UNIVERSITAT DE BARCELONA

# Phenomenology and Models of Exchange Bias in Core /Shell Nanoparticles


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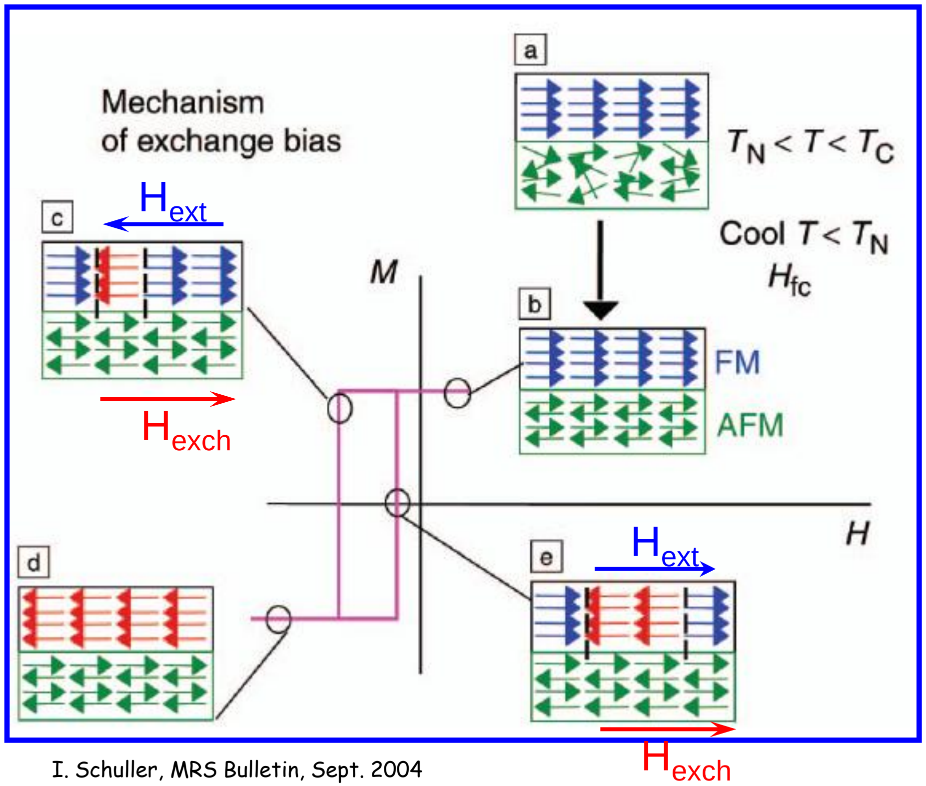
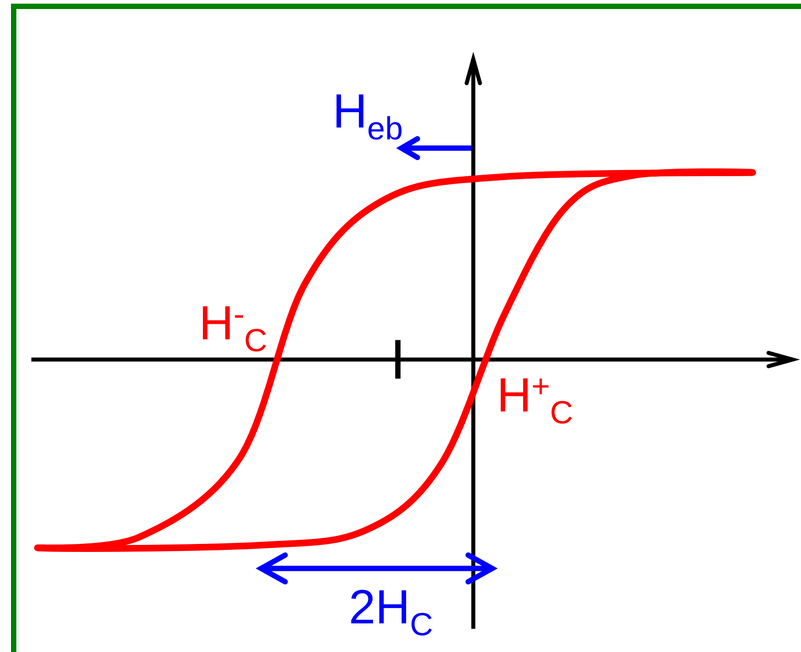
FM film on top of AFM




I. Schuller, MRS Bulletin, Sept. 2004

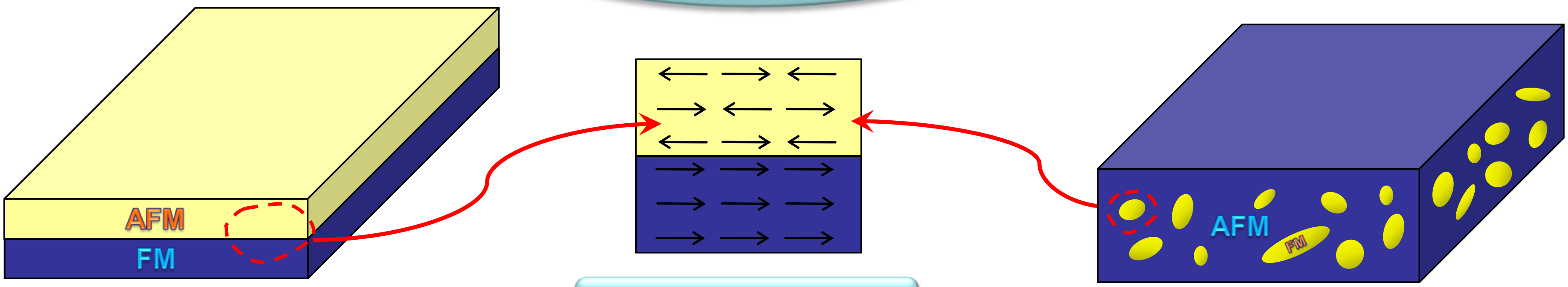



Displacement of loop after FC due to coupling of the FM to the AFM

$$H_{eb} = (H^+_c + H^-_c)/2$$

$$H_C = (H^+_c - H^-_c)/2$$

## Microscopic Origin of Exchange Bias?




Close contact between FM and AFM phases

- Proximity effects
- Phenomena at interface (and bulk?)

Atomic details are important

- Local magnetic moments , $\mu_i$
- Exchange constants, $J_{ij}$
- Anisotropy constants, $K_i$
- Lattice structure, $r_{ij}$

## KEY INGREDIENTS

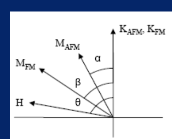
- Pinned Antiferromagnet ⇒ High anisotropy $K_{AFM}$
- Exchange coupling at the interface ⇒ FM or AFM
- Uncompensated moment of the AFM ⇒ Loop displacements

## OPEN QUESTIONS

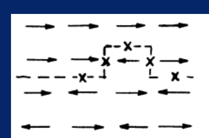
- Nature of interface interaction.
- Quantifying the loop shifts.
- Reversal mechanisms.
- Hysteresis loop asymmetry.

## MODELS

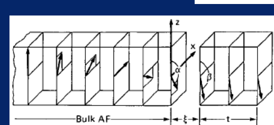
- **Meiklejohn, Bean (1956) ⇒**
  *Uncomp. Interface*
  *Too large shift*



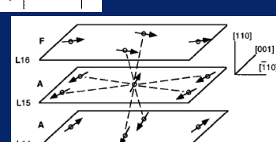

- **Malozemoff (1987) ⇒**
  *Random field*
  *Interf. roughness*



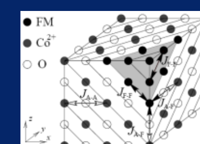
- **Mauri (1987) ⇒**
  *Interface AF Domain Wall*



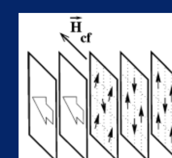

- **Koon (1997) ⇒**
  *Spin-flop coupling*



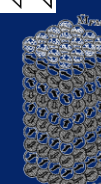

- **Schulthess, Butler (1998) ⇒**
  *Magnetostatic interations*



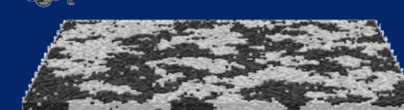

- **Kiwi (1999) ⇒**
  *Frozen interface model*



- **Stiles, McMichael (1999) ⇒**
  *Polycrystalline interface*
  *AFM grains*



- **Nowak, Usadel (2000) ⇒**
  *Domain state model*
  *Diluted AFM*



## ➢ Experimental systems showing EB


*W. H. Meiklejohn and C. P. Bean*
*Phys. Rev. 102, 1413 (1956); 105, 904 (1957)*

Bilayered thin films → AF on top of a FM material: $FeF_2$/Fe, $MnF_2$/Fe, CoO/Py,…

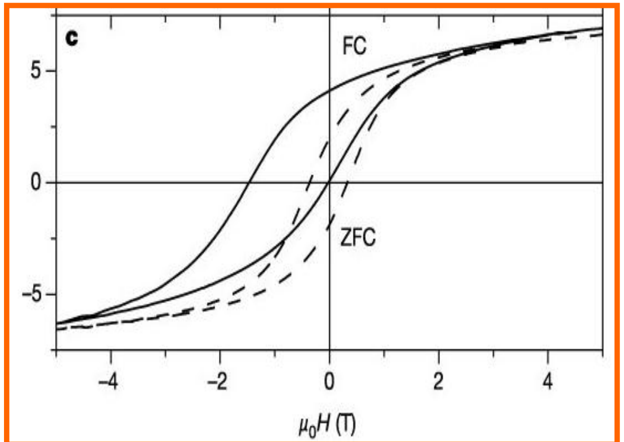
Ferrimagnetic and AF oxide NPs → NiO, CoO, CuO, FeOOH… $NiFe_2O_4$, γ-$Fe_2O_3$, $LaCaMnO_3$,…

FM particles embedded in AFM matrix → Co in CoO, Fe in $FeCl_2$, Fe in $FeF_2$,…

Core /Shell NPs → Usually FM core + AF shell: CoO/Co, Fe/FeO,…

**Review Article:**
***Exchange Bias phenomenology and models of core/shell nanoparticles***
O. Iglesias, A. Labarta and X. Batlle
**J. Nanoscience and Nanotechnology 8, 2761-2780 (2008)**
Preprint: Cond-Mat/0607716

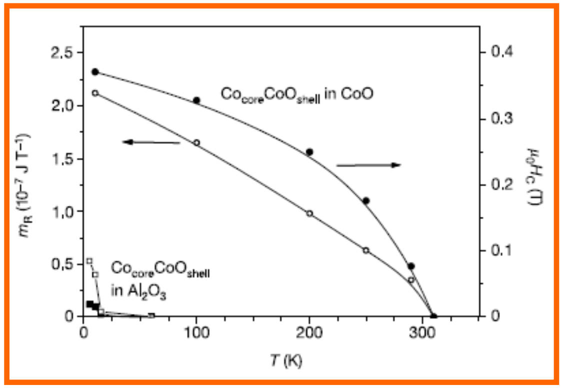
## Shifted loops, increased $H_c$




V. Skumryev at al.
Nature **423**, 850 (2003)

Co/CoO

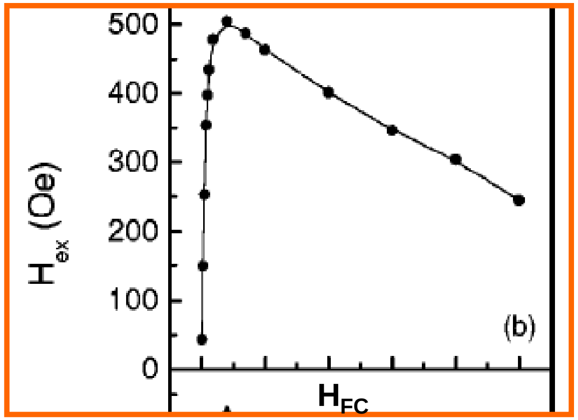
## Increased $T_B$




V. Skumryev at al.
Nature **423**, 850 (2003)

Co/CoO

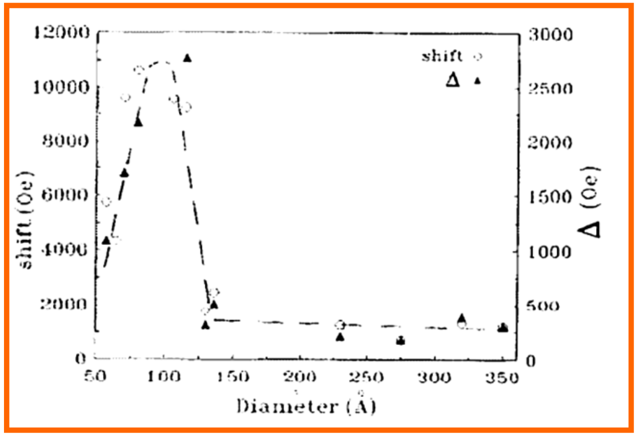
## Field cooling dependence




Del Bianco et al.
PRB **70**, 052401 (2004)

Fe/FeO

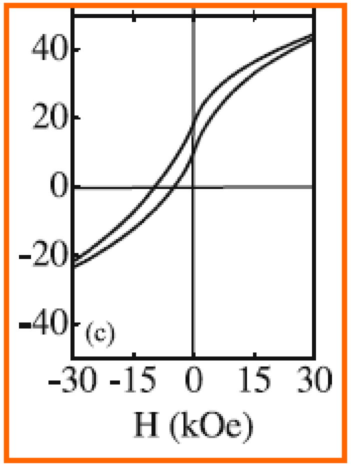
## Particle size dependence




Gangopadhyay S et al.
JAP **73**, 6964 (1993)

Co/CoO

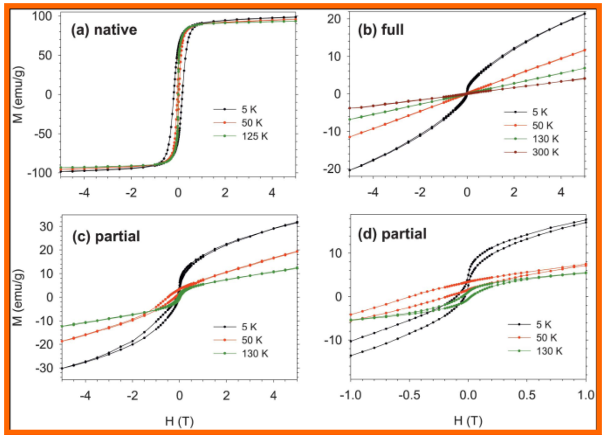
## Vertical shifts




Zhou et al.
ApplPhysA **81**, 115 (2005)

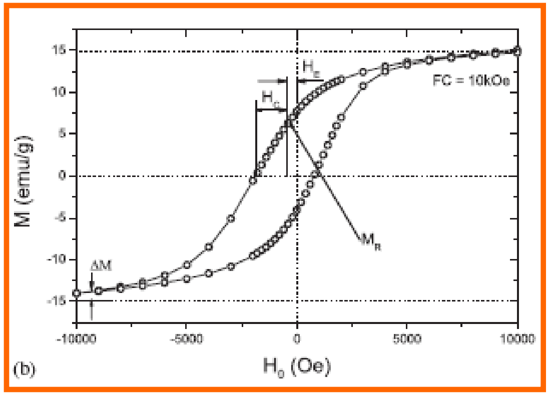
Co/CoO

## Oxidation state




Tracy et al.
PRB 72, 064404 (2005)

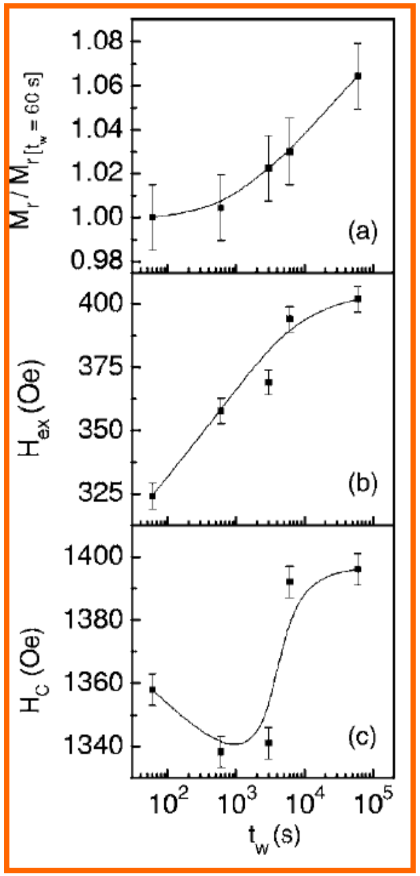
Co/CoO




Passamani et al.
JMMM **299**, 11 (2006)

$Fe/MnO_2$

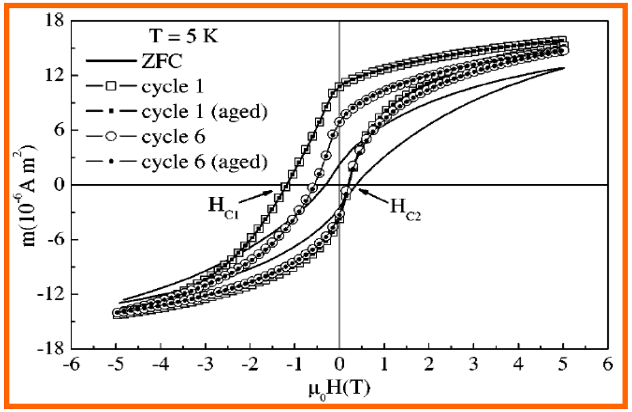
## Glassy dynamics




Fiorani et al.
PRB **73**, 092403 (2006)

Fe/FeO

## Training effects



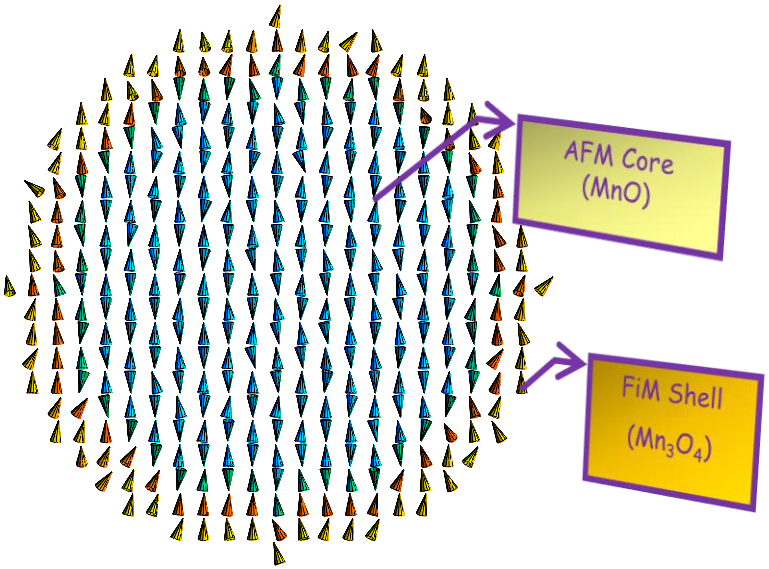

Zheng et al.
PRB **69**, 214431 (2004)

$Fe/\gamma Fe_2O_3$

## ➢ Phenomenology in Core/Shell NPs

### EB in Inverted core/shell NPs

$R_{Total}$= 12a , $R_{Shell}$= 3a




**Doubly inverted Core/Shell NPs**

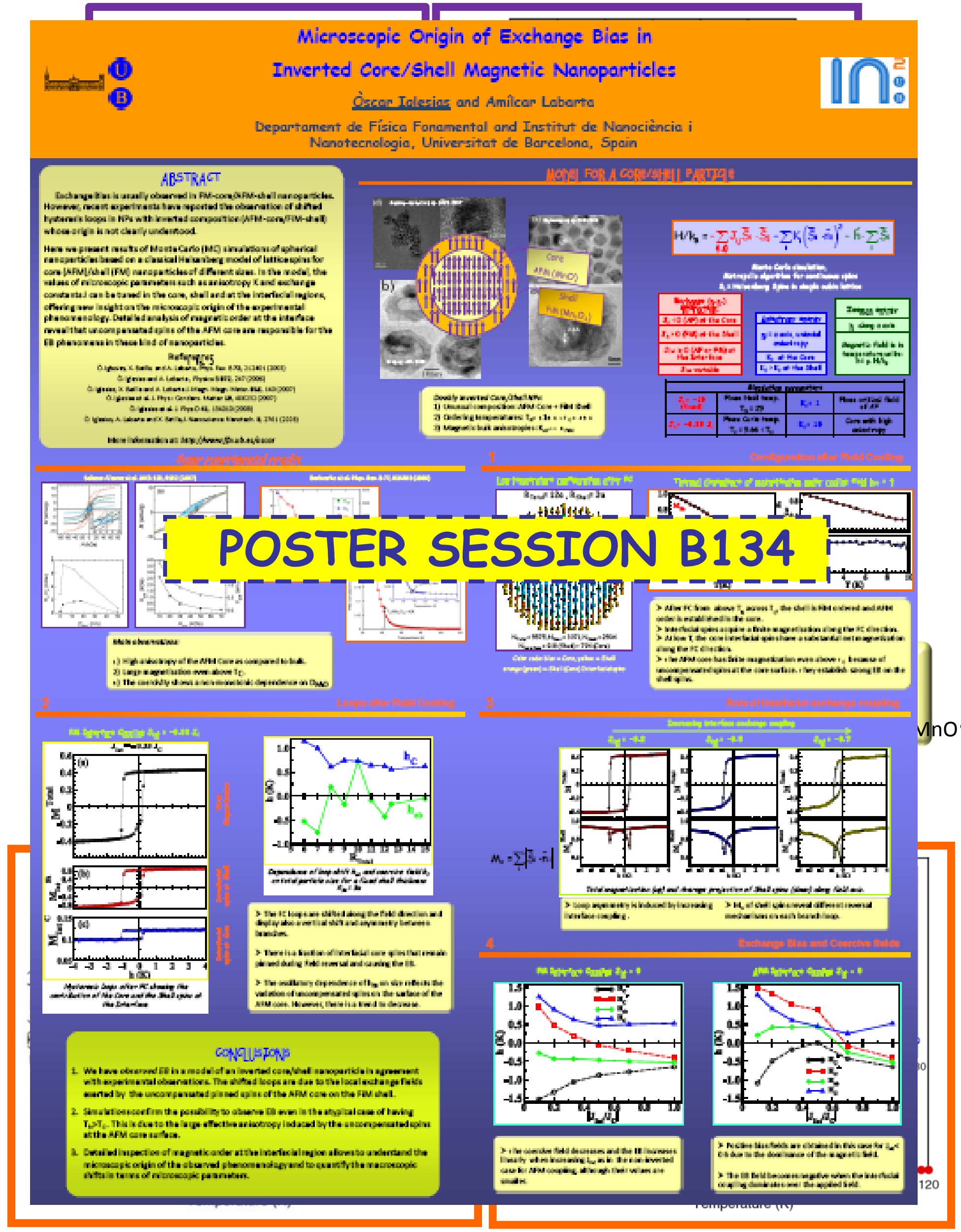
Composition
AFM Core + FiM Shell

Unusual

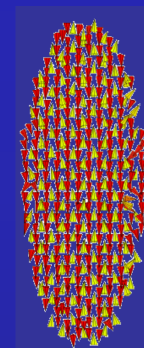
Ordering Temp.
$T_N$= 118 K >$T_C$ = 43 K

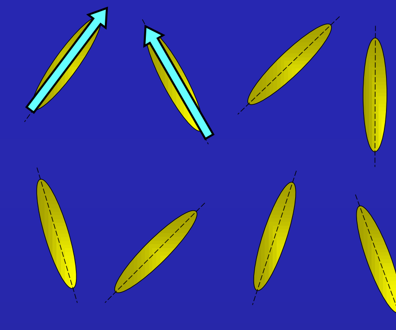
Unusual

Anisotropy
$K_{AF} >> K_{FiM}$



• Interplay with Surface Effects and Interparticle Dipolar Interactions ⇒

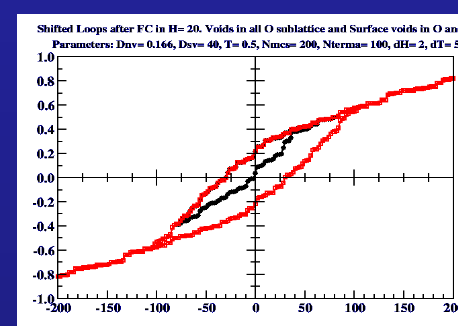




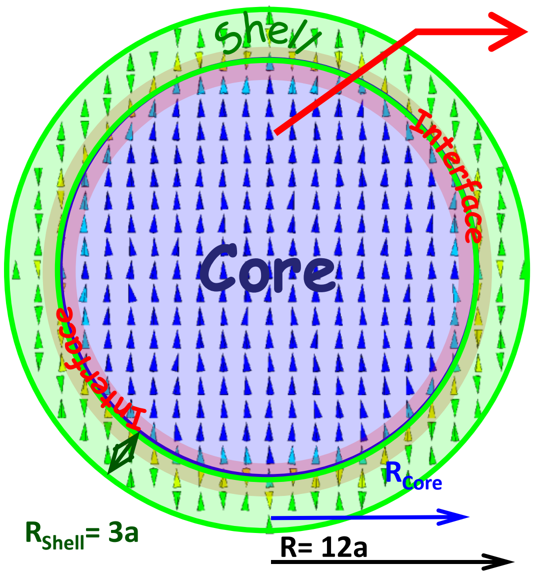
• Magnitude of the EB and coercive fields ⇒

• Distributed properties and role of $T_B$ ⇒

• EB vs. Minor loop Effects ⇒



## ➢ Model for a Core/Shell NP

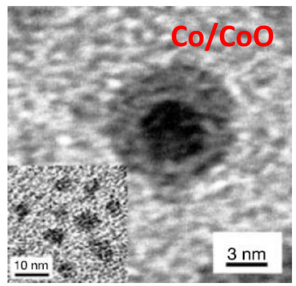



**Core: ferromagnetic (Co)**

**Shell: antiferromagnetic (oxide)**

**Interface: spins at C/Sh with nearest neighbors at the Sh/C**

Skumryev et al. Nature 2003




**In a core/shell particle, the interface is not well-defined as in bilayers.**

**Interface spins are not compensated nor uncompensated.**

O. Iglesias et al., PRB 72, 21240 (2005)

$N_{Total} = 5575 N_{Core} = 3071$, $N_{Shell} = 2504$

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

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

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

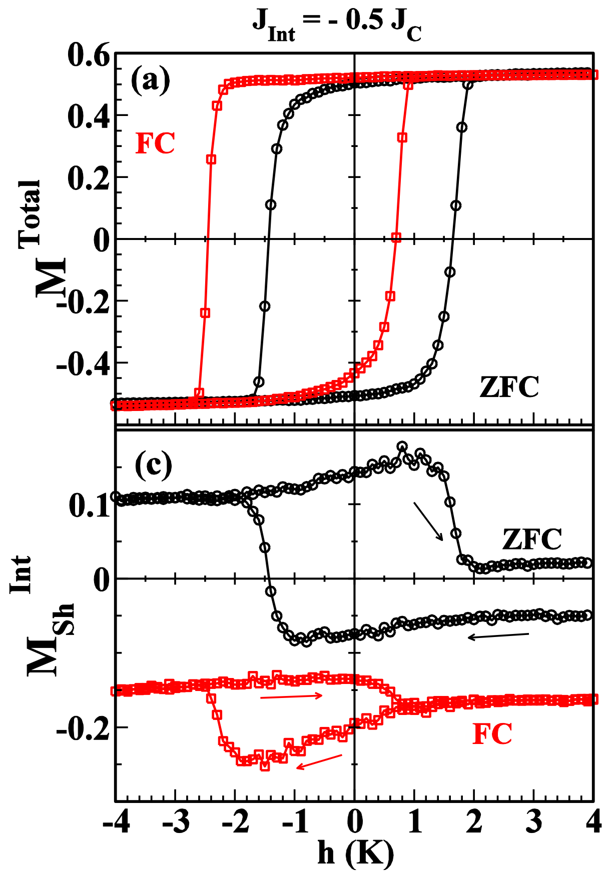
**Monte Carlo simulation,**

**Metropolis algorithm for continuous spins**

**$S_i$ = Heisenberg Spins in simple cubic lattice**

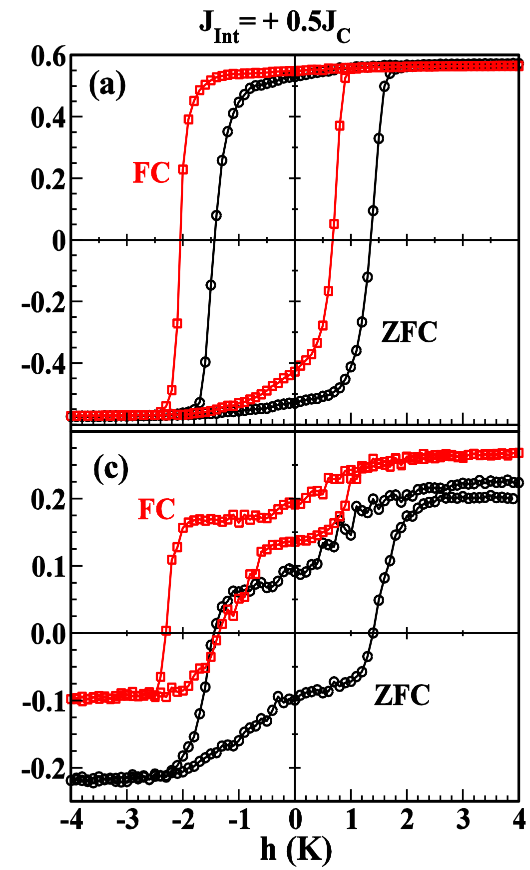
| | | |
|---|---|---|
| **Zeeman energy** | **h** along z axis | Magnetic field is in temperature units: $h = \mu H/k_B$ |

## AF Interface Coupling




$J_S = -0.5, J_{Int} = -0.5$

## FM Interface Coupling




$J_S = -0.5, J_{Int} = +0.5$

- ➢ Loop after FC is displaced towards negative field direction with respect to ZFC loop.
- ➢ Notice also the vertical shift of the shell magnetization.

- ➢ Shell behavior is dictated by coupling with the core through $J_{int}$ .
- ➢ Changing the sign of the interface coupling influences the net magnetization at the interface.

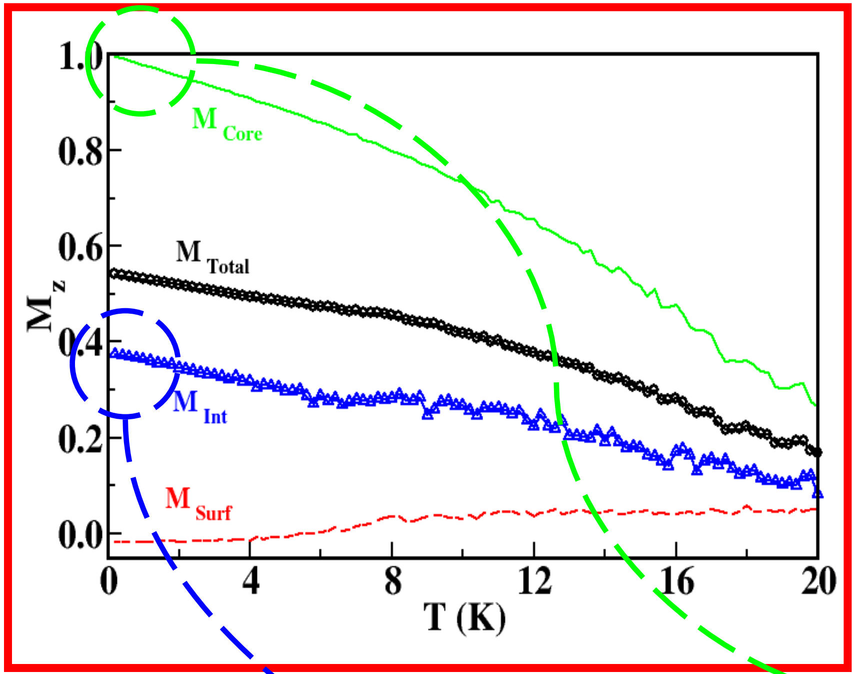
O. Iglesias, X. Batlle and A. Labarta, Phys. Rev. B 72, 212401 (2005)

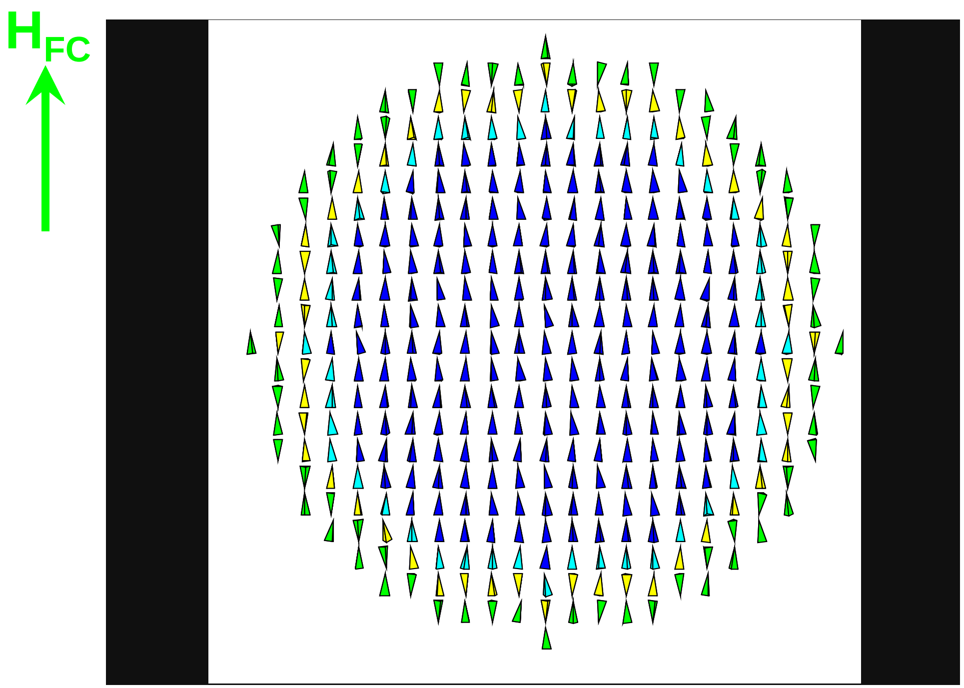
# ➢ Results: Field Cooling

COLOR CODE: dark blue ⇒ core, green ⇒ shell

yellow (cyan) ⇒ shell (core) interfacial spins

**Temperature dependence of magnetization under cooling field $h_{FC} = 4$**



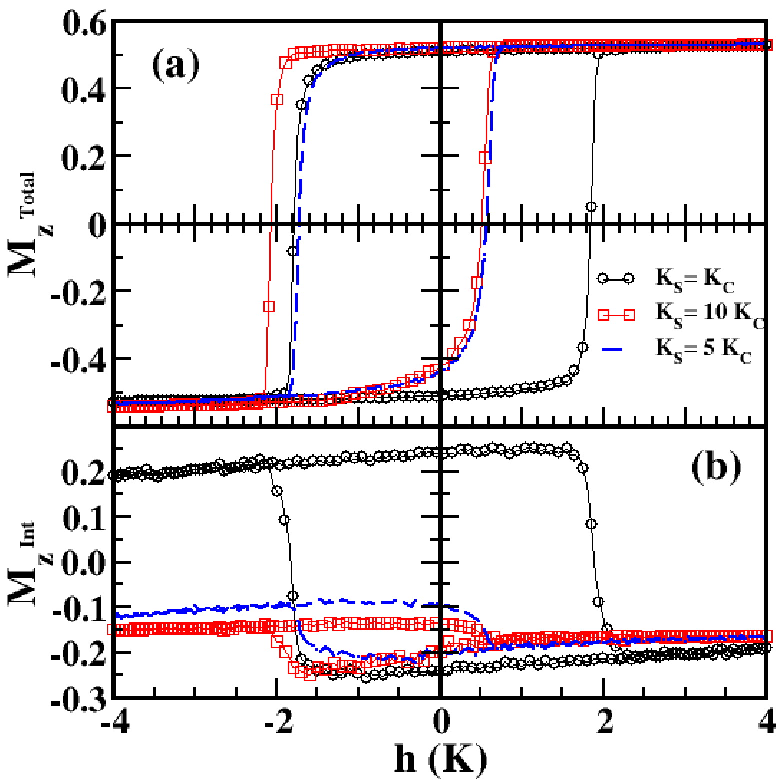



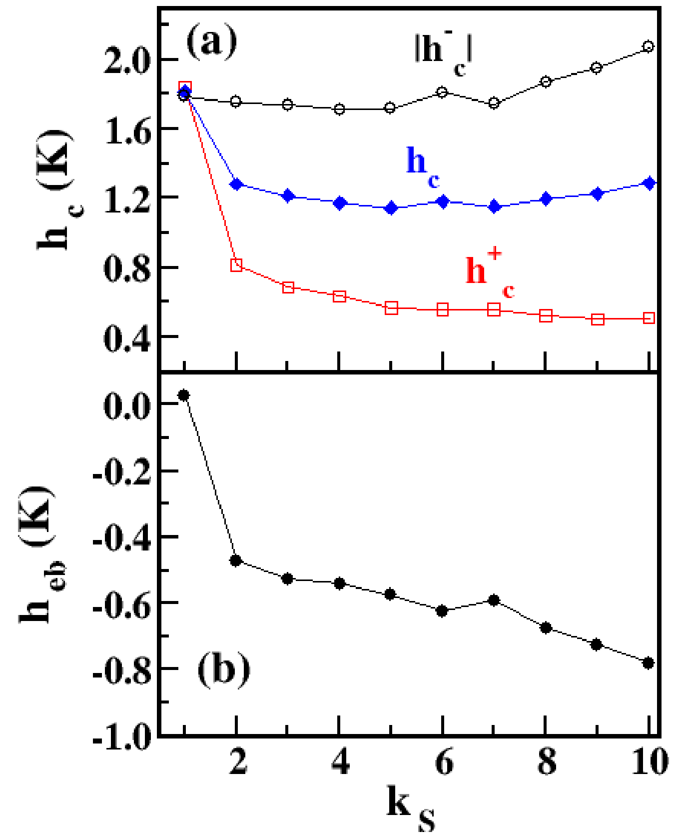

O. Iglesias and A. Labarta, Physica B 372, 247 (2006)

After FC from high temperature $T > T_N$ :

- ➢ Core with FM order.
- ➢ Shell with AF order.
- ➢ Interface spins have net magnetization along z-axis.

## Increasing the anisotropy of the AF shell




For low $K_S$, shell spins are dragged by core spins during reversal.

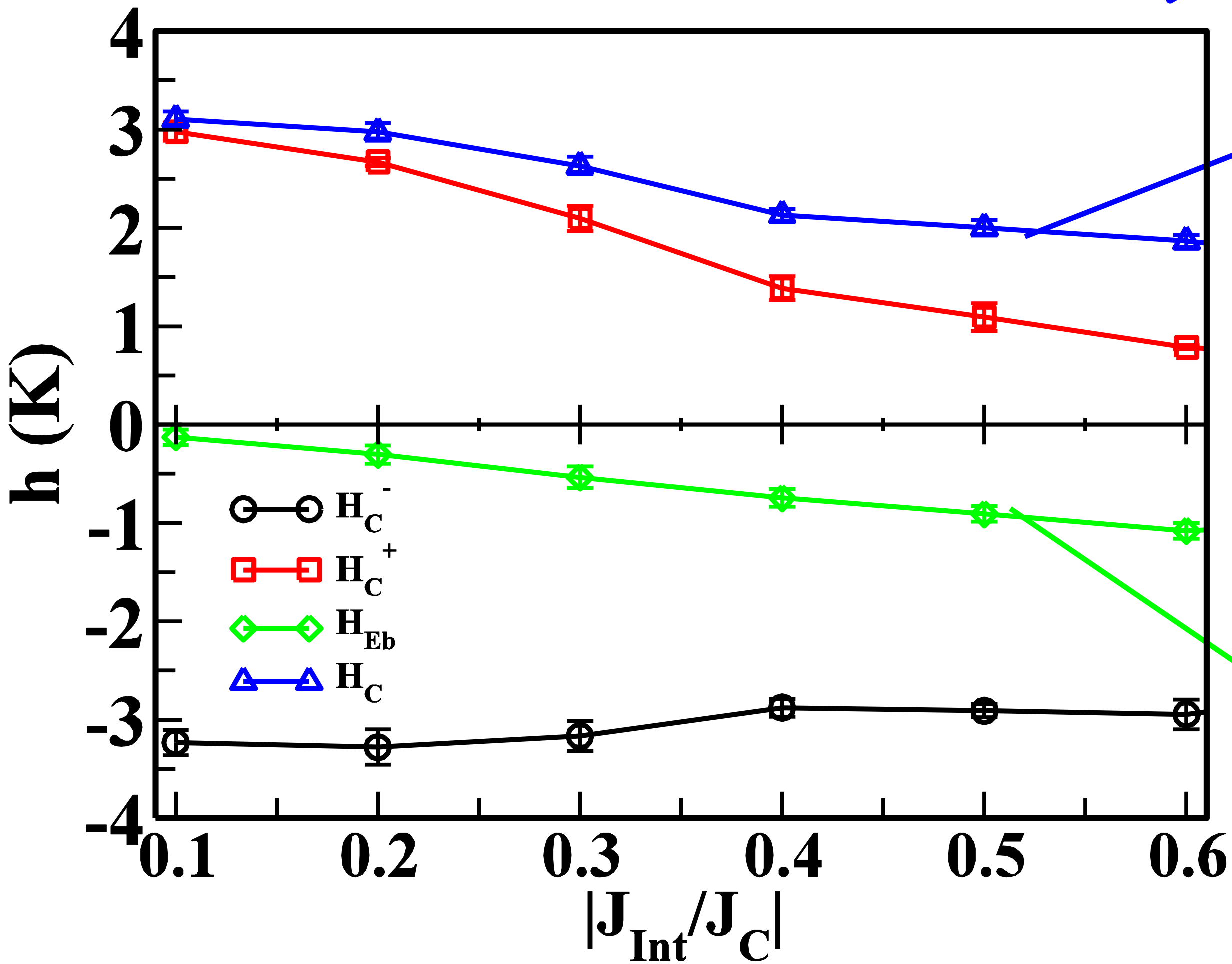
- There is a minimum value of $K_S$ for observing EB.
- $h_C$ does not change appreciably.

O. Iglesias, X. Batlle and A. Labarta, J. Phys.: Condens. Matter 19, 406232 (2007)

# Results: $h_{EB}$ and $H_c$

Role of the increasing Interface AF Coupling $J_{Int}$

$R = 12a$, $R_{Sh} = 3a$, $K_{Sh} = 10\ K_C$




**$H_c$ decreases**

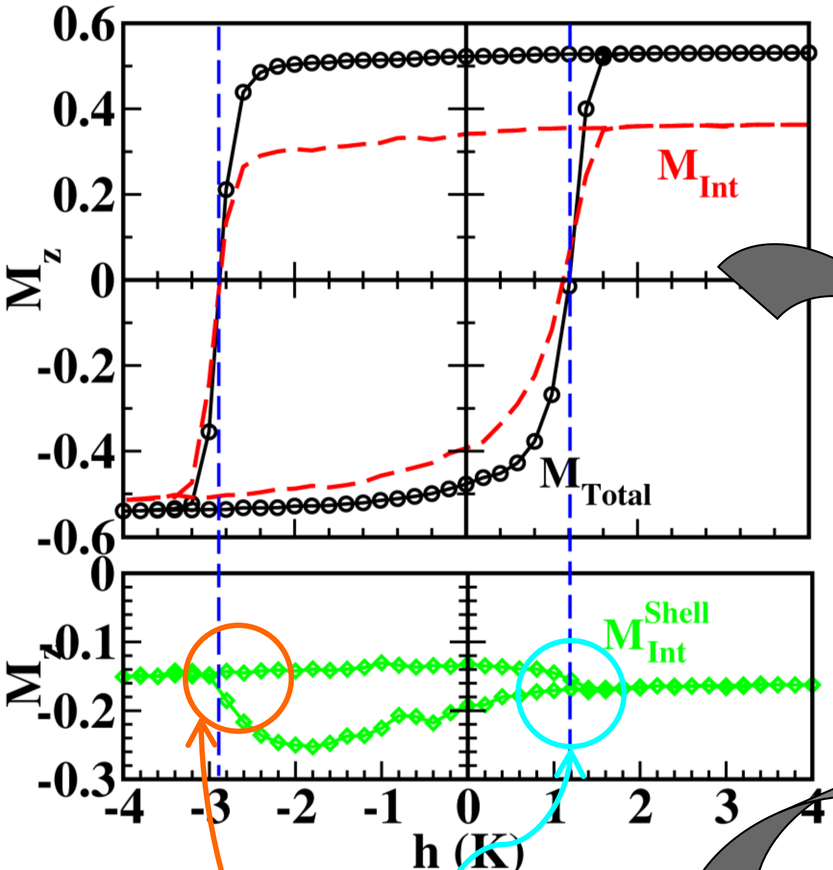
Coupling of the core to the shell helps the reversal

**$H_{eb}$ increases**

**Linear** variation with $J_{Int}$, due to the higher local exchange field acting on the core spins.

O. Iglesias, X. Batlle and A. Labarta, Phys. Rev. B 72, 212401 (2005)

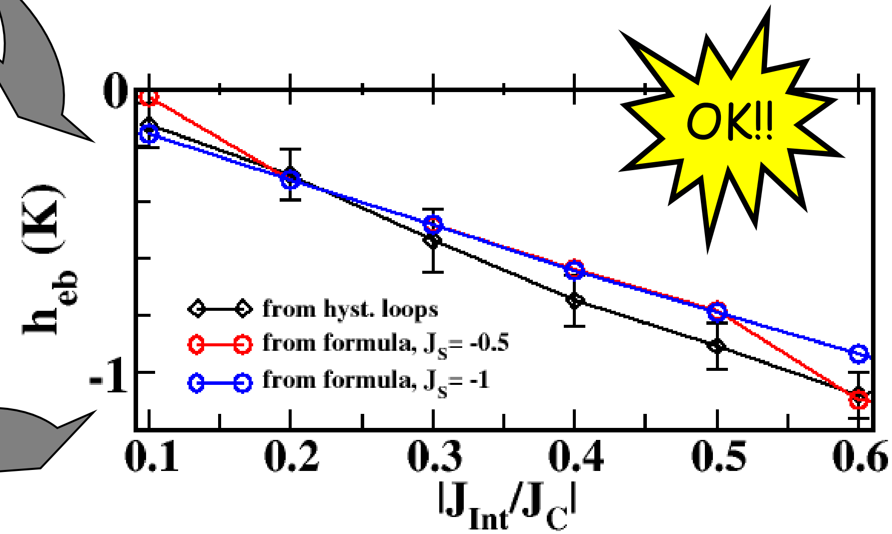
## ➢ Microscopic Origin of EB




Spins at the interface, two contributions:

*Irreversible spins:* pinned through the hysteresis loop. Small fraction!

*Reversible spins:* reverse with the core due to $J_{Int}$, do not cause EB.




$$H_{eb} = J_{Int}\frac{M^{+}_{Int} + M^{-}_{Int}}{2}$$

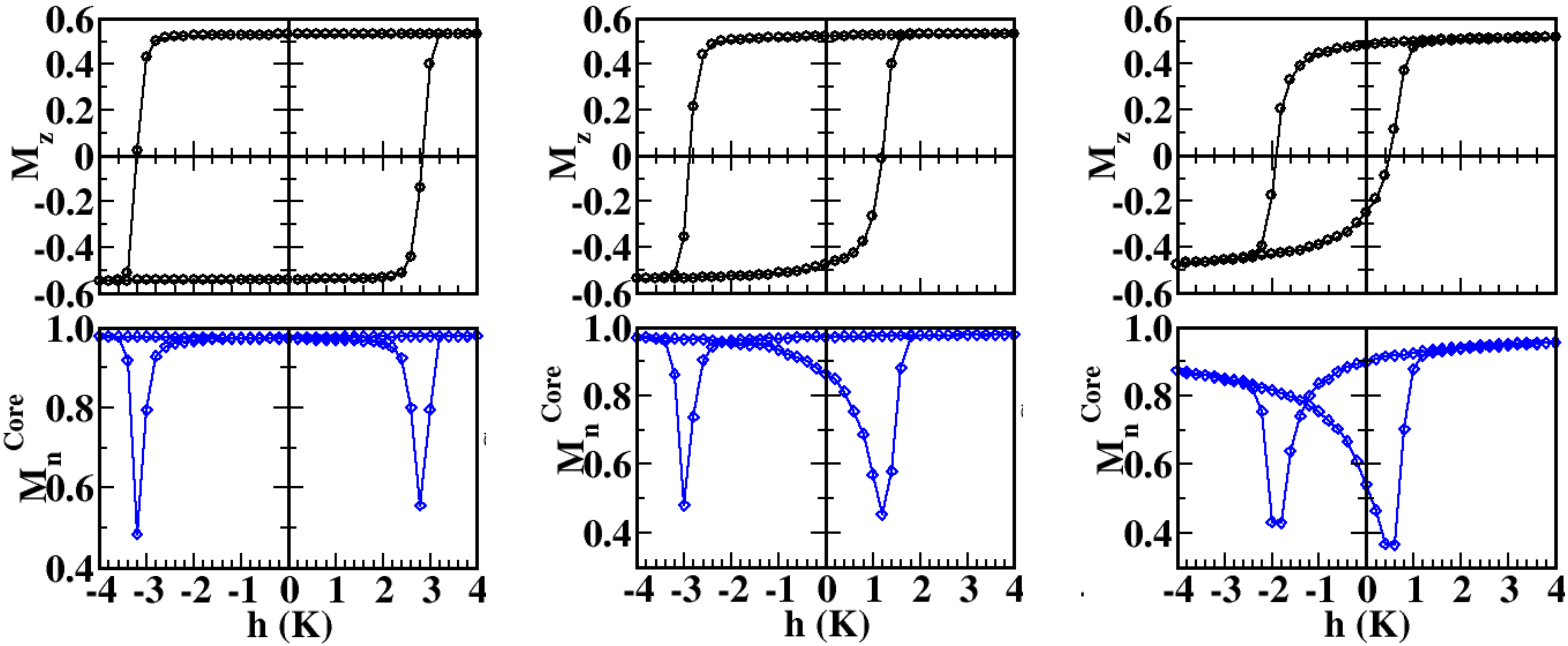
$$M^{+}_{Int} = \sum_{i\in\{Sh,Int\}} z_i S^z_i$$

- ➢ EB field is associated to the net uncompensated magnetization of the pinned interface spins at the shell.
- ➢ It can be quantified from the model !!

O. Iglesias, X. Batlle and A. Labarta, Phys. Rev. B 72, 212401 (2005)

**Increasing interface exchange coupling**

$J_{Int}$ = -0.2 $J_{Int}$ = -0.5 $J_{Int}$ = -1



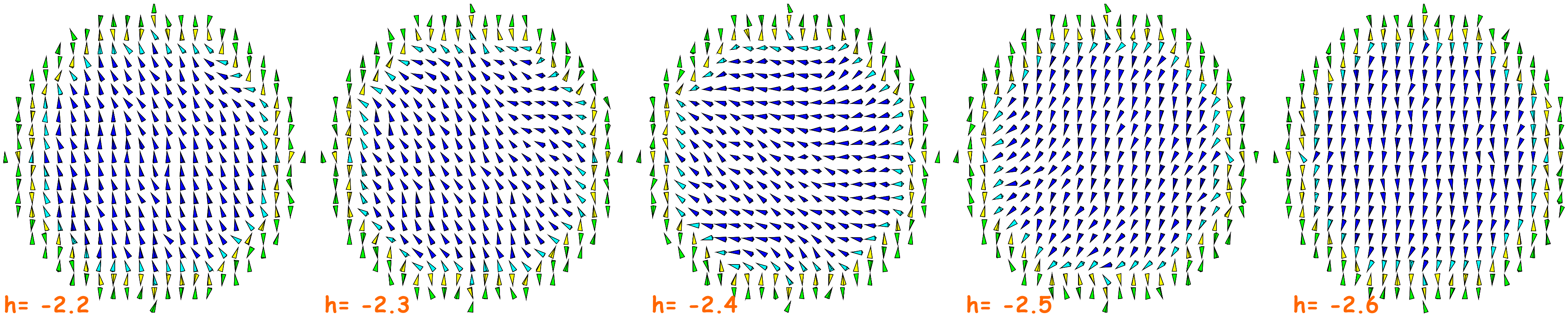

$$M_n = \sum_i \left| \vec{S}_i \cdot \hat{n}_i \right|$$

$M_n \Rightarrow$ Magnetization projection along easy-axis

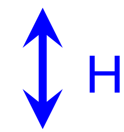
**Loop asymmetry is induced by the increasing interface coupling**

## Descending branch

**COHERENT ROTATION**

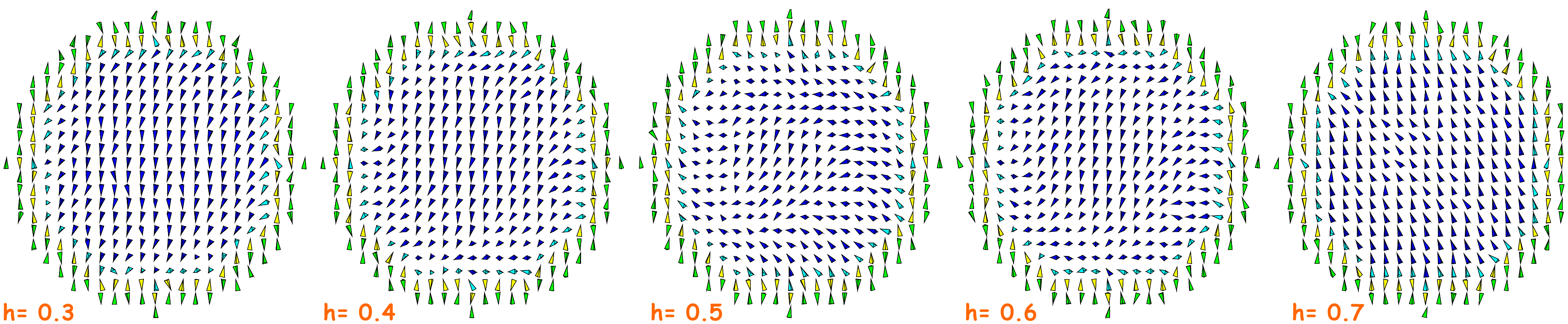



Loop asymmetry is due to different reversal mechanisms and increases with $J_{Int}$

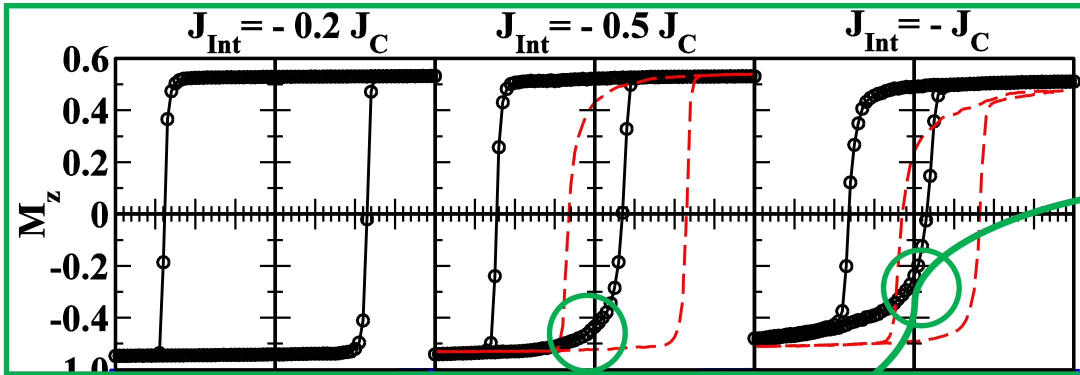


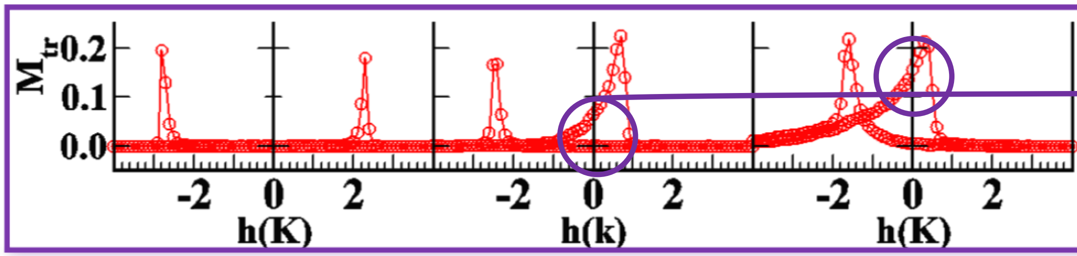

## Increasing branch

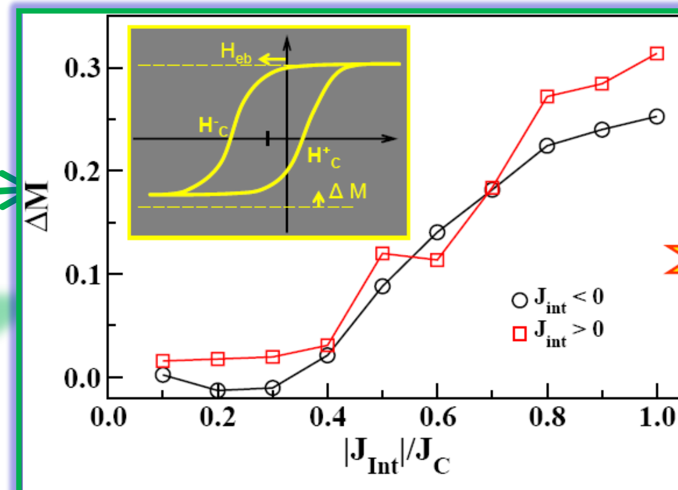
**NUCLEATION + PROPAGATION**



## ➢ Results: Vertical Shifts



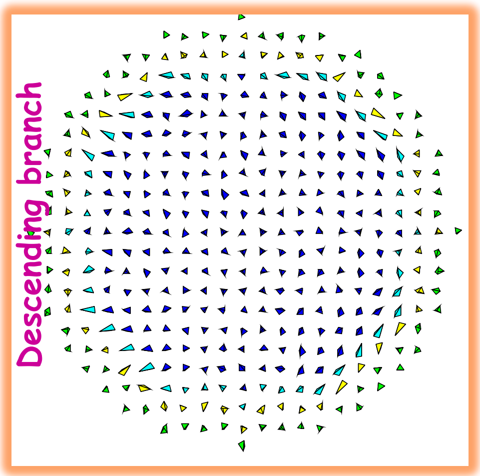



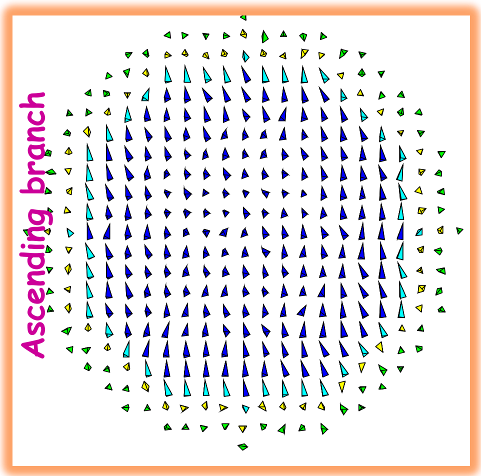




*Vertical loop displacements as a function of interface exchange coupling*

O. Iglesias et al., J. Nanosci. Nanotechnol. 8, 2761 (2008)

**Configurations at remanence**

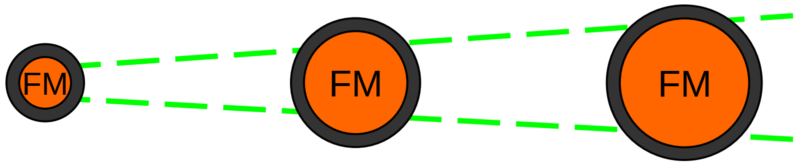


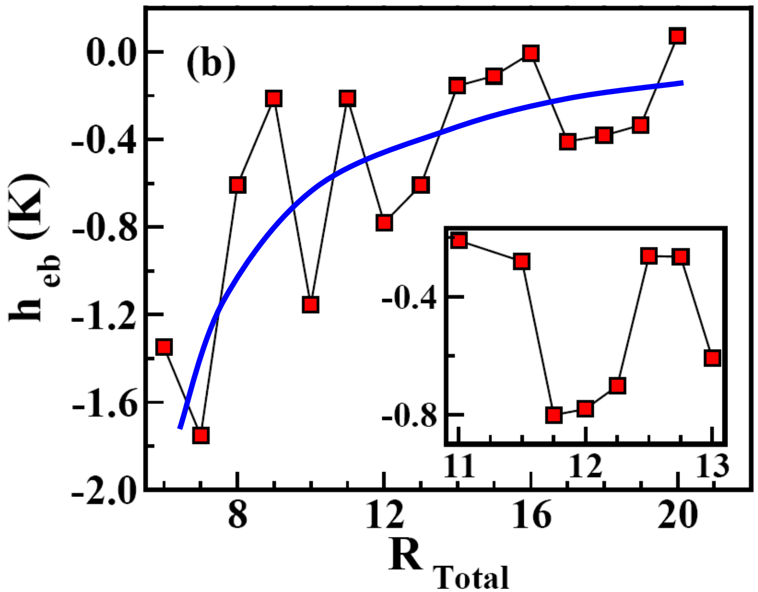




**Microscopic origin of the vertical shift is the different reversal mechanisms on the two loop branches**

## ➢ Results: Particle Size Dependence

### *Particle Size dependence*




➢ Oscillatory dependence on particle size.

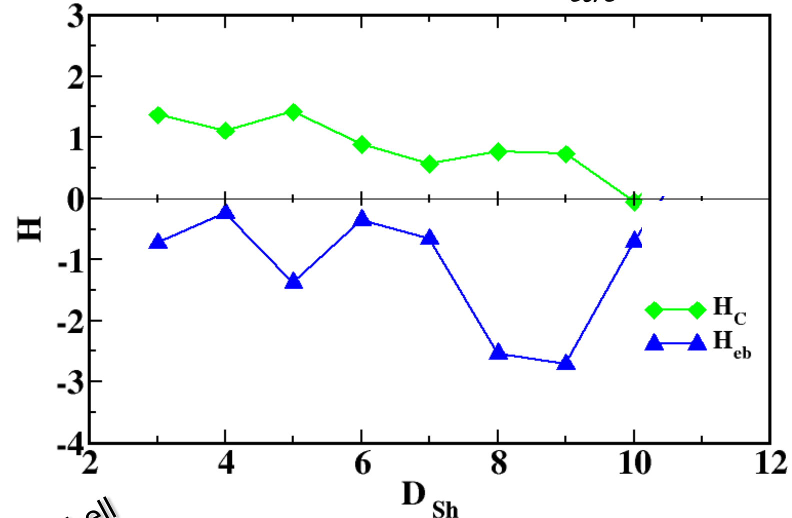
➢ $h_{EB}$ shows a trend to decrease as size increases as in experiments:

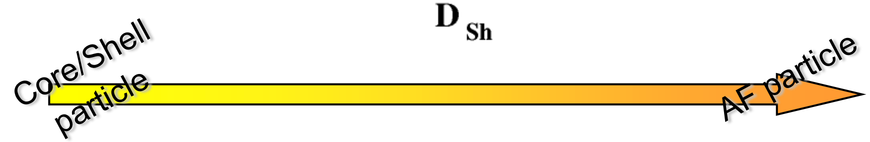
$$h_{eb} \sim 1/R_{Core}$$

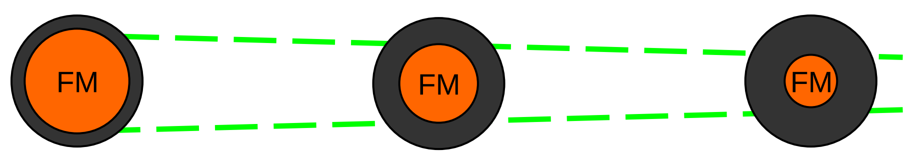
O. Iglesias et al., J. Phys. D 41, 134010 (2008)

### *From core/shell to AFM NPs*

*Particle with fixed diameter $D_{Core}$ = 12 a*



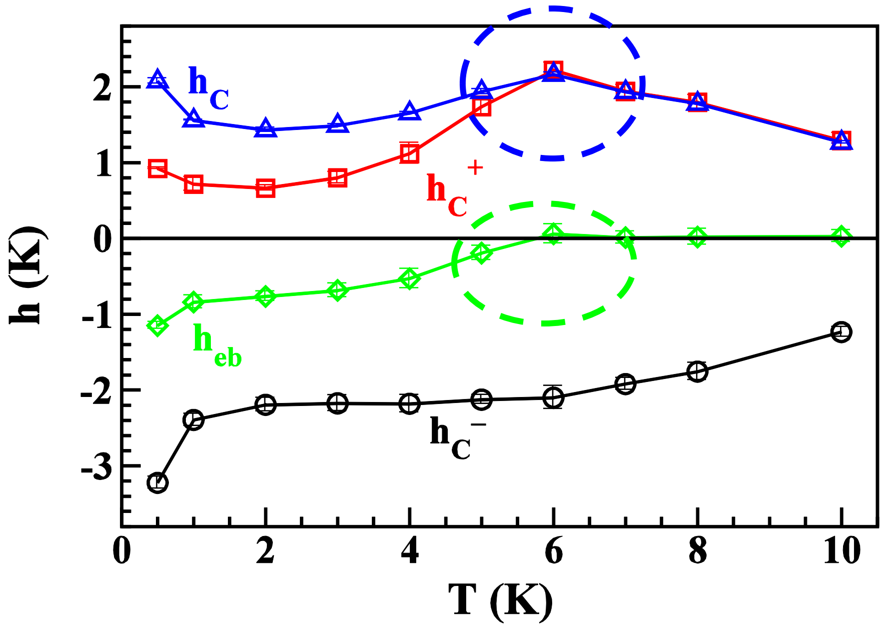



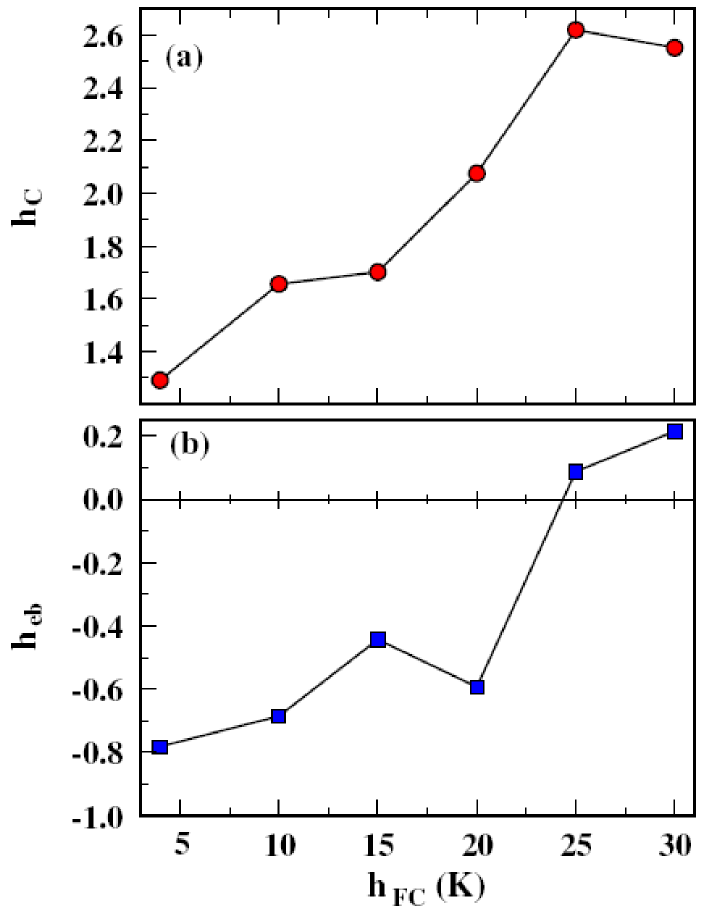

O. Iglesias et al., J. Nanosci. Nanotechnol. 8, 2761 (2008)

## ➢ Results: Temperature and $h_{FC}$ dependence

*Temperature dependence*




*Cooling field dependence*




➢ $h_{eb}$ decreases with T and vanishes above 6 K.

➢ $h_C$ decreases also with T, but presents a local maximum at the vanishing $h_{eb}$ temperature.

O. Iglesias et al., J. Nanosci. Nanotechnol. 8, 2761 (2008)

O. Iglesias et al., J. Phys. D 41, 134010 (2008)

# V. CONCLUSIONS

1. ***Monte Carlo simulations*** at the ***atomistic*** level are useful to understand microscopic origin of ***magnetic phenomenology of nanomagnets***.
2. The ***microscopic origin*** of EB has been unveiled and quantified. We have shown that $h_{EB}$ is due to the exchange field acting on the particle core, generated by the net magnetization of ***uncompensated of shell spins at the interface***.
3. ***Asymmetry*** between the descending and ascending branches of the loops has been observed which increases with the strength of the interface coupling $J_{Int}$. ***Different reversal mechanisms***: (uniform rotation, nucleation-propagation) are responsible for it.
4. Vertical shifts, particle size, cooling field and temperature dependence can be understood from the simulation results.
5. Surface and interaction effects compete with EB and complicate interpretations.
6. Further simulation studies of interacting core/shell particles with internal structure and particles embedded in a matrix are under progress.

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