Exchange bias in core/shell magnetic nanoparticles: experimental results and numerical simulations

Xavier Batlle, A. Labarta, Ò. Iglesias, M. García del Muro and M. Kovylina

Goup of Magnetic Nanomaterials
Institute of Nanoscience and Nanotechnology
University of Barcelona ***(UB)***

I. Motivation

- Magnetic nanoparticles
- Why interesting? – Size effects (1940s):
  - enhanced properties with respect to bulk
  - finite size and surface effects + interactions (dipolar)

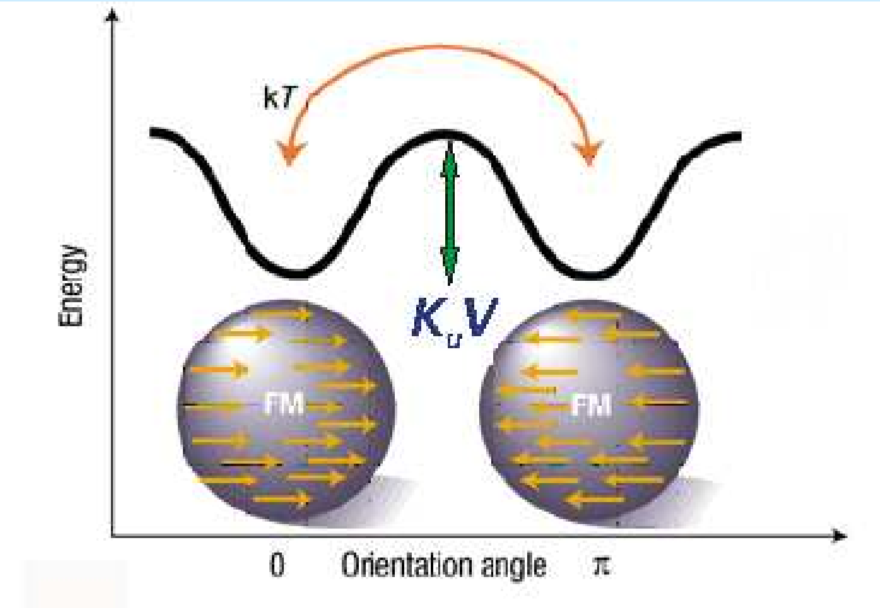
  Feature size ≤ correlation length

  Exchange length, domain wall width and single domain radius
- Why useful? – Technological applications:
  - Magnetic recording
  - Biomedical applications

Magnetic recording *vs* biomedical applications

The superparamagnetic limit: thermal fluctuations overcome the magnetic anisotropy barrier

$$t = t_0 e^{K_u V / kT}$$



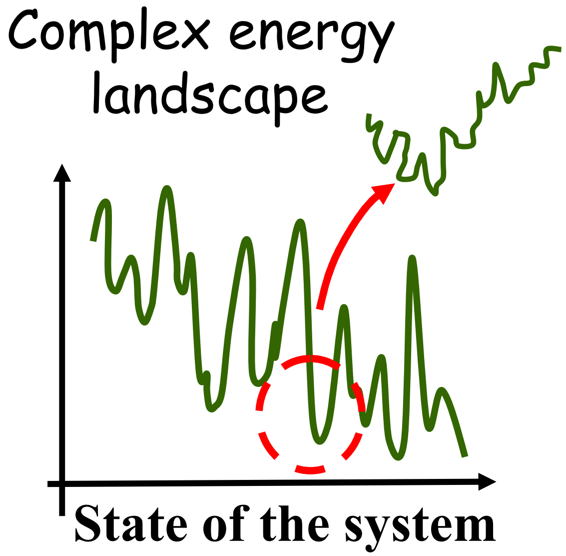
Magnetic recording (t ≈ 10 years)

With the increase in recording density (reduction in volume), we need to keep the magnetic stability (patterned media, high anisotropy materials, exchange bias…)

Requirements for bio-applications (typically)

- Superparamagnetic behavior
- High magnetization
- Limiting size *(in vivo)*
- Biocompatibility and functionality

II. Magnetic nanoparticles:
Finite-size, surface effects and collective behavior

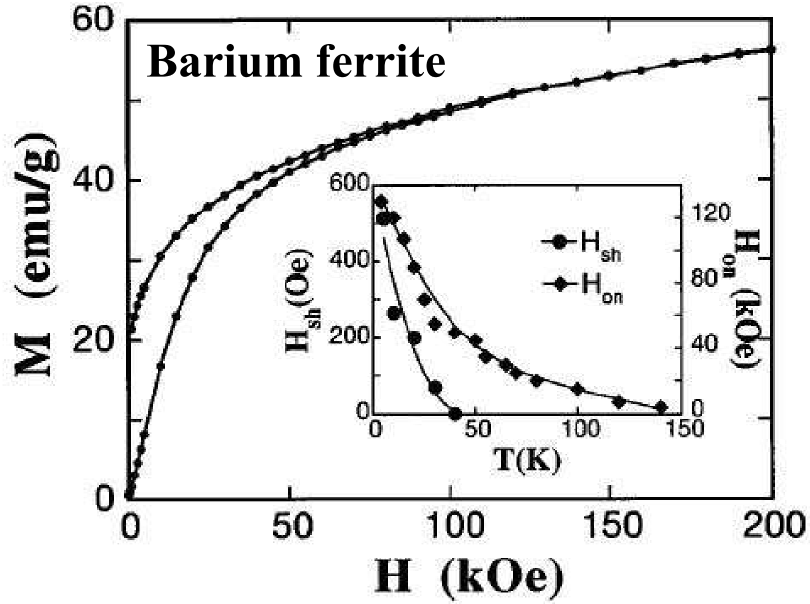


Review Papers

Finite size effects in fine particles: magnetic and transport properties
X. Batlle and A. Labarta,
Journal of Physics D: Applied Physics **35**, R15 (2002)

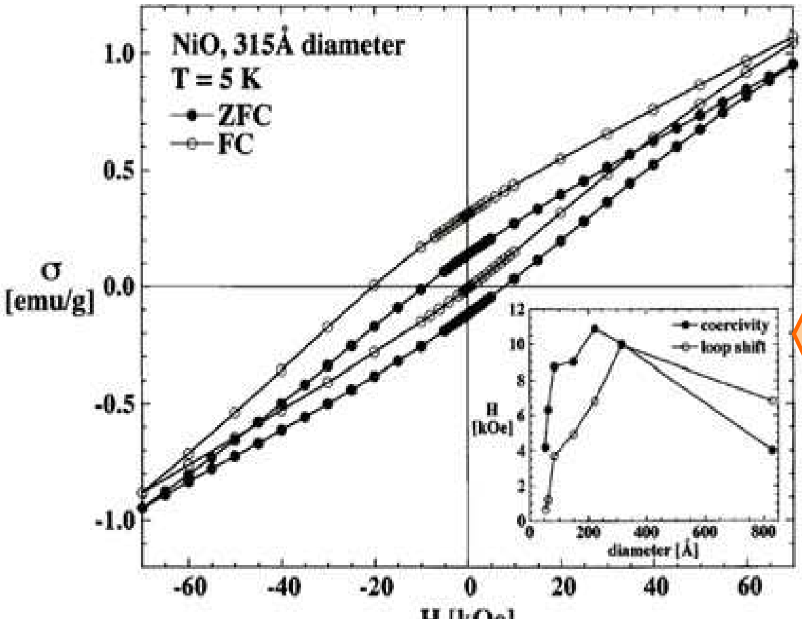
From finite-size and surface effects to glassy behaviour in ferrimagnetic nanoparticles
O. Iglesias, X. Batlle and A. Labarta
Surface effects in magnetic nanoparticles; D. Fiorani Editor; Springer (2006)

Low saturation magnetization,
high field irreversibility,
high closure fields
(broken symmetry at surface)



M. García et al., PRB **59**, 13594 (99) **UB**

Shifted hysteresis loops after FC

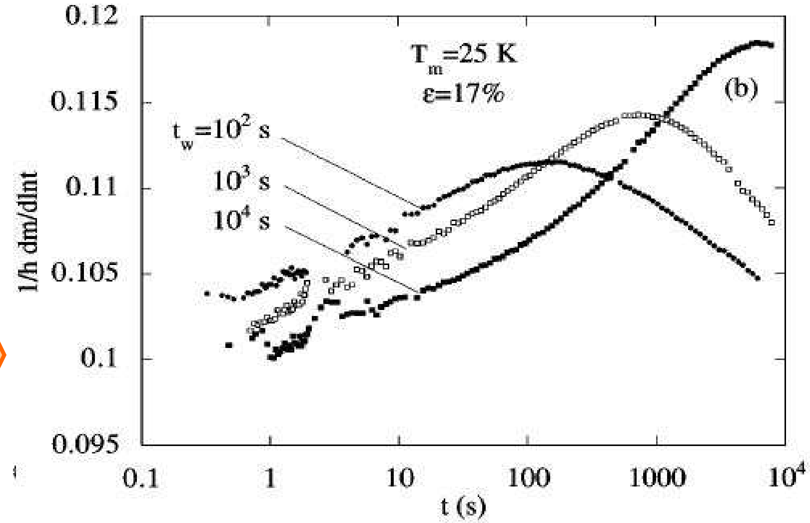


R. H. Kodama et al., PRL 79, 1393 (1997)

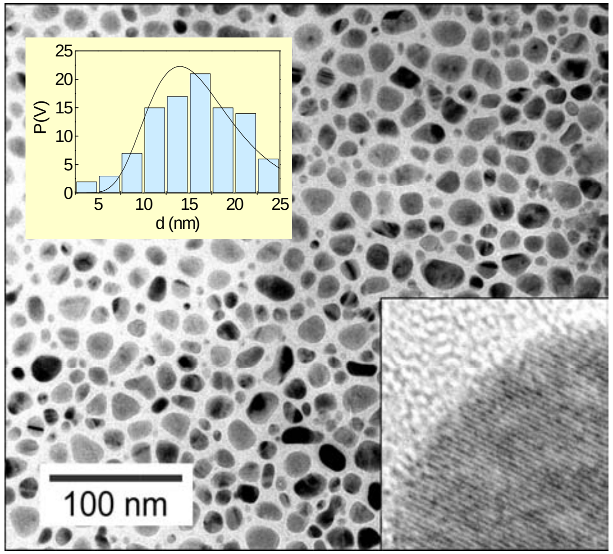
Ageing effects

(magnetic properties
depend on waiting time)

T. Jonsson et al. PRL **75**, 4138 (95)



Size distribution



Co-ZrO$_2$

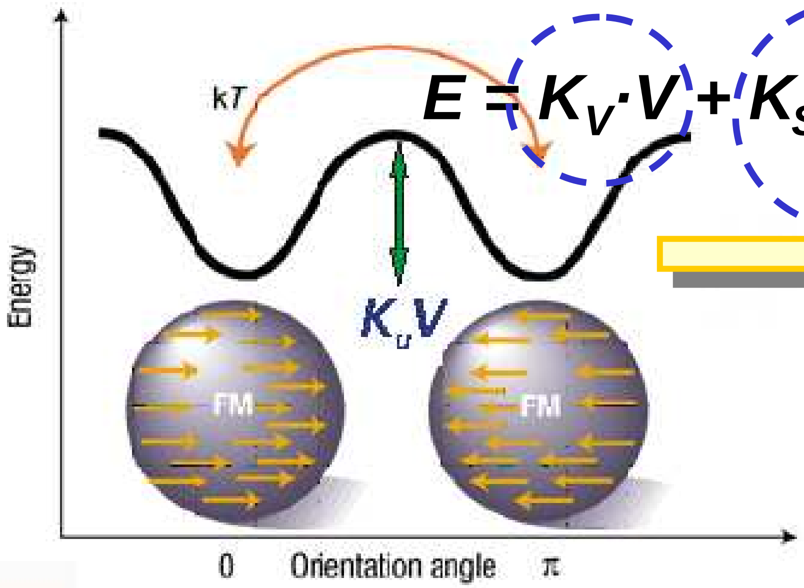
B.J. Hattink et al., PRB **67**, 033402 (2003) **UB**
N. Pérez et al., Nanotechnology **19**, 475704 (2008) **UB**

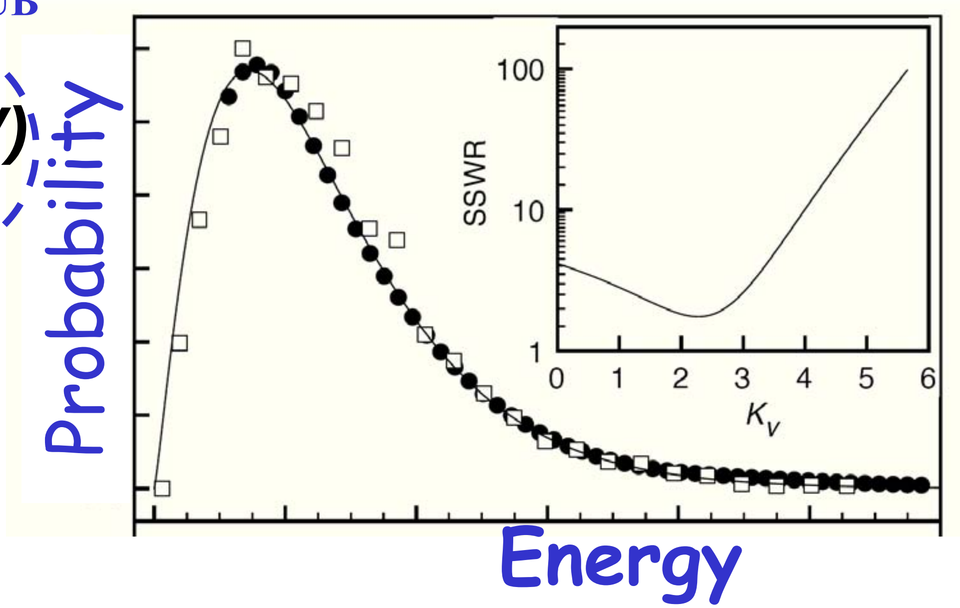
Non-uniform distribution (log-normal)

$$f(V) = \frac{1}{\sqrt{2\pi}\sigma V} \exp\left(-\frac{\ln^2 (V/V_0)}{2\sigma^2} \right)$$

Effective distribution of energy barriers for magnetization reversal

$$E = K_V \cdot V + K_S \cdot S(V)$$

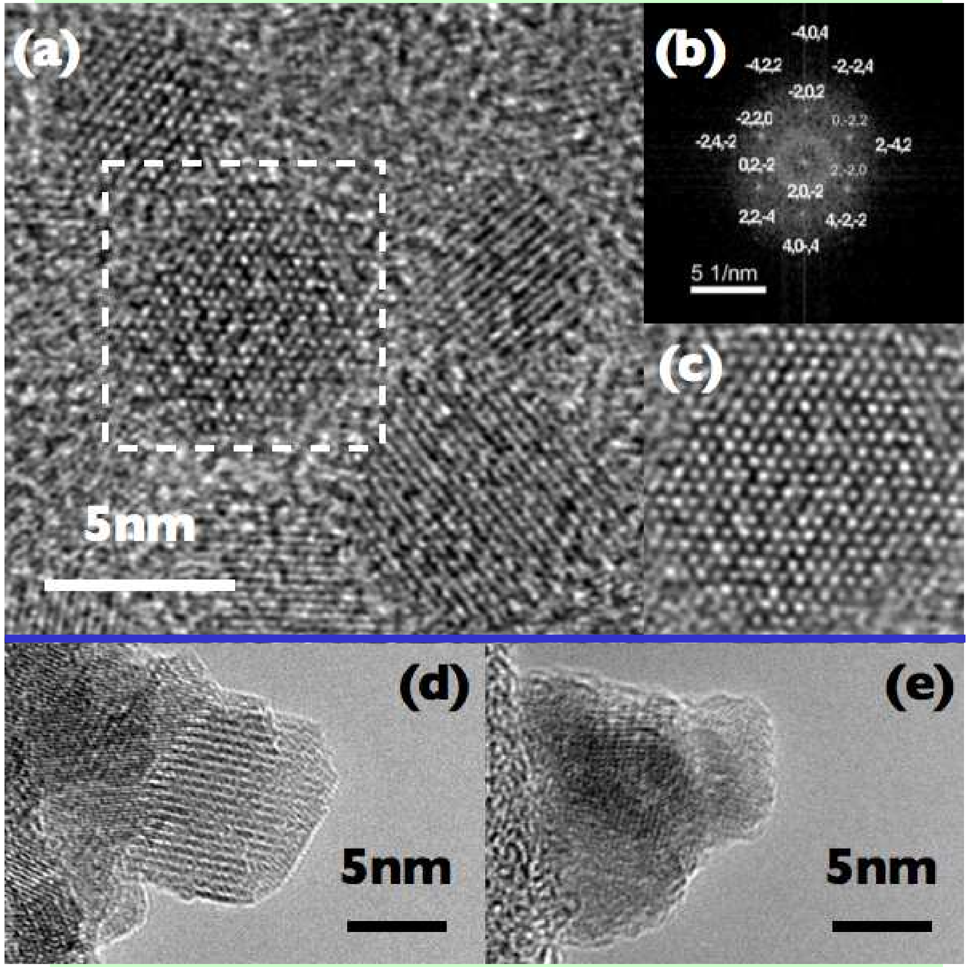




COATING EFFECTS

5 nm Fe_3O_4 particles

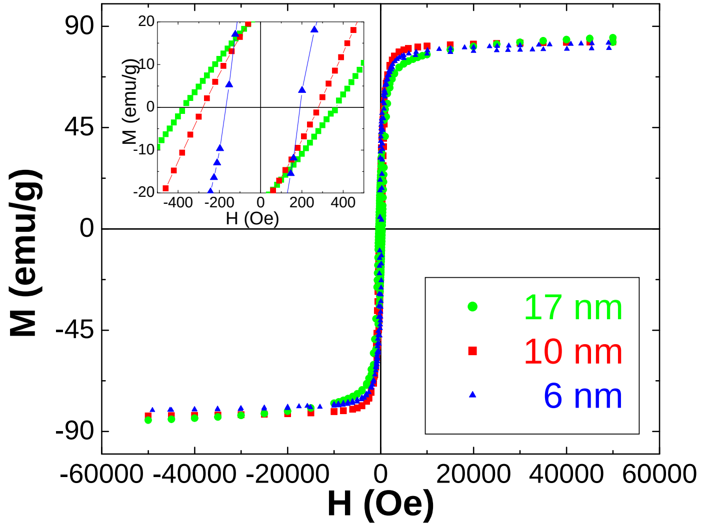
Covalent bond (oleic acid)

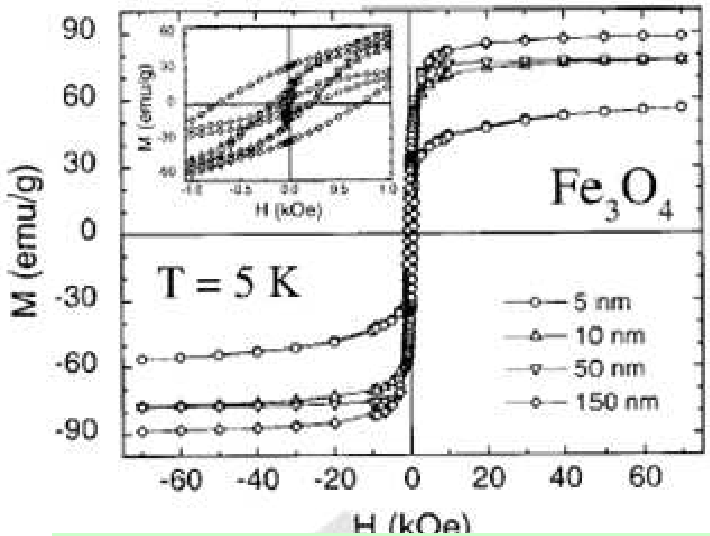


Adsorbed coating (PVA)

N. Pérez et al., APL **94**, 093108 (2009) **UB**

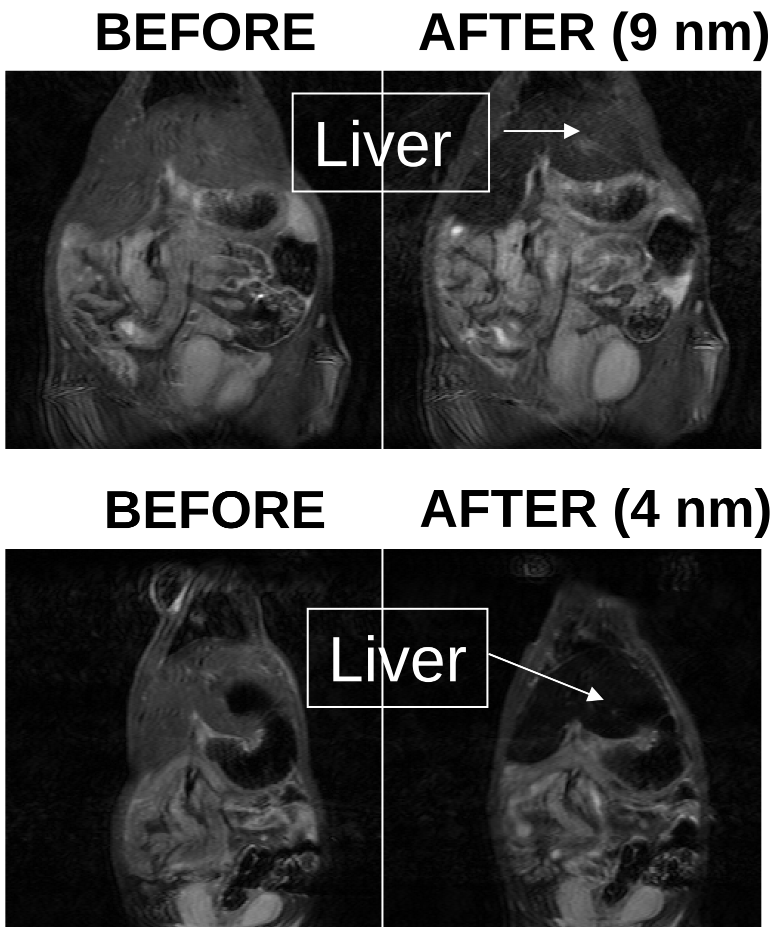
Size-independent, bulk magnetization





Size-dependent, reduced magnetization

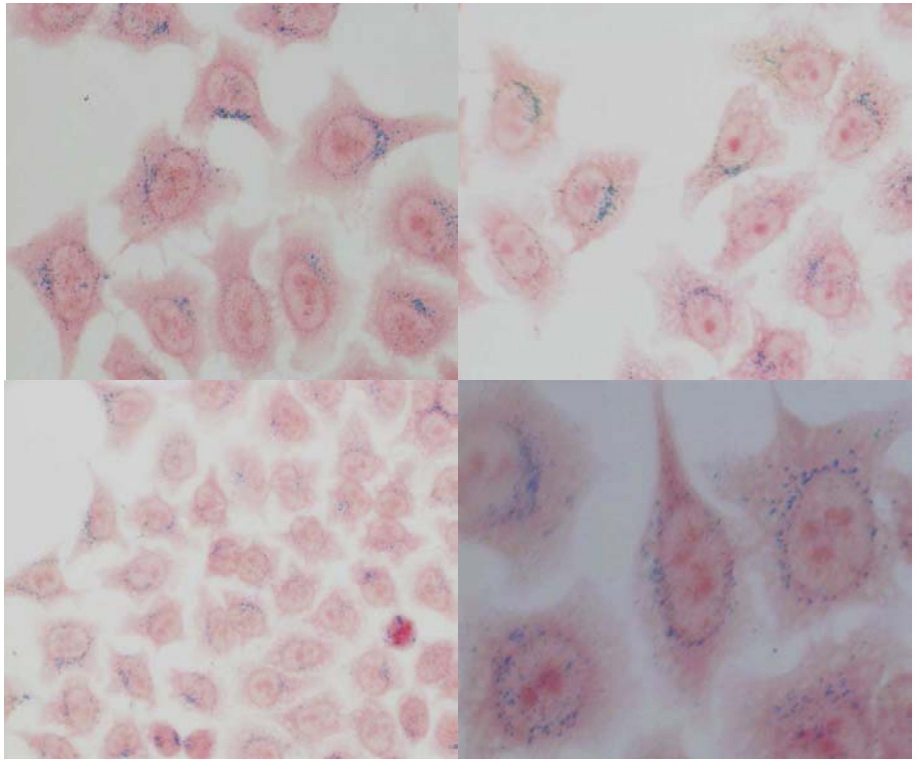
MRI



Contrast enhancement

M.P. Morales et al., (submitted) **UB**

Incubation with HeLa cells



Internalization around the cell membrane

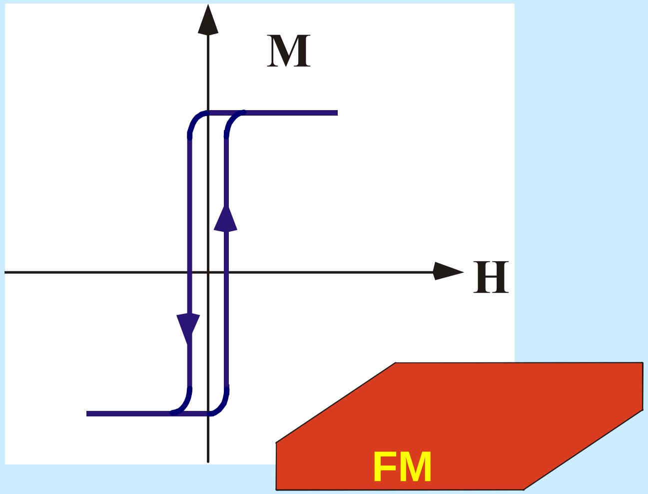
III. Exchange bias:
A (very short) survey

Review Paper

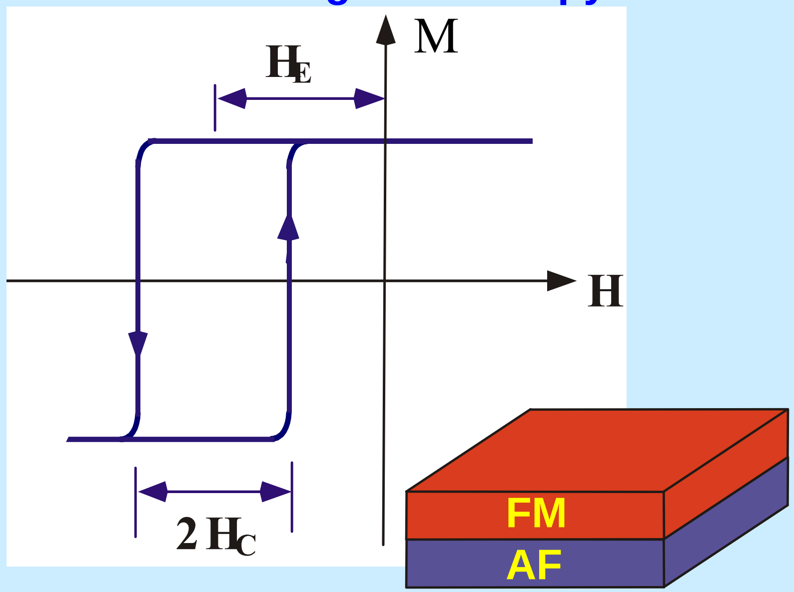
Exchange bias phenomenology and models of core/shell nanoparticles
O. Iglesias, A. Labarta and X. Batlle
Journal of Nanosciences and Nanotechnology **8**, 2761 (2008)

Reminder

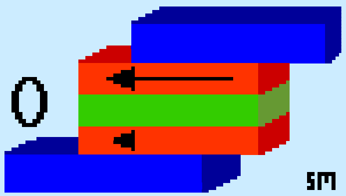
- Exchange bias: unidirectional anisotropy induced by the AF into the FM via exchange coupling at the interface



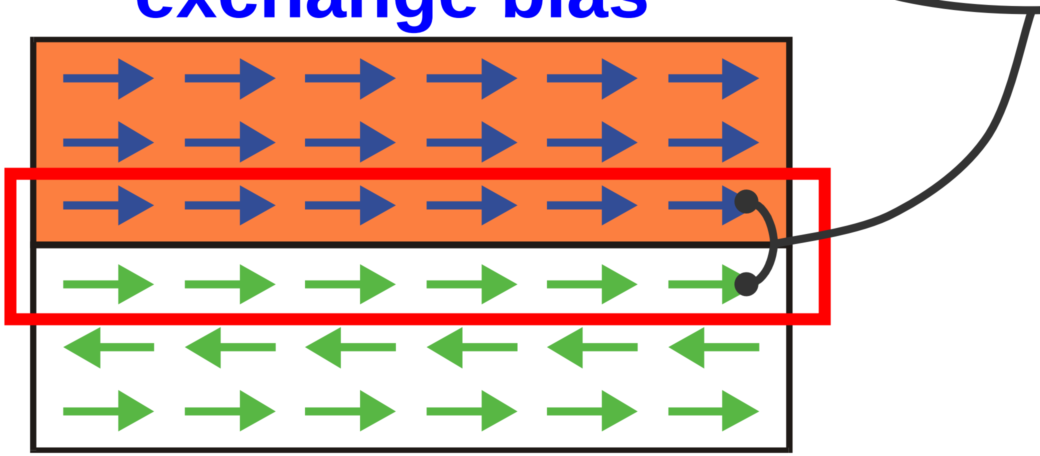
M(H) after field cooling $T_N<T<T_C$
AFM with high anisotropy

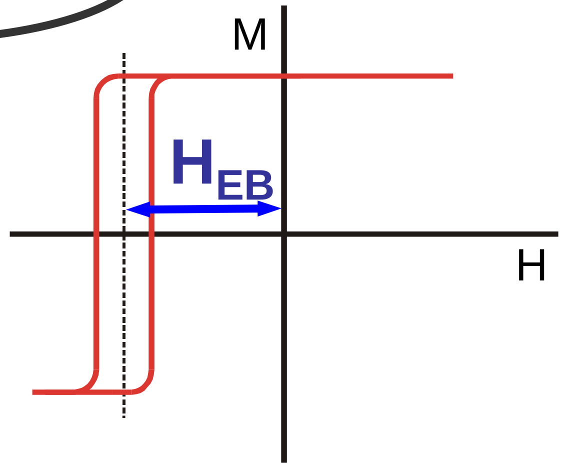


- Reference spin state (read heads, MRAM and magnetic sensors)



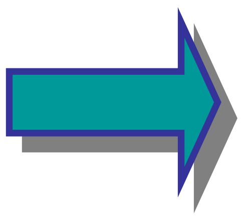
Microscopic origin of exchange bias





$$H_{EB} = n \frac{JS_{AF}S_{FM}}{t_{FM}M_{FM}}$$

n ?



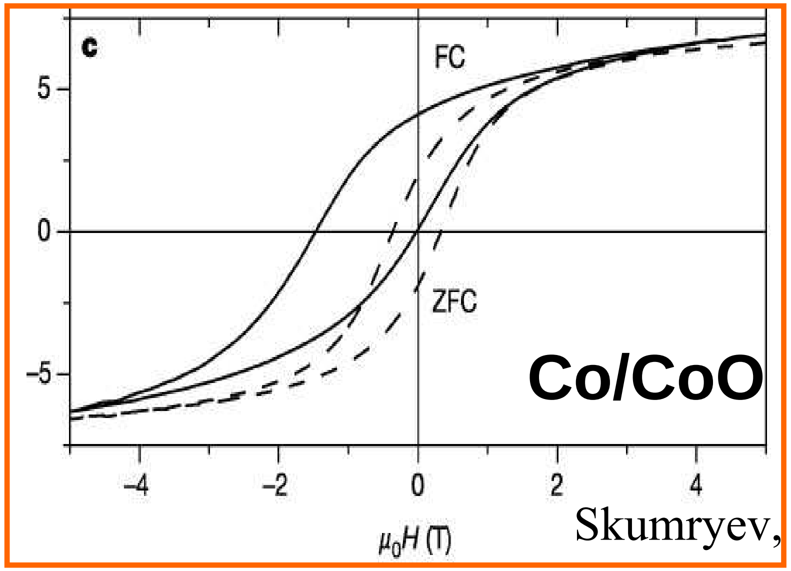
1. Uncompensated (3 – 7%) pinned spins in the AF, either at the interface or far from it.
   - Ohldag, PRL **91**, 017203 (2003)
   - Kappenberger, PRL **91**, 267202 (2003)
   - Roy, PRL **95**, 047201 (2005) **UB**

2. Asymmetric reversal due to broken symmetry, leading to *in-volume* domains in the FM.
   - Li, PRL **96**, 217205 (2003) **UB**
   - Morales, APL **89**, 072504 (2006); **95** (2009) **UB**

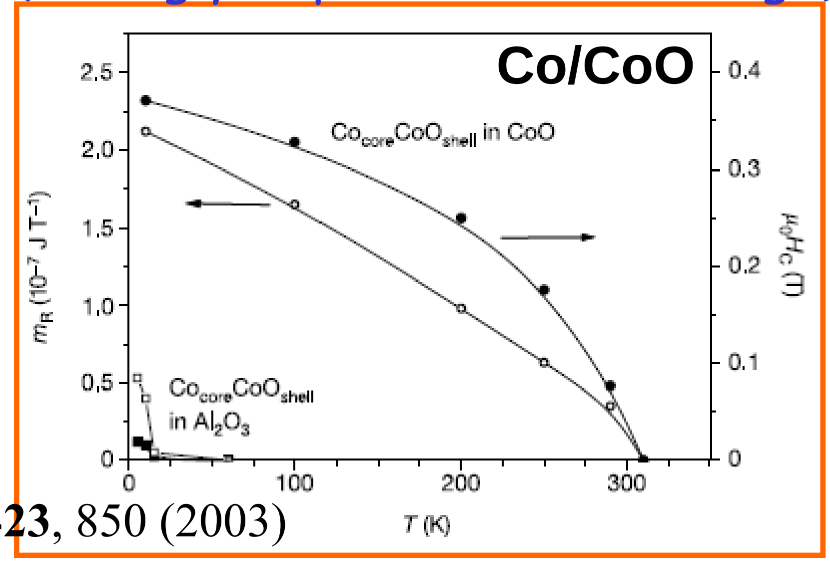
3. Key role of relative size of *in-plane* FM/AF domains
   - Roshchin, EPL **71**, 297 (2005) **UB**
   - Petracic, APL **87**, 222509 (2005) **UB**

Phenomenology in core/shell NP

Shifted loops, increased H_c (spin dragging)

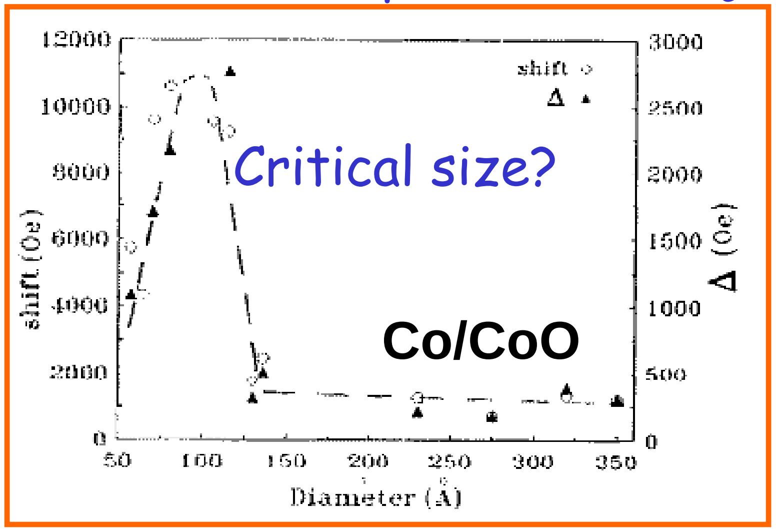


Increased blocking temperature (strongly dependent on coverage)



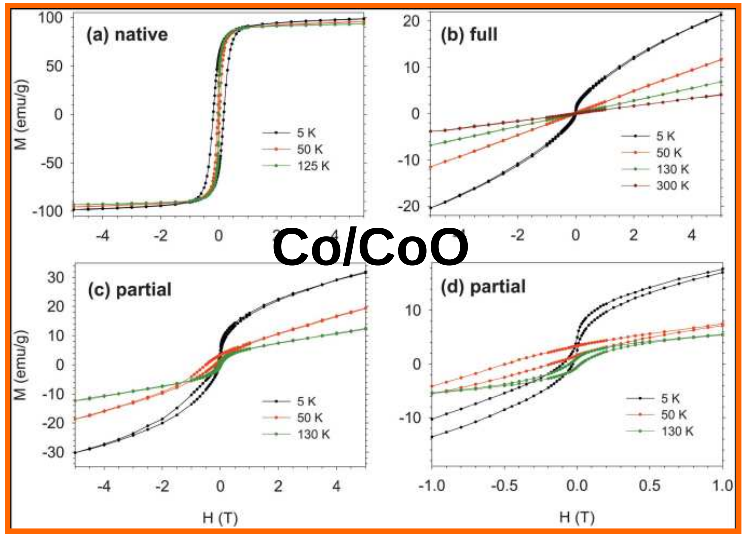
Skumryev, Nature **423**, 850 (2003)

Particle size dependence (~D_C^{-1})



Gangopadhya, JAP **73**, 6964 (1993)

Oxidation state (FM-AF ratio)



Tracy, PRB **72**, 064404 (2005)

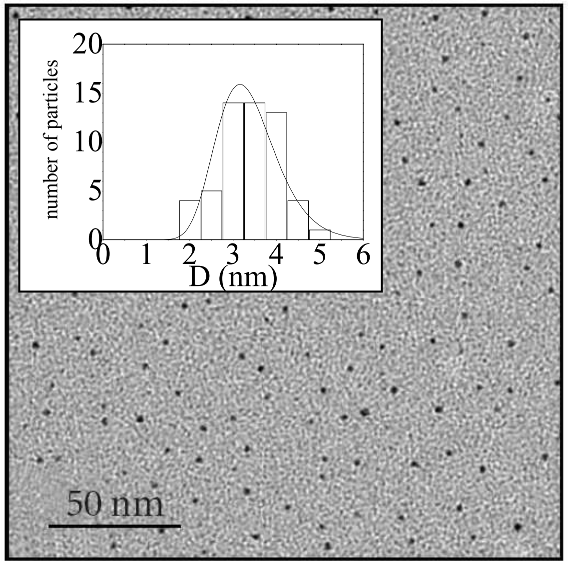
IV. Results:

EB in Co-CoO nanoparticles embedded in a matrix

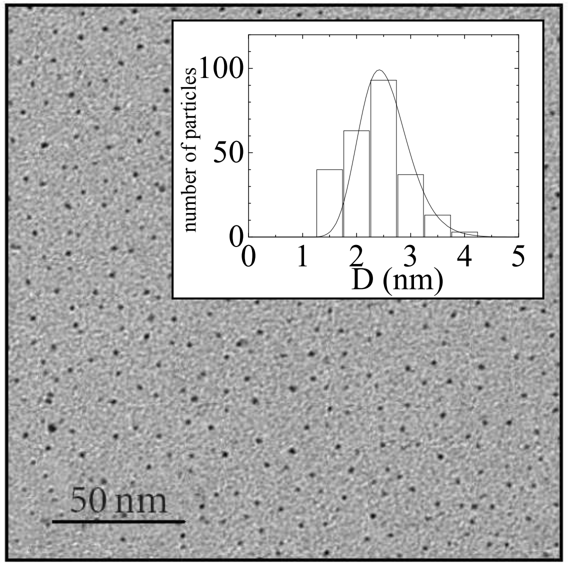
M. Kovylina, M. García del Muro, Z. Konstantinović, O. Iglesias
M. Varela, A. Labarta and X. Batlle,

Nanotechnology **20**, 175702 (2009)

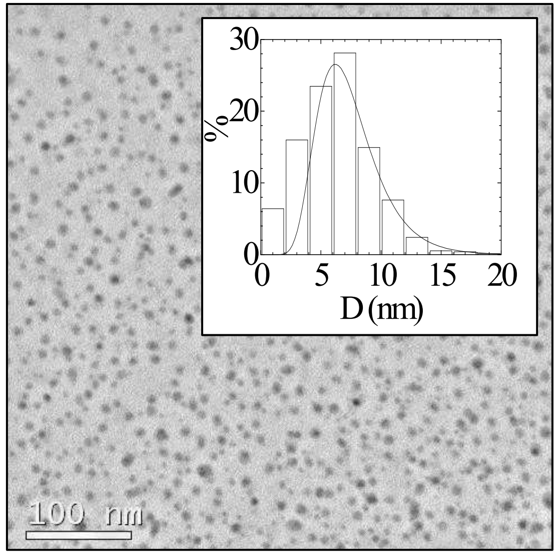
Co_x-$(ZrO_2)_{1-x}$ thin films by pulsed laser ablation



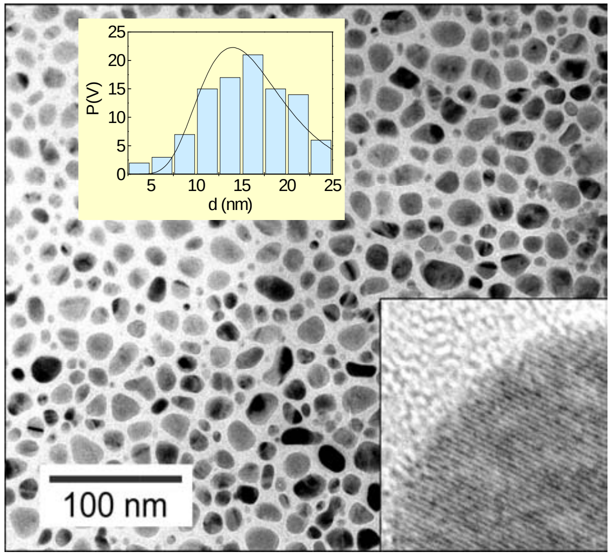
x (% vol.) = 0.06



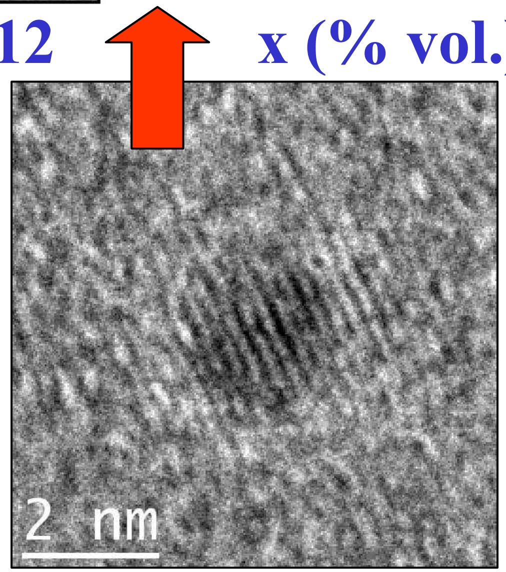
x (% vol.) = 0.12



x (% vol.) = 0.25



x (% vol.) = 0.30



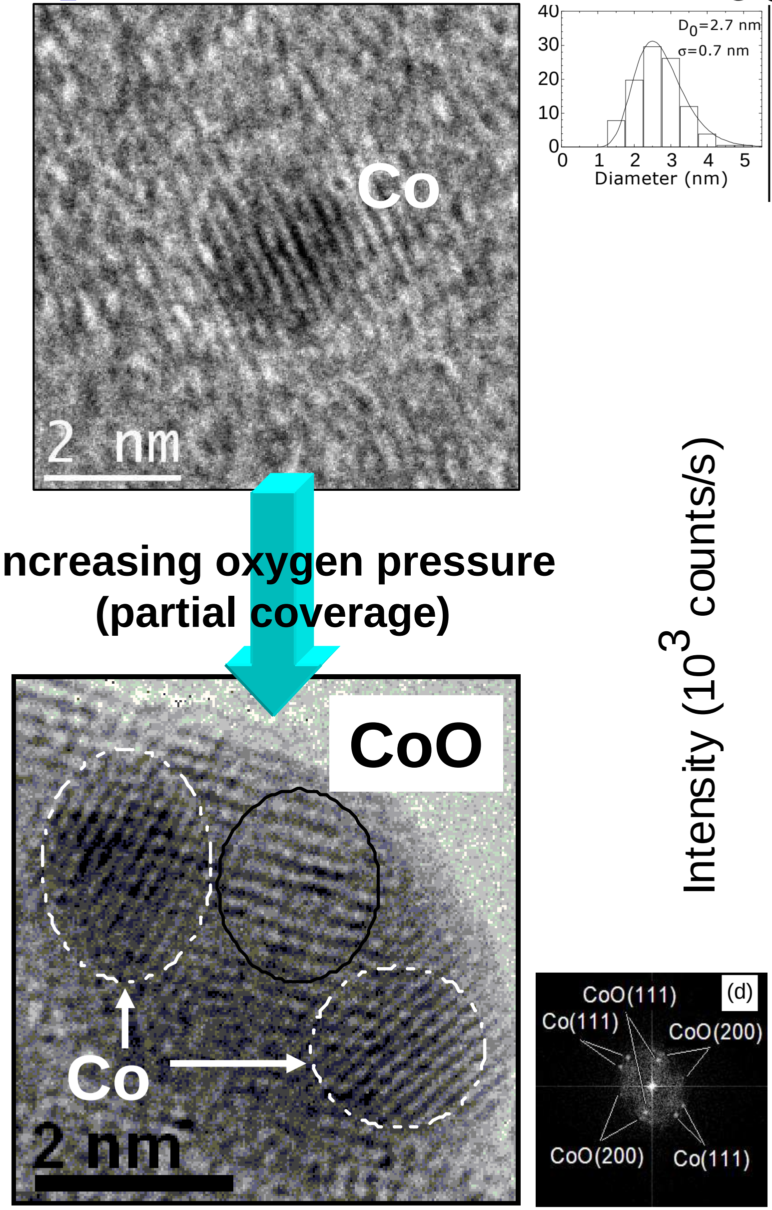
Z. Konstantinovic et al., Nanotechnology **17**, 4106 (2006) **UB**

Z. Konstantinovic, APL **91** 052108 (2009); **90**, 182506 (2009) **UB**

B.J. Hattink et al., PRB **73**, 45418 (2006); **79**, 94201 (2009) **UB**

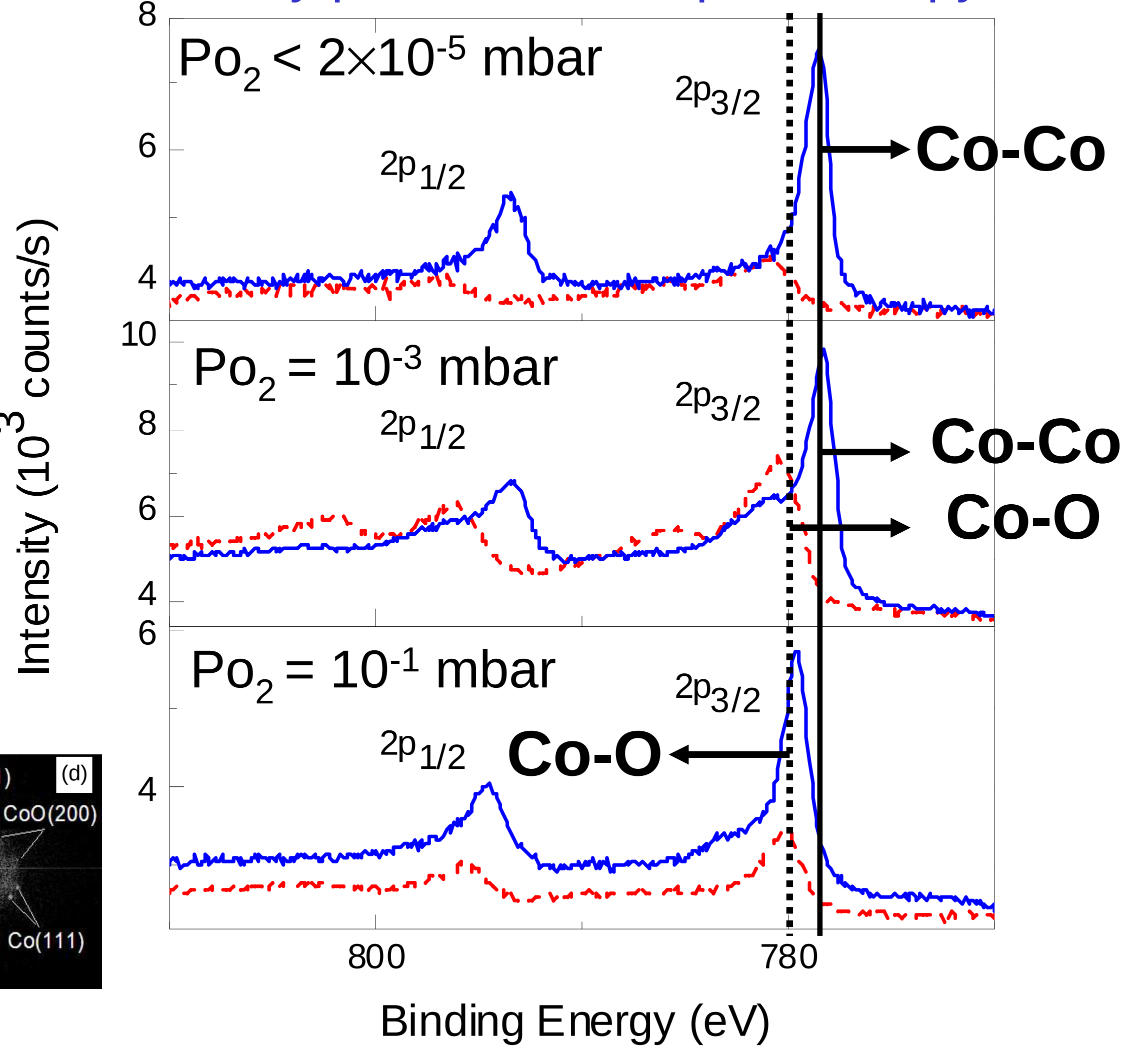
Co-ZrO_2 thin films deposited under oxygen pressure ($x_v(Co) \approx 0.2$)

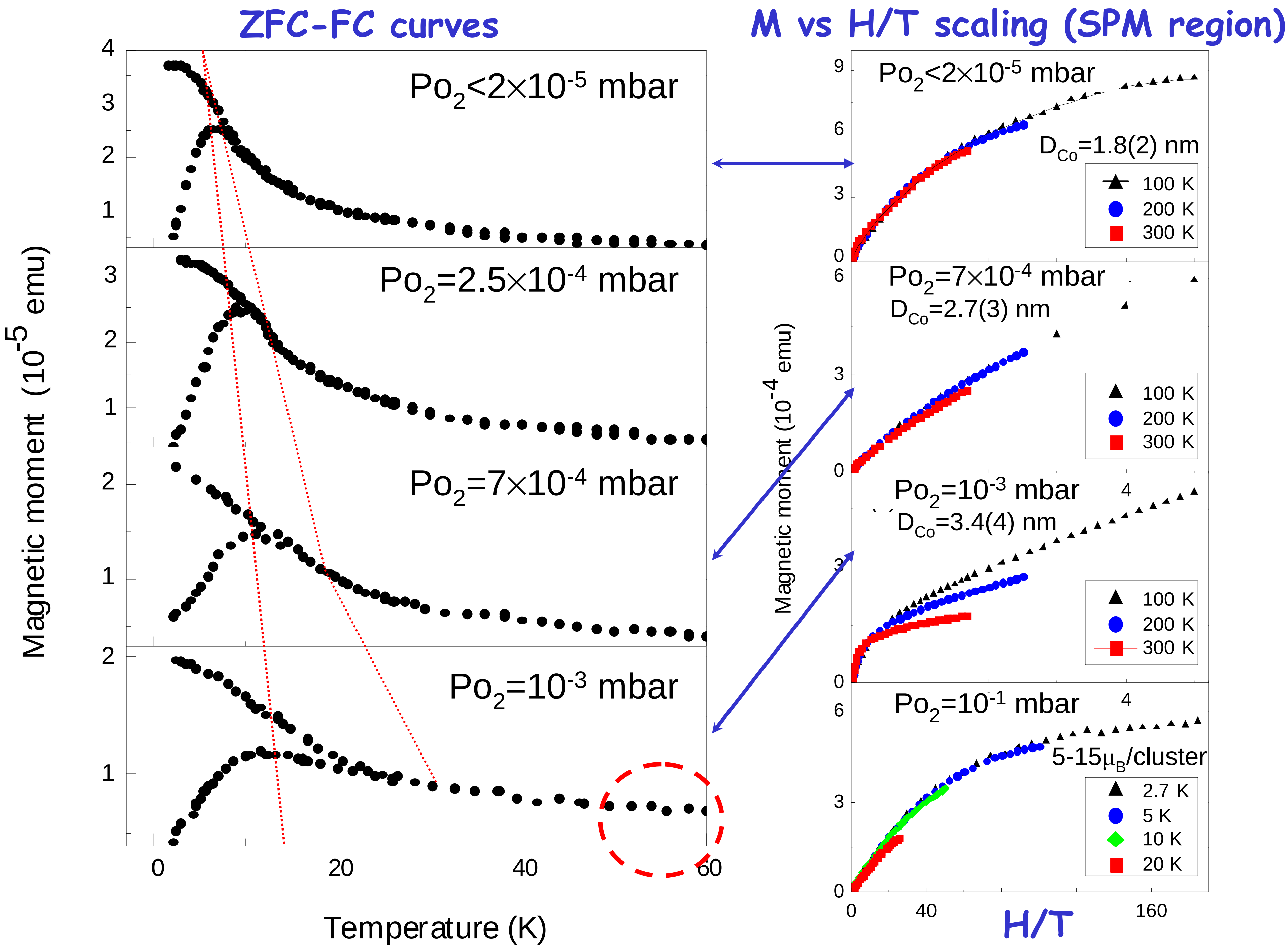
$Po_2 < 2\times10^{-5}$ mbar (base)



$Po_2 = 5\times10^{-4}$ mbar

X-ray photoelectron spectroscopy

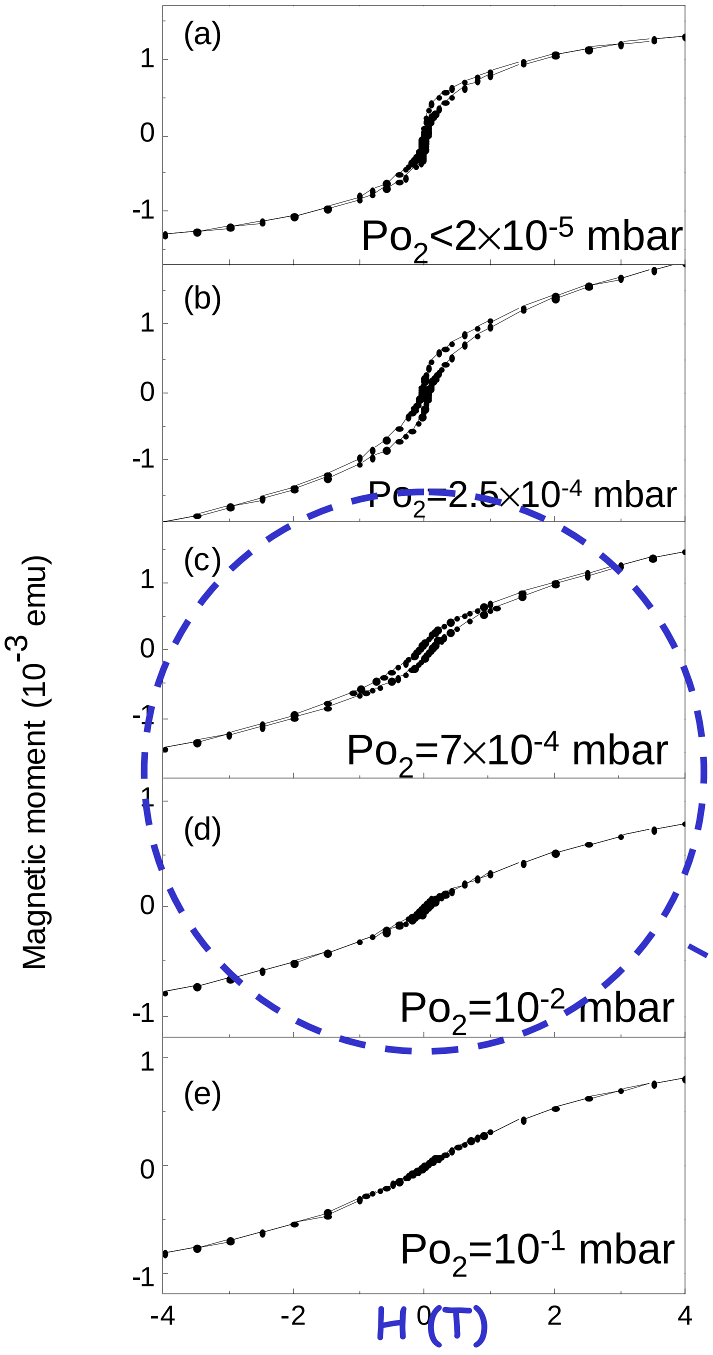


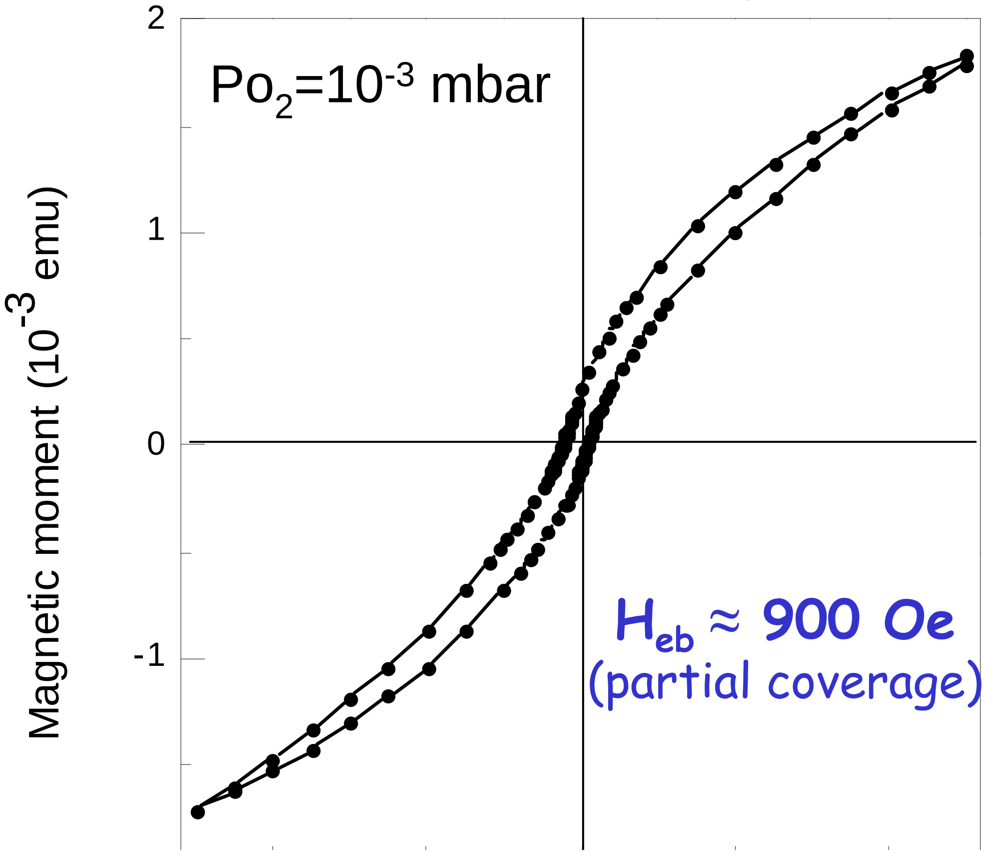


ZFC-FC curves
M vs H/T scaling (SPM region)
Po2<2×10-5 mbar
Po2=2.5×10-4 mbar
Po2=7×10-4 mbar
Po2=10-3 mbar
Magnetic moment (10-5 emu)
Temperature (K)
DCo=1.8(2) nm
100 K
200 K
300 K
Po2=7×10-4 mbar
DCo=2.7(3) nm
Po2=10-3 mbar
DCo=3.4(4) nm
Po2=10-1 mbar
5-15μB/cluster
2.7 K
5 K
10 K
20 K
Magnetic moment (10-4 emu)
H/T

M(H) @ 5 K after ZFC

M(H) @ 1.8 K after H_{FC} = 50 kOe

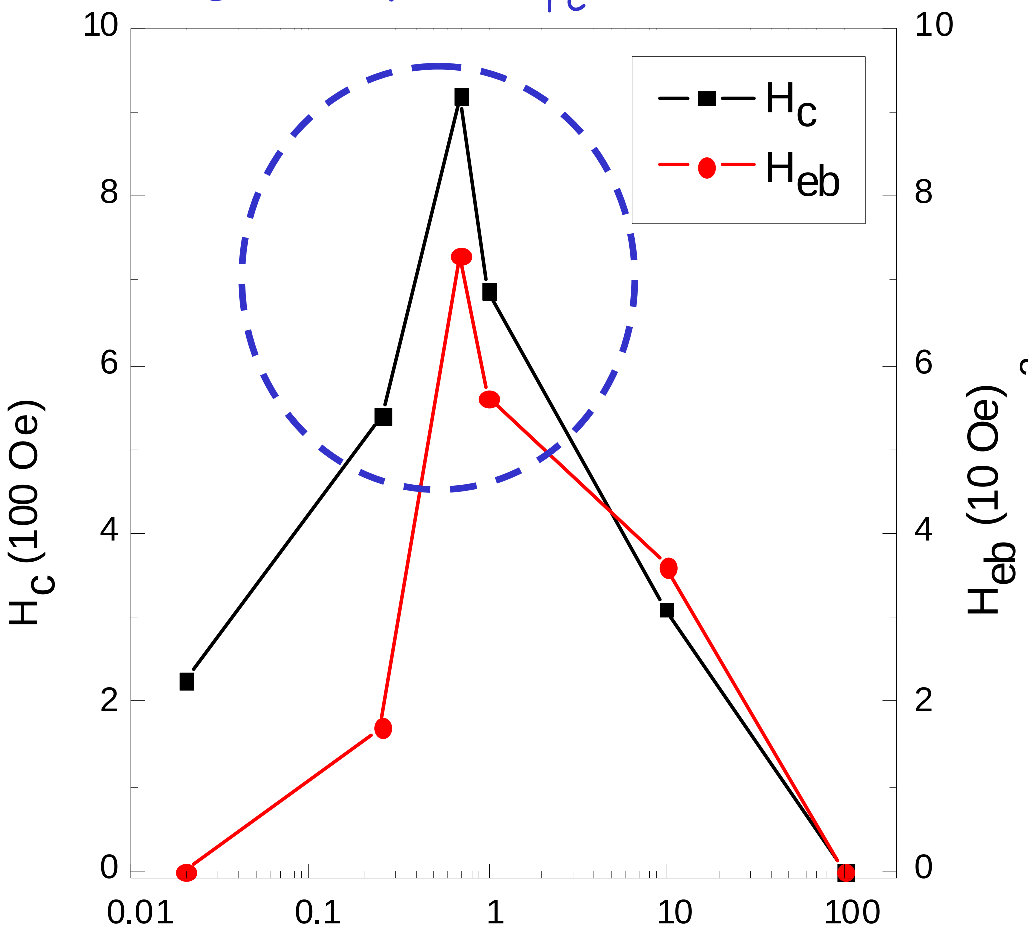




High irreversibility disappears and the small moment in the AF unblocks due to the absence of exchange coupling and magnetic frustration.

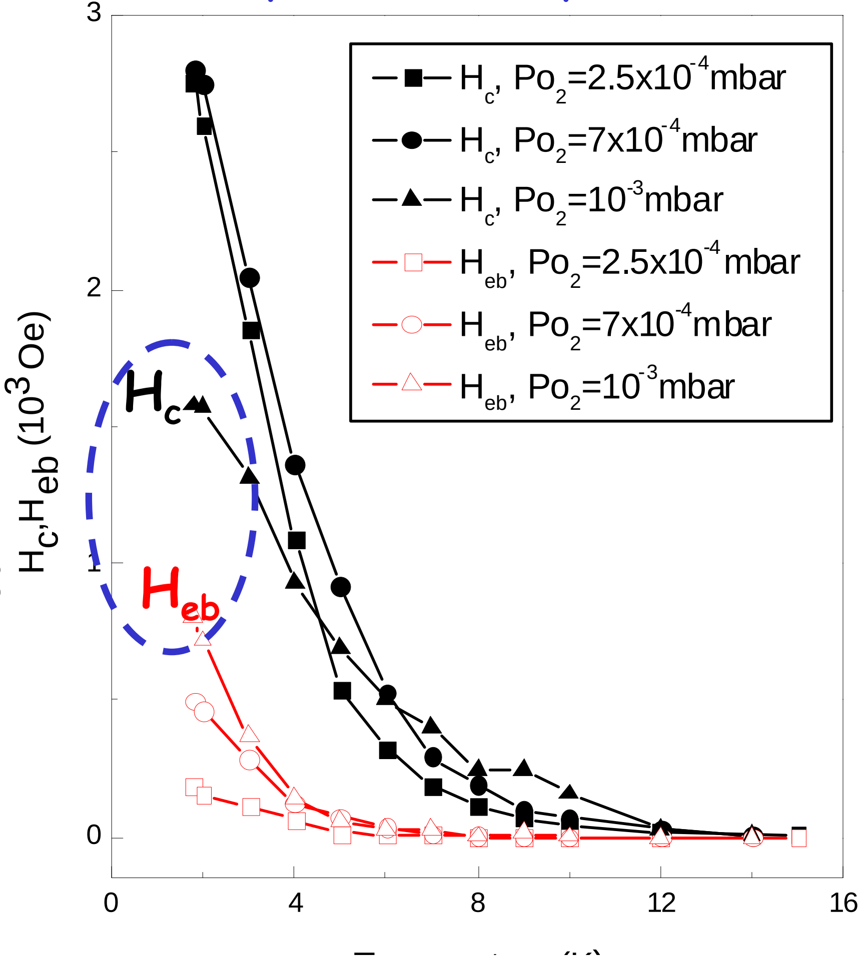
EB requires a minimum size for both the FM and AF components to show up.

Coercive field (H_c) and loop shift (H_{eb}) @ 5 K after H_{FC} = 50 kOe



Po_2 (10^{-3} mbar)

Temperature dependence



Temperature

Thermal stabilization of the FM due to exchange coupling?

V. Results:

Monte Carlo simulations

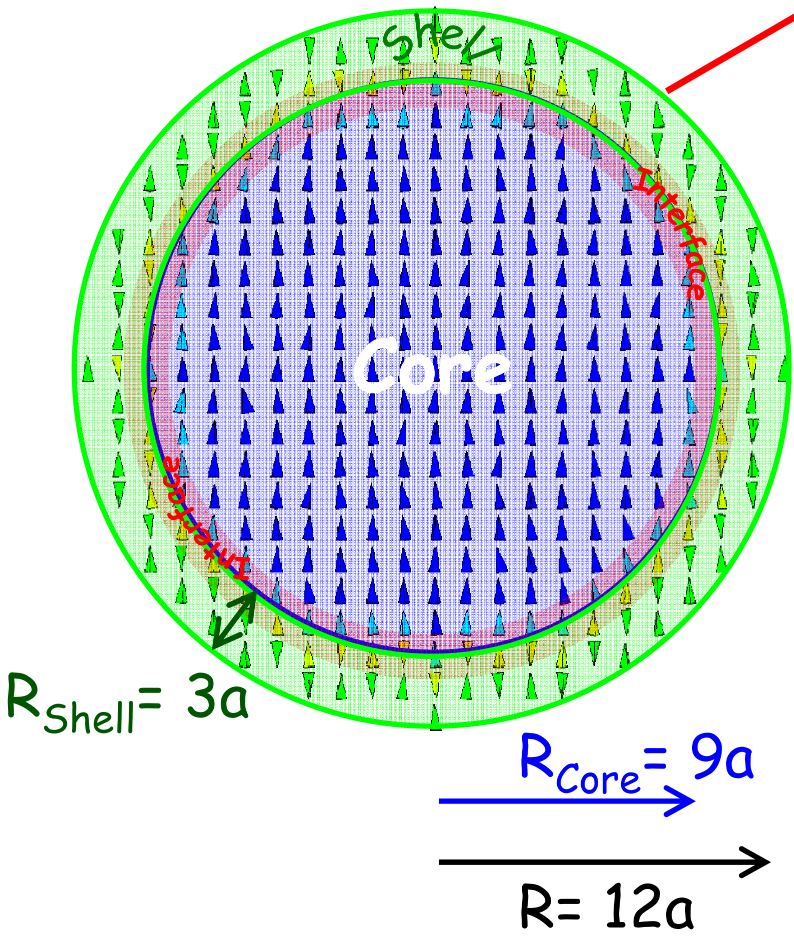
References

Òscar Iglesias
18:45 (Today)

O. Iglesias, X. Batlle and A. Labarta,
Phys. Rev. B **72**, 212401 (2005)
J. Magn. Magn. Mater. **316**, 140-142 (2007)
J. Phys.: Condens. Matter **19**, 406232 (2007)
J. Phys. D: Appl. Phys **41**, 134010 (2008)

Exchange bias phenomenology and models of core/shell nanoparticles
O. Iglesias, A. Labarta and X. Batlle
Journal of Nanosciences and Nanotechnology **8**, 2761 (2008) REVIEW

Model: single core/shell NP (to avoid collective effects)



Core: ferromagnetic (Co)

Shell: antiferromagnetic (oxide)

Interface: spins at C (Sh) with nearest neighbors at the Sh (C)

In a core/shell particle, the interface is not well-defined as in bilayers and finite-size effects appear

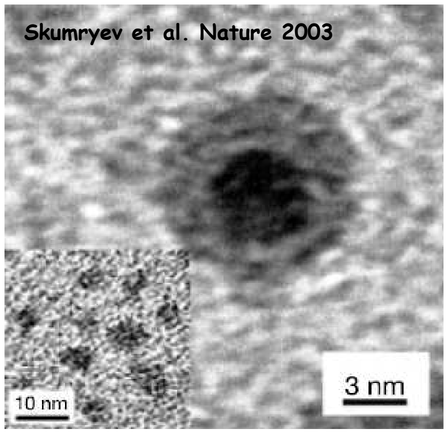
Interface incorporates roughness, disorder and local compensation/non-compensation (number of neighbors depend on position)

Number of spins (a = 0.3 nm; unit cell)

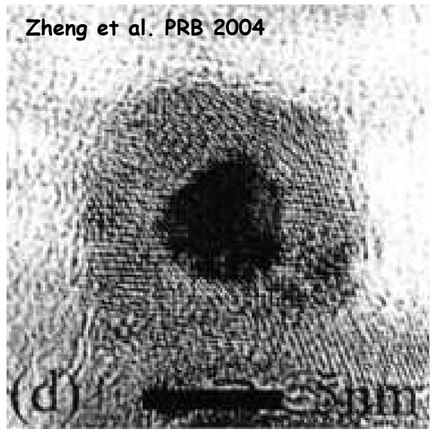
N_{Total} = 5575

N_{Core} = 3071, N_{Shell} = 2504

$N_{Interface}$ = 918 (Shell) + 794 (Core)



Co/CoO



Fe/γ-Fe_2O_3

$$H/k_B = -\sum_{\langle i,j\rangle} J_{ij}\vec{S}_i \cdot \vec{S}_j - \sum_i K_i \left(\vec{S}_i \cdot \hat{n}_i\right)^2 - \vec{h}\cdot\sum_i \vec{S}_i$$

Monte Carlo simulation, Metropolis algorithm for continuous spins

S_i = Heisenberg Spins in simple cubic lattice

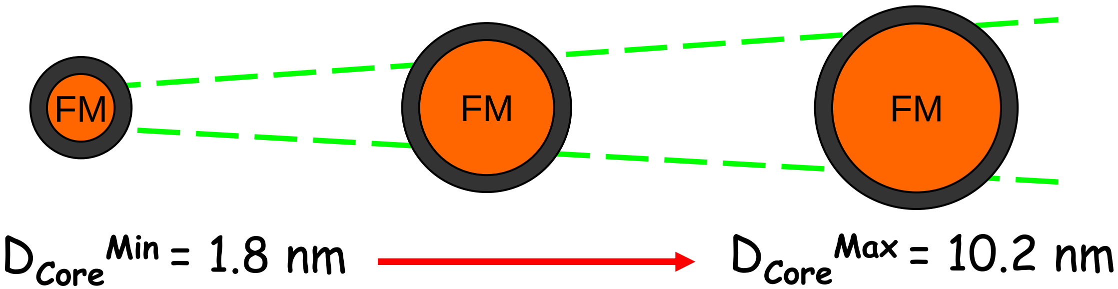
Exchange (n.n.) interaction:
$J_C > 0$ (FM) at the Core
$J_S < 0$ (AF) at the Shell
$J_{Int} >< 0$ (FM or AF) at the Interface
J_{Int} variable within $\pm J_C$

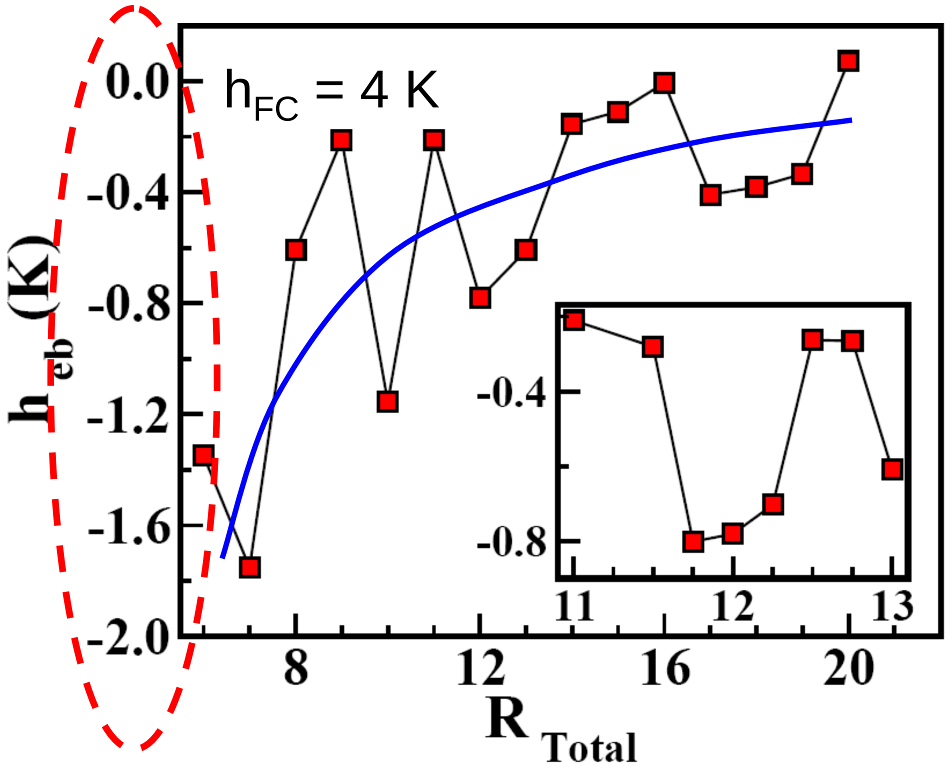
Anisotropy energy
n_i = z axis, uniaxial anisotropy
K_C at the Core
$K_S > K_C$ at the Shell

Zeeman energy
h along z axis
Magnetic field is in temperature units: $h = \mu H/k_B$

Simulation parameters (all in temperature units)			
J_C= 10 (fixed)	Fixes Curie temp. $T_C = 29$	**K_C= 1 (per site)**	Fixes coercive field of FM
J_S= -0.5 J_C	Fixes Neél temp. $T_N = 14.5 < T_C$	**K_S= 10 (per site)**	Shell with high anisotropy

Particle size dependence





O. Iglesias, X. Batlle and A. Labarta, J. Phys. D **41**, 134010 (2008)

Oscillatory dependence on particle size

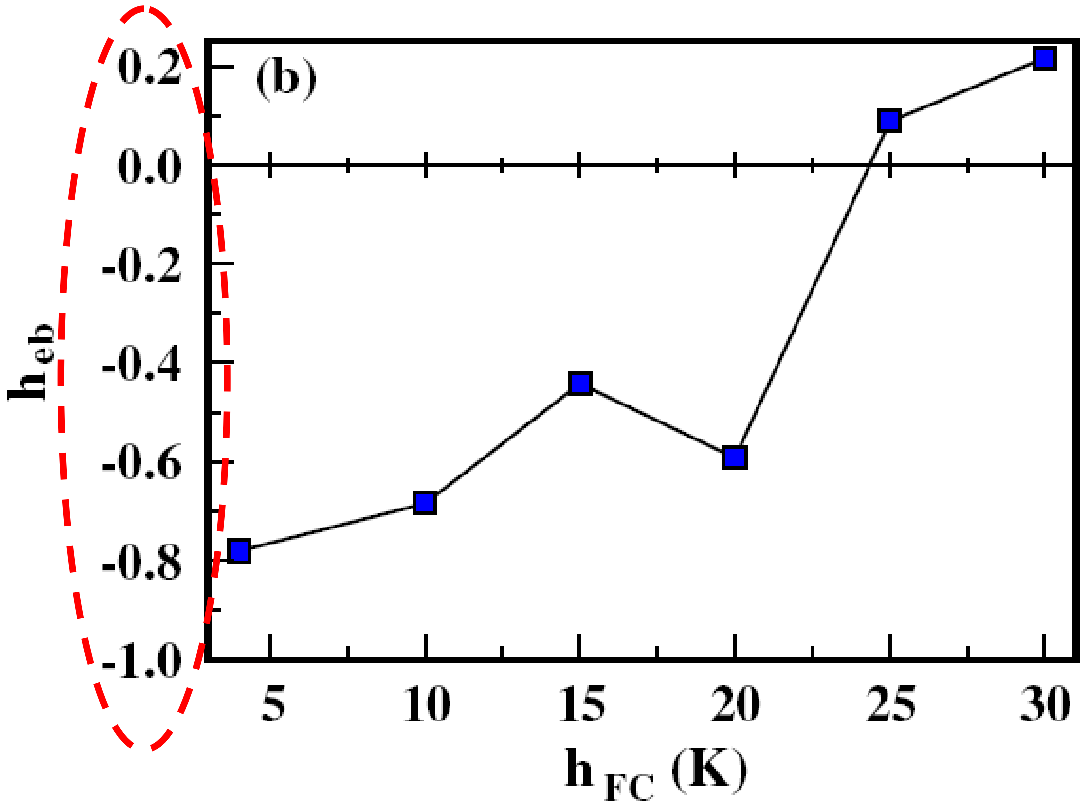
$\mathbf{h_{eb}}$ decreases as size increases (experiments)

$\mathbf{h_{eb} \sim 1/R_{Core}}$

The net magnetization of the AF shell spins at interface oscillates with particle size

Small changes in the core radius induce different geometric arrangements of interfacial shell spins, due to the intersection of the sphere with the lattice sites

Field cooling dependence



O. Iglesias, X. Batlle and A. Labarta,

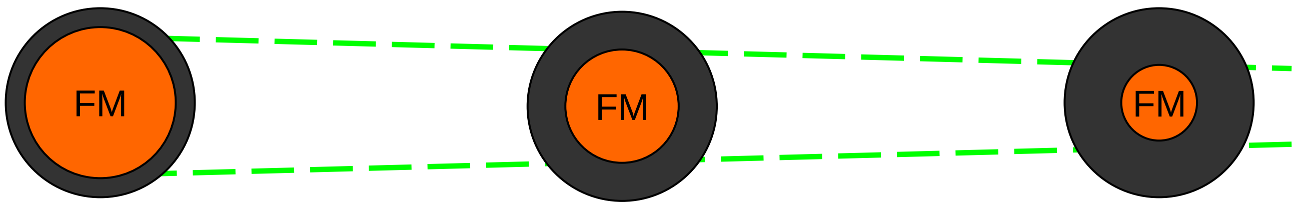
J. Phys. D **41**, 134010 (2008)

h_{eb} decreases as the cooling field increases (as in experiments)

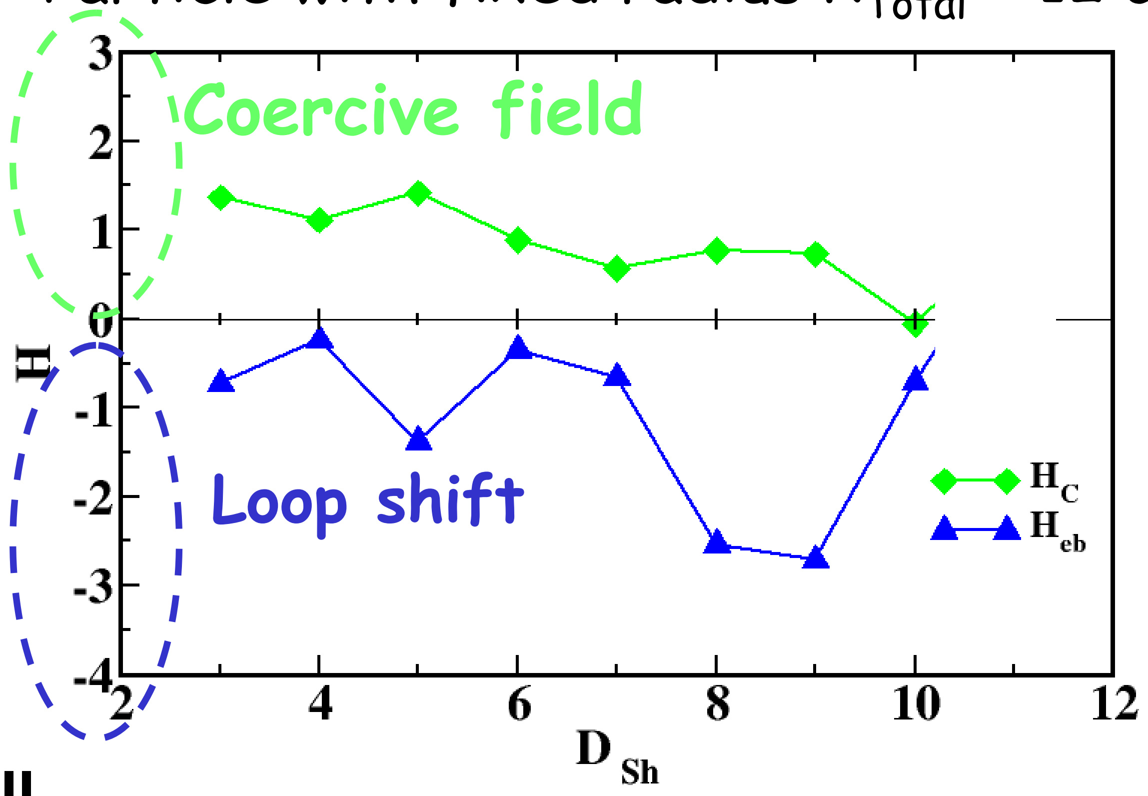
The increasing cooling field progressively reverses the interfacial shell spins along the field direction (as in *positive* EB), reducing the exchange field on the FM

The loops become more symmetric

Shell thickness dependence



Particle with fixed radius R_{Total} = 12 a



Core/Shell particle → **AF particle**

Conclusions

1. EB effects and glassy behavior are difficult to decouple.
2. Core/shell NPs naturally incorporate roughness and non-compensation at the interface.
3. EB in core/shell Co-CoO can be tuned as a function of the oxygen pressure.
4. Atomistic Monte Carlo simulations can be used to study finite-size and surface effects at the microscopic level.
5. Simulations of a model of core/shell NP unveils and quantifies the **microscopic origin** of EB: loop shift is due to the exchange field acting on the particle core, generated by the net magnetization of **uncompensated, pinned shell spins at the interface**.
6. EB-related phenomenology such as **particle size, shell thickness, shell anisotropy, cooling field and interface coupling dependences**, together with loop **asymmetry, reversal mechanisms and vertical shift**, are successfully accounted for by the results of the simulation.