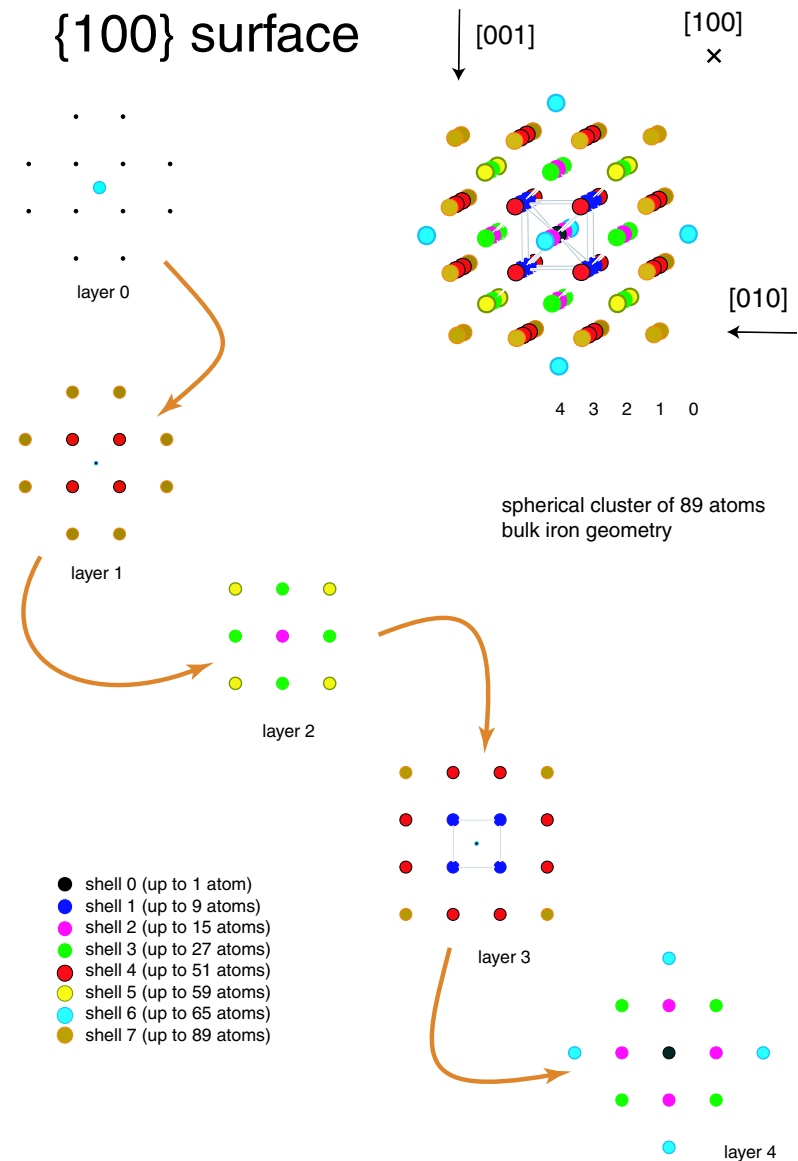


# Clusters and crystal surfaces



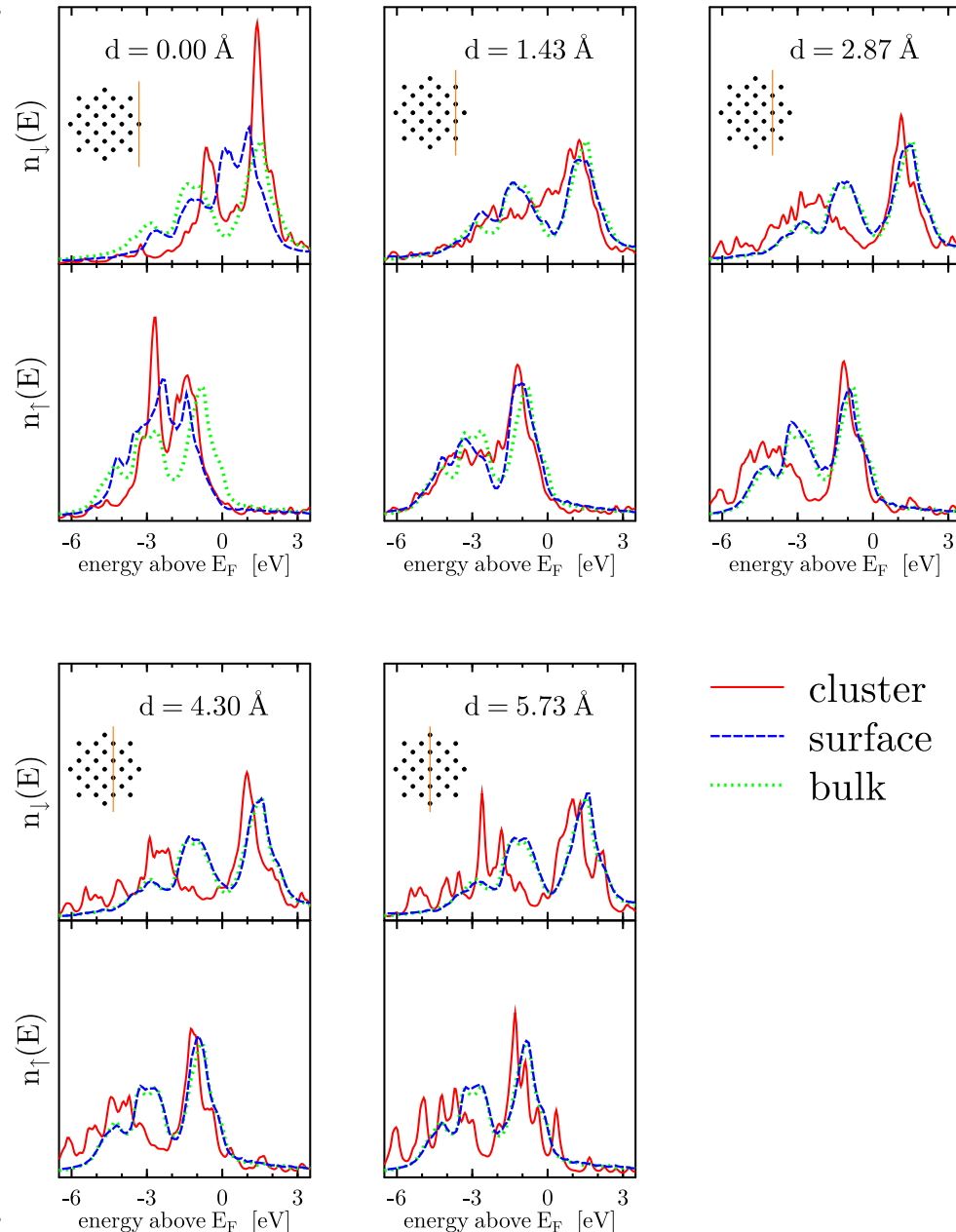
# Clusters vers. surfaces: HOWTO

- take free iron cluster of 89 atoms
- drill a hole into this cluster
- inspect DOS,  $\mu_{\text{spin}}$  and  $\mu_{\text{orb}}$  around you and compare them with what you see beneath a crystal surface
- explore various “crystallographic directions”

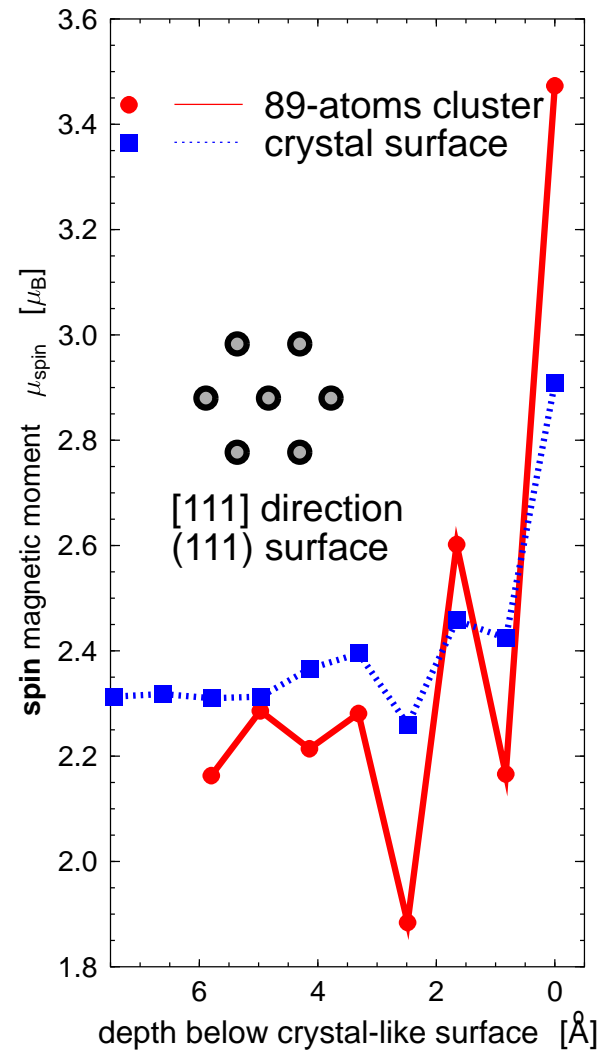
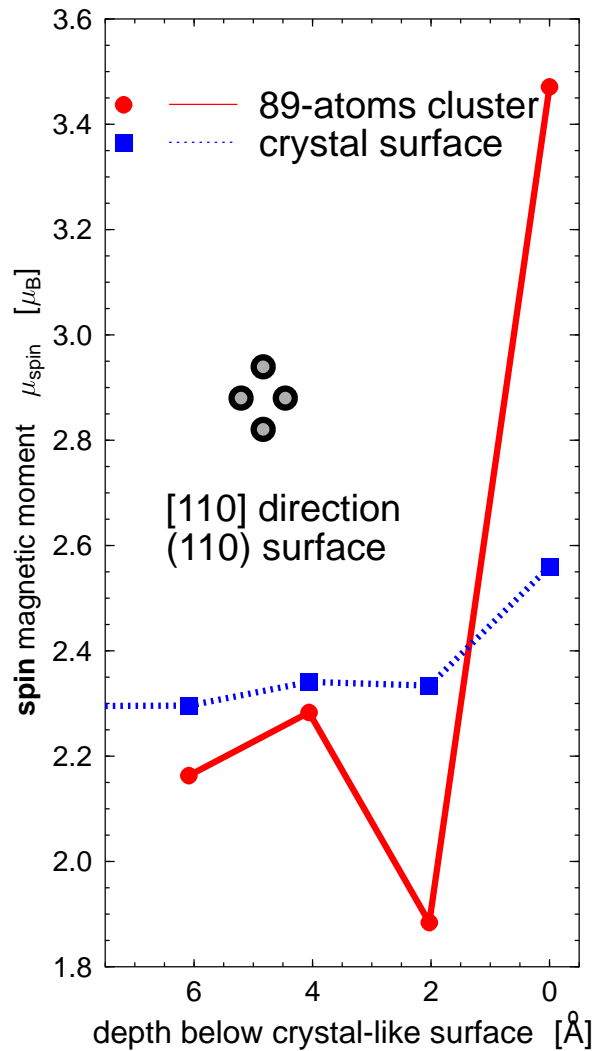
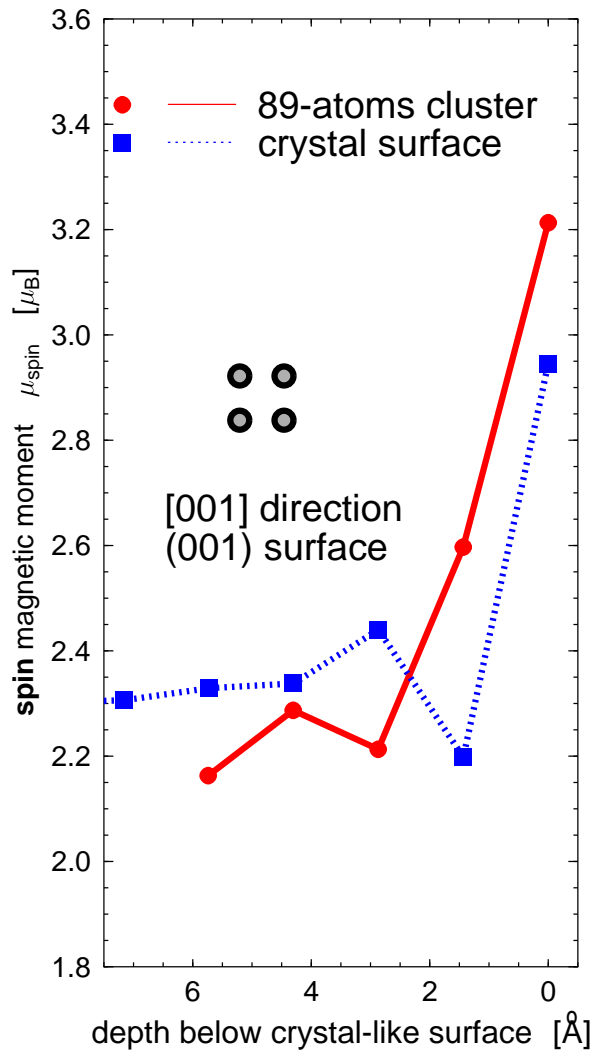


# DOS profile in clusters and at surfaces

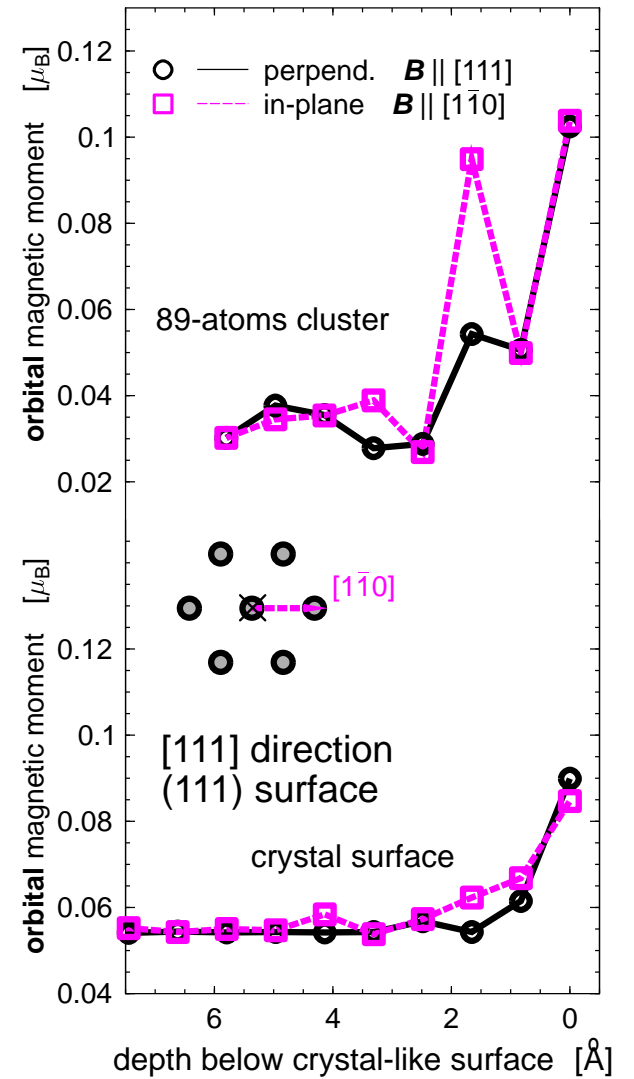
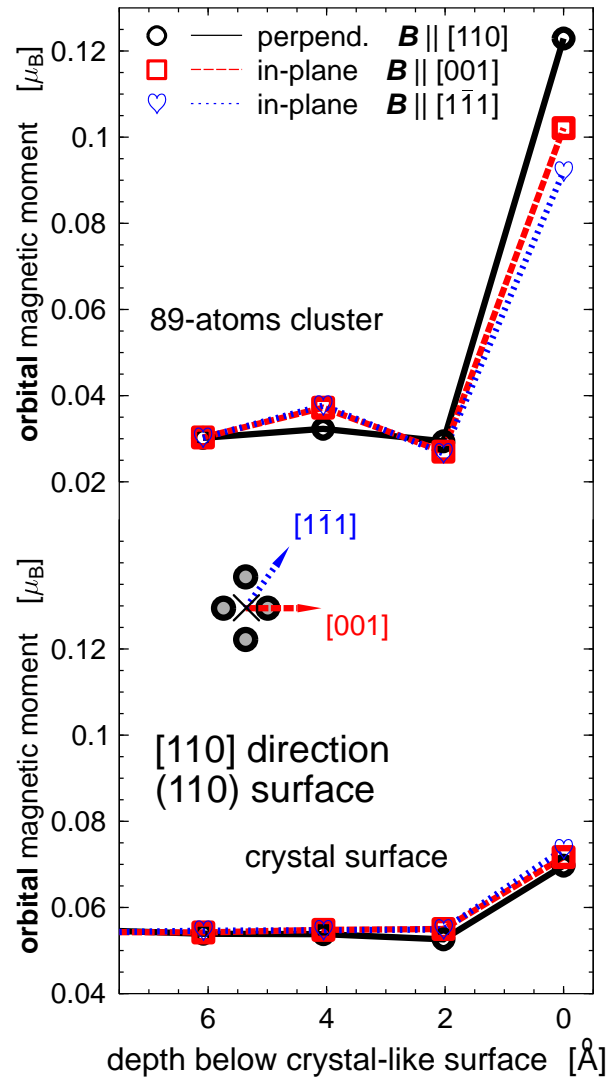
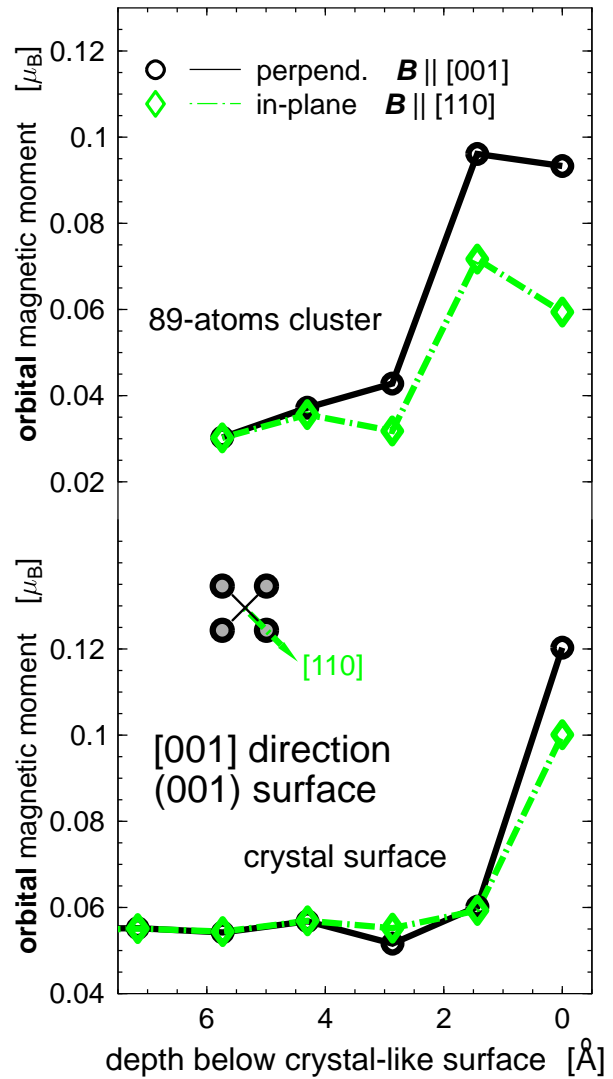
- 89-atoms cluster
- (001) crystal surface
- Comparing “most analogous atoms” of both systems
- Surface converges to bulk much more quickly than clusters



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



# 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

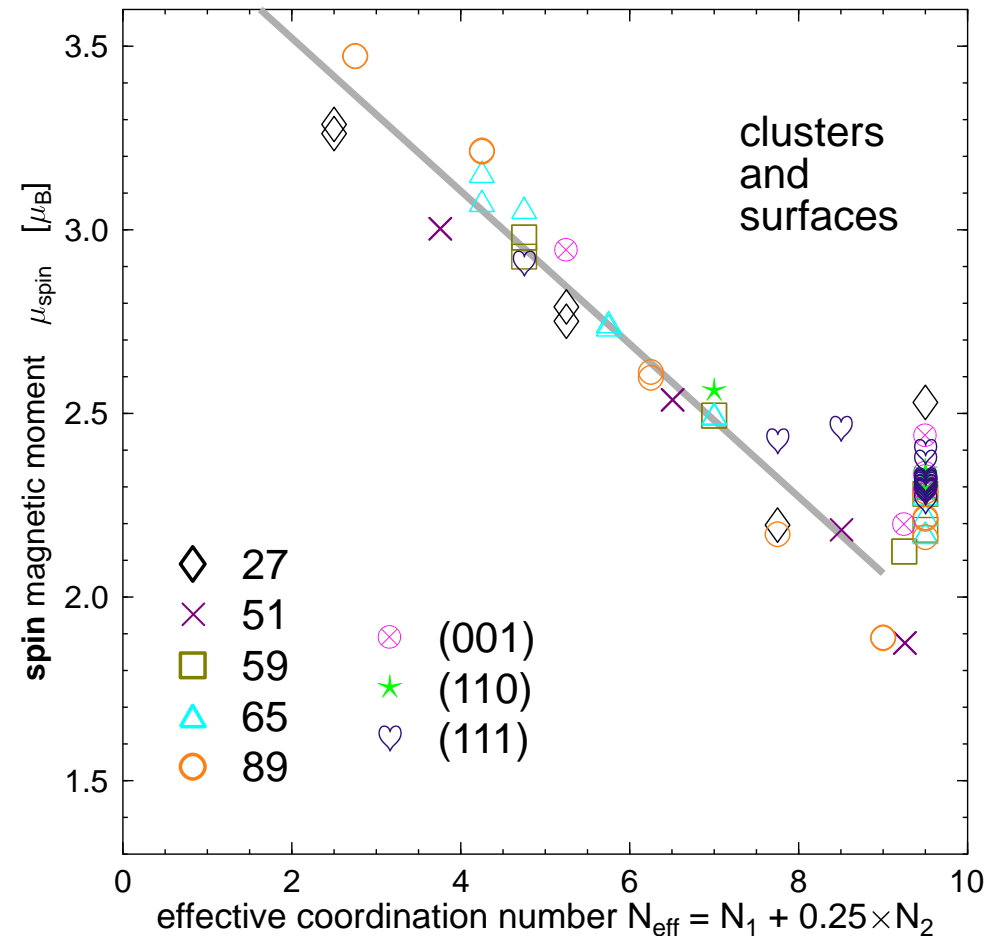
$$N_{\text{eff}} = N_1 + 0.25 \times N_2,$$

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 Letters  
A **205**, 308 (1995)]

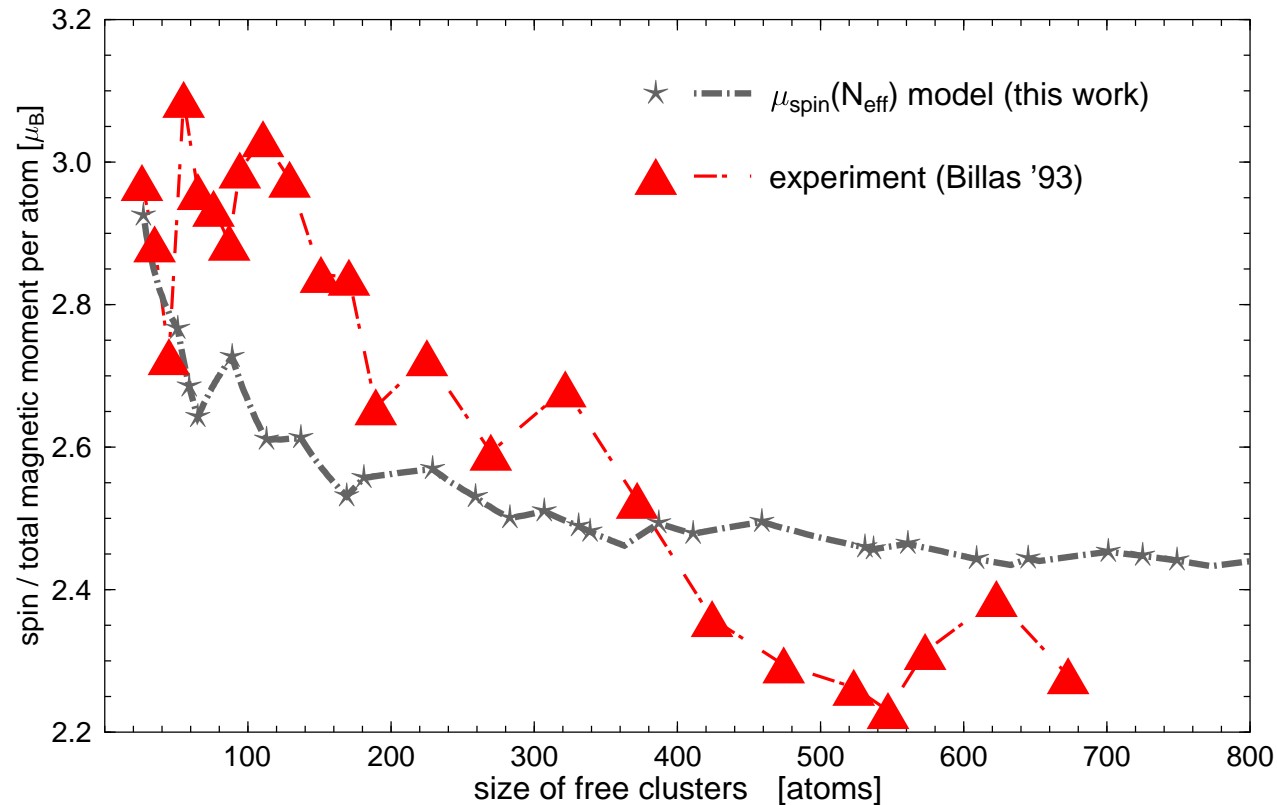
Empirical model dependence:

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



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

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

# Magnetism in clusters: summary

- 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  $M$ . However, the anisotropy in  $\mu_{\text{orb}}$  *averaged* over whole coordination spheres is very small.
- **Oscillations** both in  $\mu_{\text{spin}}$  and in  $\mu_{\text{orb}}$  are a general feature of magnetic profiles in clusters and 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  $N_{\text{eff}}$



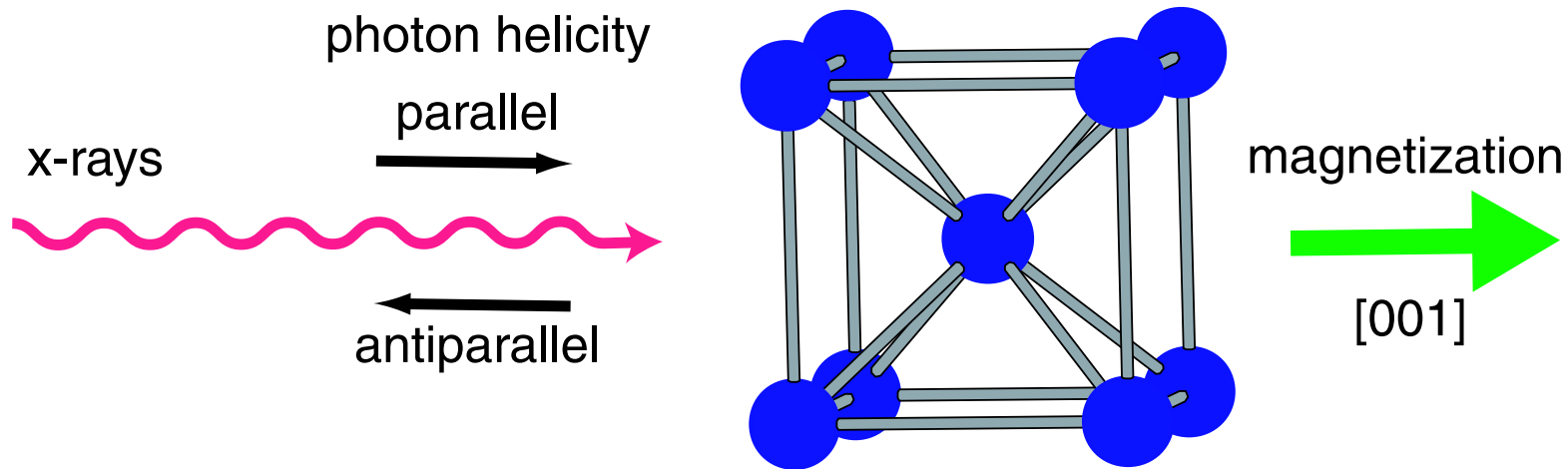
# Spectroscopy

# What can XMCD do for us?

- XMCD spectroscopy probes the magnetic properties of materials
- Through the sum rules, XMCD can inform about  $\mu_{\text{spin}}$  and  $\mu_{\text{orb}}$  separately
  - $L_{2,3}$  edge: sum rules give access to the  $d$  components of  $\mu_{\text{spin}}$  and  $\mu_{\text{orb}}$  (for transition metals, that's what we want)
  - $K$  edge: sum rule gives access to the  $p$  component of  $\mu_{\text{orb}}$
- Employing sum rules on experimental data may require substantial theoretical input
- Theoretical modelling should provide an intuitive understanding of what is going on

# Our setup

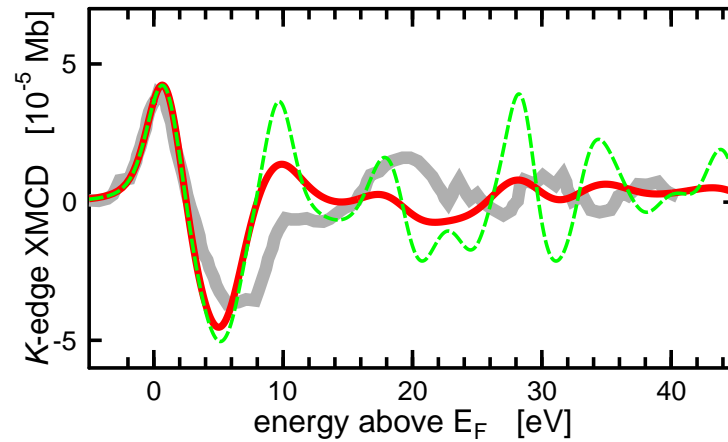
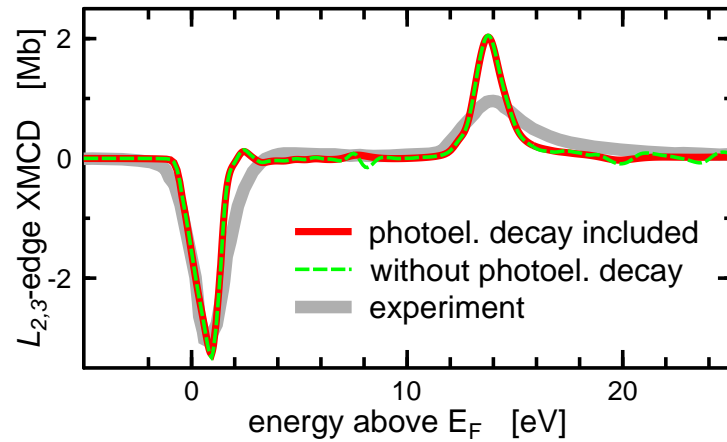
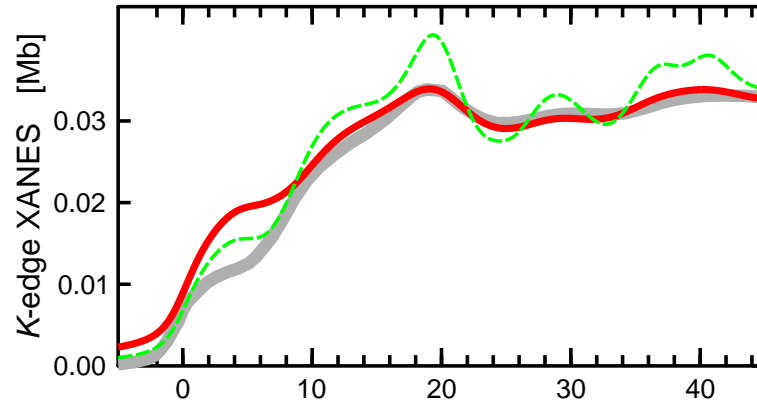
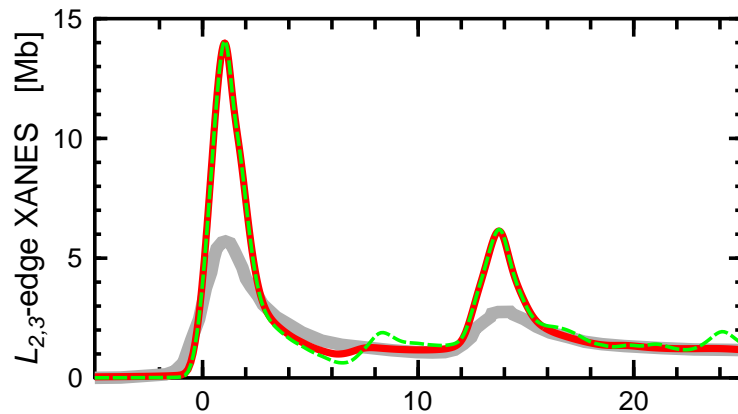
Helicity of the incoming photons is parallel or antiparallel with the cluster magnetization  $M$  (coincides with the [001] direction in the parental crystal)



# Some more details

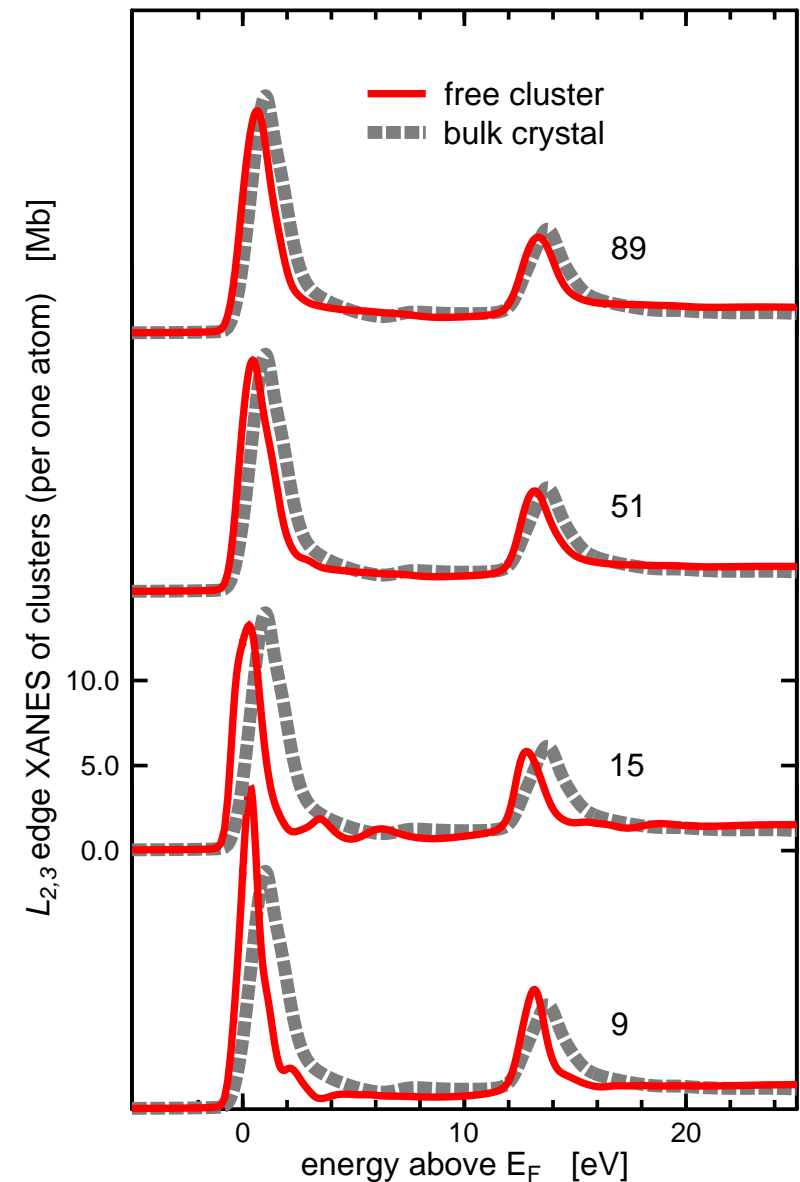
- Spectrum of cluster is a **superposition** of spectra at edges of individual atoms
- The spectra do **not** depend on the direction of  $M$ 
  - magnetic anisotropy in bcc-like Fe clusters is practically negligible
  - average of  $\mu_{\text{orb}}$  over all atoms does not depend on  $M$  either
- Core hole neglected
- Fe  $L_{2,3}$  edge: localized, should not be very sensitive to cluster geometry (i.e. size)
- Fe  $K$  edge: delocalized, **should be sensitive** to cluster size

# $L_{2,3}$ and $K$ edge spectra of Fe crystal



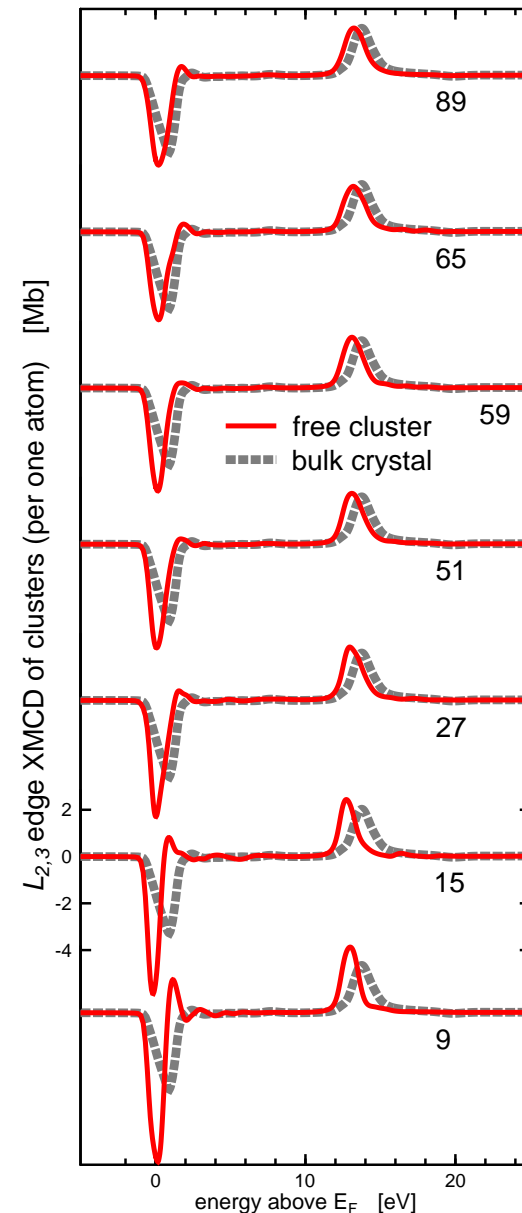
# $L_{2,3}$ edge XAS of clusters

- No significant variation with cluster size
- Fine structure just after the  $L_3$  white line — presence of **truly discrete** states (vacuum level is 5–8 eV above  $E_F$ )
- Smoothing of peaks for larger clusters

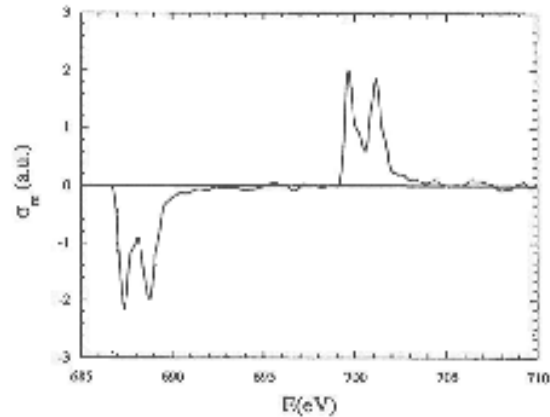


# $L_{2,3}$ edge XMCD of clusters

- Similar shape for clusters and for the bulk
- Peak *intensity* systematically decreases and peak *width* increases with increasing cluster size
- No systematic variations for **areas** of peaks (cluster magnetization oscillates with cluster size)
- Small yet **distinct positive hump** just after the main  $L_3$  peak

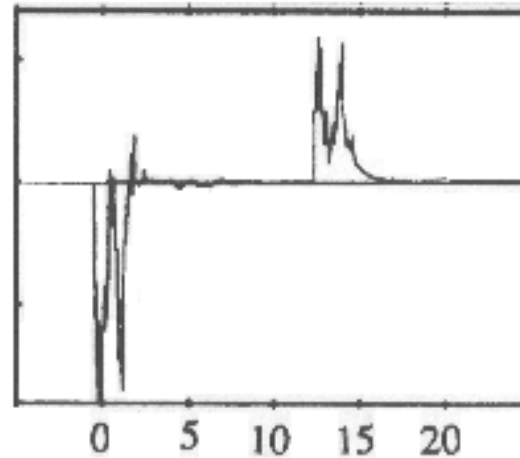


# Where have all the structures gone?



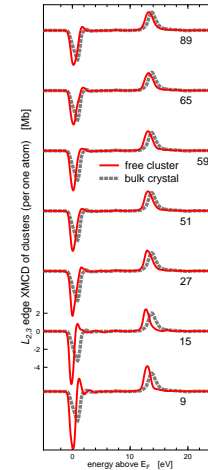
Fe(001) surface

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

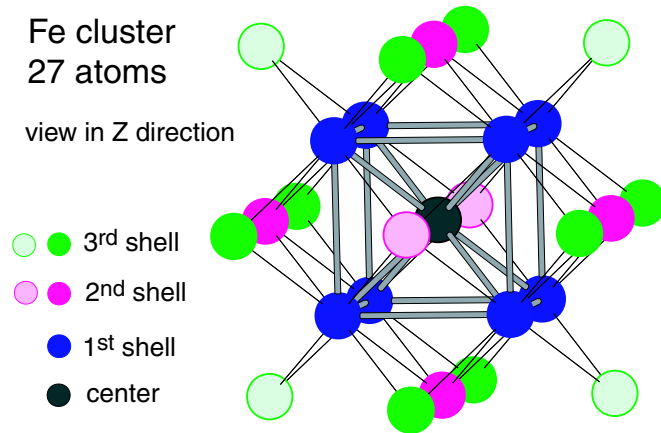
Calculated XMCD of clusters display no such fine structure.



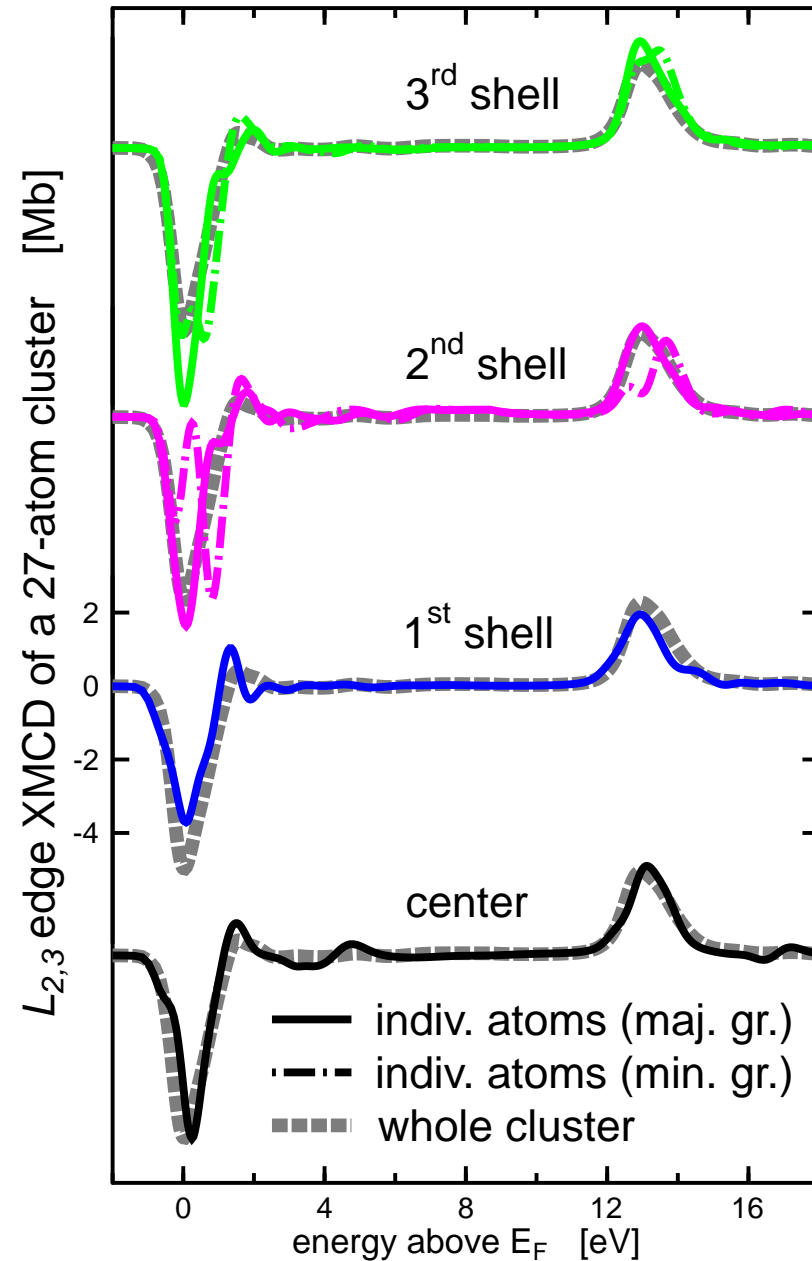
# The wiggles in XMCD mutually cancel!

Fe cluster  
27 atoms

view in Z direction

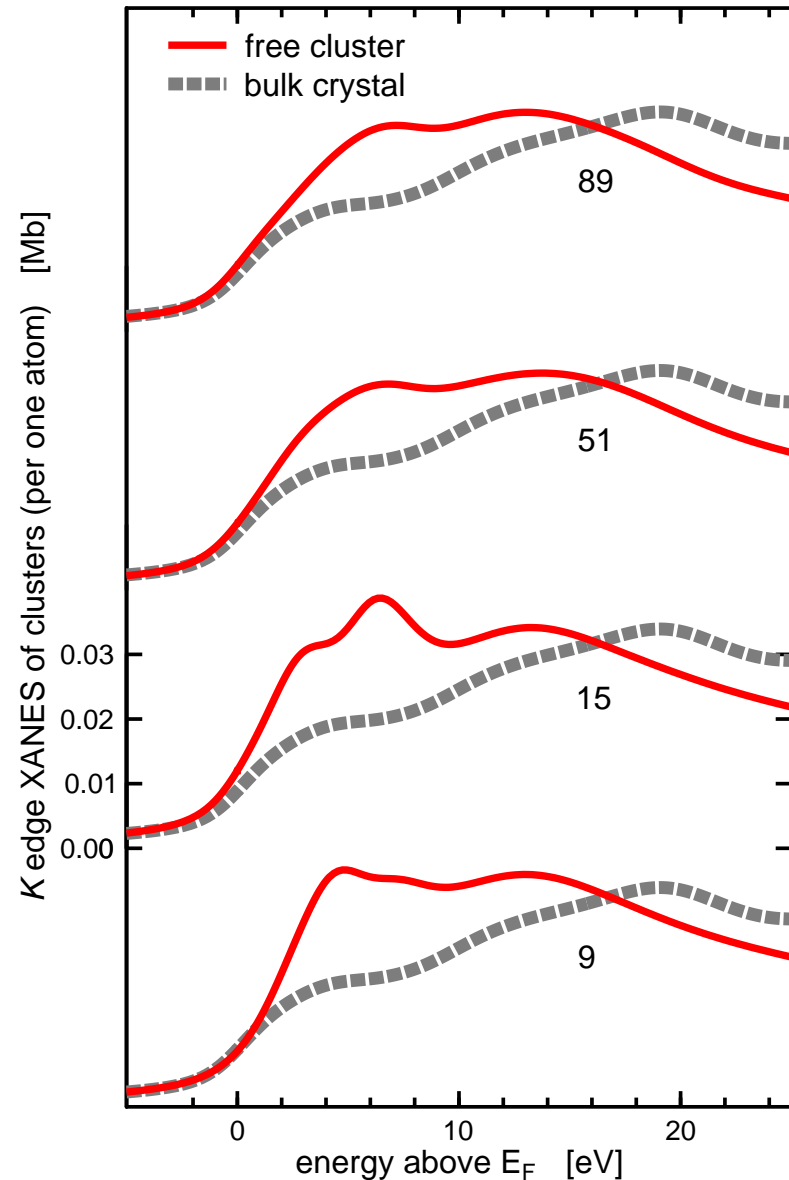


Spectrum of the whole cluster is a **superposition** of signals from all individual atoms



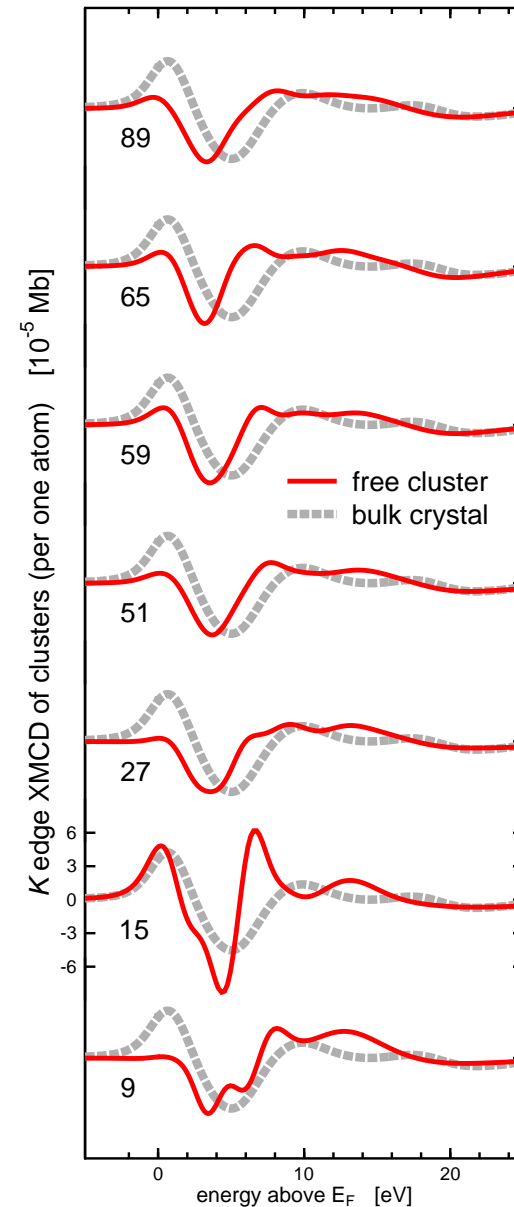
# *K* edge XAS of clusters

- Difference between clusters and bulk larger than in the case of  $L_{2,3}$  edge
- Small clusters give rise to higher intensities in the low-energy lobe of the main peak
- Even for the 89-atom cluster, difference between cluster and bulk XAS remains



# *K* edge XMCD of clusters

- Size affects not only shape and intensity of individual oscillations but also their positions
- Peak around 1 eV suppressed for most clusters
- *K* edge XMCD more sensitive to the cluster size than  $L_{2,3}$  edge



# XAS and XMCD of clusters: summary

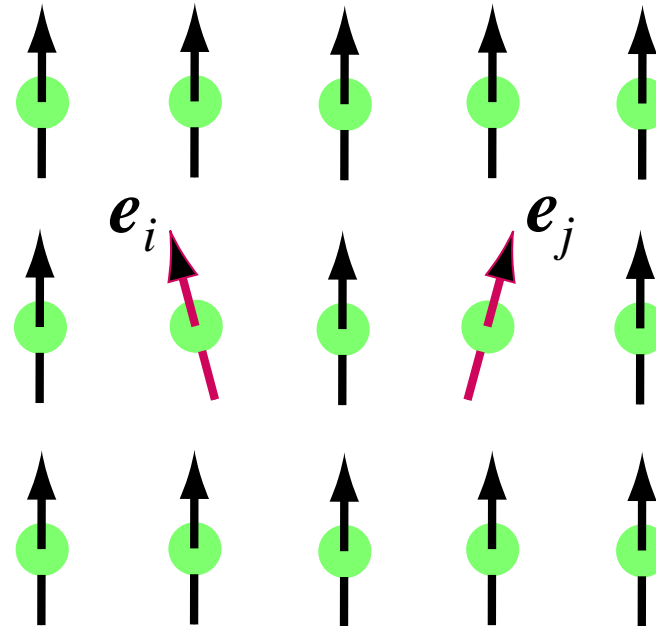
- Difference between electronic structure of Fe clusters and of a Fe crystal is reflected by the difference in their XMCD
- This difference is **more significant at the  $K$  edge** than at the  $L_{2,3}$  edge
- The  $L_{2,3}$  edge XMCD of the clusters differ from the bulk **only quantitatively** through higher intensities of the dominant peaks.
- Small yet distinct positive hump just after the  $L_3$  peak — a marker of “clusterization” in XMCD spectra?
- The  $K$  edge XMCD spectra of clusters **differ significantly** from the bulk

# Magnetic properties of clusters at $T \neq 0$

# Finite temperature magnetism

For localized moments, finite temperature magnetism can be described by a classical Heisenberg hamiltonian

$$H_{\text{eff}} = - \sum_{i \neq j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j$$



# Mapping DFT onto Heisenberg

Comparing energy associated with **infinitesimal rotations of local magnetic moments**  $\implies$

$$J_{ij} = -\frac{1}{4\pi} \text{Im} \int^{E_F} dE \text{Tr} \left[ (t_{i\uparrow}^{-1} - t_{i\downarrow}^{-1}) \tau_{\uparrow}^{ij} (t_{j\uparrow}^{-1} - t_{j\downarrow}^{-1}) \tau_{\downarrow}^{ji} \right]$$

[Liechtenstein et al. (1986), involving multiple-scattering formalism, linear response theory, spin-polarized local force theorem and long wave approximation]

Valid only if magnetism can be described by localized magnetic moments (fine for Fe)

# From $J_{ij}$ to $M(T)$

- Mean magnetization  $M(T)$  of a system described by a classical Heisenberg hamiltonian is

$$M(T) = \frac{\sum_k M_k \exp(-\frac{E_k}{k_B T})}{\sum_k \exp(-\frac{E_k}{k_B T})}$$

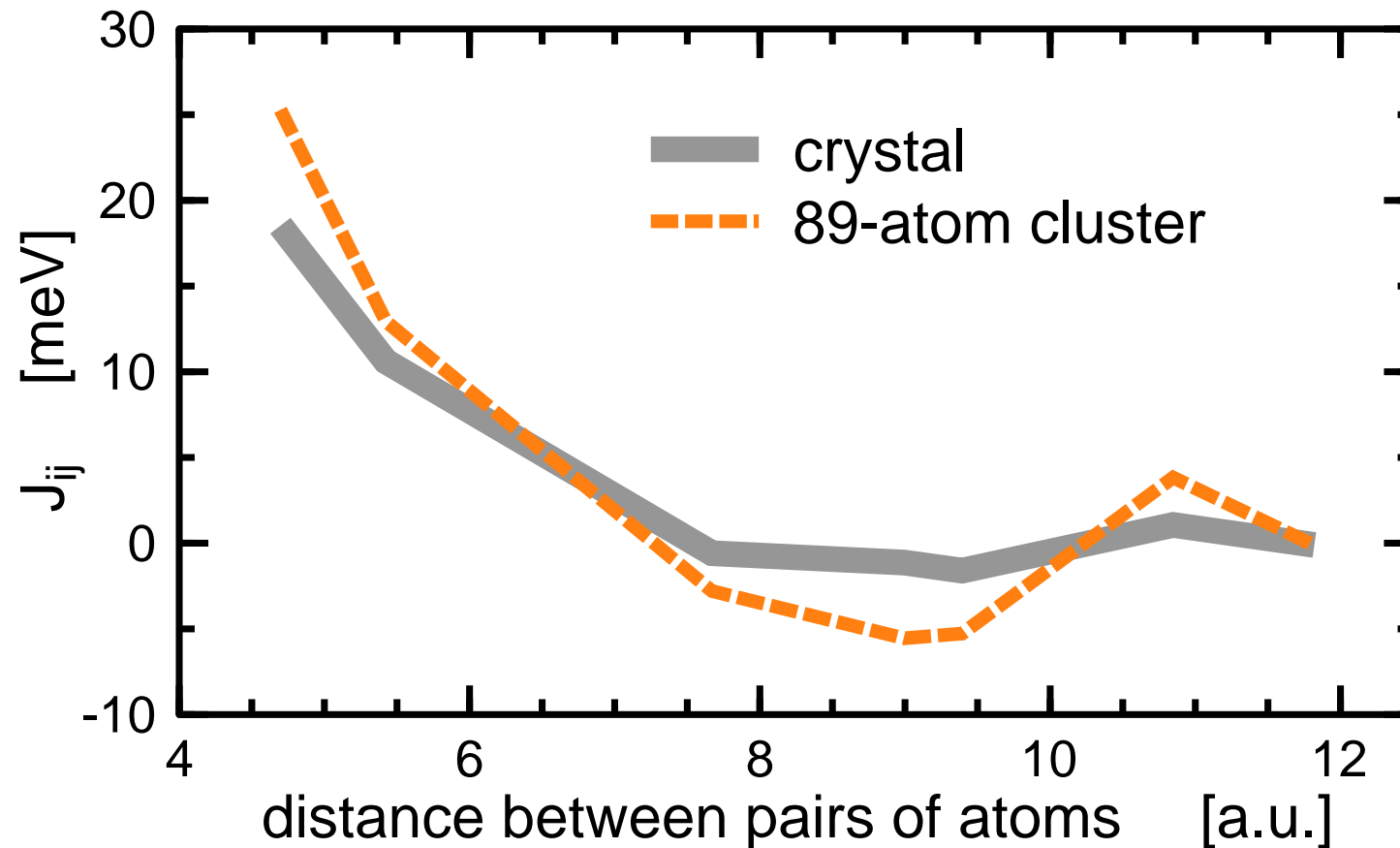
where  $M_k$  is the magnetization of the system for a particular configuration  $k$  of the directions of spins and  $E_k$  is the energy of such a configuration

- Practical evaluation: Monte Carlo method with the importance sampling Metropolis algorithm
- For **bulk Fe**, this procedure yields finite-temperature results that are in a **good agreement** with experiment



# Dependence of $J_{ij}$ on the distance

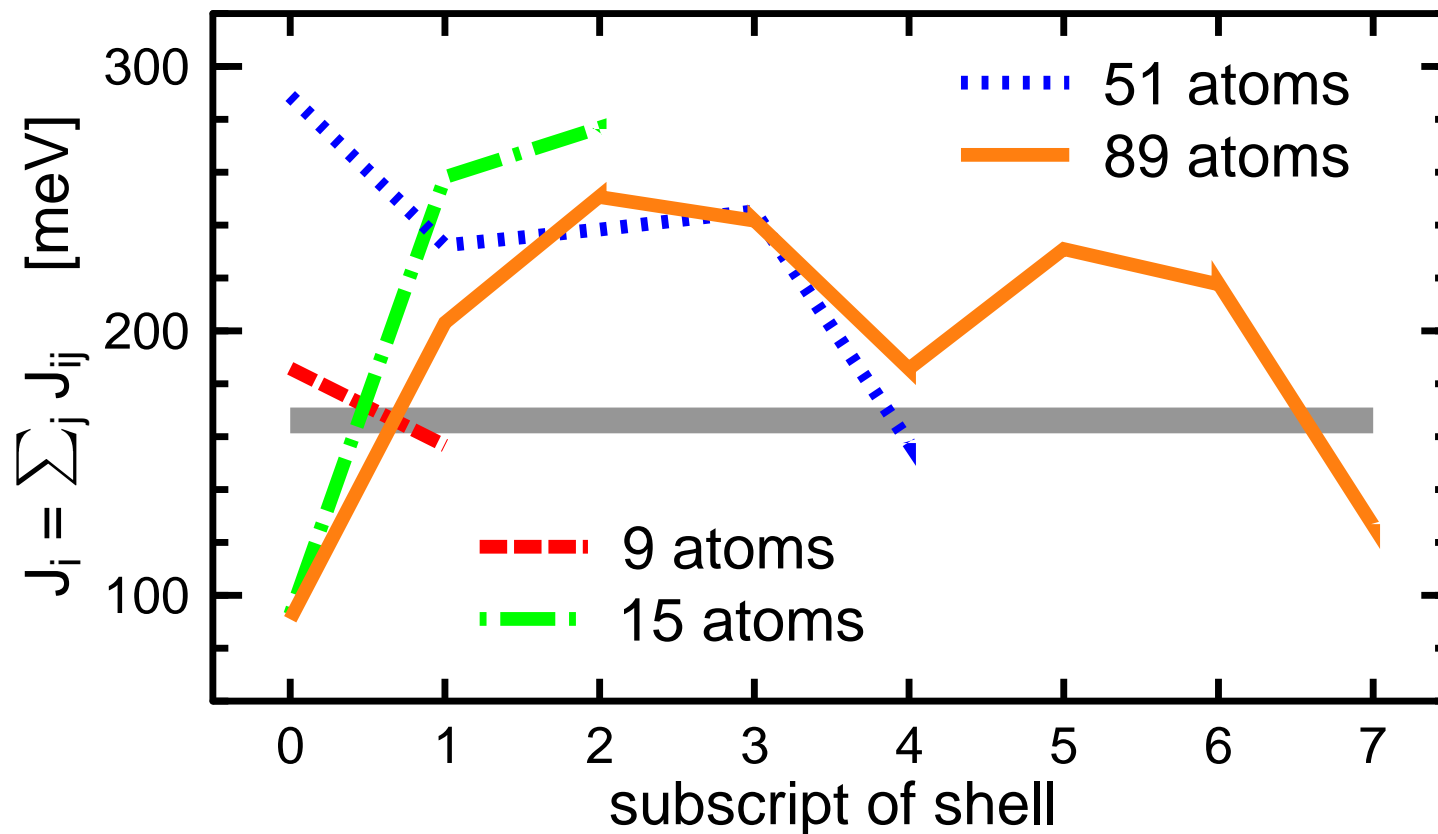
Atom  $i$  is in the center of an 89-atom cluster and the atom  $j$  belongs to subsequent coordination shells of that cluster



# Site-dependence of $\sum_{j \neq i} J_{ij}$

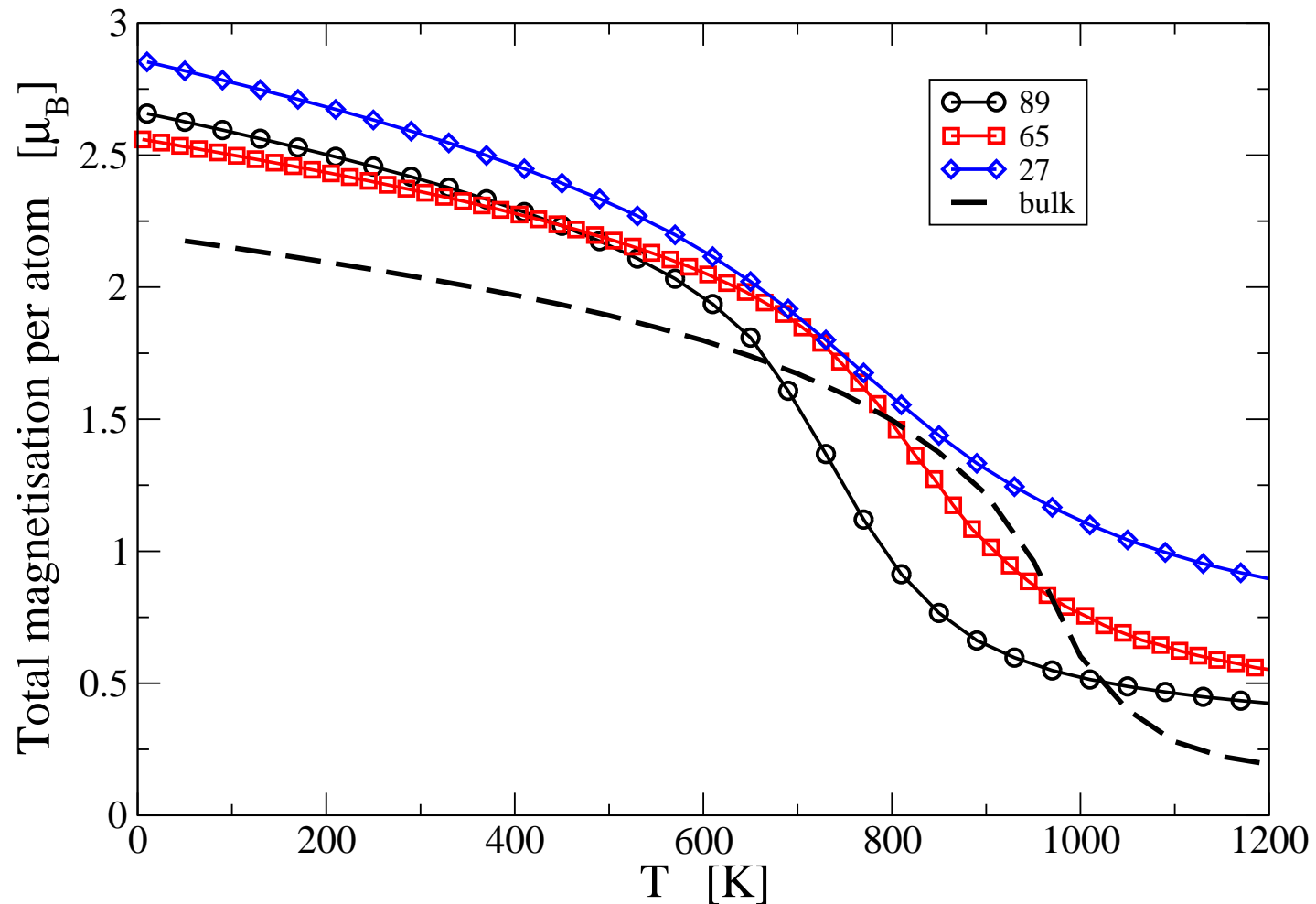
Energy needed to flip the spin of atom  $i$  while keeping all the remaining spins collinear:

$$J_i = \sum_{j \neq i} J_{ij} ,$$



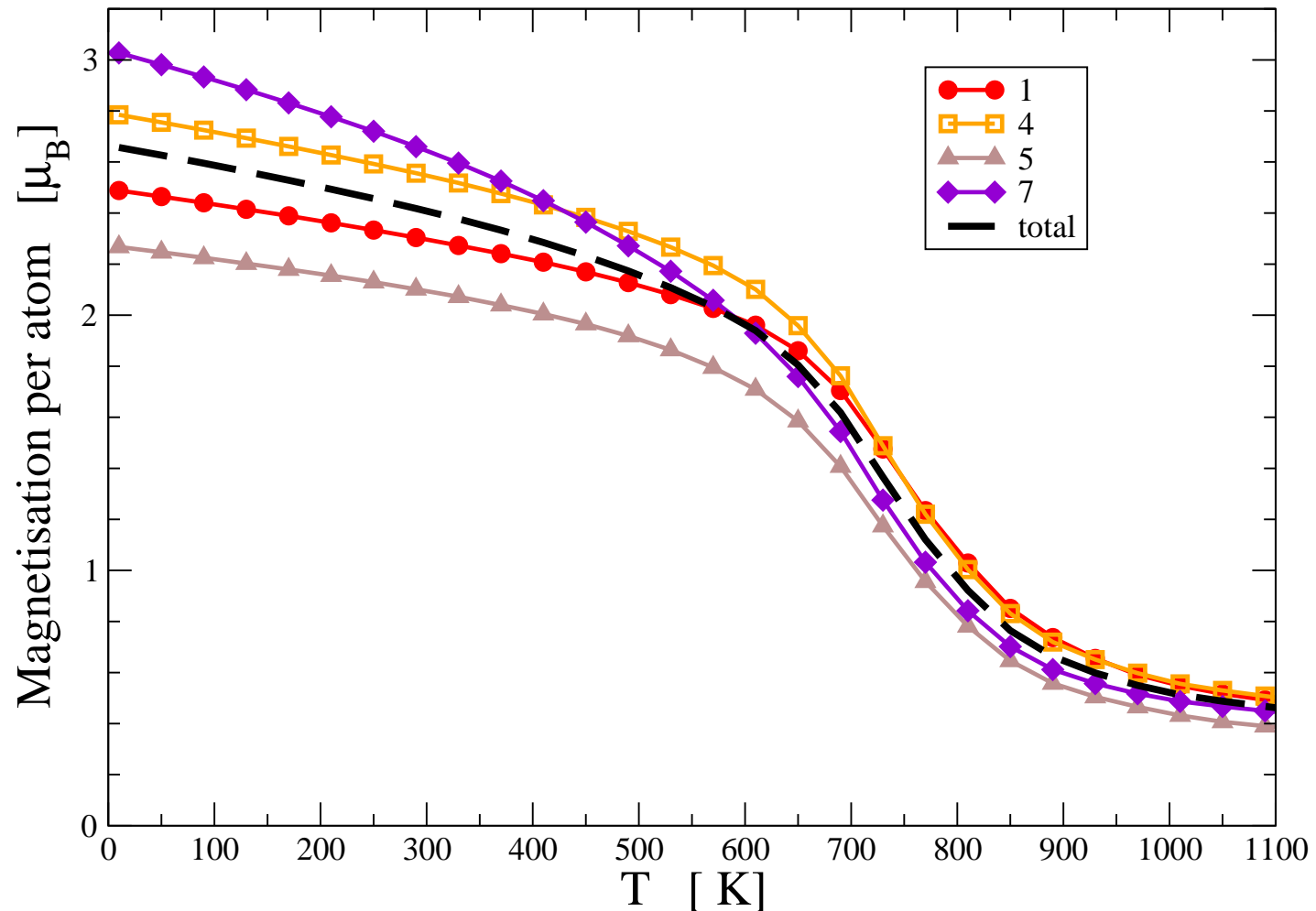
# $M(T)$ in clusters and in bulk

$M(T)$  curves are more shallow in clusters (no phase transition for finite systems)



# Shell-resolved magnetization

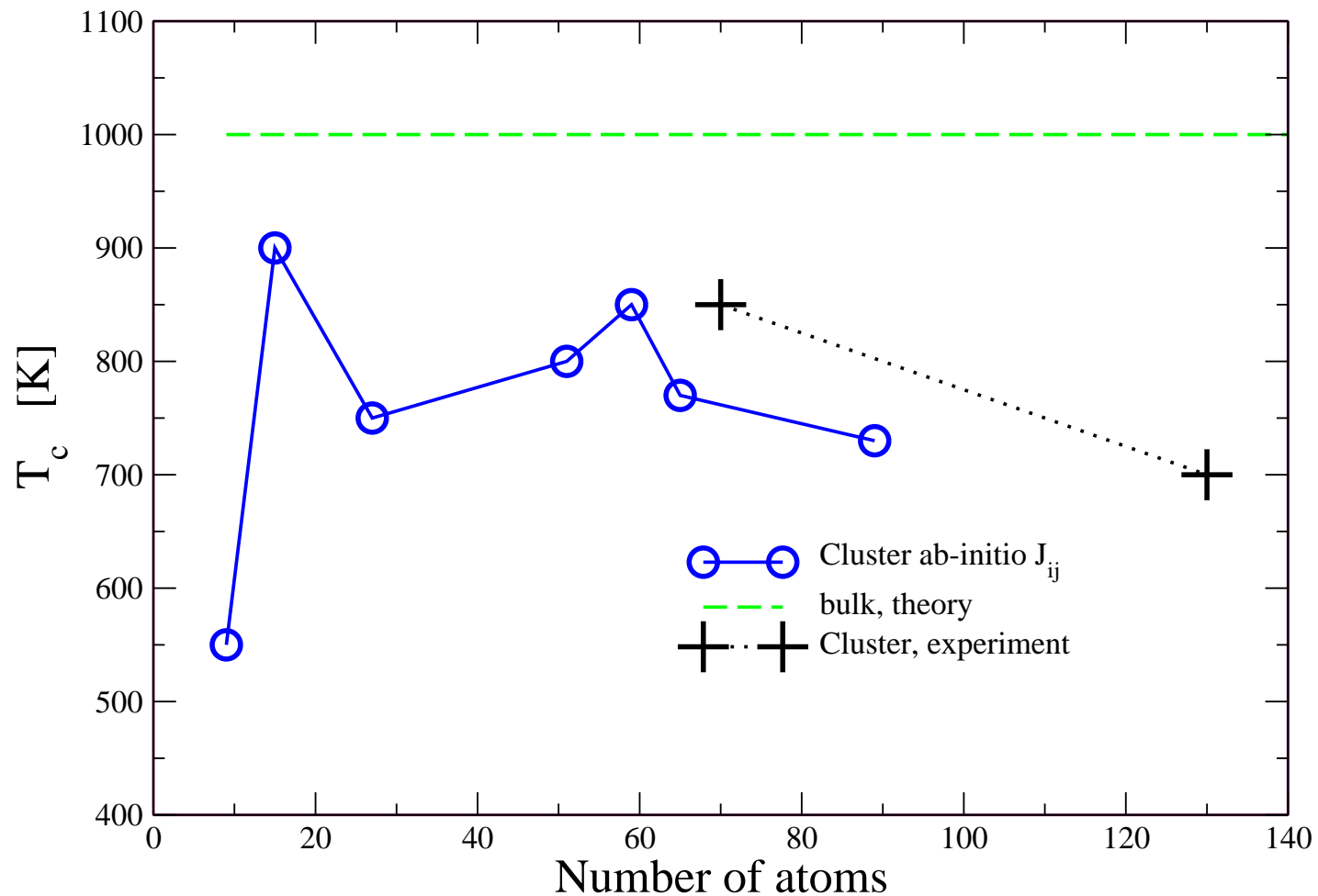
Projecting magnetization of given shell onto the direction of the magnetic moment of the whole 89-atom cluster



# Dependence of $T_c$ on cluster size

Critical temperature defined as the inflection point of  $M(T)$  curves  
Extrapolation techniques used for bulk (fourth order cumulant)

Experiment of Billas et al. (1993)



# $T \neq 0$ magnetism: summary

- Exchange coupling constants  $J_{ij}$  in clusters differ from the bulk, with **no obvious systematics** ( $\Rightarrow$  one **has to calculate** it. . . )
- Magnetization  $M(T)$  curves are more shallow from small clusters than for large clusters
- Magnetization of the outer shells decreases with temperature more quickly than magnetization of inner shells (usually. . . )
- Critical temperature  $T_c$  **oscillates** with cluster size

# Cluster physics in a nutshell

- Anything that can oscillate, will oscillate
- Using bulk data (potentials, exchange constants, ...) for cluster calculations does no good
- For best results, use the `SPRKKR` code 