

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

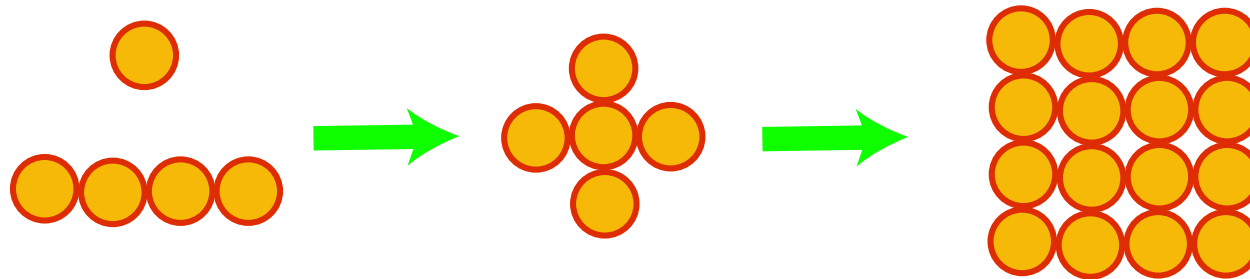
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Germany

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 and on how do they get revealed through XMCD

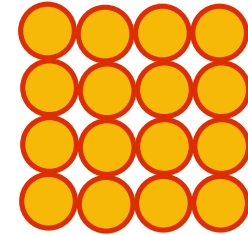
Magnetic properties of iron



atom



surface



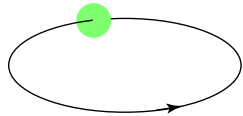
bulk



$$m_{spin} = 4 \mu_B$$

$$m_{spin} = 2.5-3.0 \mu_B$$

$$m_{spin} = 2.2 \mu_B$$



$$m_{orb} = 2 \mu_B$$

$$m_{orb} = 0.07-0.12 \mu_B$$

$$m_{orb} = 0.05 \mu_B$$

(clusters go in between)

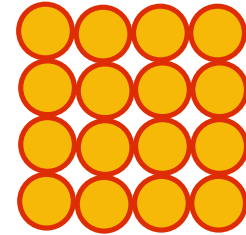
Magnetic properties of iron



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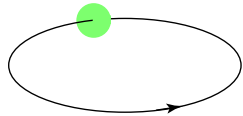
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Clusters contain a high portion of surface atoms
⇒ ought to have larger magnetic moments.

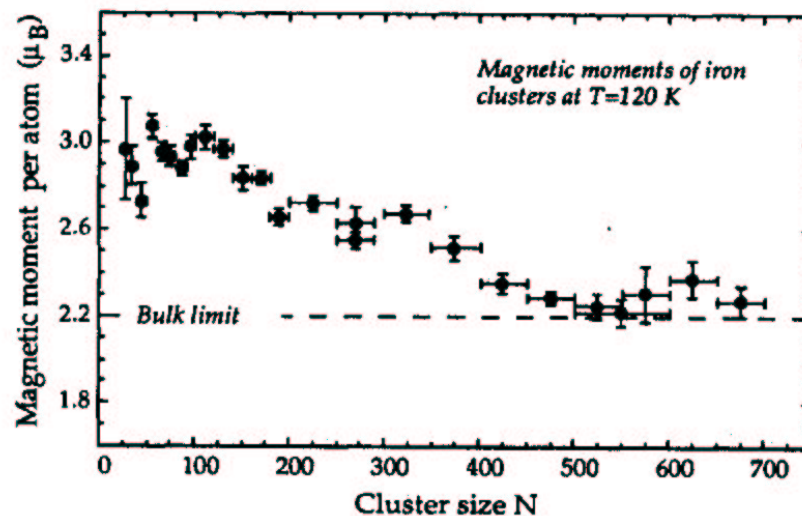
Magnetism of iron clusters (1)

Selected knowledge about iron clusters containing 25–700 atoms:

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

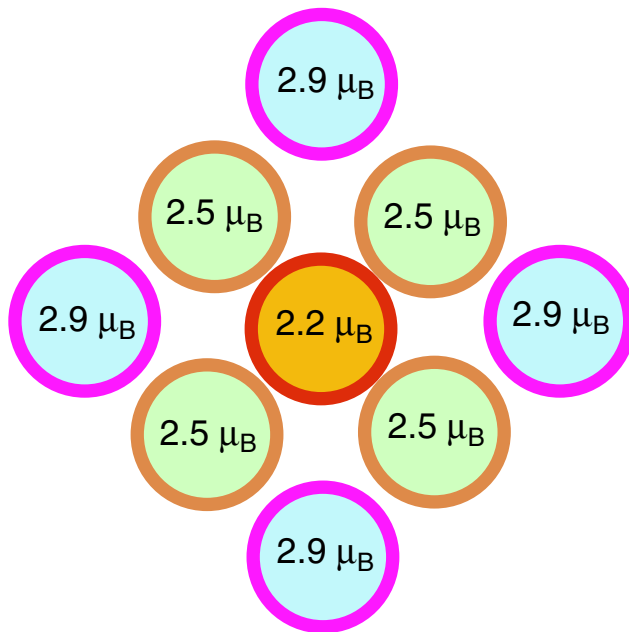
$$m_{tot} = m_{spin} + m_{orb} \approx 2.2 - 3.1 \mu_B ,$$

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).]

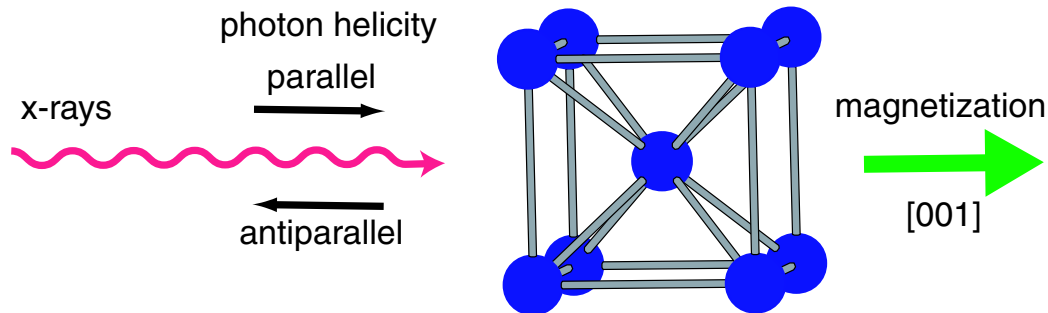
Our aim

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

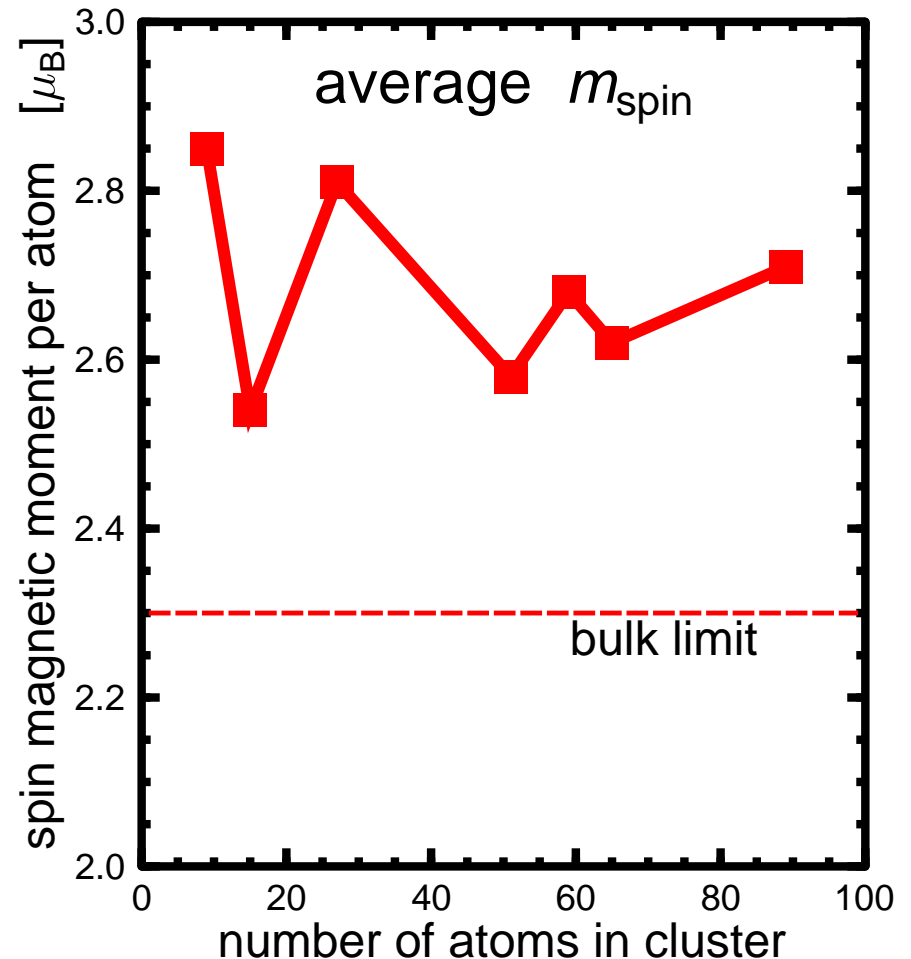
- magnetic moments and XMCD spectra calculated in real space via a fully-relativistic spin-polarized multiple-scattering technique as implemented in the `SPRKKR` code
[H. Ebert: in “Electronic structure and physical properties of solids” (Springer, Berlin 2000), vol. 535, p. 191]
- spherical ASA approximation, clusters surrounded by empty spheres
- scattering potential obtained from SCF- X_α 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)

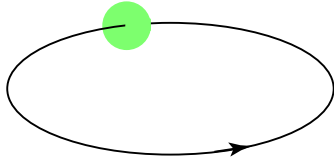


- Average *spin* magnetic moments do not approach bulk limit for clusters of $\lesssim 100$ atoms.

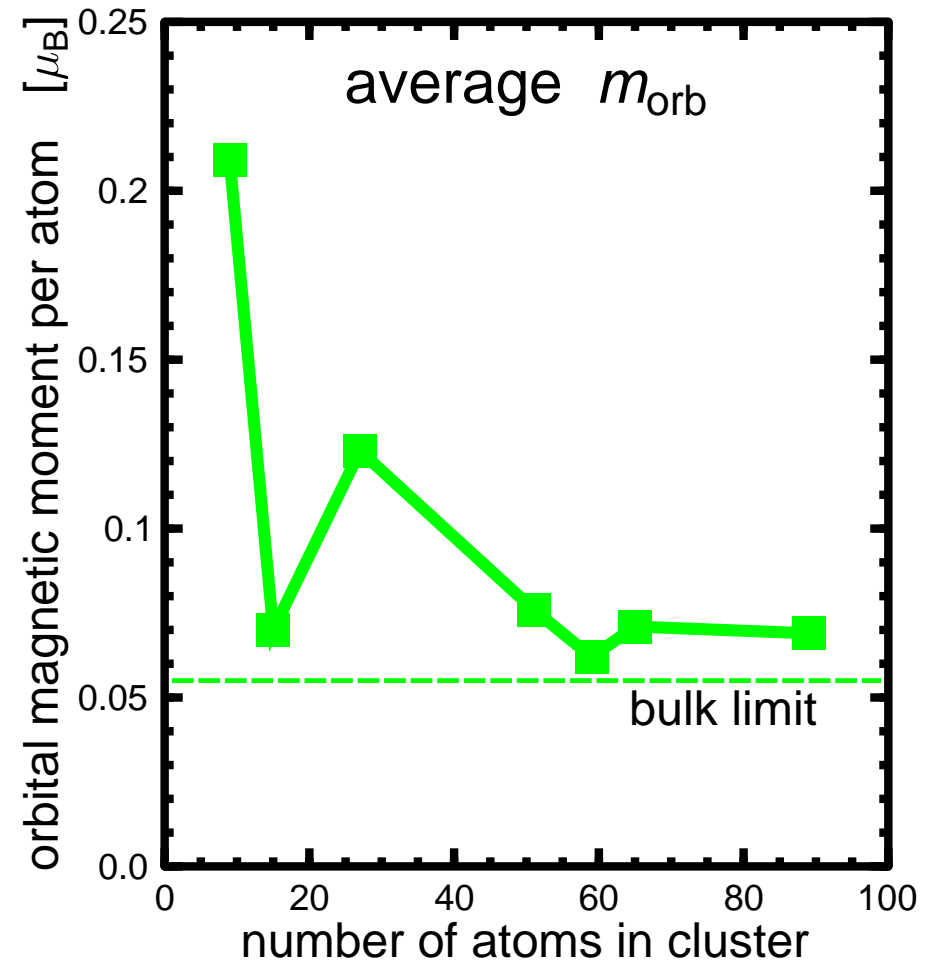
Different calculations by different authors provide different oscillatory structure



Magnetic moments of clusters (2)



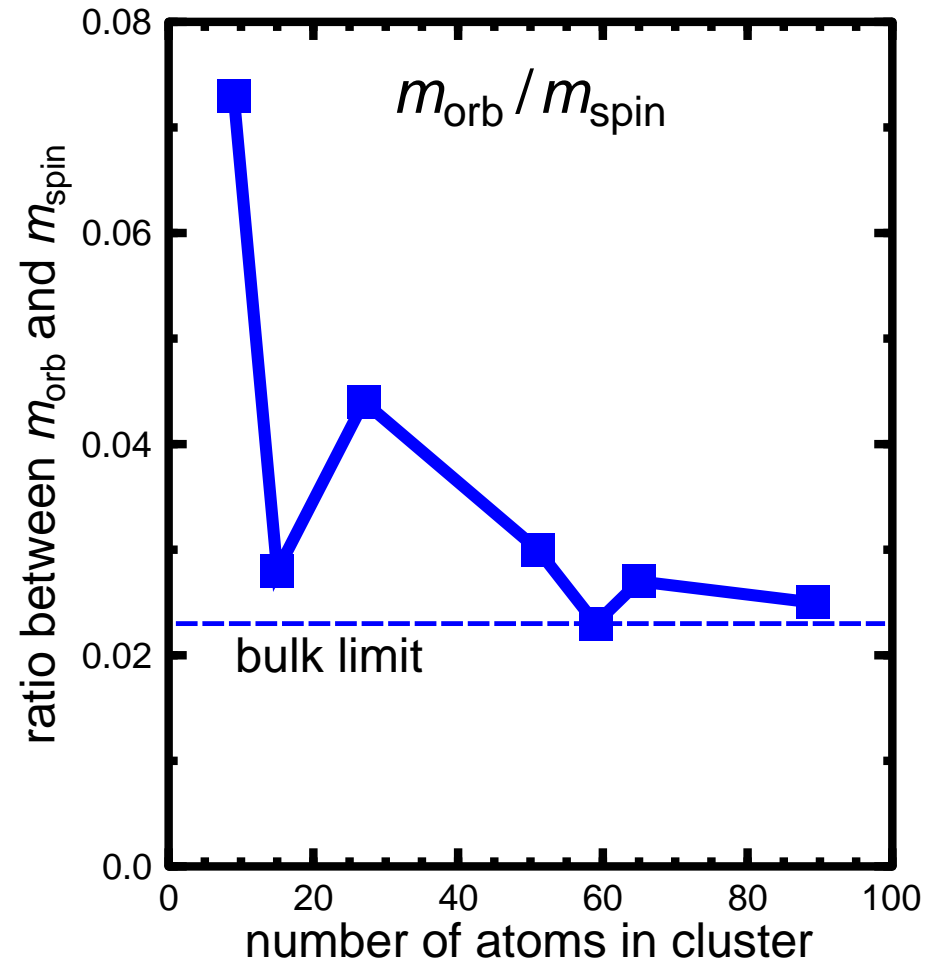
- Average *orbital* magnetic moments have not converged to bulk values either ...



Magnetic moments of clusters (3)



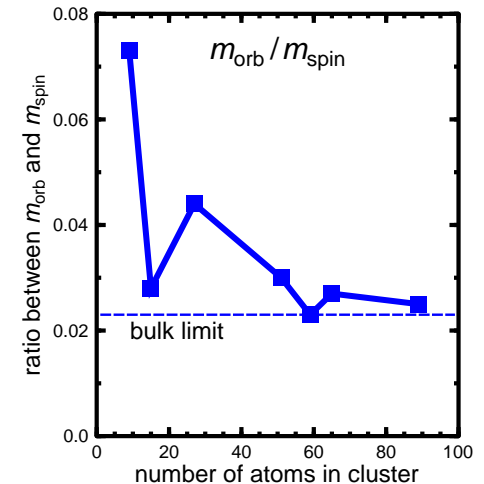
- The ratio m_{orb}/m_{spin} attains bulk values for clusters larger than ≈ 60 atoms !



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).]

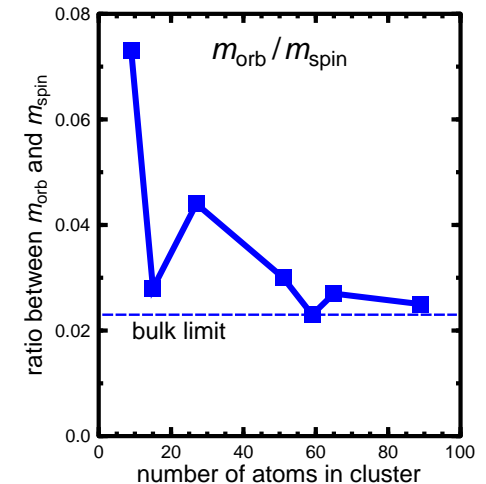


???

No real conflict with experiment...

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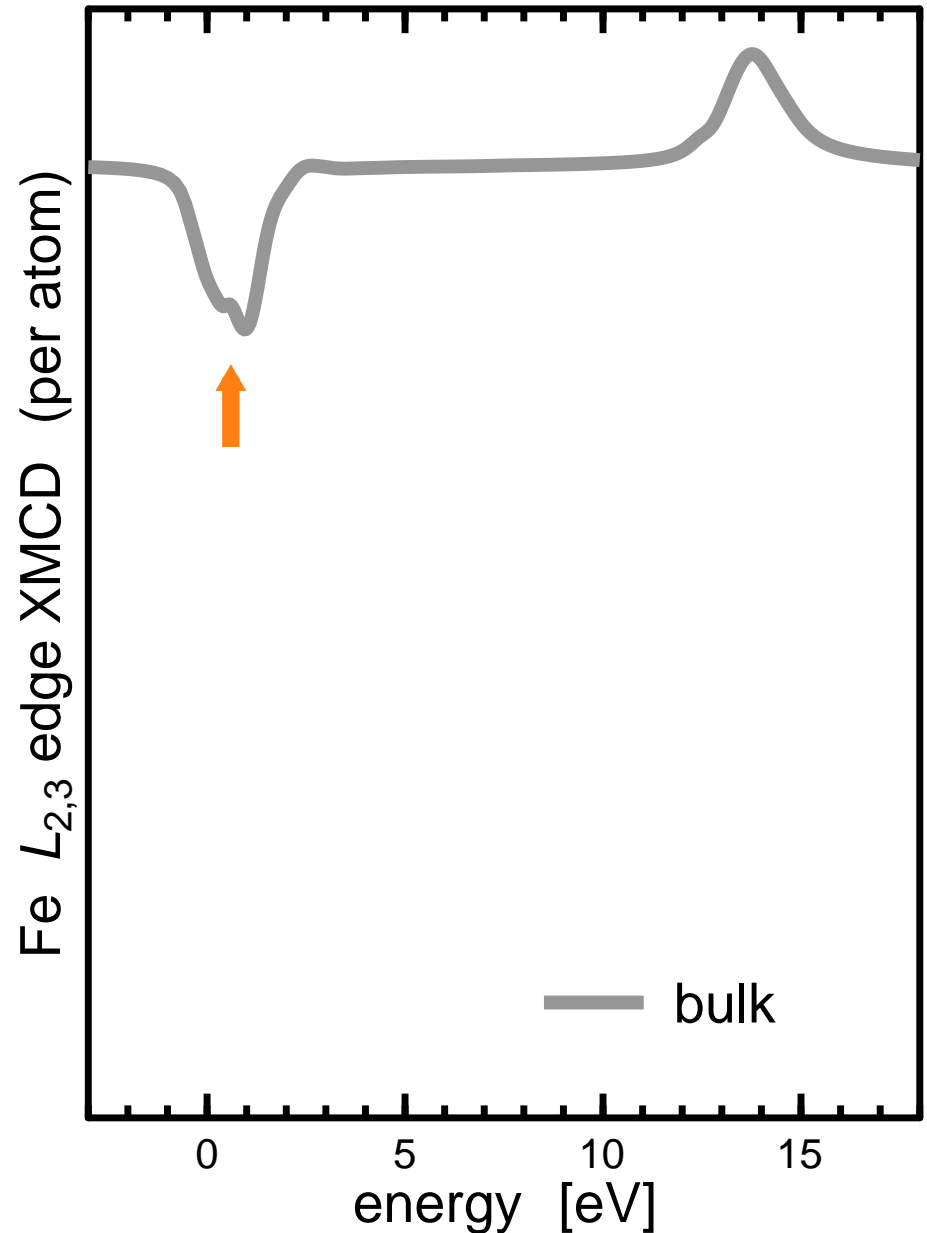
???

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.

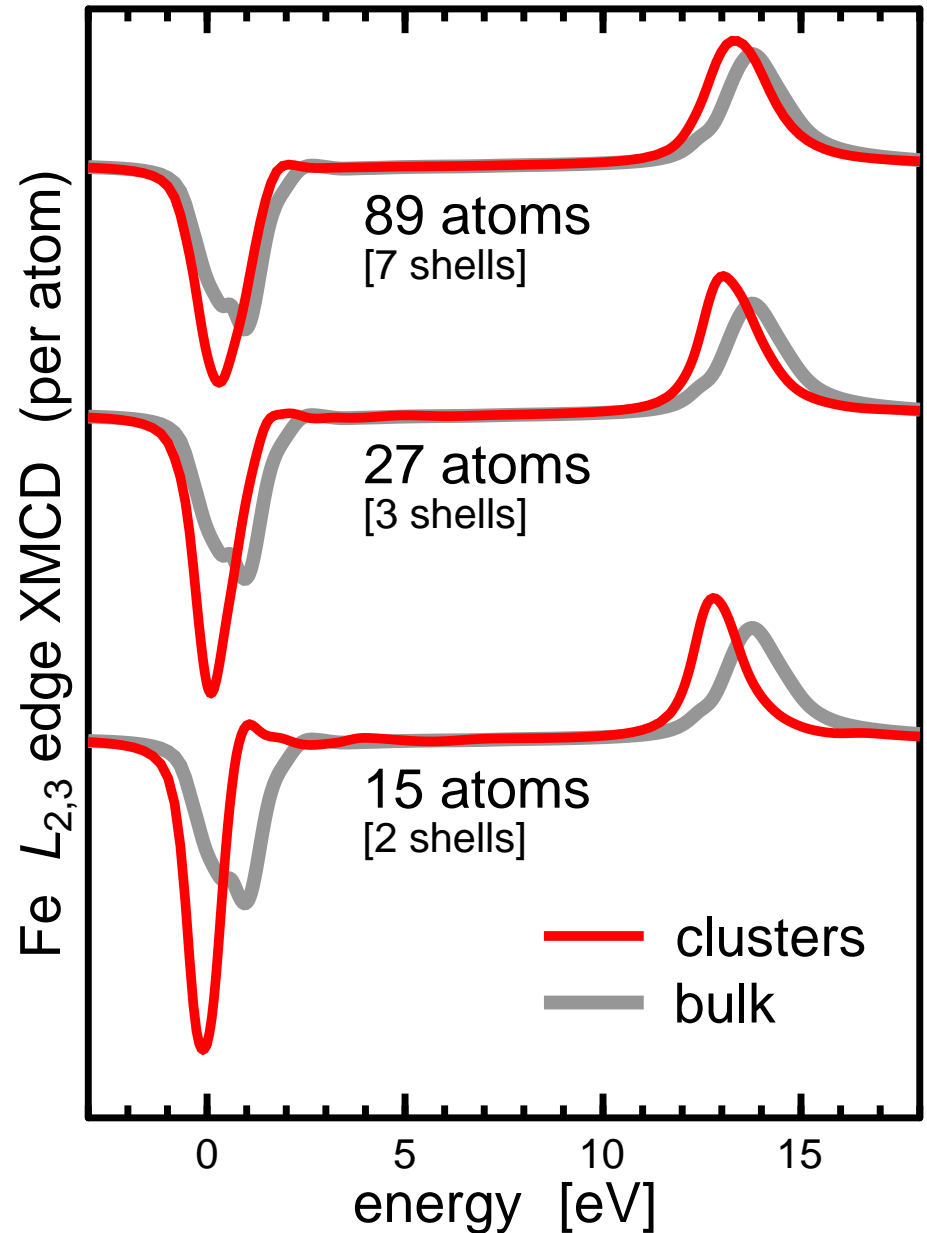
XMCD of iron clusters

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



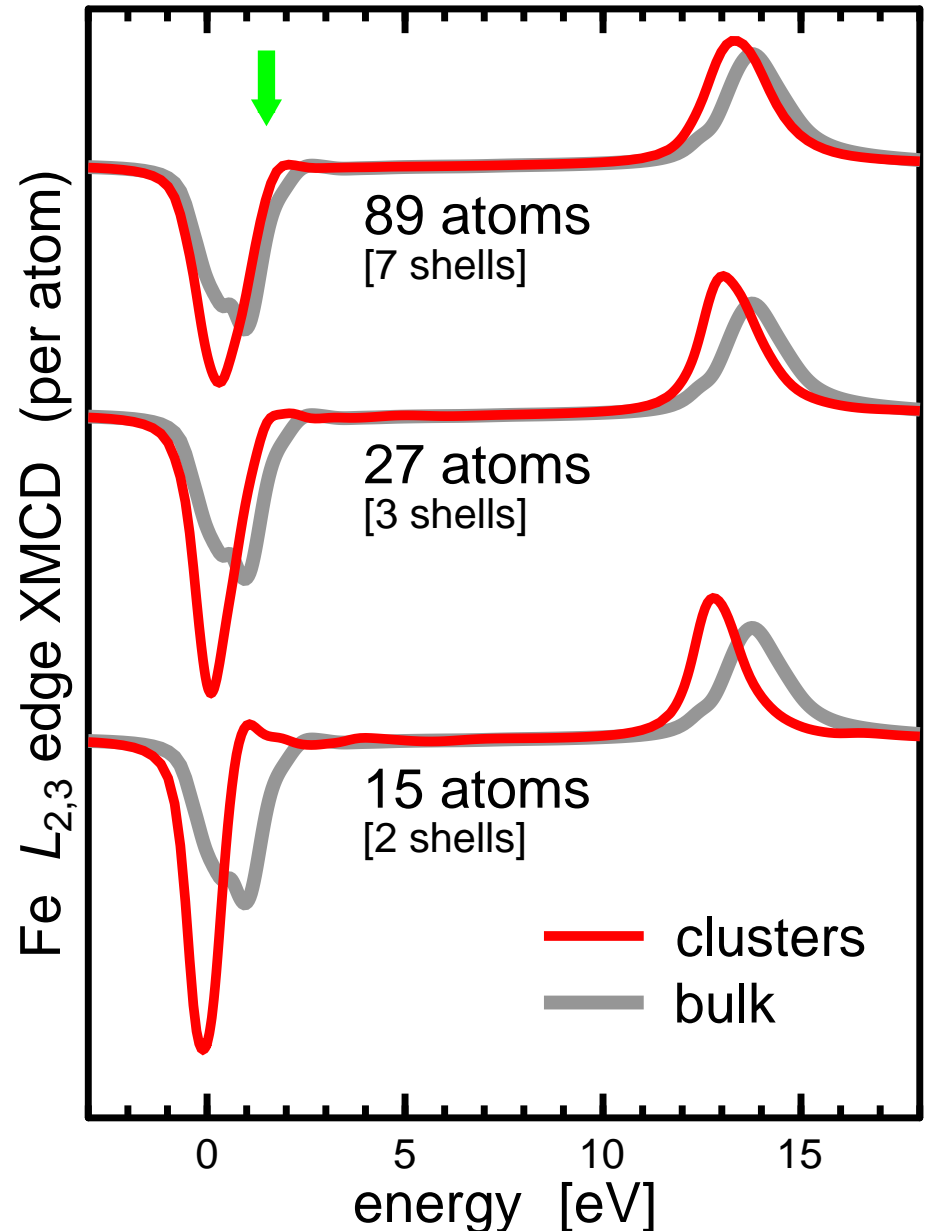
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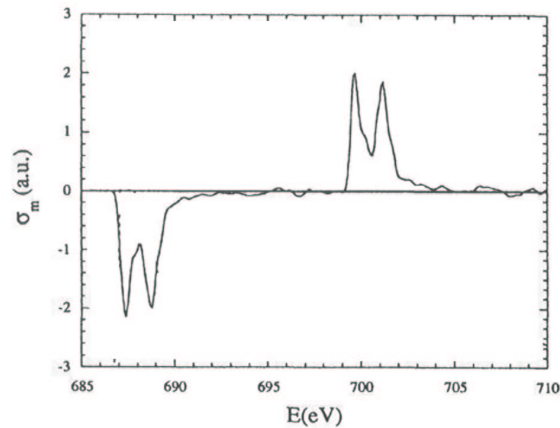
- Splitting of the bulk L_3 peak not seen in experiment (but present in full-potential calculations). Energy resolution?
- Narrowing and enhancement of main peaks (more apparent at L_3 than at L_2).
- Peaks tilted towards the low-energy side.



XMCD of iron clusters

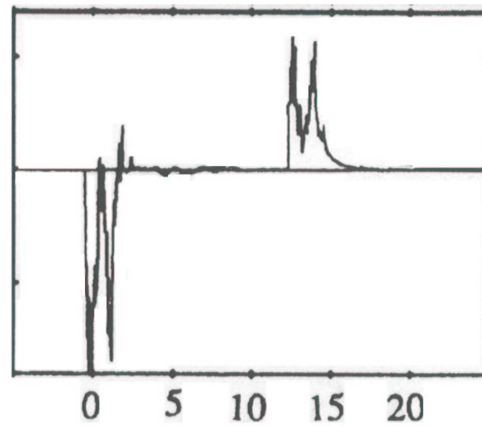
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- Narrowing and enhancement of main peaks (more apparent at L_3 than at L_2).
- Peaks tilted towards the low-energy side.
- Small positive peak just after the main L_3 minimum.





Fe(001) surface

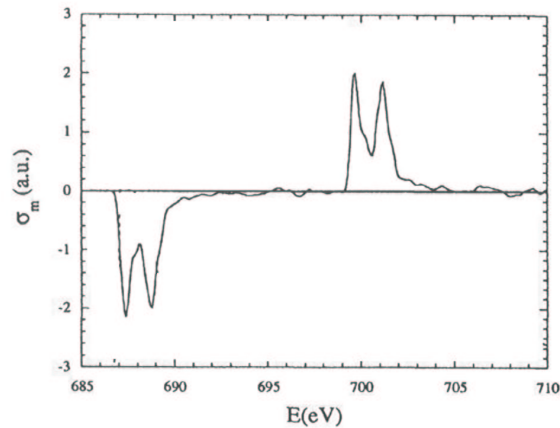
[Wu et al. PRL 71, 3581 (1993)]



Fe₂Cu₆ (001) multilayer

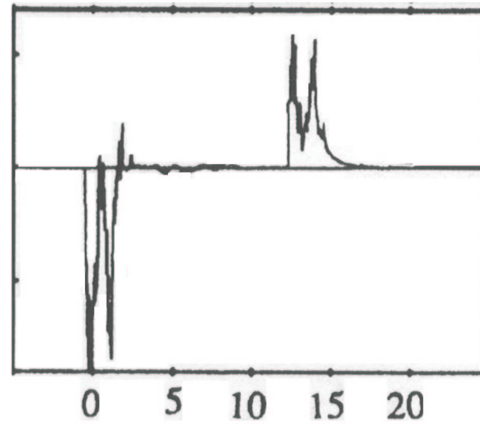
[Guo et al PRB 50, 3861 (1994)]

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



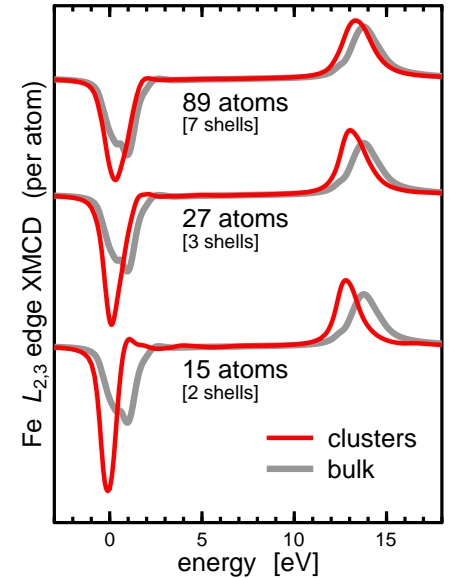
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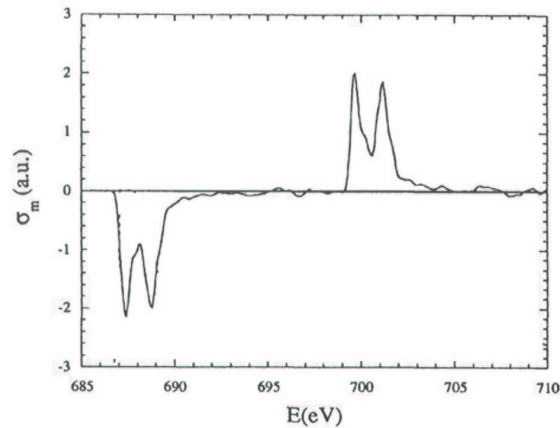
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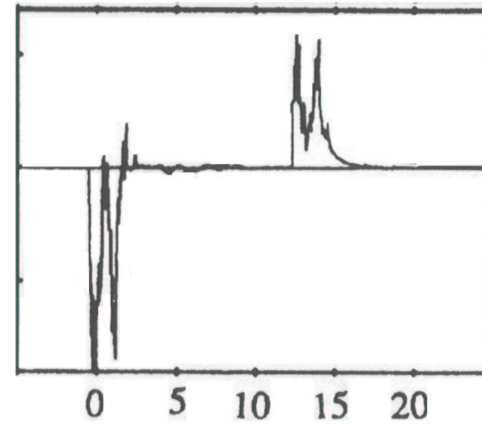
Calculated XMCD of clusters display no such fine structure.

Where have all the structures gone?



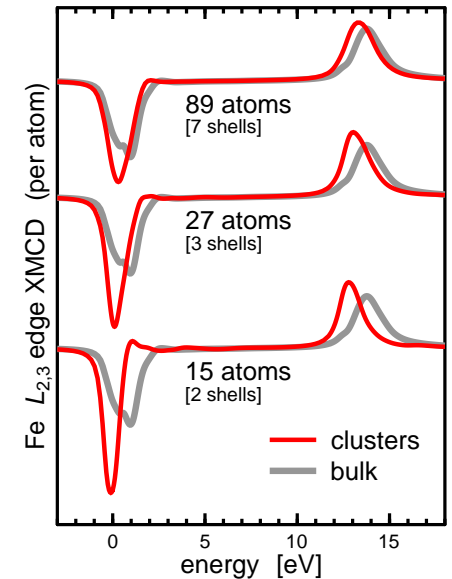
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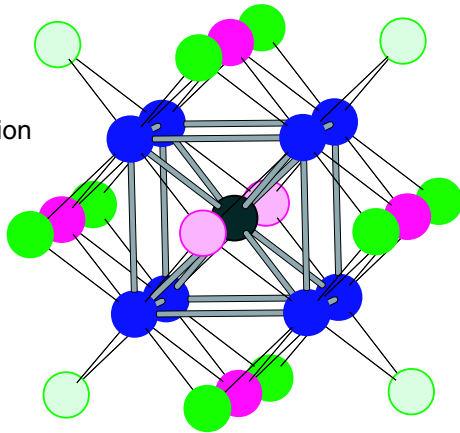
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Fe cluster
27 atoms

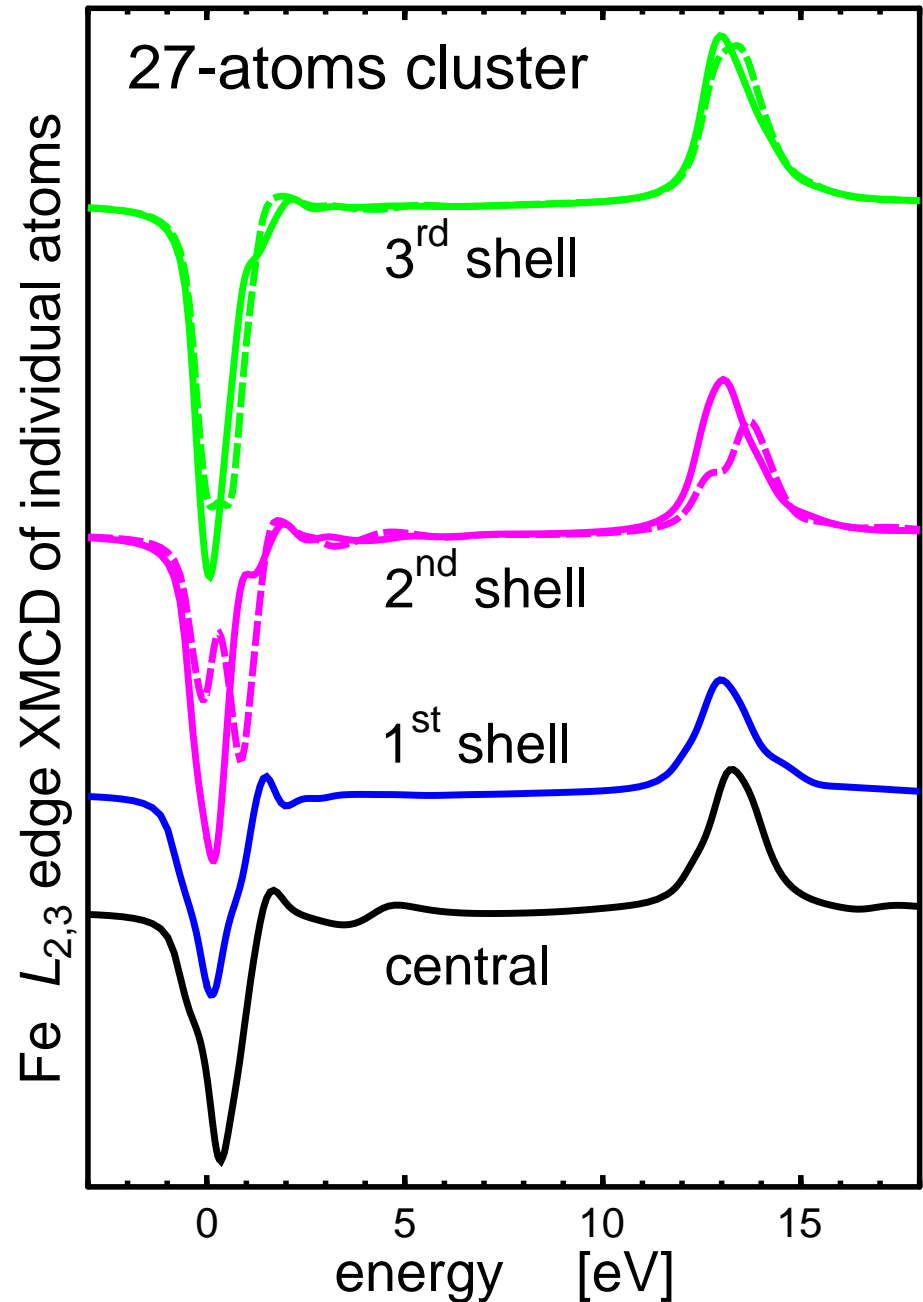
view in Z direction

- 3rd shell
- 2nd shell
- 1st 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

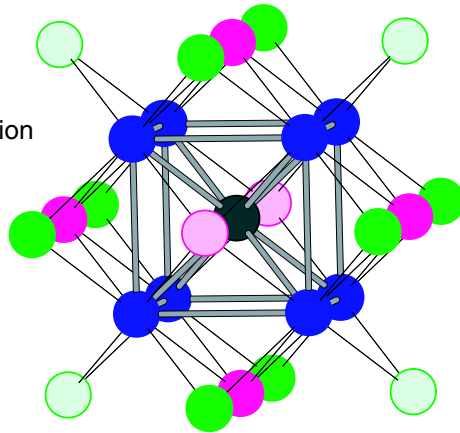


The wiggles cancel each other!

Fe cluster
27 atoms

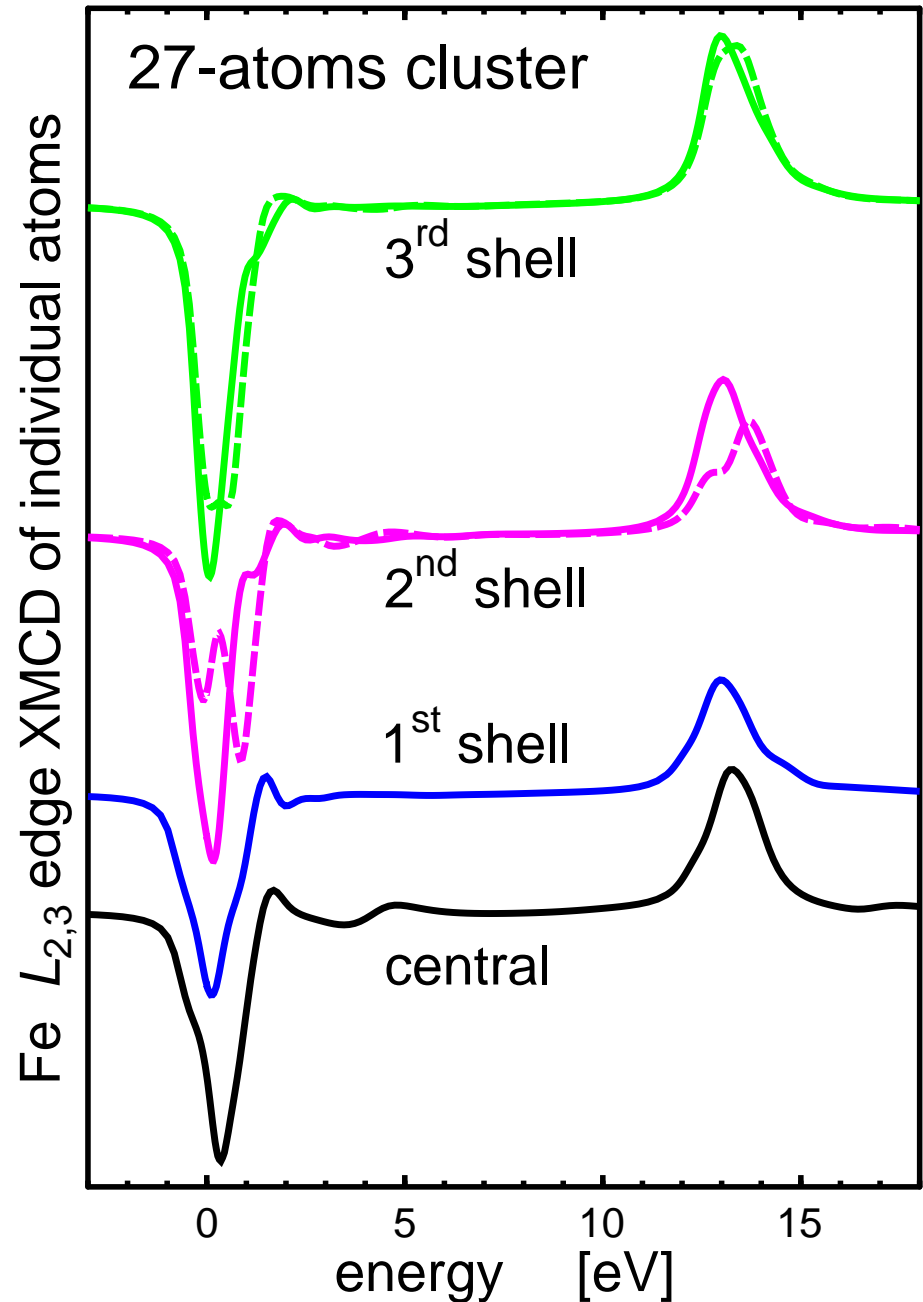
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Yet another look at XMCD profiles

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

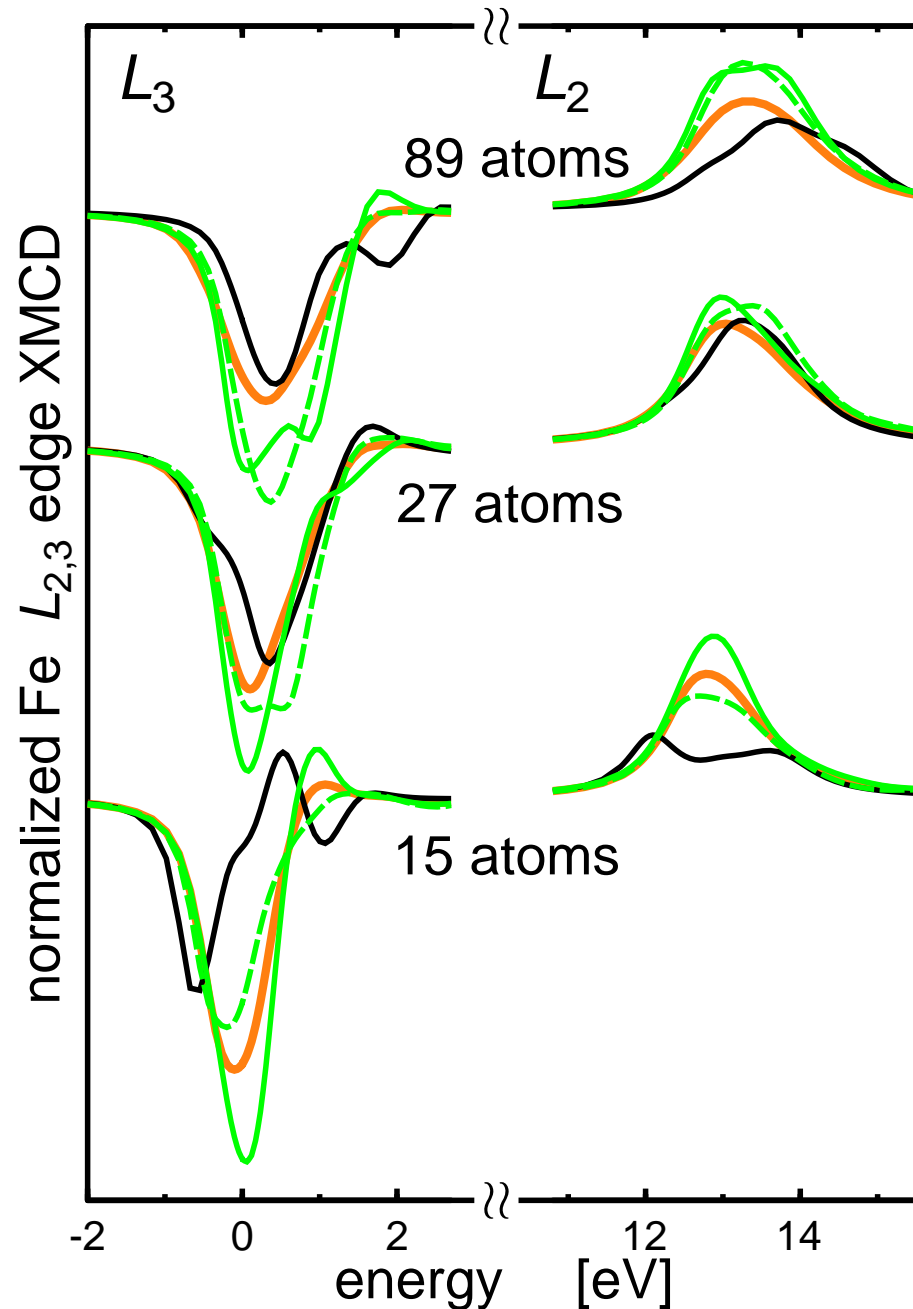
Yet another look at XMCD profiles

- 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 ?