Exchange bias in a superspin glass system of ferromagnetic particles in an antiferromagnetic matrix

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OUTLINE

I) Exchange Bias concepts (role of the disorder)

II) Magnetic behaviour of granular Co-Mn films: Co nanoparticles embedded in Mn matrix (comparison with Co-Ag films)

• Exchange bias properties of Co-Mn films
Devices governed by interface exchange coupling

HARD DISK

MRAMs

Spin valve structure
Interface exchange coupling (IEC)

IEC can be exploited as a tunable source of anisotropy (in magnetic recording spring magnets, magnetic sensors, spintronic devices) obtaining:

- Improvement of thermal stability of FM magnetization through exchange anisotropy (increase of coercive field, nanoparticle blocking temperature) in FM/AF systems (Exchange Bias)

![Diagram showing M vs. H for FM, FM + AFM, and FM + AFM + H](image)

- Control of the coercive field in FM(hard)/FM(soft) systems (exchange coupled magnetic recording media, spring magnets)

- Supersoft and superhard properties in exchange coupled soft and hard nanograins
Composite exchange coupled perpendicular media

Tuning of coercivity, through the control of exchange coupling strength (via the non magnetic interlayer thickness) to improve media writability.

Main advantage of exchange coupled media:
Controlled reduction of coercivity, still keeping a high thermal stability factor $K_u V/K_B T$
FeSiO/PdSi(1-4nm)/(Co/PdSi)$_{14}$

$K_a/V/K_bT = 74$ (single hard layer)

= 58 (proper coupling)

$[(K_a/V/K_bT)/H_{sf}]_{PC} = 2 [(K_a/V/K_bT)/H_{sf}]_{SHL}$
“Beating the superparamagnetic limit with exchange bias”

FM(Co)/AFM(CoO) interface exchange coupling increases the thermal stability of FM magnetization particle (increase of $T_B$; Increase of $H_c$; exchange bias)

Non-magnetic matrix: $T_B \approx 30K$

AFM matrix $T_B \approx T_N \text{CoO}$

Particle size: 3-4 nm
Exchange bias

Interface exchange interaction between the ferromagnetic core and the antiferromagnetic surface shell (EXCHANGE ANISOTROPY)

After FC from $T>T_N$ to $T<T_N$:
- Shifted hysteresis loop (unidirectional anisotropy)
- Increased coercivity

$\mu_0 H_E \approx 0.2 \, T$

Meiklejohn and Bean, Phys. Rev. 102 (1956) 1413, Phys. Rev. 105 (1957) 904
Exchange Bias Effect

\[ T_{\text{Néel}} < T < T_{\text{Curie}} \]

Field Cooling

\[ T < T_{\text{Néel}} \]

THEORETICAL MODEL: IDEAL SYSTEM


ASSUMPTIONS
- MONOCRYSTALLINE SYSTEMS
- ABSENCE OF FM AND AFM DOMAINS
- UNCOMPENSATED AFM SPIN INTERFACE
- SPIN COLLINEARITY (PARALLEL FM AND AFM EASY AXES)
- FERROMAGNETIC INTERFACE SPIN COUPLING
- COHERENT SPIN ROTATION

APPLIED FIELD EFFECT ON FM LAYER
\[ E = -HM_{FM} t_{FM} \cos(\vartheta - \beta) + K_{FM} t_{FM} \sin^2(\beta) + K_{AFM} t_{AFM} \sin^2(\alpha) - J_{INT} \cos(\beta - \alpha) \]

FM ANISOTROPY EFFECT

AFM ANISOTROPY EFFECT

INTERFACIAL COUPLING EFFECT

\[ K_{FM} t_{FM} \ll K_{AFM} t_{AFM} \]

\[ E = -HM_{FM} t_{FM} \cos(\vartheta - \beta) + K_{AFM} t_{AFM} \sin^2(\alpha) - J_{INT} \cos(\beta - \alpha) \]

\[ H_E = \frac{J_{INT}}{M_{FM} t_{FM}} \]

\[ K_{AFM} t_{AFM} \gg J_{INT} \]
**Realistic system**: interfacial disorder (roughness, defects, grain boundary) and domains.
Role of disorder in EB

- **Random field model** (A.P. Malozemoff, PRB 35, 3679 (1987))
  Random fields at the interface, due to random roughness and defects, cause the AFM to break up into domains (with domain walls perpendicular to the interface) uncompensated at the surface, generating EB.
  Domain size: $\pi (A_{AFM} K_{AFM})^{1/2}$
  $H_{EB} = (K_{eff} A_{eff})^{1/2}/M_{FM} t_{FM}$
  Randomness in exchange interactions at the interface

- **Domain state model** (U. Nowak et al, PRB 66, 014430, 2002)
  Disorder and frustration induced by dilution in the AFM.
  FM layer coupled to a diluted (non magnetic substitution, defects) AFM layer ($Co_{1-x}M_xO; C_{1-y}O$).
  Increase of $H_{EB}$ with dilution, which promotes the formation of domains with net magnetization in the volume of AFM
  (Monte Carlo simulations and experiments)

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Fig. 1. Sketch of the model with one FM layer and three diluted AFM layers. The dots mark defects (non-magnetic ions).

Fig. 2. Tanner domain pattern of a diluted AFM conducting...
Types of Exchange Bias Systems

- Layered films
- Patterned structures (dots..)
- Nanoparticles
- Inhomogeneous materials (inhomogeneous concentrated Spin Glasses)
Exchange Bias in an inhomogeneous SG

Frustration of magnetic interactions (coexistence of FM and AFM interactions) and disorder (statistical fluctuations in the local Mn concentration) determine the formation of **AFM and FM domains**

# Nanoparticle Exchange Bias Systems

## Core/shell nanoparticles

<table>
<thead>
<tr>
<th>Type</th>
<th>Examples</th>
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</thead>
<tbody>
<tr>
<td>FM/AFM</td>
<td>Co/CoO, Ni/NiO</td>
</tr>
<tr>
<td>FM/FMI</td>
<td>Fe/Fe$_3$O$_4$, Fe/γ-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>FMI/SG</td>
<td>NiFe$_2$O$_4$, γ-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>AFM/SG</td>
<td>NiO</td>
</tr>
</tbody>
</table>

## Nanoparticles dispersed in a matrix

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<td>FM/AFM</td>
<td>Co/CoO (core/shell NP in matrix)</td>
</tr>
<tr>
<td></td>
<td>Fe/Cr$_2$O$_3$, Fe/FeCl$_2$</td>
</tr>
<tr>
<td>FM/SG</td>
<td>Fe/FeO$_x$ (core/shell NP in matrix)</td>
</tr>
</tbody>
</table>
NiFe2O4 particles

R. H. Kodama et al, JAP 81, 5552, 1997

Core shell FMI/SG particles: ordered core surrounded by a disordered shell

![Graph showing magnetic properties of milled NiFe₂O₄](image)
FM/AFM

only two energetically equivalent spin configurations for the AFM phase

FM(AFM,FI)/SG

multiple equivalent spin configurations for the spin-glass phase
Spin glasses: multiminima energy structure

Hierarchical organization of the metastable states as a function of $T$
Since:

- the SG phase is intrinsically disordered (random bonds: $J_{ij}$ distribution gaussian)
- magnetically frustrated (competing F and AF magnetic interactions)
- characterized by aging effects and slow dynamics
- its multivalley energy structure is strongly modified by the magnetic field

**the following E.B. features are expected:**

- **Multiple random interfaces** (random mixture of ferromagnetic and antiferromagnetic interface interactions): distribution of $H_{ex}$ and $T_B$
- **Different interface spin configurations** are selected varying $H_{cool}$ (variation of $H_{ex}$ and $H_c$)
- **Effect of the magneto-thermal history** ($H_{cool}$, $T_{cool}$, cooling rate, aging) on exchange bias
Exchange bias in a superspin glass system of ferromagnetic particles in an antiferromagnetic matrix

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and J. Tejada\textsuperscript{b}

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\textsuperscript{c}Department of Physics and AStronomy, University of Leicester, UK
Films of Cobalt particles in Mn matrix (Co-Mn)

Films thickness: 200 nm
(co-deposition by gas aggregation cluster source and MBE)

Comparison with magnetic properties of Co particles in Ag matrix
(same particle size, same volume fraction: 4.7%)

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co in Mn</td>
<td></td>
<td></td>
<td>4.7%</td>
<td></td>
<td>8.9%</td>
<td></td>
</tr>
<tr>
<td>Co in Ag</td>
<td>9.2%</td>
<td>4.7%</td>
<td>1.3%</td>
<td>4.7%</td>
<td>1.5%</td>
<td></td>
</tr>
</tbody>
</table>

\( \phi \sim 1.8 \text{ nm} \)
Co cluster size distribution

Co hcp (from EXAFS measurements on Co/Ag)

Log-normal distribution of particle size
Mn matrix
Mn matrix

ZFC/FC $\chi$ curves

Disordered antiferromagnet (AFM domains of different size with uncompensated moments blocked at low temperature)
Mn-edge XMCD signal

Spin inbalance, mostly coming from the layers close to the surface.

(The drain current signal is generated mostly within the top 5 nm of the sample)

(Film thickness: 50 nm)
DC susceptibility measurements
Theoretical blocking temperature for Co-Ag, (1.8 nm hcp Co, magnetocrystalline bulk anisotropy, $K_a = 4.5 \times 10^6$ erg/cm$^3$): $T_B = 4k$

(from the Arrhenius law: $K_a V = 25 k_b T_B$)

Evidence of strong surface anisotropy

Co-Mn: spin-glass like behaviour
$T_{max}$ of $\chi$(ZFC): 65 K
Plateau of $\chi$(FC) below 30 K
$T_{irr}/T_{max} = 1.2$
Collective freezing behaviour

Leiden, June 18 - 22, 2007
AC susceptibility measurements
AC susceptibility measurements

Co/Ag ($\nu = 0.3 - 30$ Hz)

Co/Mn ($\nu = 0.3 - 30$ Hz)

Co/Mn ($\nu = 0.1 - 1000$ Hz)

Much weaker frequency dependence for Co/Mn:

$\Delta T_{\text{max}}(\nu)/<T_{\text{max}}>$ $\Delta \log \nu = 0.01$  (0.10 for Co/Ag)

Co/Ag

Arrhenius law

$\tau = \tau_0 \exp(K_a V / K_b T)$

$\tau = t_m = 1/f_f$ for $T = T_B$

$\tau_0 = 6 \times 10^{-11}$ s  $K_a = 2 \times 10^7$ erg/cm$^3$

Co/Mn

Power law

$\tau = \tau_0 \left[ T_g / (T_{\text{max}}(\nu)) - T_g \right]^\alpha$

$\alpha = 8.2$; $T_g = 62$ K; $\tau_0 = 10^{-9}$ s
Critical dynamics in spin - glasses

Critical slowing down of dynamics approaching the phase transition from high temperature

Critical power law:

\[ \tau = \tau_0 \left[ \frac{T_g}{T_{\text{max}}(\nu) - T_g} \right]^\alpha \]

\[ \alpha = z\nu \]

\[ \tau \sim \xi^z \]

\[ \xi = \left[ \frac{T_g}{T - T_g} \right]^\gamma \]

In SG, \( \alpha = 7 - 9 \)

For Co/Mn: \( \alpha = 8.2 \)

\( T_g = 62 \, K; \, \tau_0 = 10^{-9} \, s \)

SG like behaviour: superspin glass

(collectively frozen disordered state of Co particle moments)

Long range interactions between Co particle moments propagated through the disordered Mn matrix (interface exchange interactions between Co particle moment and AFM Mn domains with uncompensated moments).
Hysteresis cycles

measurements
M vs H measurements

Co in Ag

\begin{tabular}{|c|c|c|c|}
\hline
Co in Ag & \(H_c\) & \(M_s\) & \(M_{rem}/M_s\) \\
\hline
S5 & 8.9\% & 350 Oe & 400 emu/cm\(^3\) & 0.15 \\
S4 & 4.7\% & 275 Oe & 875 emu/cm\(^3\) & 0.25 \\
S6 & 1.5\% & 200 Oe & 1225 emu/cm\(^3\) & 0.23 \\
\hline
\end{tabular}

Co in Mn

\begin{tabular}{|c|c|c|c|}
\hline
Co in Mn & \(H_c\) & \(M_s\) & \(M_{rem}/M_s\) \\
\hline
S1 & 9.2\% & 1800 Oe & 39 emu/cm\(^3\) & 0.27 \\
S2 & 4.7\% & 1600 Oe & 29 emu/cm\(^3\) & 0.24 \\
S3 & 1.3\% & 470 Oe & 6 emu/cm\(^3\) & 0.11 \\
\hline
\end{tabular}
Co/ Mn and Co/ Ag: Comparison between hysteresis cycles features

<table>
<thead>
<tr>
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<th>Co@Mn ZFC</th>
<th>Co@Ag ZFC</th>
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<tbody>
<tr>
<td>$M_s$ (emu/cm$^3$)</td>
<td>30</td>
<td>900</td>
</tr>
<tr>
<td>$H_c$ (Oe)</td>
<td>1600</td>
<td>280</td>
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**Table:**

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<table>
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<tr>
<td>$4.7%$ Co</td>
<td>$H_c$ (Oe)</td>
<td>$M_s$ (emu/cm$^3$)</td>
</tr>
<tr>
<td>$T = 5$ K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co/Mn</td>
<td>1600</td>
<td>30</td>
</tr>
<tr>
<td>Co/Ag</td>
<td>280</td>
<td>900</td>
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Co L-edge XMCD signal

Pure Co clusters

Co clusters in Ag or Mn (VF=4-5%)

T=305 K  B=0.6T

$m_L = 0.31 \pm 0.02 \mu_B,$

$m_S = 2.2 \pm 0.3 \mu_B$

T=24K (ZFC) B=0.6T

Co in Ag

Co in Mn
Mn-Edge XMCD signal

Drain current

Transmission

Film thickness:

4.7% Co: 125 nm
22% Co: 23 nm
Co L-edge XMCD signal

red: 4.7% Co
black: 23.2% Co
Exchange Bias properties
**Co/ Mn: Exchange Bias**

$H_{\text{cooling}} = 2 \, \text{T},$

from 300 K

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**After field cooling:**
- Shift of the cycle (EB, $H_{\text{EB}} = 750 \, \text{Oe}$)
- Increase of $H_c$
- Increase of $M_r$

<table>
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<tr>
<th>$T = 5 , \text{K}$</th>
<th>$H_c (\text{Oe})$</th>
<th>$M_r/M_s$</th>
</tr>
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<tbody>
<tr>
<td>Co/Mn (ZFC)</td>
<td>1600</td>
<td>0.25</td>
</tr>
<tr>
<td>Co/Mn (FC)</td>
<td>2250</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Temperature dependence of $H_{EB}$, $H_c$ and $M_r$

Onset of exchange bias ($T_b$) and increase of coercivity and remanence after FC (4 kOe) occur below 30 K, the temperature below which $\chi$(FC) becomes temperature independent.

Co/Ag: FC, ZFC $H_c$ and $M_r$ coincide
Temperature dependence of $H_{EB}$ and $H_c$

Exponential temperature dependence of $H_{EB}$ (as expected for non continuous AFM structure) and $H_c$:

$$H_i = H_{i0} \exp(-T/T_0)$$

$H_{EB0} = 2000$ Oe; $T_0 = 5$ K
$H_{c0} = 3700$ Oe; $T_0 = 11$ K

$H_{EB}(5K) = 750$ Oe
$H_{EB}(5K, (Co(24A)/Mn(14))_{12}) = 250$ Oe

(Stoner- Wolfarth temperature dependence of $H_c$ for Co/Ag: $H_c = H_{c0}(1-(T/T^*)^{1/2})$)
Monte Carlo simulations

FM/AFM core/shell spherical particles
Random Anisotropy in the shell

Exponential decrease of Hex with temperature
(K. Trohidou, private communication)

\[ Y = A \exp(-x/b) \]

- \( H_c \) \( (A=0.2252; b=1.0774) \)
- \( \text{Hex} (A=0.1314; b=0.3305) \)
Field cooling dependence of the Hex, $H_c(FC)$ and $M_r$

Dependence on the Field of Cooling ($H_{FC}$):

- **Hex (Oe)**
- **$H_c$ (T)**
- **$M_{rem}$ (%)**

Nanospin Sample 2, Co in Mn at 4.7%
Co/ Mn: Relaxation of $M_r$ (from saturation) after ZFC from 300K

Logarithmic relaxation $\rightarrow$ Wide distribution of energy barriers

$$M_r = M_0[1 - S(T)\ln(t/t_0)]$$
Normalized viscosity vs T

Power law dependence of $S/T \sim n(E) = (a+bT)^{-5}$

$n(E) = E^{-1}$ barrier distribution for surface SG
(R.H. Kodama et al, PRL 77, 394 (1996))

\[
M(t) = M_0 \left(1 - \int_0^{E_c/T_{max}} e^{-t/\tau} n(E)dE\right)
\]

\[
M(t) = M_0[1-n(<E>)KbTln(t/\tau_0)]
\]

\[
S = -(1/M_0)dM/d\ln t = n(<E>)KT
\]

\[
S/T \sim n(<E>)
\]

\[
<E> = KTln(<\tau>/\tau_0)
\]

Mean energy barrier for the experimental time window characterized by a mean relaxation time $<\tau>$
Wolhfarth’s relationship for an assembly of non interacting SD particles with UA anisotropy: \( I_d(H) = 1 - 2 I_r(H) \)

Deviations from linearity may be visualized through the \( dI(dM) \) plots:

Modified Wolhfarth’s equation: \( \delta I(\delta M) = I_d(H) - [1 - 2 I_r(H)] \) (Henkel plot)
Henkel Plots

Henkel Plots

\[ I_d (H) = 1 - 2 I_r (H) \]

\[ \delta I (\delta M) = I_d (H) - [1 - 2 I_r (H)] \]

\[ \delta M = 0, \text{ no interaction} \]

Demagnetizing interactions much stronger in Co/Mn

DCD remanence curves
Irreversible susceptibility (derivative of the remanence curve),
switching fields distribution (after ZFC and FC)

The switching fields distribution shifts to higher fields and flattens from Co/Ag to Co/Mn.
FC induces a maximum (large) in the distribution.
Conclusions

**Superspin glass** behavior in Co particles dispersed in a disordered Mn matrix

Interparticle long range interactions mediated through Mn AFM domains, via interface exchange coupling

With respect to Co-Ag (same particle size, same volume fraction):

- Increase of thermal stability of particle magnetization
- **Exchange Bias** (with coercivity and remanence enhancement after field cooling)
- Collective magnetic behaviour
- Broadening and shift of energy barrier and switching field distribution to larger values

*Activity within the “Nanospin” UE project (Coordinator: C. Binns)*
6th International Conference on Fine Particle Magnetism (ICFPM)
“New trends in nanoparticle magnetism”
Rome, October 9-12, 2007

This is the 6th edition of the International Conferences series, previously held in Rome (1991), Bangor (1996), Barcelona (1999), Pittsburg (2002) and London (2004). The aim of the conference is to bring together the experts in the field of nanoparticle magnetism at a single forum for discussing recent developments and new trends.

Main topics:
- Organization of magnetic arrays (self assembled nanoparticles, nanopatterned media)
- Multifunctional nanomagnets
- Magnetic core/shell nanocomposites
- Metamaterials
- Surface/interface induced phenomena
- Spin dynamics
- Magnetotransport
- Sensors and devices
- Biomedical applications

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Deadline for abstract submission: May 15, 2007
Web-site: www.icfpm.mlib.cnr.it (starting from Oct. ‘06)

Contact persons: D. Fiorani (dino.fiorani@ism.cnr.it) Conference Chairman
E. Agostinelli (elisabetta.agostinelli@ism.cnr.it) Chairman Local Organizing Committee
Concentration dependence of $H_c(FC)$ and $H_{EB}$

$H_c(FC)$ and $H_{EB}$ increase with Co particles concentration.

$T_b$ is concentration independent.
Exchange Bias: training effect

Reduction of 46% between the first and the second cycle
NiFe/ CoO
$H_{ex}$ for different CoO thicknesses
Sample Preparation for XMCD for XAS
Measured in Transmission

Circularly polarised soft X-rays (700-800eV) from synchrotron
Thin magnetic sample
Applied magnetic field

TEM grid 60% transmission
Mn Edge XMLD

Drain current

Transmission

D. Fiorani (ISM-CNR)
Ultrasoft magnetic properties
Exchange-coupled nanograin

Anisotropy averaged over many particles:
 extremely small

\[ K = 10^4 \text{ J/m}^3 \]
\[ D = 10\text{nm}, \quad \delta_g = 100\text{nm} \]
\[ \alpha = 10 \quad K = 10^{-2} \text{ J/m}^3 \]
The magnetic field (4 kOe) is applied at 50 K for different times (waiting time: $t_w$) before starting the cooling down to 5 K, where the cycle is measured.

$t_w = 60 \text{ s}; \quad H_{ex} = 324 \text{ Oe}; \quad t_w = 60000 \text{ s}; \quad H_{ex} = 402 \text{ Oe}$
Exchange Bias Effect

Ideal system
(Meiklejohn and Bean, 1956)
for (FM) / AFM interfaces

\[ H_{ex} = \frac{\sigma}{(M_{FM} \ t_{FM})} = n \ J_{int} \ \frac{S_{FS} S_{AF}}{(M_{FM} \ t_{FM})} \]

\[ K_{AFM} t_{AFM} > J_{int} \]

- \( \sigma \): interfacial exchange energy density
- \( n \): number of exchange bonds per unit area
- \( J_{int} \) = exchange constant across the FM/AFM interface per unit area.
- \( M_{FM}, t_{FM} \): magnetization and thickness of the FM layer
- \( K_{AFM}, t_{AFM} \): anisotropy constant and thickness of the AFM layer

\[ T_{N\acute{e}el} < T < T_{Curie} \]

Field Cooling

\[ T < T_{N\acute{e}el} \]