Size vs. Disorder effects in the electronic properties of nanosized intermediate valence metals

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Magnetic Nanoparticles:

Issues to solve for Technical applications:

- Core/shell coupling: superparamagnetic limit
- Interparticle coupling: Magnetoelectrical properties
- Clustering: Natural or Artificial
- Disorder: Transitions?

Superparamagnetism:

Single Domain – Energy Barrier

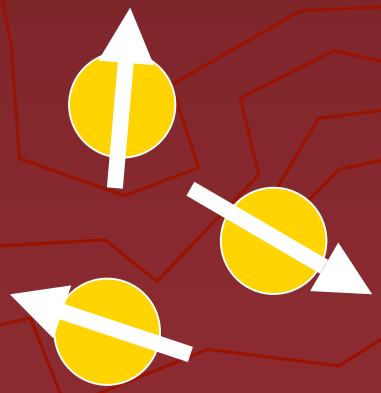
Competition between magnetic anisotropy and thermal fluctuations

Arrenhius law:

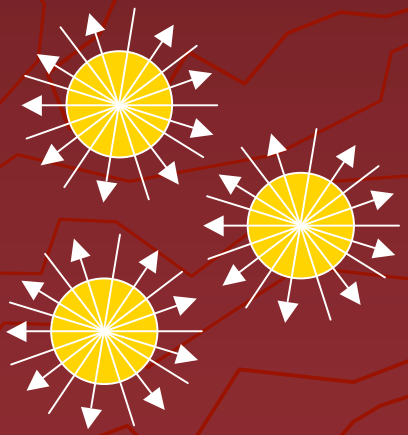
$$\tau = \tau_0 e^{E_B / k_B T}$$

If $\tau = t_m$ then $T = T_B$

$T << T_B$



$T >> T_B$



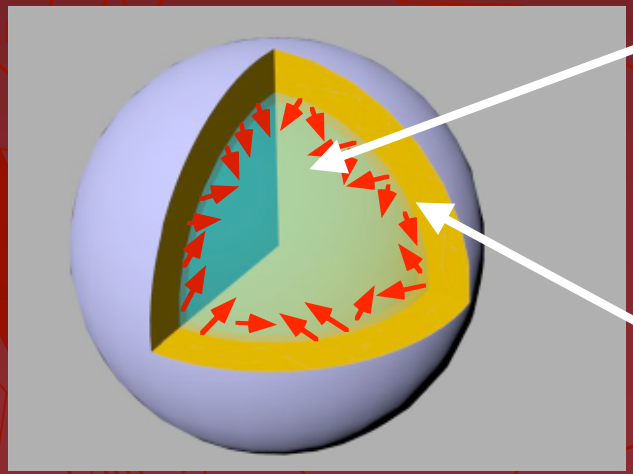
Core/Shell: Amorphous Fe-B

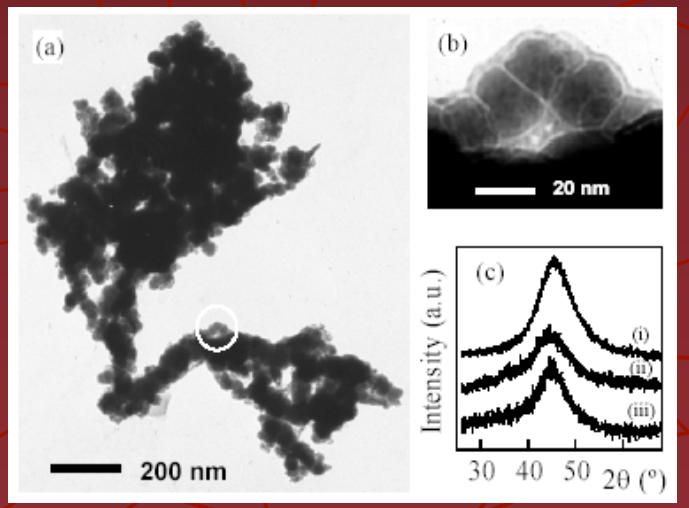
Antiferromagnetic/Ferromagnetic Coupling

Nanoparticles obtained by chemical reduction of NaBH4

Phys. Rev. B 69, 212401 (2004)

Amorphous Fe-B Core, 22 nm

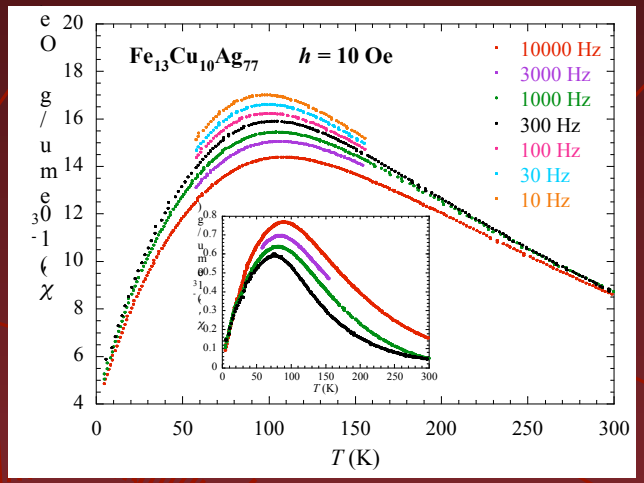




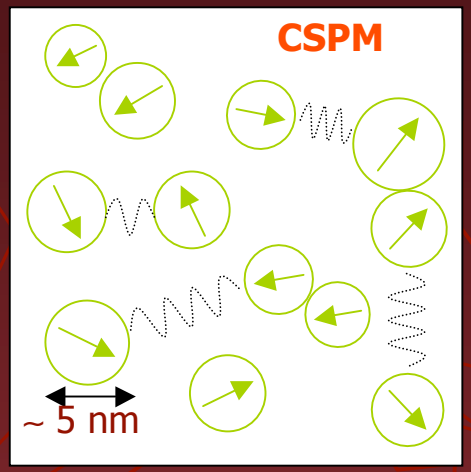
Exchange pinned Interface, 0.3 nm

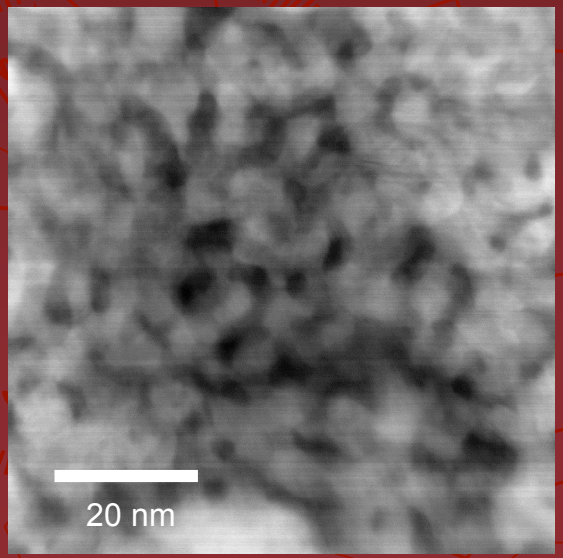
Interparticle Coupling: GMR Fe-Cu-Ag

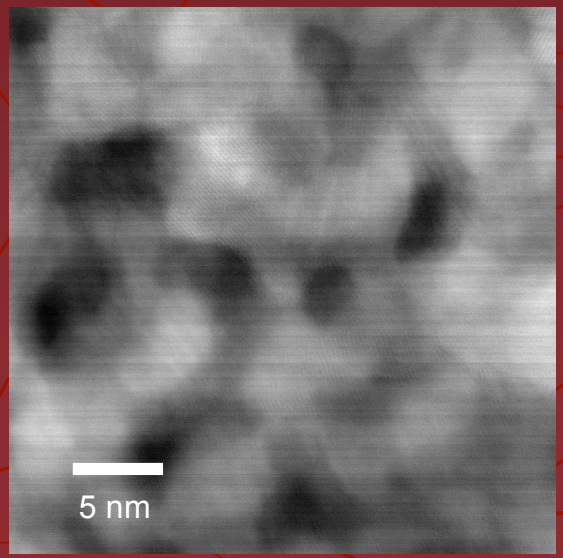
AC-susceptibility



Phys Rev B 64, 104433 (2001)
Phys Rev B 76 , 172404 (2007)







SuperSTEM

Rutherford scattering

Resolution: < 1 Å

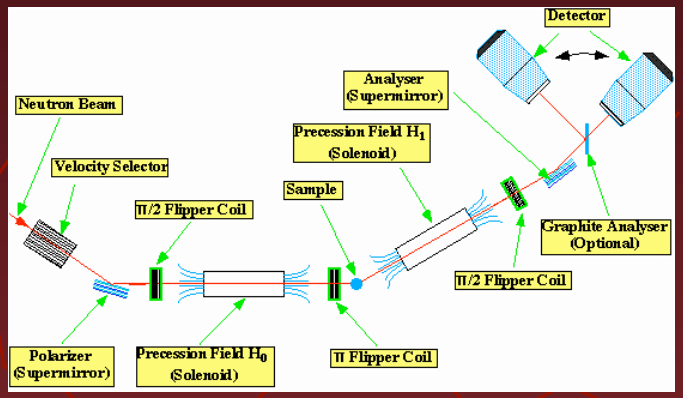
Colours

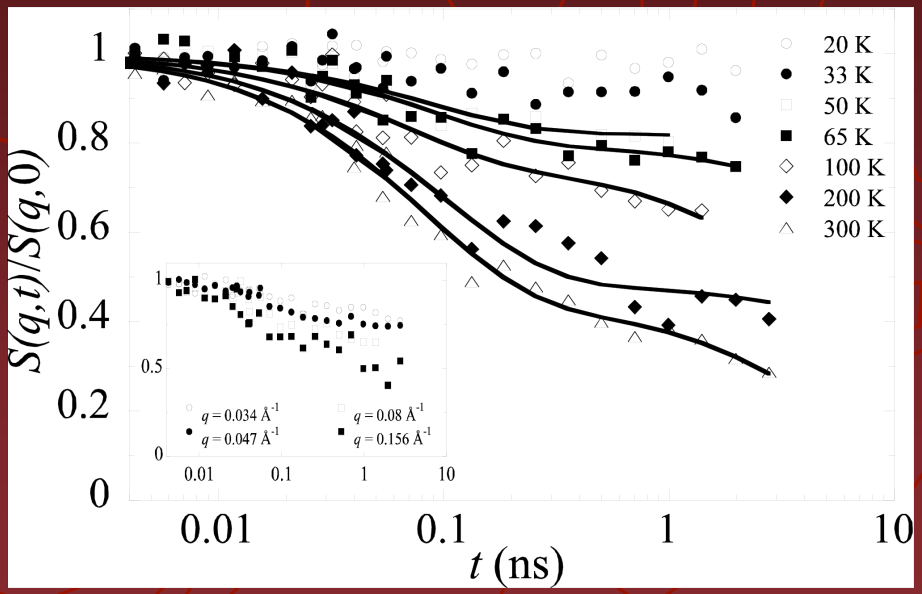
Z^2 : composition

Black: Fe(Cu) particles 4.5 nm

White: Ag

Neutron Spin-Echo, Inst. Laue-Langevin (France)

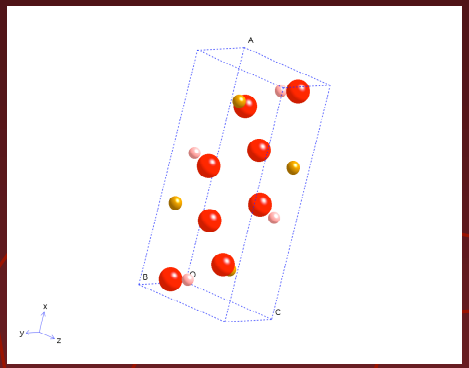




Phys Rev B 76 , 172404 (2007)

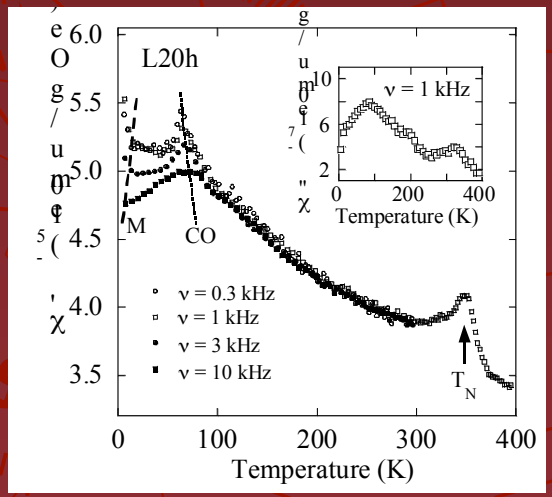
- Spin-Spin correlation which becomes weaker with increasing time
- Model of depolarization using the Superparamagnetic relaxation with B parameter $\beta = kT/KV$

Natural Clusters: The goethite case

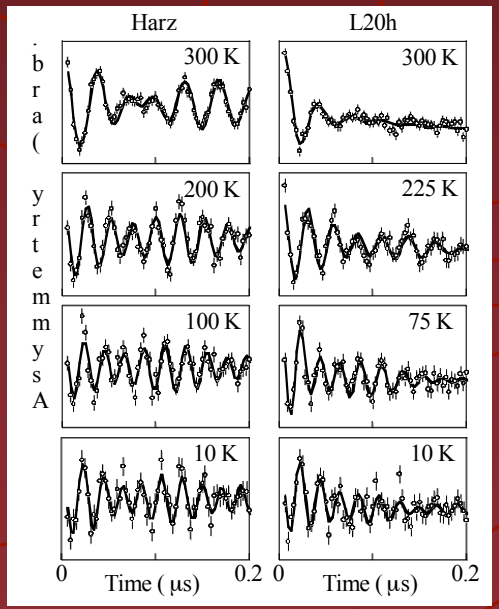


FeOOH: AFM Orthorombic (canted)

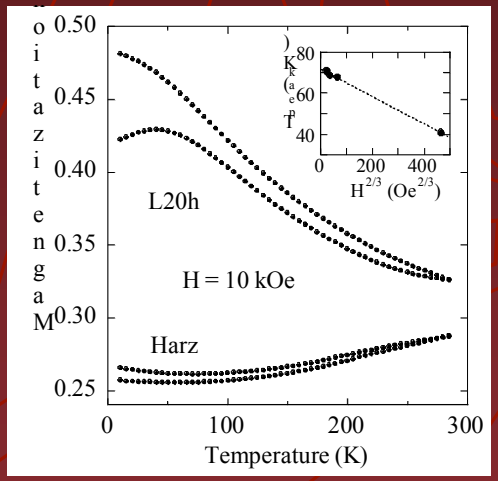
AC-susceptibility:



Muon spin relaxation:

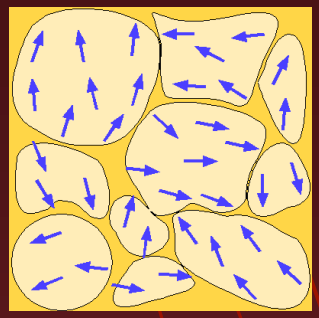


DC-magnetisation:

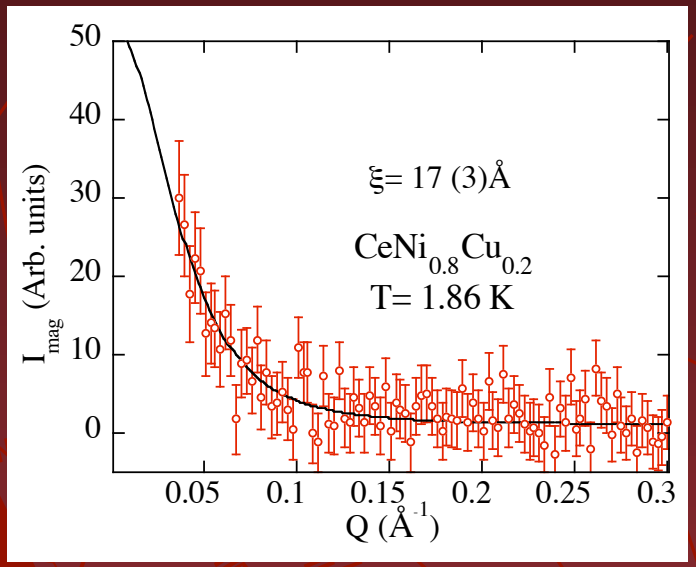


Phys Rev B (to be submitted, 2008)

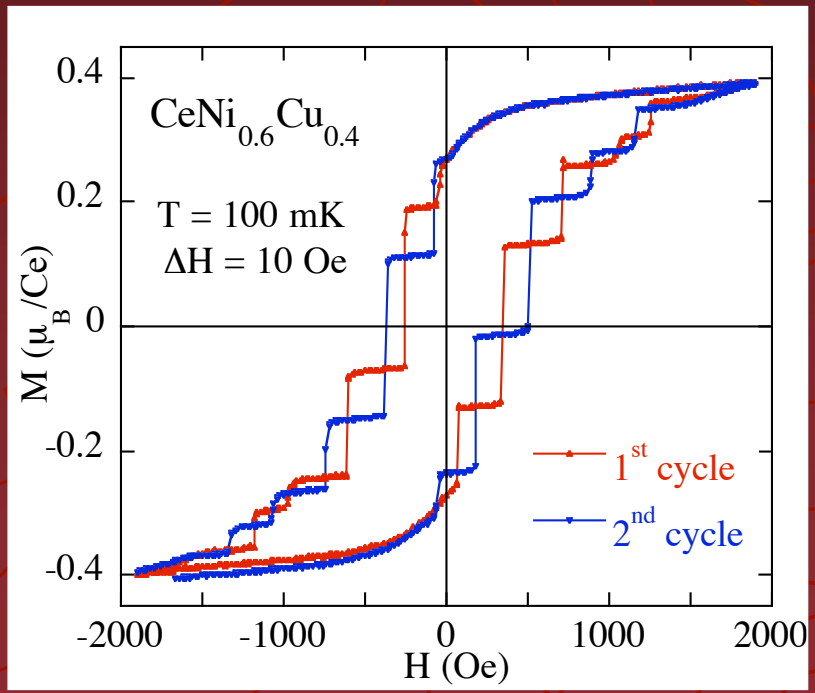
Artificial Clusters: Ce-Ni-Cu



Small-Angle Neutron Scattering (I Laue Langevin)



Orthorombic structure, reduced Ce moments due to hybridization



Phys. Rev. Lett 98, 166406 (2007)
& Phys Rev B 76, 224419 (2007)

- **Non-repetitive on cycling**
- **Strong temperature dependence**

What is the influence of size and disorder?

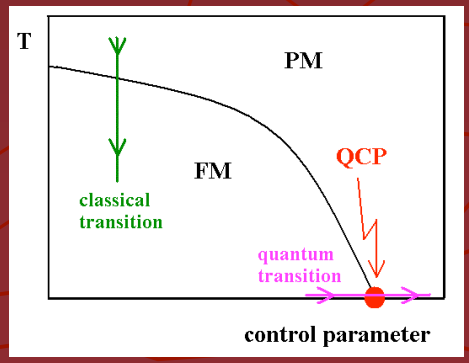
Study of milled $YbAl_3$ alloys

Strongly correlated electron systems

- Intermediate valence
- Non-Fermi liquid behaviour: modified

Cp …log T (miliK)

- Magnetic Instability
- Heavy fermions: 4f,5f -> Ce,Yb,U
- Quantum Phase transitions: Tc -> 0



Intermediate Valence, non-magnetic behaviour

Electronic configuration: Ce3+, Yb3+ (4f-electrons)

Proximity of the 4f level to the Fermi energy, hybridization

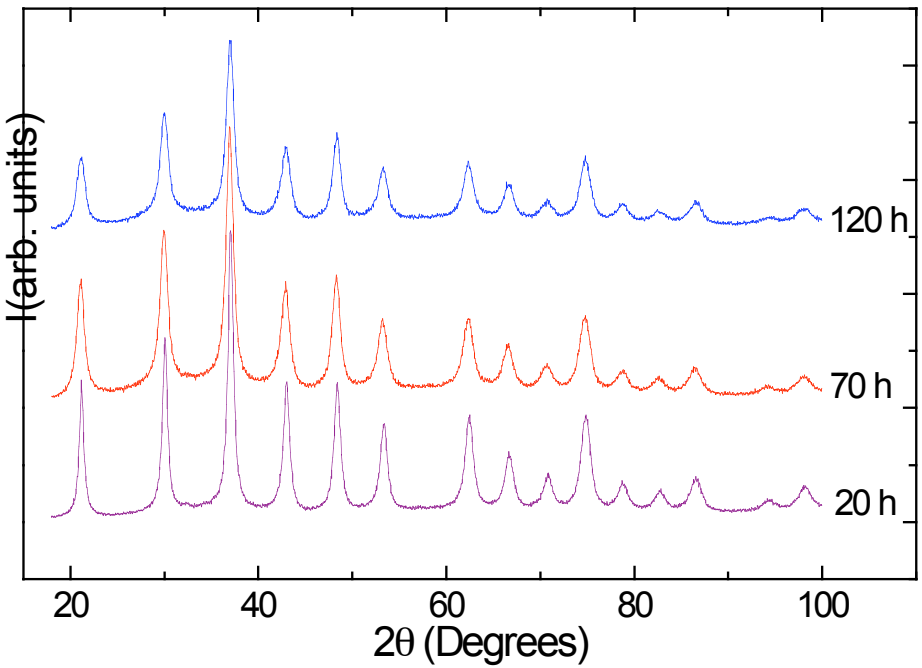
Competition between RKKY and Kondo effect

Instability of the magnetic moment and of charge configuration:
intermediate valence

Yb3+ is magnetic whereas Yb2+ is not

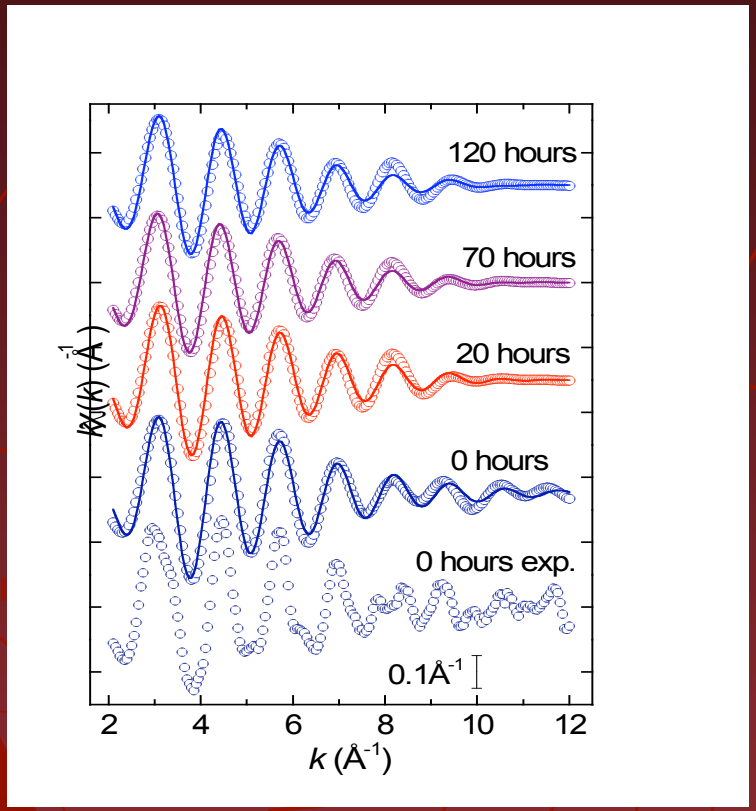
Work on mechanically milled (Argon) $YbAl_3$

Crystallographic structure: XRD



Rietveld analysis: Cubic structure *a* = 4.2057(7) Å, constant lattice parameter, line broadening due to size decrease and strain effects

Short-range order (EXAFS)



Spline (ESRF, Grenoble) + Spring8 (Japan)

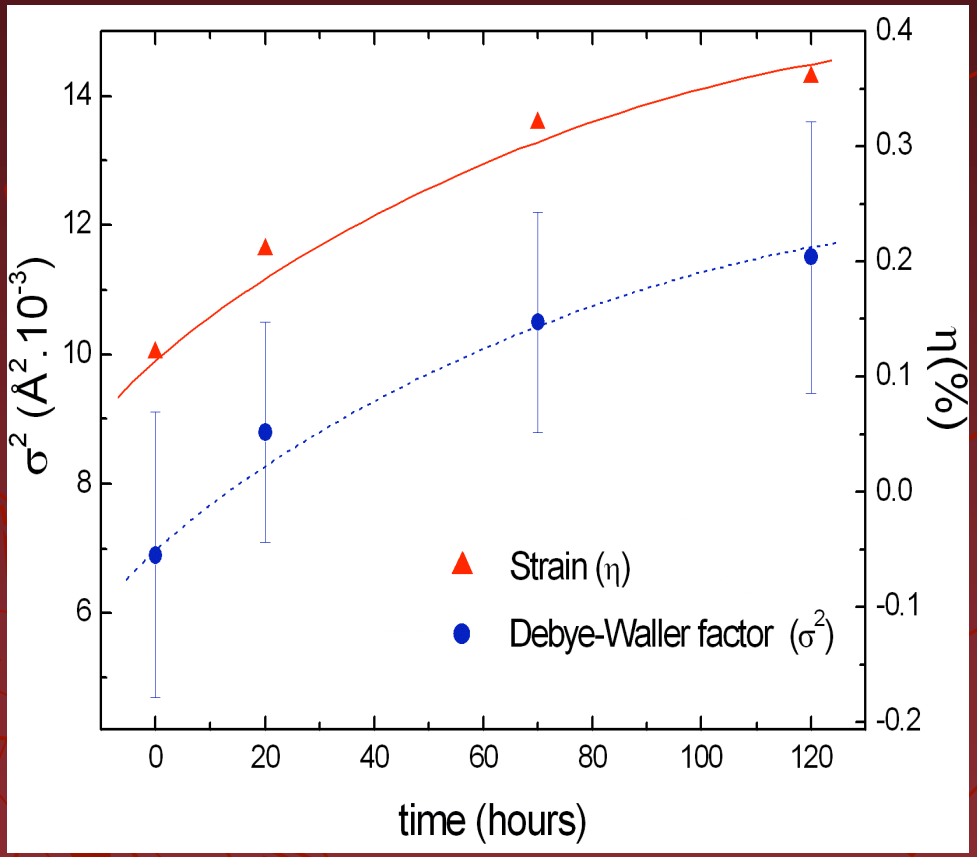
Yb-Yb distance: 2.96 Å

Local structure as shown in XRD does not change

N=12

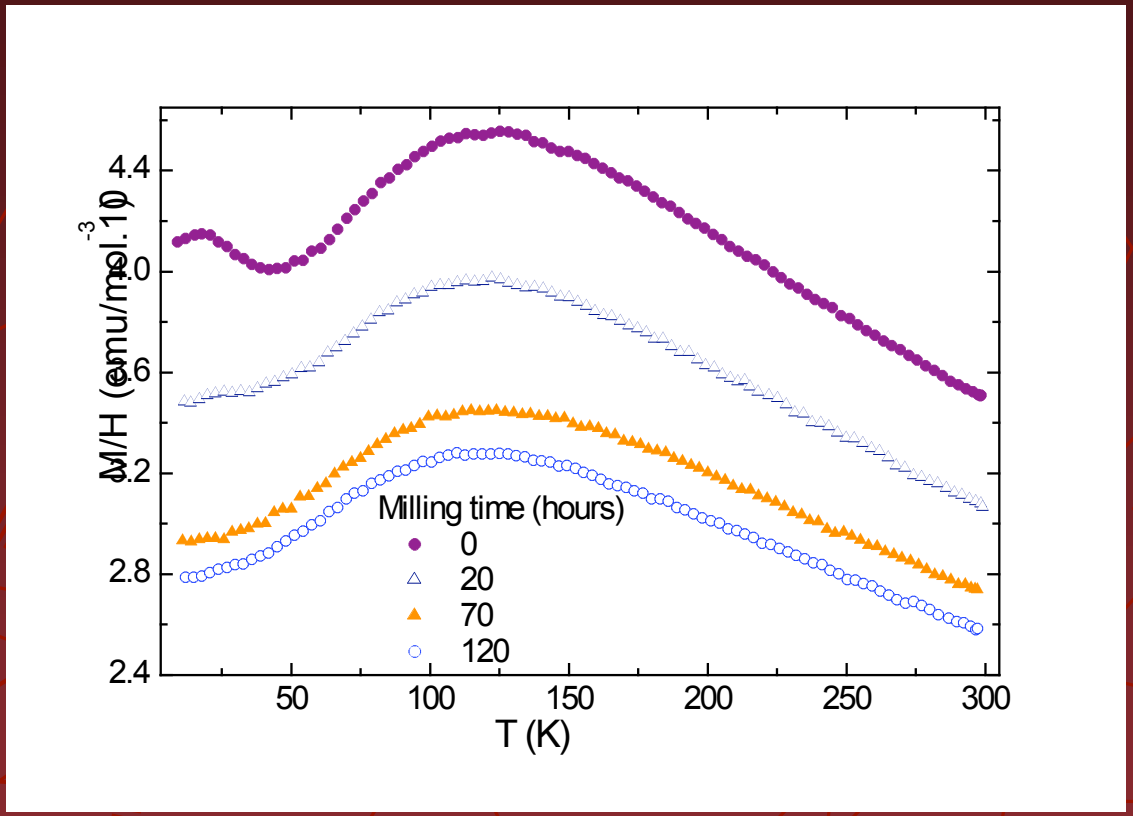
Milling time	r(Å)	σ^2	R-factor
0 hours	2.96(1)	0.0069(22)	0.045
20 hours	2.96(2)	0.0088(17)	0.037
70 hours	2.96(2)	0.0105(17)	0.034
120 hours	2.96(3)	0.0115(21)	0.051

Disorder parameters:



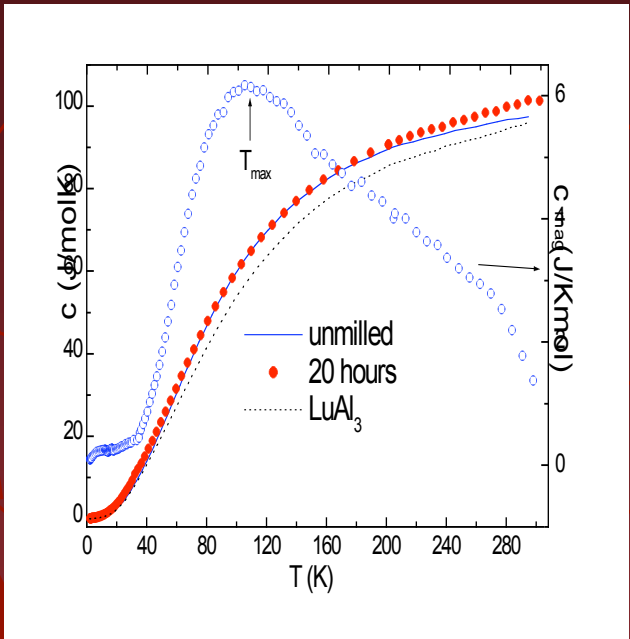
- Similar tendency of the lattice strain η (XRD) and Debye-Waller factor σ (EXAFS)
- Both parameters increase continuously

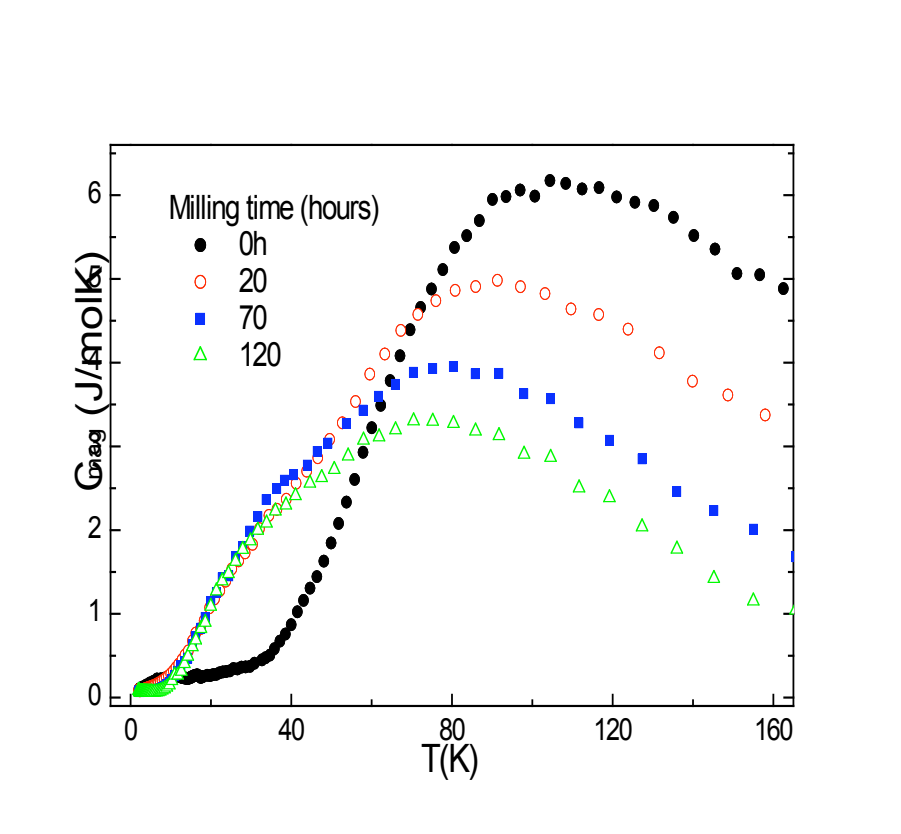
Susceptibility



With the increase of milling time the magnetic signal (susceptibility = M/H) becomes weaker towards the non-magnetic state

Specific Heat

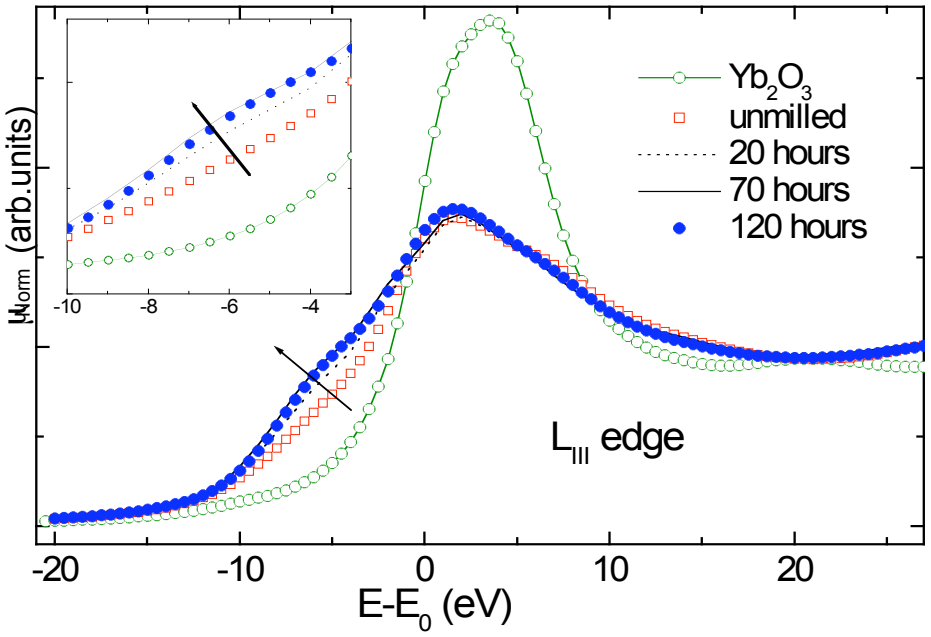




We have produced non-magnetic isostructural LuAl3 to obtain the magnetic Cp

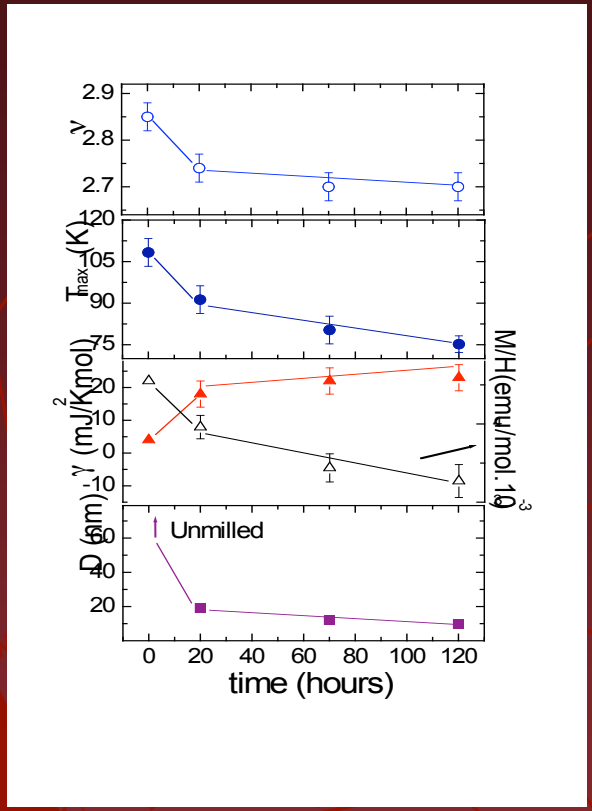
With the increase of milling time the magnetic signal becomes weaker towards the non-magnetic state!

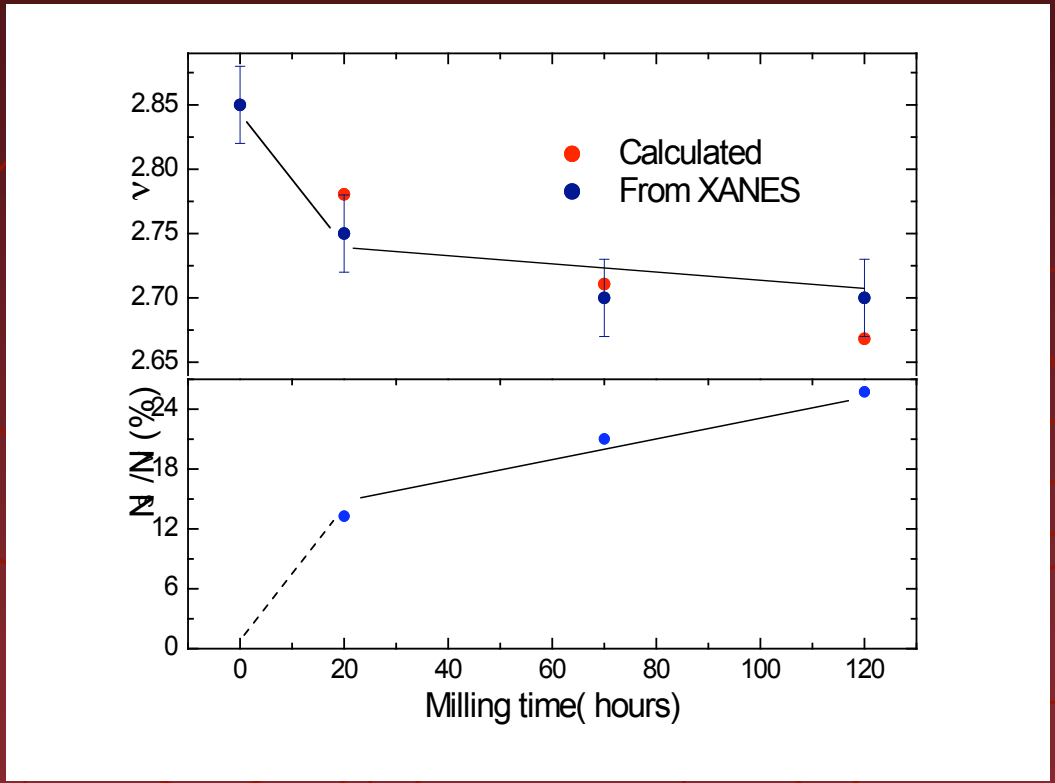
Electronic state (XANES)



The XANES signal reveals clearly a change in the electronic configuration, with a modification of the valence

Electronic parameters:





The abrupt change in size is followed by electronic parameters, in contrast to the continuous modification of disorder

Conclusion

Our results indicate that the driving parameter is the reduction of the size of the particles leading to an increase of the surface/volume ratio and to
the divalent contribution of the Yb atoms on the surface.

Neutrons & Nano

- Sociedad Española de Tecnicas de Neutrones (SETN): Users (> 100)
- Participation in the ILL and the Rutherford-Appleton Lab (ISIS) (approx 3%)
- Instruments CRG: D1B & D15 (ILL)