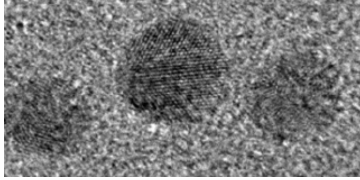
New perspectives in Rare Earth metallic nanoparticles: Spin glass phases, Crystal fields and Kondo decoherence

Luis Fernández Barquín

Dept. CITIMAC, Universidad de Cantabria (Santander, SPAIN)

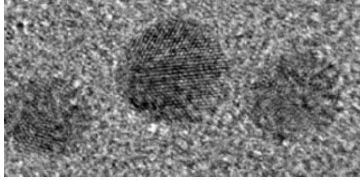
barquinl@unican.es

Club Español de Magnetismo



Outline

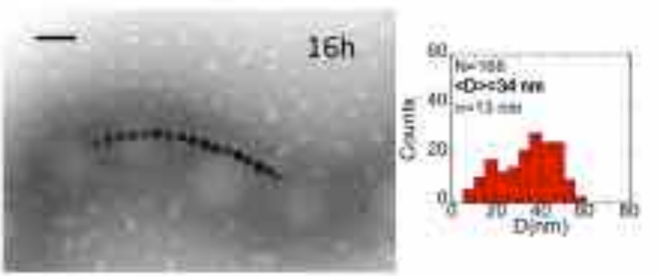
- ► I. Context: 3d-4f-Nanoparticles
- II. RX_2 Nanoparticles
- III. $YbAl_3$ NPs: Intro + Structure + Resistivity



I. Context: Nanoparticles (3d/4f-compounds)

Interest: Size effects, Surface Effects, Interaction & Core (disorder)-Shell

Applications: Biomedicine, Fe-oxides (Review, QA Pankhurst et al., J Phys D (2003)) + Waste Management…



3d

GMR

Ultrasoft

Magnetite/Maghemite:

40000 articles!

Superparamagnetic

Fe-Oxides: P. Bender et al., Sci Rep (2017); L. Marcano et al., Nanoscale(2018), ...

4f

$GdAl_2$: Zhou et al., PRL (1994)

$YbAl_3$, $YbNi_2$: D. P. Rojas et al., PRB (2008); C. Echevarria-Bonet JPCM (2018); D. P. Rojas SSC (2016) + JMMM (2018).

$TbCu_2$: C. Echevarria et al., PRB Rapid (2013); JPCM (2015), M de la Fuente et al., J. Nano Res (2017).

$TbAl_2$: D. P. Rojas et al., Mat Res Ex (2015)

NanoMag

SEVENTH FRAMEWORK PROGRAMME

SCIENTIFIC REPORTS

OPEN

Structural and magnetic properties of multi-core nanoparticles analysed using a generalised numerical inversion method

Received: 13 December 2016
Accepted: 06 March 2017
Published: 11 April 2017

P. Bender[1], L. K. Bogart[2], O. Posth[3], W. Szczerba[4,5], S. E. Rogers[6], A. Castro[7], L. Nilsson[7,8], L. J. Zeng[9], A. Sugunan[10], J. Sommertune[10], A. Fornara[10], D. González-Alonso[1], L. Fernández Barquín[1] & C. Johansson[11]

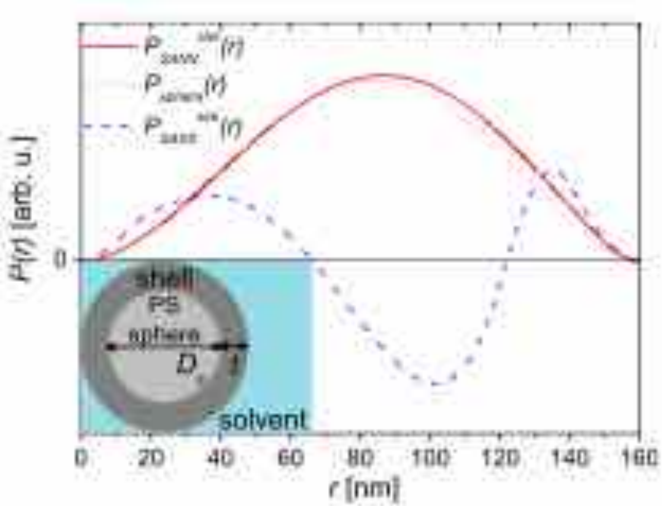


Figure 2. Simulated PDDFs. Comparison of simulated PDDFs for small angle scattering via neutrons ($P^{sim}_{SANS}(r)$) and X-rays ($P^{sim}_{SAXS}(r)$) from a 120 nm poly(styrene) sphere with a 20 nm thick shell embedded in water, as well as the calculated profile of a homogeneous sphere with $D = 160$ nm (equation 3). Assumed scattering length densities for neutrons and X-rays are provided in Table 1.

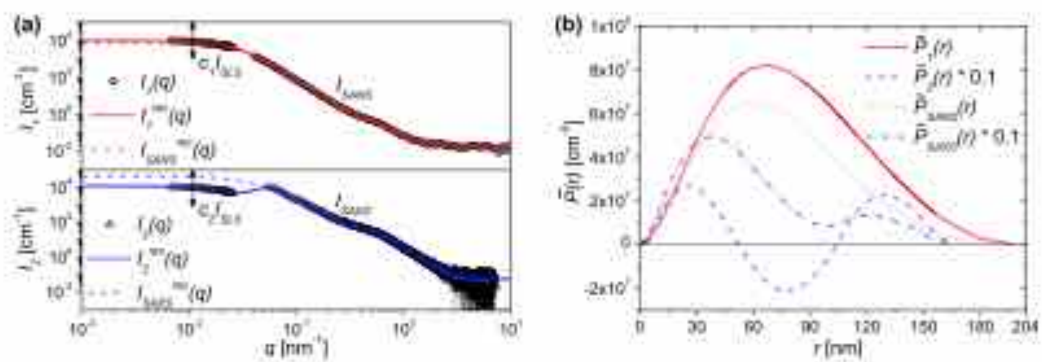
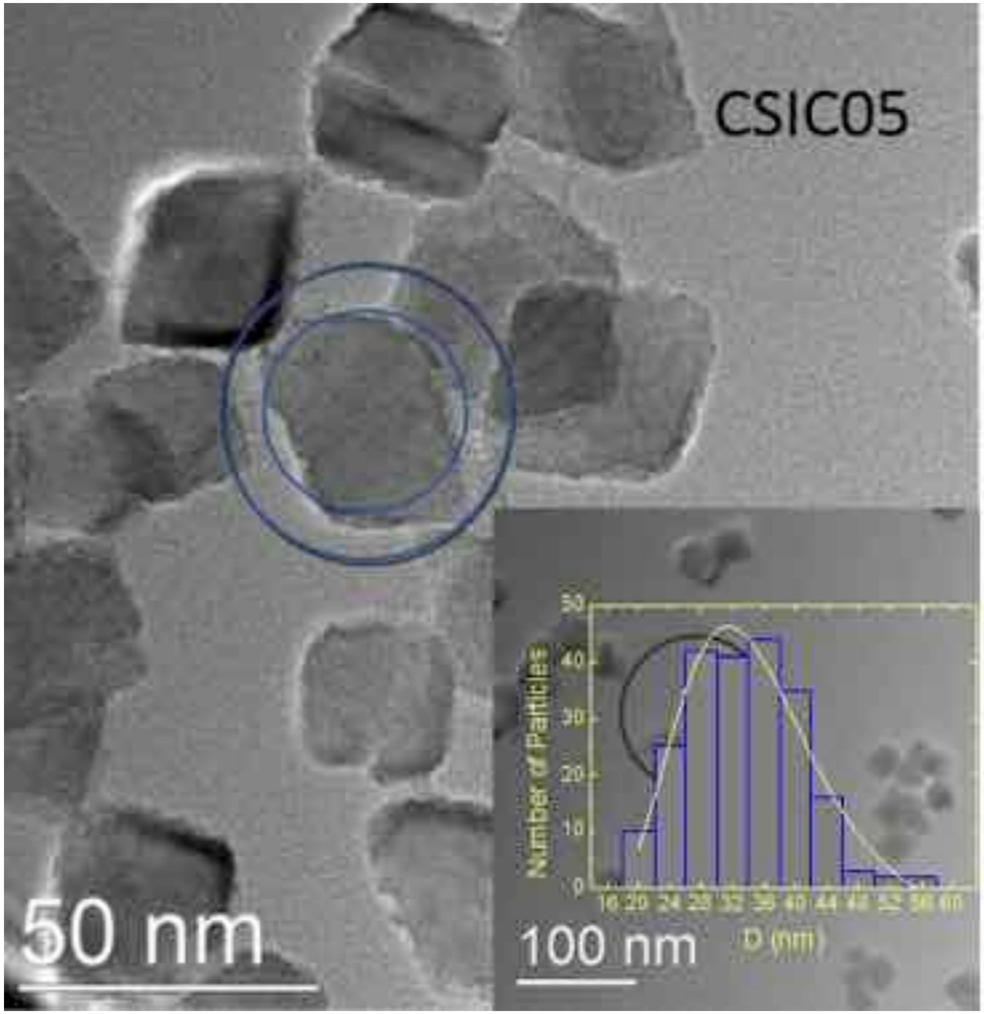


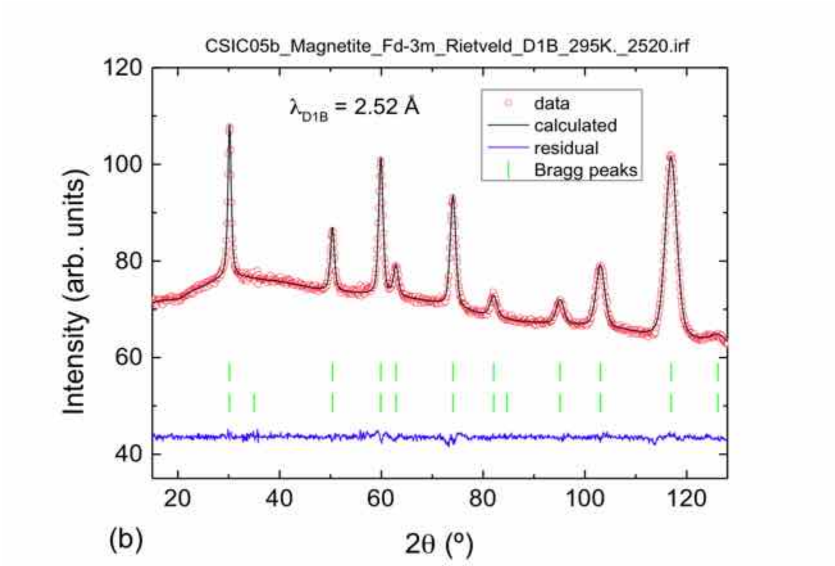
Figure 3. Results of the structural characterisation of the multi-core particles via SANS, SAXS and SLS. (a) The experimentally measured scattering intensities $I_{SANS}(q)$, $I_{SAXS}(q)$ and $I_{SLS}(q)$. The static light scattering intensity was scaled by c_1 and c_2, respectively. The reconstructed curves $I_1^{rec}(q)$, $I_2^{rec}(q)$, $I_{SANS}^{rec}(q)$ and $I_{SAXS}^{rec}(q)$ were calculated for the distributions $\bar{P}_1(r)$, $\bar{P}_2(r)$, $\bar{P}_{SANS}(r)$ and $\bar{P}_{SAXS}(r)$ from Fig. 3(b). (b) The pair distance distribution functions $\bar{P}_1(r)$, $\bar{P}_2(r)$, $\bar{P}_{SANS}(r)$ and $\bar{P}_{SAXS}(r)$ determined by an indirect Fourier transform of $I_1(q)$, $I_2(q)$, $I_{SANS}(q)$ and $I_{SAXS}(q)$.

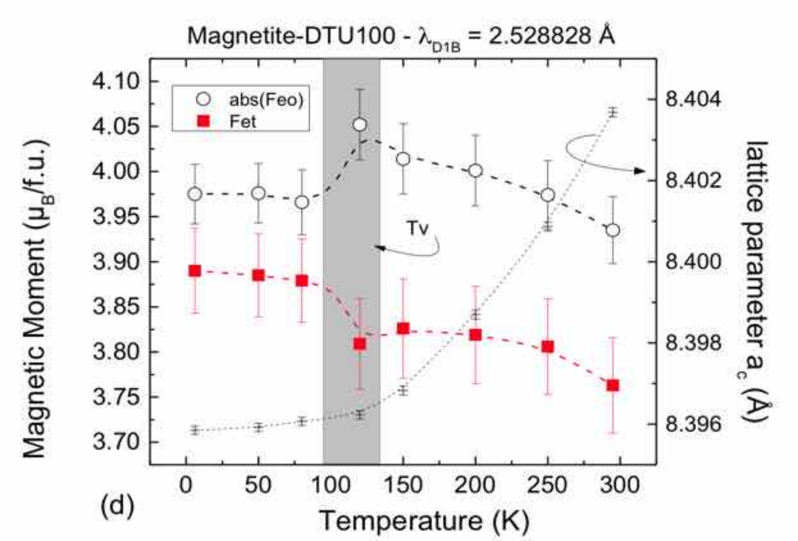
CEMAG, Gijón 2018

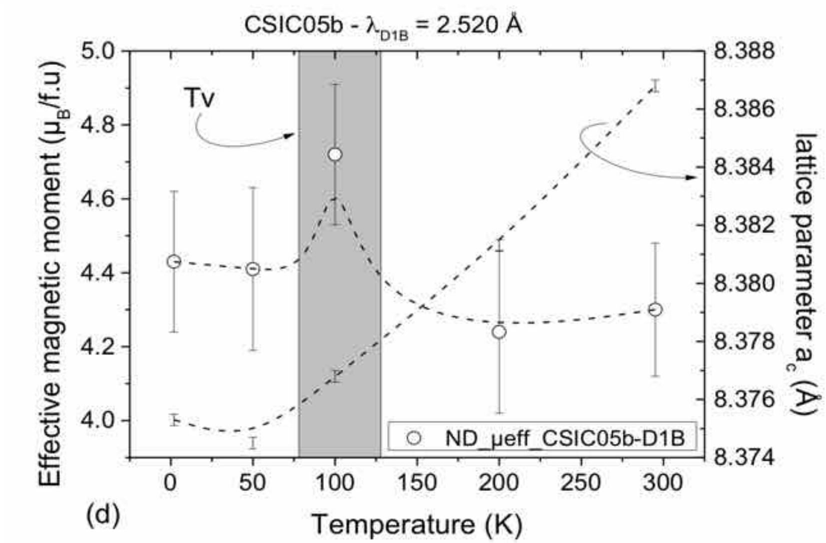
Fe-oxide Nanoparticles CSIC05
(Puerto Morales)



Neutrons revealing Verwey (Inst. Laue-Langevin, Grenoble)



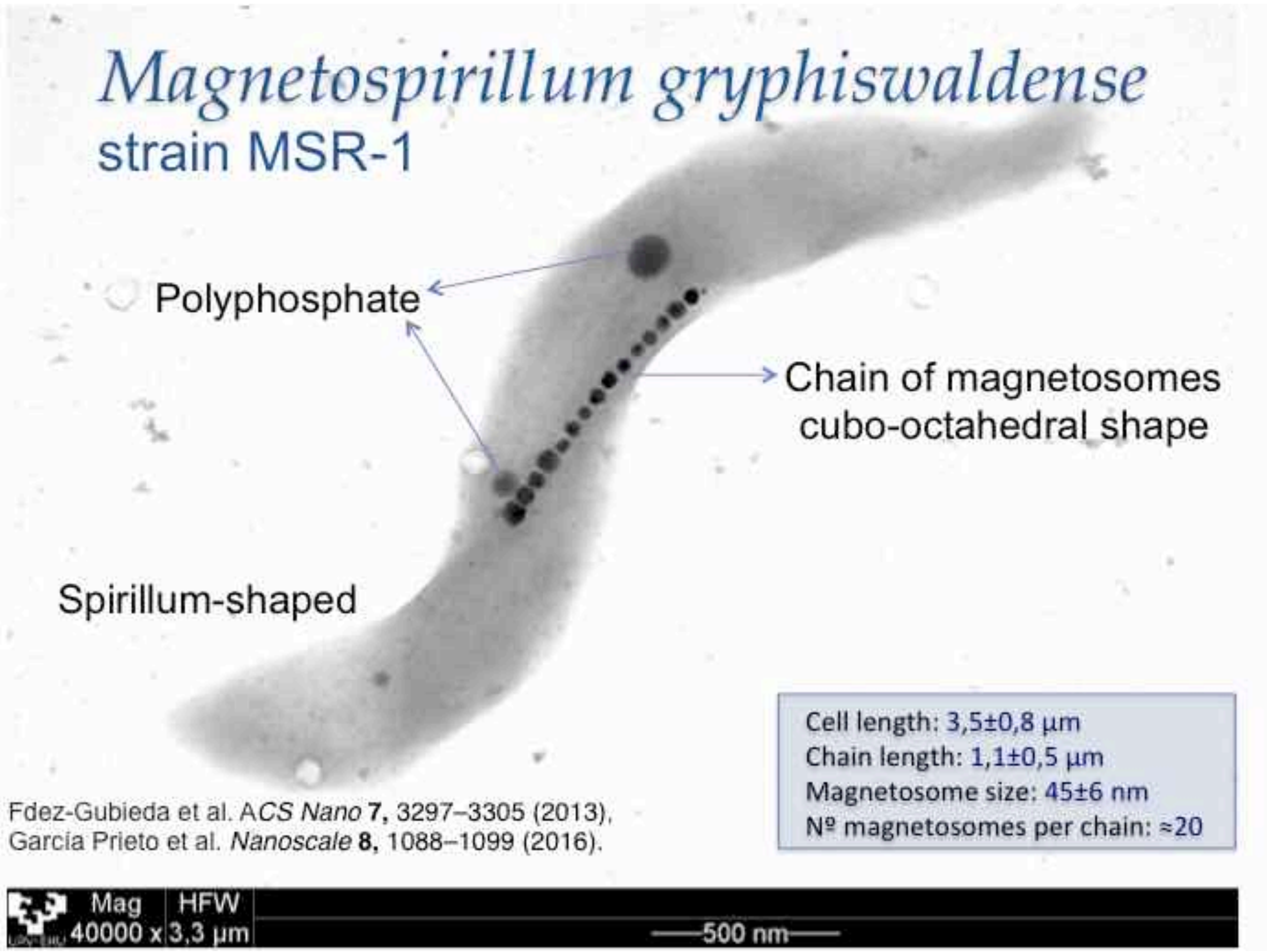


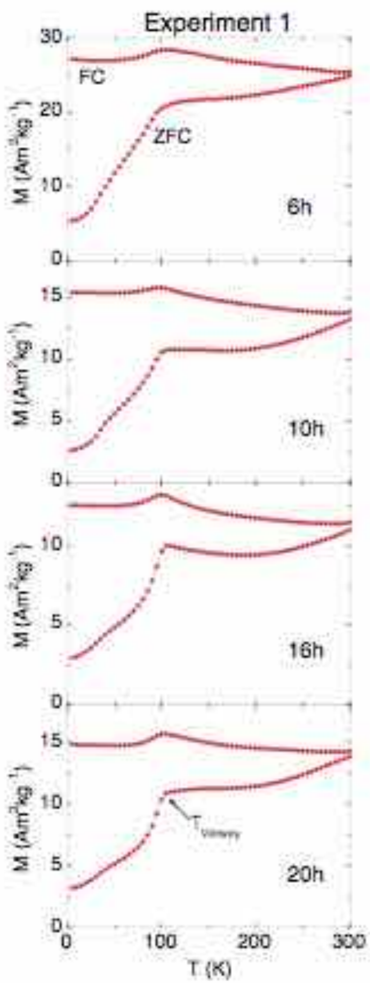


SEVENTH FRAMEWORK PROGRAMME

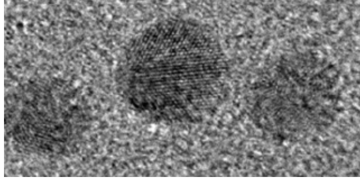
CEMAG, Gijón 2018

Magnetotactic Bacteria (UPV/EHU)
Alicia Muela, M.L. Fdez-Gubieda,...





I. Context: Nanoparticles (3d/4f-compounds)



Interest: Size effects, Surface Effects, Interaction & Core (Disorder)-Shell
Applications: Biomedicine, Fe-oxides (Review, QA Pankhurst et al., J Phys D (2003)) + Waste Management...

GMR
Ultrasoft

$GdAl_2$: Zhou et al., PRL (1994)

3d

4f

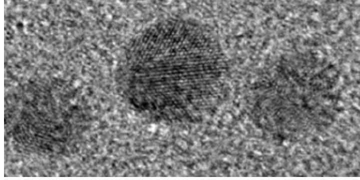
$YbAl_3$, $YbNi_2$: D. P. Rojas et al., PRB (2008); C. Echevarria-Bonet JPCM (2018); D. P. Rojas SSC (2016). D. P. Rojas JMMM (2018).

Magnetite/Maghemite: 40000 articles!
Superparamagnetic

Fe-Oxides: P. Bender et al., Sci Rep (2017); L. Marcano et al., Nanoscale(2018), ...

$TbCu_2$: C. Echevarria et al., PRB Rapid (2013); JPCM (2015), M de la Fuente et al., J. Nano Res (2017).

$TbAl_2$: D. P. Rojas et al., Mat Res Ex (2015)



Context: RE-NPs

Conventional MAGNETIC 4f-ALLOYS

- Binary Alloys (R=Tb, Nd,…, X=Al,Cu, ⋯): FM or AFM...RX_2

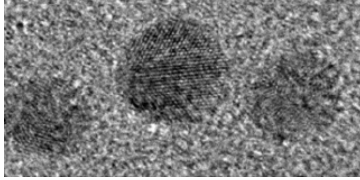
- Dilution
- Disorder
- Small record in nanoparticles
- Surfaces

➢ - Permanent Magnets

➢ - CEF influence

➢ - Spin glass

4f

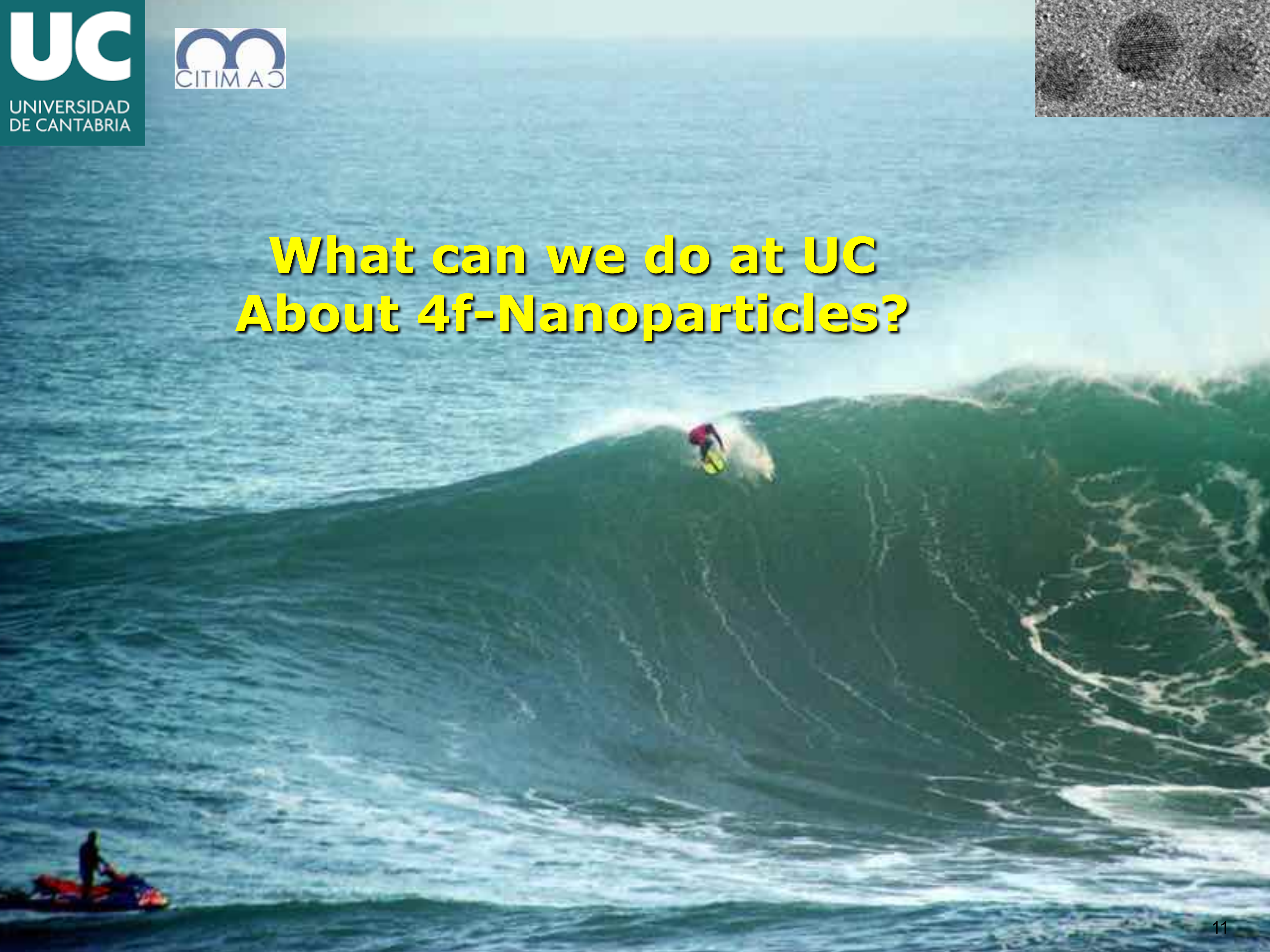


Context: RE-NPs

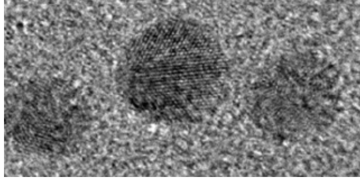
ANOMALOUS EFFECTS IN 4f- ALLOYS

- Unconventional behaviour in Yb, Ce, Sm or Eu alloys
- Strongly Correlated Electron Systems (SCES)
- Unconventional Physics
- Very scarce record in nanoparticles. Surfaces.

- ➢ Kondo effect
- ➢ Heavy fermions
- ➢ Intermediate valence



What can we do at UC About 4f-Nanoparticles?



Outline

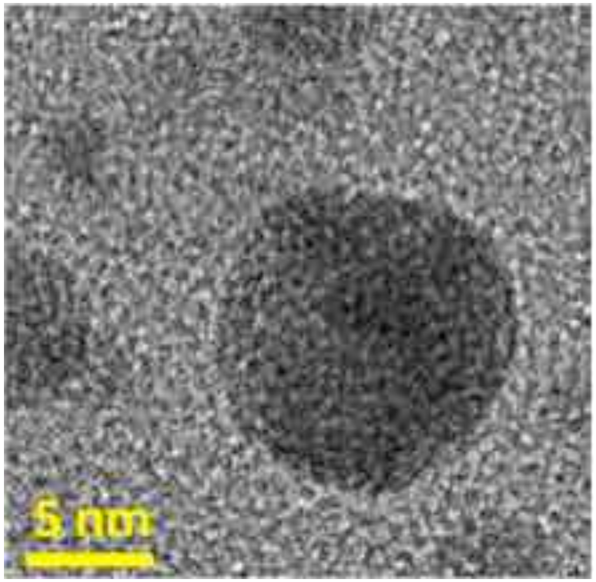
- I. Context: 3d-4f-Nanoparticles
- II. RX_2 Nanoparticles
- III. $YbAl_3$ NPs: Intro + Structure + Resistivity

UC
UNIVERSIDAD
DE CANTABRIA

CITIMAC

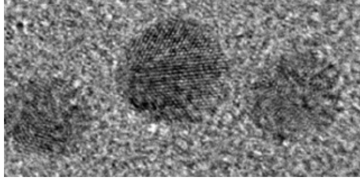
Synthesis of 4f-RX_2 NPs

High-Energy Inert-atmosphere Milling
(CW, ZrO_2)



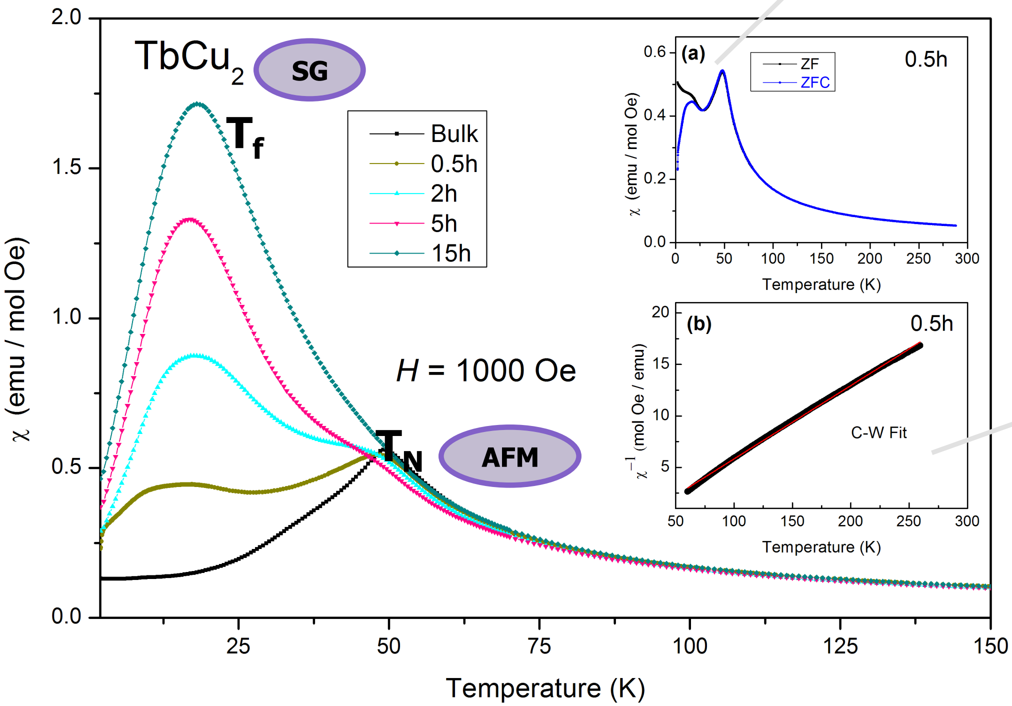
- Mass production of Metallic Nanoparticles
- Decent size distribution
- Presence of oxides (Controlled).
- Cost effective. Re-scalable (technology)

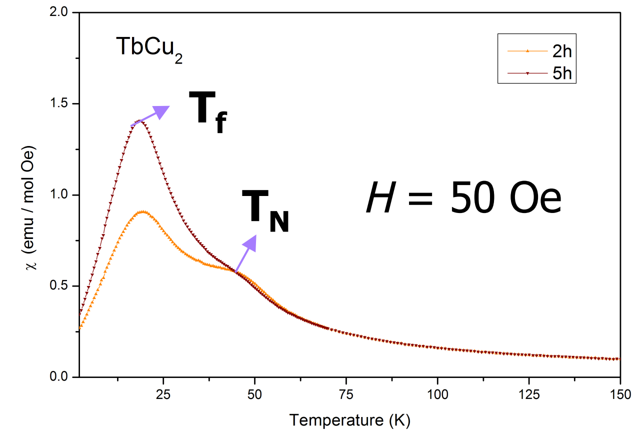
Nano-RX_2, R = Tb, X = Cu



▶ Susceptibility-DC:

ZFC- FC: Irreversibility
→ magnetic disorder



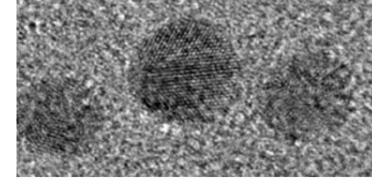


Tb^{3+} (J = 6) μ_{eff} = 9.72 μ_B

t = 0.5 h → μ_{eff} = 10.56(2) μ_B
θ_p = 18.2(3) K

***t* (h)**	**D (nm)**	**T_N (K)**	**T_f (K)**
Bulk	--	49.1(1)	--
0.5	13(1)	48.2(1)	16.7(1)
2	8(1)	47.4(1)	17.5(1)
5	7(1)	47.1(1)	16.4(1)
15	6(1)	--	18.4(1)

increase *t* :
AFM → SG, ↓ T_N
→ ↑ T_f



Disorder in $TbCu_2$

▶ AC-susceptibility:

$z\nu$ = 5.7

$\tau_0 = 1.3 \times 10^{-5}$ s

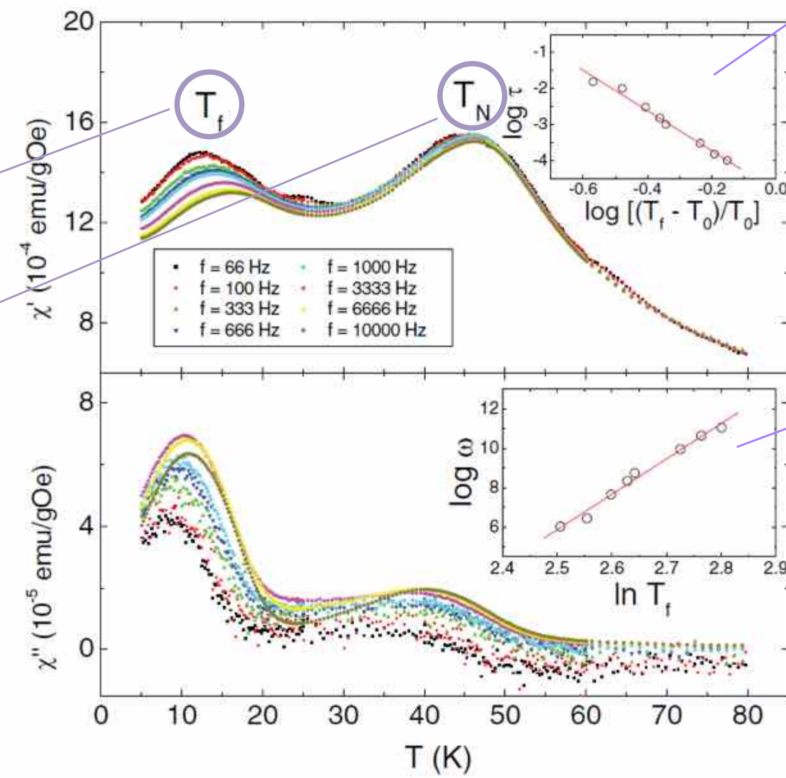
D = 9 nm

SG

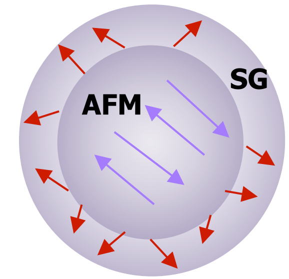
$T_f \approx 10$ K

AFM

$T_N \approx 47$ K



δ = 0.057



core-shell

Core → AFM
Shell → SG

Nps $TbCu_2$

Super-AFM

Coexistence of AFM+SG…as in bulk, for example, multiferroic PbFeNbO, PRL (2010)

PRL **105**, 257202 (2010) PHYSICAL REVIEW LETTERS week ending 17 DECEMBER 2010

Coexistence of Antiferromagnetic and Spin Cluster Glass Order in the Magnetoelectric Relaxor Multiferroic $PbFe_{0.5}Nb_{0.5}O_3$

W. Kleemann,* V. V. Shvartsman,† and P. Borisov‡

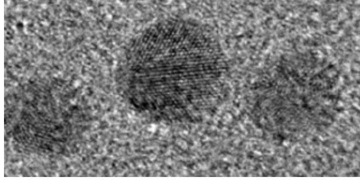
Angewandte Physik, Universität Duisburg-Essen, Lotharstrasse 1, D-47048 Duisburg, Germany

A. Kania

Institute of Physics, University of Silesia, PL-40-007 Katowice, Poland

(Received 29 July 2010; published 13 December 2010)

C. Echevarria-Bonet et al., PRB 87, 180407(R) (2013)



Anisotropy, $TbCu_2$

▶ M(H):

Metamagnetic transition → typical AFM

mechanism spin – flip sublattice AFM → FM

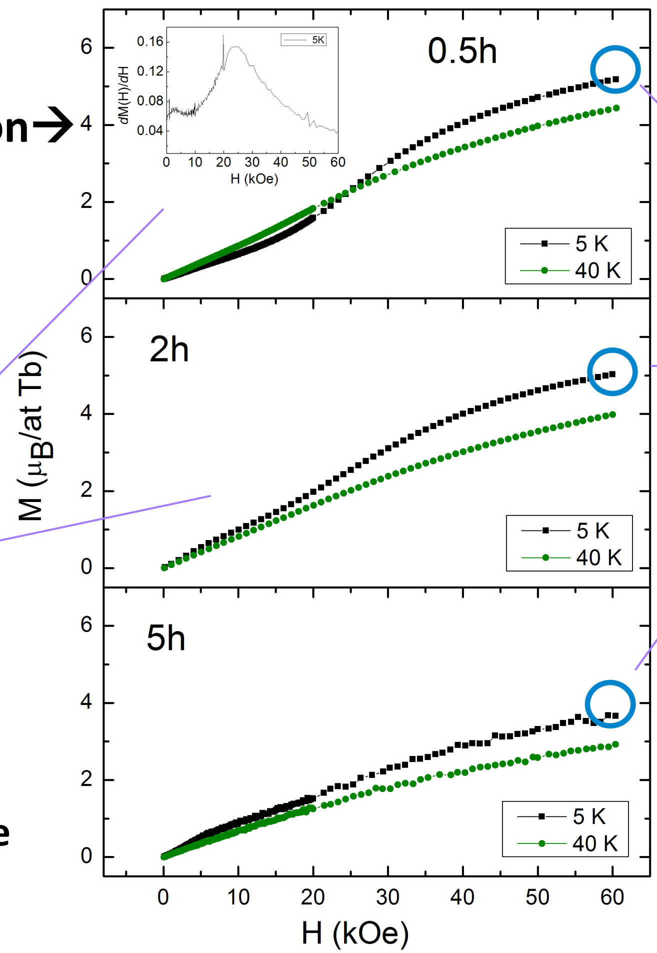
H_{SF} = 19 kOe Bulk

H_{SF} = 24 kOe (D = 13 nm)

H_{SF} = 23 kOe (D = 8 nm)

SAFM + SG

Size decrease → AFM core ↓, disordered shell ↑



No magnetic saturation ~ 8.8 m_B Bulk

bulk CEF prevents saturation

5 K

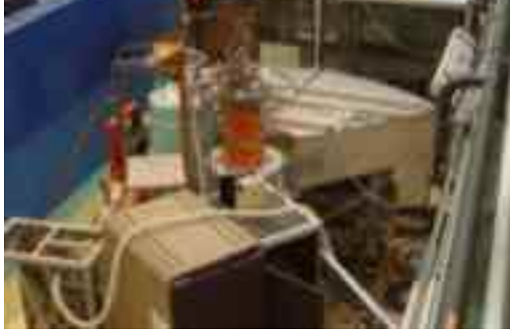
5.2 m_B/at Tb (D = 13 nm)

5.0 m_B/at Tb (D = 8 nm)

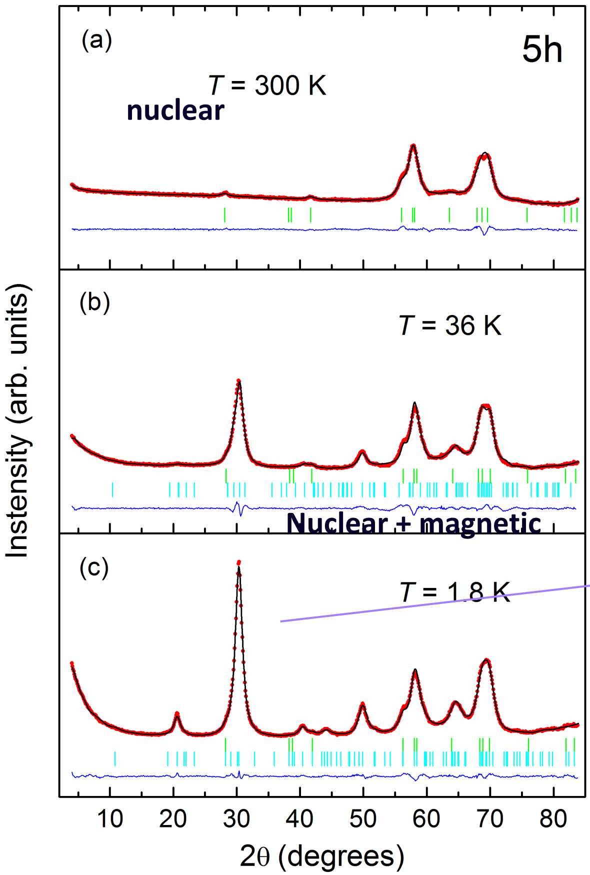
3.8 m_B/at Tb (D = 7 nm)

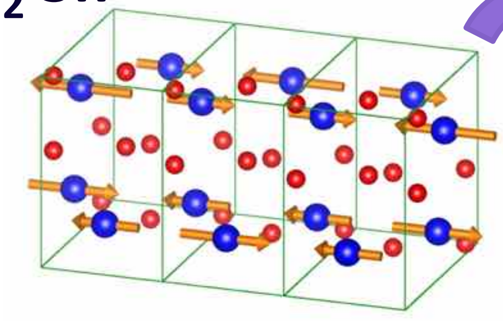
M_s decreasing size → Shell moments with high anisotropy

Neutron Diffraction (LLB G4.1), F. Damay



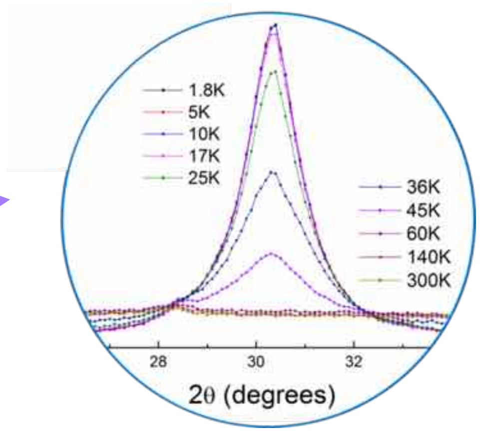
▶ Magnetic structure $TbCu_2$ 5h





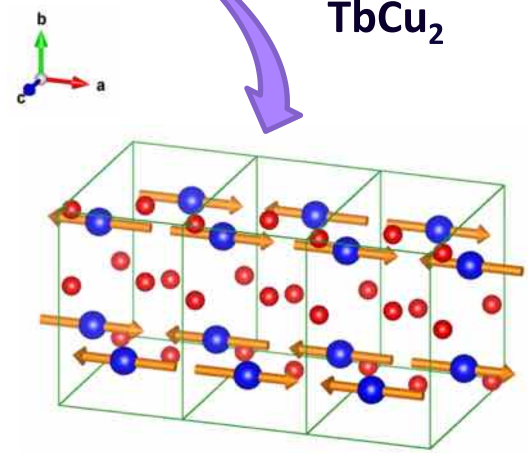
D ≈ 8 nm

T = 36 K



Sima et al, JMMM (1986)

Structure $TbCu_2$

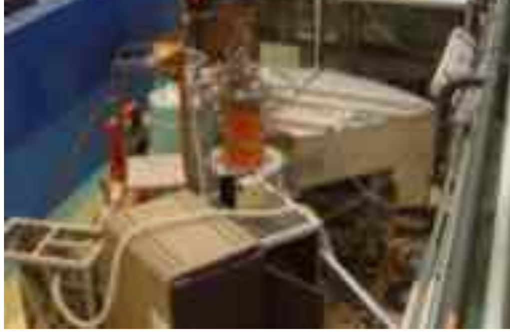


T = 1.8 K

AFM commensurate

Propagation vectors { (0,0,0) (1/3,0,0)

High CEF anisotropy

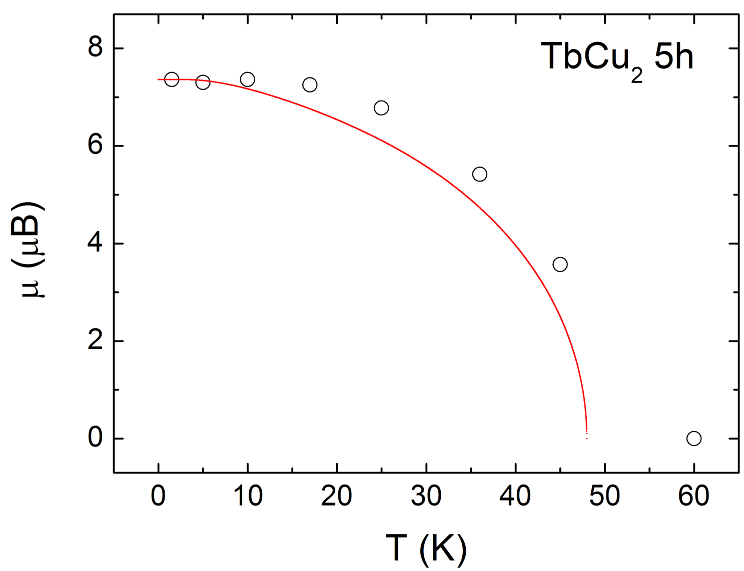


Neutron diffraction

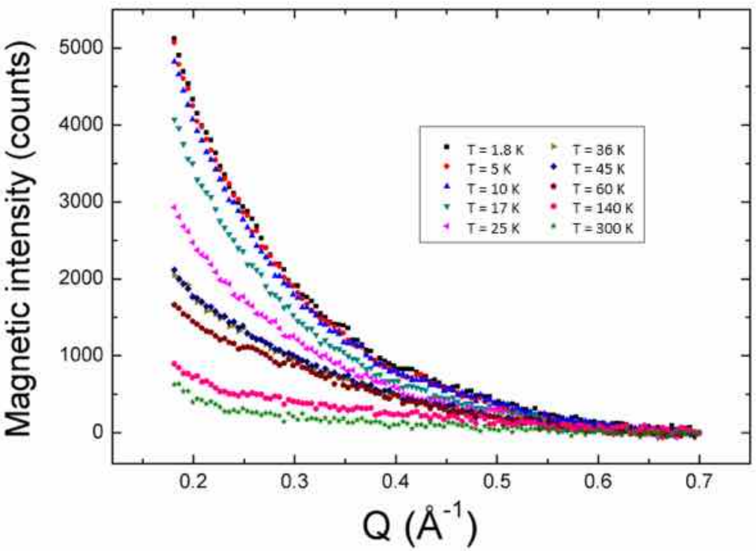
▶ Magnetic moment evolution $TbCu_2$ 5h

5h $\mu_{Tb^{3+}}$ = 7.3(5) μ_B ➡ **reduction μ ~ 20% → disordered moments**

Bulk $\mu_{Tb^{3+}}$ = 8.8 μ_B



Brillouin J = 6



Low T nanoparticle correlation

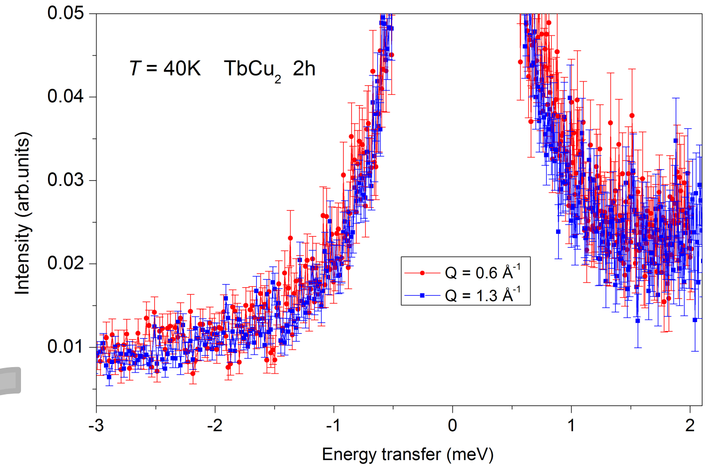
UNIVERSIDAD DE CANTABRIA

CITIMAC

Inelastic Neutron Scattering (INS), B. Fåk (Inst Laue-Langevin)

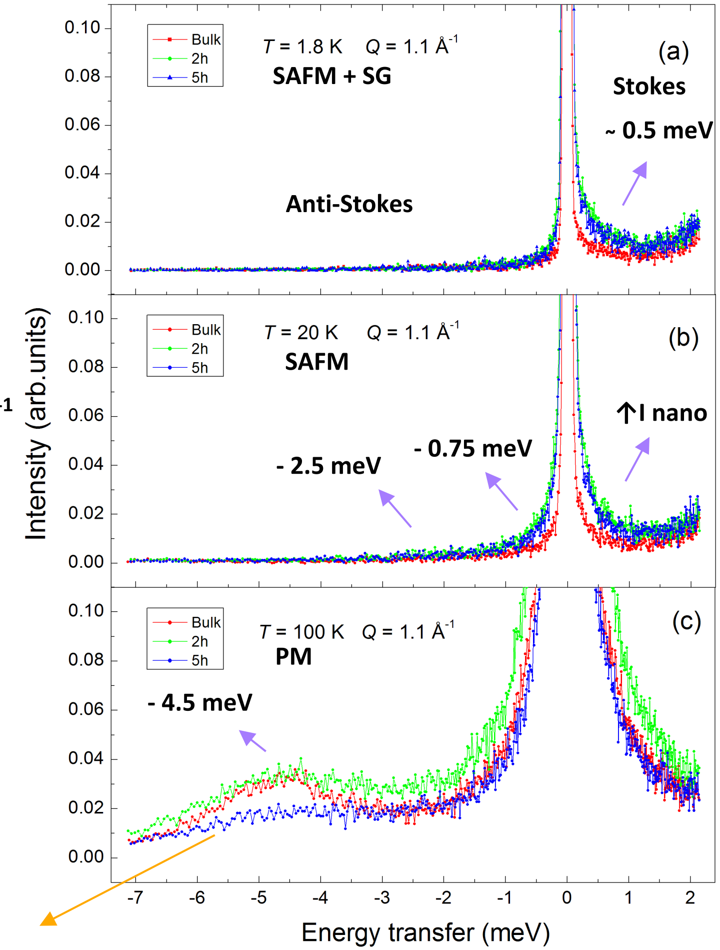
► Experiment IN6: $TbCu_2$ Bulk, 2h y 5h

T = 1.8, 8, 20, 40, 100 y 300 K



λ = 5.1 Å

$0.6\ Å^{-1} \leq Q \leq 1.3\ Å^{-1}$



I(Q) Vs E : feeble ↓I when ↑Q → magnetic + Incoherent phonon contribution

Lower Intensity in nano-$TbCu_2$ → less defined multiplets

Distributions of CEF

I ↑ when ↑T, CEF excitations

SANS
(D. Alba, RAL-ISIS)

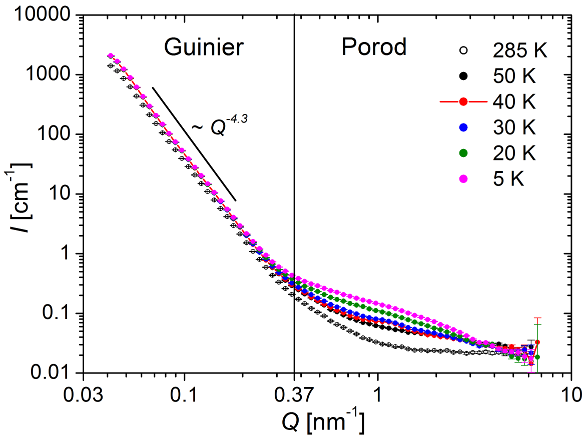
- **RAL-ISIS: SANS2D, $TbCu_2$ 5h**

Guinier zone:

I (Q) independent of T→ Guinier (low Q)

↓

Nuclear: NP's spherical, pores



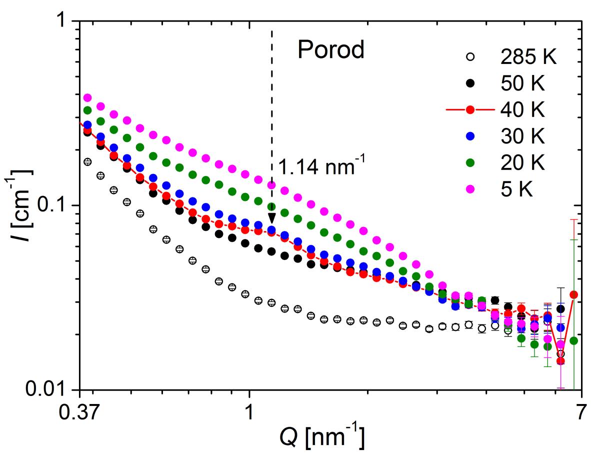
Porod Zone:

I (Q) varies with T→ Porod (high Q)

↓

Magnetic contribution

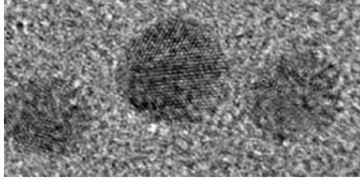
T = 40 K, Peak Q~1.14 nm^{-1}



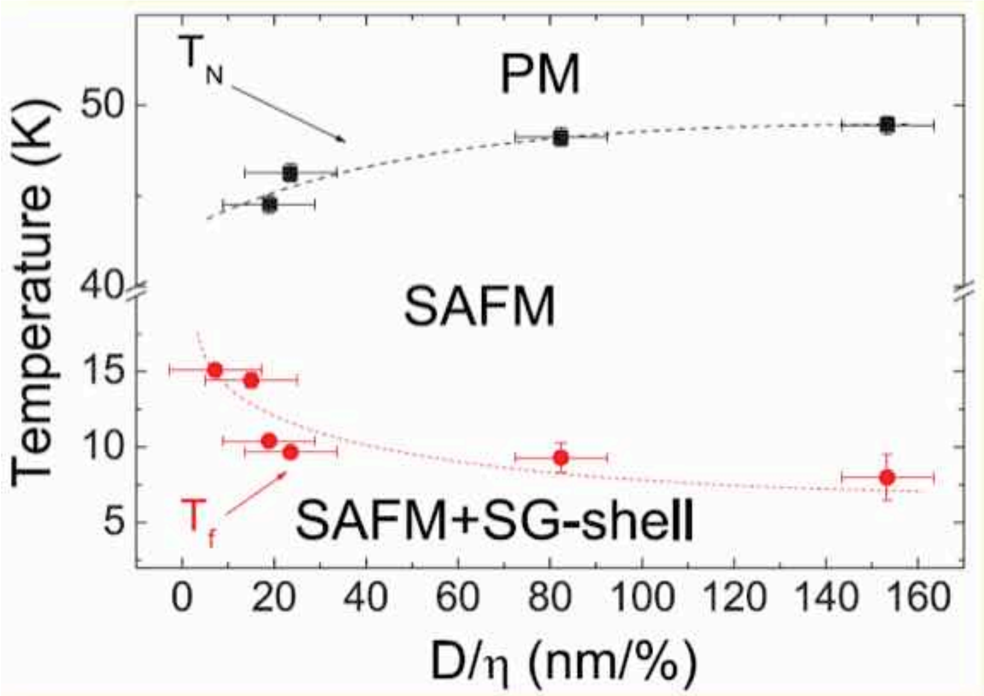
Magnetic Peak (open):
- Correlation of neighbouring MNPs, chains?

2.- helicoidal→Tb Bulk?

$TbCu_2$ phase diagram



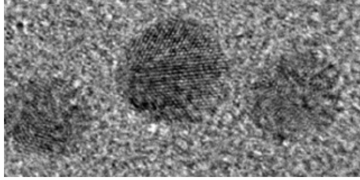
- Progressive variation of magnetic disorder + SAFM
- High anisotropy (SG influence)
- Variation of CEF levels due to disorder
- Disorder is crucial



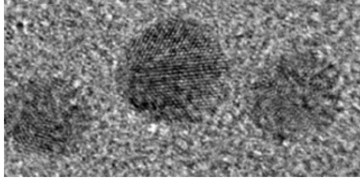
C. Echevarria-Bonet et al., JPCM (2015)

Work in$TbCu_{2NPs,}$ with oleic acid, (surfactant), seperating NPs….
see J. Nanopart. Res (2017)

Outline



- I. Context: 3d-4f-Nanoparticles
- II. RX_2 Nanoparticles
- **III. $YbAl_3$ NPs: Intro + Structure + Resistivity**



Context: Intermediate Valence

ANOMALOUS EFFECTS IN 4f- ALLOYS

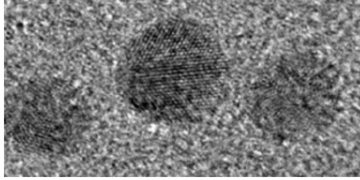
Electronic configurations are well defined when Fermi level and 4f-band are well separated. For an Yb ion:

If $E_F >> E_{4f}$ ⇨ Yb^{3+} ; $4f^{13}$ ⇨ localised magnetism.
If $E_F << E_{4f}$ ⇨ Yb^{2+} ; $4f^{14}$ ⇨ non-magnetic state.

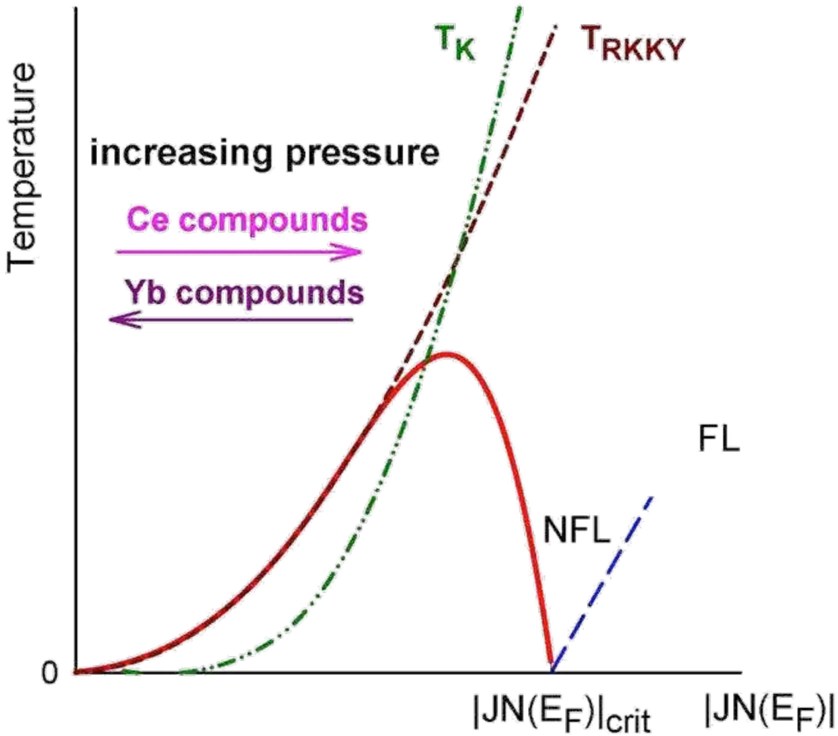
If $E_F \sim E_{4f}$ ⇨ hybridisation of states ⇨ Anomalous effects:

Heavy fermions.
Intermediate valence.
Kondo effect.

Different characteristics but same origin.



Context: Doniach diagram

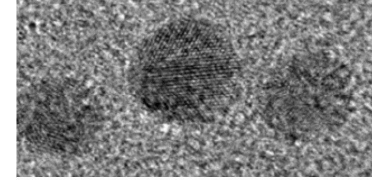


[S. Doniach, *Physica B* 91, 231 (1977)]

$$T_{RKKY} \propto \mathcal{J}^2 N(E_F)$$

$$T_K \propto e^{-\left(\frac{1}{\mathcal{J}N(E_F)}\right)}$$

- **Several behaviours:**
  - If $T_{RKKY} >> T_K$: the system is ordered magnetically.
  - If $T_K >> T_{RKKY}$: non-magnetic.
  - If $T_K < T_{RKKY}$: μ reduced by the screening of the Kondo effect, but the system can be ordered at a reduced T_C.
  - If $T_K \approx T_{RKKY}$: HF.
- QPT: NFL. Magnetic instability.



Context-$YbAl_3$

$YbAl_3$ bulk

cubic
susceptibility maximum: intermediate valence
valence: 2.86

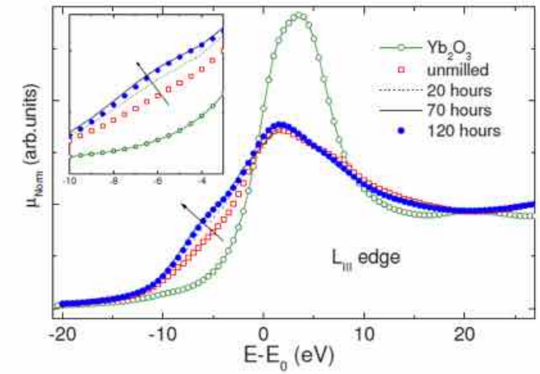
PHYSICAL REVIEW B 78, 094412 (2008)

Reduction of the Yb valence in $YbAl_3$ nanoparticles

D. P. Rojas, L. Fernández Barquín, J. I. Espeso, and J. Rodríguez Fernández
CITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain

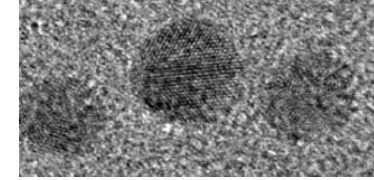
J. Chaboy
Instituto de Ciencia de Materiales de Aragón and Departamento de Física de la Materia Condensada, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain

(Received 29 November 2007; revised manuscript received 23 July 2008; published 16 September 2008)



- **XANES, BM25A ESRF & SPRING8 (Japan)**
- **Yb LIII. Change from Yb^{3+} to Yb^{2+} due to surface atoms**

Inspiring work/convesations:
Bulk, $YbAl_3$,$YbAl_2$,T. Görlach et al., PRB (2005); P. Schlottman PRB (2002);
YbAl3 nano, De et al., JAC (2017); B. Coqblin (privste…)

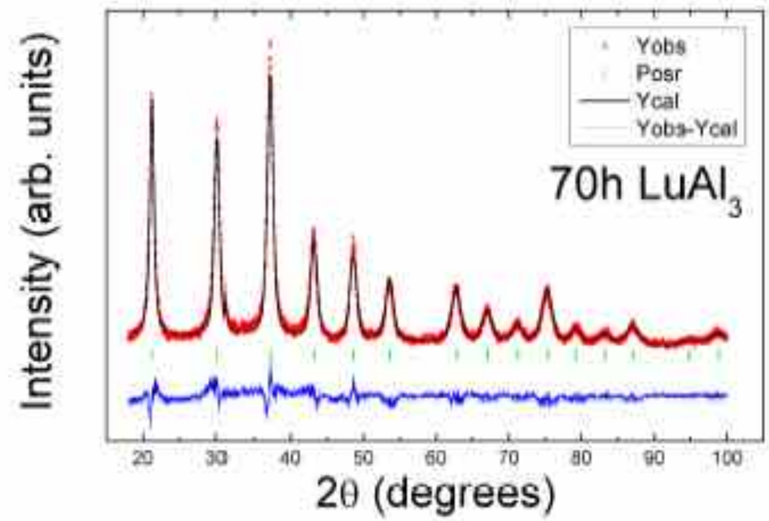


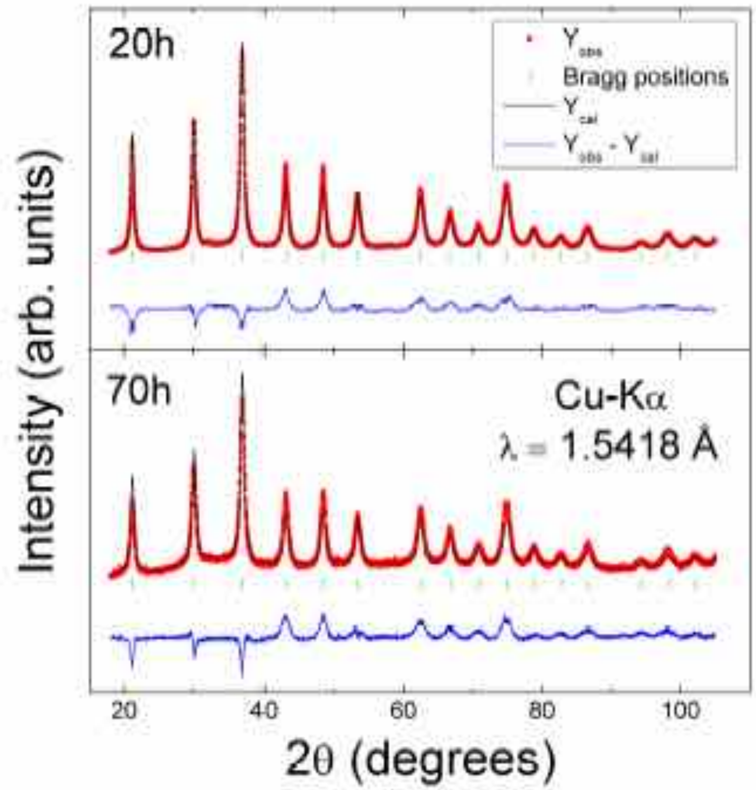
Nano-structure

Cubic *Pm-3m*

$YbAl_3$:

$LuAl_3$:



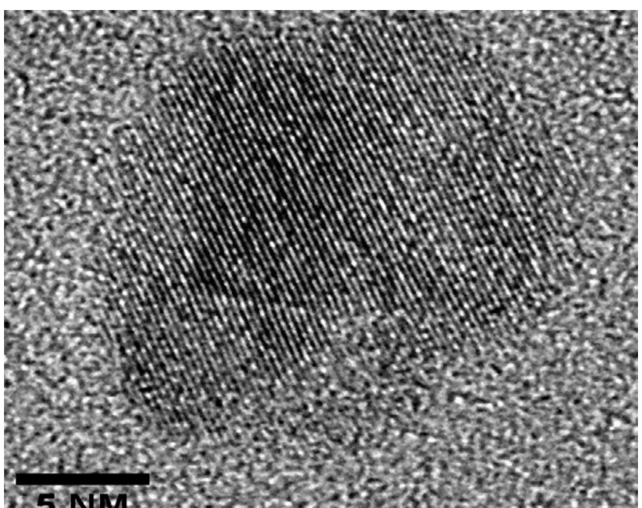


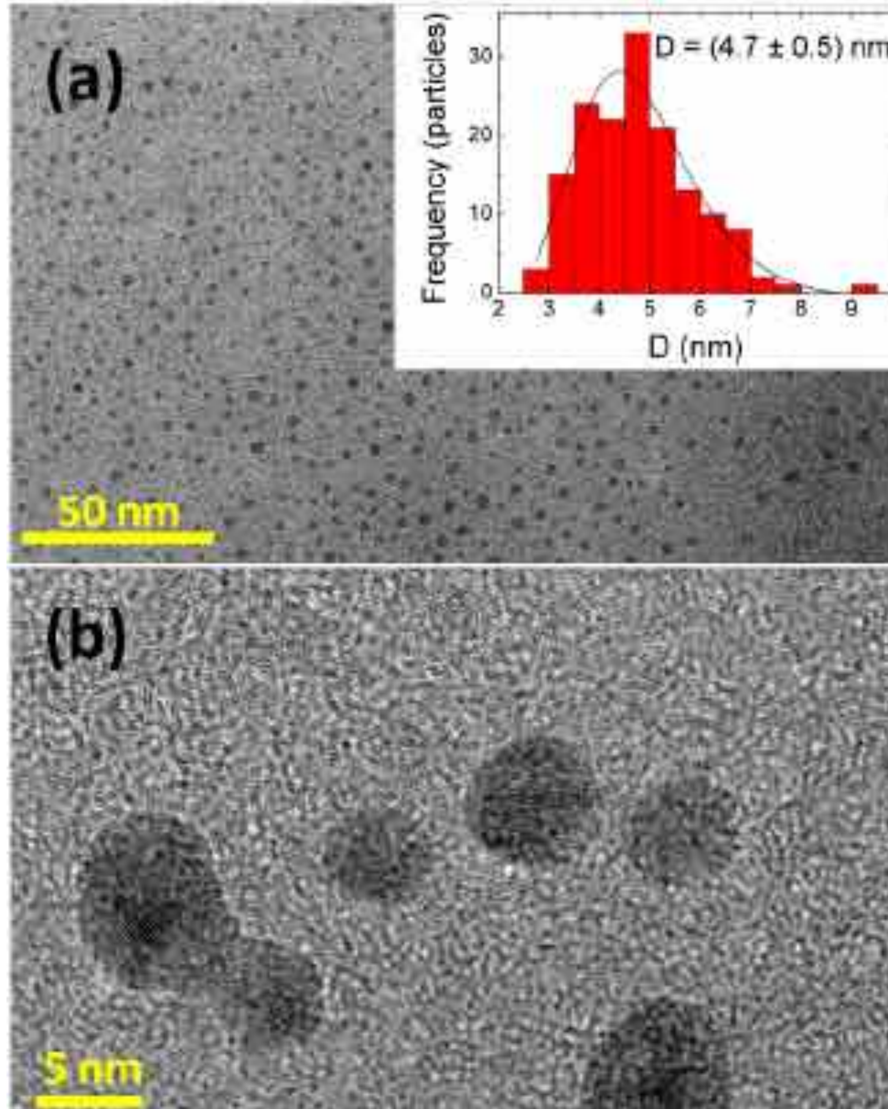
20h, D = 20 nm
70 h, D = 12 nm

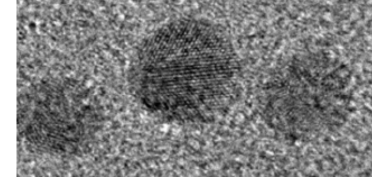
70 h, D = 11 nm

Structure (TEM at UC)

- The milling of $YbAl_3$ results in a decrease of particle size as it is also deduced from the TEM analysis.
- The size distribution of nanoparticles relatively narrow.

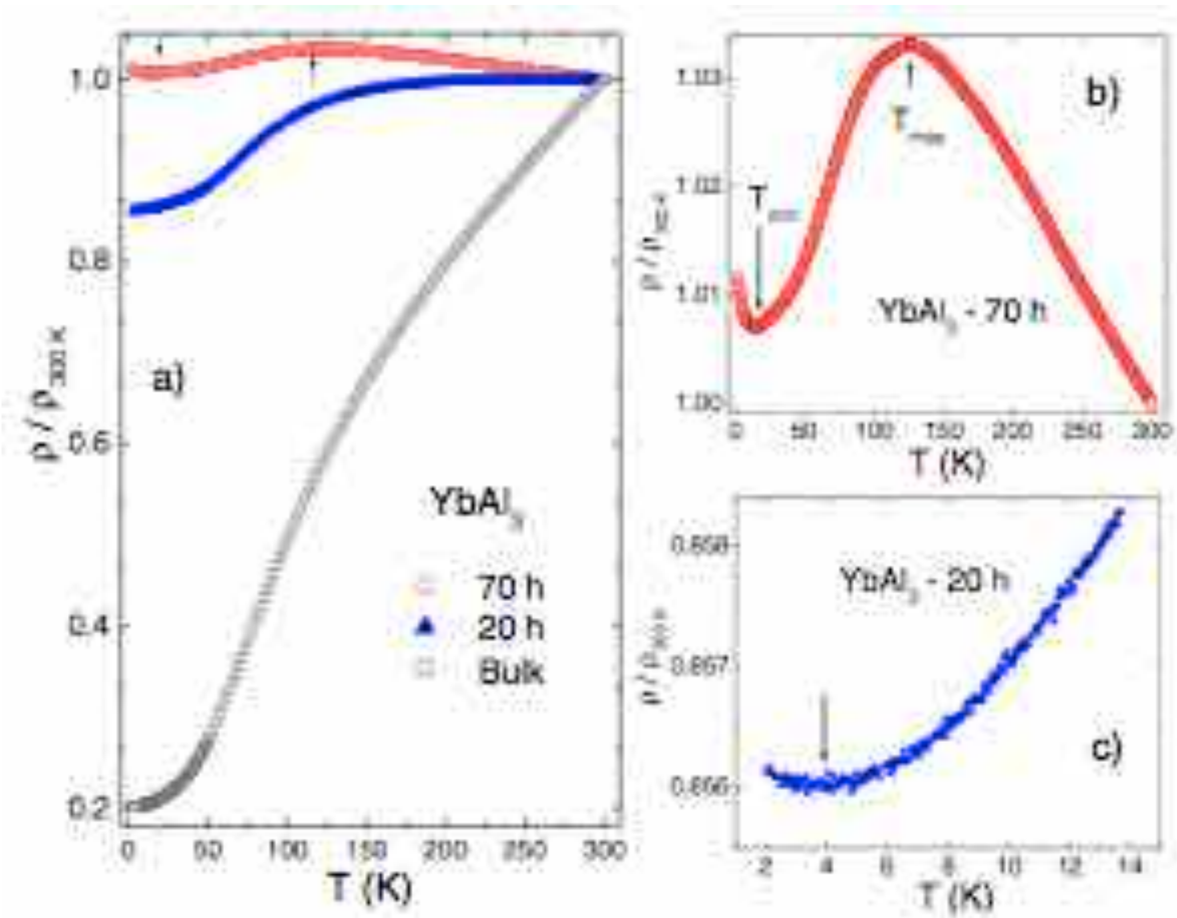


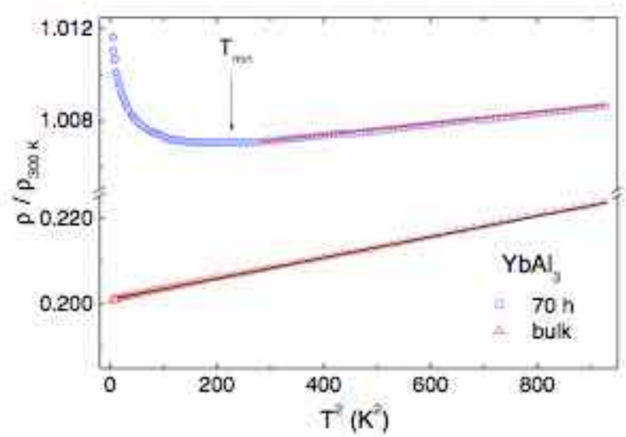




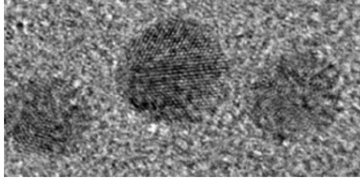
Resistivity in $YbAl_3$

Evolution from Fermi liquid to Kondo Minimum

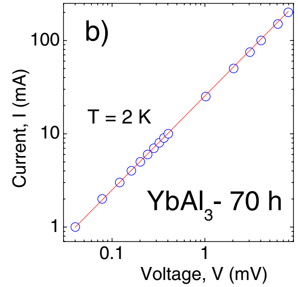




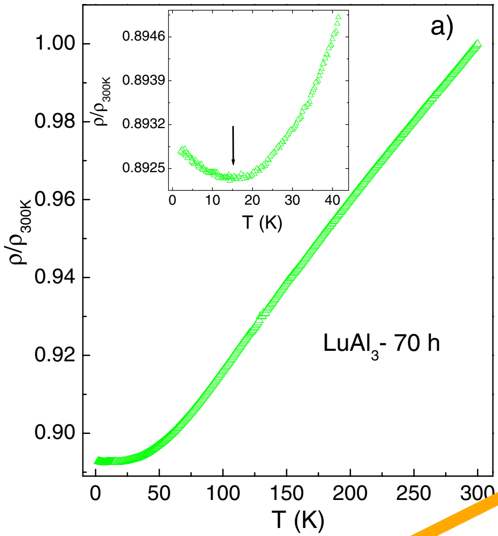
Resistivity-Analysis

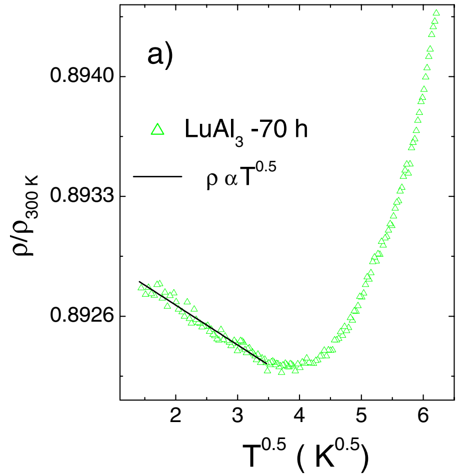


1.- Ohmic $YbAl_3$:



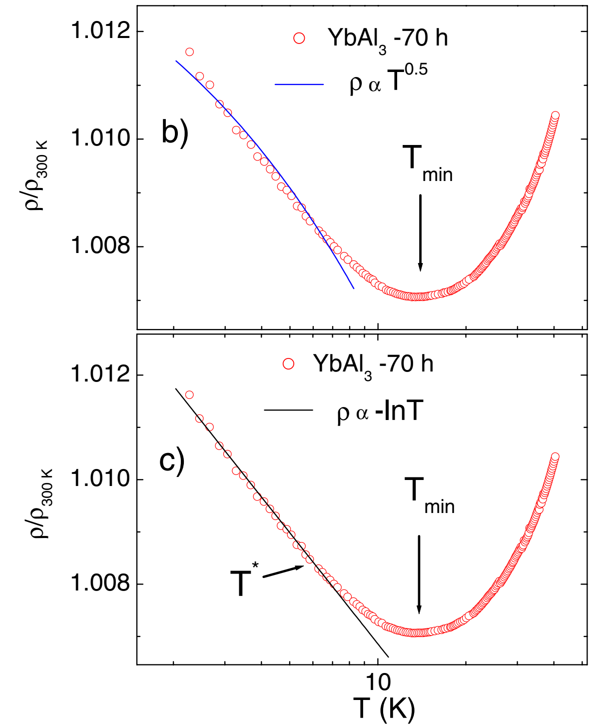
2.- QIE Effects in $LuAl_3$:



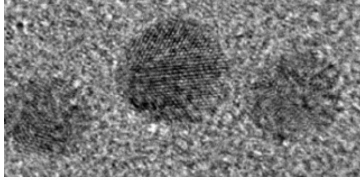


$$\Delta\sigma_{ee} = \frac{1.3}{\sqrt{2}}\frac{e^2}{2\pi\hbar}F_0\sqrt{\frac{2\pi k_B T}{\hbar D'}},$$

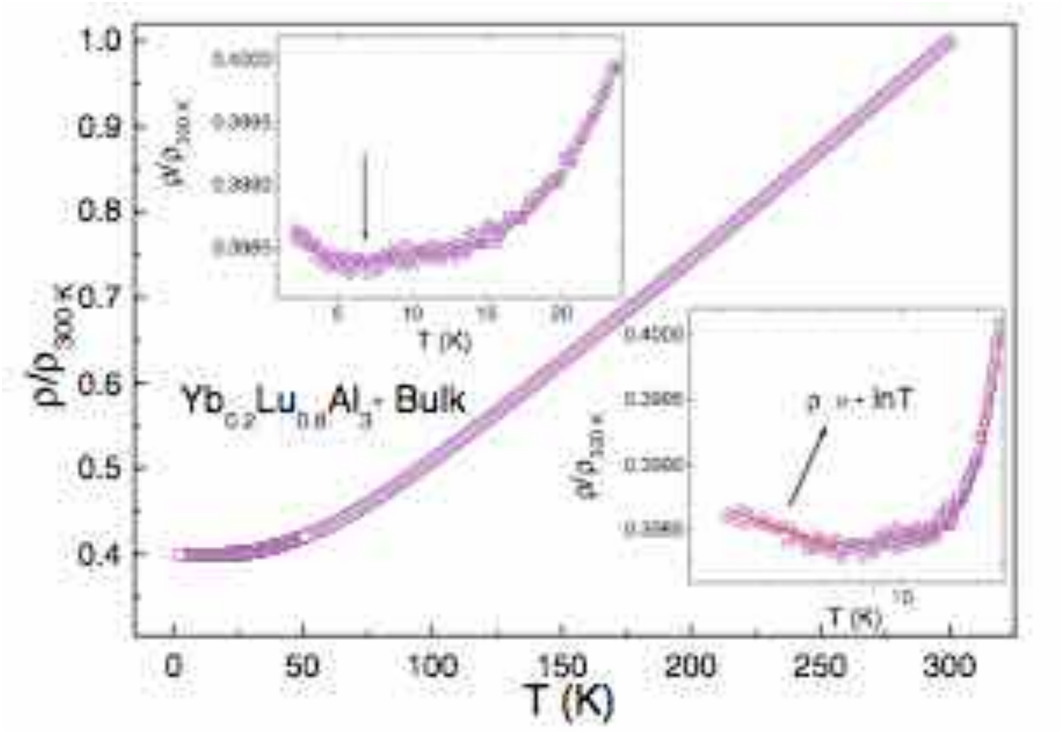
3.- ρ α LnT vs. $T^{1/2}$, $YbAl_3$



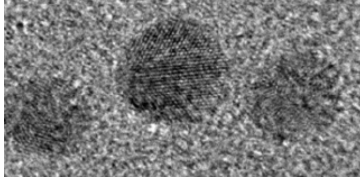
For example: Lee P A and Ramakrishnan T V 1985 Rev. Mod. Phys. 57 287



4.- In Bulk? Dilution with Lu (in $YbLuAl_3$) also favours the existence of resistivity minimum

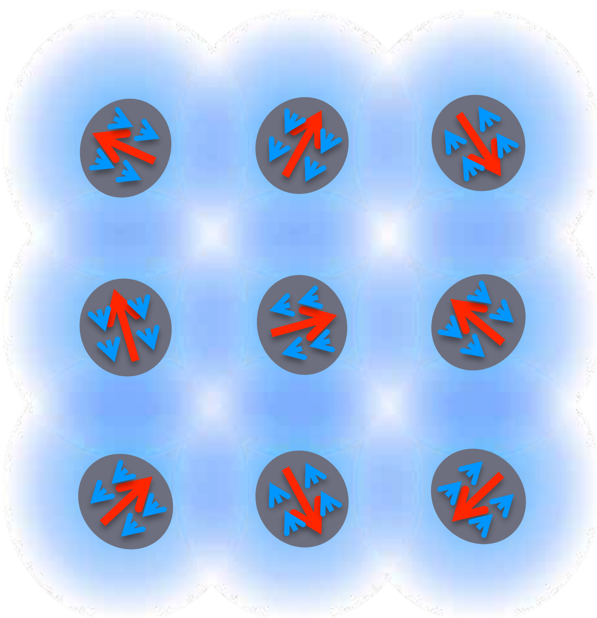


C. Echevarria-Bonet et al., JPCM 30, 135604 (2018)

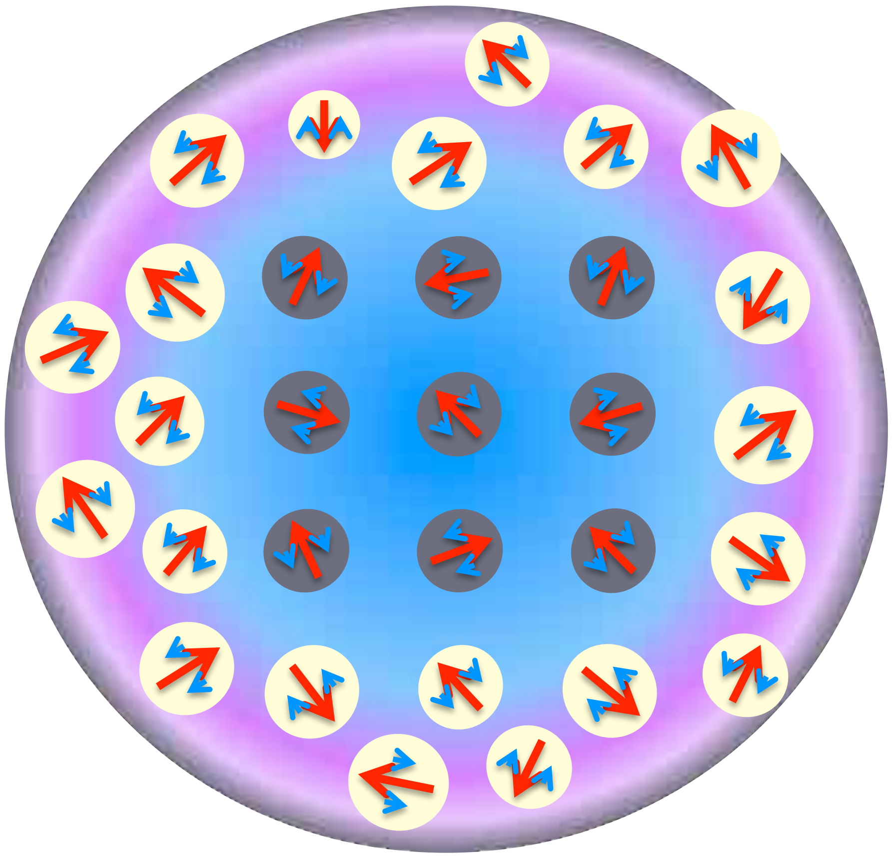


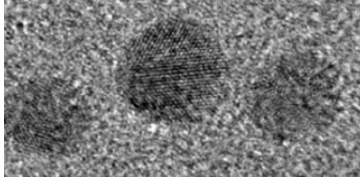
Just a sketch!

Coherence (Kondo lattice) in bulk



Kondo + Surface disorder in NPs





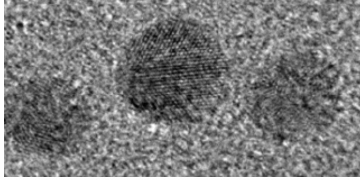
Conclusions

- The milling of RX_2 produces NPs with an AFM core and a SG shell in a SAFM behavior. Disorder in the Shell changes CEF levels, forced by distortions?

- The milling of $YbAl_3$ enables the production of large quantities of nanoparticles below 10 nm which show a drastic change in the electrical resistivity with decoherence effects. QIE (Electron-Electron Int) likely to be present ($LuAl_3$).

Near Future:

- **$NdCu_2$ INS + SANS, modeling (Jesús Blanco, Oviedo)**
- **RX_2 NPs: Y-La dilutions: magnetic properties**
- **$YbNi_2$ NPs, heavy fermion FM, $YbAL_3$ dots?**
- **Ho,Tb-NPs (Andreas Michels, U Luxembourg)**
- **Griffiths Phase + SG in Magnetocaloric TbLaSiGe (bulk) (Noelia Marcano, Zaragoza, Spain)**
- **Verwey (Charge order) in Fe-oxides NPs in Magnetotactic Bacteria (ML Fdez, Bilbao, Spain)**



In cooperation with:

María de la Fuente, Elizabeth Martín Jefremovas, **Cristina Echevarría Bonet**, J. C. Gómez Sal, P. Bender, D. González Alonso, I de Pedro, J. Rodríguez, Jose I. Espeso

Universidad de Cantabria (Santander, Spain)

Daniel P. Rojas
Universidad Politécnica de Madrid (Madrid, Spain)

Lidia Rodríguez Fernández
SERMET (Santander, Spain)

Sergio G. Magalhaes
UFRGS, Porto Alegre (Brazil)

Sebastien Burdin
U. Bordeaux (Bordeaux, France)

Jesús A. Blanco
Universidad Oviedo (Oviedo, Spain

Ana García Prieto, Lourdes Marcano, Maria L. Fdez-Gubieda
U. País Vasco (Bilbao, Spain)

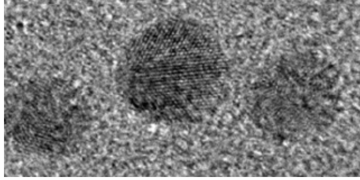
Ernst Bauer
Tech. Uni. Vienna (Vienna, Austria)

Gilles André, Francoise Damay
LLB (Gif-Orsay, France)

Björn Fak
(ILL, Grenoble, France)

Diego Alba
RAL-ISIS, Didcot (UK)

Funding Acknowledgement:
Spanish MINECO + EU-FP7 Large



Thank you!

Muchas Gracias