Phenomenology and Models of Exchange Bias in Core /Shell Nanoparticles

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II. WHAT IS EXCHANGE BIAS

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

Exchange Bias Basics

\[ H_{eb} = \frac{(H^+_C + H^-_C)}{2} \]

\[ H_C = \frac{(H^+_C - H^-_C)}{2} \]
I. INTRODUCTION

Microscopic Origin of Exchange Bias?

- Close contact between FM and AFM phases

Microscopic Origin of Exchange Bias?

- 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, $r_{ij}$

Modeling Exchange Bias
II. WHAT IS EXCHANGE BIAS

KEY INGREDIENTS

• Pinned Antiferromagnet \( \Rightarrow \)
  High anisotropy \( K_{AFM} \)

• Exchange coupling at the interface \( \Rightarrow \)
  FM or AFM

• Uncompensated moment of the AFM \( \Rightarrow \)
  Loop displacements

OPEN QUESTIONS

• Nature of interface interaction.

• Quantifying the loop shifts.

• Reversal mechanisms.

• Hysteresis loop asymmetry.

MODELS

• Meiklejohn, Bean (1956) \( \Rightarrow \)
  Uncomp. Interface
  Too large shift

• Malozemoff (1987) \( \Rightarrow \)
  Random field
  Interf. roughness

• Mauri (1987) \( \Rightarrow \)
  Interface AF Domain Wall

• Koon (1997) \( \Rightarrow \)
  Spin-flop coupling

• Schulthess, Butler (1998) \( \Rightarrow \)
  Magnetostatic interactions

• Kiwi (1999) \( \Rightarrow \)
  Frozen interface model

• Stiles, McMichael (1999) \( \Rightarrow \)
  Polycrystalline interface
  AFM grains

• Nowak, Usadel (2000) \( \Rightarrow \)
  Domain state model
  Diluted AFM
III. EB PHENOMENOLOGY

Experimental systems showing EB

- Bilayered thin films
- AF on top of a FM material: FeF₂/Fe, MnF₂/Fe, CoO/Py...
- Ferrimagnetic and AF oxide NPs
- NiO, CoO, CuO, FeOOH...
- NiFe₂O₄, γ-Fe₂O₃, LaCaMnO₃,...
- FM particles embedded in AFM matrix
- Co in CoO, Fe in FeCl₂, Fe in FeF₂,...
- 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

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

Phenomenology in Core/Shell NPs

**Shifted loops, increased $H_c$**
- V. Skumryev et al.

**Increased $T_B$**
- V. Skumryev et al.
- 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)

**Vertical shifts**
- Zhou et al.
- Co/CoO

Co/CoO
III. EB PHENOMENOLOGY

**Oxidation state**

Tracy et al.
PRB 72, 064404 (2005)

Co/CoO

Passamani et al.
JMMM 299, 11 (2006)

Fe/MnO₂

**Glassy dynamics**

Tracy et al.
PRB 72, 064404 (2005)

Co/CoO

Zheng et al.
PRB 69, 214431 (2004)

Fe/γFe₂O₃

Fiorani et al.
PRB 73, 092403 (2006)

Fe/FeO

**Training effects**

Passamani et al.
JMMM 299, 11 (2006)

Fe/MnO₂
III. EB PHENOMENOLOGY

EB in Inverted core/shell NPs

\[ R_{\text{Total}} = 12a, \quad R_{\text{Shell}} = 3a \]

**AFM Core**

**MnO**

**FiM Shell**

\((\text{Mn}_3\text{O}_4)\)

**Doubly inverted Core/Shell NPs**

- Composition: AFM Core + FiM Shell
- Anisotropy: \(K_{\text{AF}} >> K_{\text{FiM}}\)
- Ordering Temp.: \(T_N = 118 K > T_C = 43 K\)

**Unusual**
III. EB PHENOMENOLOGY

➢ Key Questions in EB Phenomenology

• 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 ⇒
IV. MICROSCOPIC MODEL

Model for a Core/Shell NP

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)

Core: ferromagnetic (Co)
Shell: antiferromagnetic (oxide)

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

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

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

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

Zeeman energy
- $\mathbf{h}$ along z axis
- Magnetic field is in temperature units: $h = \mu H / k_B$
Results: ZFC-FC Loops

- 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 $J_{\text{int}}$.
- Changing the sign of the interface coupling influences the net magnetization at the interface.
Results: Field Cooling

After FC from high temperature $T > T_N$:

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

**COLOR CODE:**
- **dark blue** ⇒ core
- **green** ⇒ shell
- **yellow (cyan)** ⇒ shell (core) interfacial spins

IV. MICROSCOPIC MODEL

Results: Increasing anisotropy

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.

IV. MICROSCOPIC MODEL

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

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

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

- $H_C$ 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.

IV. MICROSCOPIC MODEL

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 $J_{\text{Int}}$, do not cause EB.

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

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

IV. MICROSCOPIC MODEL

Results: Loop asymmetries

Increasing interface exchange coupling

\[ J_{\text{Int}} = -0.2 \quad J_{\text{Int}} = -0.5 \quad J_{\text{Int}} = -1 \]

Loop asymmetry is induced by the increasing interface coupling

\[ M_n = \sum_i \left| \vec{S}_i \cdot \hat{n}_i \right| \quad \text{M}_n \Rightarrow \text{Magnetization projection along easy-axis} \]
Results: Reversal Mechanisms

Loop asymmetry is due to different reversal mechanisms and increases with $J_{\text{int}}$.

COHERENT ROTATION

NUCLEATION + PROPAGATION

Descending branch

Increasing branch

$h = -2.2$

$h = -2.3$

$h = -2.4$

$h = -2.5$

$h = -2.6$

$h = 0.3$

$h = 0.4$

$h = 0.5$

$h = 0.6$

$h = 0.7$
Results: Vertical Shifts

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

Results: Particle Size Dependence

- Oscillatory dependence on particle size.
- \( h_{eb} \) shows a trend to decrease as size increases as in experiments:
  \[
  h_{eb} \approx \frac{1}{R_{Core}}
  \]


Results: Temperature and $h_{FC}$ 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.

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 \( J_{\text{Int}} \). **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](http://www.ffn.ub.es/oscar)