

Phenomenology and Models of Exchange Bias in Core /Shell Nanoparticles

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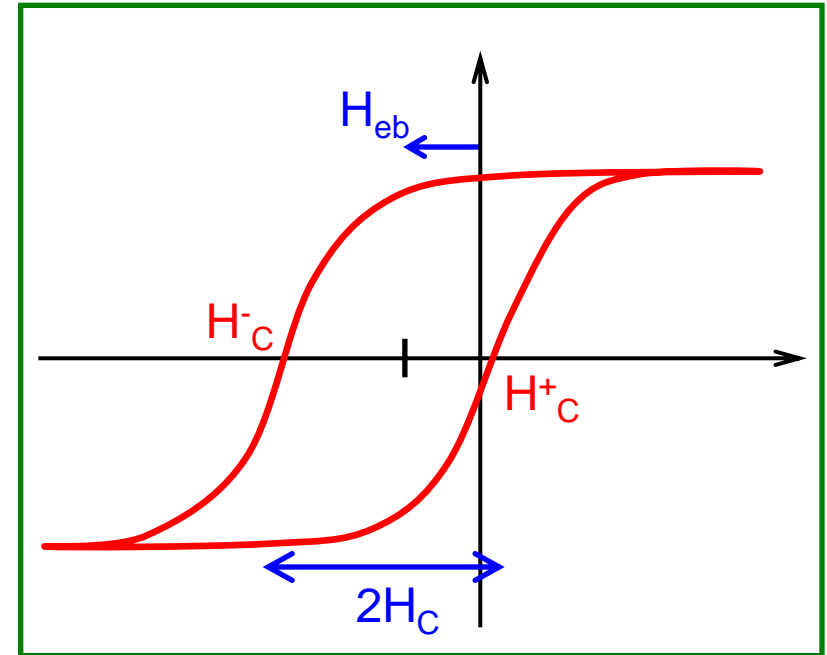
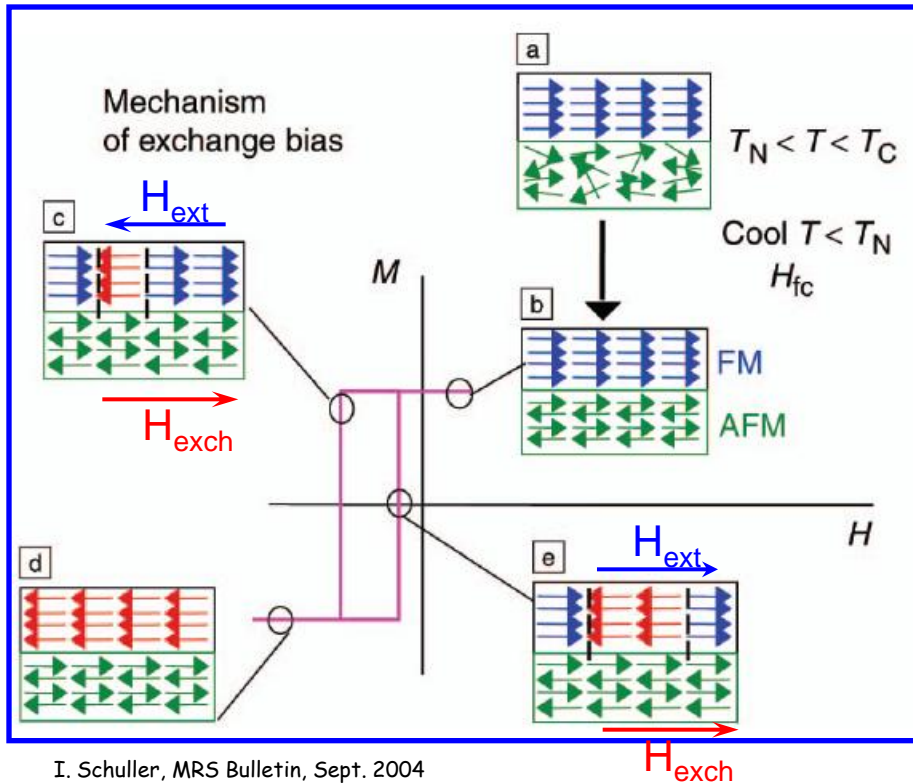


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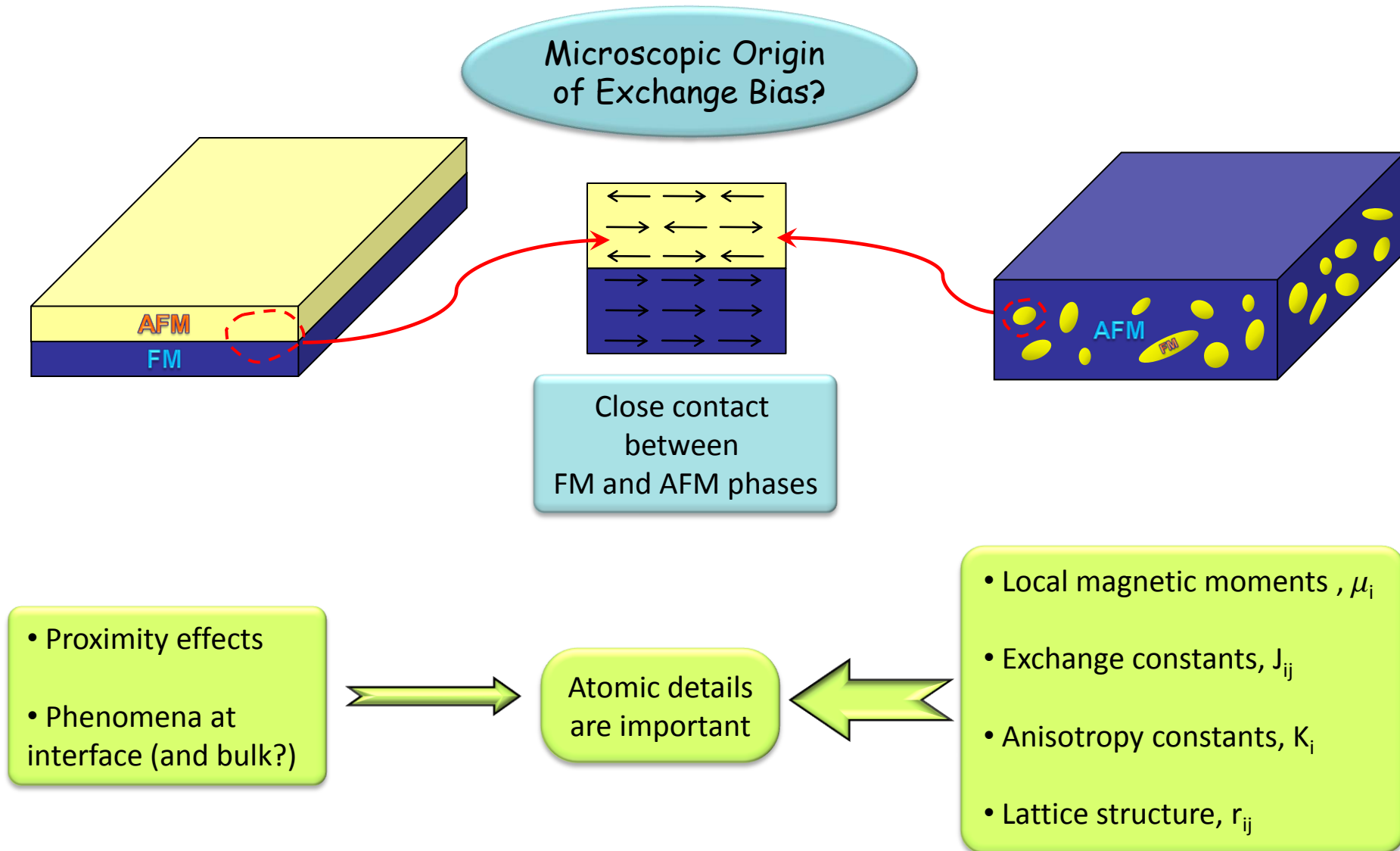
FM film on top of AFM



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

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

$$H_C = (H_c^+ - H_c^-) / 2$$



KEY INGREDIENTS

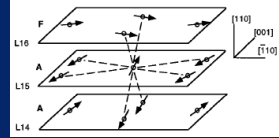
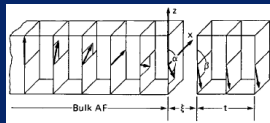
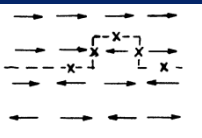
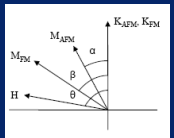
- Pinned Antiferromagnet ⇒ High anisotropy K_{AFM}
- Exchange coupling at the interface ⇒ FM or AFM
- Uncompensated moment of the AFM ⇒ Loop displacements

OPEN QUESTIONS

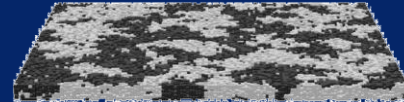
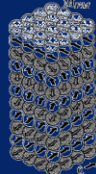
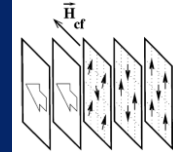
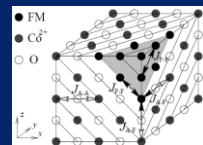
- Nature of interface interaction.
- Quantifying the loop shifts.
- Reversal mechanisms.
- Hysteresis loop asymmetry.

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*

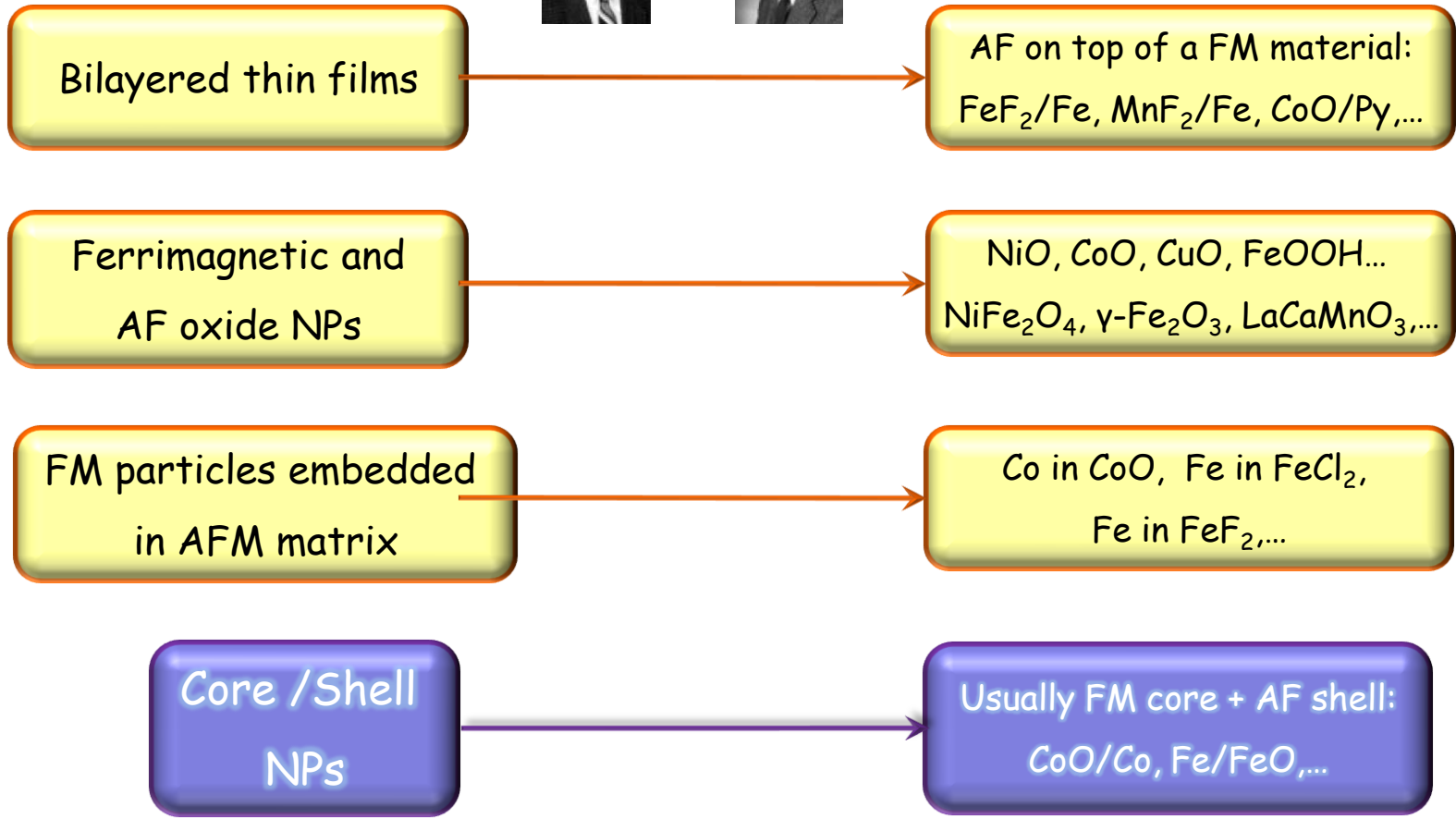


- Schulthess, Butler (1998) ⇒ *Magnetostatic interactions*
- Kiwi (1999) ⇒ *Frozen interface model*
- Stiles, McMichael (1999) ⇒ *Polycrystalline interface AFM grains*
- Nowak, Usadel (2000) ⇒ *Domain state model Diluted AFM*



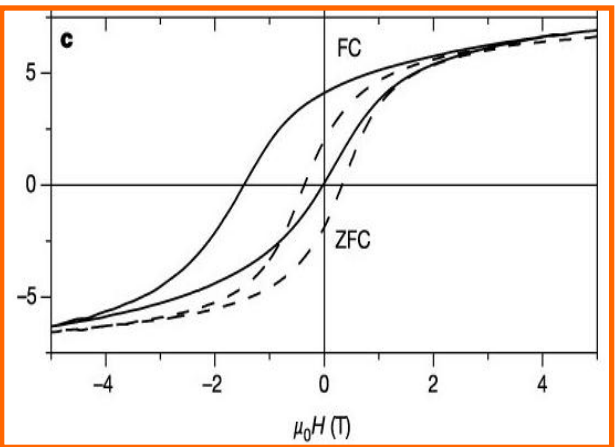


W. H. Meiklejohn and C. P. Bean
Phys. Rev. 102, 1413 (1956); 105, 904 (1957)



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

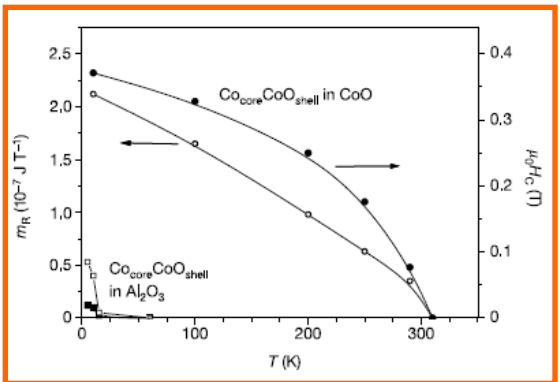
Shifted loops, increased H_c



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

Co/CoO

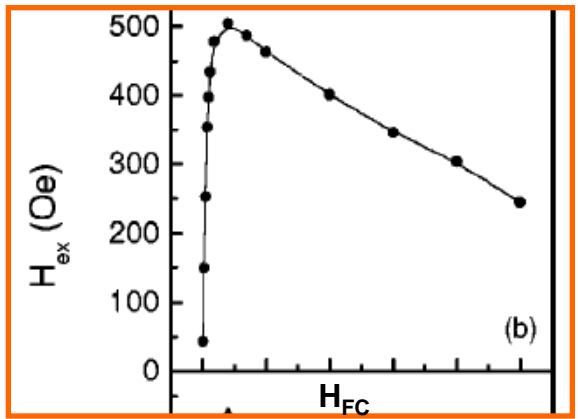
Increased T_B



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

Co/CoO

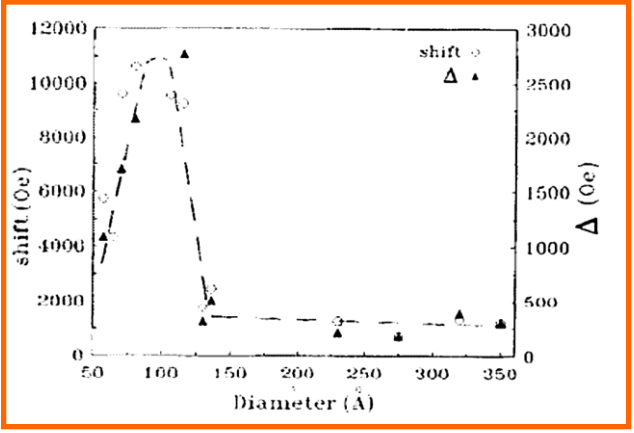
Field cooling dependence



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

Fe/FeO

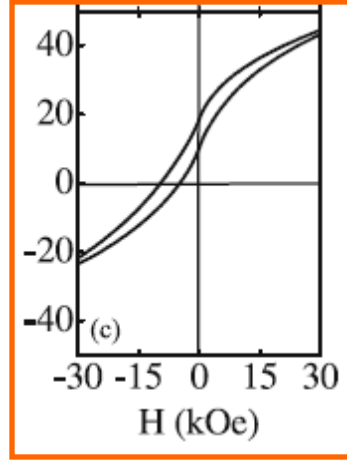
Particle size dependence



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

Co/CoO

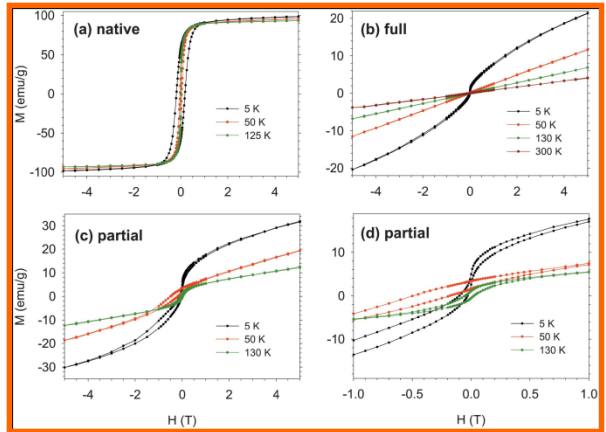
Vertical shifts



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

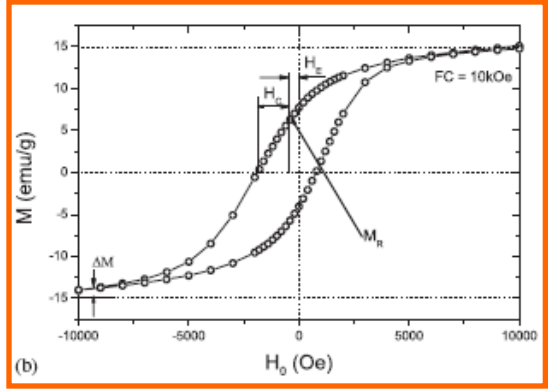
Co/CoO

Oxidation state



Tracy et al. PRB 72, 064404 (2005)

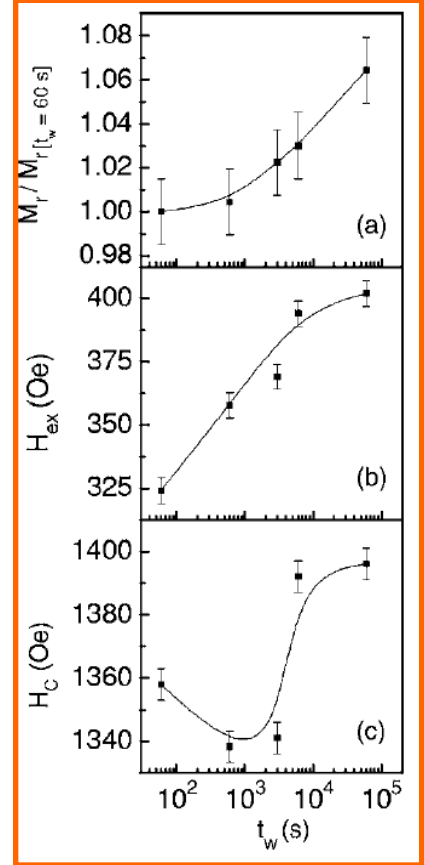
Co/CoO



Passamani et al. JMMM 299, 11 (2006)

Fe/MnO₂

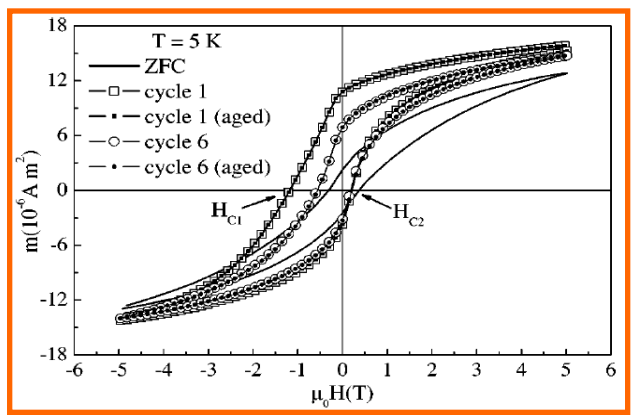
Glassy dynamics



Fiorani et al. PRB 73, 092403 (2006)

Fe/FeO

Training effects

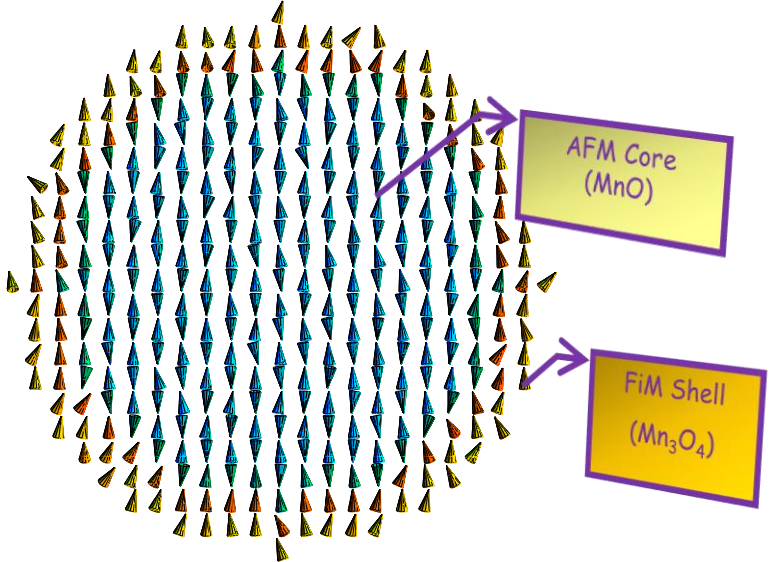


Zheng et al. PRB 69, 214431 (2004)

Fe/ γ Fe₂O₃

EB in Inverted core/shell NPs

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



AFM Core (MnO)

FiM Shell (Mn₃O₄)

Doubly inverted Core/Shell NPs

Composition
AFM Core + FiM Shell

Unusual

Anisotropy
 $K_{\text{AF}} \gg K_{\text{FiM}}$

Ordering Temp.
 $T_N = 118 \text{ K} > T_C = 43 \text{ K}$

Unusual

Microscopic Origin of Exchange Bias in Inverted Core/Shell Magnetic Nanoparticles

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ABSTRACT

Exchange bias is usually observed in FM-coe (FM-shell) nanoparticles. However, recent experiments have reported the observation of shifted hysteresis loops in FiM-coe inverted core/shell (FiM-coe/FM-shell) whose origin is not clearly understood. Here we present results of Monte Carlo (MC) simulations of spherical nanoparticles based on a classical Heisenberg model of lattice spins for core (AFM) and shell (FiM) nanoparticles of different sizes. In the model, the values of microscopic parameters such as anisotropy K and exchange constant J can be fixed in the core, shell and at the interfacial region, offering new insight on the microscopic origin of the experimental phenomenology. Detailed analysis of magnetic order at the interface reveals that uncompensated spins of the AFM core are responsible for the EB phenomenon in these kind of nanoparticles.

References

- Ó Iglesias, A. Labarta, and Amílcar Labarta, *Phys. Rev. B* **79**, 014404 (2009)
- Ó Iglesias, A. Labarta, *Phys. Rev. B* **80**, 200406 (2009)
- Ó Iglesias, A. Labarta, *Phys. Rev. B* **80**, 140401 (2009)
- Ó Iglesias, A. Labarta, *Phys. Rev. B* **80**, 140401 (2009)
- Ó Iglesias, A. Labarta, *Phys. Rev. B* **80**, 140401 (2009)

Micro-Information at: <http://www.ub.edu/~oiglesias>

KEYWORDS FOR A CONFERENCE PRESENTATION

Monte Carlo simulation, Heisenberg algorithm for continuous spins, B.E. hysteresis loops in single cubic lattice

Exchange Bias (EB)

- 1. H_E (at $M=0$) of the Core
- 2. H_E (at $M=0$) of the Shell
- 3. H_E (at $M=0$) of the Interface
- 4. H_E (at $M=0$) of the Shell

Energy spectra

- 1. E vs θ (core), E vs θ (shell)
- 2. E vs θ (core), E vs θ (shell)
- 3. E vs θ (core), E vs θ (shell)

Exchange properties

H_E (at $M=0$)	Phase shift θ_{EB}	Phase of the field of EB
$H_E > 0$	$\theta_{EB} > 0$	Core with high anisotropy
$H_E < 0$	$\theta_{EB} < 0$	Core with low anisotropy

POSTER SESSION B134

1. Microscopic origin of EB in inverted core/shell NPs

High anisotropy in the AFM core as compared to bulk.
Large magnetic anisotropy above T_C .
The anisotropy shows a non-monotonic dependence on T_{shell} .

2. Exchange bias after field cooling

MC Simulations: H_E vs T_{shell} , H_E vs T_{core} , H_E vs $T_{\text{interface}}$.
Dependence of H_E on T_{shell} and T_{core} fields, on total particle size and on shell thickness.

3. Role of interface exchange coupling

Strongly anisotropic coupling.
Total temperature shift and change projection of H_E (core) along H_E (shell).

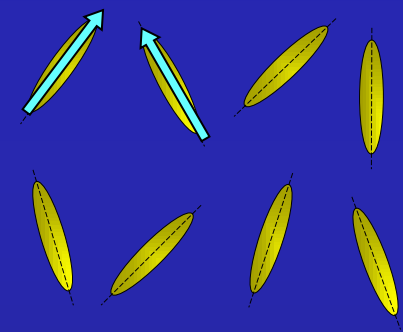
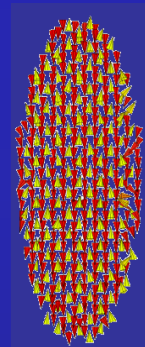
4. Exchange bias and coercive field

MC Simulations: H_E vs T_{shell} , H_E vs T_{core} , H_E vs $T_{\text{interface}}$.
The coercive field decreases and the EB increases (linearly) with increasing T_{shell} in the core-cooled case by AFM cooling, although their values are small.
The EB becomes negative when the interfacial coupling considers over the applied field.

CONCLUSION

- We have observed EB in a model of an inverted core/shell nanoparticle in agreement with experimental observations. The shifted loops are due to the local exchange fields exerted by the uncompensated pinned spins of the AFM core on the FiM shell.
- Simulation confirms the possibility to observe EB even in the atypical case of having $T_N > T_C$. This is due to the large effective anisotropy induced by the uncompensated spins at the AFM core surface.
- Detailed inspection of magnetic order at the interfacial region allows to understand the microscopic origin of the observed phenomenology and to quantify the microscopic J 's in terms of microscopic parameters.

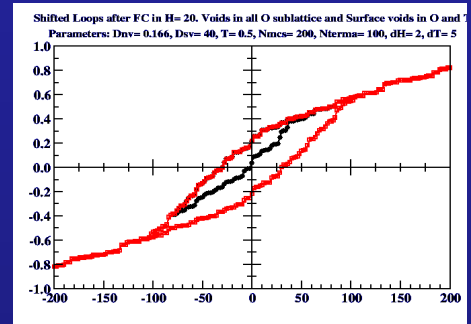
- Interplay with Surface Effects and Interparticle Dipolar Interactions ⇒

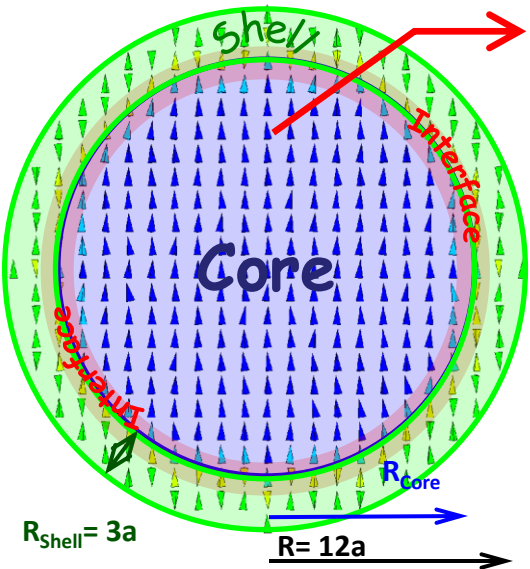


- Magnitude of the EB and coercive fields ⇒

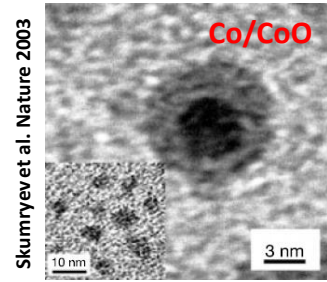
- Distributed properties and role of T_B ⇒

- EB vs. Minor loop Effects ⇒





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.
 Interface spins are not compensated nor uncompensated.

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

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

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

Exchange (n.n.) interaction:

- $J_C > 0$ (FM) at the Core
- $J_S < 0$ (AF) at the Shell
- $J_{Int} \geq 0$ (AF or FM) at the Interface
- J_{Int} variable

Anisotropy energy

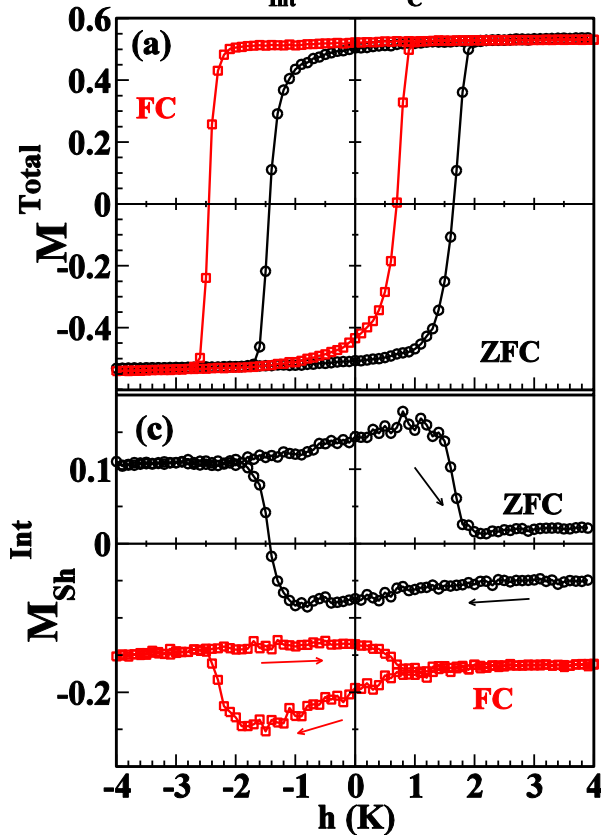
- $n_i = z$ axis, uniaxial anisotropy
- K_C at the Core
- $K_S > K_C$ at the Shell

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

Monte Carlo simulation,
 Metropolis algorithm for continuous spins
 $S_i =$ Heisenberg Spins in simple cubic lattice

AF Interface Coupling

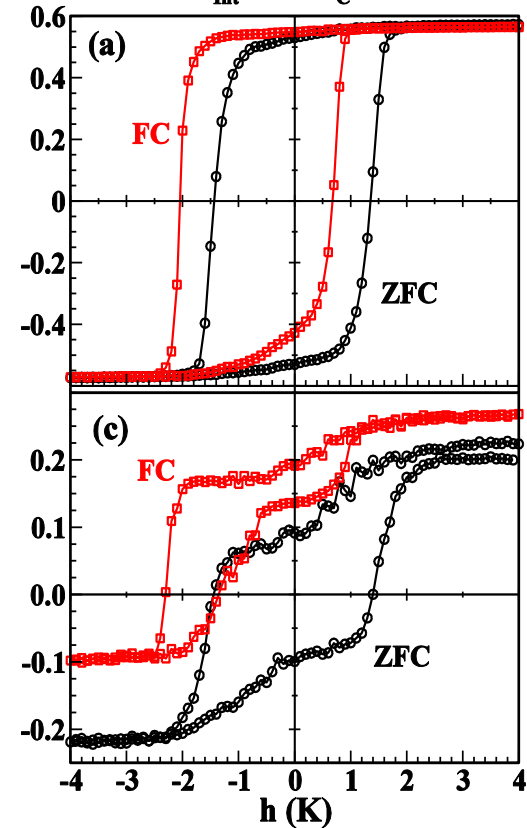
$$J_{Int} = -0.5 J_C$$



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

FM Interface Coupling

$$J_{Int} = +0.5 J_C$$



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

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

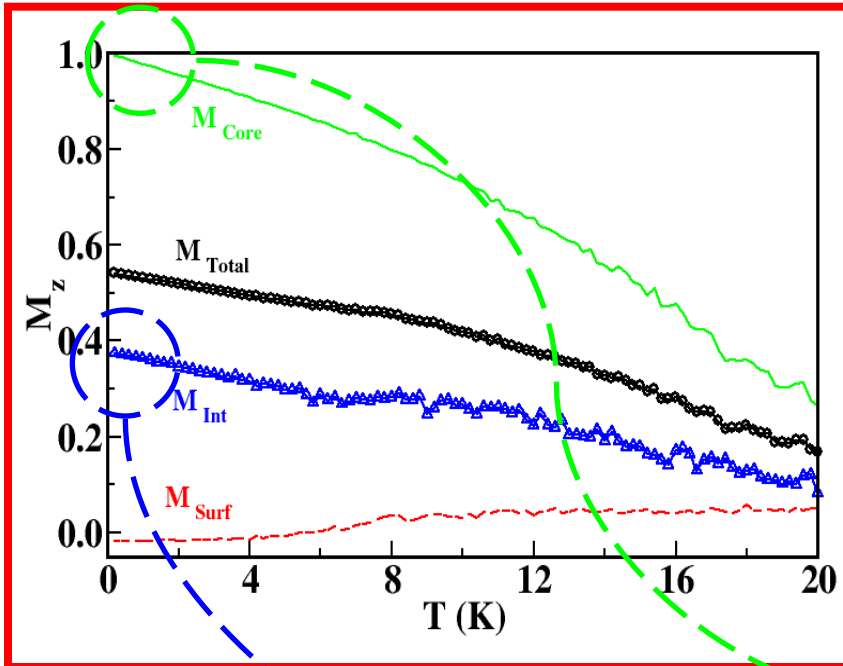
- Shell behavior is dictated by coupling with the core through J_{int} .
- Changing the sign of the interface coupling influences the net magnetization at the interface.

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

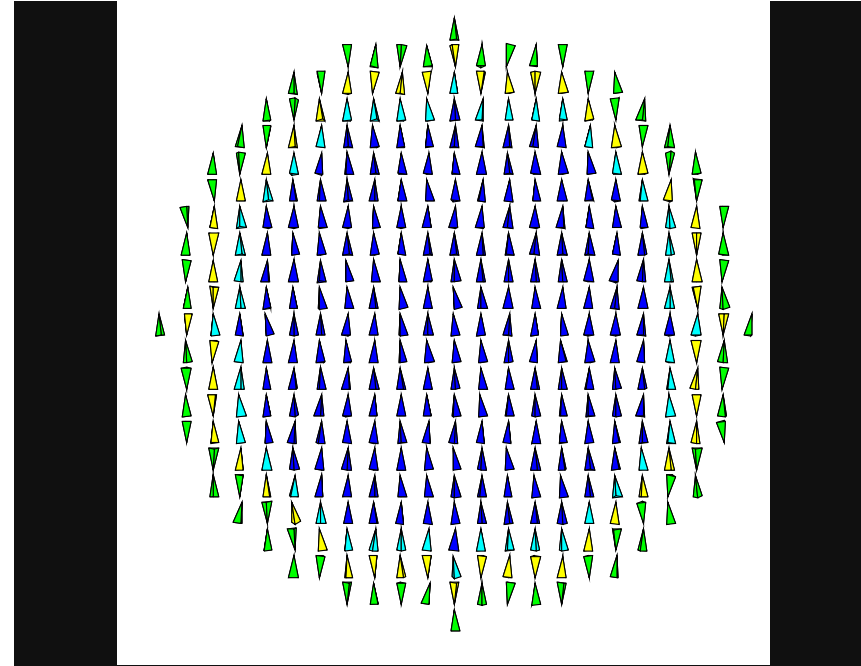
COLOR CODE: dark blue \Rightarrow core, green \Rightarrow shell

yellow (cyan) \Rightarrow shell (core) interfacial spins

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



H_{FC}
↑

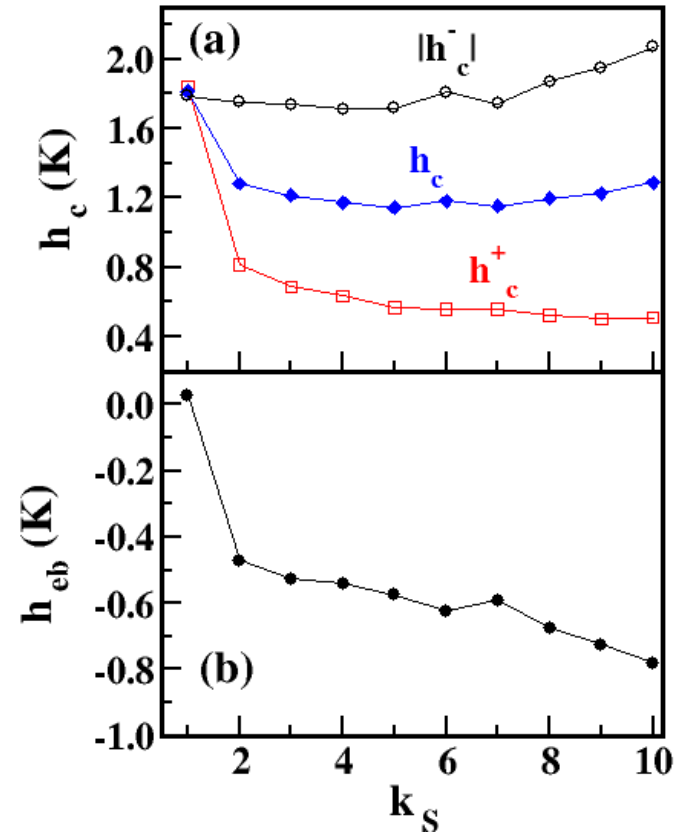
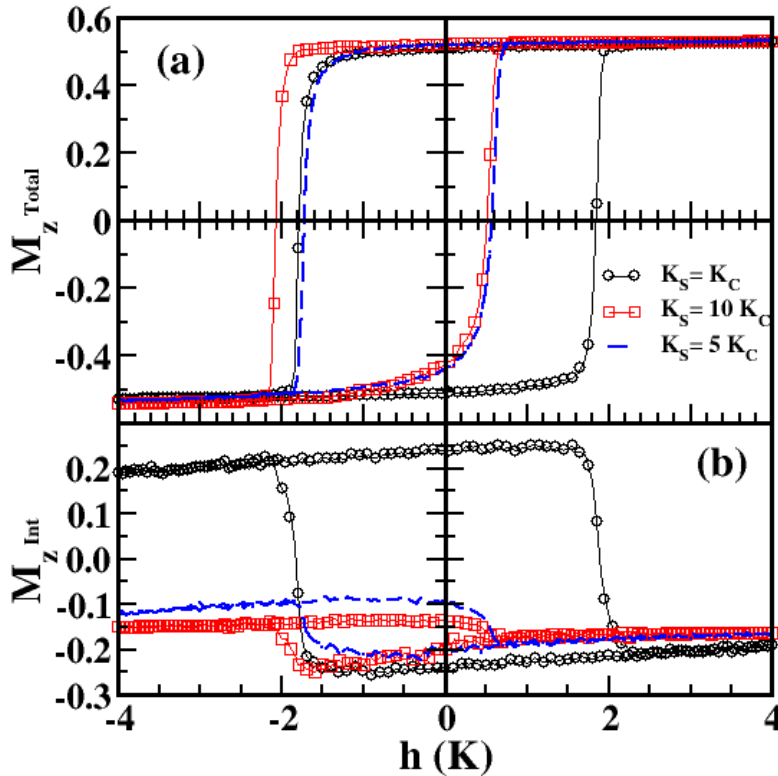


O. Iglesias and A. Labarta, *Physica B* 372, 247 (2006)

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



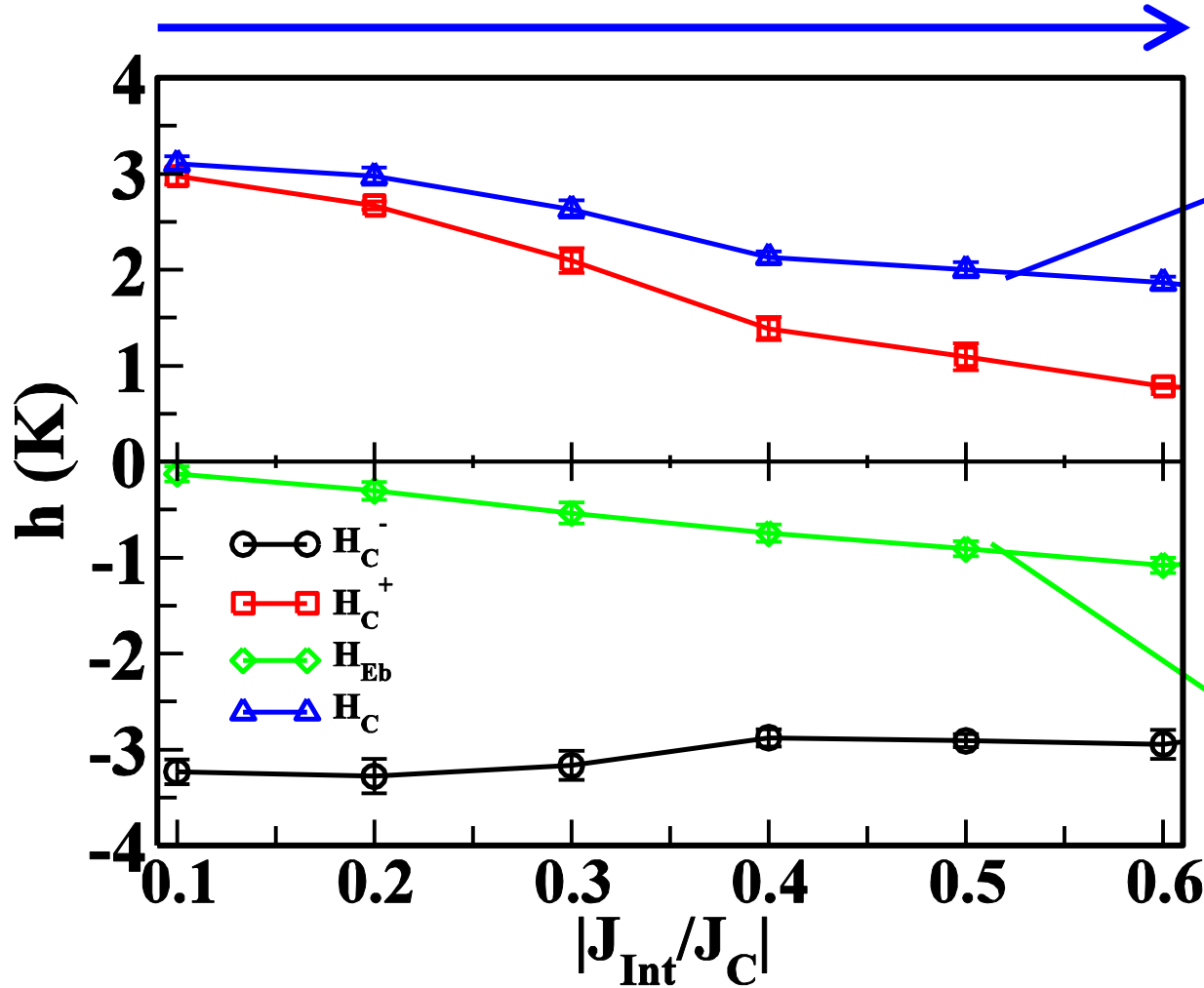
For low K_S , shell spins are dragged by core spins during reversal.

- 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)

Role of the increasing Interface AF Coupling J_{Int}

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



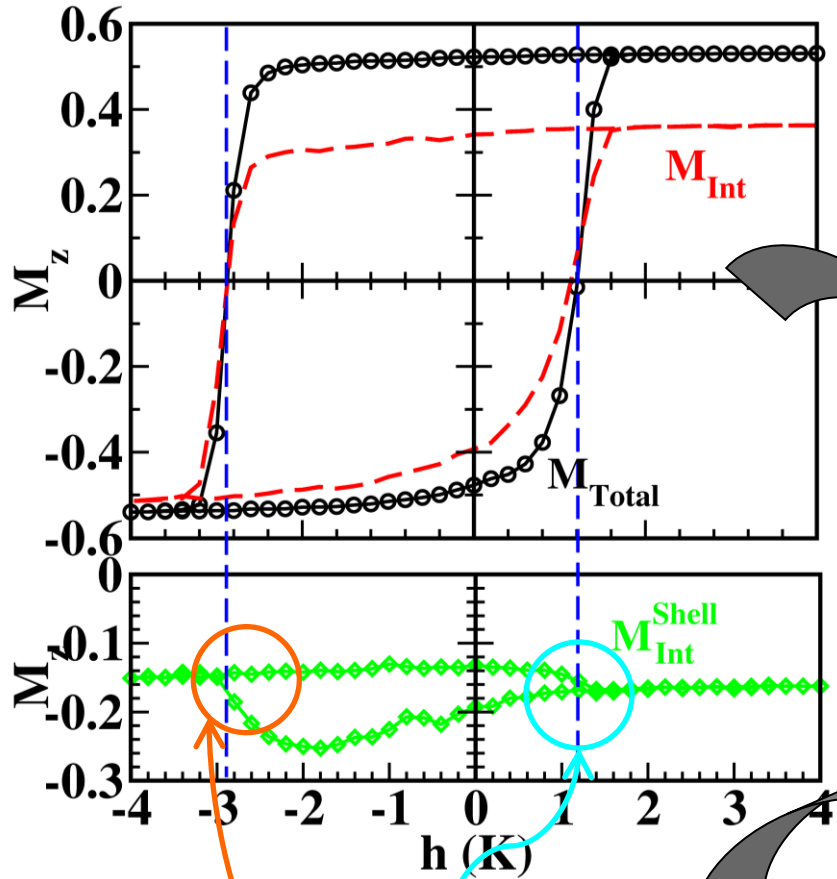
H_c decreases

Coupling of the core to the shell helps the reversal

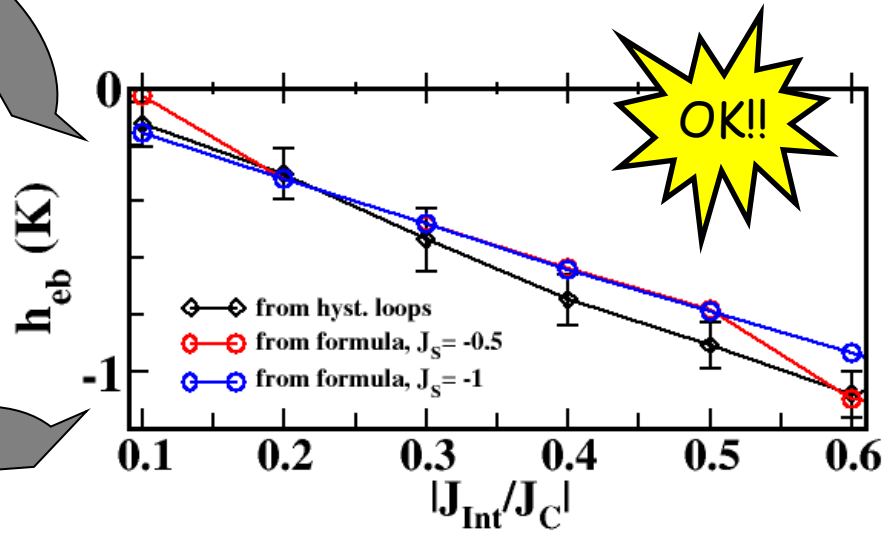
H_{eb} increases

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)



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.



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

$$M_{Int}^+ = \sum_{i \in \{Sh, Int\}} z_i S_i^z$$

➤ 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)

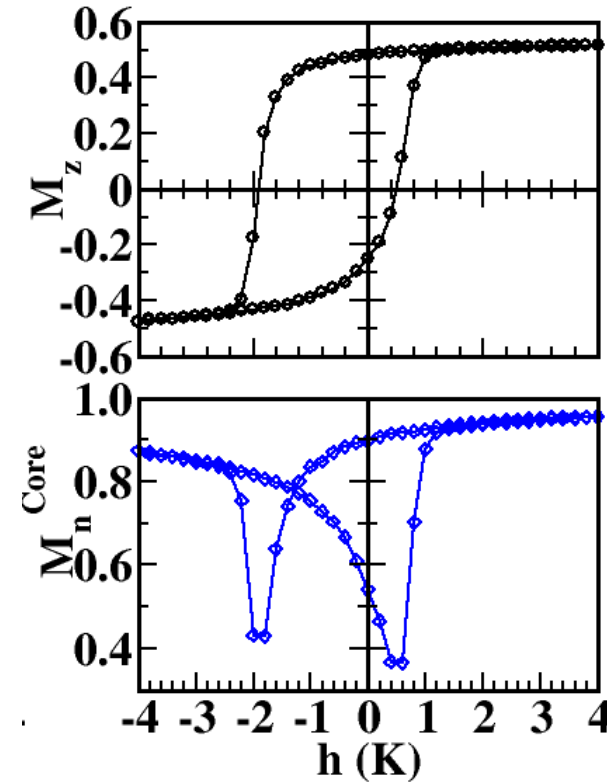
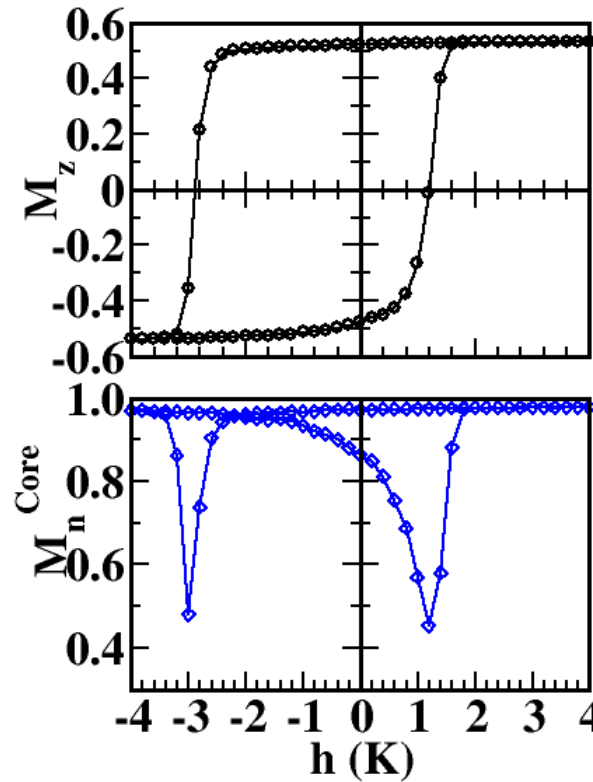
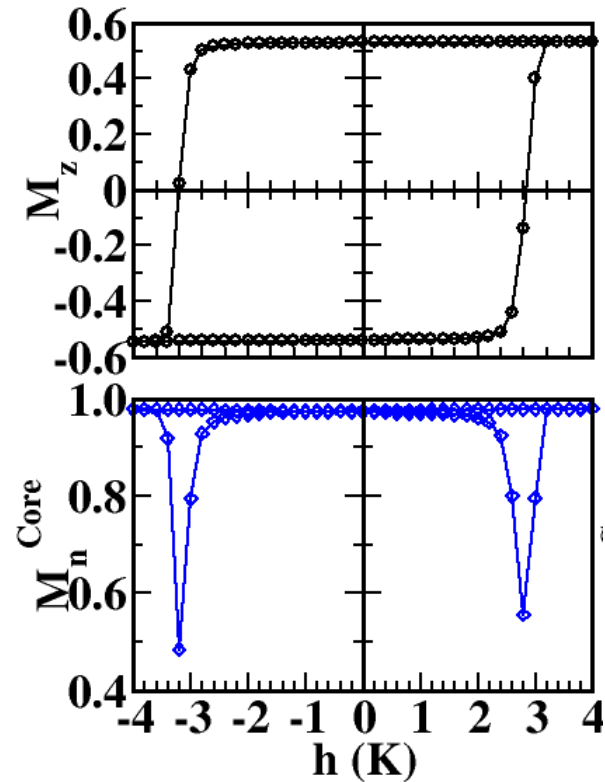
Increasing interface exchange coupling



$J_{Int} = -0.2$

$J_{Int} = -0.5$

$J_{Int} = -1$



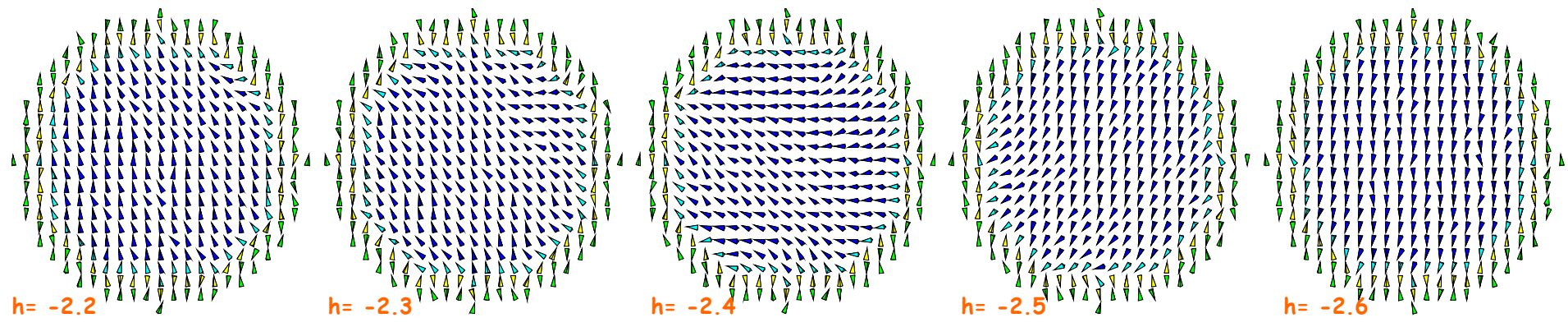
$$M_n = \sum_i \left| \vec{S}_i \cdot \hat{n}_i \right|$$

$M_n \Rightarrow$ Magnetization projection along easy-axis

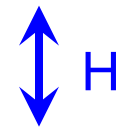
Loop asymmetry is induced by the increasing interface coupling

Descending branch

COHERENT ROTATION

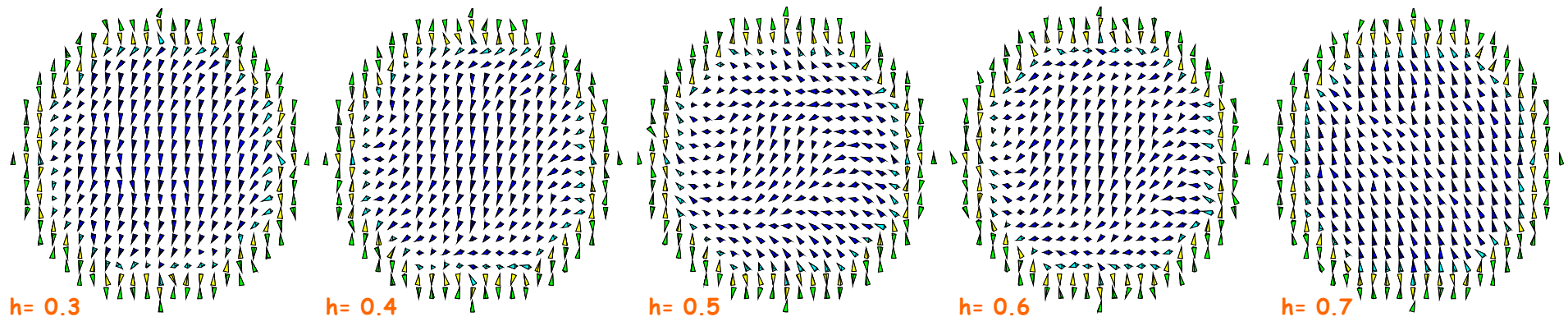


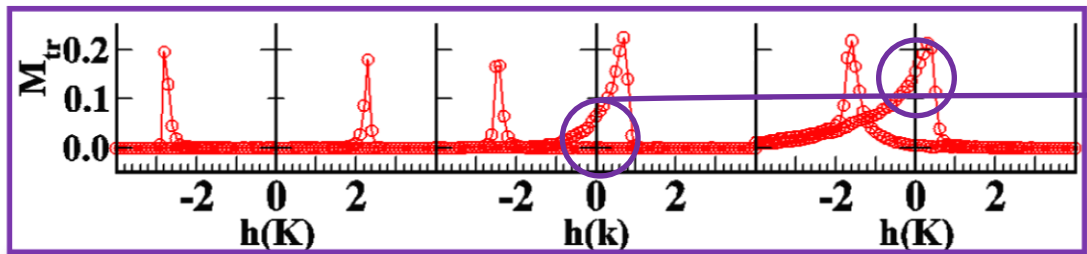
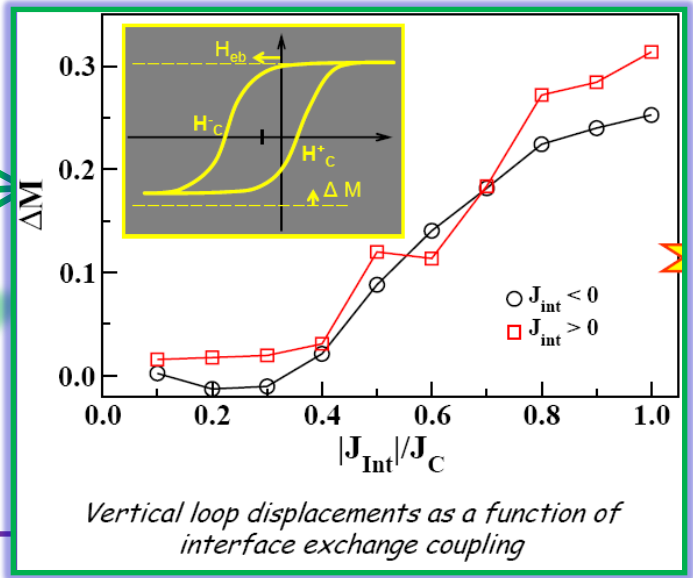
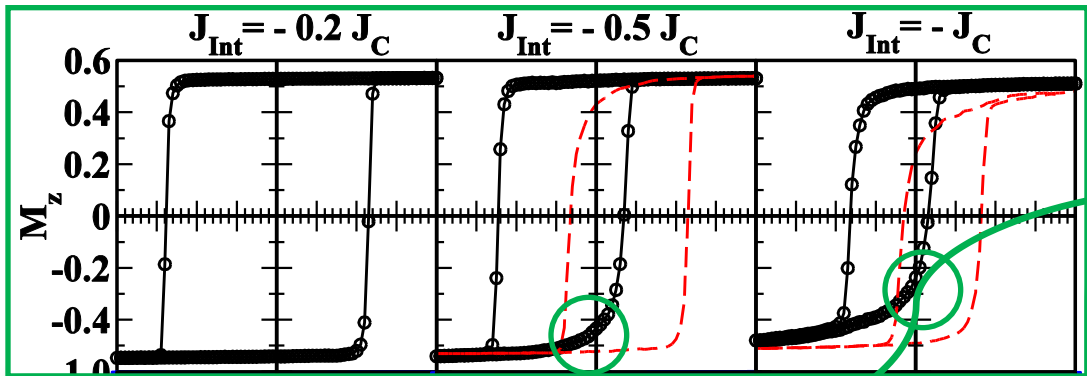
Loop asymmetry is due to different reversal mechanisms and increases with J_{Int}



Increasing branch

NUCLEATION + PROPAGATION



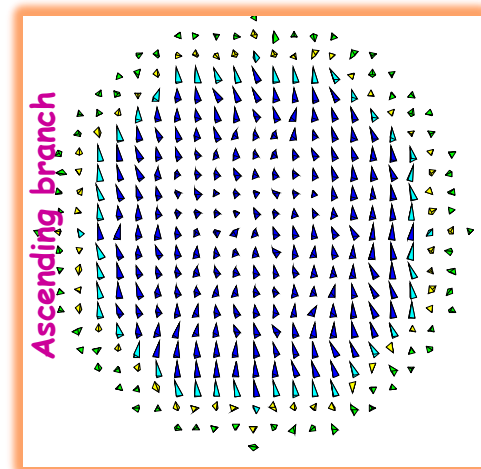
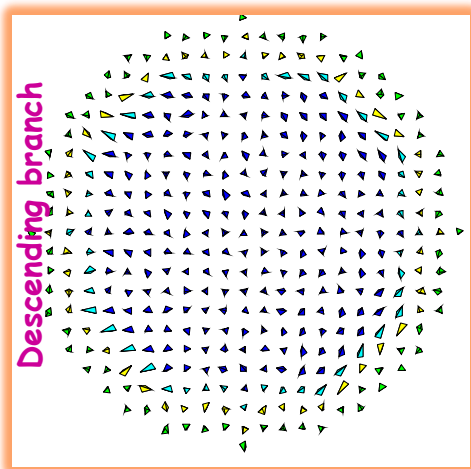


Vertical loop displacements as a function of interface exchange coupling

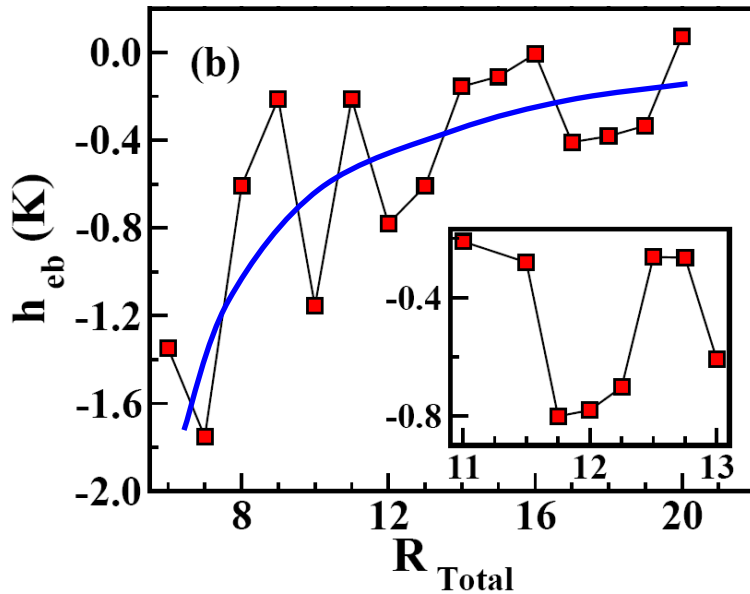
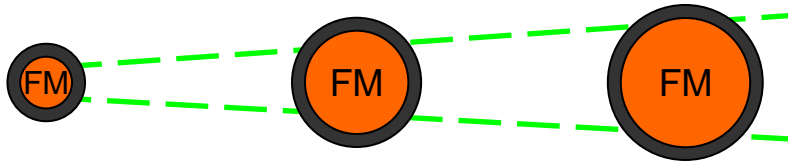
O. Iglesias et al., J. Nanosci. Nanotechnol. 8, 2761 (2008)

Configurations at remanence

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



Particle Size dependence



➤ Oscillatory dependence on particle size.

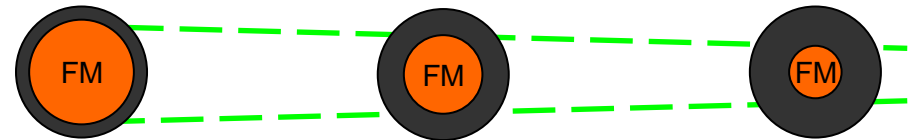
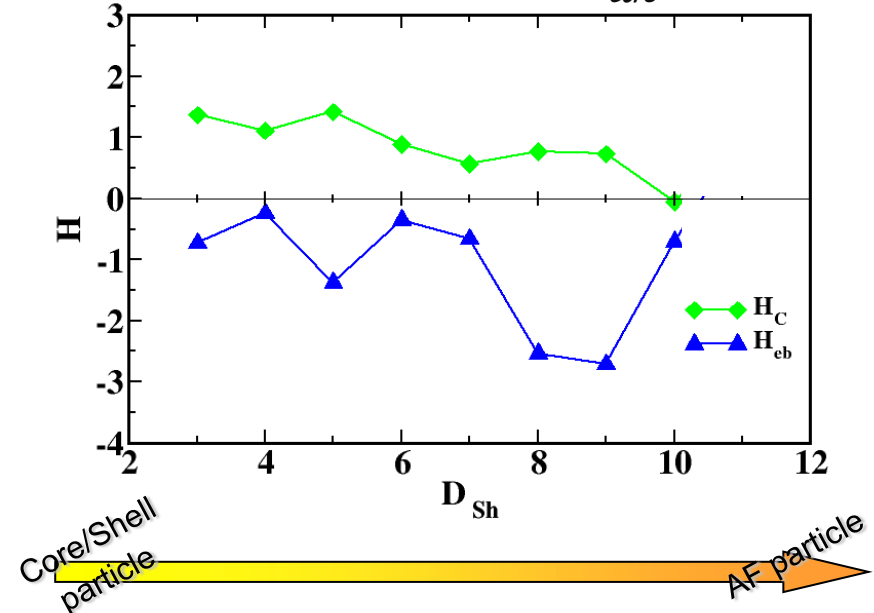
➤ h_{EB} shows a trend to decrease as size increases as in experiments:

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

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

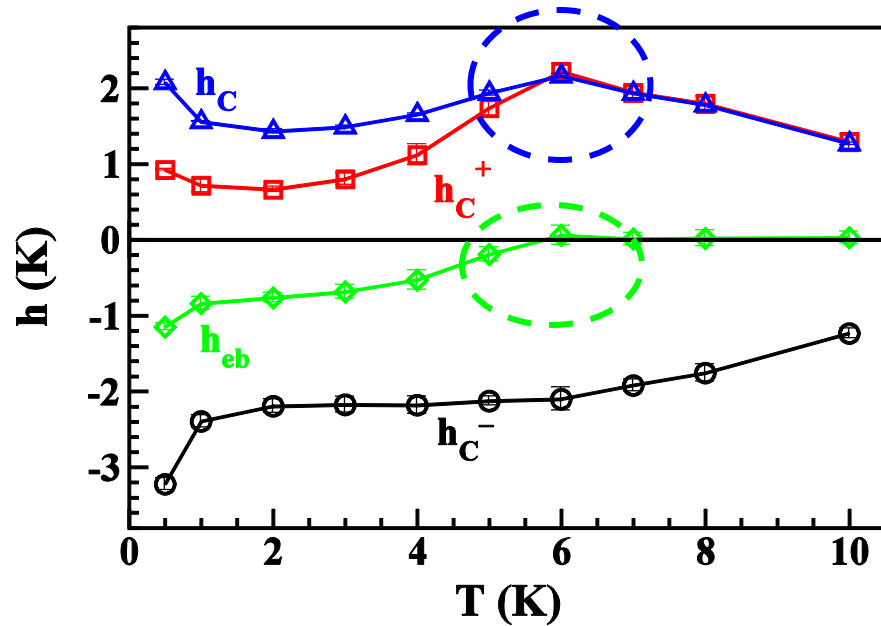
From core/shell to AFM NPs

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



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

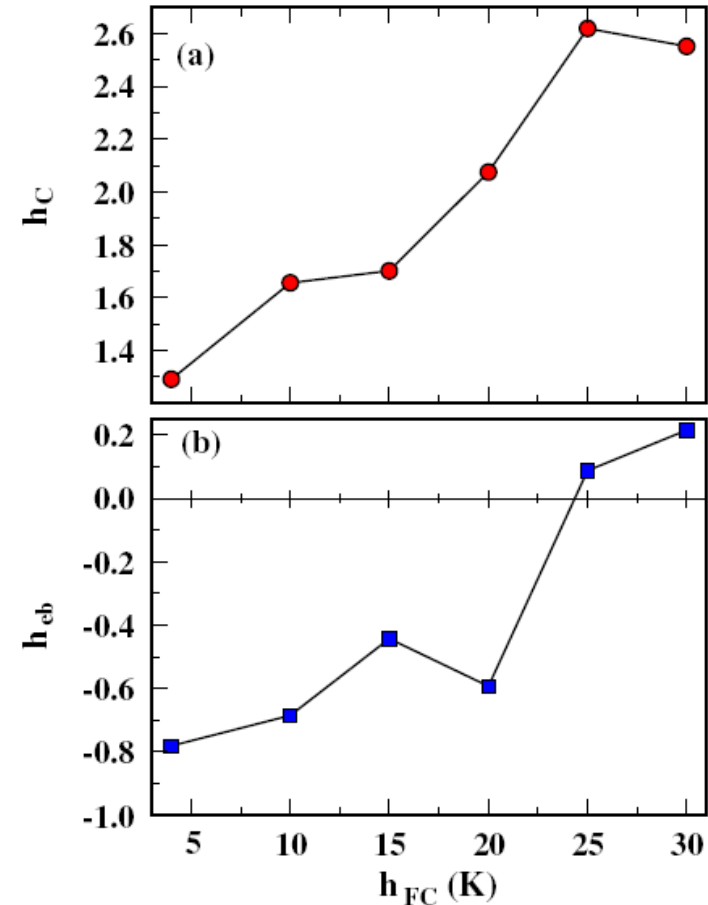
Temperature dependence



➤ 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.

Cooling field dependence



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

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

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.

More up to date information at the web page: <http://www.ffn.ub.es/oscar>