Size- and site-dependence of XMCD spectra of iron clusters from ab-initio calculations

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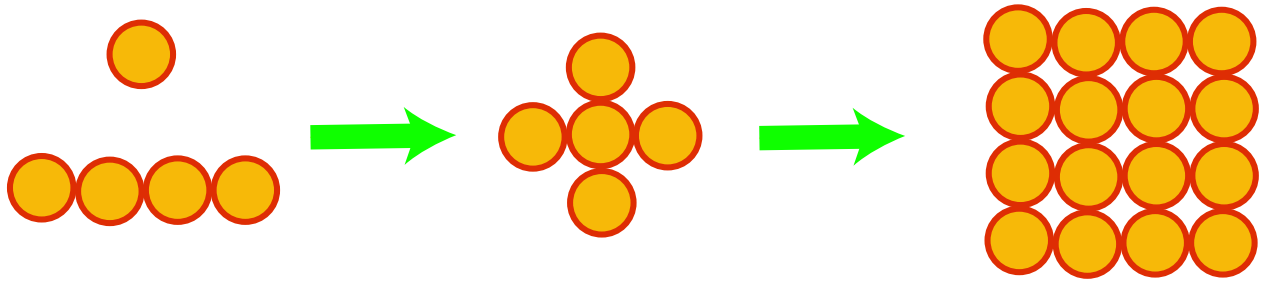
What are the clusters about?

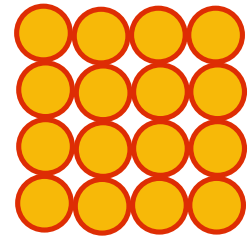
- Clusters mark the transition between atoms, surfaces and bulk systems



- Interesting phenomena (and a lot of fun) can be expected
- We concentrate on their magnetic properties and on how do they get revealed through XMCD

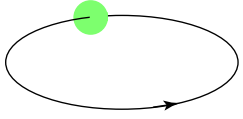
Magnetic properties of iron





atom | surface | bulk

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

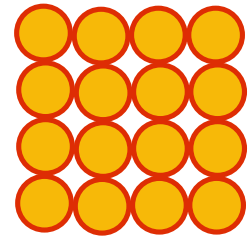


$m_{orb} = 2\ \mu_B$ | $m_{orb} = 0.07\text{–}0.12\ \mu_B$ | $m_{orb} = 0.05\ \mu_B$

(clusters go in between)

Magnetic properties of iron





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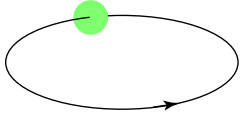

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(clusters go in between)

Clusters contain a high portion of surface atoms
$\Rightarrow$ ought to have larger magnetic moments.

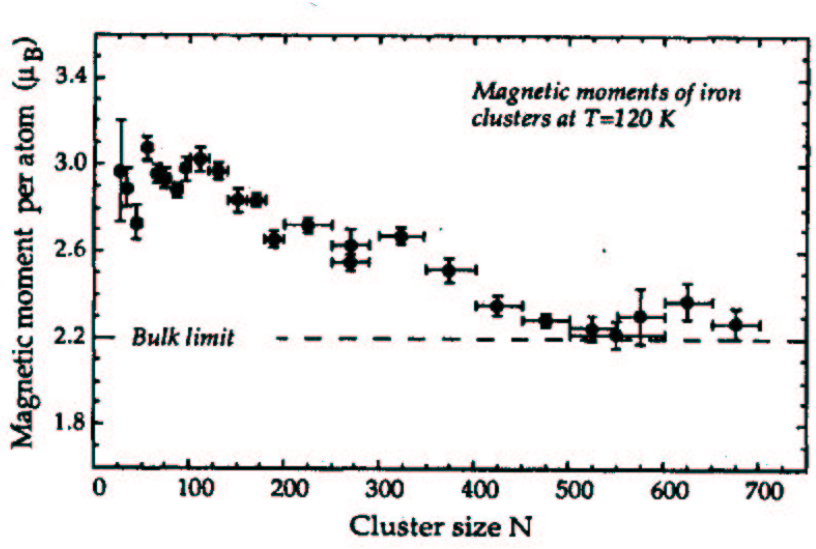
Magnetism of iron clusters (1)

Selected knowledge about iron clusters containing 25–700 atoms:

- Stern-Gerlach-type experiments [Billas *et al.* PRL **71**, 4067 (1993)] $\longrightarrow$ average total magnetic moment per atom is larger in clusters than in bulk,

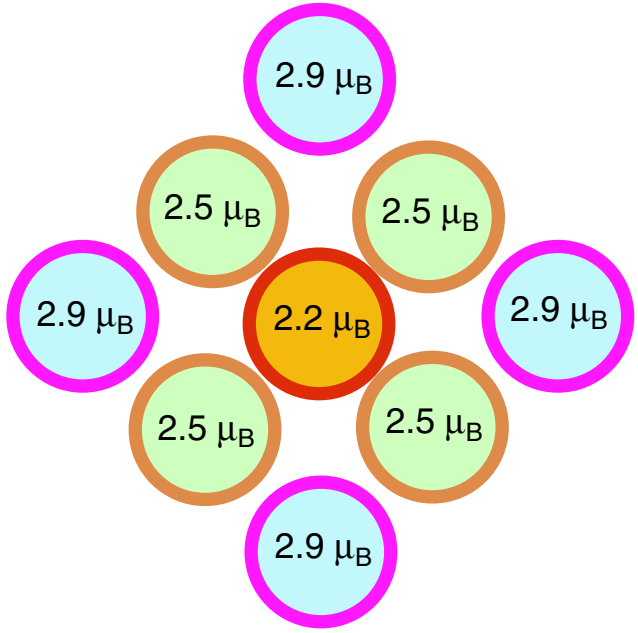
$$m_{tot} = m_{spin} + m_{orb} \approx 2.2\text{–}3.1\mu_B \ ,$$

and approaches the bulk limit in an oscillatory way.



Magnetism of iron clusters (2)

- Theoretical results on the site-dependence of magnetic moments of atoms in clusters (“magnetic profile”) differ quite a lot one from another.



Ch.Y. Yang *et al.* Phys. Rev. B **24**, 5673 (1981)

G.M. Pastor *et al.* Phys. Rev. B **40**, 7642 (1989)

A. Vega *et al.* Phys. Rev. B **47**, 4742 (1993)

J.A. Franco *et al.* Phys. Rev. B **60**, 434 (1999)

Can XMCD help?

Is there a way to learn more about cluster magnetism through XMCD spectra?

- Through the sum rules, XMCD can inform about m_{spin} and m_{orb} separately. Even more reliably, about the *ratio* m_{orb}/m_{spin}.

- Experiments on supported clusters suggest an essential enhancement of m_{orb} and of m_{orb}/m_{spin} in comparison with bulk (m_{spin} remains unchanged or even decreases).

  [K.W. Edmonds *et al.* Phys. Rev. B **60**, 472 (1999); P. Ohresser *et al.* Phys. Rev. B **62**, 5803 (2000).]

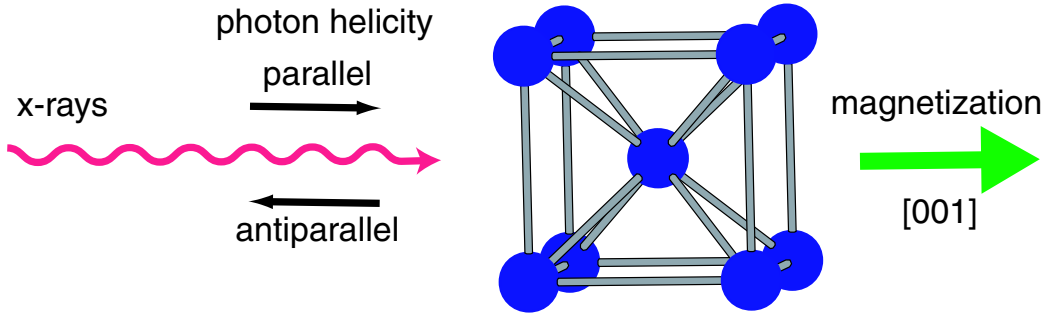
Our aim

The task we subscribed to:

- Calculate the magnetic structure and Fe $L_{2,3}$ edge XMCD spectra of free iron clusters
- Compare calculated spectra for different cluster sizes one with another and with the bulk
- Search for “markers of clusterization”

System we study

- free spherical-like clusters with geometry taken as if they were cut from a bcc Fe crystal
- cluster size range between 9 atoms (one coordination shell) and 89 atoms (seven coordinations shells)
- helicity of the incoming photons parallel or antiparallel with the cluster magnetization (coincides with the [001] direction in the parental crystal)



- we focus on iron only [visit the Thursday 11:45 talk in the Materials section to learn more about other systems]

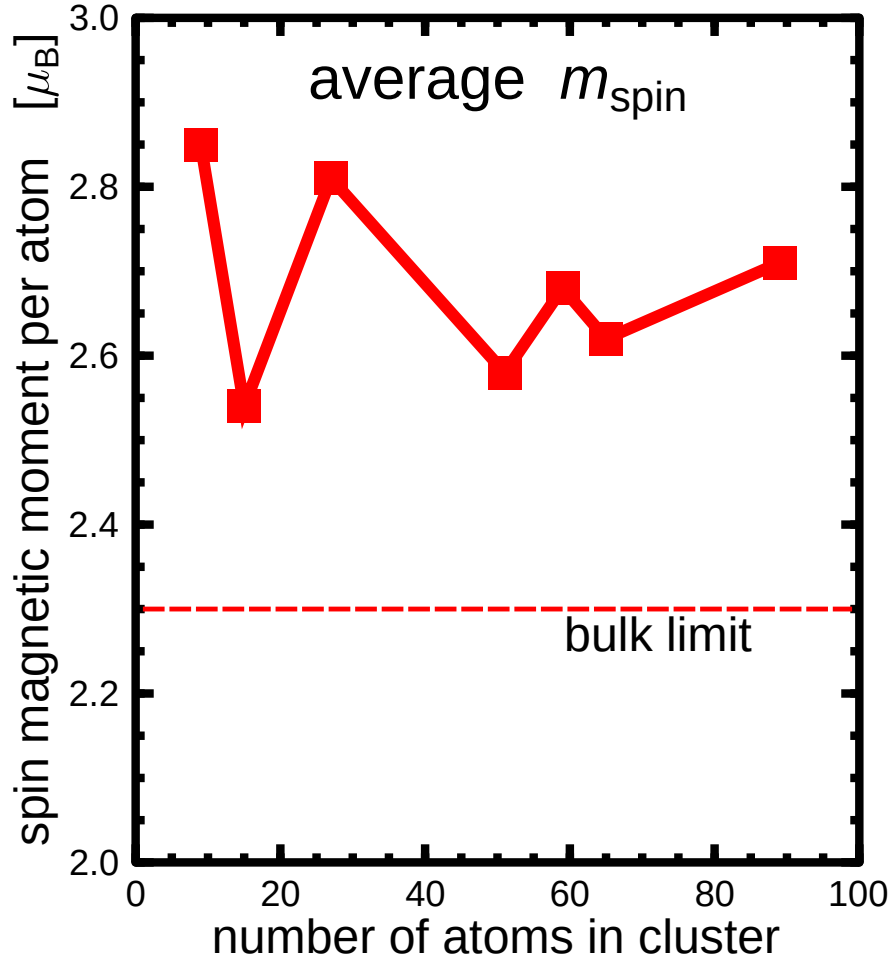
Theoretical formalism

- magnetic moments and XMCD spectra calculated in real space via a fully-relativistic spin-polarized multiple-scattering technique as implemented in the SPRKKR code
  [H. Ebert: in “Electronic structure and physical properties of solids” (Springer, Berlin 2000), vol. 535, p. 191]
- spherical ASA approximation, clusters surrounded by empty spheres
- scattering potential obtained from SCF-Xα calculations applied to molecular clusters
- total XMCD of a cluster obtained by superposing calculated XMCD signals from all the constituting atoms
- details in Šipr and Ebert, Czech. J. Phys. **53**, 55 (2003)

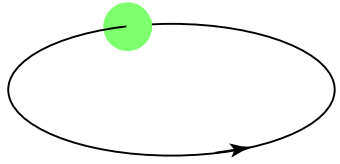
Magnetic moments of clusters (1)

- Average *spin* magnetic moments do not approach bulk limit for clusters of $\lesssim 100$ atoms.

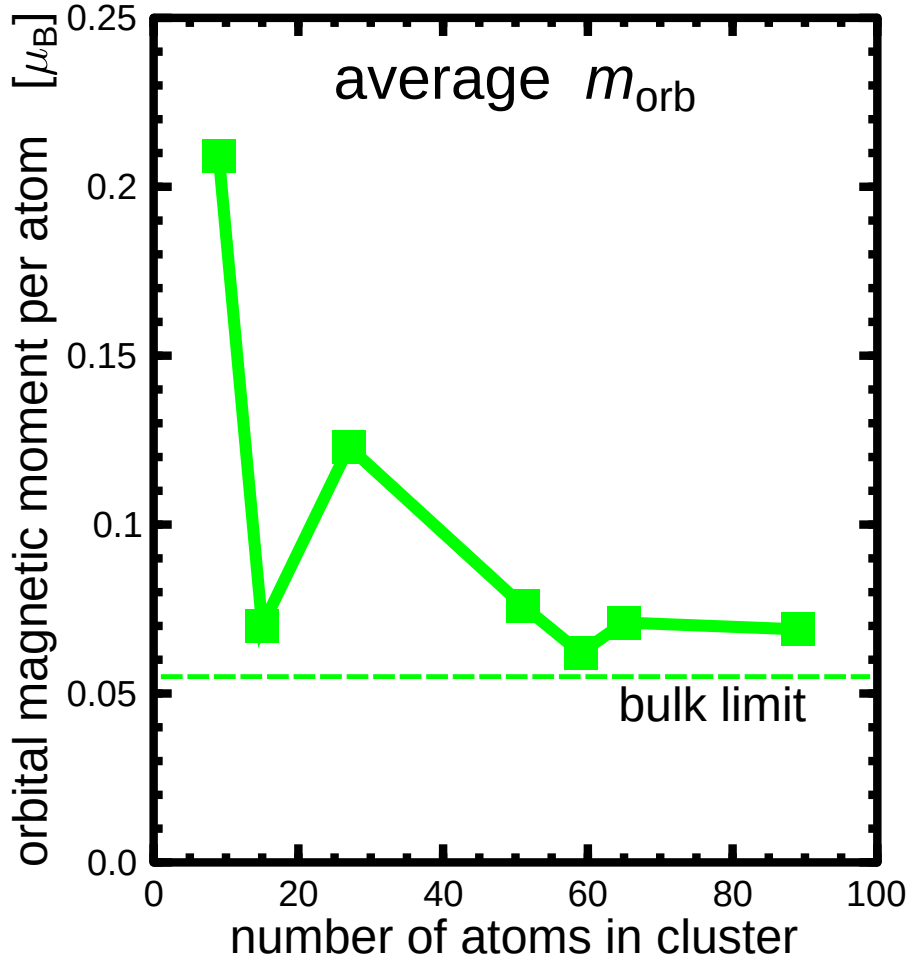
Different calculations by *different* authors provide *different* oscillatory structure



Magnetic moments of clusters (2)

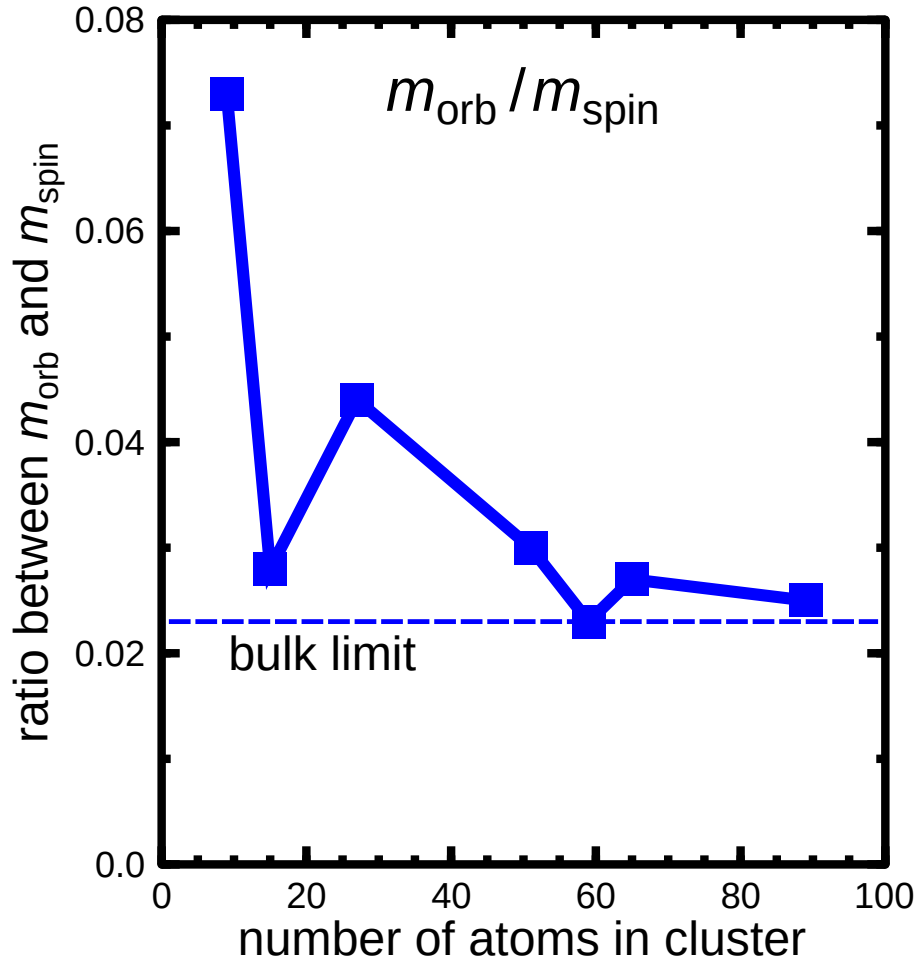


- Average *orbital* magnetic moments have hot converged to bulk values either . . .



Magnetic moments of clusters (3)

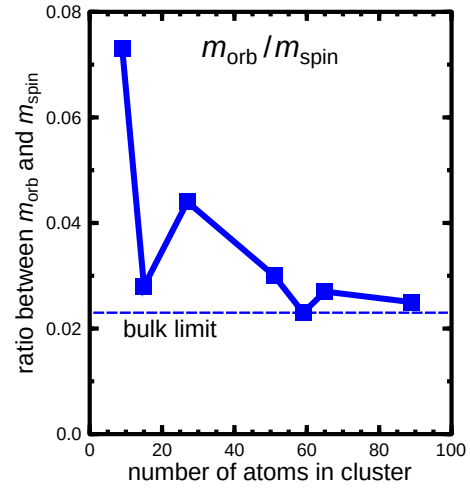
- The ratio m_{orb}/m_{spin} attains bulk values for clusters larger than $\approx$60 atoms !



Conflict with experiment ?

Theory: Ratio m_{orb}/m_{spin} converges to bulk for $N \approx 60$ atoms.

Experiment: For clusters of few hundreds of atoms the ratio m_{orb}/m_{spin} as deduced via sum rules is about twice as high as in the bulk! [K.W. Edmonds *et al.* Phys. Rev. B **60**, 472 (1999); P. Ohresser *et al.* Phys. Rev. B **62**, 5803 (2000).]



???

No real conflict with experiment...

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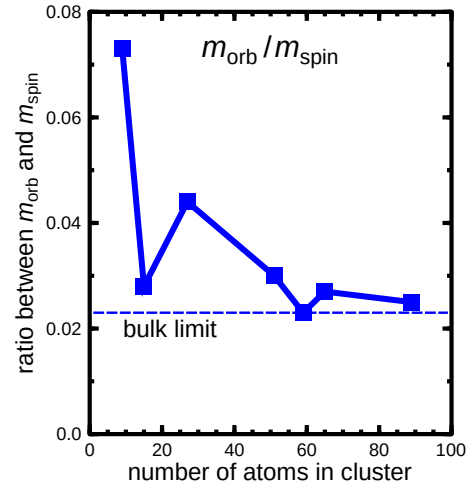


???

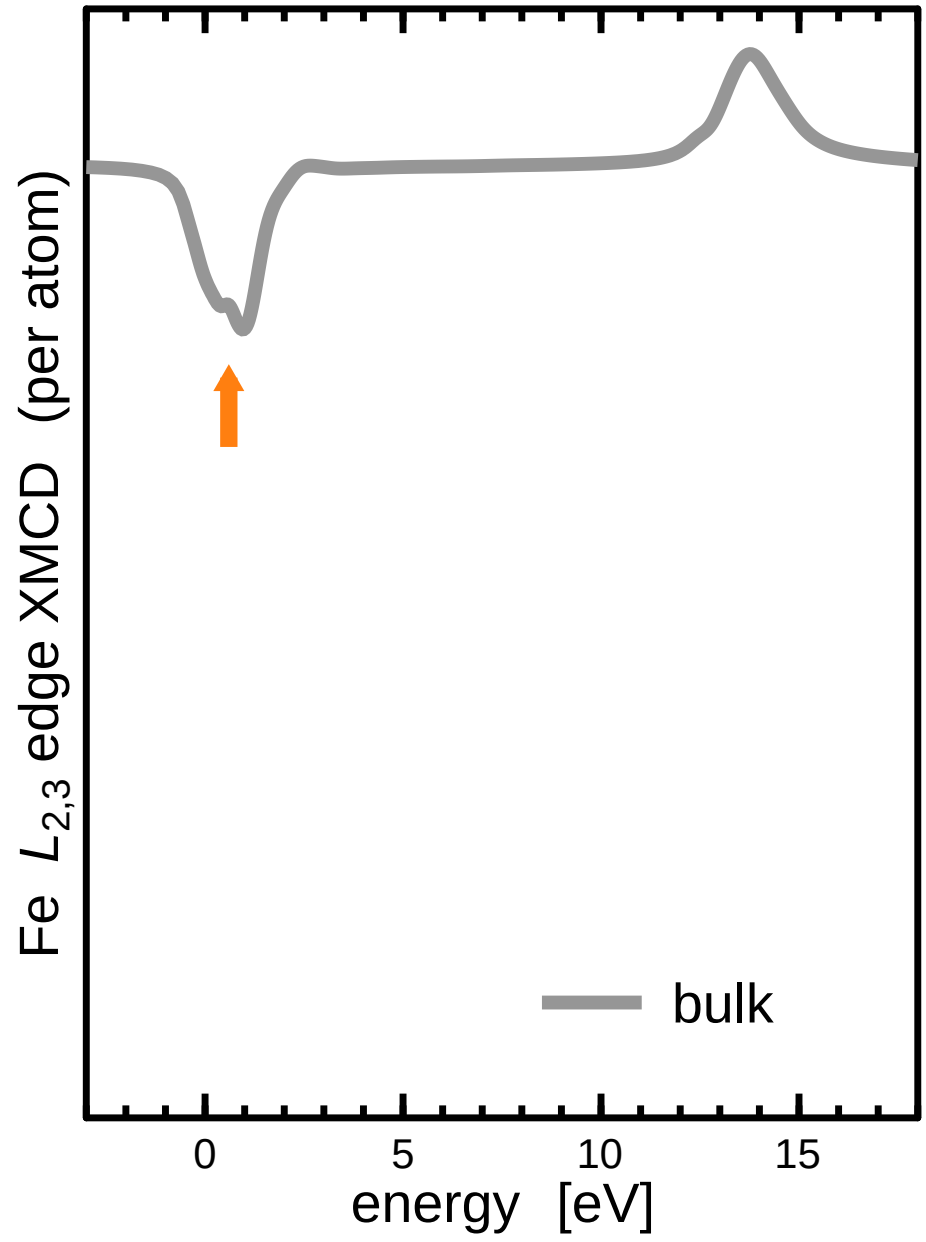
There is no need for a contradiction!

→ Experiment investigated supported clusters — rather flat than spherical, large portion of edge atoms.

→ Our calculations deal with free clusters.

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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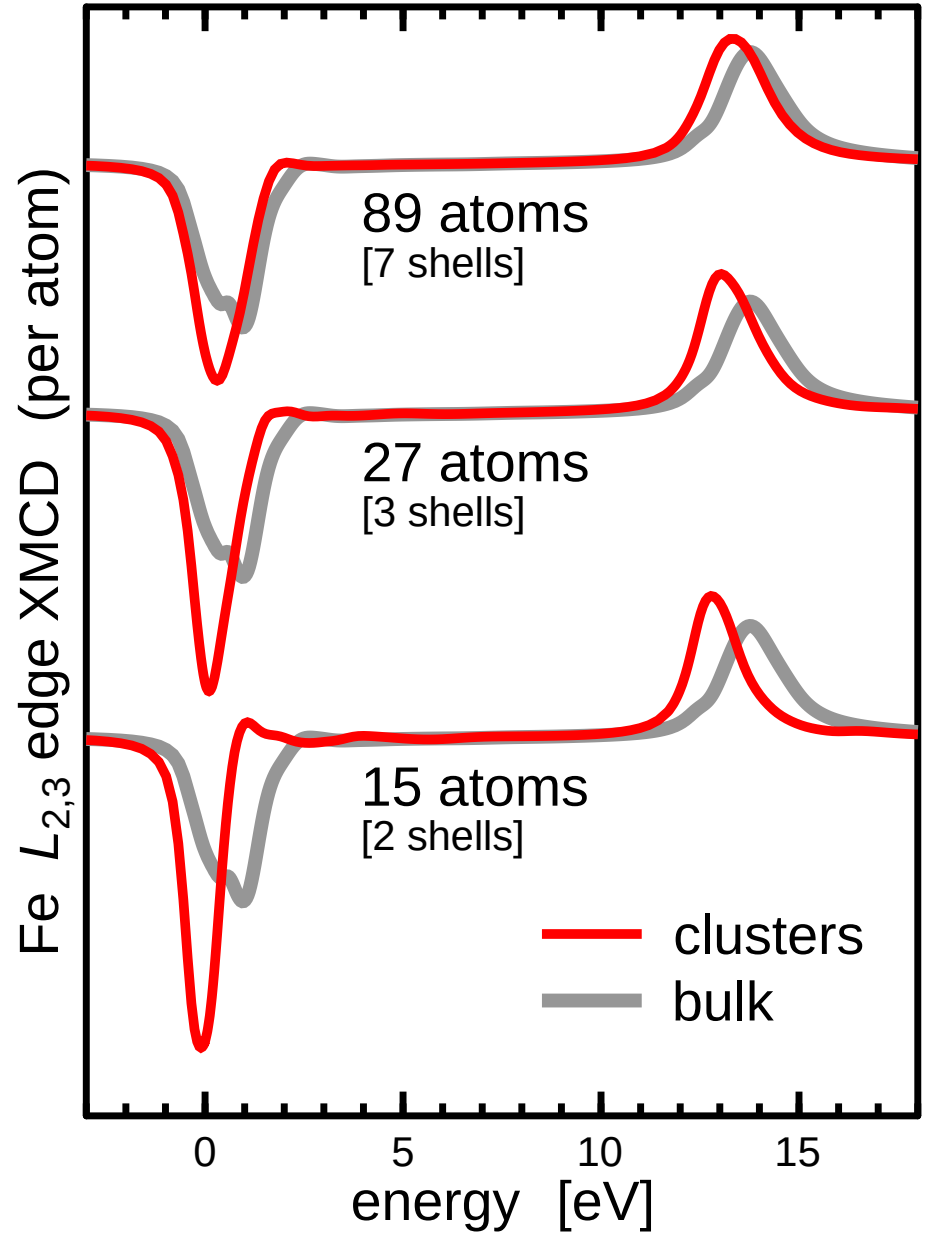

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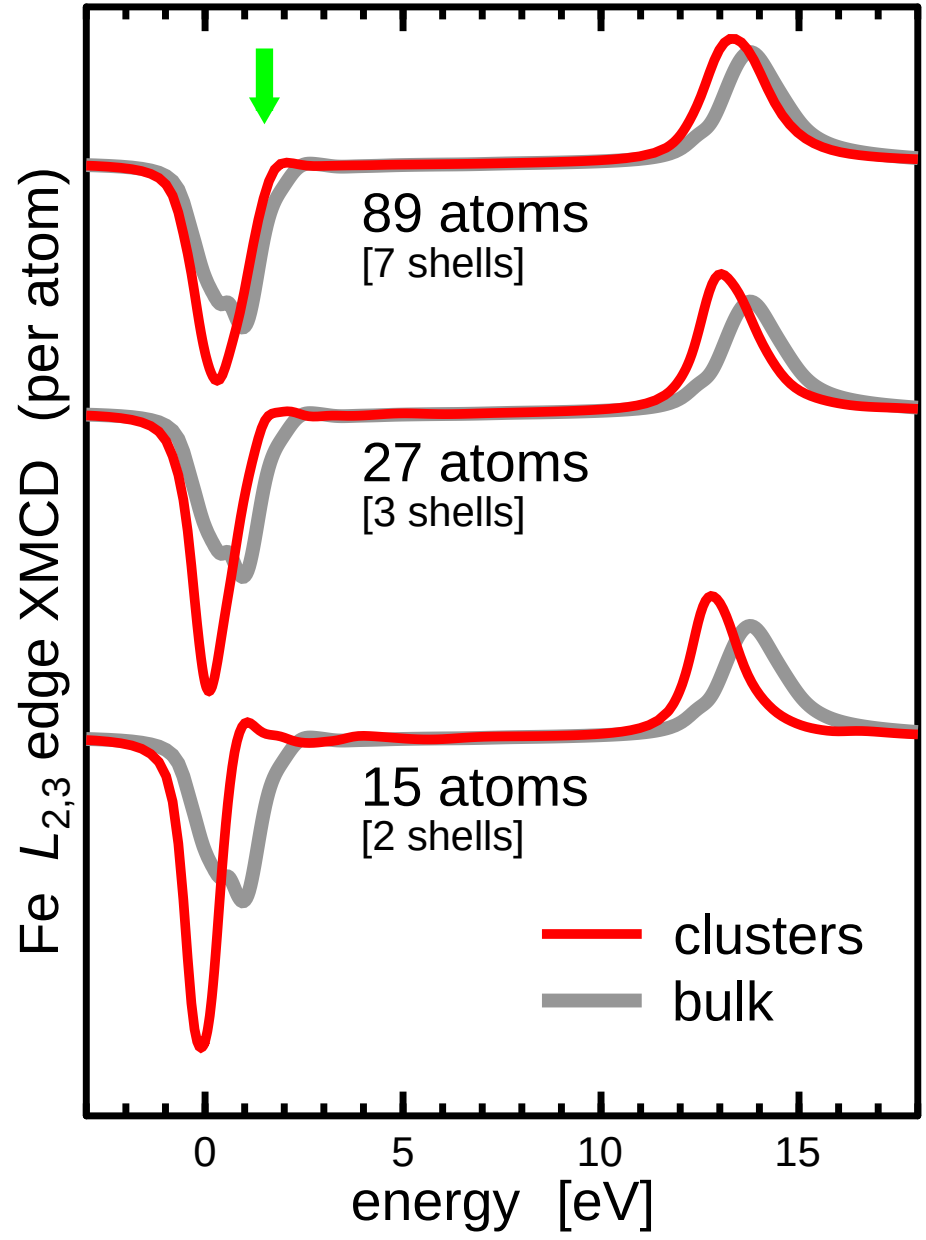
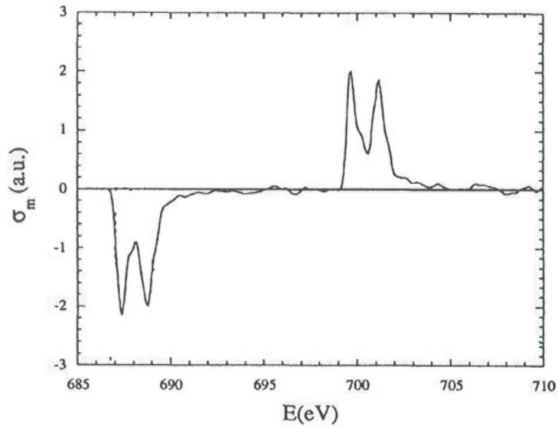
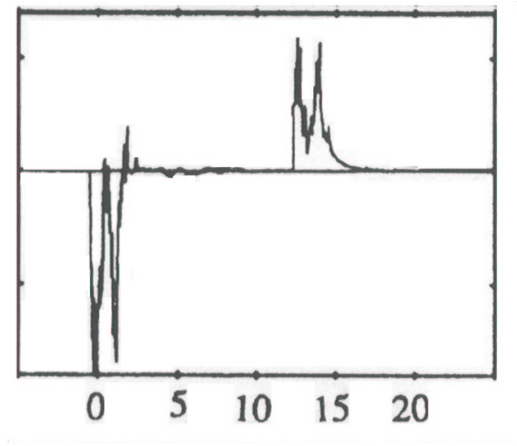
- Small positive peak just after the main L_3 minimum.





Fe(001) surface

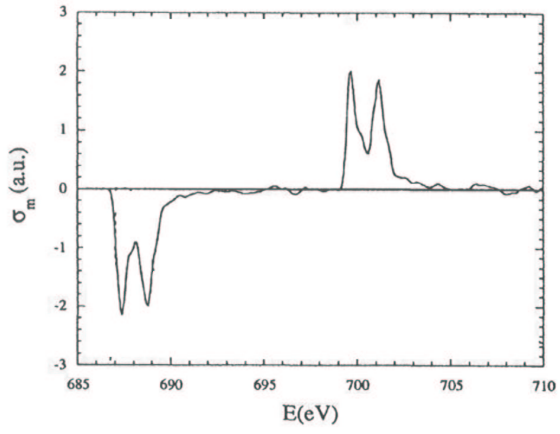
[Wu et al. PRL 71, 3581 (1993)]



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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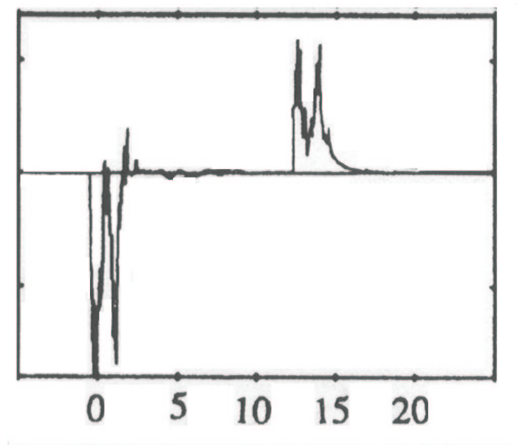

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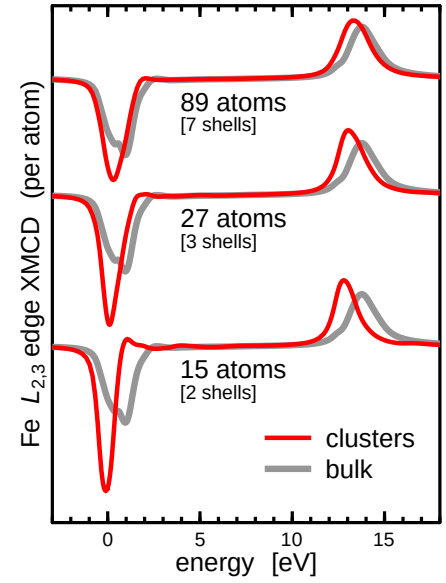

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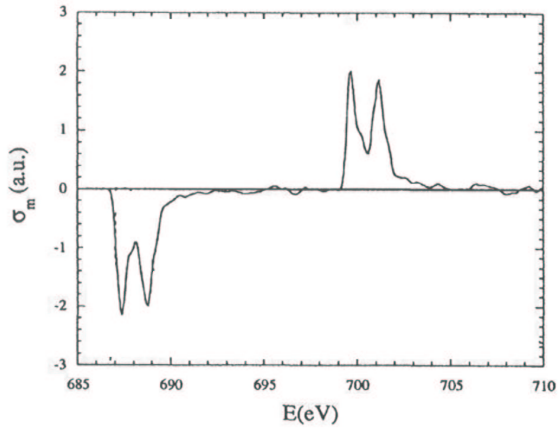
Calculated XMCD of clusters display no such fine structure.

Where have all the structures gone?



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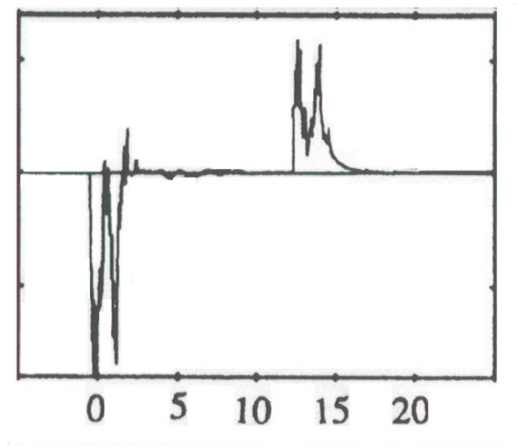

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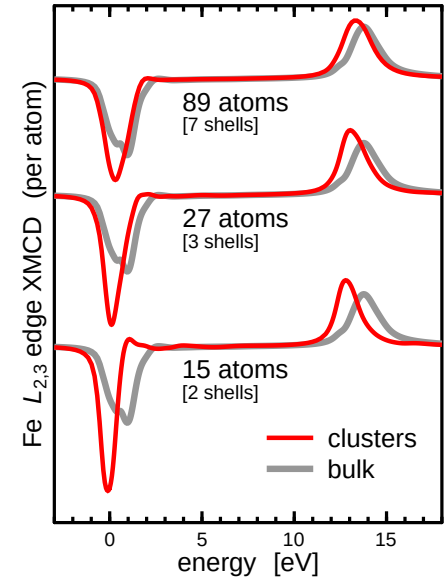

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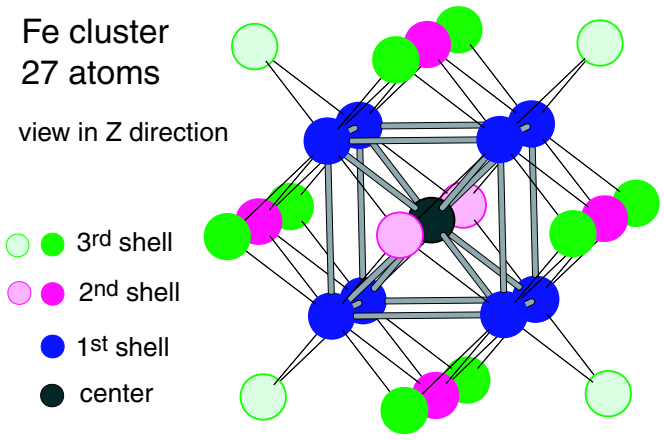
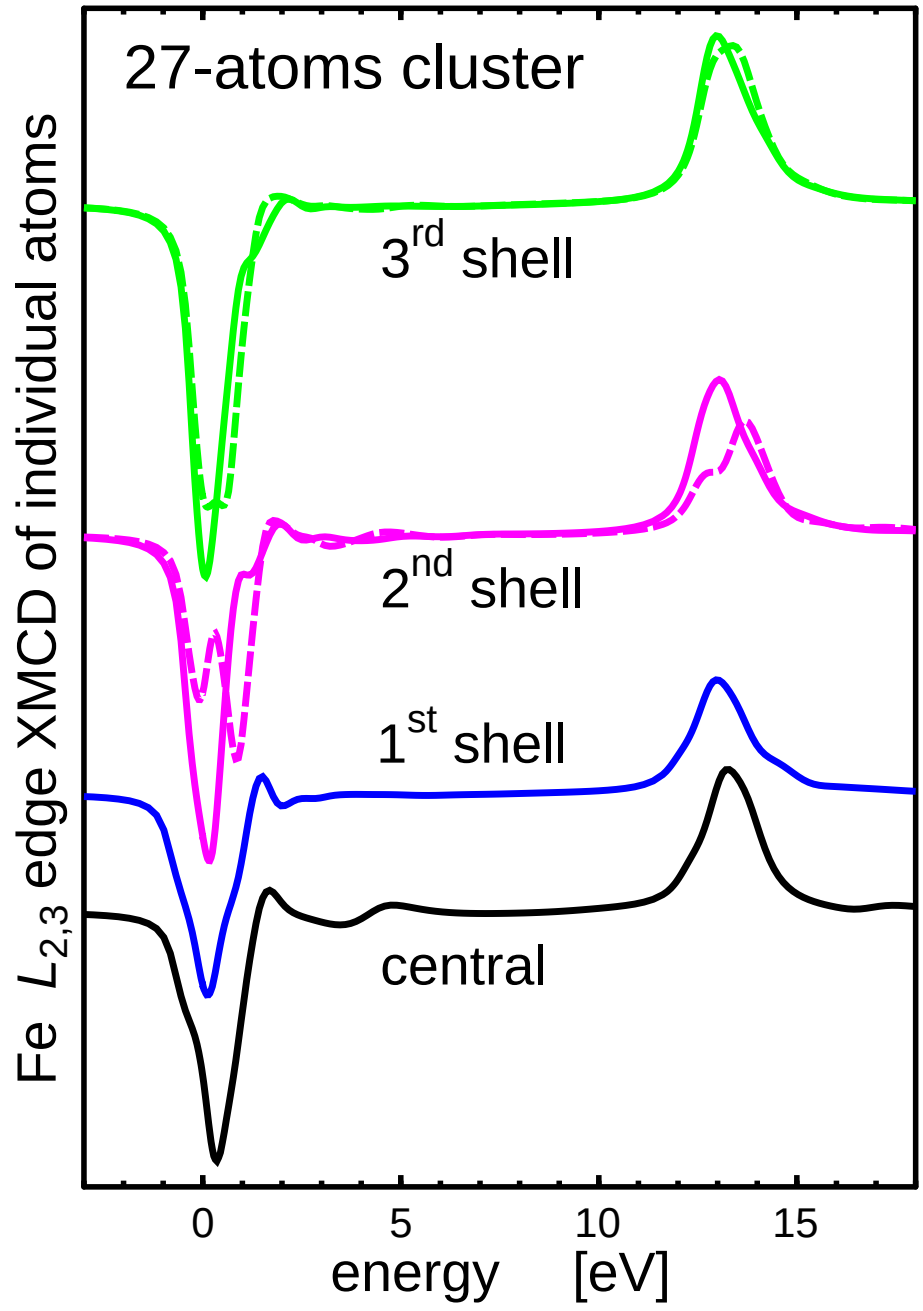
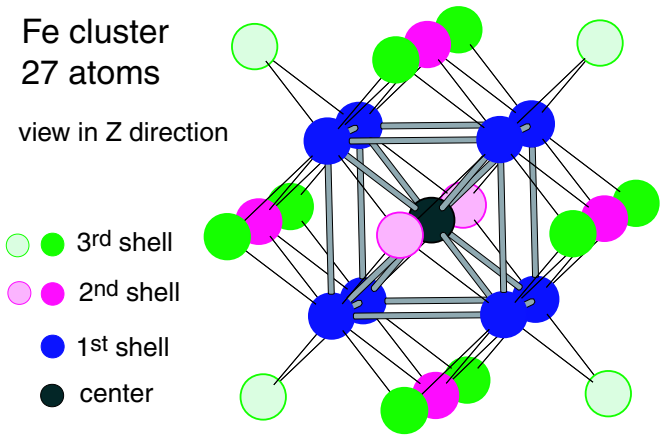


Spectrum of the whole cluster is a superposition of signals from all individual atoms

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



The wiggles cancel each other!



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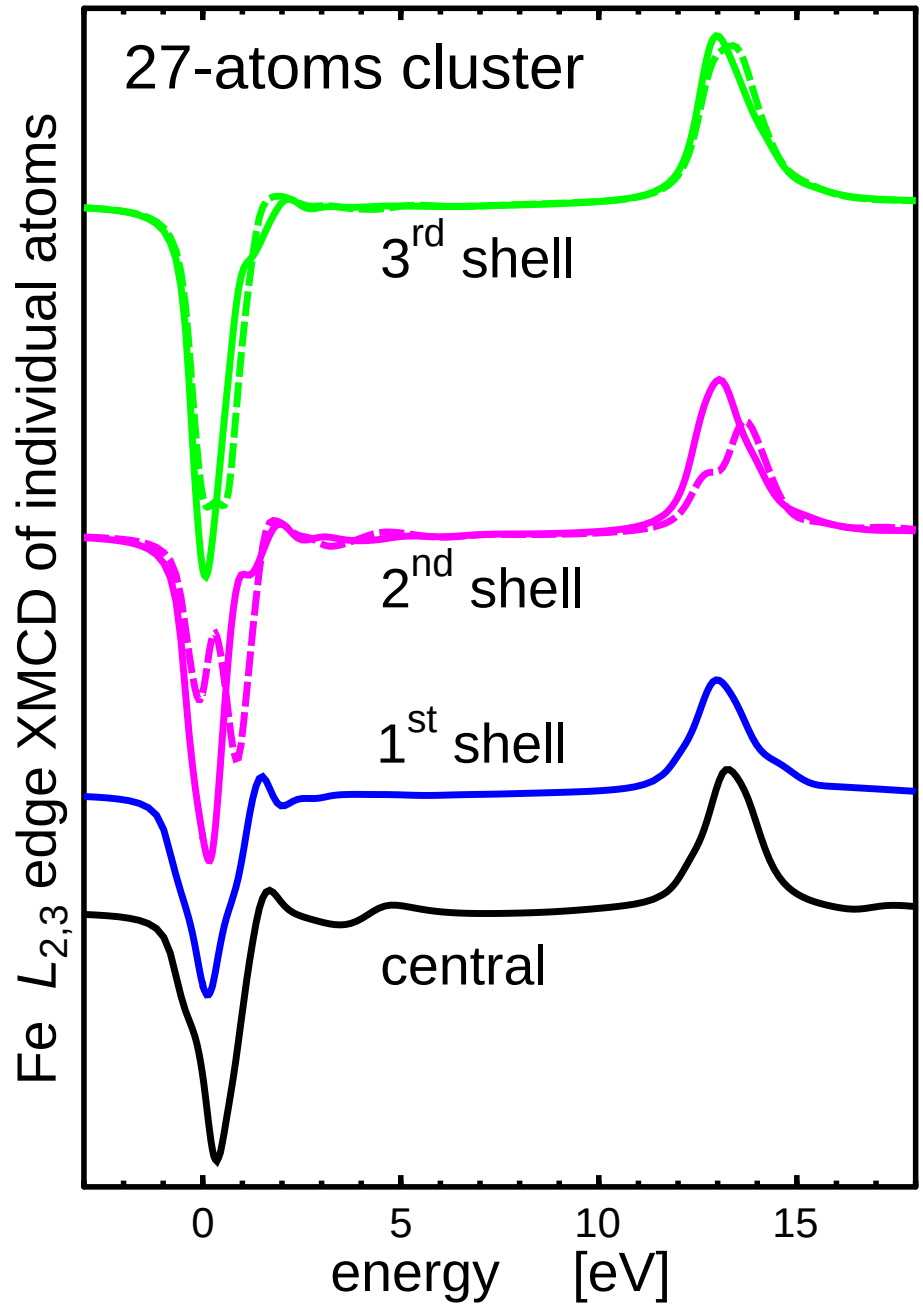


Yet another look at XMCD profiles

Individual spectra of the central atoms and of the atoms of the outermost shell

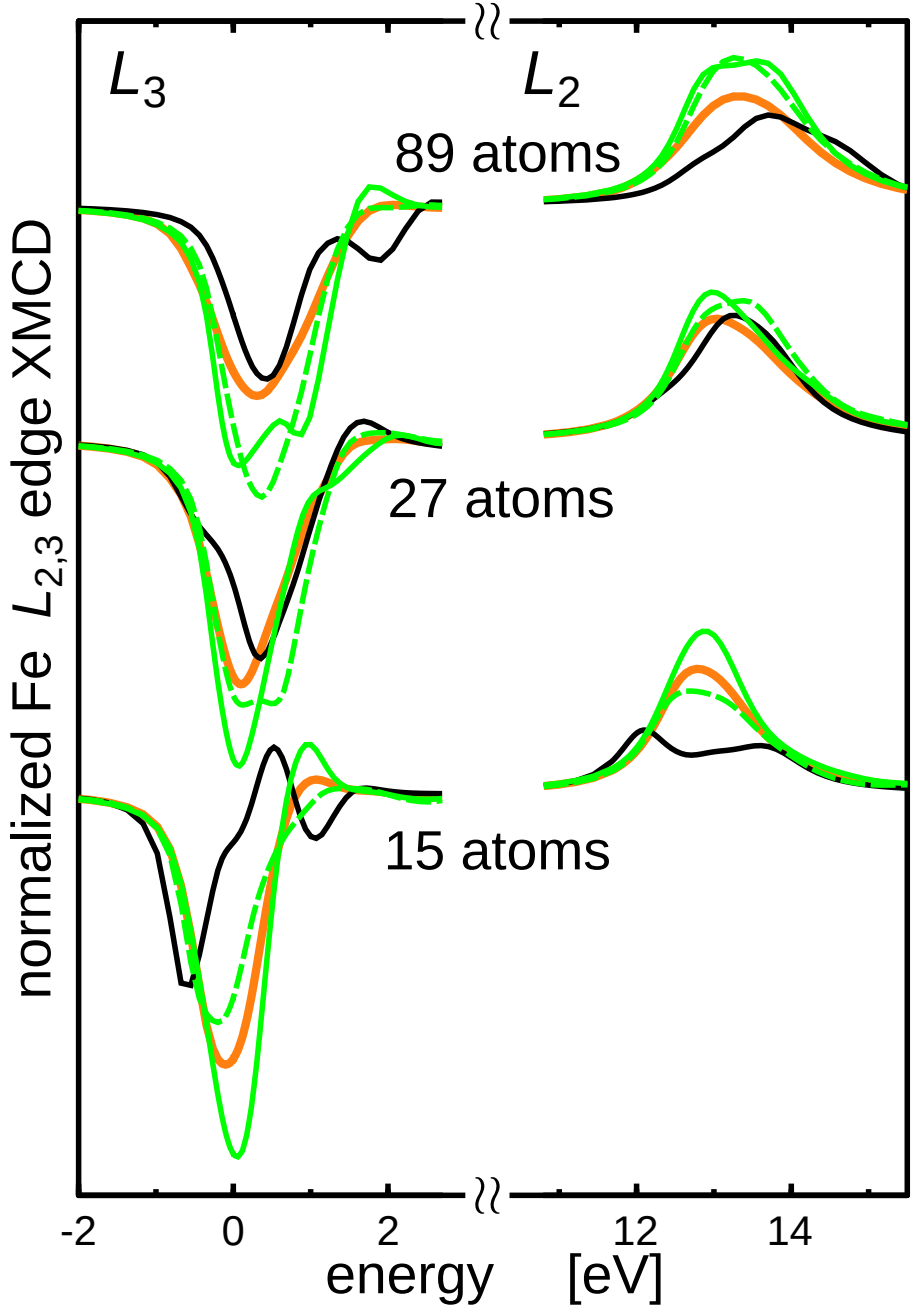
Yet another look at XMCD profiles

whole cluster
central atom
outermost atom (maj symm)
outermost atom (min symm)

Individual spectra of the central atoms and of the atoms of the outermost shell

Pronounced features mutually cancel and/or get smeared if they are superposed

No unique pattern, no general rule



Conclusions

- The ratio m_{orb}/m_{spin} converges in clusters quickly towards bulk values
- XMCD spectra of clusters distinguish from XMCD of bulk through leaner and enhanced peaks
- Bold fine structure in XMCD of individual atoms gets smeared in the combined spectrum of whole cluster
- Small yet distinct positive hump just after the L_3 peak — a general marker of clusterization ?