

Thin films and Nanostructures

Julio Camarero

*Laboratorio de Física de Superficies, Dpto. de Física de la
Materia Condensada and Instituto “Nicolás Cabrera”,
Universidad Autónoma de Madrid UAM, Spain*

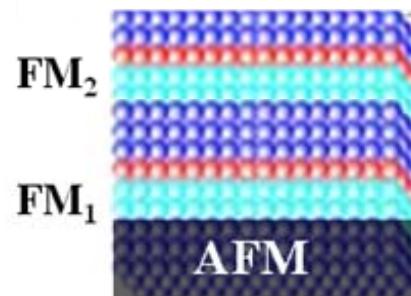
Nanomagnetism Group, Inst. Madrileño de Estudios Avanzados en Nanociencia, IMDEA-nanoscience, Campus de la UAM, Madrid, Spain

julio.camarero@uam.es

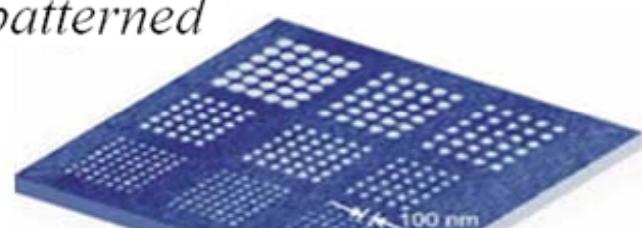
thin films



multilayers

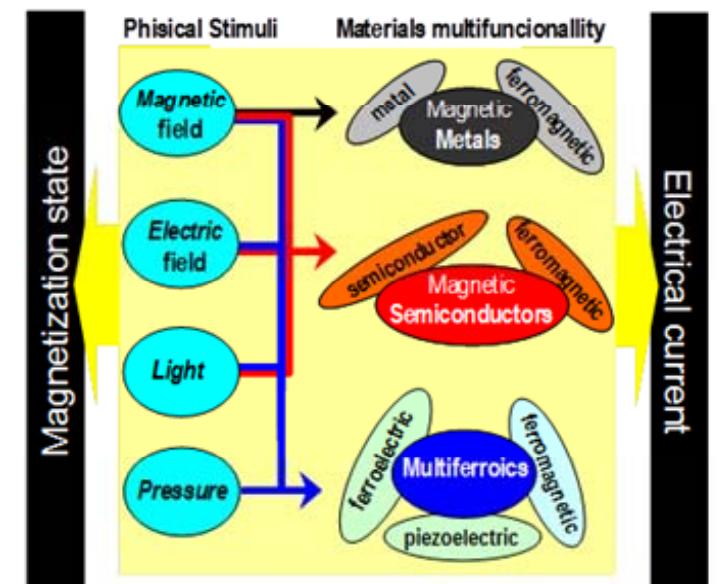


patterned



<http://lasuam.fmc.uam.es/lasuam>

multifunctional



<http://www.nanociencia.imdea.org/>

FROM *MACROSCOPIC* down
TO *NANOSCOPIC SIZES*

Nowadays we can design 'complex magnetic systems' by controlling materials at the atomic scale, that is layer by layer, row by row, and ultimately atom by atom

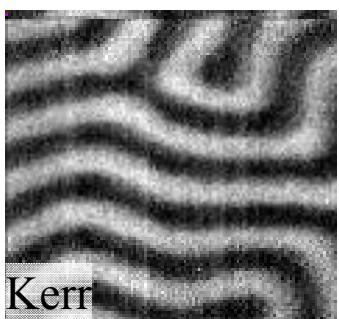
10 μm 1 μm

100 nm

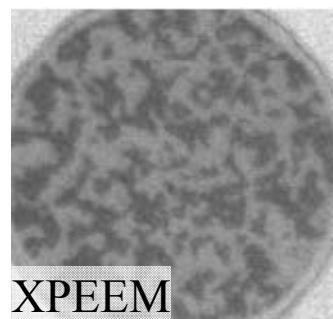
10 nm

1 nm

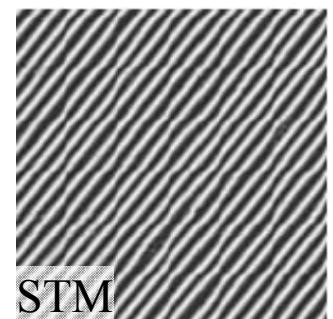
0.1 nm



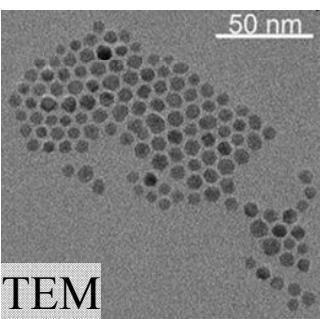
Kerr



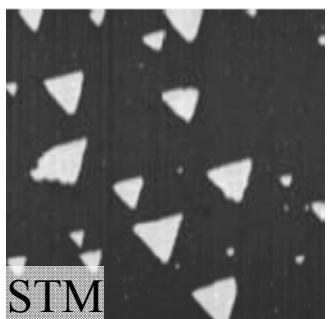
XPEEM



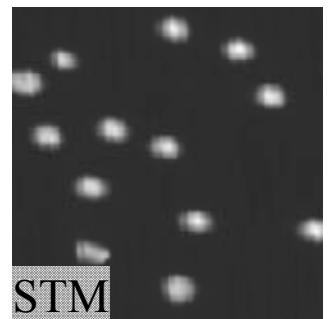
STM



TEM



STM

STM
0D impurities
single molecules

Magnetic domains in 2D films

1D chains & 3D-2D nanoparticles

Magnetic thin films & nanostructures exhibit a wide range of fascinating phenomena:

- **Low dimensional effects:** (tailoring) anisotropies, critical temperatures, magnetic moments...
- **Proximity effects:** induced magnetization in non-magnetic systems (noble metals)...
- **Interfaces:** exchange coupling (FM/AFM), oscillatory coupling (FM/NM/FM),...
- **Magnetoresistance:** Giant Magneto-Resistance GMR, Tunneling Magneto Resistance TMR,...

OUTLINE

Driven forces at the nanoscale

Tailoring Magnetic Properties

Critical Temperatures

Magnetic anisotropy

Interfacial Phenomena

Induced Moments

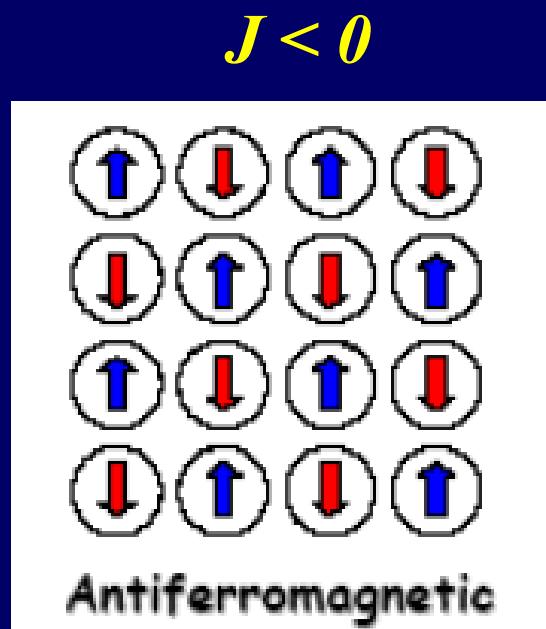
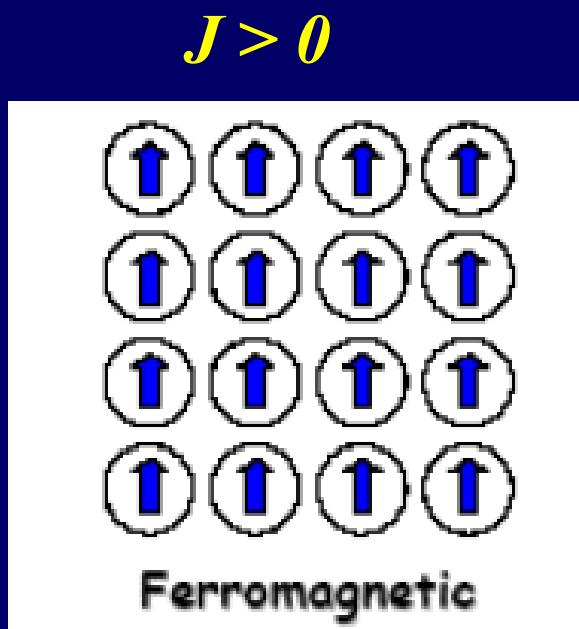
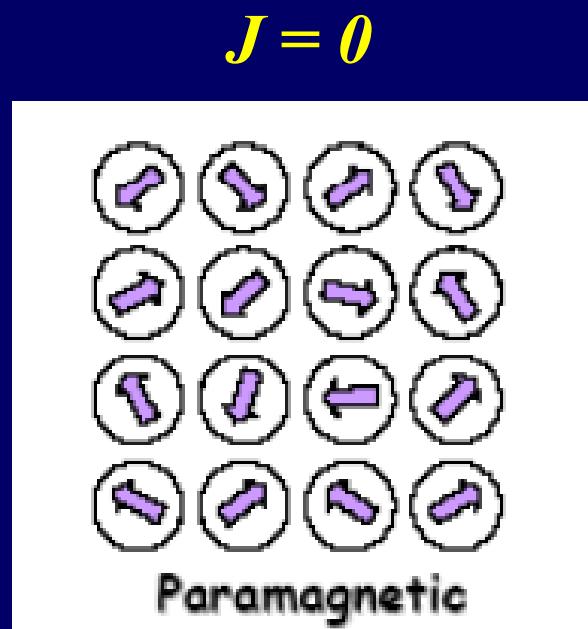
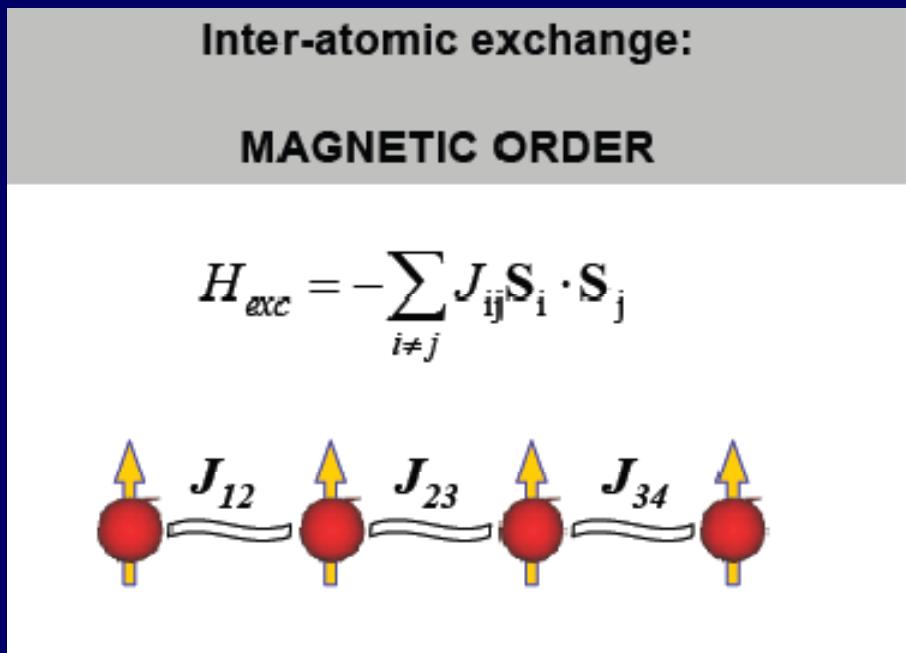
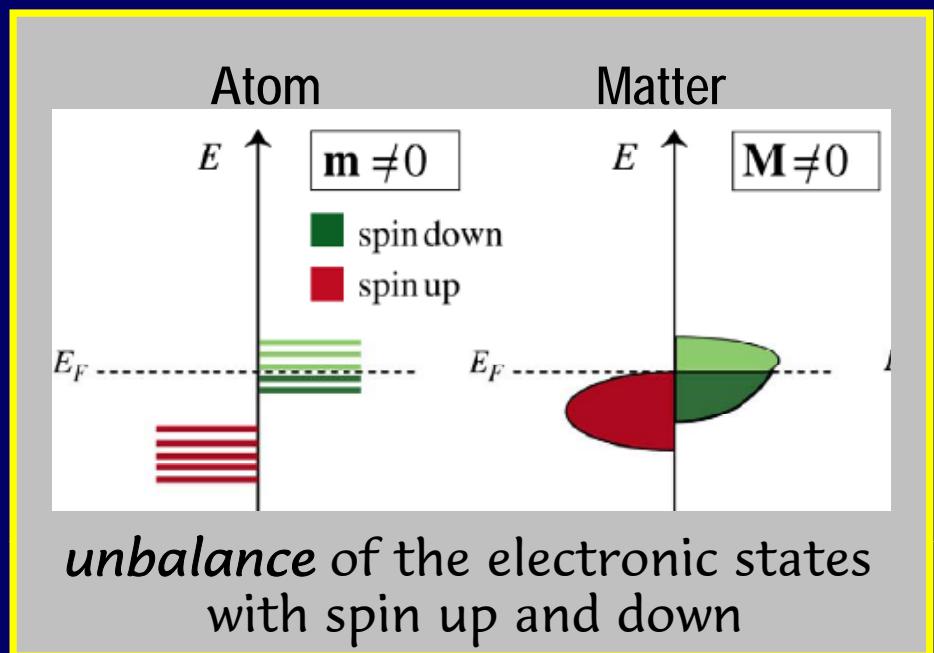
Exchange

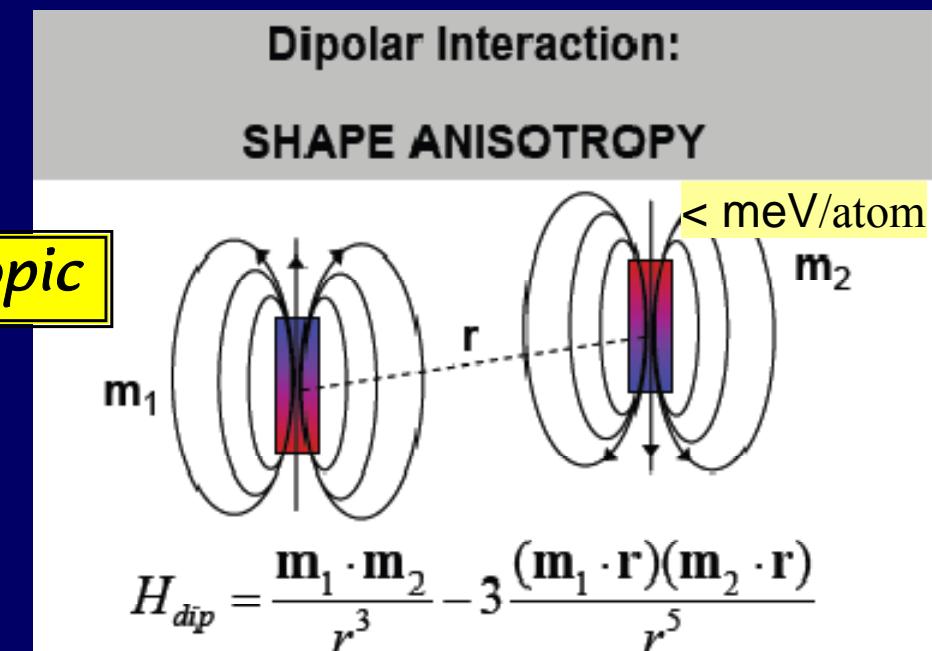
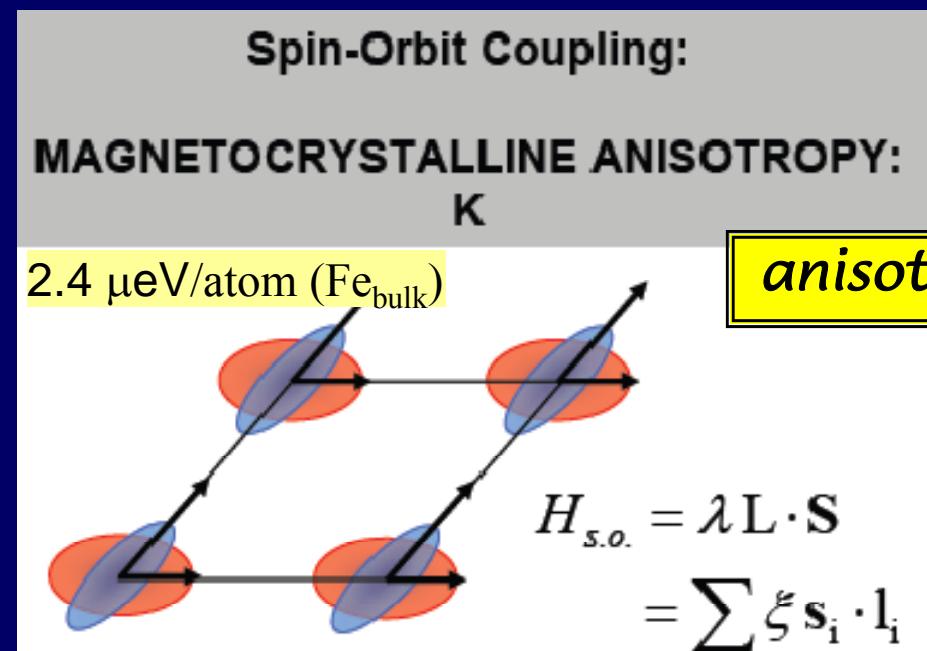
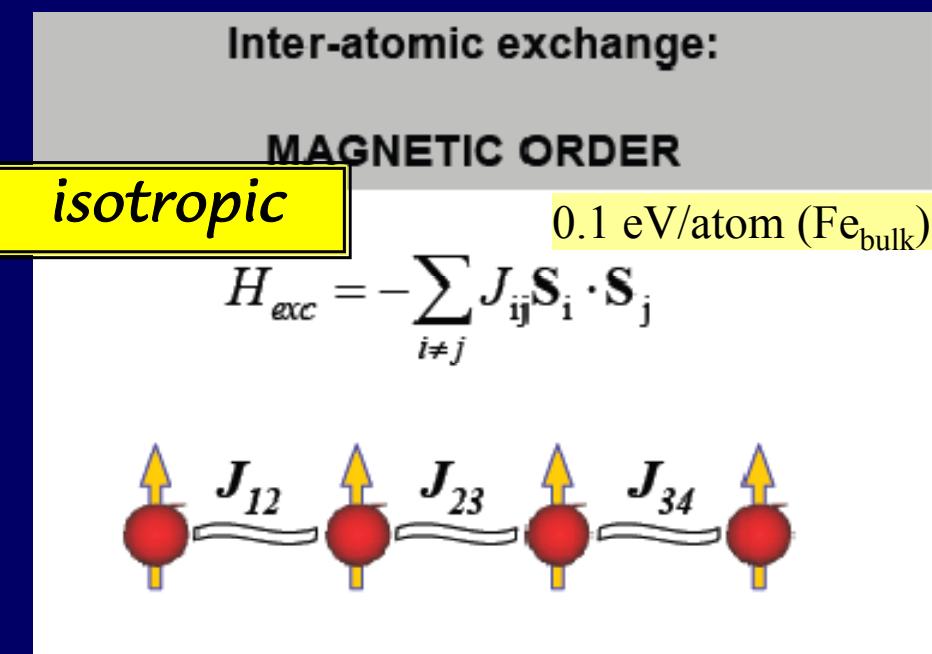
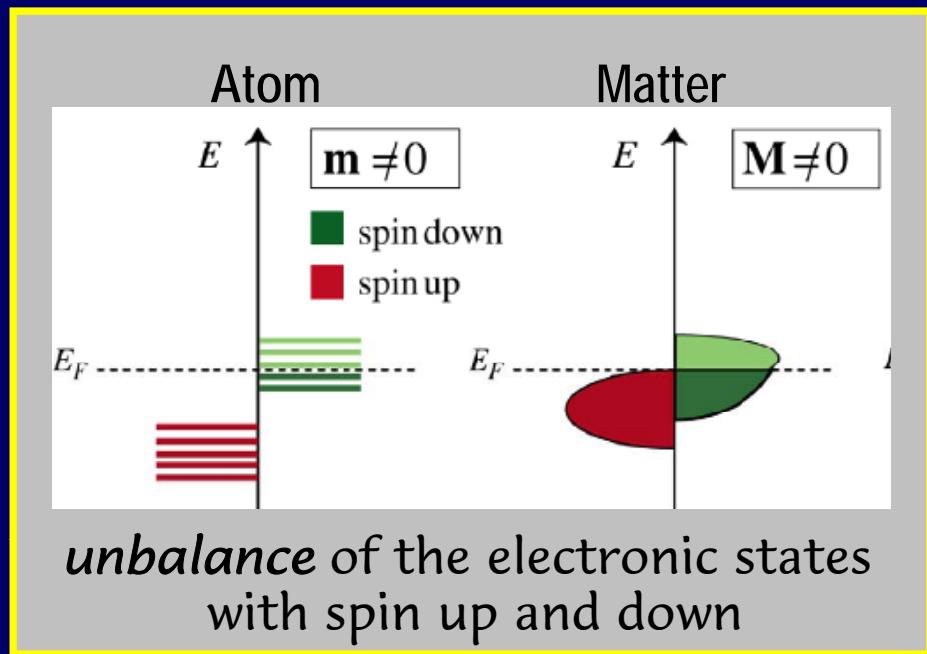
Reversal processes

Size and time scales

Magnetic Symmetry

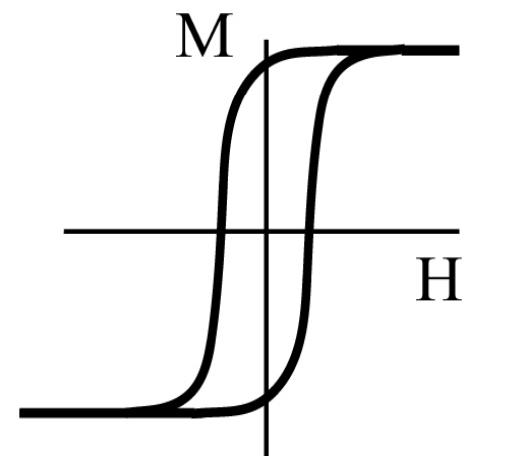
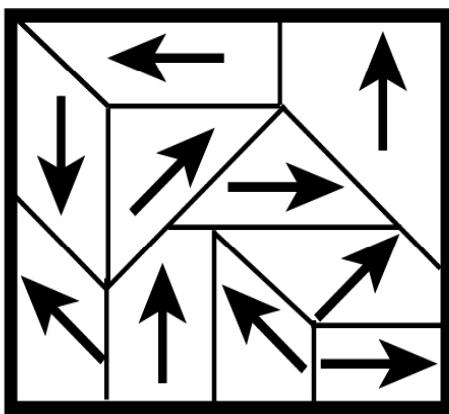
Future Trends



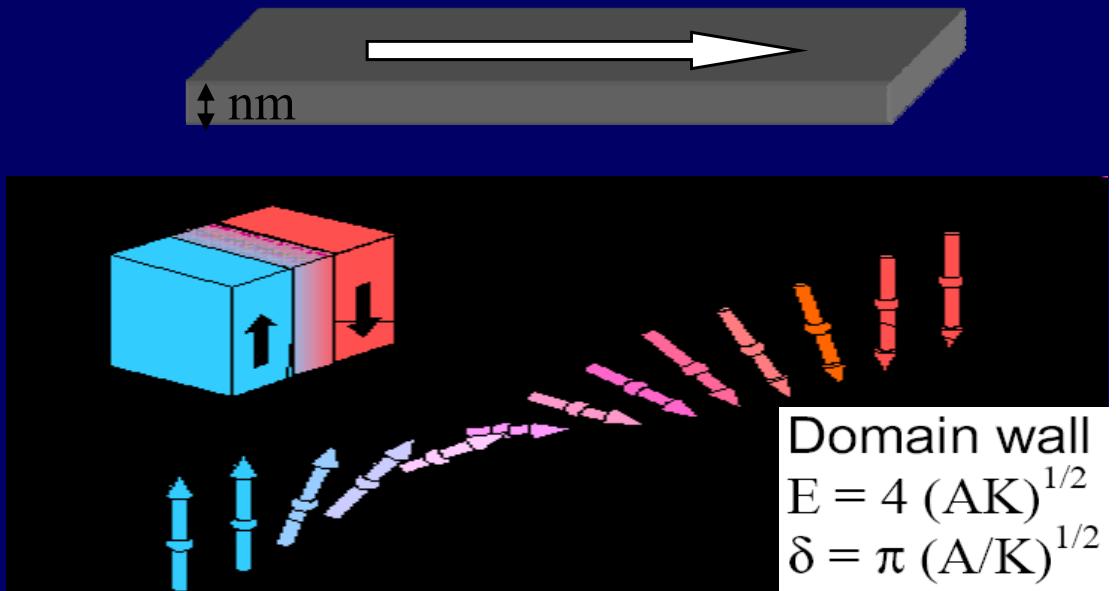
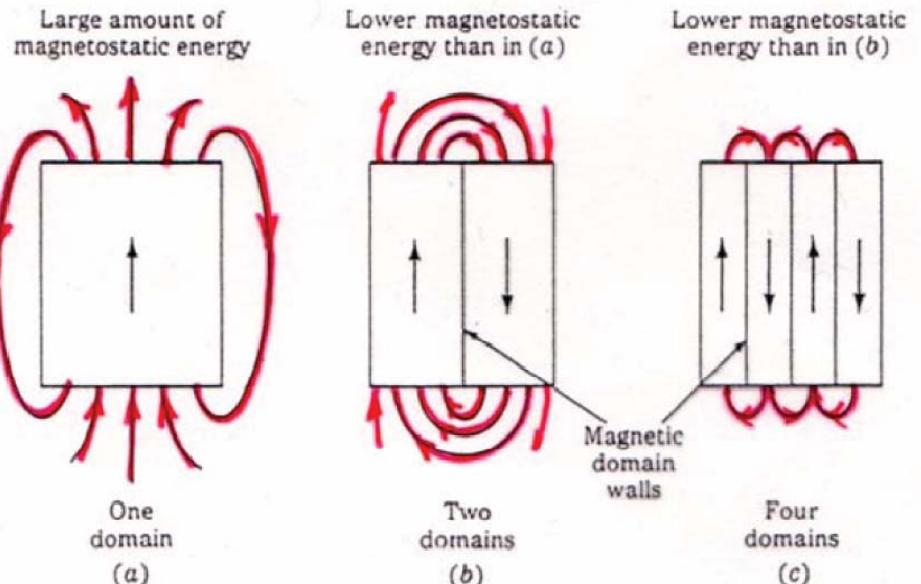


MAGNETIC DOMAINS AND DOMAIN WALLS

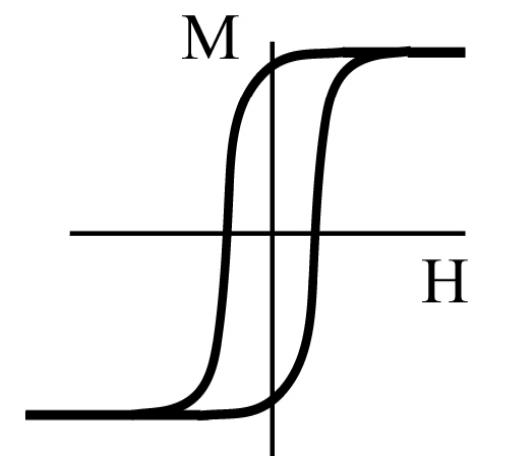
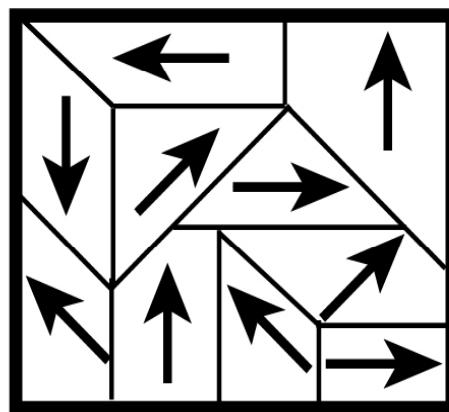
Multi-domain



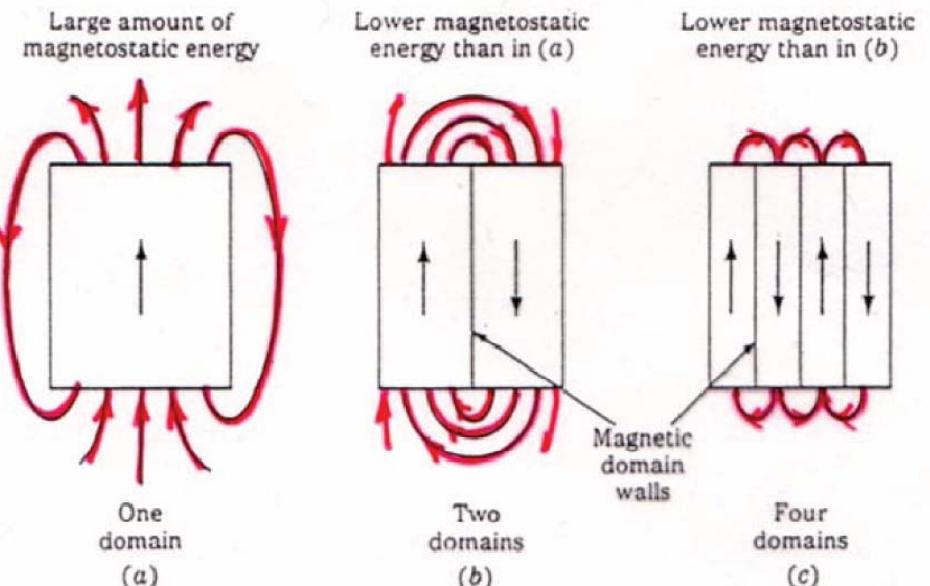
MAGNETOSTATIC ENERGY *Magnetic domain formation*



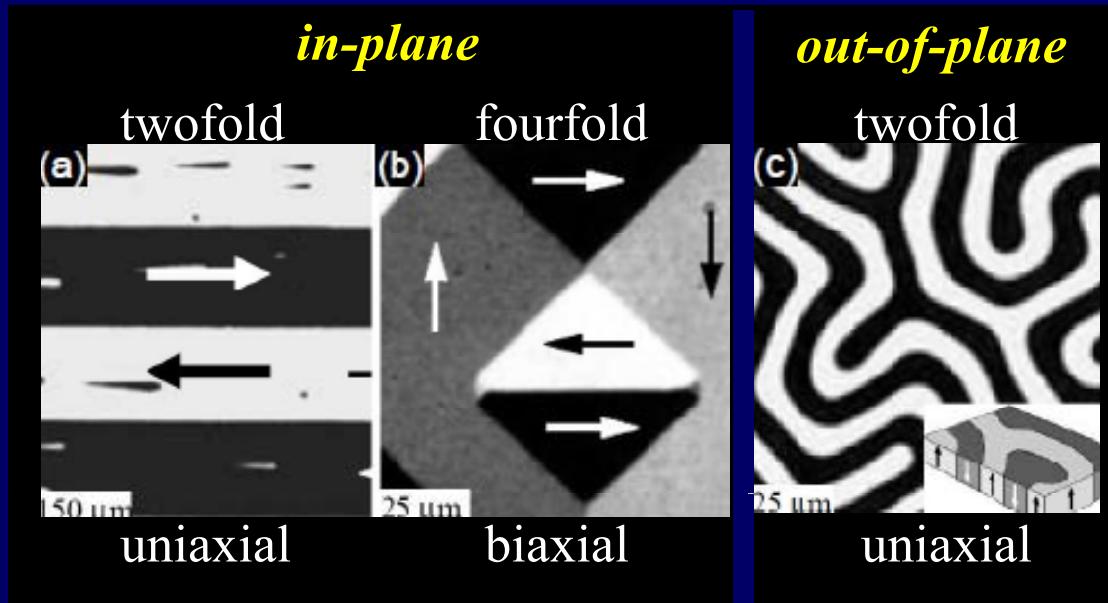
Multi-domain



MAGNETOSTATIC ENERGY *MAGNETIC DOMAIN FORMATION*



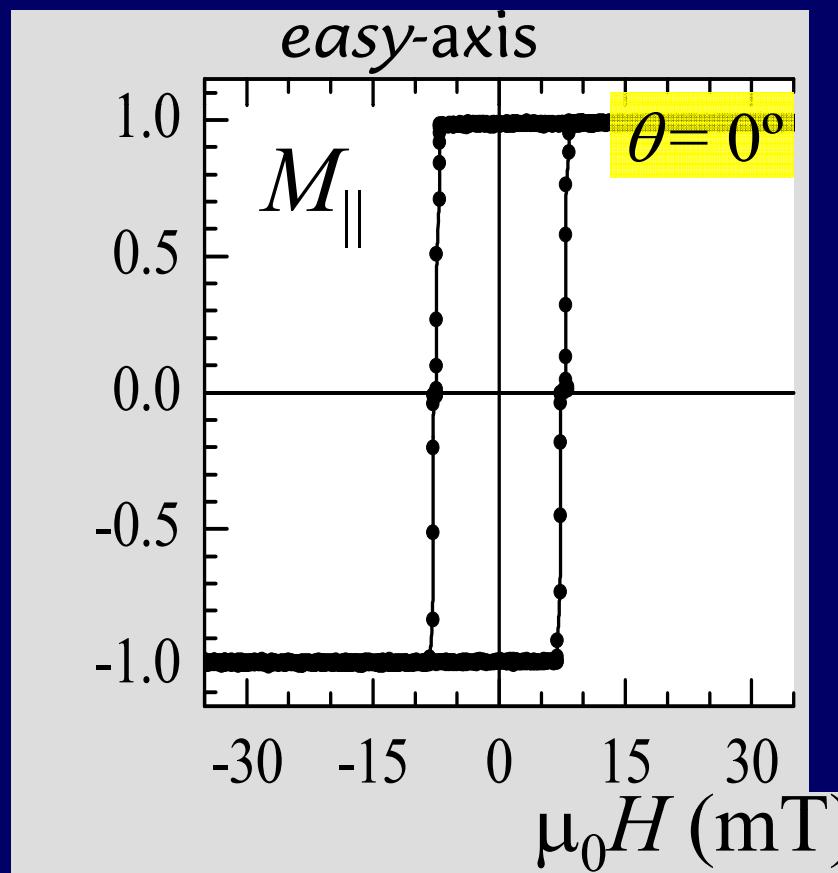
MAGNETIC ANISOTROPY *PREFERENTIAL DIRECTION OF THE MAGNETIZATION*



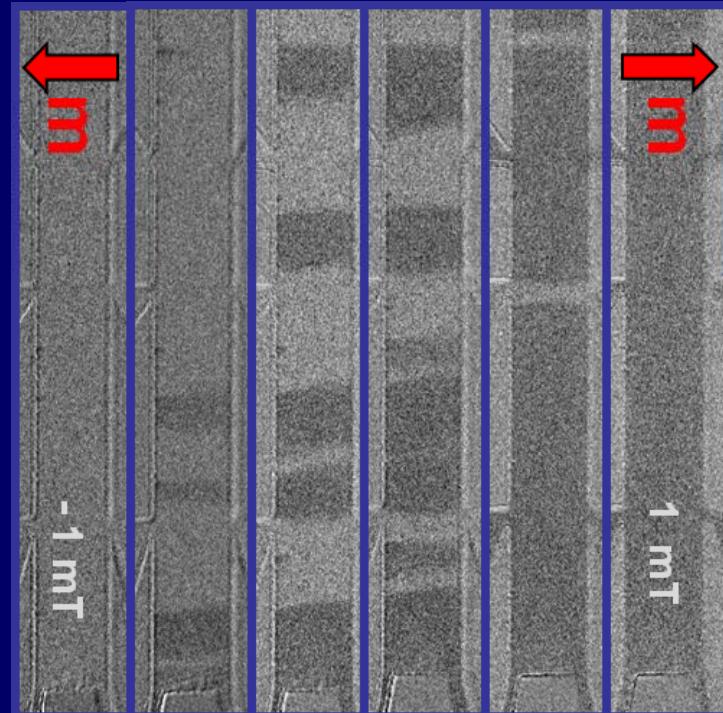
MAGNETIC ANISOTROPY

Magnetic anisotropy is the direction dependence of a material's magnetic properties.

A magnetically *isotropic* material has *no preferential direction* for its magnetic moment in zero field, while a magnetically *anisotropic* material will align its moment to an *easy axis*.



FM ultrathin film with uniaxial anisotropy,

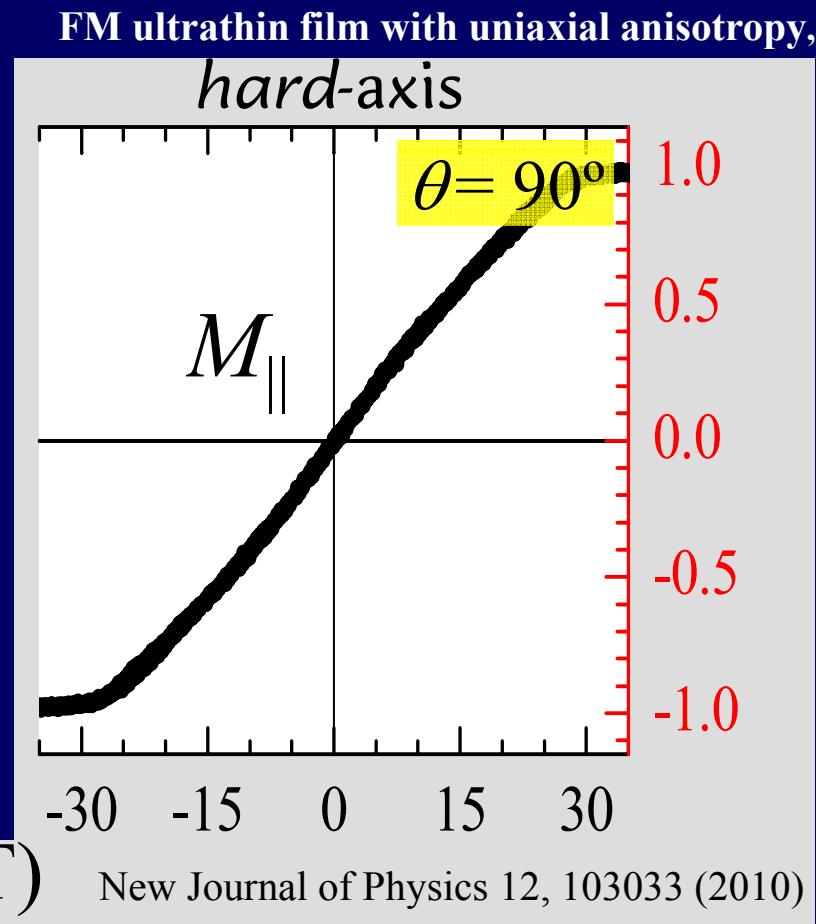
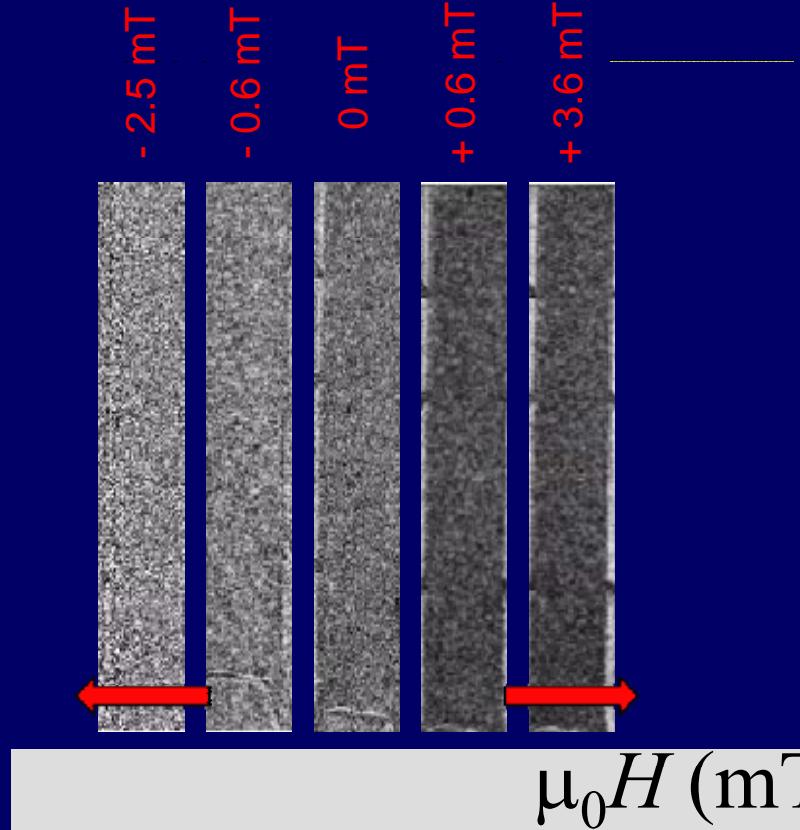


New Journal of Physics 12, 103033 (2010)

MAGNETIC ANISOTROPY

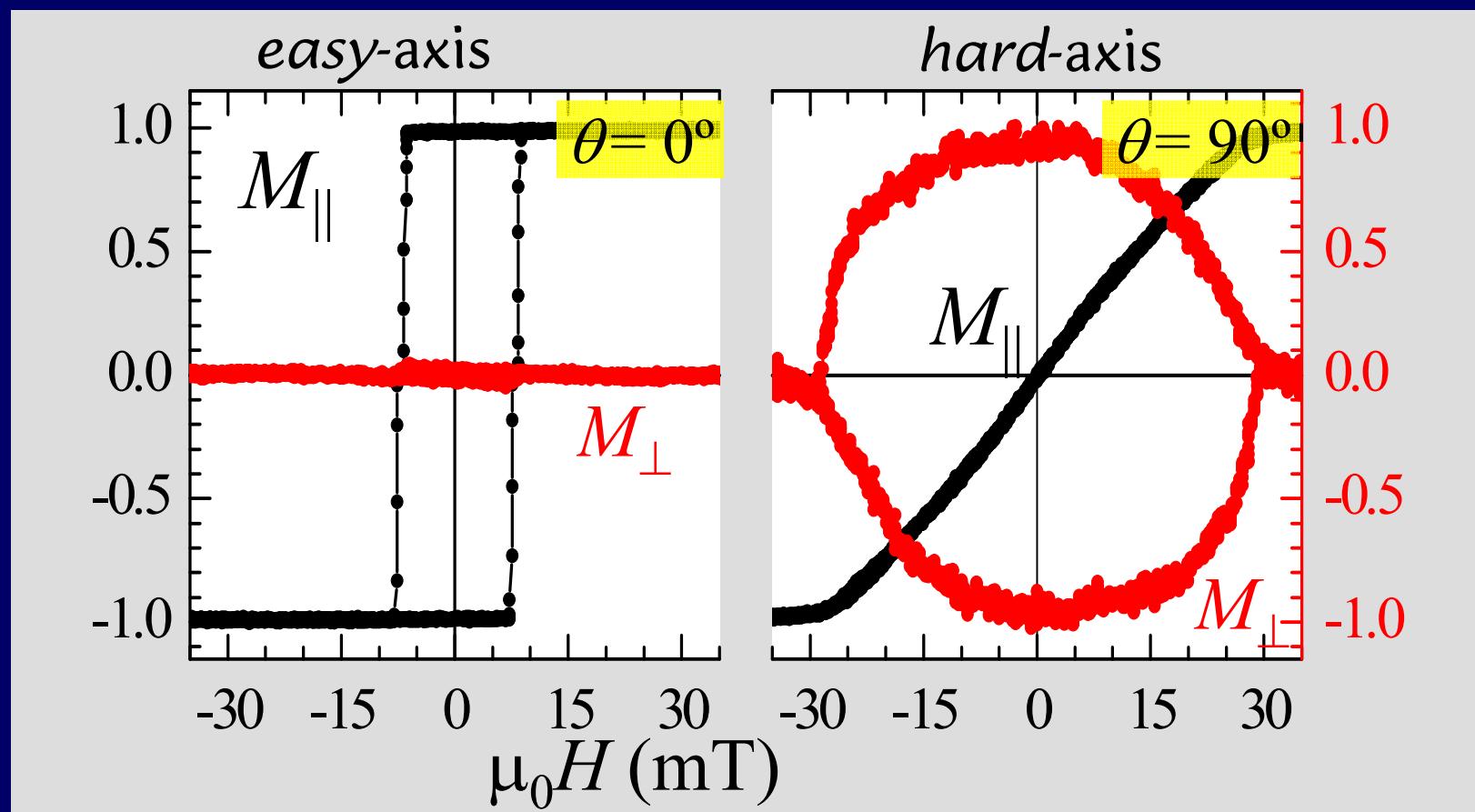
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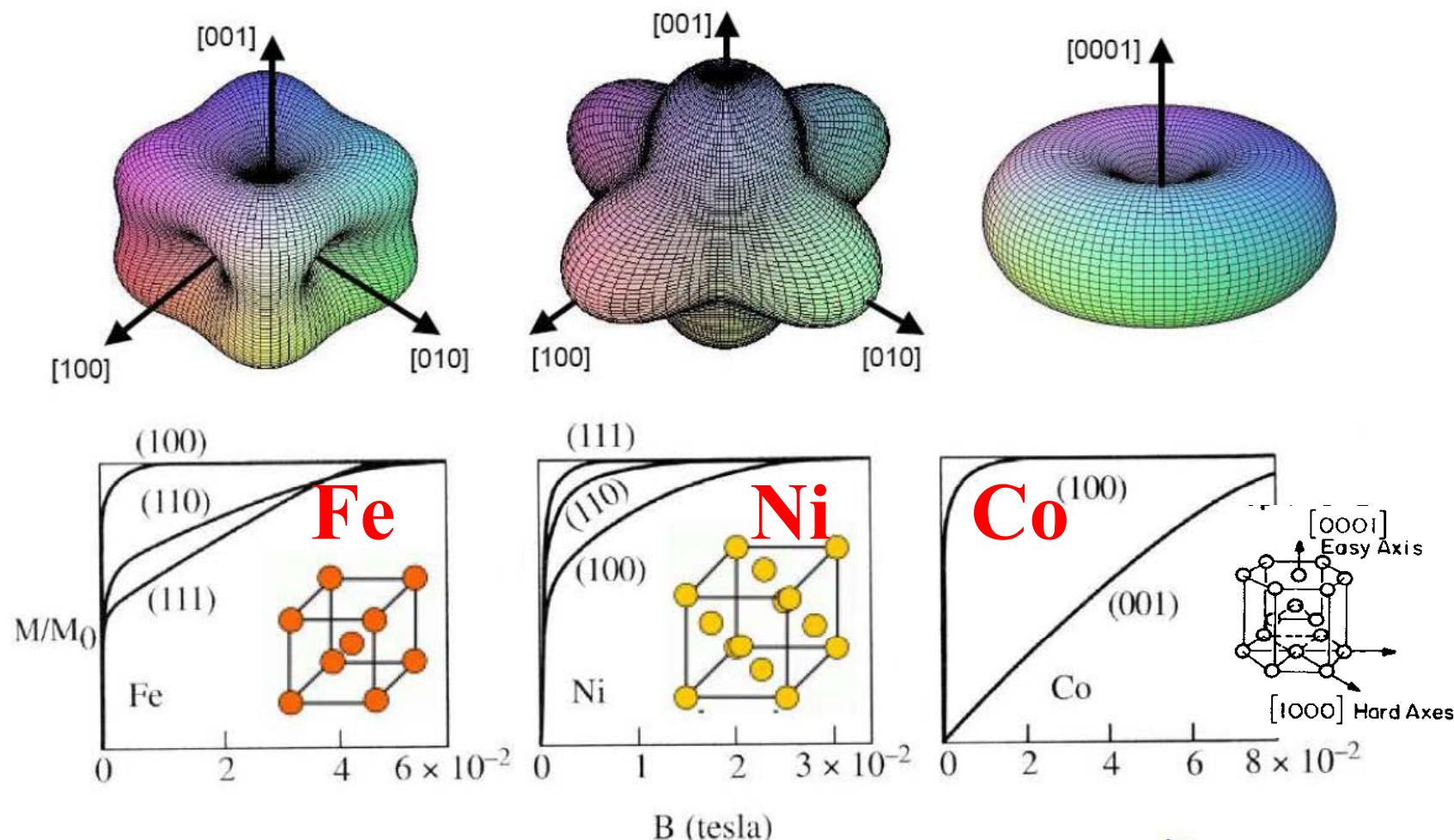
by VECTORIAL MAGNETOMETRY

FM ultrathin film with uniaxial anisotropy, Appl. Phys. Lett. 90 032505 (2007)



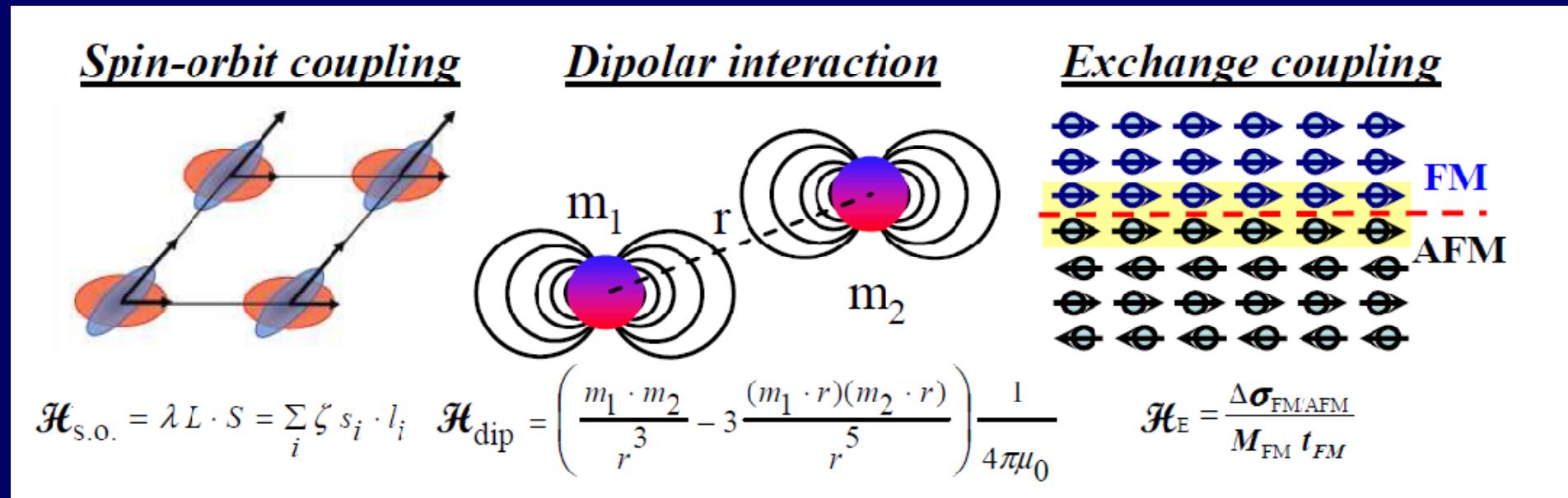
SOURCES of MAGNETIC ANISOTROPY (*broken symmetry*)

- Magnetocrystalline anisotropy (crystal & surface lattice symmetry)



SOURCES of MAGNETIC ANISOTROPY (*broken symmetry*)

- Magnetocrystalline anisotropy (crystal & surface lattice symmetry)
- Magnetoelastic anisotropy (strain)
- Shape anisotropy (demagnetizing fields)
- Exchange anisotropy (e.g., FM/AFM)



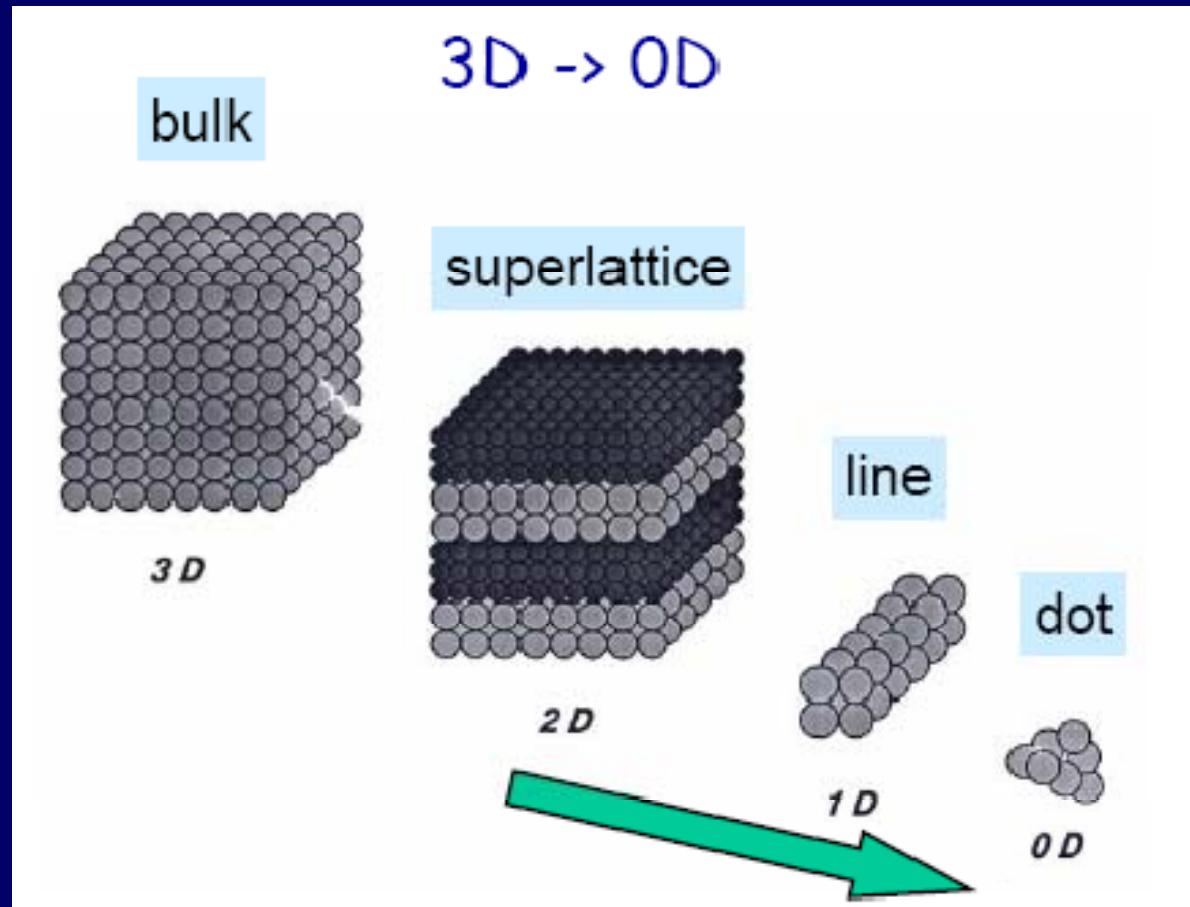
TAILORING MAGNETIC PROPERTIES ← INTERFACIAL PHENOMENA

Critical Temperature

Induced Moments

Magnetic anisotropy

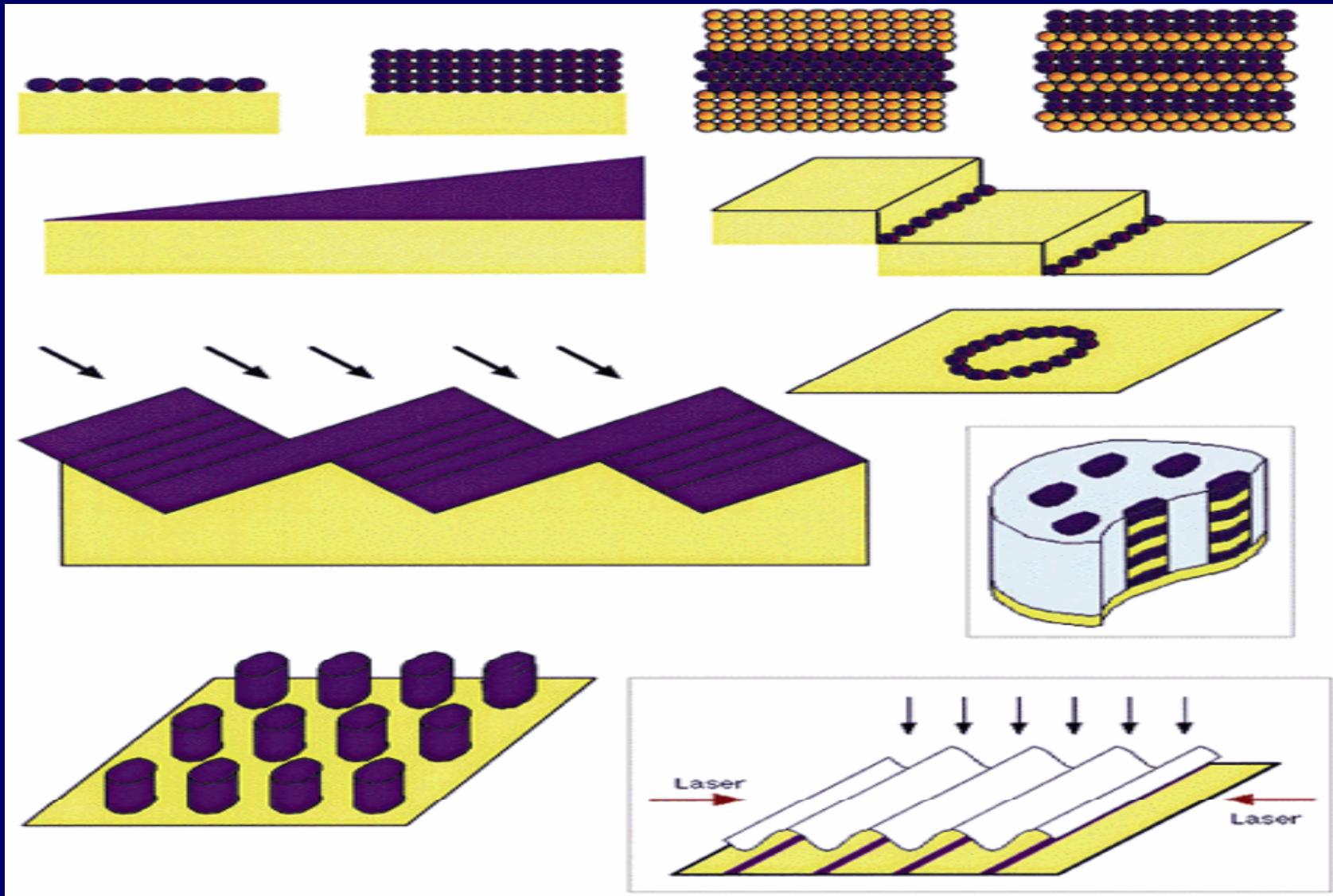
Exchange



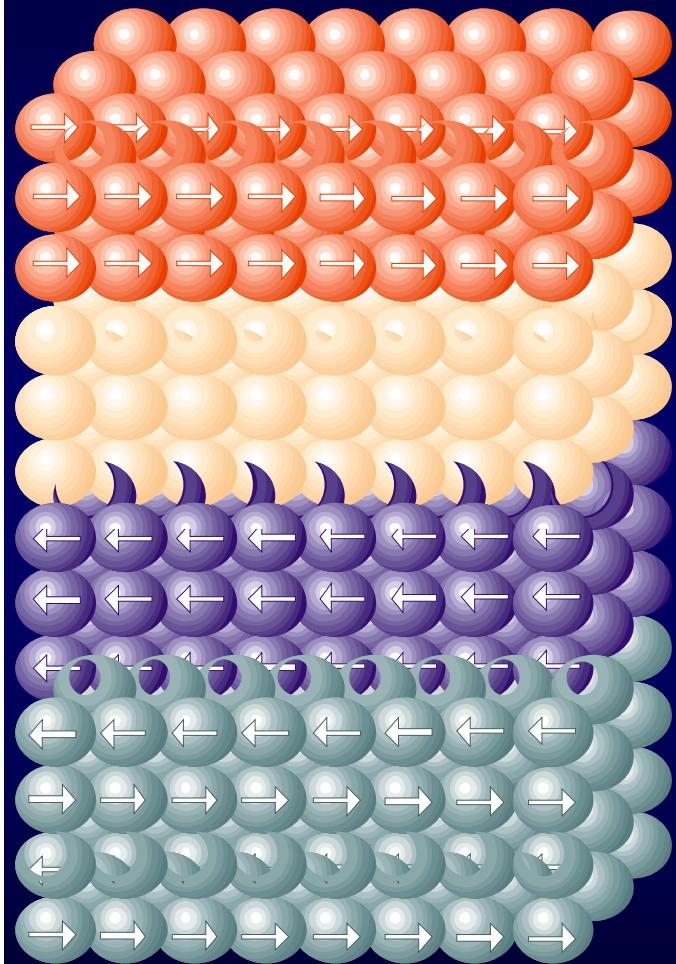
THERMAL EVAPORATION

- Sputtering
- Pulsed laser deposition (PLD)
- Chemical vapor deposition (CVD)
- Molecular beam epitaxy (MBE)

Ultra-high-vacuum UHV conditions



ULTRATHIN film MAGNETIC SUPERLATTICES



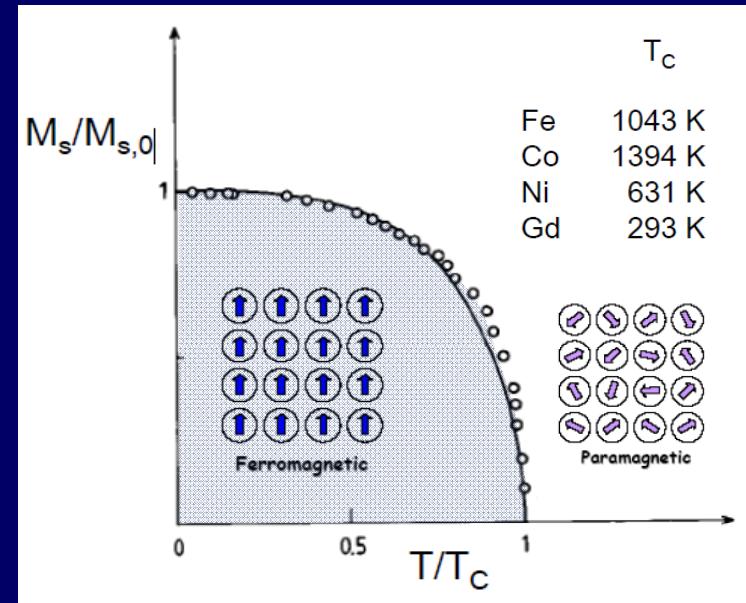
Exchange-biased spin-valve
MTJ

Critical Temperature in Magnetic Materials

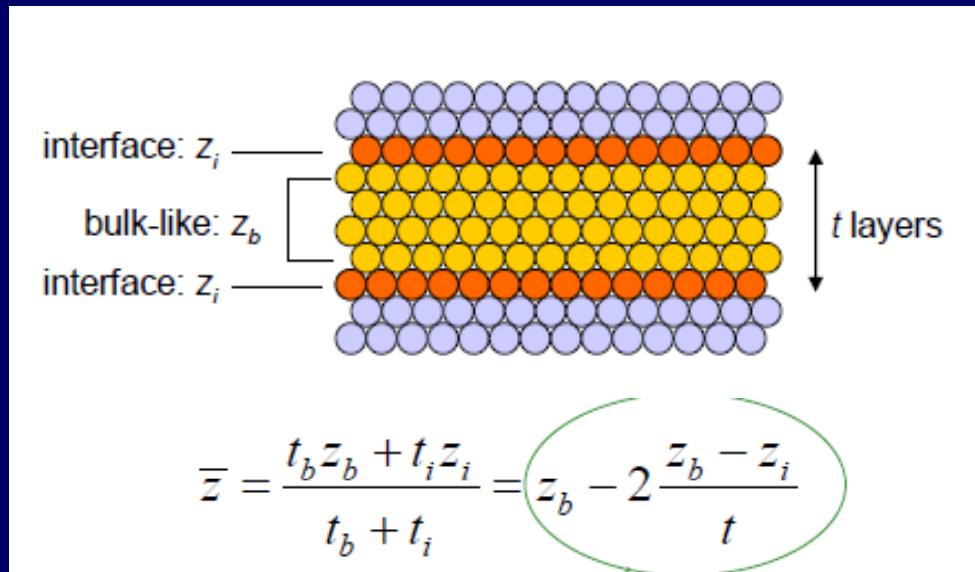
The Curie temperature depends on the number of nearest neighbors z .

$$T_C = \frac{S+1}{3S} \frac{J_{exc} z}{k}$$

E.g., for bulk bcc Fe, $z = 8$,
 $T_C = 1040$ K, $S \approx 2$, $J \approx 0.02$ eV

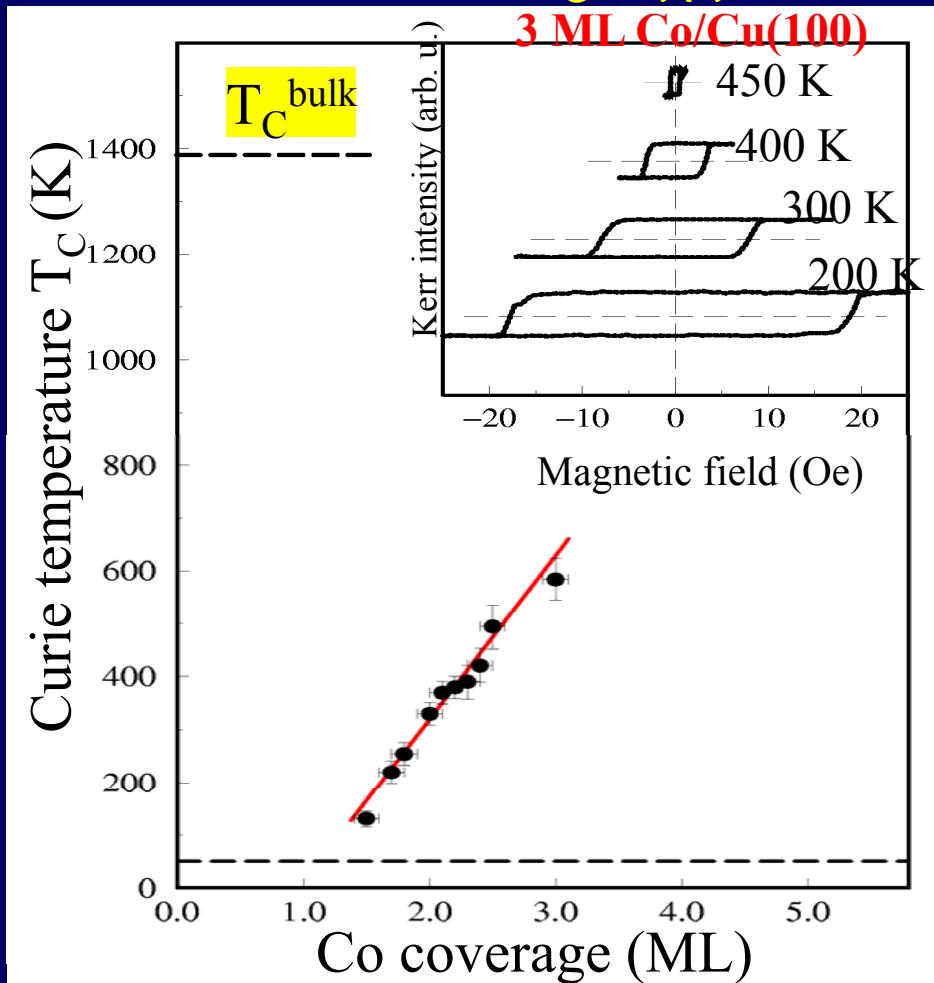


Thin films → reduced number of magnetic neighbors



$1/t_{FM}$ dependence

XMCD $\rightarrow T_C(t_{FM})$



Schneider *et al*, Phys. Rev. Lett **64**, 1059 (1990)

XMLD $\rightarrow T_N(t_{AFM})$

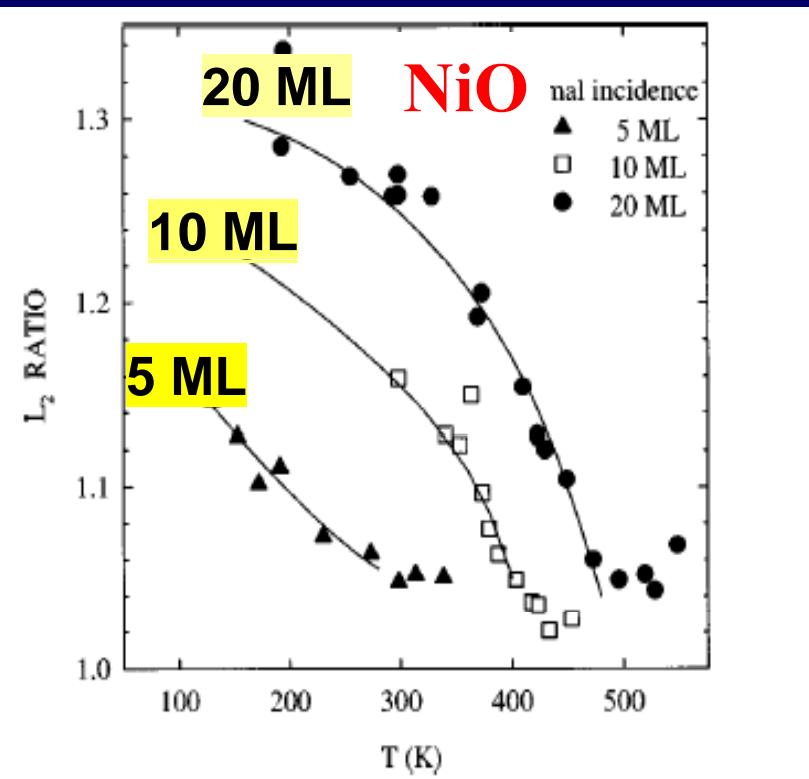


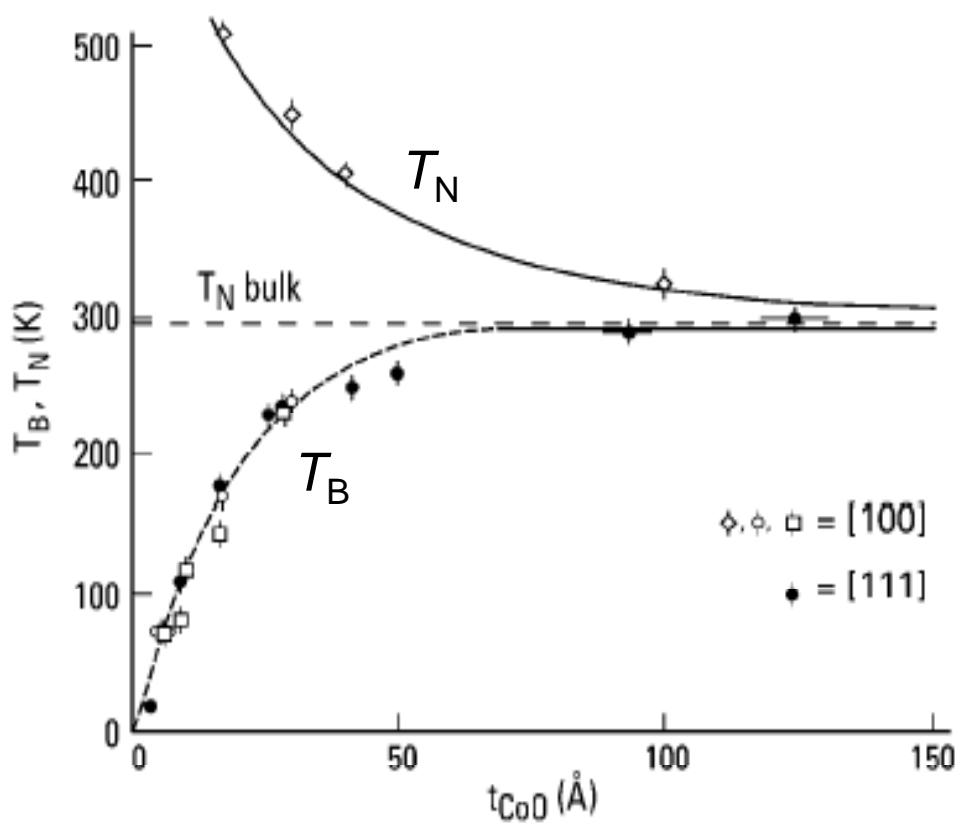
FIG. 12. Temperature and thickness dependence of the ratio of the two peaks in the Ni L_2 -XAS of NiO(100) thin films, taken at normal incidence. Néel temperatures of $T_N = 295, 430$, and 470 K can be found for the 5, 10, and 20 monolayer films, respectively.

Alders *et al*, Phys. Rev. B **57**, 11623 (1998)

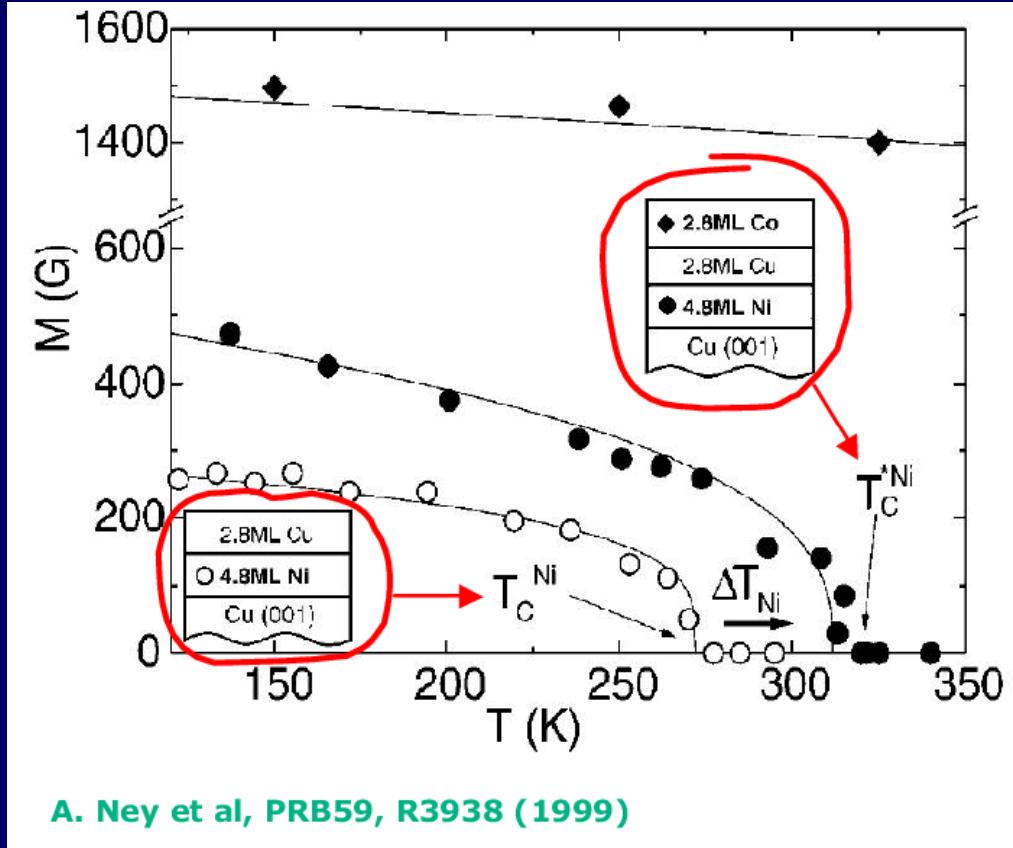
*Critical temperature decreases when thickness decreases
 ⇔ dimensionality effect*

The ordering temperature of the AFM layers (FM nanoparticles) layers is *enhanced* above the bulk T_N (T_C) due to the proximity of magnetic FM (AFM) layers.

EXCHANGE-COUPING INCREASES OF T_N



EXCHANGE-COUPING INCREASES OF T_C



Van der Zaag et al, Phys. Rev. Lett. **84**, 6102 (2000)

Induced magnetic moments have been found in non magnetic materials such as Pt, Pd, Cu, W, Ir, C, N in contact with ferromagnetic ones

Magnetic and element selective tool \Rightarrow XMCD

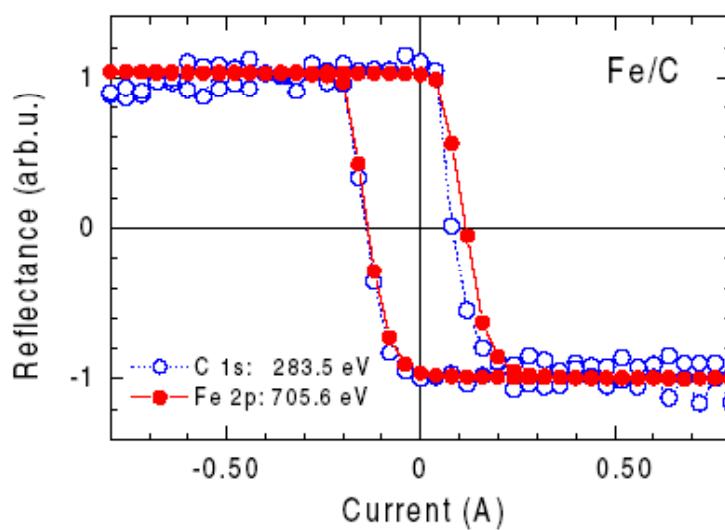
First evidence in Co/Cu multilayers by Samant *et al*, Phys. Rev. Lett **72**, 1112 (1994)

Europhys. Lett., **66** (5), pp. 743–748 (2004)

DOI: [10.1209/epl/i2003-10253-5](https://doi.org/10.1209/epl/i2003-10253-5)

Direct observation of local ferromagnetism on carbon in C/Fe multilayers

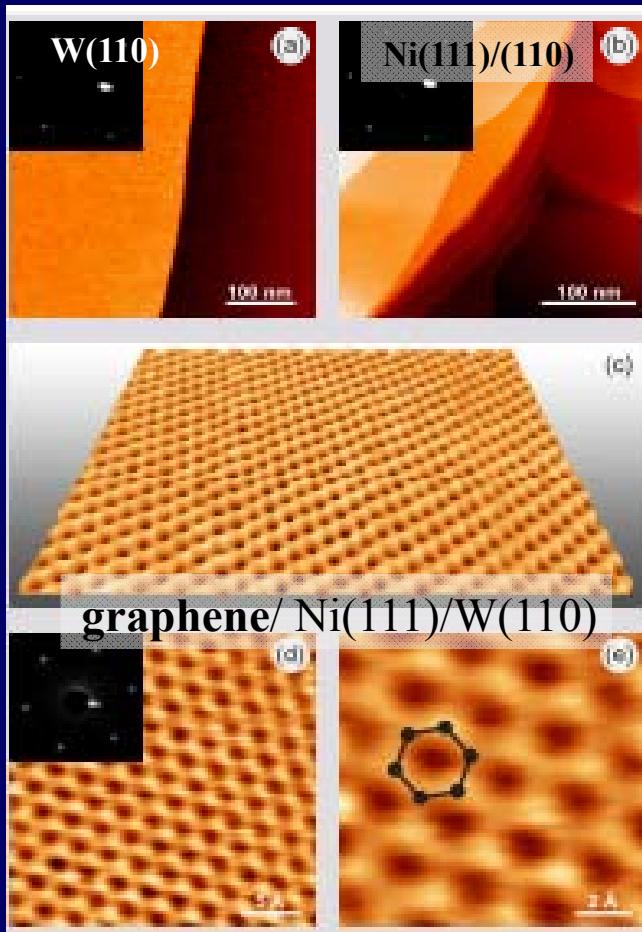
H.-Ch. MERTINS¹(*), S. VALENCIA², W. GUDAT², P. M. OPPENEER³,
O. ZAHARKO⁴ and H. GRIMMER⁴



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Magnetic and element selective tool \Rightarrow XMCD

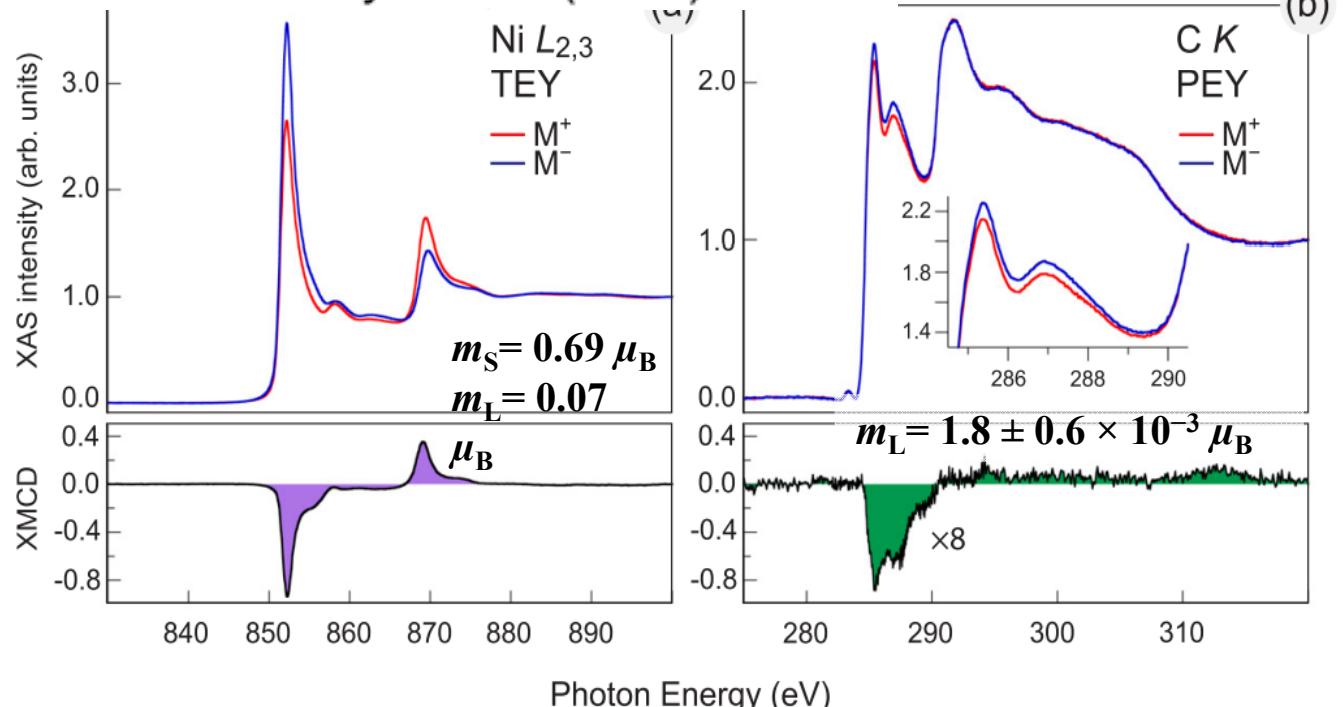
First evidence in Co/Cu multilayers by Samant *et al*, Phys. Rev. Lett **72**, 1112 (1994)

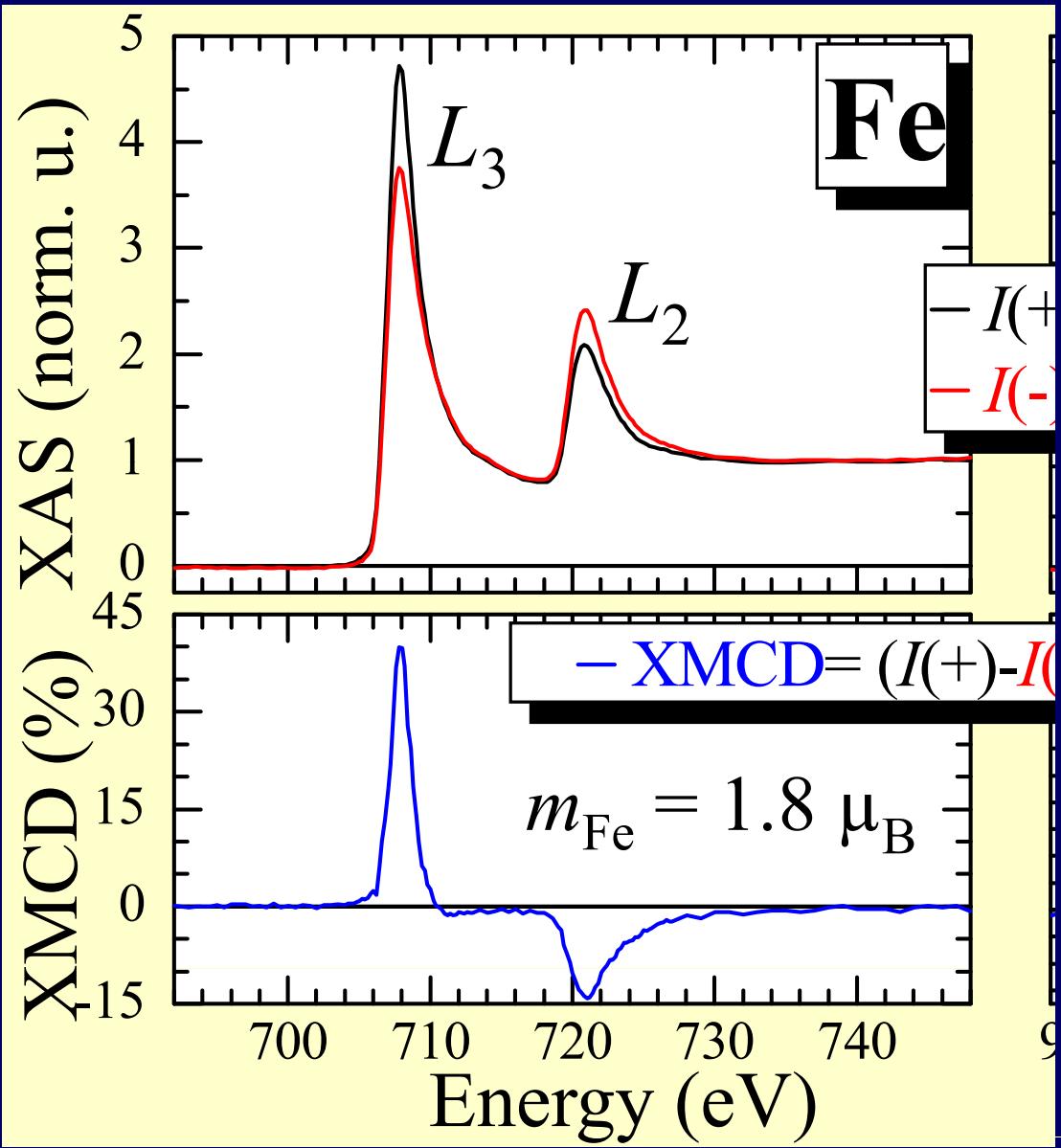


XAS \rightarrow existence of interface states, originating from partial charge transfer from Ni to C atoms (*strong hybridization*)

\rightarrow induced magnetic moment in the graphene layer

New Journal of Physics **12** (2010) 125004

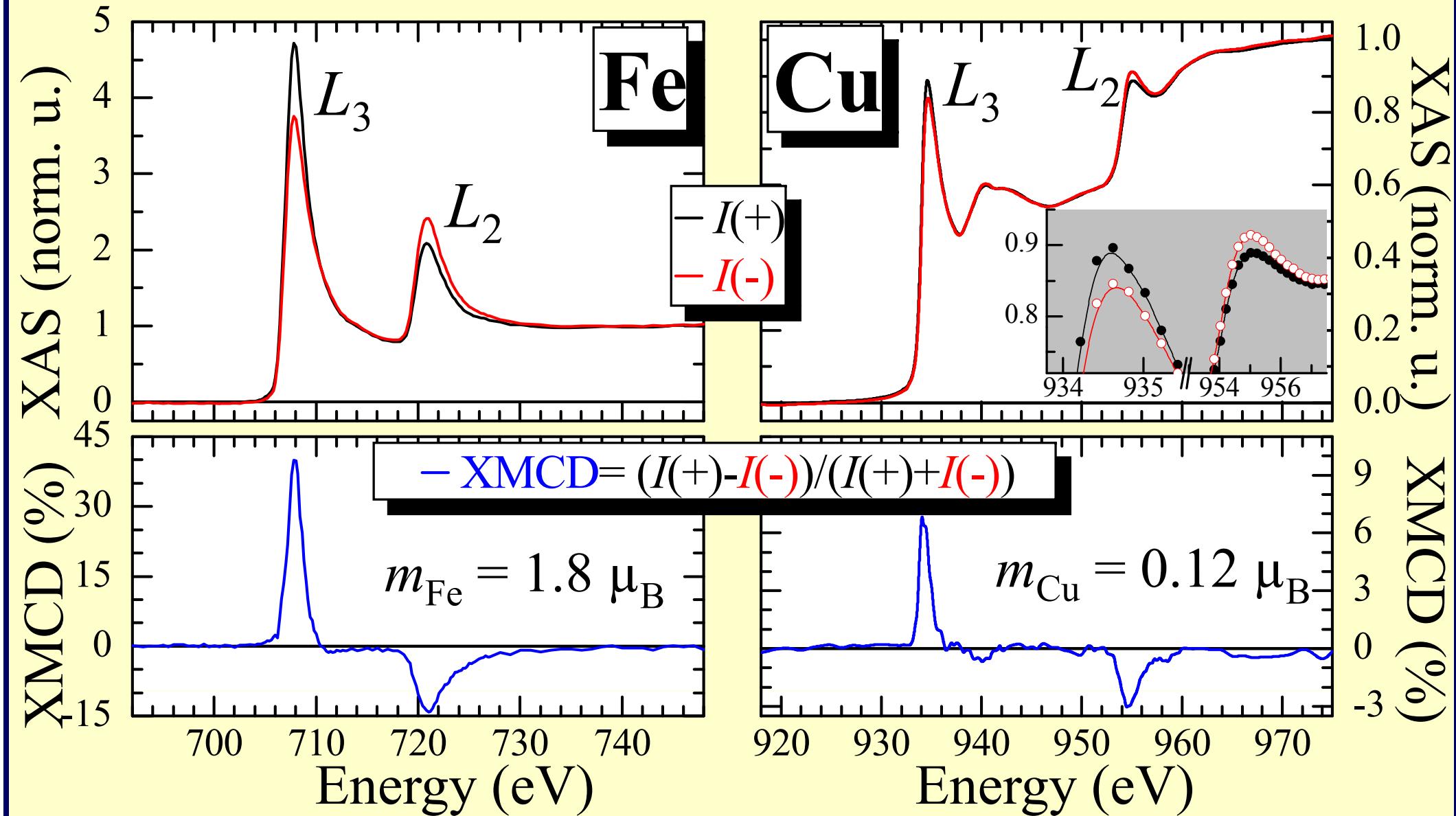


element-selective magnetic properties of 37 ML $\text{Fe}_{55}\text{Cu}_{45}$ 

Fe-Cu *codeposition* on (4x4)Pb/Cu(111)
→ atomically disordered FeCu alloys
with fcc-fct structure.

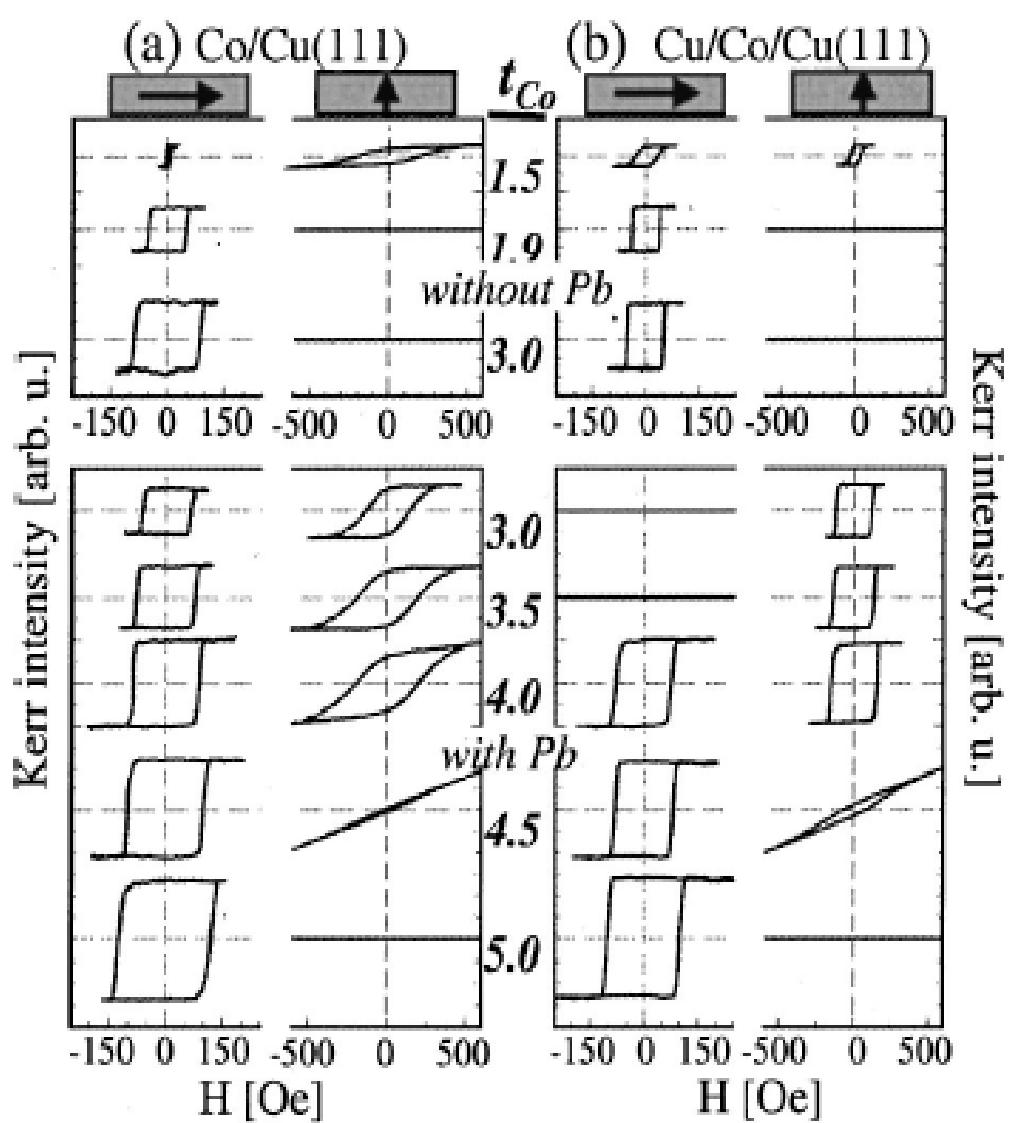
Niño *et al*,
J. Phys.: Cond. Matt. **20**, 265008 (2008)

element-selective magnetic properties of 37 ML $\text{Fe}_{55}\text{Cu}_{45}$



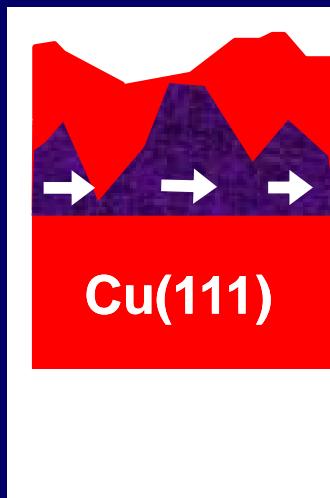
Parallel alignment between Fe and Cu (*induced*) magnetic moments

SURFACE-INTERFACE EFFECTS

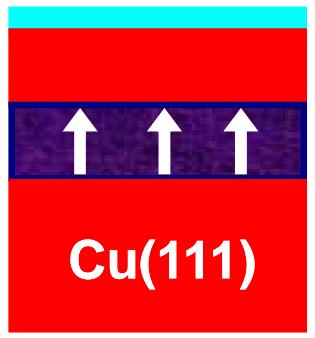


INTERFACE ENGINEERING
PERPENDICULAR MAGNETIC ANISOTROPY (PMA)

two FM/NM interfaces



4 ML Cu
3 ML Co



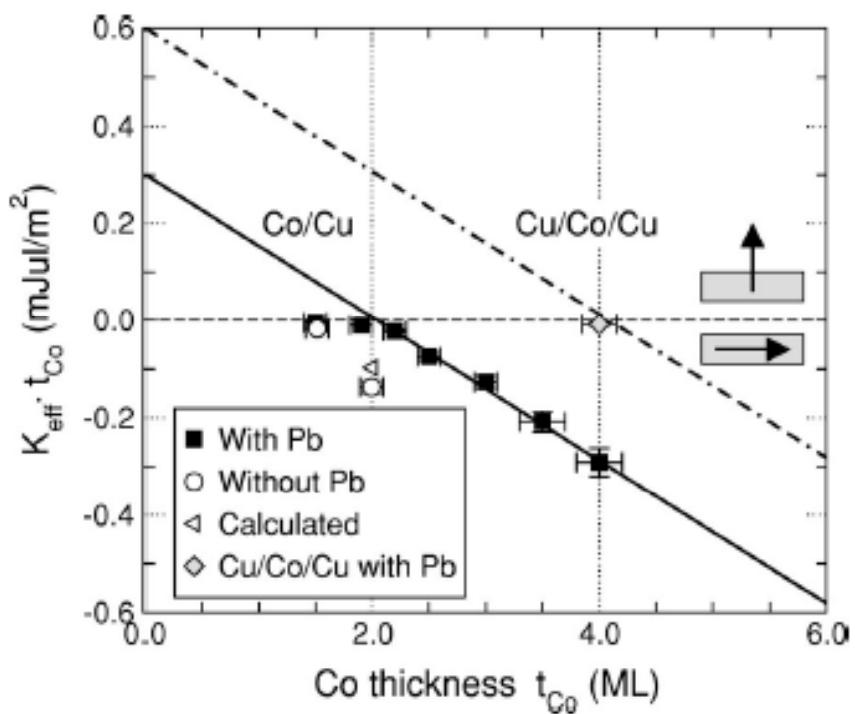
Cu(111)
with *Pb*
as surfactant

roughness vanishes interfacial effects

Camarero *et al* Phys. Rev. Lett. **76**, 4428 (1996)

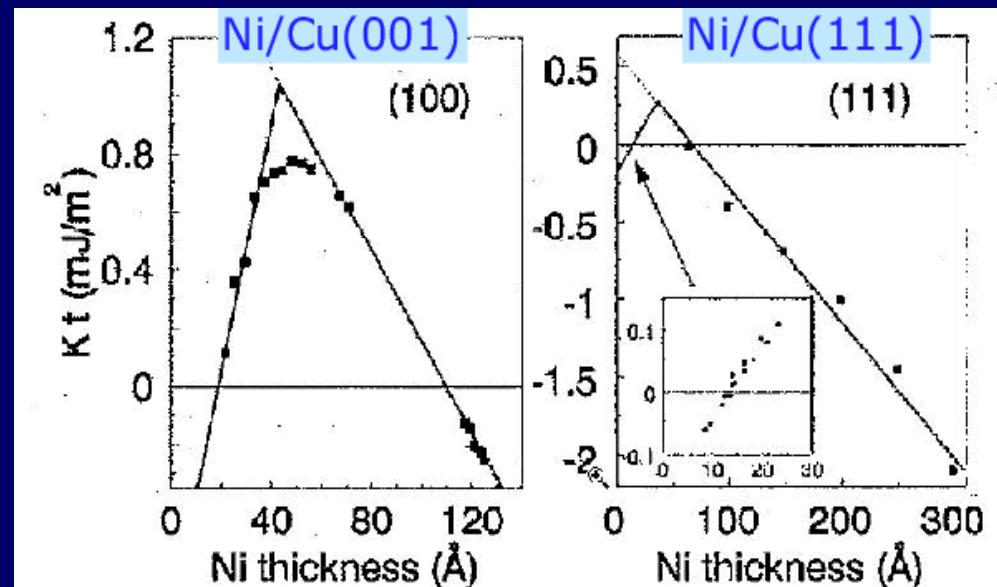
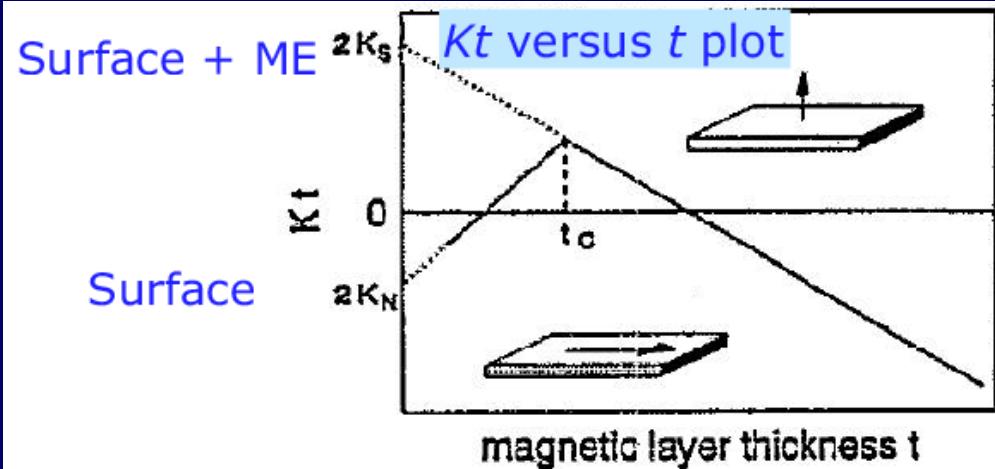
SURFACE-INTERFACE EFFECTS

$$K_{eff} = K_V + nK_S \left(\frac{1}{t} \right),$$



Camarero *et al* Phys. Rev. B **64** 125406 (2001)

MAGNETOELASTIC EFFECTS

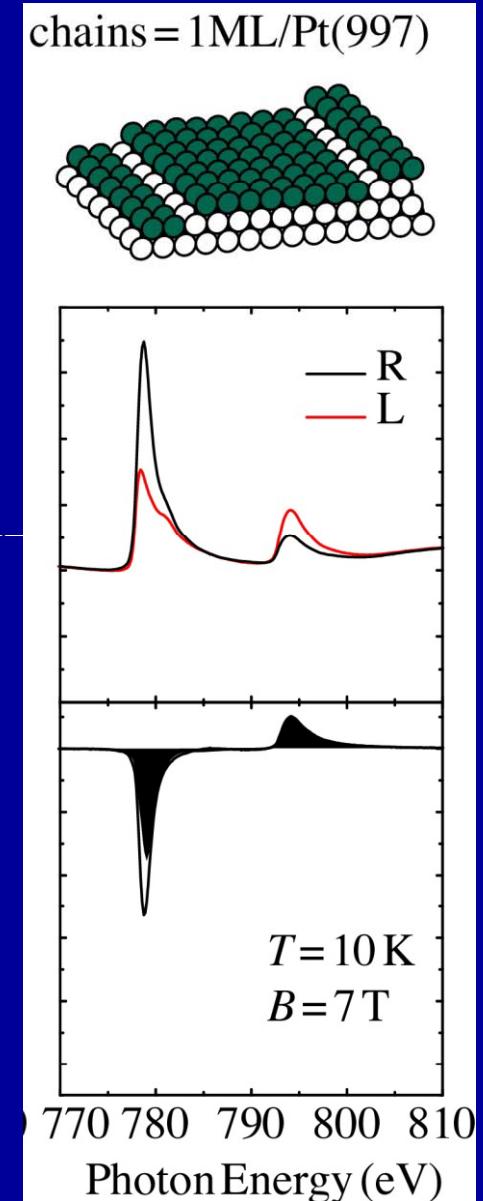


R. Jungblut *et al.*, JAP75, 6424 (1994)



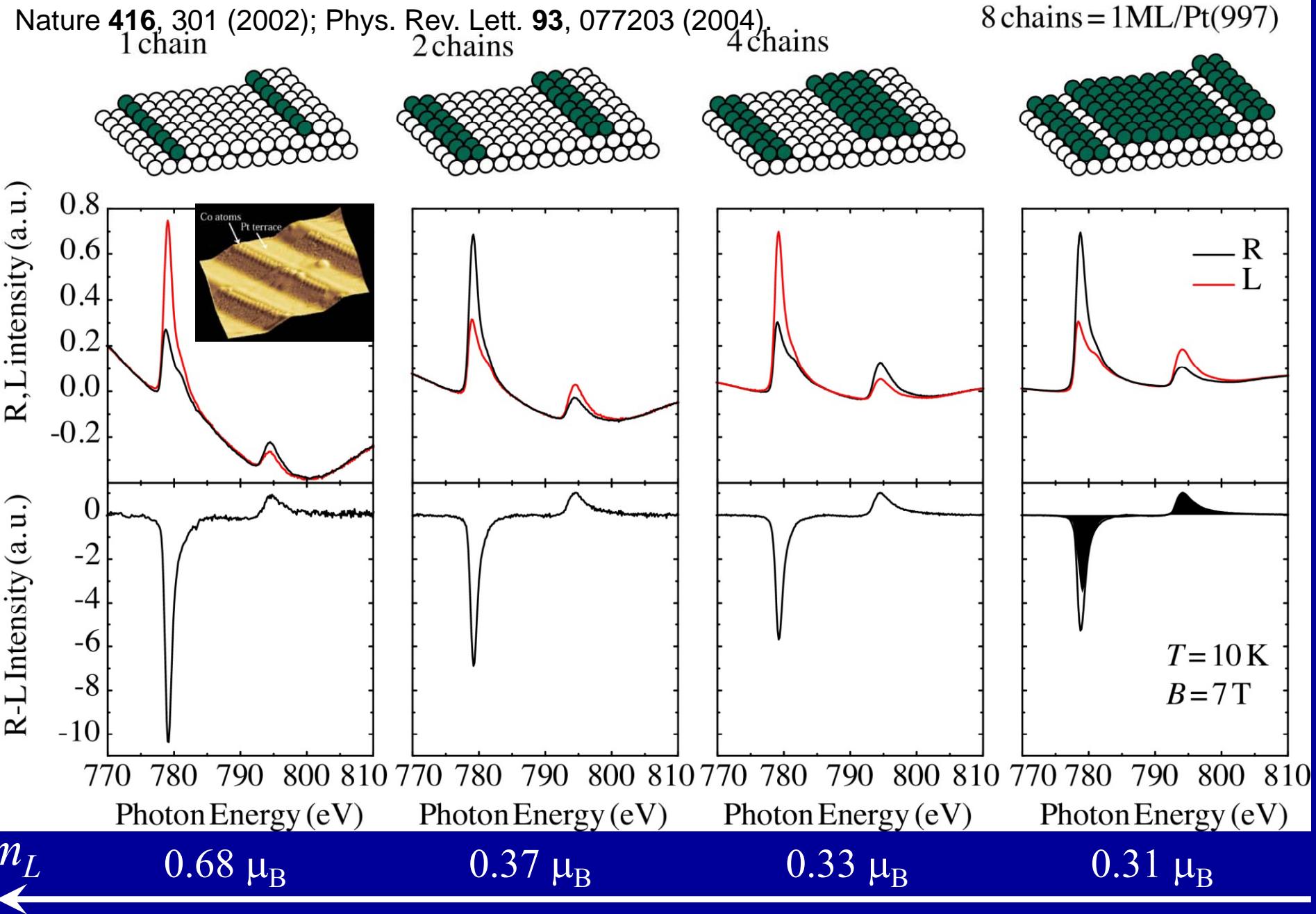
DI^MENSION-DE^PENDENT MAGNETIC ANISOTROPY

P. Gambardella *et al.*, Nature **416**, 301 (2002); Phys. Rev. Lett. **93**, 077203 (2004).



Dimension-dependent magnetic anisotropy

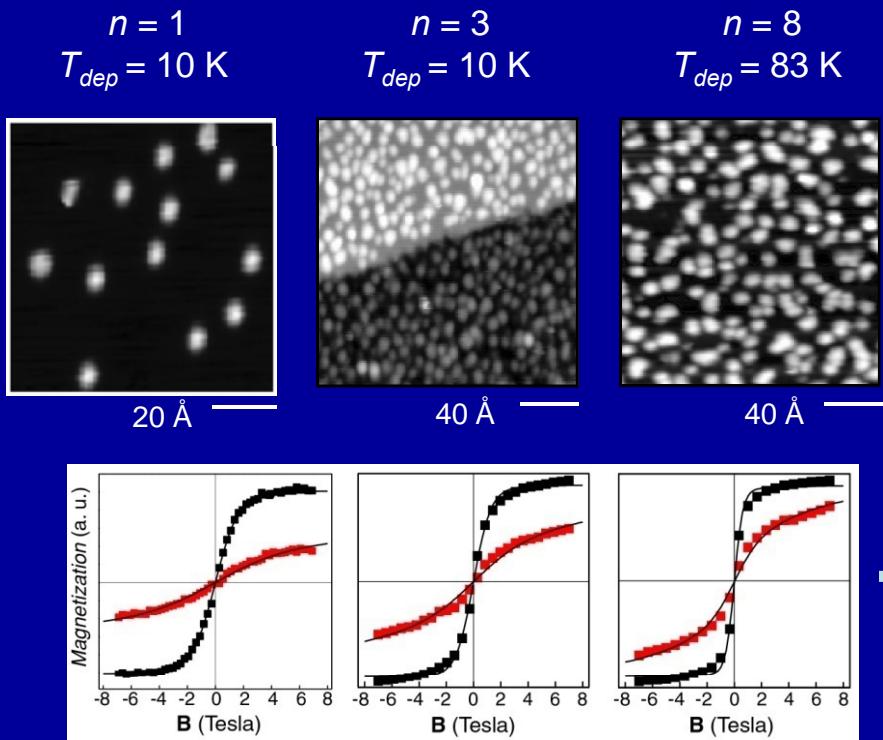
enhanced orbital magnetic moment in 1D wires



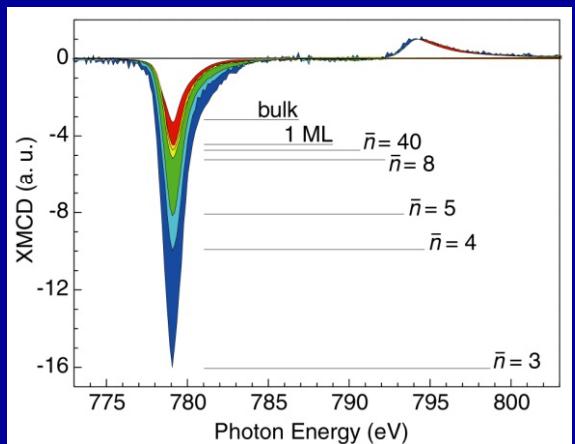


Dimension-dependent magnetic anisotropy

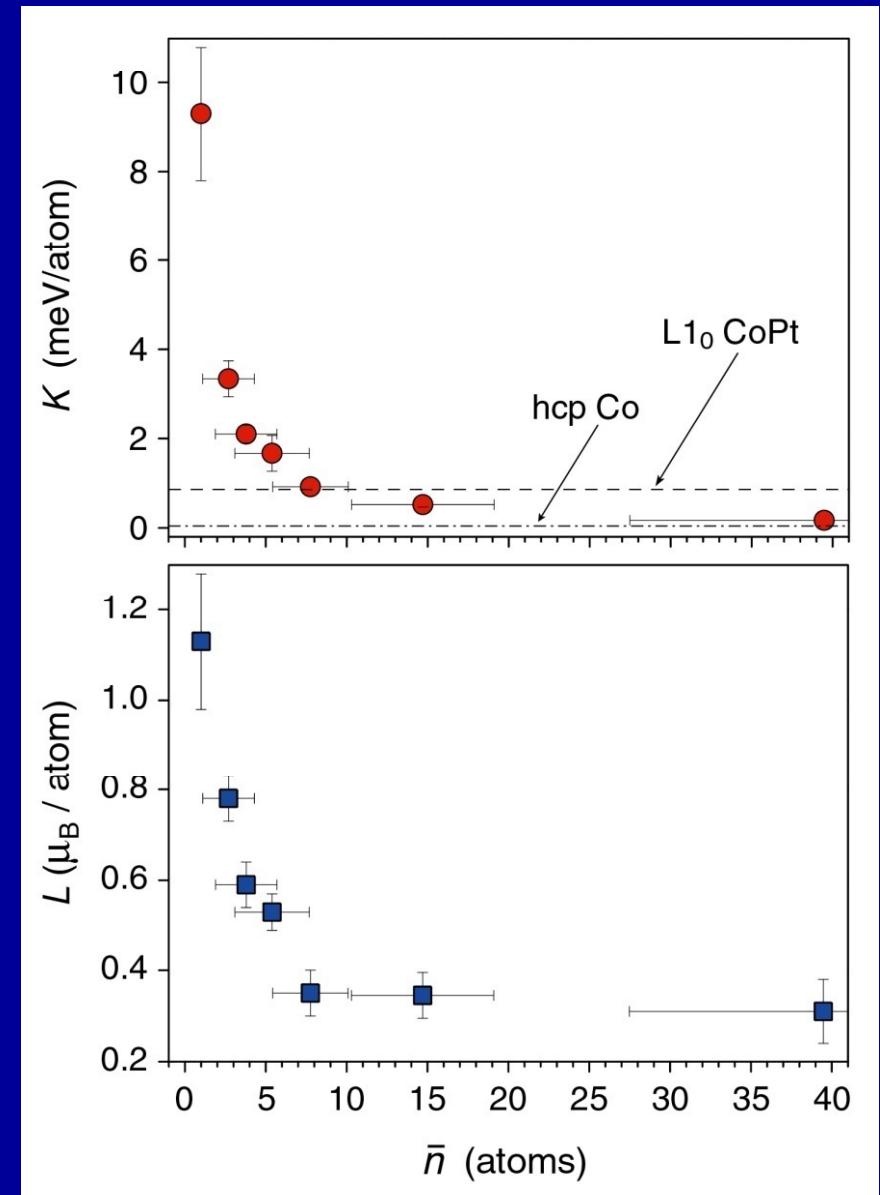
finite-sized particles: the rise and fall of the magnetic anisotropy



P. Gambardella *et al.*, Science 300, 1130 (2003)



COORDINATION EFFECT



ORIGIN OF PERPENDICULAR MAGNETIC ANISOTROPY: ORBITAL MOMENT IN METAL FILMS: INTERFACE EFFECT

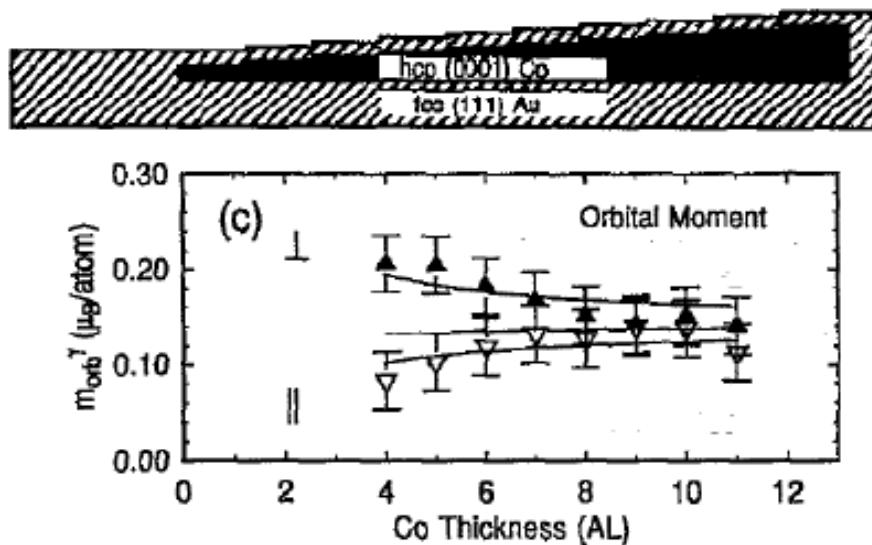
VOLUME 75, NUMBER 20

PHYSICAL REVIEW LETTERS

13 NOVEMBER 1995

Microscopic Origin of Magnetic Anisotropy in Au/Co/Au Probed with X-Ray Magnetic Circular Dichroism

D. Weller,¹ J. Stöhr,¹ R. Nakajima,² A. Carl,^{1,*} M. G. Samant,¹ C. Chappert,³ R. Mégy,³ P. Beauvillain,³ P. Veillet,³ and G. A. Held⁴

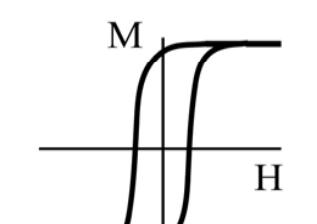
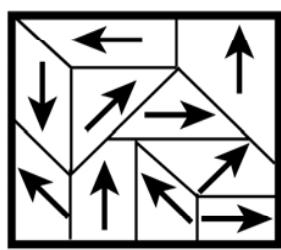


Co film free-standing $W_d^{\parallel} > W_d^{\perp} \Rightarrow m_L^{\perp} < m_L^{\parallel}$

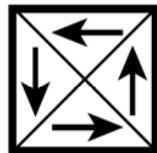
Co film on Au $W_d^{\parallel} < W_d^{\perp} \Rightarrow m_L^{\perp} > m_L^{\parallel}$

balance of the exchange, anisotropy, and magnetostatic energies

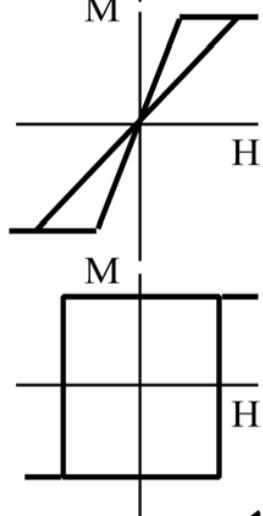
Multi-domain



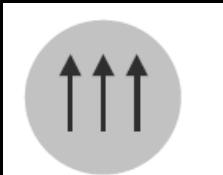
Closure-domain



Single-domain



for spherical single crystal nanoparticles $\rightarrow \Phi_{\text{critical}} \sim 6 \text{ nm (Fe)}; 30 \text{ nm (Co)}; 760 \text{ nm (SmCo}_5\text{)}$



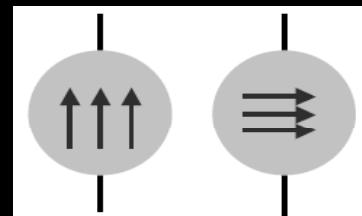
Exchange: $A(d\theta/dz)^2$
short range

Domain wall

$$E = 4 (AK)^{1/2}$$

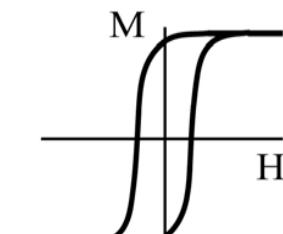
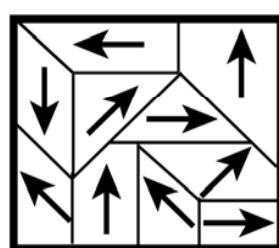
$$\delta = \pi (A/K)^{1/2}$$

Anisotropy: $K \sin^2 \theta$
local

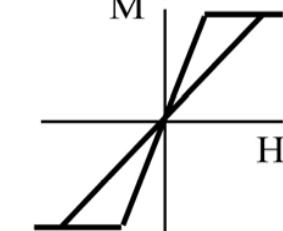
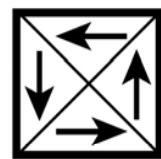


Thermal effects

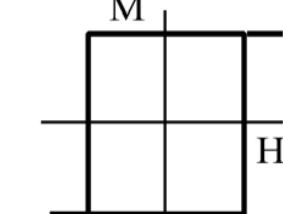
Multi-domain



Closure-domain



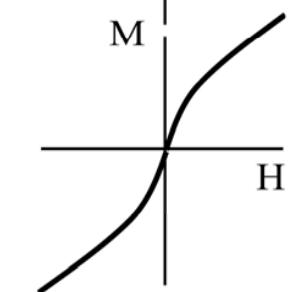
Single-domain



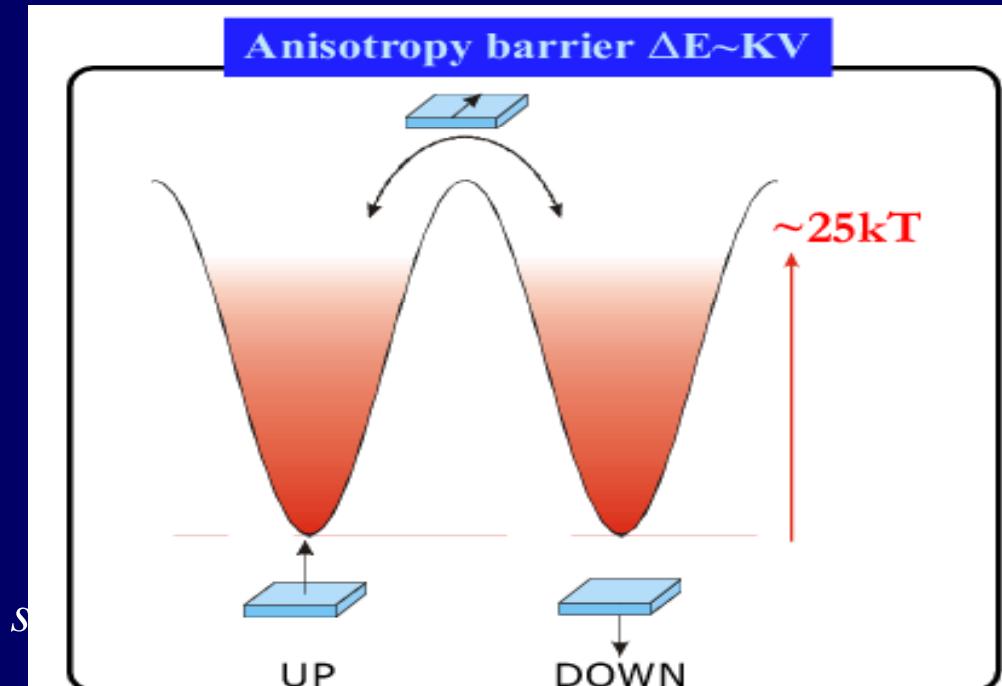
Superparamagnetic



below blocking temperature T_B



Superparamagnetism for $T > T_B = KV/25k_B$



Arrhenius law

L. Néel, Ann. Geophys. 5, 99 (1949)

Brown , PRB 130,1677 (1963)

Phenomenological thermal activation

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right)$$

$\tau_0 \sim 10^{-9} \text{ s}$

Precession

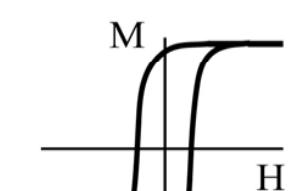
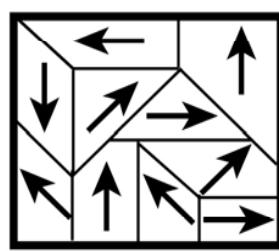
$$\Rightarrow \Delta E = k_B T \ln(\tau / \tau_0) \sim 25 k_B T$$

$\tau \sim 1 \text{ s}$

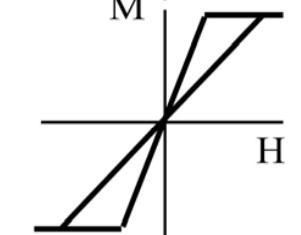
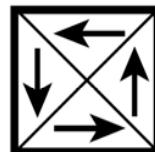
Experiments

J.I. Martín *et al.*, J. Magn. Magn. Mater. **256**, 449 (2003)

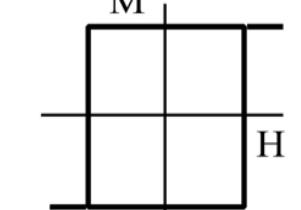
Multi-domain



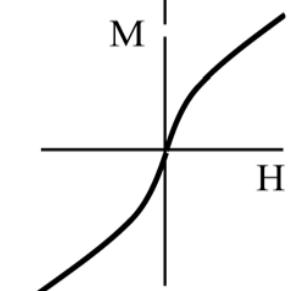
Closure-domain



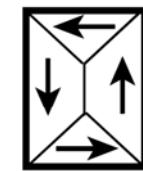
Single-domain



Superparamagnetic



ASPECT RATIO EFFECTS

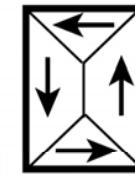


Closure-domain

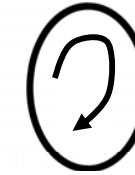


Single-domain

SHAPE EFFECTS



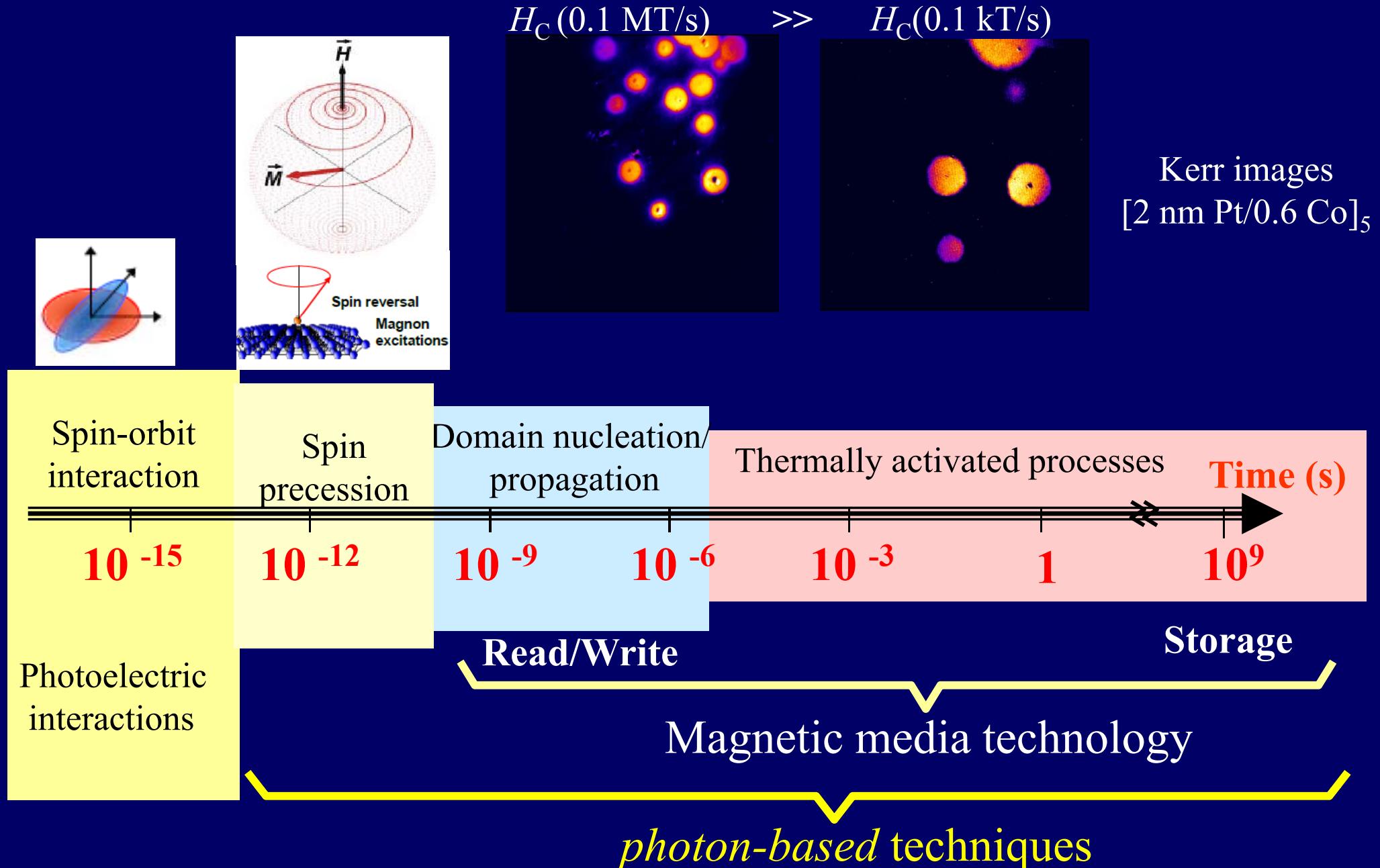
Closure-domain



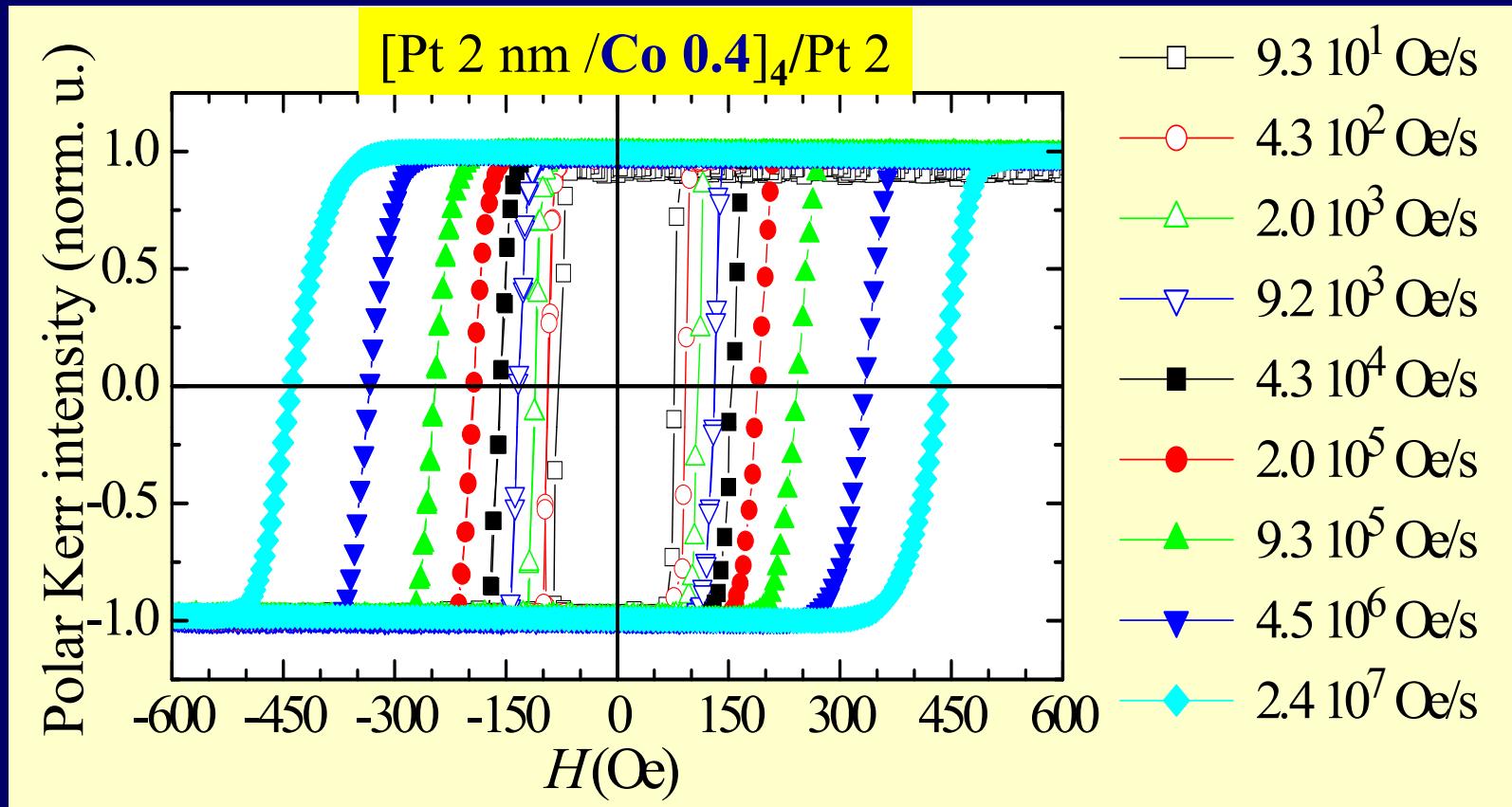
Vortex



TIMESCALES IN MAGNETIC MATERIALS



Camarero *et al*, Phys. Rev. B Rapid Comm. **69**, 180402 (2004); *ibid* **71**, 100402 (2005)



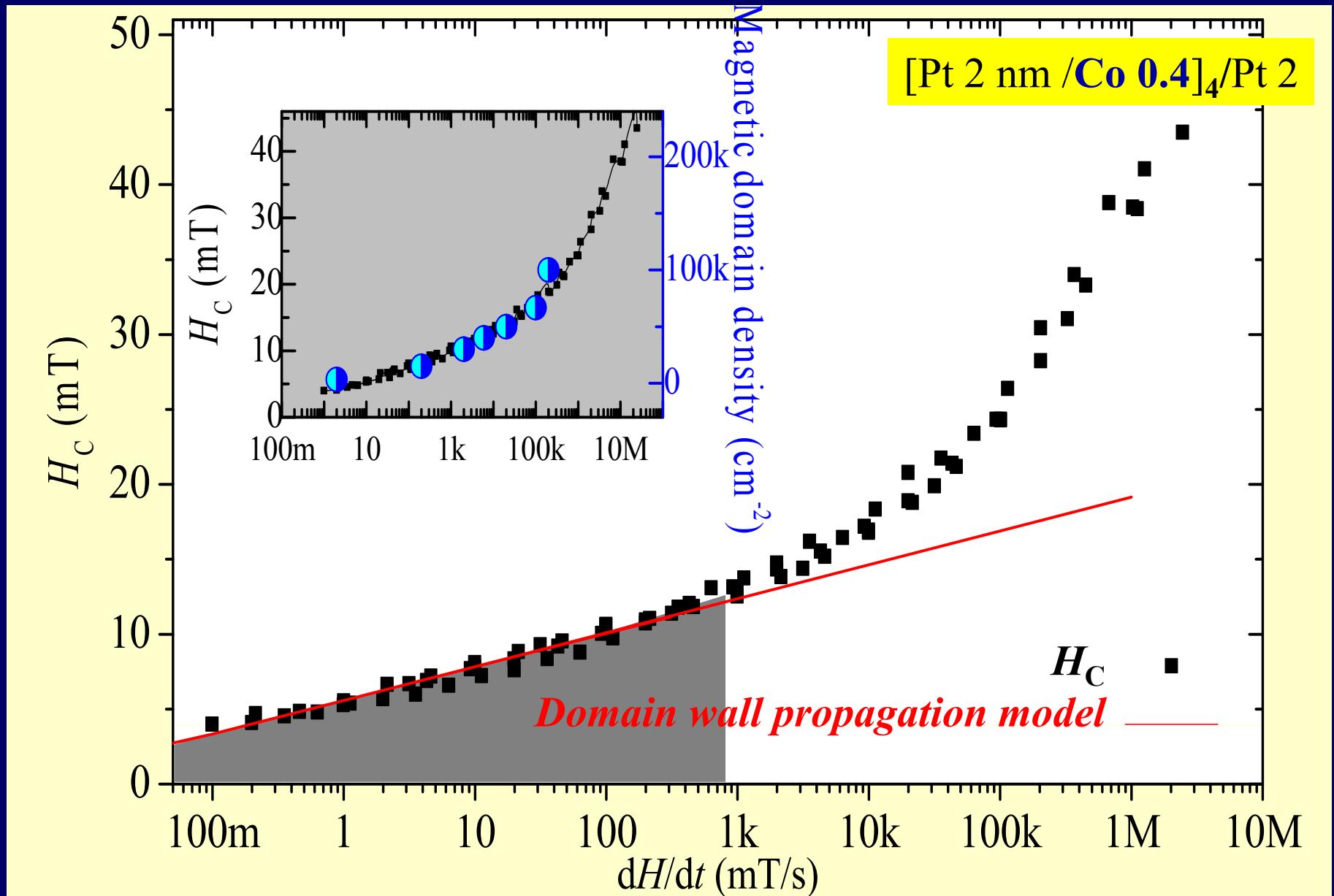
The evolution of both (i) shape and (ii) coercivity H_C with dH/dt stresses a *transition between propagation to nucleation regime increasing dH/dt*

(i) square (**lower dH/dt**) \Leftrightarrow governed by **DW propagation** process;
 smooth (**higher dH/dt**) \Leftrightarrow **domain nucleation** process dominates.

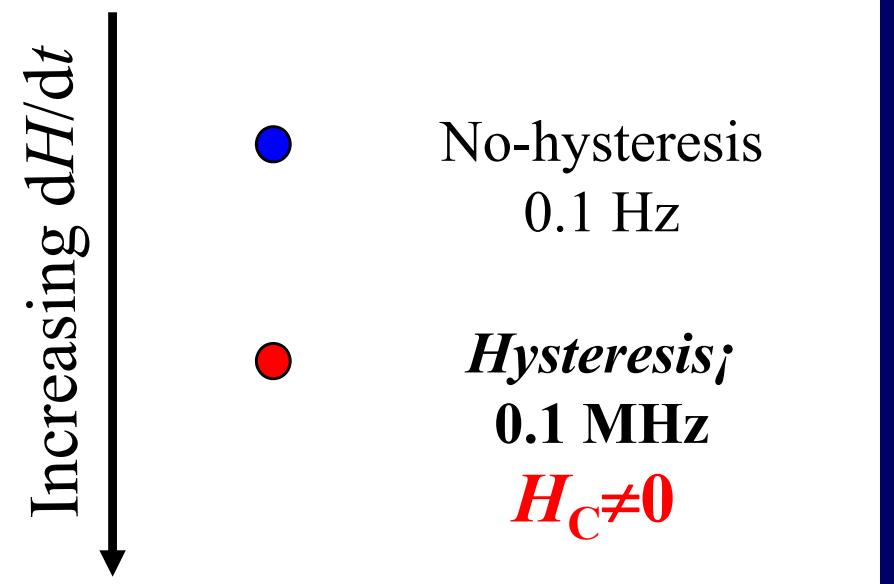
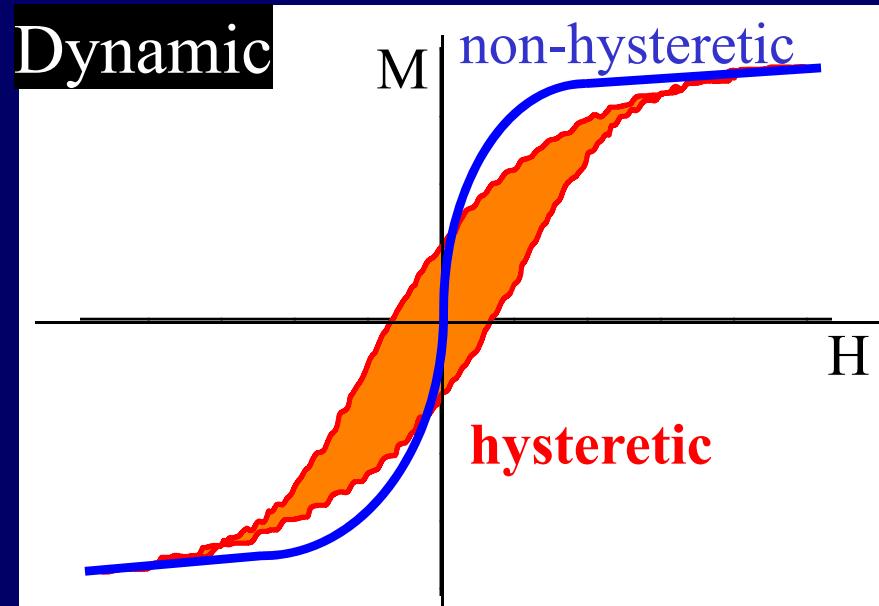
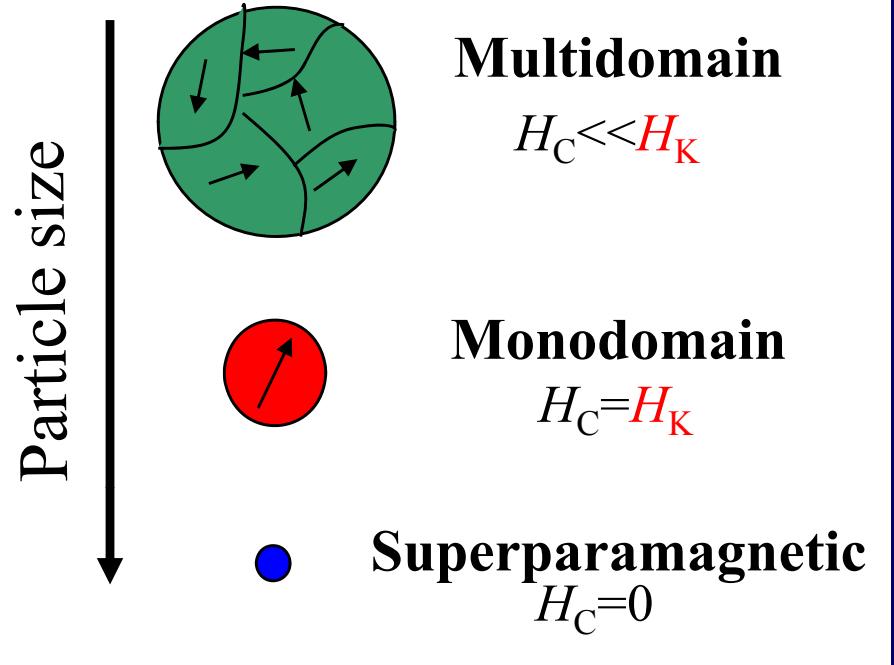
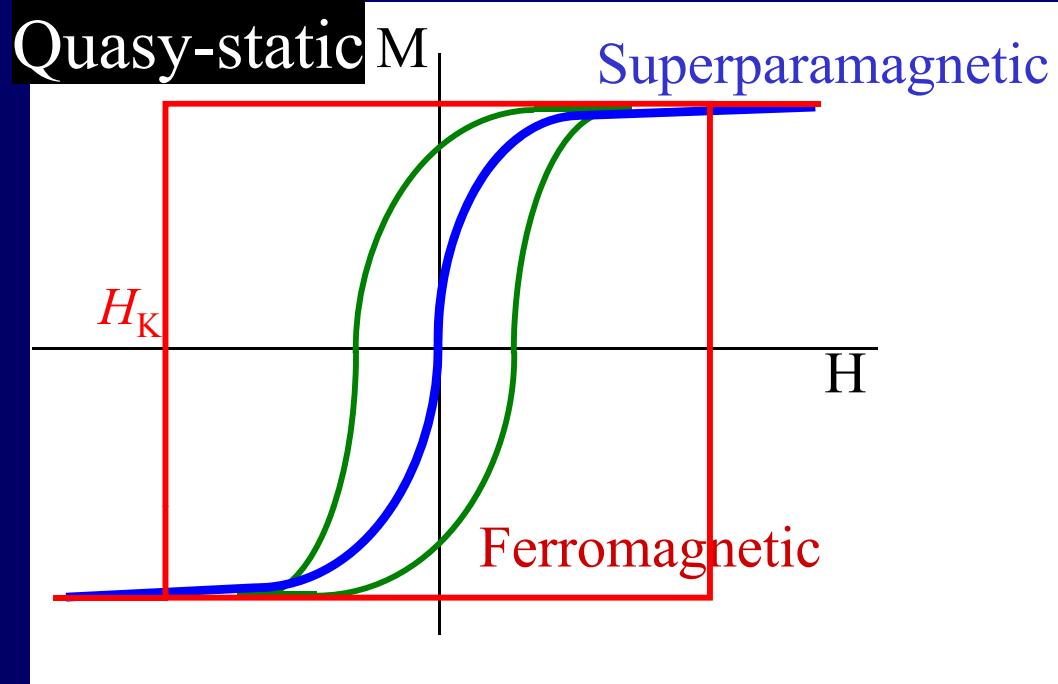
(ii) H_C increases as dH/dt increases

MAGNETIZATION REVERSAL: dynamics vs quasi-static

Camarero *et al*, Phys. Rev. B Brief Report **64**, 172402 (2004); J. Appl. Phys. **89**, 6585 (2001)



SIZE + THERMAL EFFECTS: *SUPERPARAMAGNETIC limit*



METALLIC SPACER

- Ferromagnetic direct coupling

PINHOLES



NON METALLIC SPACER

- Ferromagnetic direct coupling.

METALLIC SPACER

- Ferromagnetic direct coupling

PINHOLES



- Oscillatory exchange coupling with spacer thickness. (~ several nm)

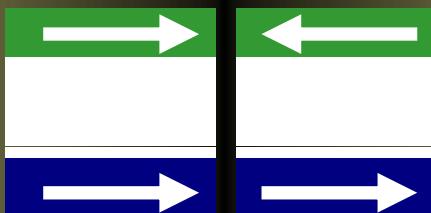
Fe/Cr/Fe: Grunberg *et al*, PRL **57**, 2442 (86)

Co/Cu/Co: Cebollada *et al*, PRB **39**, 9726 (89)
Parkin *et al*, PRL **66**, 2152 (91)

- Interactions propagated by s-p e-.
- Topology of the spacer metal Fermi surface (RKKY-type coupling).

Bruno and Chappert, PRL **67**, 1602 (91).

SPIN POLARIZED CURRENT



NON METALLIC SPACER

- Ferromagnetic direct coupling.

- Monotonic nonoscillatory variation with spacer thickness.

Slonczewski, PRB **39**, 6995 (1989);

• Fe/Si/Fe: Toscano *et al* JMMM **114**, L6 (92)
Fullerton *et al* JMMM **117**, L301 (92)

- Fe/MgO/Fe/Co, AF coupling bellow 1nm
Faure-Vincent *et al*, PRL **89** 107206 (02)
- Spin asymmetry of the reflections at the interfaces. Bruno, PRB **49**, 13 231 (94).

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- Ferromagnetic direct coupling

pinholes



- Oscillatory exchange coupling with spacer thickness. (~ several nm)

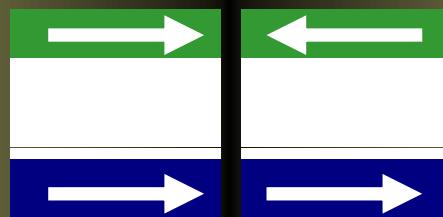
Fe/Cr/Fe: Grunberg *et al*, PRL **57**, 2442 (86)

Co/Cu/Co: Cebollada *et al*, PRB **39**, 9726 (89)
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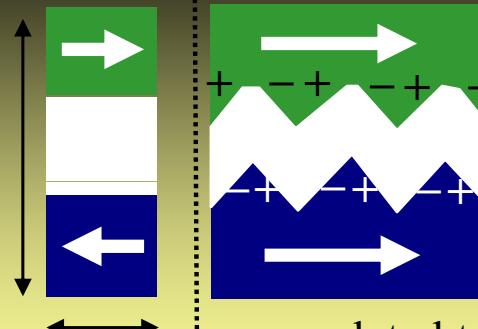
“stray-field” coupling

Moon *et al*, APL **64**, 3690 (99)

Negative interaction between magnetic charges created by the reduced in-plane dimensions of the structure.

- ⇒ uncompensated magnetic poles at the edges
- ⇒ antiferromagnetic coupling

MAGNETOSTATIC



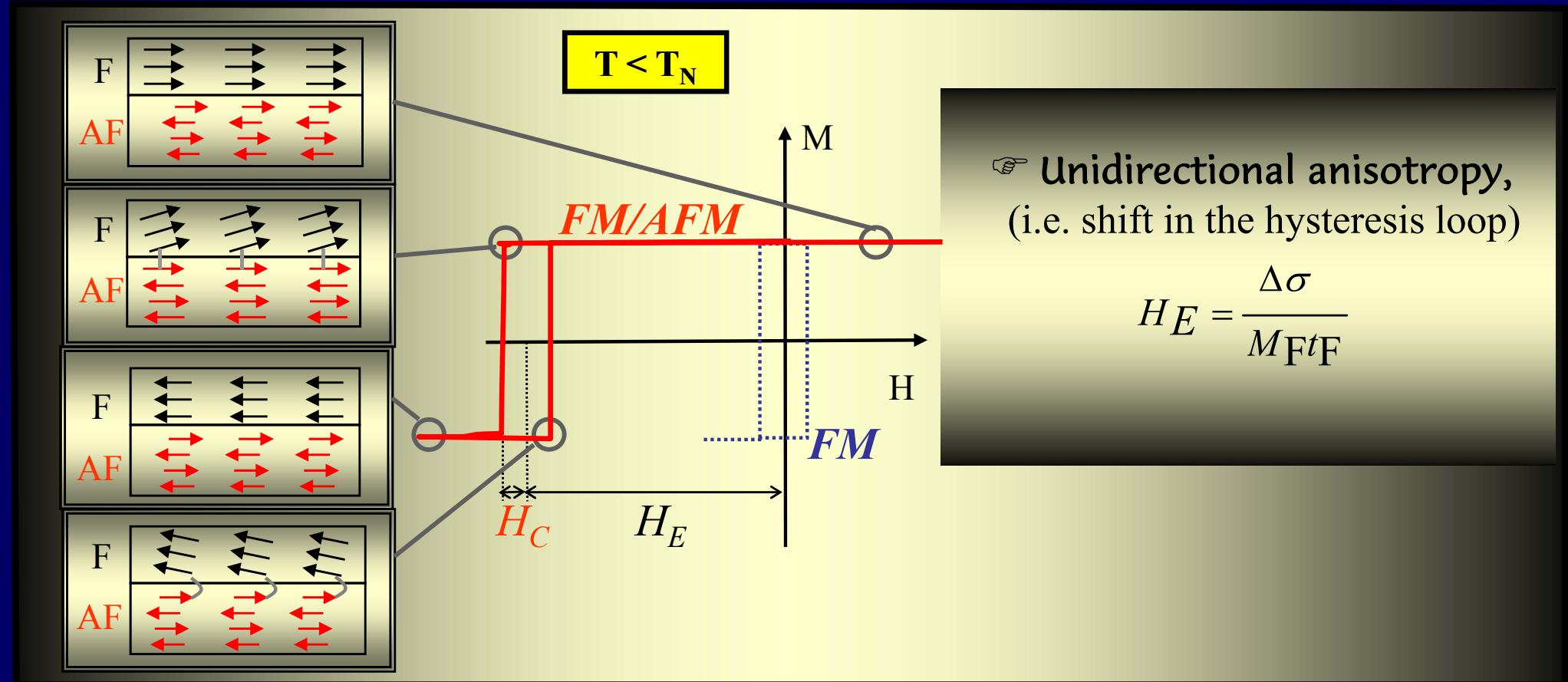
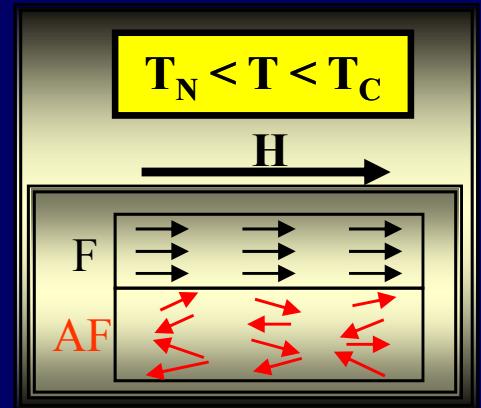
Néel Orange-peel coupling

L. Néel, Comptes Rendus **255**, 1676 (62)

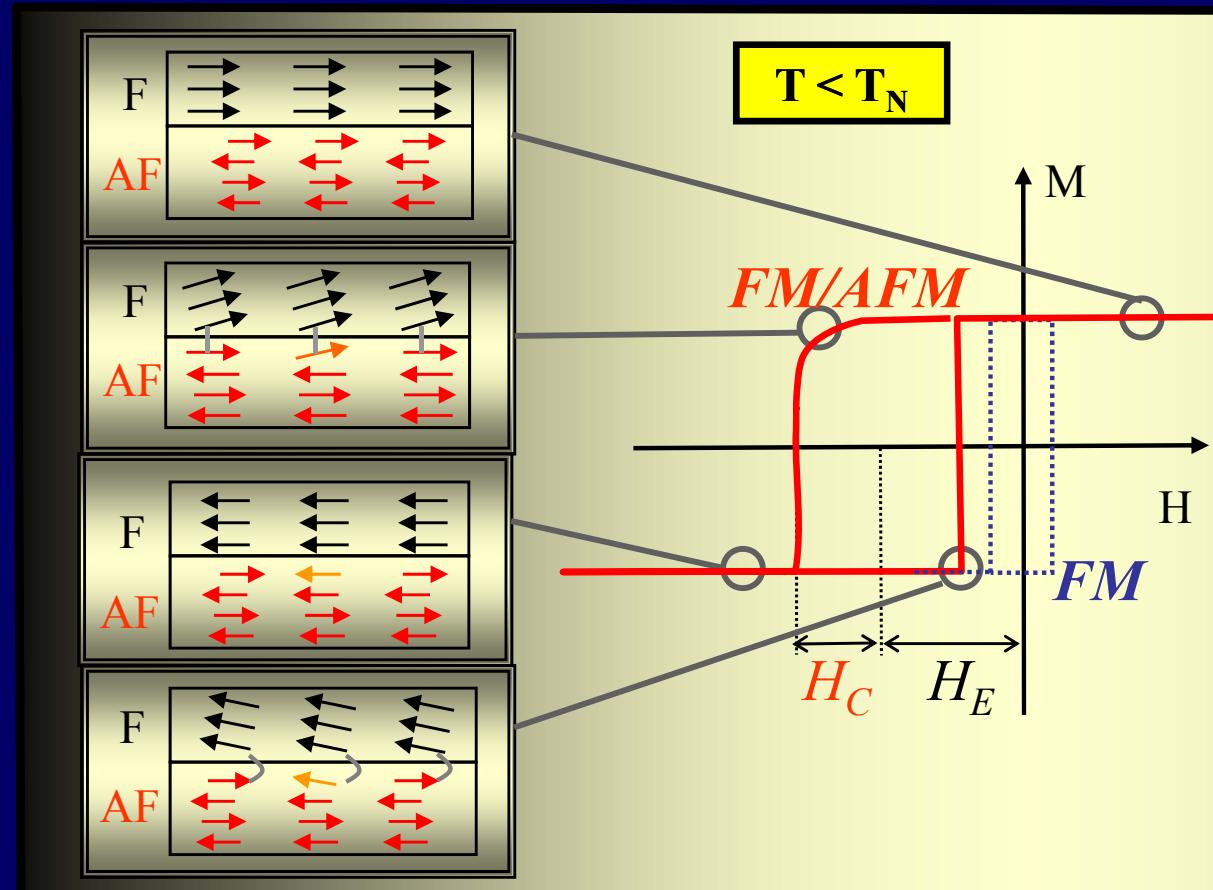
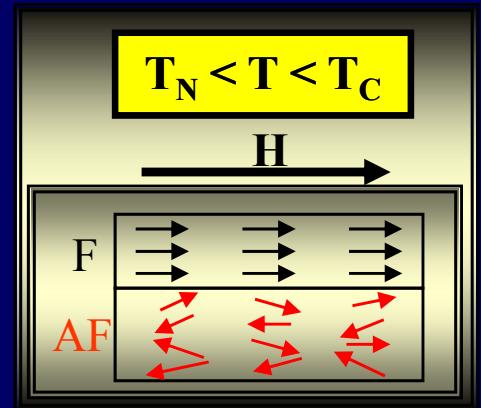
$$H_N = \frac{J}{M_{\text{soft}} t_{\text{soft}}} = \frac{(\pi A)^2}{t_{\text{soft}} \sqrt{2\lambda}} M_{\text{hard}} \exp(-2\pi\sqrt{2}t_{\text{NM}}/\lambda)$$

- correlated topological roughness at F/NM interfaces
- ⇒ magnetic charges on topological bumps.
- ⇒ ferromagnetic coupling

1956 "A new type of magnetic anisotropy has been discovered which is best described as an exchange anisotropy. This anisotropy is the result of an interaction between an antiferromagnetic material and a ferromagnetic material"
 W.H. Meiklejohn and C.P. Bean, Phys Rev B **102** (1956), 413.



1956 “A new type of magnetic anisotropy has been discovered which is best described as an exchange anisotropy. This anisotropy is the result of an interaction between an antiferromagnetic material and a ferromagnetic material”
 W.H. Meiklejohn and C.P. Bean, Phys Rev B **102** (1956), 413.



Main experimental evidences

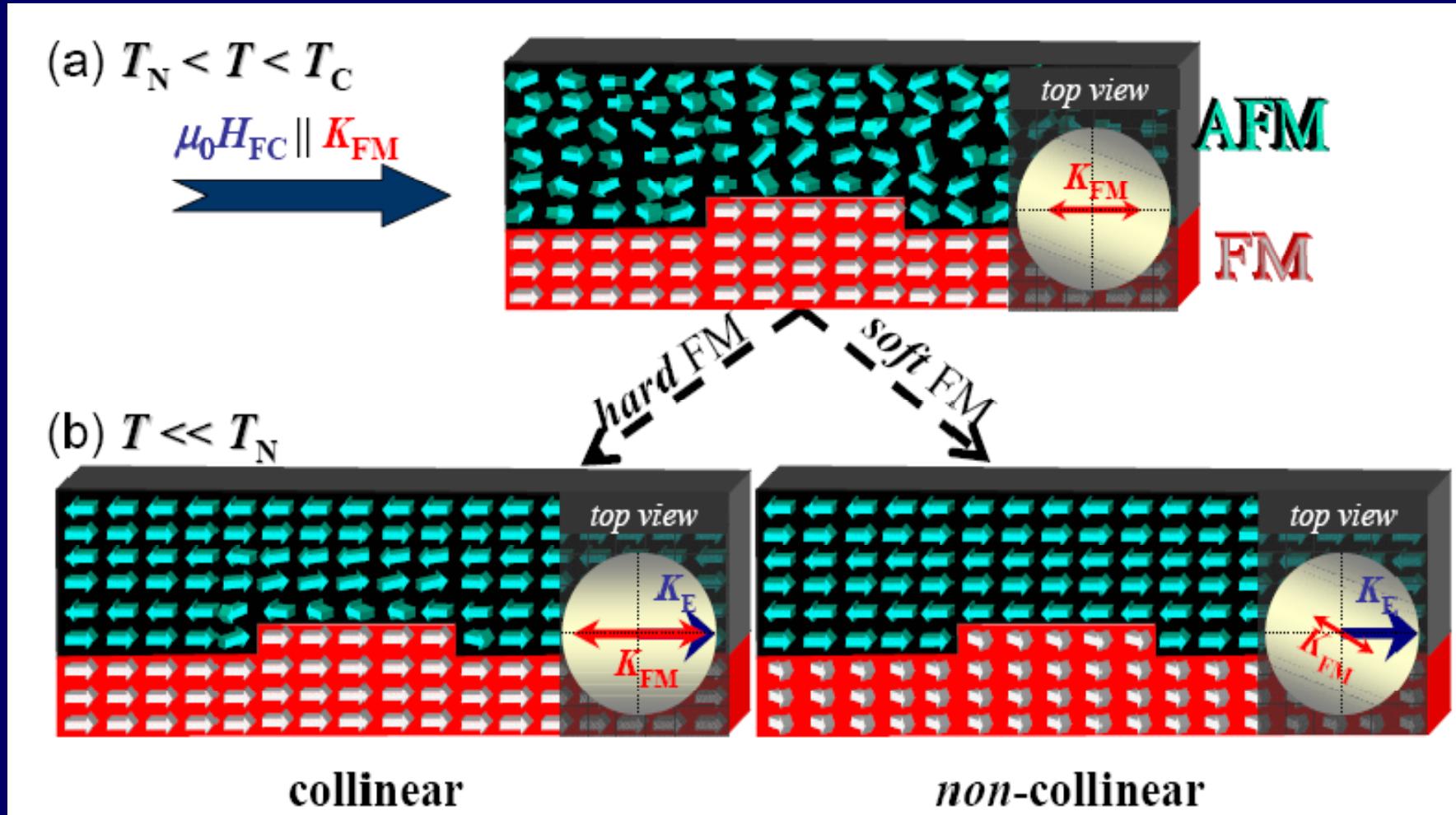
- ☞ Unidirectional anisotropy, $\Delta\sigma$
- $$H_E = 0.01 \times \frac{\Delta\sigma}{M_F t_F}$$
- ☞ Enhanced coercivity:

$$H_C(\text{FM/AFM}) > H_C(\text{FM})$$
- ☞ Magnetization reversal asymmetry
- ☞ also in perpendicular anisotropy systems

INTERFACIAL SPIN FRUSTRATION EFFECTS IN FM/AFM SYSTEMS



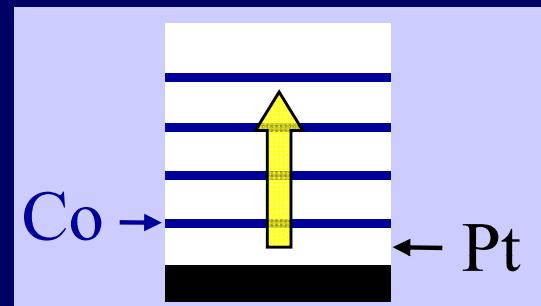
Jimenez *et al.* Phys. Rev. B **80**, 014415 (2009), J. Appl. Phys. **109**, 07D730 (2011)



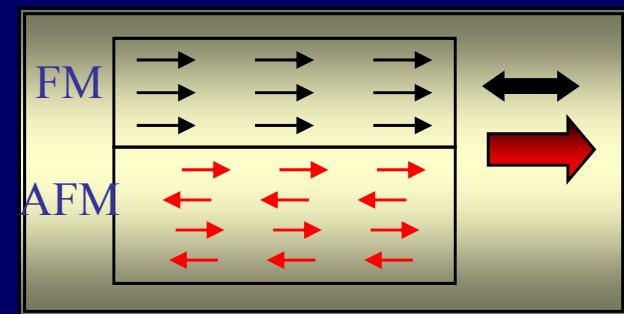
Inevitable atomically rough FM/AFM interfaces induces interfacial spin frustration
→ **magnetic reorientation in soft FM systems**

ELECTRONIC INTERACTIONS

perpendicular (hybridisation)

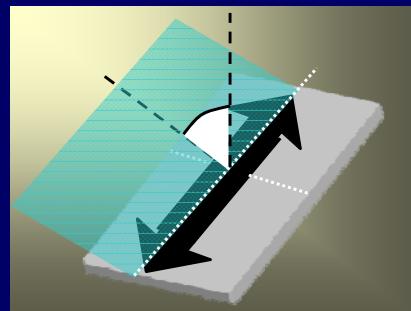


unidirectional (direct exchange)

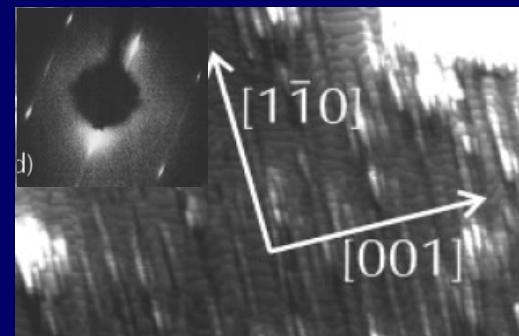


MAGNETOSTATIC INTERACTIONS

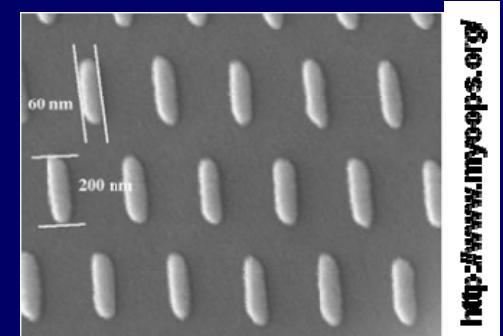
angle of deposition



uniaxial
anisotropic stress, diffusion

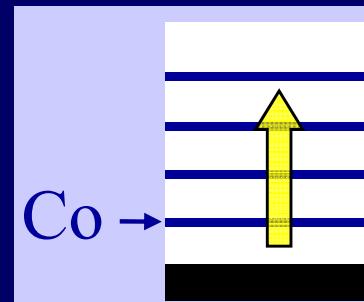


shape,...

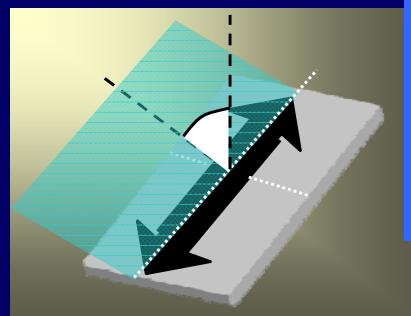


<http://www.magnetism.es>

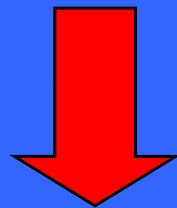
perpendicular (hybrid)



angle of deposition



new (additional) magnetic anisotropy not
only alters the anisotropy axes

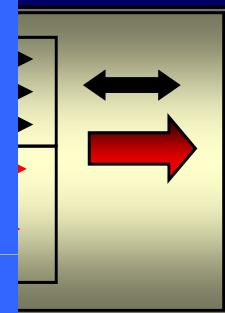


New magnetic behavior

coercivity,
remanence,
magnetic stability,

magnetization reversal processes

shape exchange)

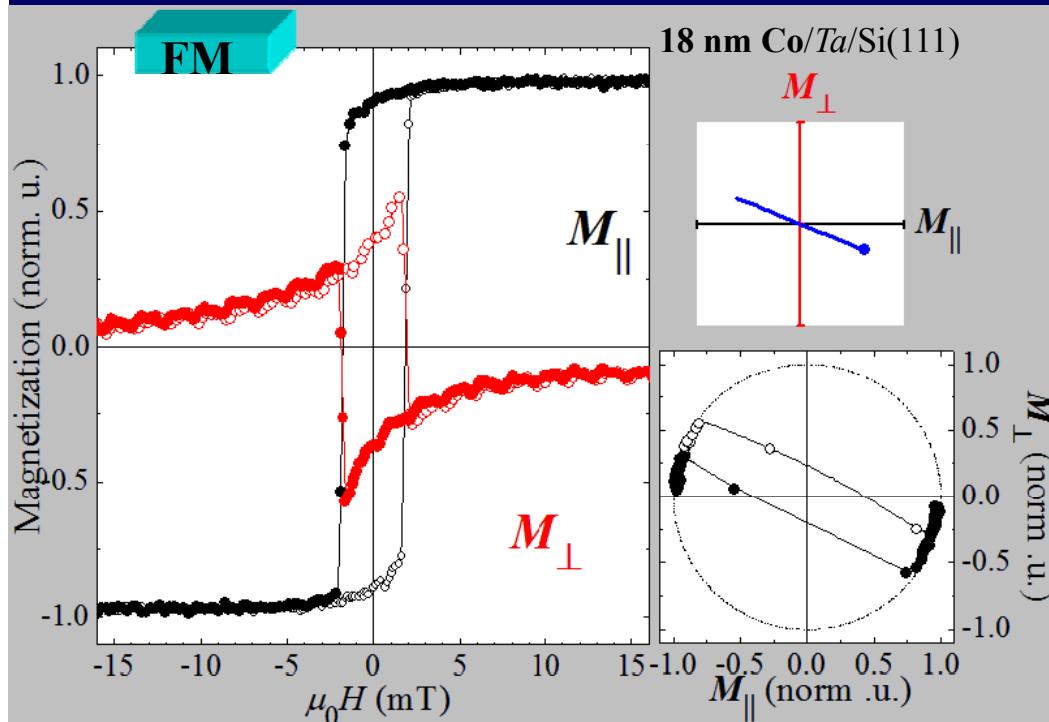


shape,...

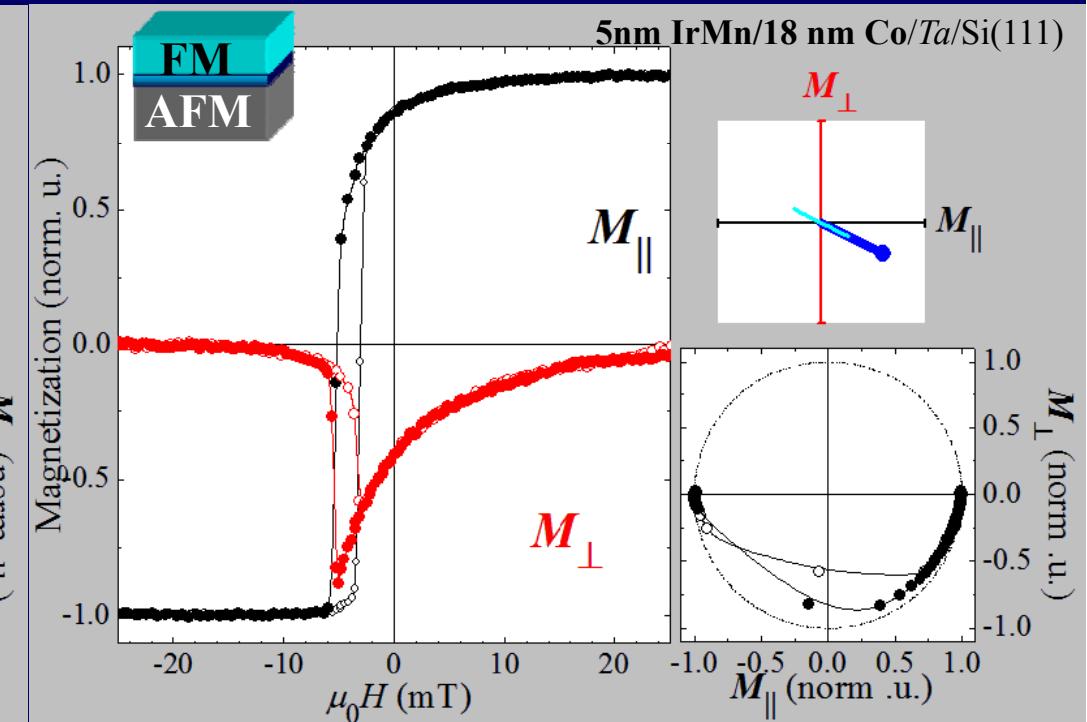


The (simultaneous) acquisition of the two in-plane magnetization components M_{\parallel} and M_{\perp} provide direct information about the magnetization reversal processes

UNIAXIAL



UNIAXIAL+UNIDIRECTIONAL

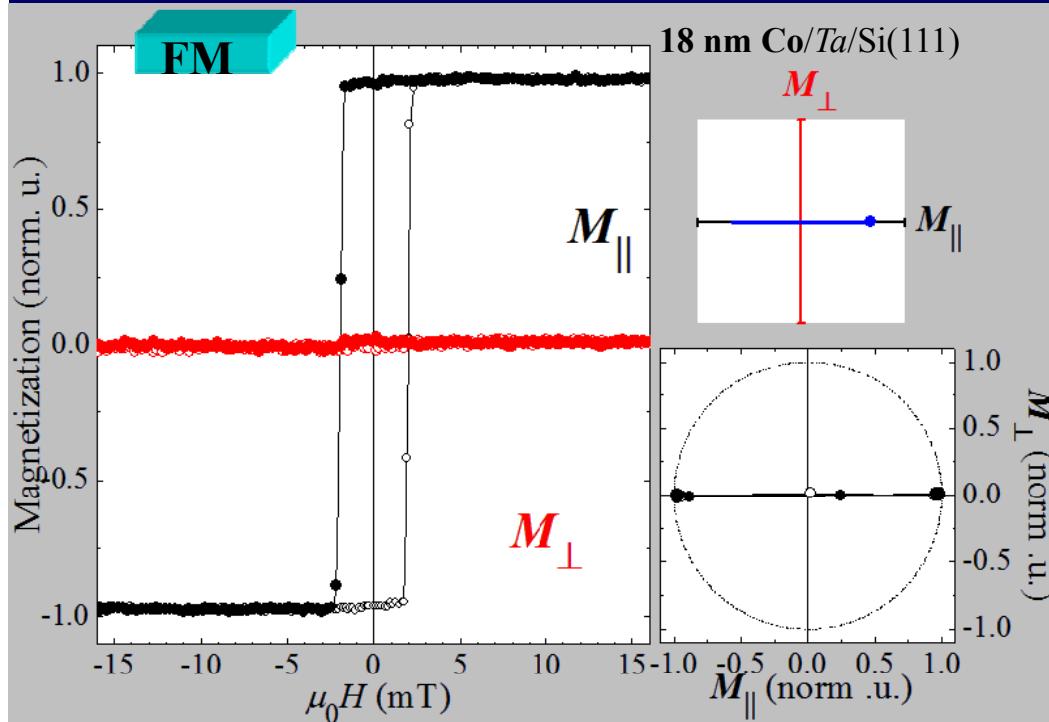


Sharp irreversible & smooth reversible transitions can be observed in both M_{\parallel} and M_{\perp}

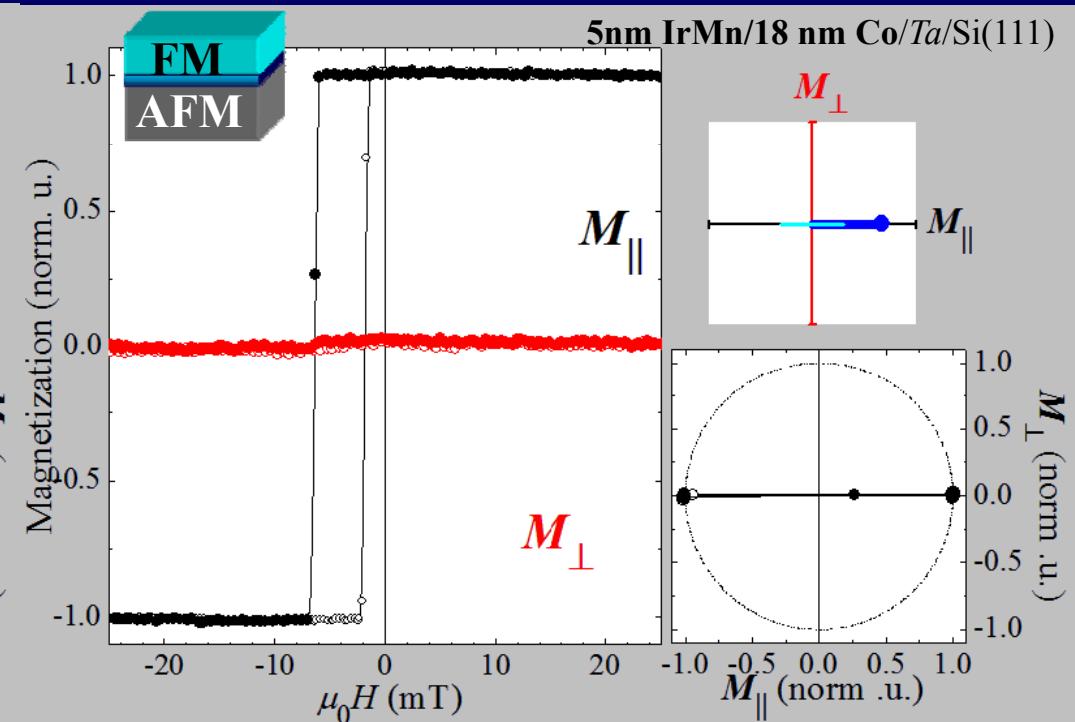
The vectorial plot, M_{\perp} vs. M_{\parallel} , reflects the direction of magnetization

The magnetization reversal is determined by the anisotropy of the system

UNIAXIAL



UNIAXIAL+UNIDIRECTIONAL



Close to the e.a.: Sharp irreversible transition dominated → magnetization reversal is governed by *nucleation of magnetic domains and further domain wall propagation*

Close to the h.a.: Smooth reversible transitions dominated → magnetization reversal is governed by in-plane magnetization rotation processes

The asymmetric reversal phenomena is intrinsic to exchange-biased FM/AFM systems

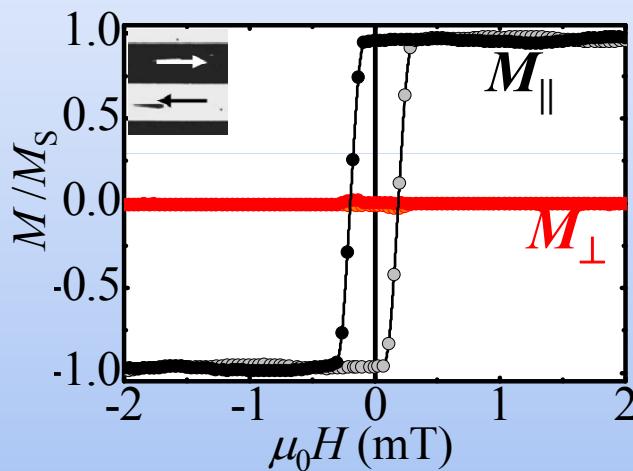


Magnetization reversal of model systems I: easy axis

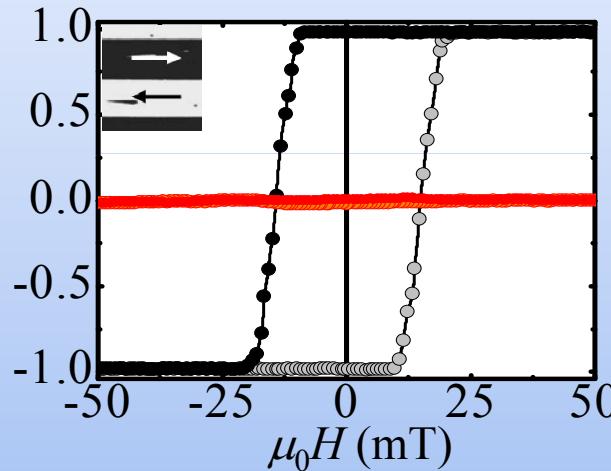
$\theta_H=0^\circ$



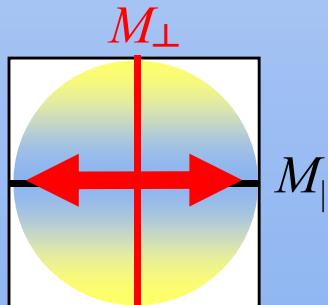
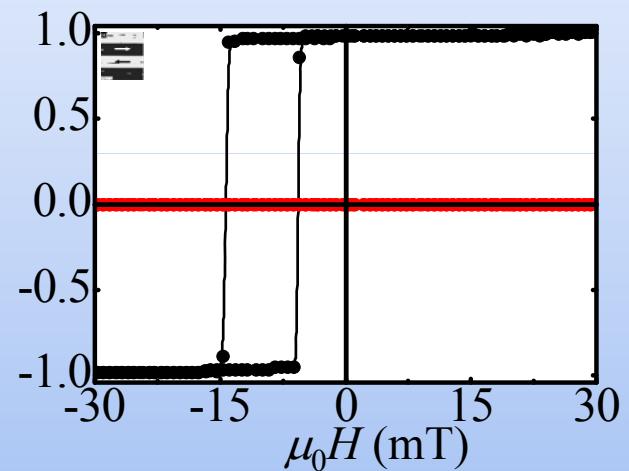
Uniaxial anisotropy



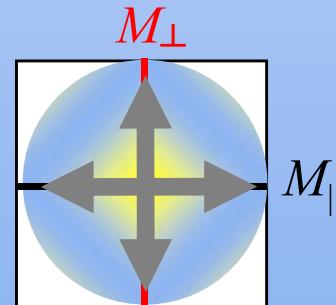
Biaxial anisotropy



*Uniaxial+Unidirectional
collinear configuration*



Jimenez et al., to be published



- Phys. Rev. B **80**, 014415 (2009)
Appl. Phys. Lett. **95**, 122508 (2009)
J. Appl. Phys. **109**, 07D730 (2011)



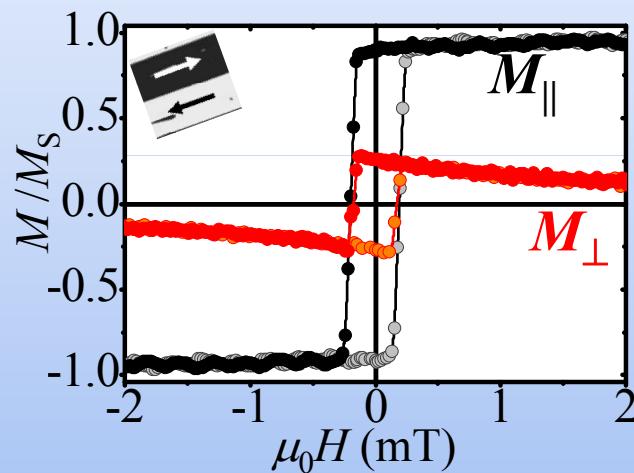
Magnetization reversal of model systems II:

$\theta_H = -18^\circ$

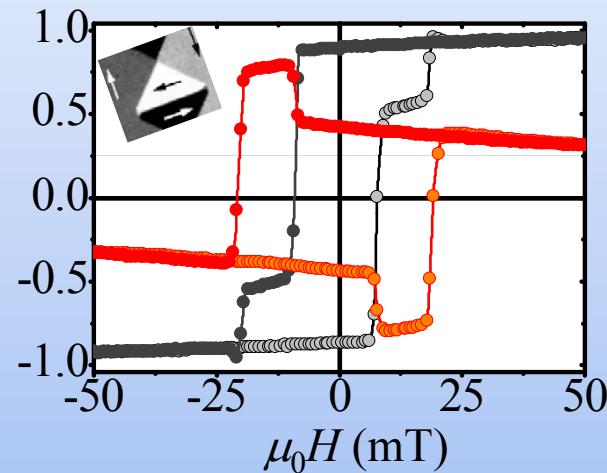
FACULTAD DE CIENCIAS
UNIVERSIDAD AUTÓNOMA DE MADRID



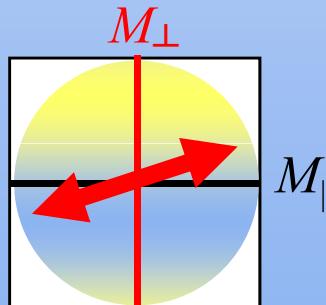
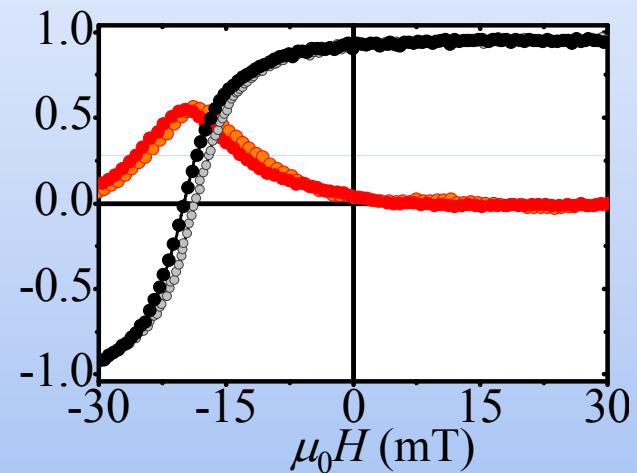
Uniaxial anisotropy



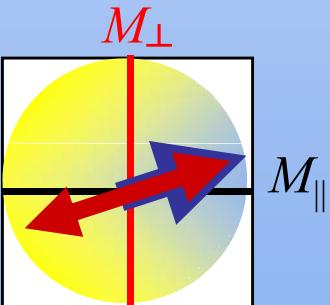
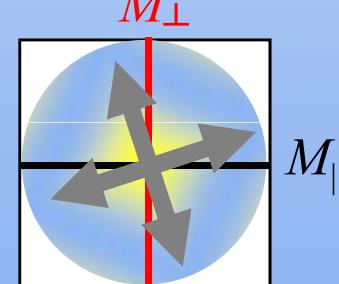
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Jimenez et al., to be published



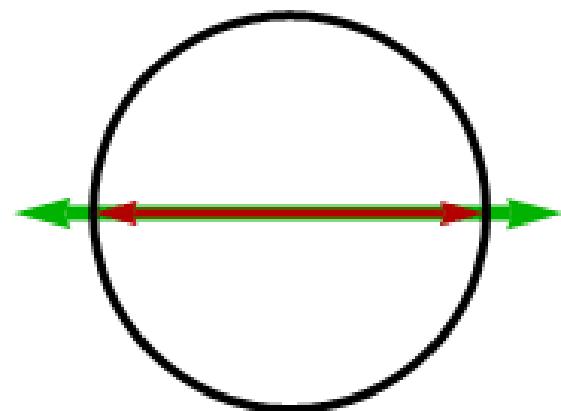
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J. Appl. Phys. **109**, 07D730 (2011)



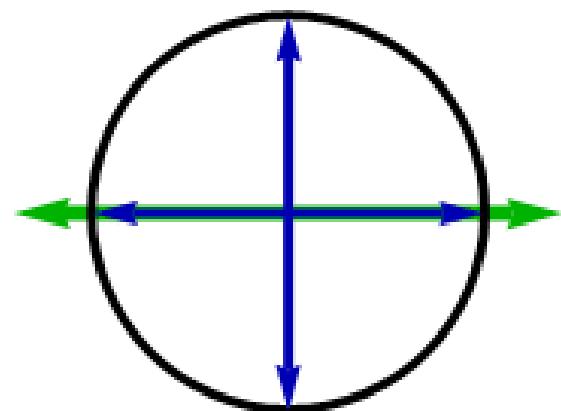
Magnetization reversal of model systems: angular dependence



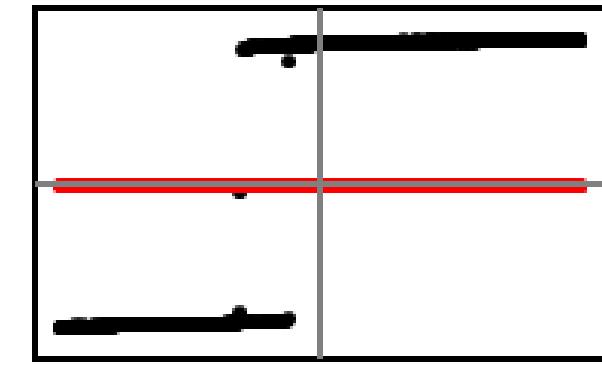
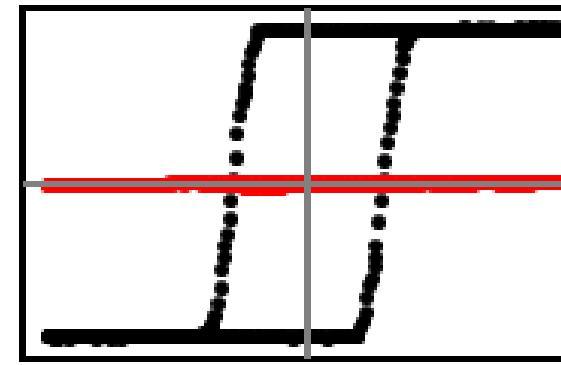
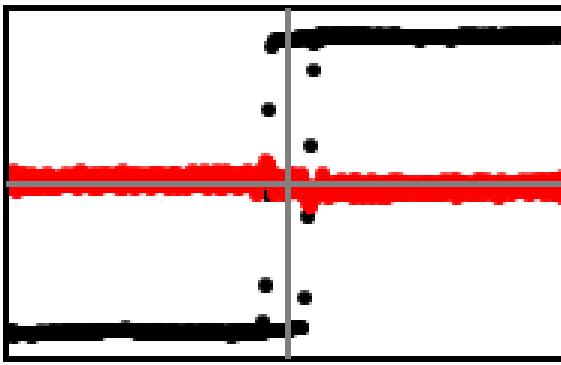
Uniaxial anisotropy



Biaxial anisotropy



Uniaxial+Unidirectional





Magnetization reversal of model systems: angular dependence



Uniaxial anisotropy

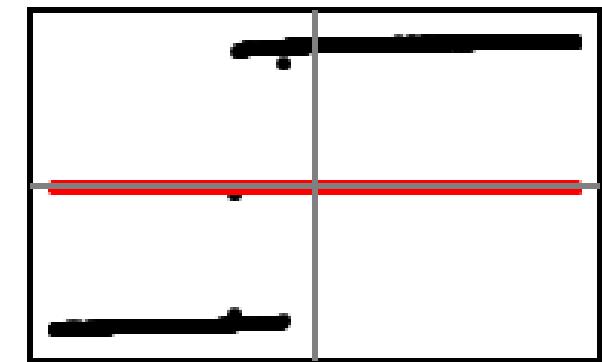
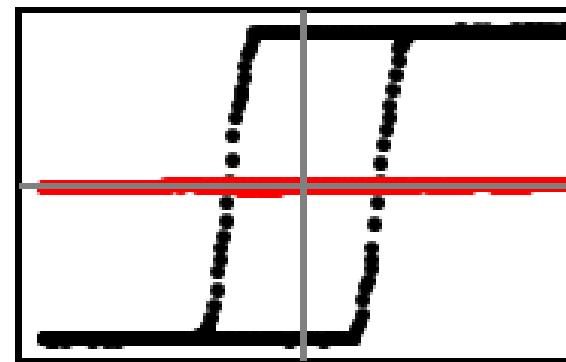
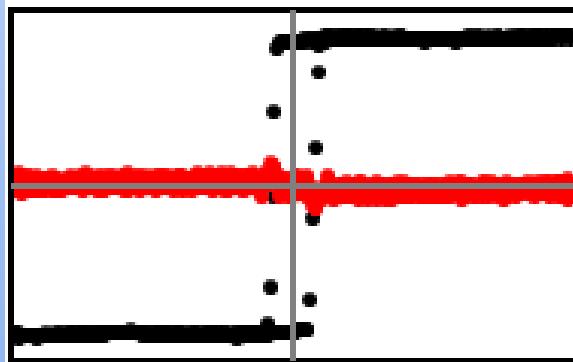


Biaxial anisotropy



Uniaxial+Unidirectional

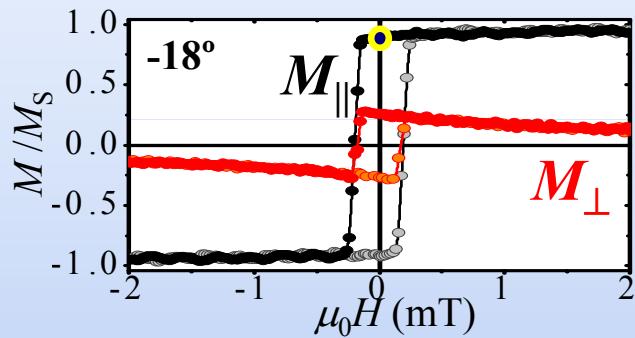
Angular-dependent magnetic studies are required in order to understand the properties of magnetic nanostructures.



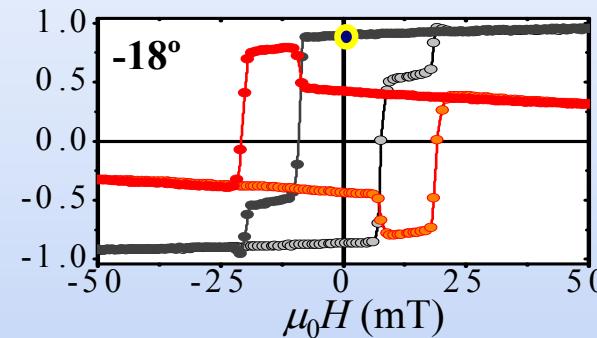


The symmetry is found in the magnetic behavior, $M_{\parallel,R}$ vs. θ_H

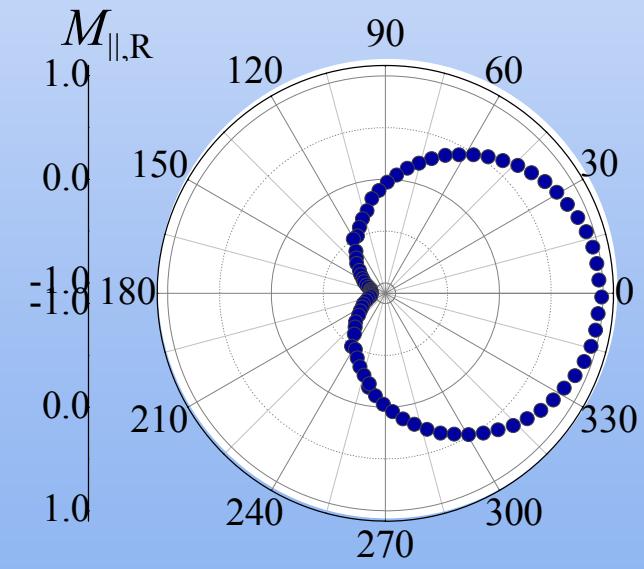
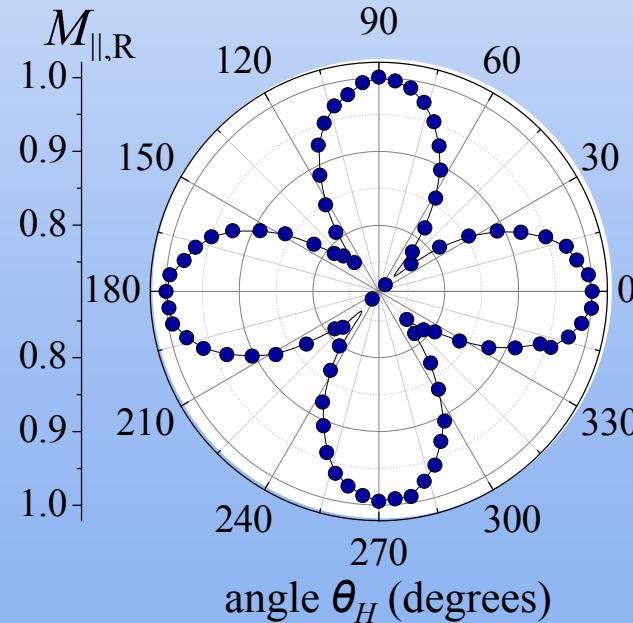
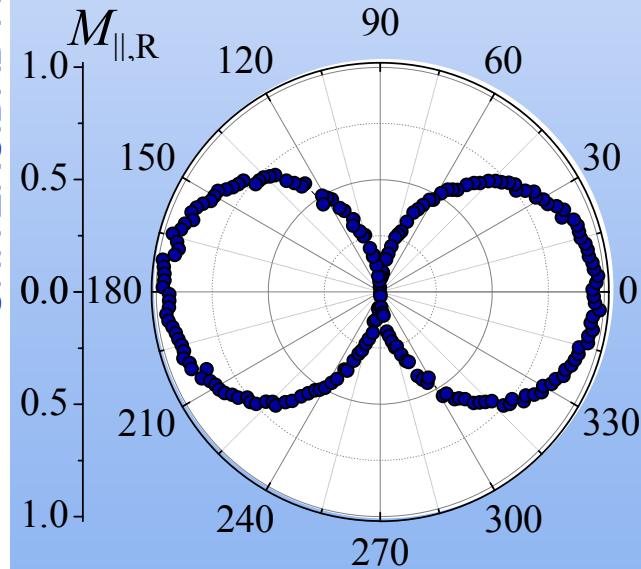
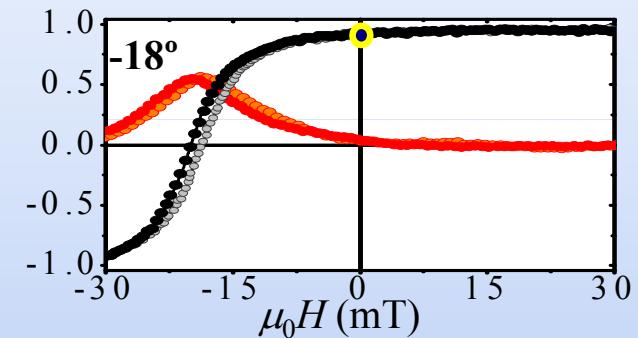
Uniaxial anisotropy



Biaxial anisotropy

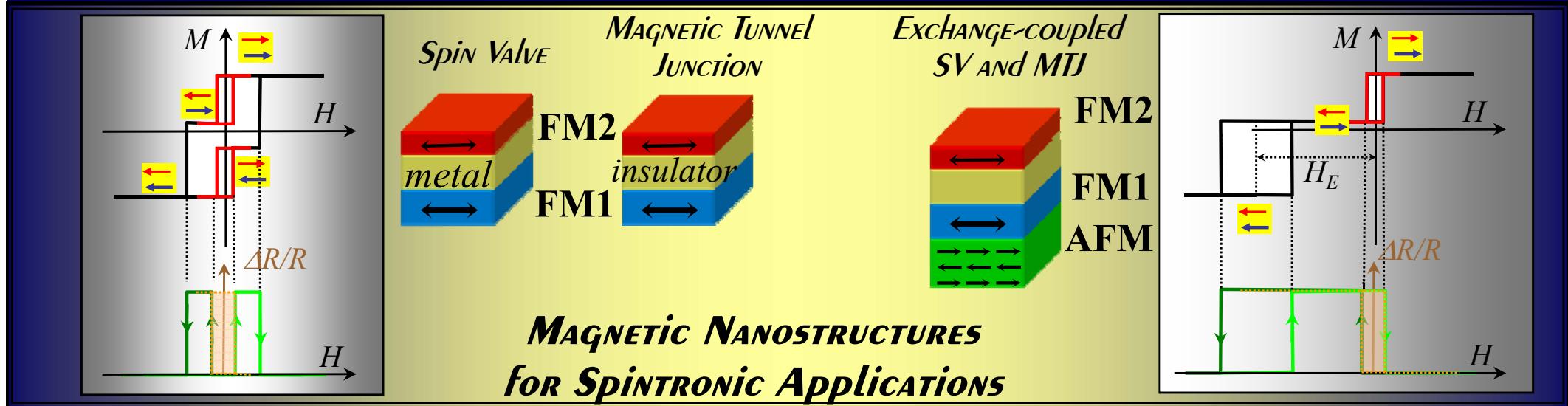


Uniaxial+Unidirectional



SpINTRONIC

Up to now, >20000 experimental works dealt with GMR phenomena of complex multilayered magnetic nanostructures with potential spintronic applications...



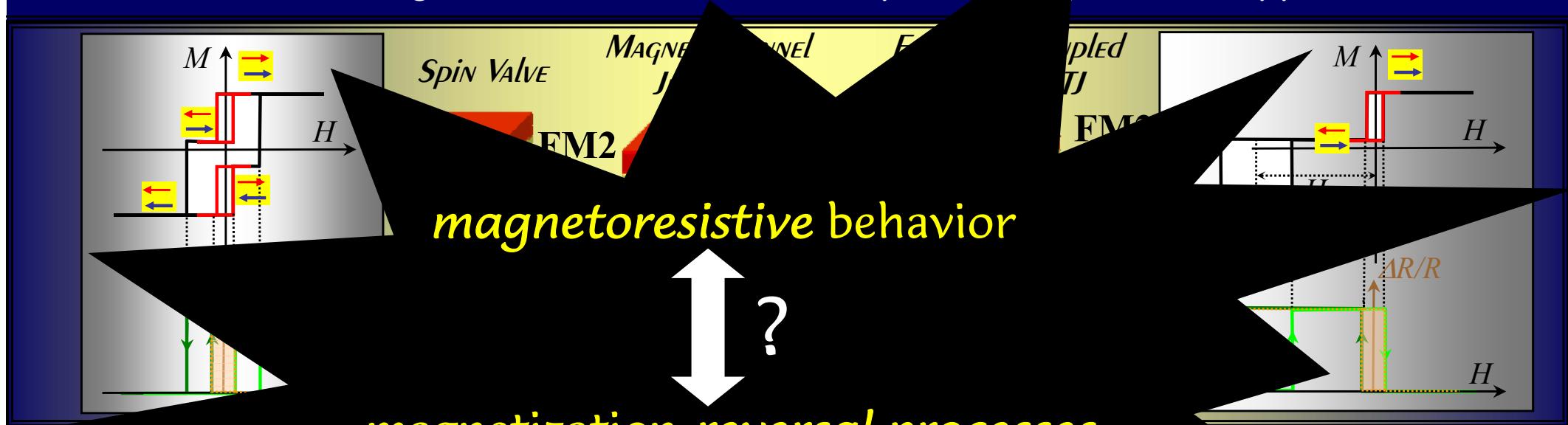
But, reported experiments rely on:

- magnetization or MR hysteresis **curves** acquired independently,
- measurements performed at a **fixed angle** of the applied field (~e.a.),
- **only the parallel component** of the magnetization curve is recorded.

In addition, widely different hysteretic magnetoresistance behaviors, including maximum MR values and curve shapes, are unexpectedly found for multilayers with similar structures.

ORIGIN OF MAGNETORESISTANCE

Up to now, >20000 experimental works dealt with GMR phenomena of complex multilayered magnetic nanostructures with potential spintronic applications...



But,
- mag
- ma

- only the pa

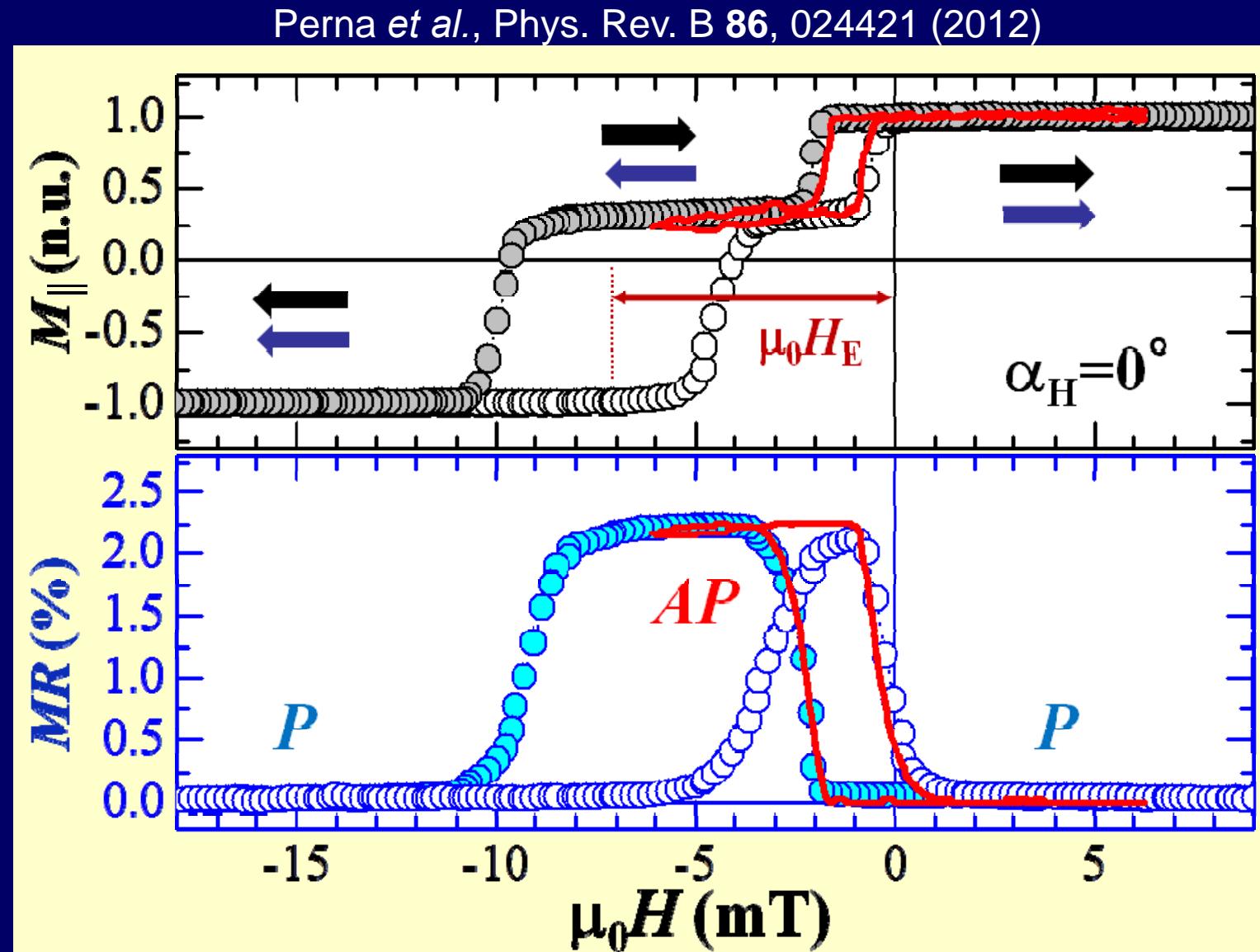
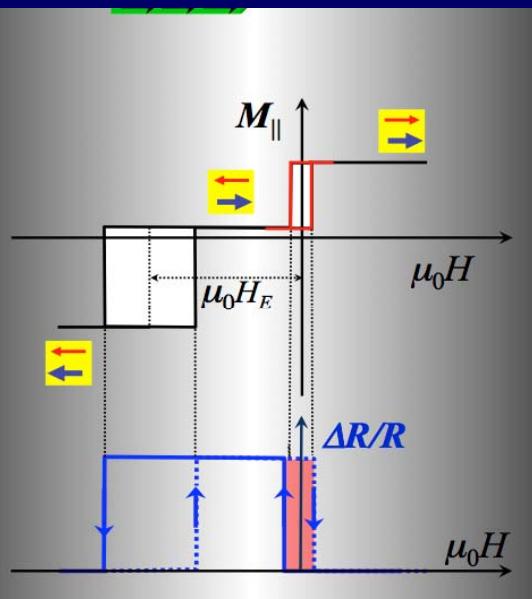
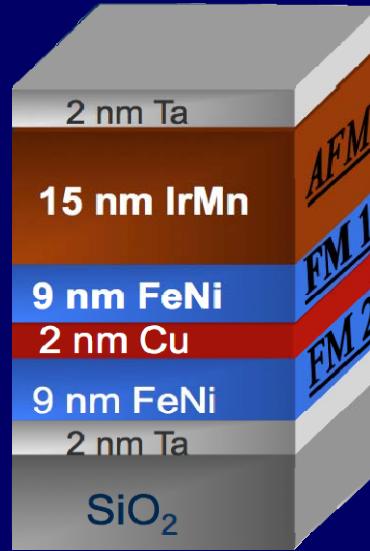
Phys. Rev. B **86**, 024421 (2012)

... independently,
in the presence of the applied field (~e.a.),
only the parallel component of the magnetization curve is recorded.

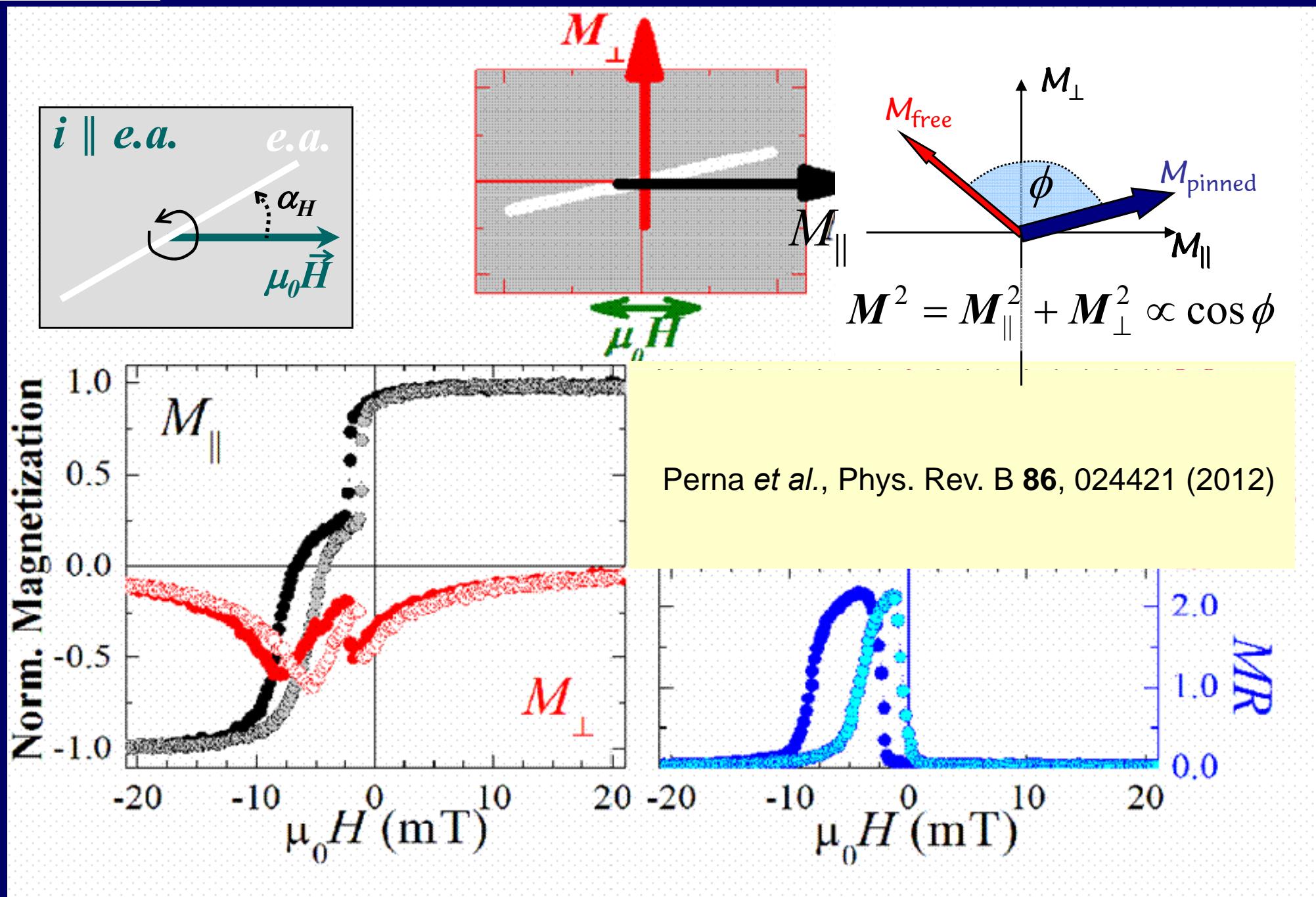
In addition, widely different hysteretic magnetoresistance behaviors, including maximum MR values and curve shapes, are unexpectedly found for multilayers with similar structures.

SIMULTANEOUS V-KERR + MR: SPIN-VALVE

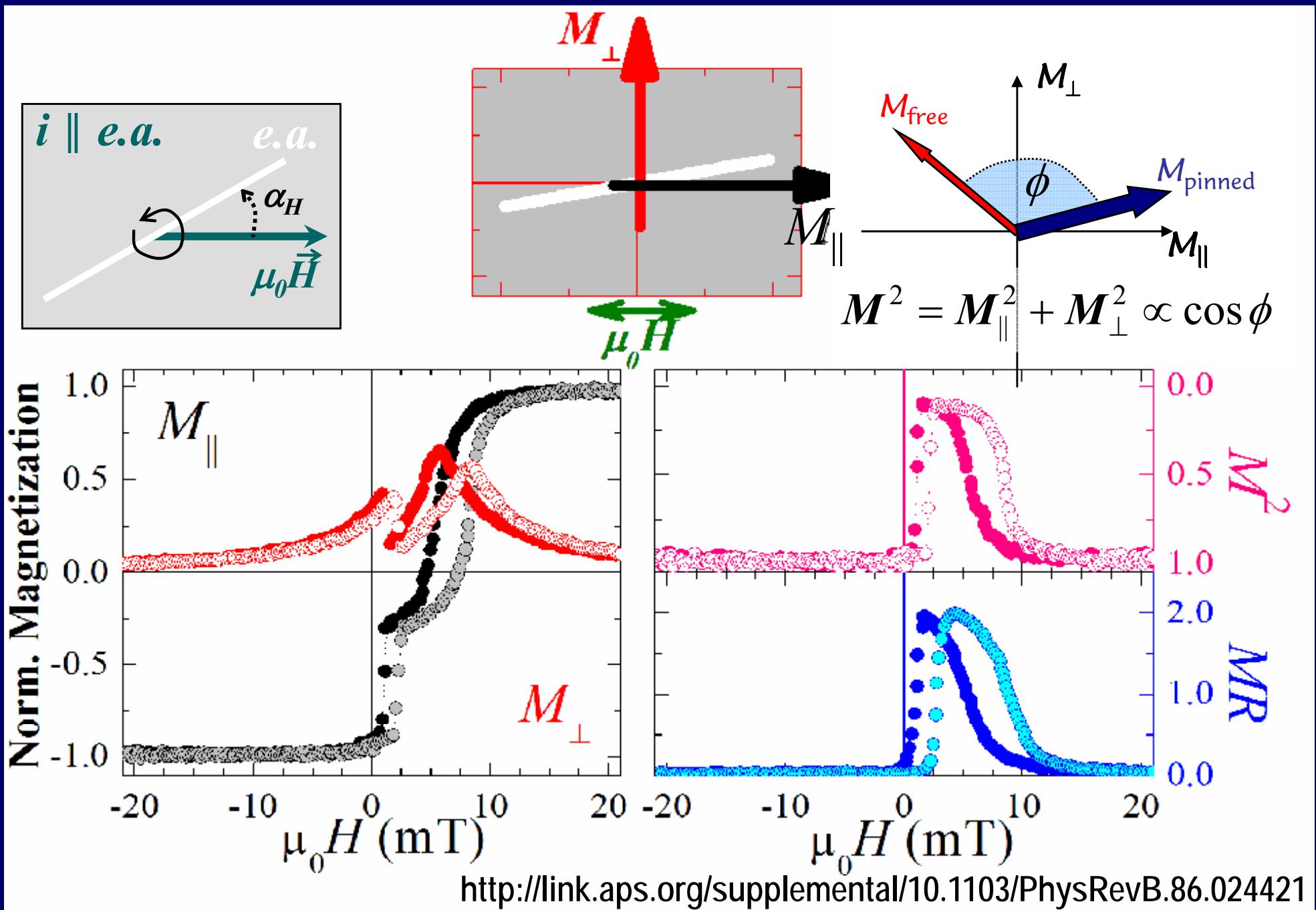
Sample fabrication: M. Muñoz, J. L. Prieto, M. Romera, J. Akermann @



COMPLETE ANGULAR study



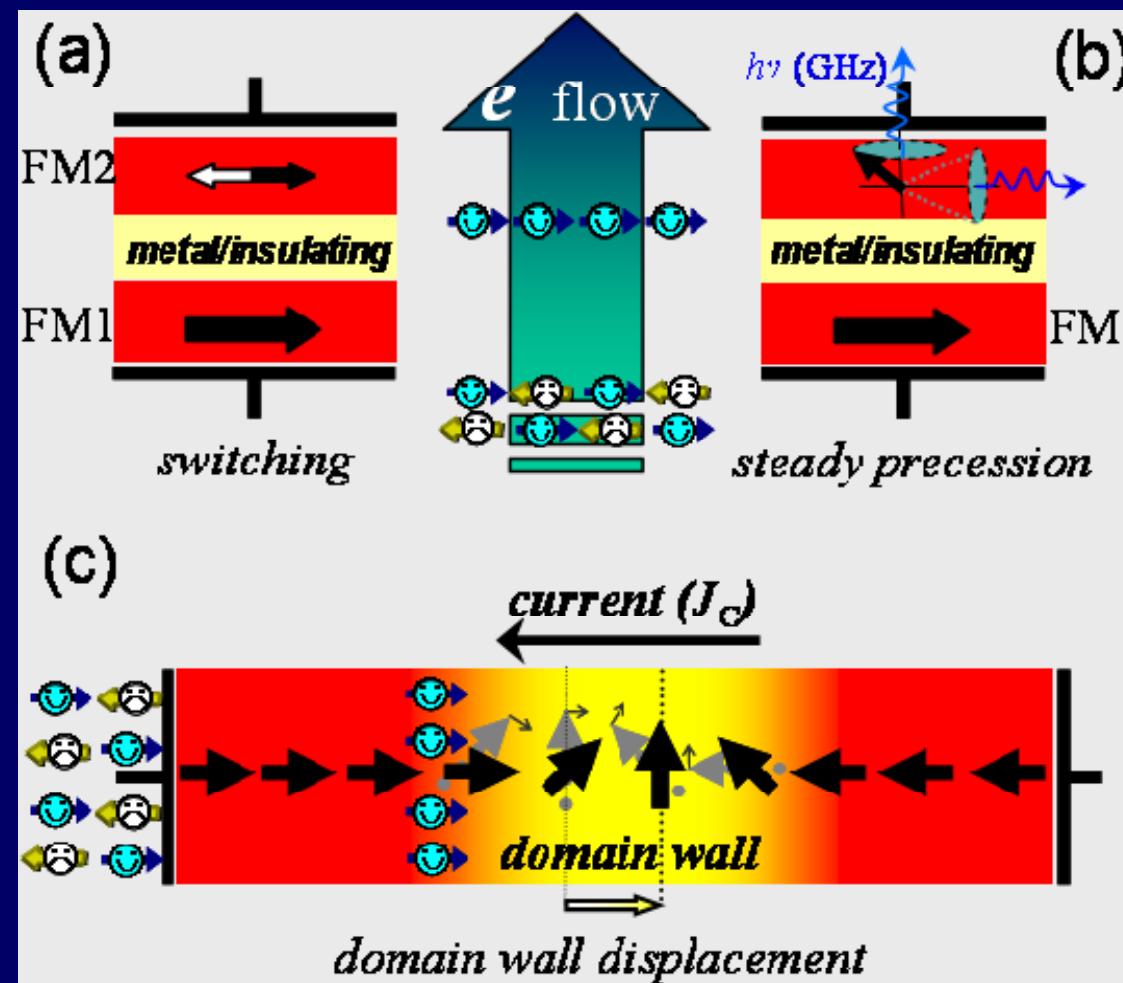
COMPLETE ANGULAR study



SPIN TRANSFER TORQUE STT EFFECT

Spin polarized current induces

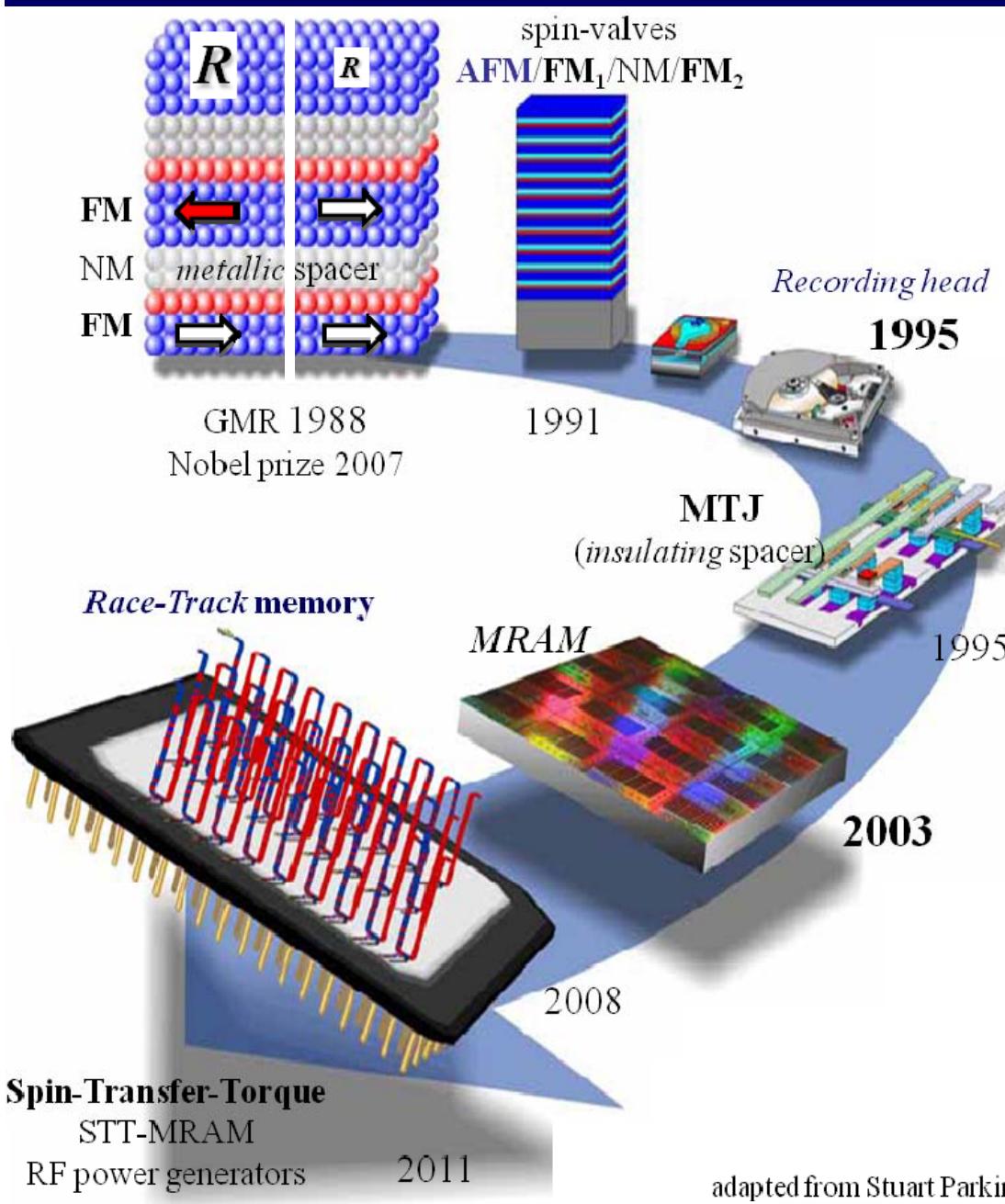
- irreversible switching
- steady precession
- domain wall displacement



J. Mater. Chem. Highlight 19, 1678 (2009)

Magnetic switching and microwave generation by spin transfer

SPINTRONIC SYSTEMS



Low dimensionality

Multilayered systems

Artificial interfaces

Shapes

Stimuli:

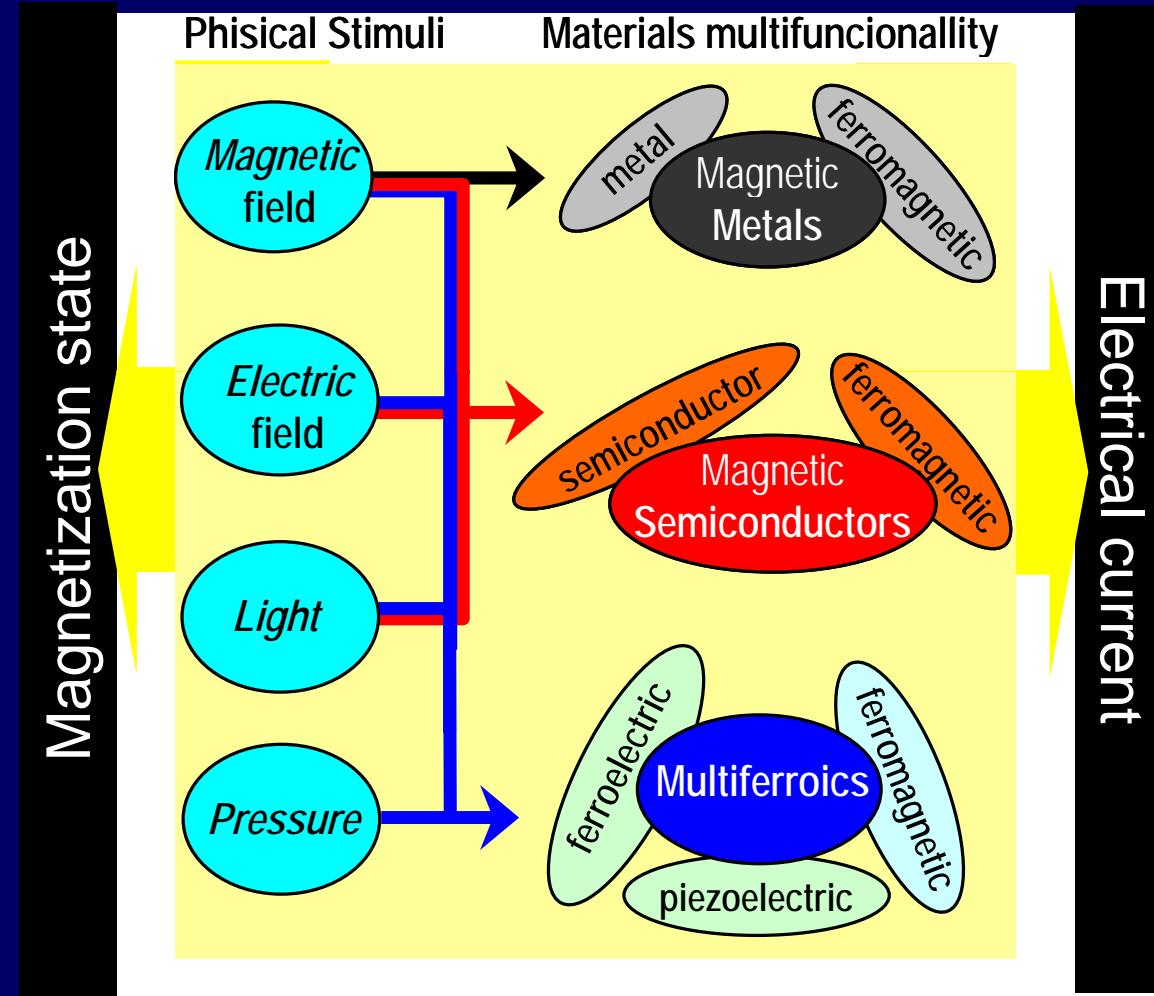
Magnetic fields (Oersted)

Electric Currents (STT)

TOWARDS MULTIFUNCTIONAL MATERIALS.

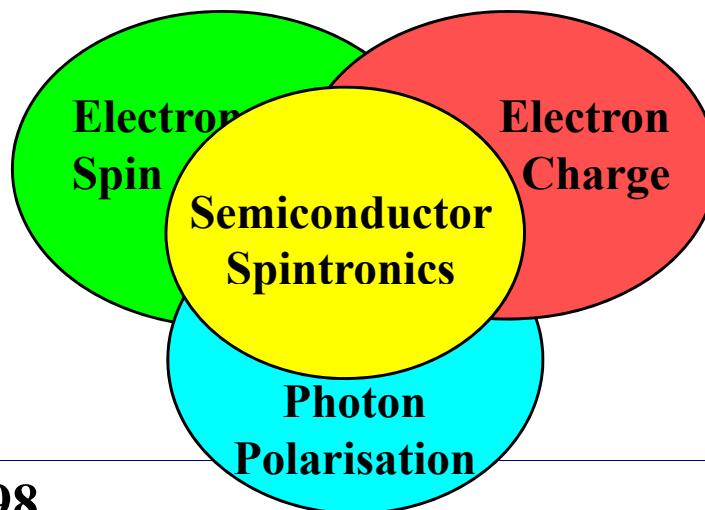
Spintronics is the link between the magnetization orientation of a material and its electrical resistance. In conventional spintronics these two properties are controlled by applying either a magnetic field or an electrical current and measuring the resistance

J. Mater. Chem. Highlight 19, 1678 (2009)



The coexistence of different functionalities allows the realization of devices with more than two-state logic, as used in conventional spintronics.

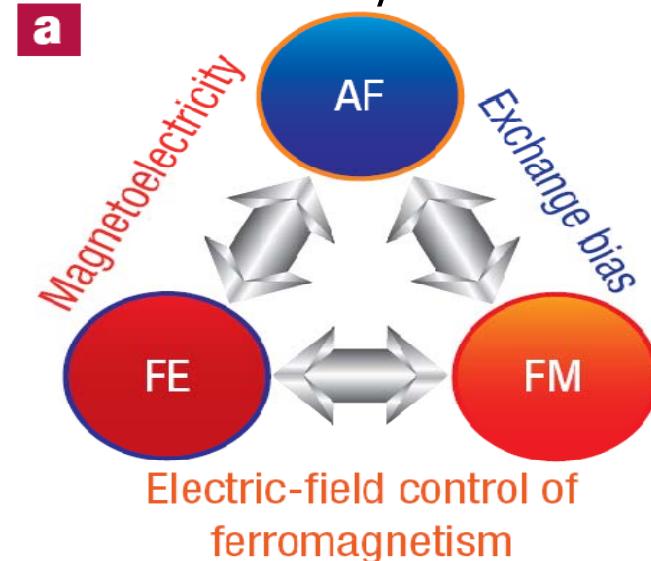
DILUTED MAGNETIC SEMICONDUCTORS



1998

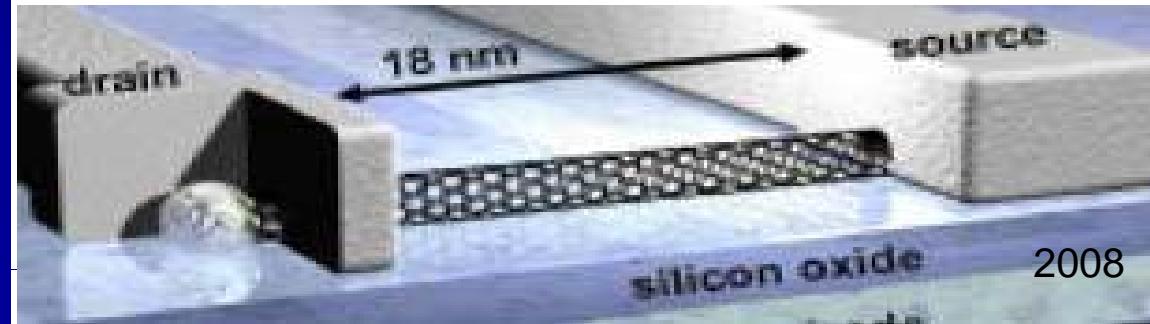
GaAs with 5% Mn, but **max. $T_c=172K$**

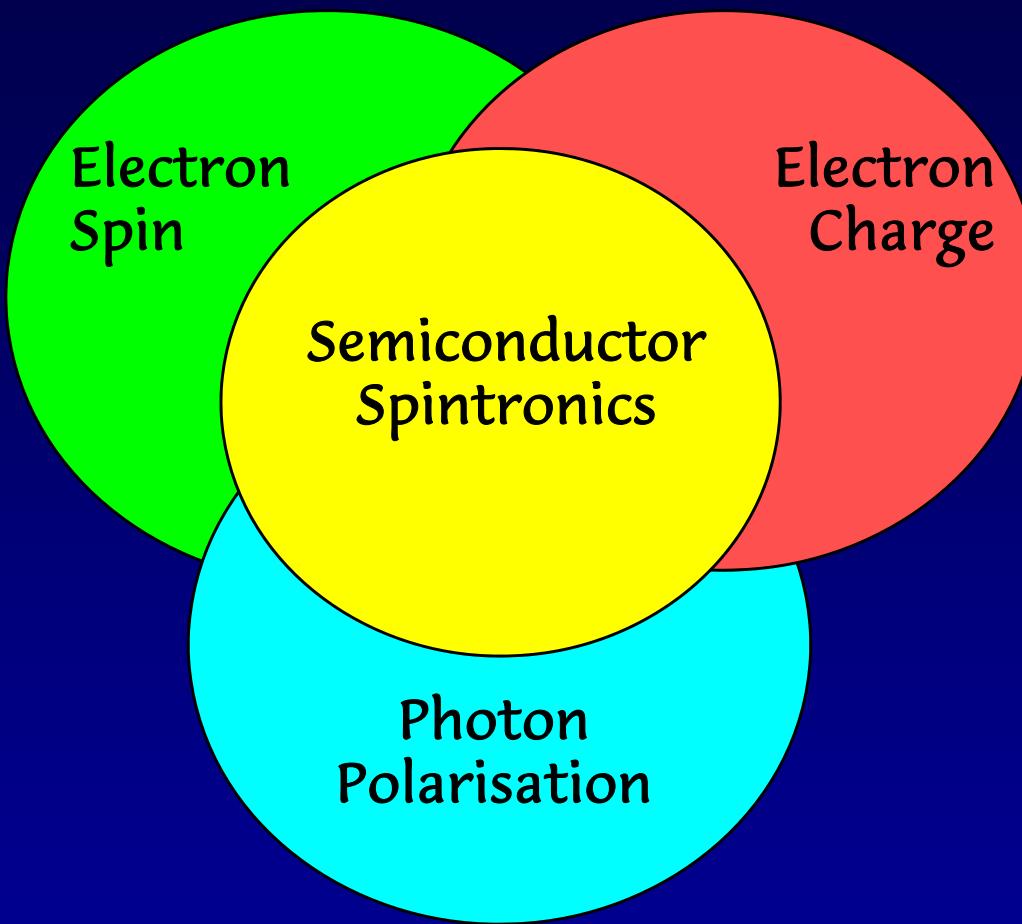
MULTIFFEROICS: MAGNETOELECTRIC MEMORY



2008

MAGNETIC MOLECULES: NEW FUNCIONALITIES



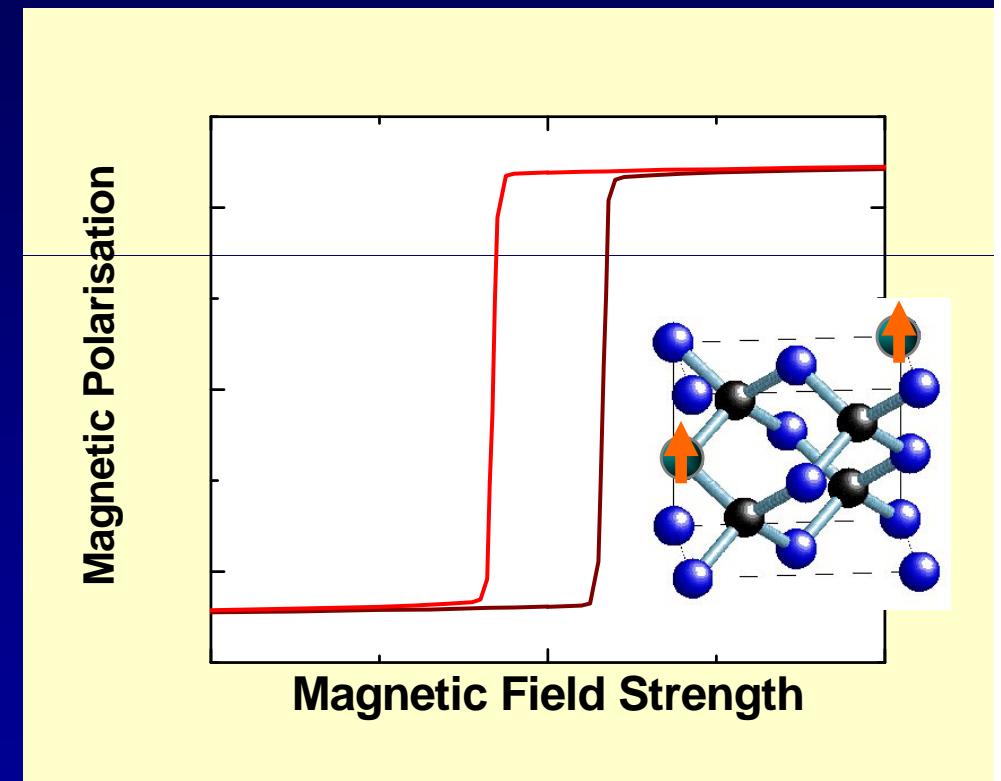


Benefits: Fast, small, low dissipation devices

Quantum computation?
New physics

$(Ga,Mn)As$

H. Ohno *et al.* (1996): ferromagnetism in GaAs thin films doped ~5% with Mn



Growth by low temperature MBE to beat equilibrium solubility limit

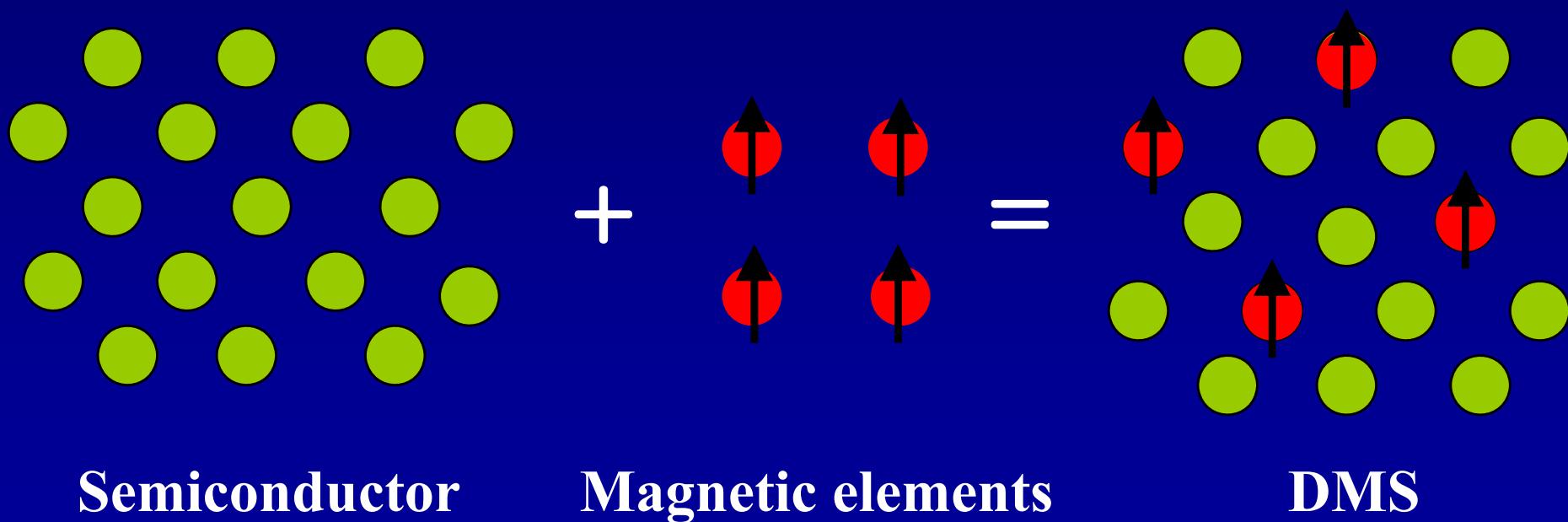
How MAKE Dilute MAGNETIC SEMICONDUCTOR

Injection of Spin-polarized electrons into semiconductor

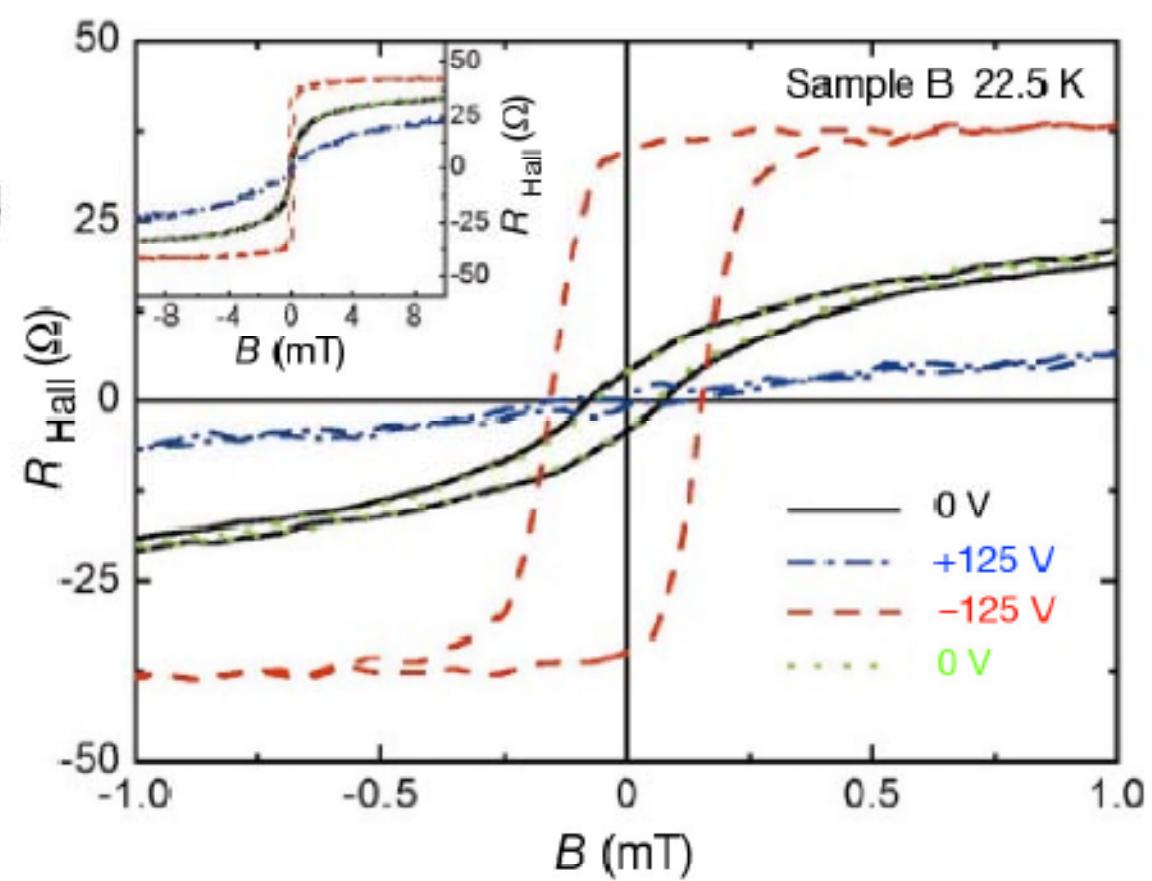
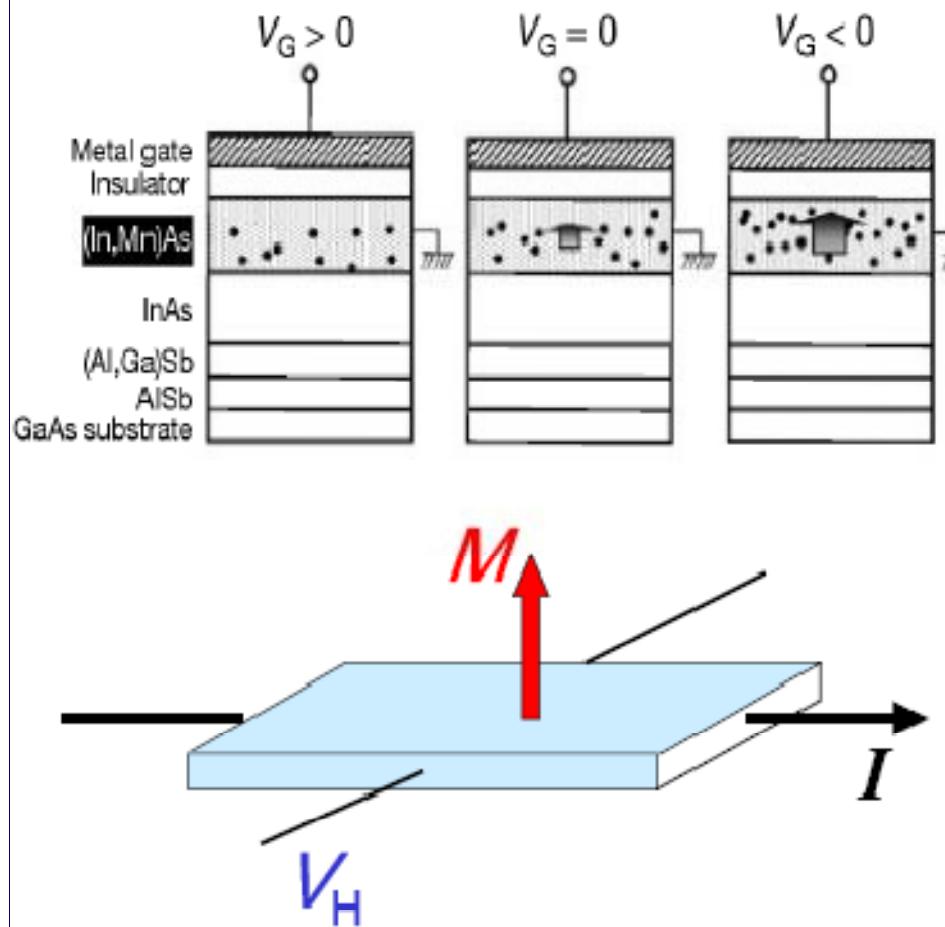
Magnetic semiconductor

Realization of Spintronics devices

* magnetic semiconductor: An alloys of non-magnetic semiconductor and magnetic elements

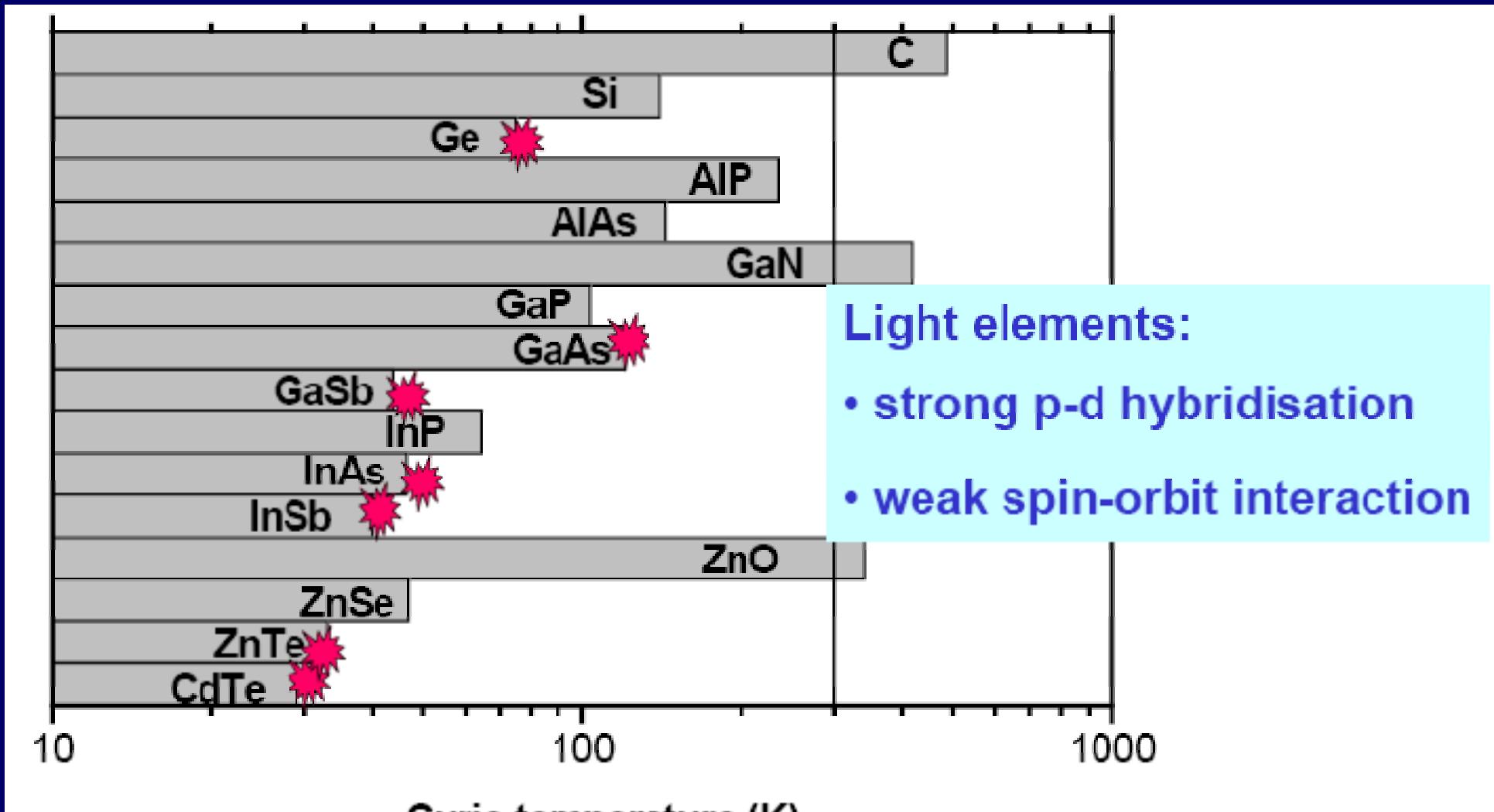


TUNING OF MAGNETIC ORDERING BY ELECTRIC FIELD (FERRO-FET) $(In,Mn)As$



Ohno et al. (Tohoku, Warsaw) Nature '00

p-d Zener model prediction of T_C 5% Mn d⁵, p= $3.5 \times 10^{20} \text{ cm}^{-3}$

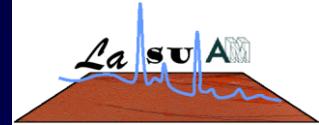


Light elements:

- strong p-d hybridisation
- weak spin-orbit interaction

T. D. et al. (Warsaw, Tohoku, Grenoble) Science'00, PRB'01

MATERIALS SHOWING HYSTERESIS AND SPONTANEOUS MAGNETIZATION AT 300 K

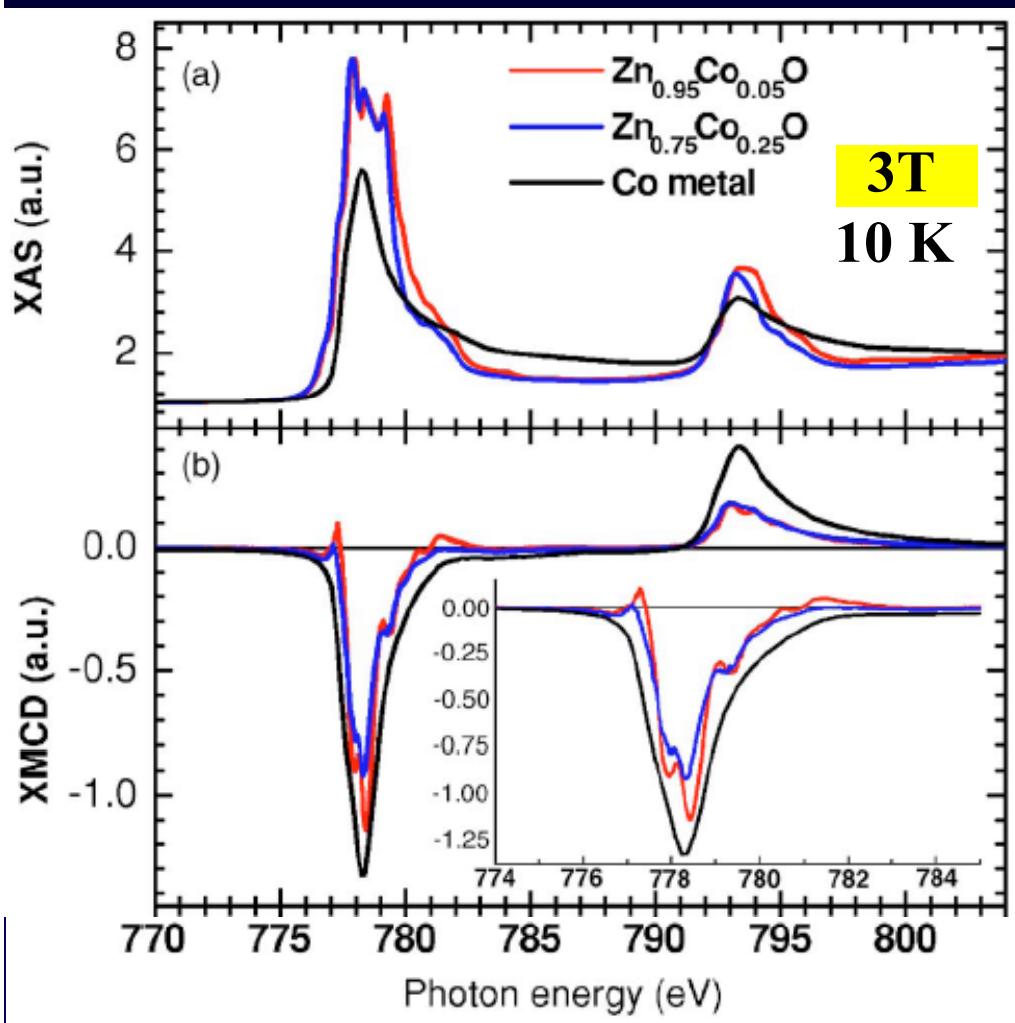


wz-c-(Ga,Mn)N, (In,Mn)N, (Ga,Cr)N, (Al,Cr)N, (Ga,Gd)N,
(Ga,Mn)As, (In,Mn)As, (Ga,Mn)Sb, (Ga,Mn)P:C
(Zn,Mn)O, (Zn,Ni)O, (Zn,Co)O, (Zn,V)O, (Zn,Fe,Cu)O
(Zn,Cr)Te
(Ti,Co)O₂, (Sn,Co)O₂, (Sn,Fe)O₂, (Hf,Co)O₂
(Cd,Ge,Mn)P₂, (Zn,Ge,Mn)P₂, (Zn,Sn,Mn)As₂
(Ge,Mn)
(La,Ca)B₆C, C₆₀, HfO...

- ☞ None proven to be 300 K ferromagnetic semiconductor
- ☞ Each brings new challenges

Moving beyond (Ga,Mn)As, Nature Materials 84, 195 (2005)

A meticulous XAS and XMCD investigation can reveal unequivocally the electronic and magnetic properties of diluted magnetic semiconductors.

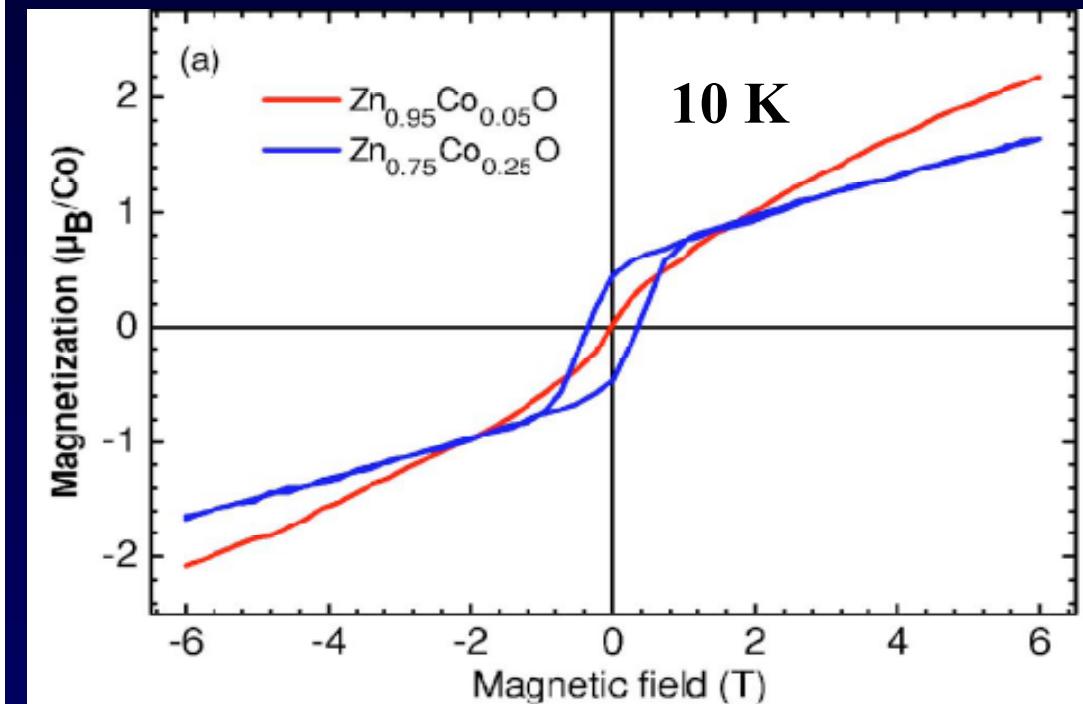
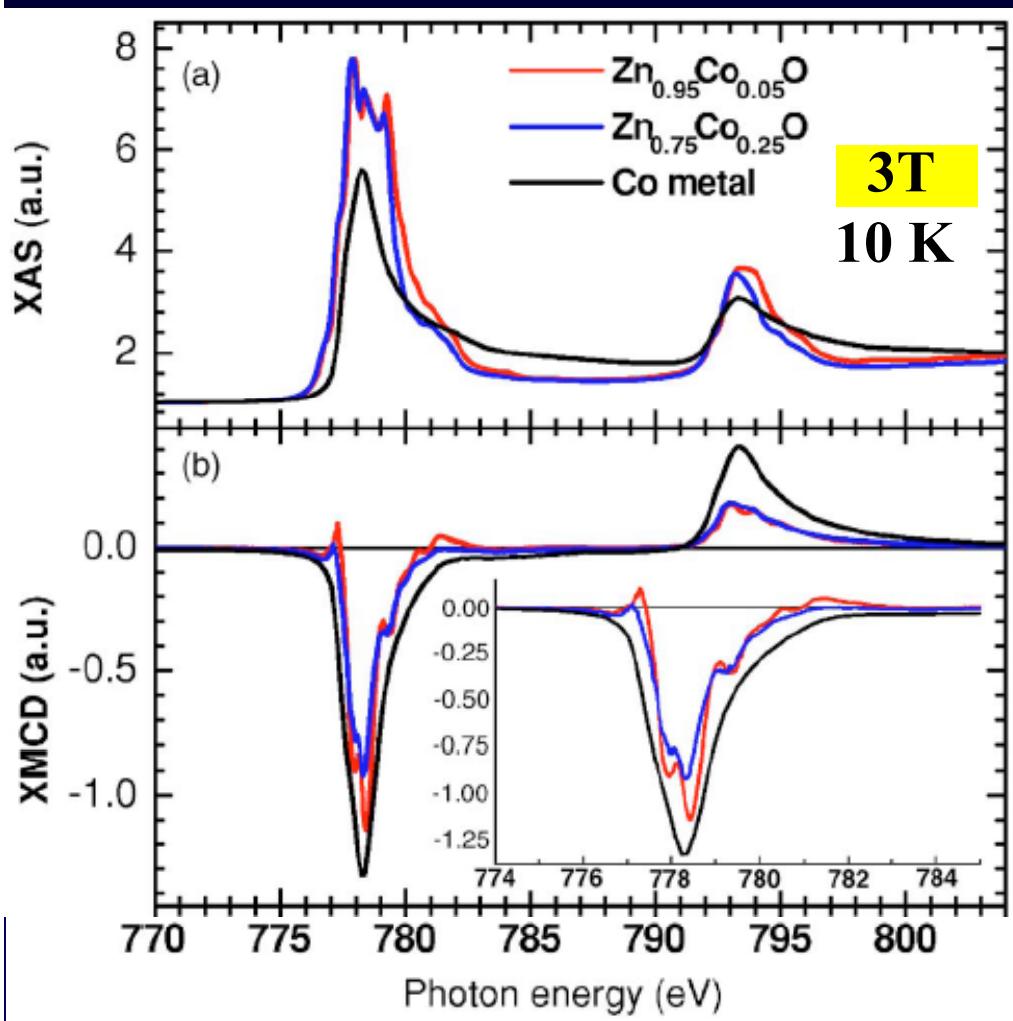


multiplets XAS → Co in an ionic state (diluted)

multiplets XMCD → the magnetic component at high magnetic field can be mainly attributed to Co in an ionic state

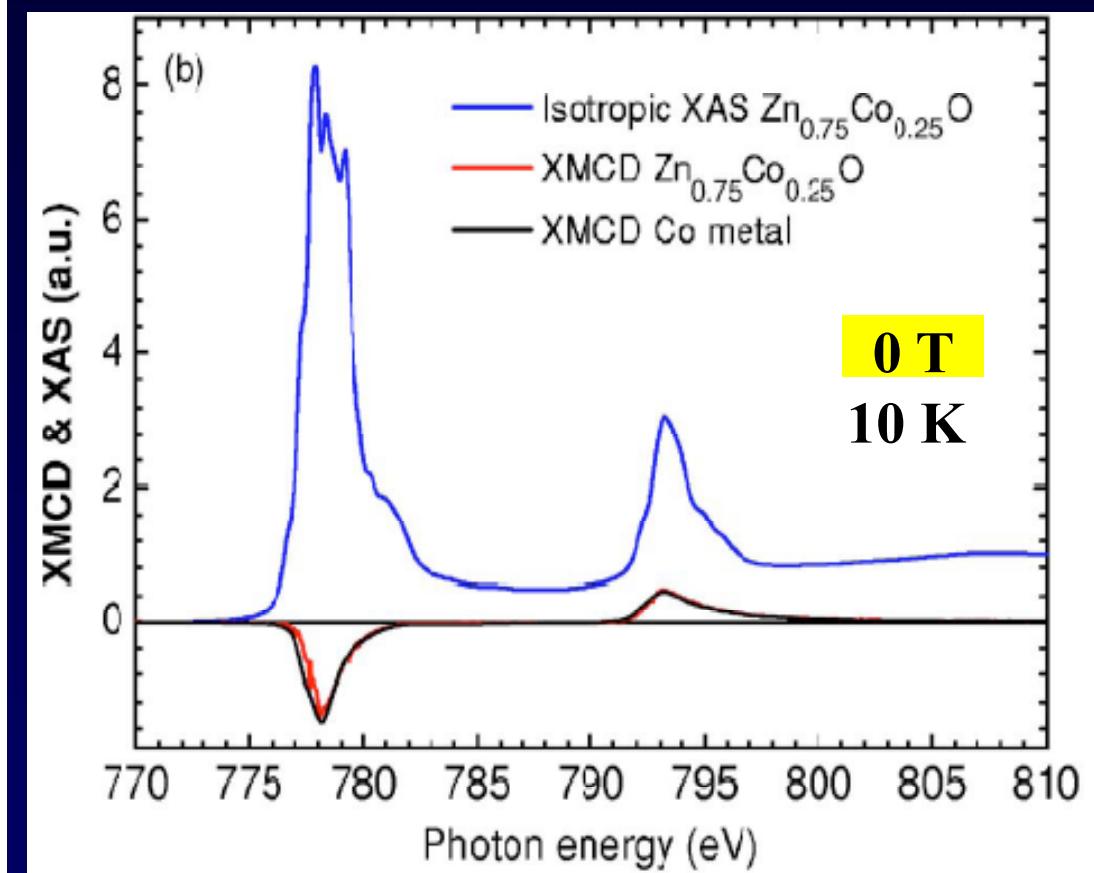
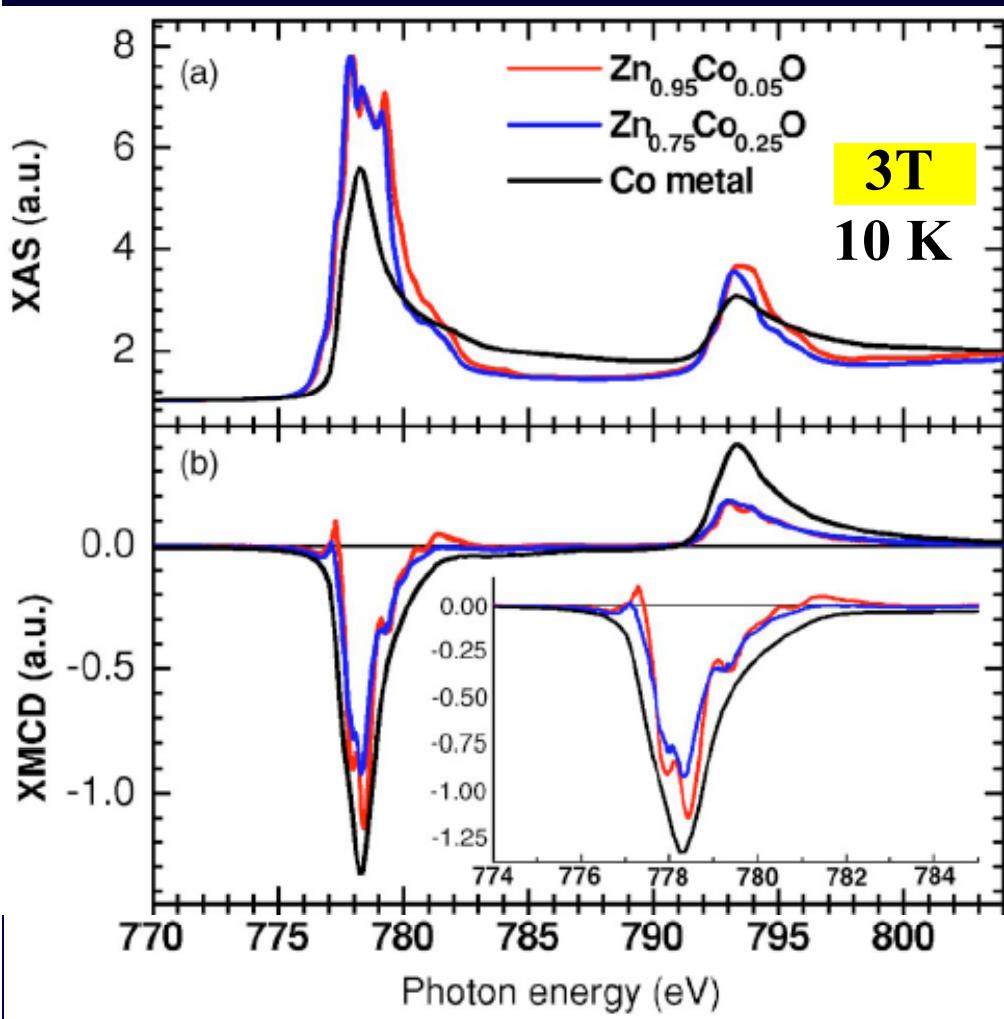
Rode *et al.*, Appl. Phys. Lett. **92**, 012509 (2008)

A meticulous XAS and XMCD investigation can reveal unequivocally the electronic and magnetic properties of diluted magnetic semiconductors.



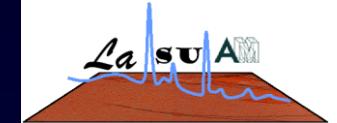
Rode *et al.*, Appl. Phys. Lett. **92**, 012509 (2008)

A meticulous XAS and XMCD investigation can reveal unequivocally the electronic and magnetic properties of diluted magnetic semiconductors.



Rode *et al.*, Appl. Phys. Lett. **92**, 012509 (2008)

Evidence that in Co-doped ZnO thin films two magnetic phases coexist, a paramagnetic phase associated to cobalt in ionic state and an **extrinsic FM phase associated to metallic cobalt clusters**.



A ten-year perspective on dilute magnetic semiconductors and oxides

Tomasz Dietl^{1,2*}

pp965 - 974

editorial

Nature December 2010,
Volume 9 No 12 pp951-957

A window on the future of spintronics

Hideo Ohno

Despite low transition temperatures, ferromagnetism in diluted magnetic semiconductors has been essential in exploring new ideas and concepts in spintronics, some of which have been successfully transferred to metallic ferromagnets.

More than just room temperature

Diluted magnetic semiconductors and oxides are interesting for fundamental science and applications even without room-temperature ferromagnetism.

Is it really intrinsic ferromagnetism?

Scott Chambers has worked on epitaxial oxide films for the past eighteen years. *Nature Materials* asked him about his view on high-temperature ferromagnetism in diluted magnetic oxides.

A model ferromagnetic semiconductor

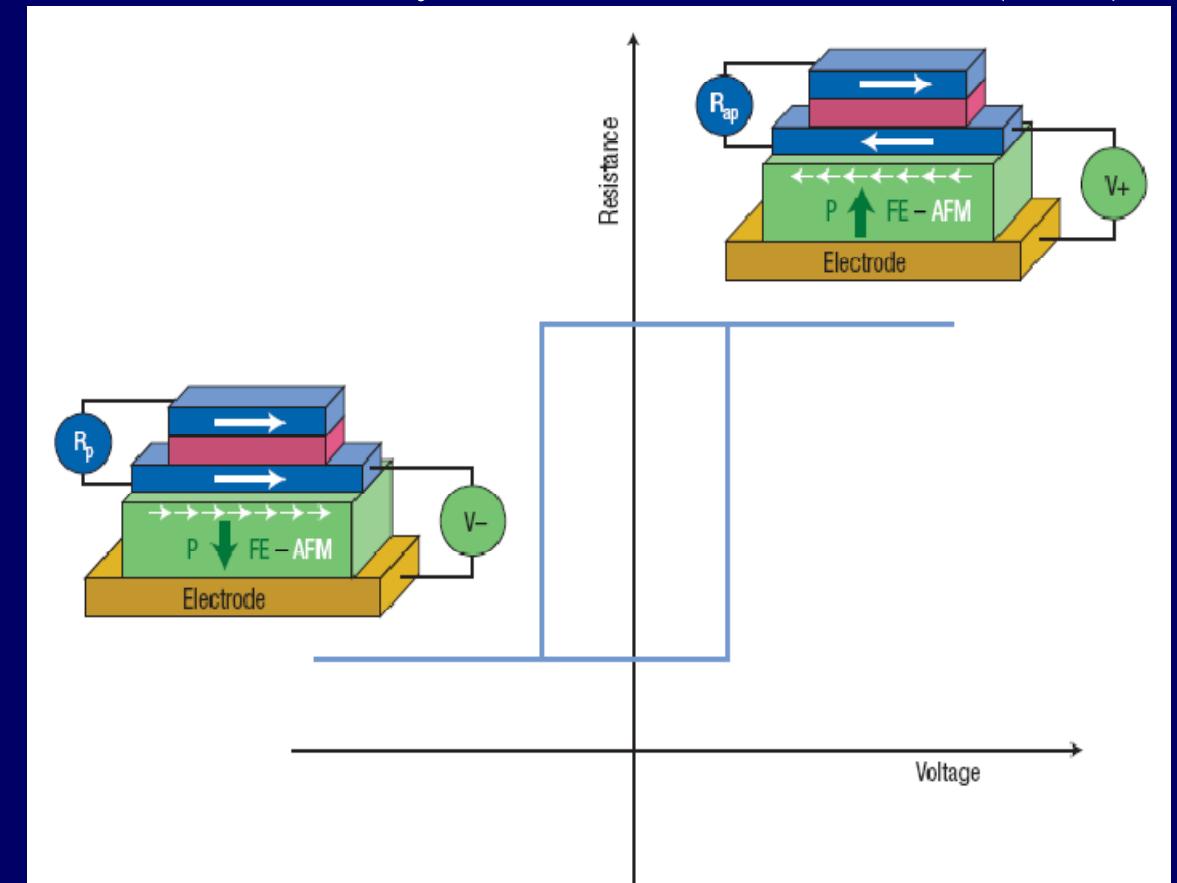
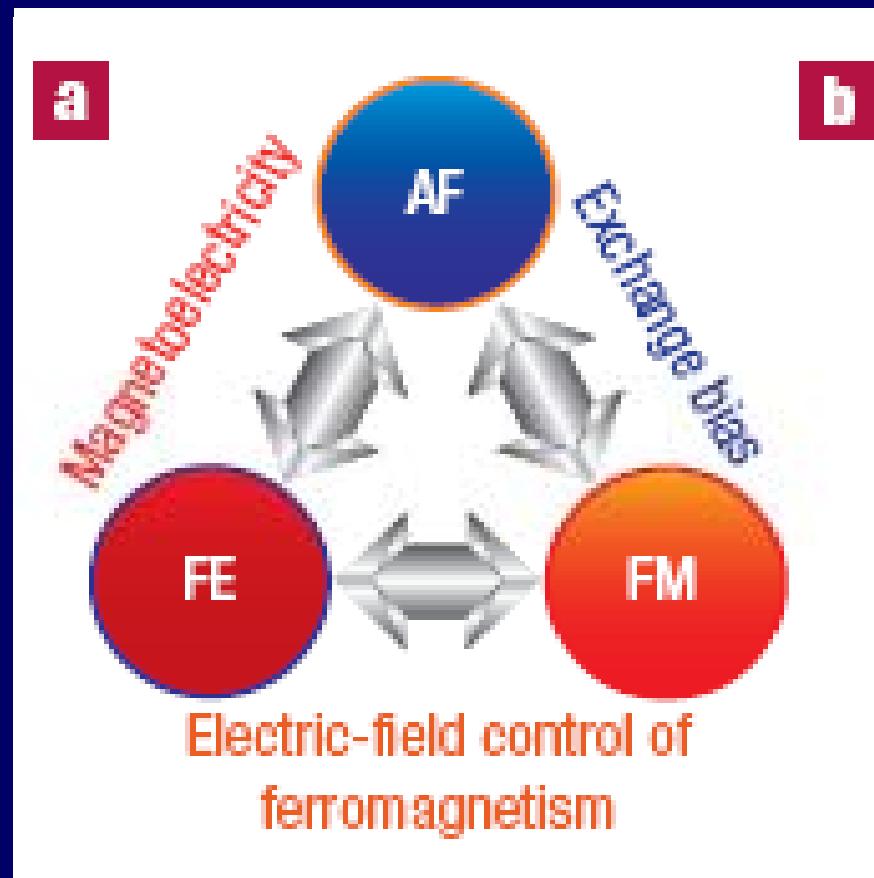
Nitin Samarth has extensive experience in studying the properties of (Ga,Mn)As. He told *Nature Materials* about the role that this compound has had in exploring the magnetic properties of semiconductors and, more generally, of spin-related phenomena.

ELECTRIC-FIELD CONTROL OF LOCAL FERROMAGNETISM USING MULTIFERROICS



Ferroelectric&AFM / FM
 BiFeO_3 / $\text{Co}_{0.9}\text{Fe}_{0.1}$

M. Bibes & A. Barthélémy, *Nature Materials* 7, 425 (2008)



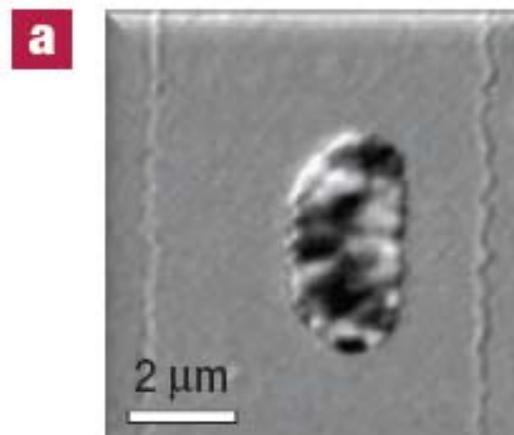
ELECTRIC-FIELD CONTROL OF LOCAL FERROMAGNETISM USING MULTIFERROICS



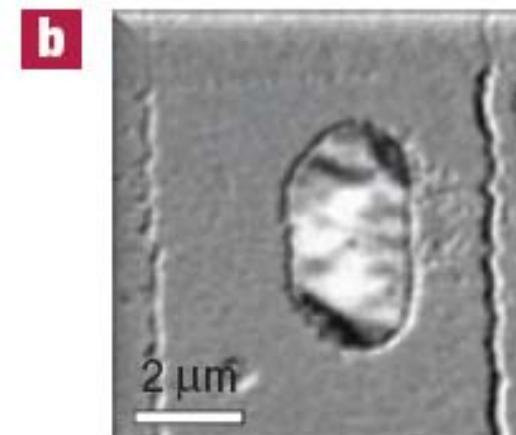
Ferroelectric&AFM / FM
 BiFeO_3 / $\text{Co}_{0.9}\text{Fe}_{0.1}$

XPEEM @ Co-edge

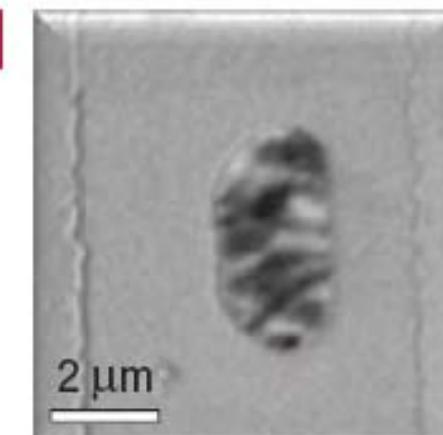
as grown



after $-E_{\text{pulse}}$



after $+E_{\text{pulse}}$



Applied field
during growth
(200 Oe)



Incoming X-ray
direction



Net magnetization of
CoFe feature

Ramesh group & SLS, *Nature Materials* 7, 478 (2008); *NanoLetters* 8, 2050 (2009)



Electric Field-Induced Modification of Magnetism in Thin-Film Ferromagnets
 Martin Weisheit, et al.
Science **315**, 349 (2007);
 DOI: 10.1126/science.11366

PRL **102**, 187201 (2009)

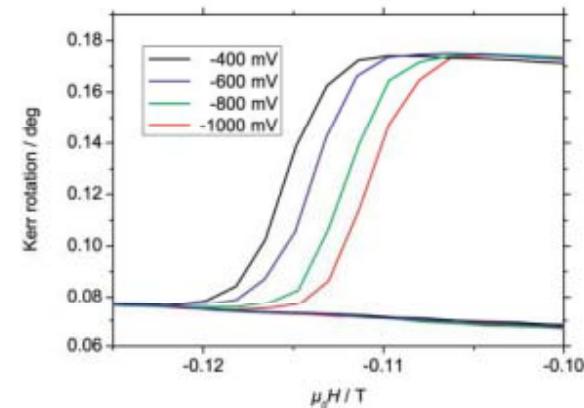
changes in the band structure introduced
 by the electric field

anisotropy

H_C

T_C

Fig. 2. Magnetization switching of the 2-nm-thick FePt film for different U values between the film and the Pt counter electrode. μ_0 , the permeability of vacuum.



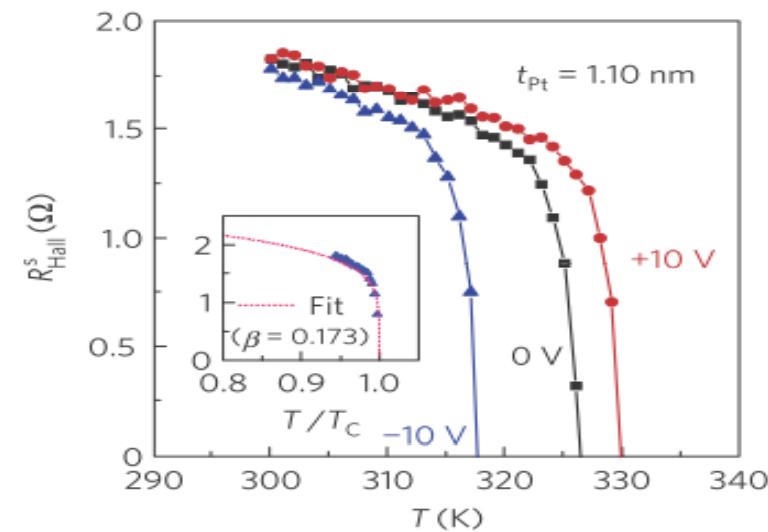
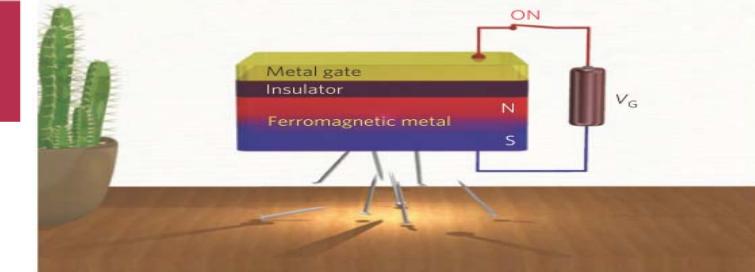
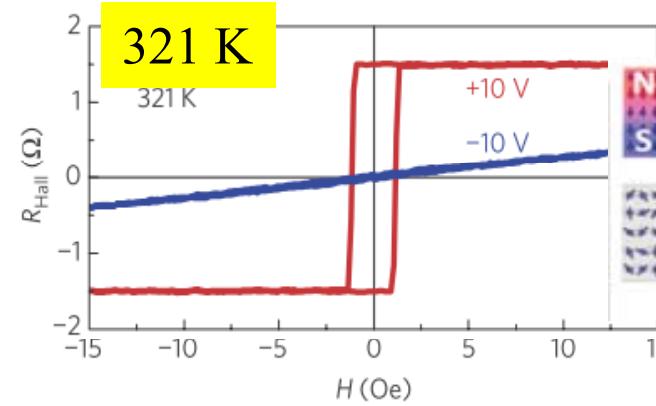
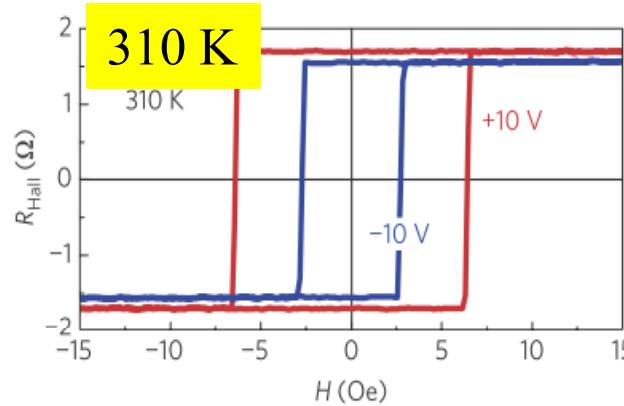
**nature
materials**

LETTERS

PUBLISHED ONLINE: 2 OCTOBER 2011 | DOI:10.1038/NMAT3130

Electrical control of the ferromagnetic phase transition in cobalt at room temperature

D. Chiba^{1,2*}, S. Fukami³, K. Shimamura¹, N. Ishiwata³, K. Kobayashi¹ and T. Ono¹



Electric toggling of magnets

Electric-field-induced toggle switching of nanoscale thin-film magnets signifies an important step towards energy-efficient magnetic data storage.

Evgeny Y. Tsymbal

NATURE MATERIALS | VOL 11 | JANUARY 2012 | www.nature.com/naturematerials

nature
materials

LETTERS

PUBLISHED ONLINE: 13 NOVEMBER 2011 | DOI: 10.1038/NMAT3172

Induction of coherent magnetization switching in a few atomic layers of FeCo using voltage pulses

Yoichi Shiota¹, Takayuki Nozaki^{1,2†}, Frédéric Bonell¹, Shinichi Murakami^{1,2}, Teruya Shinjo¹ and Yoshishige Suzuki^{1,2*}

ARTICLES

PUBLISHED ONLINE: 13 NOVEMBER 2011 | DOI: 10.1038/NMAT3171

nature
materials

Electric-field-assisted switching in magnetic tunnel junctions

Wei-Gang Wang*, Mingen Li, Stephen Hageman and C. L. Chien*

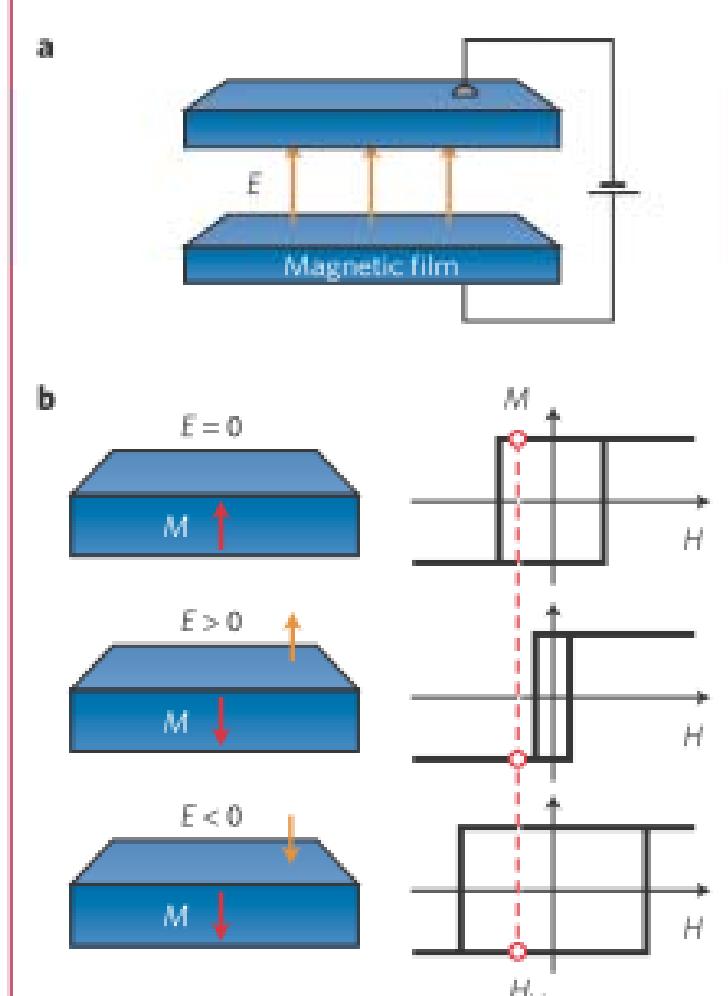


Figure 1 | Electric field effect on magnetization.

Nanoferronics is a winning combination

Manuel Bibes

Progress in controlling different ferroic orders such as ferromagnetism and ferroelectricity on the nanoscale could offer unprecedented possibilities for electronic applications.

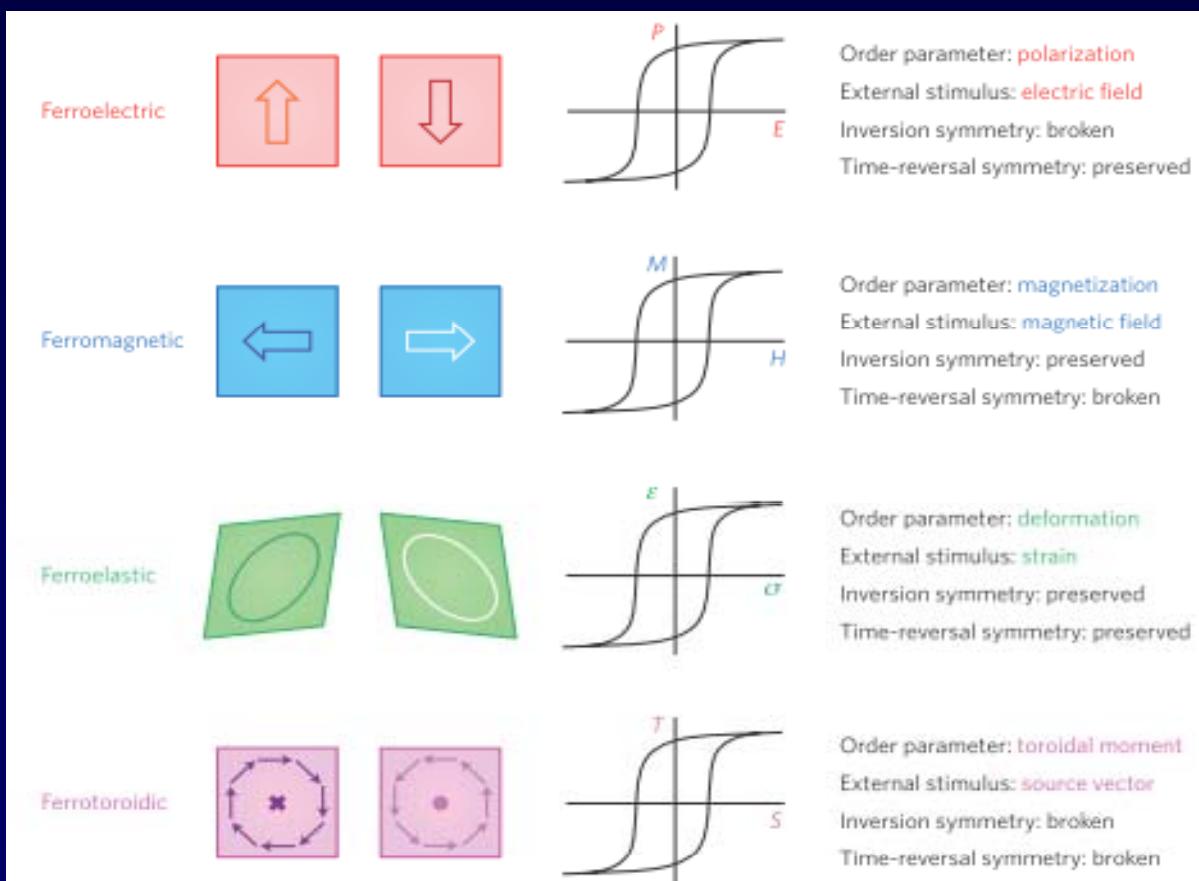


Figure 1 | Schematic representation and hysteresis cycles of the four primary ferroic orders. Figure adapted

TOWARDS ORGANIC NANOMAGNETISM

Our challenge is to start from **molecules**, existing as such in powders, suitably designed to build magnetic solid thin films and multilayer structures where:

- ☞ *intermolecular interactions are strong enough*
- ☞ *large (magnetic anisotropy times magnetization) values*

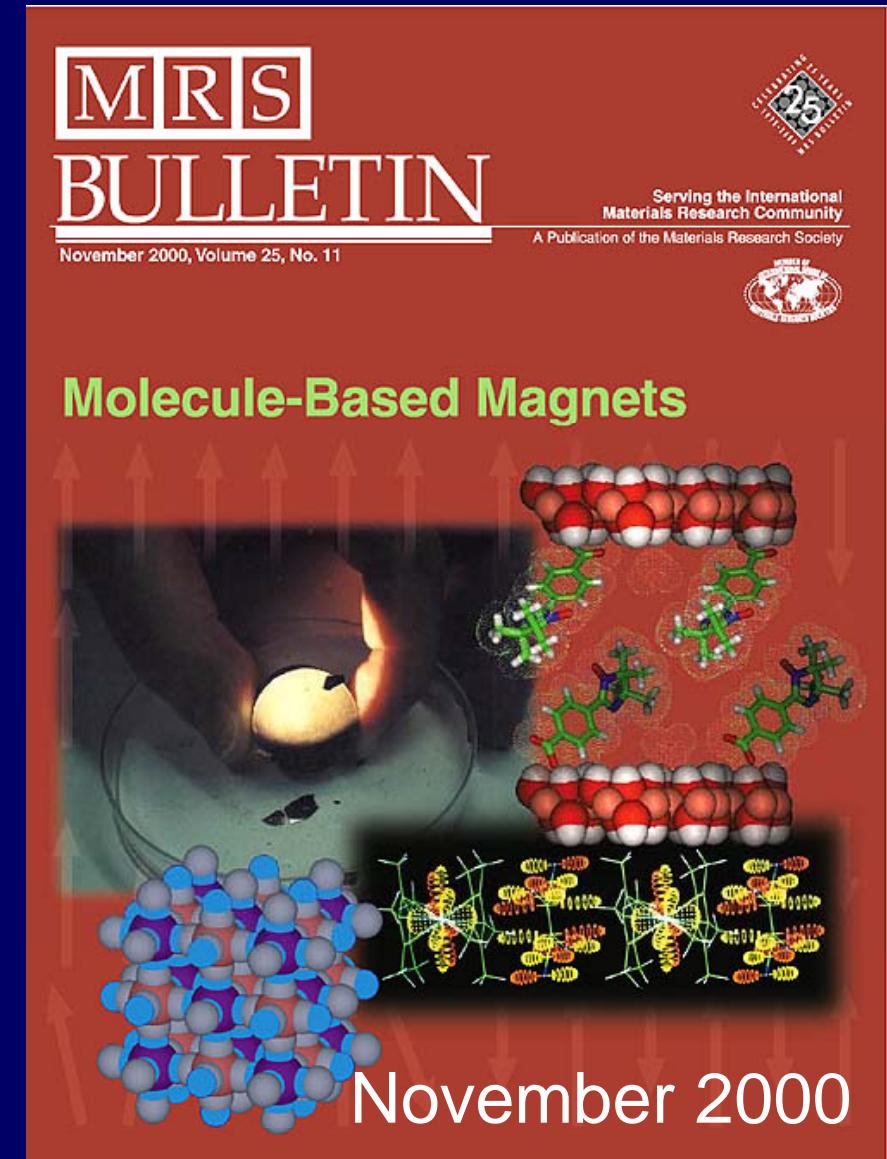
for the **magnetic ordering** to survive **at room temperature**.

Long spin diffusion length,
Multifunctionality,
Plastic technology,
Low cost,

Why Study Molecule-Based Magnets ?

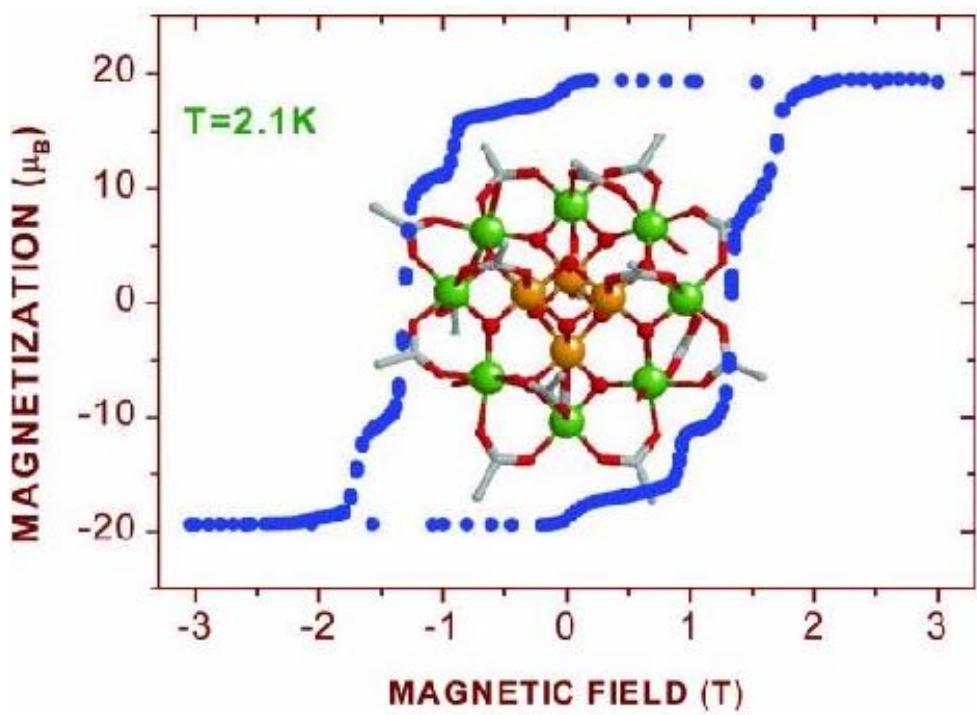
- New phenomena observed, not in conventional magnets
- Tunable properties ('magnets by design')
- Light-weight, bio-compatible alternative to conventional magnets
- Low-cost, low-temperature, flexible syntheses

adapted from A. J. Epstein, Ohio State University, USA



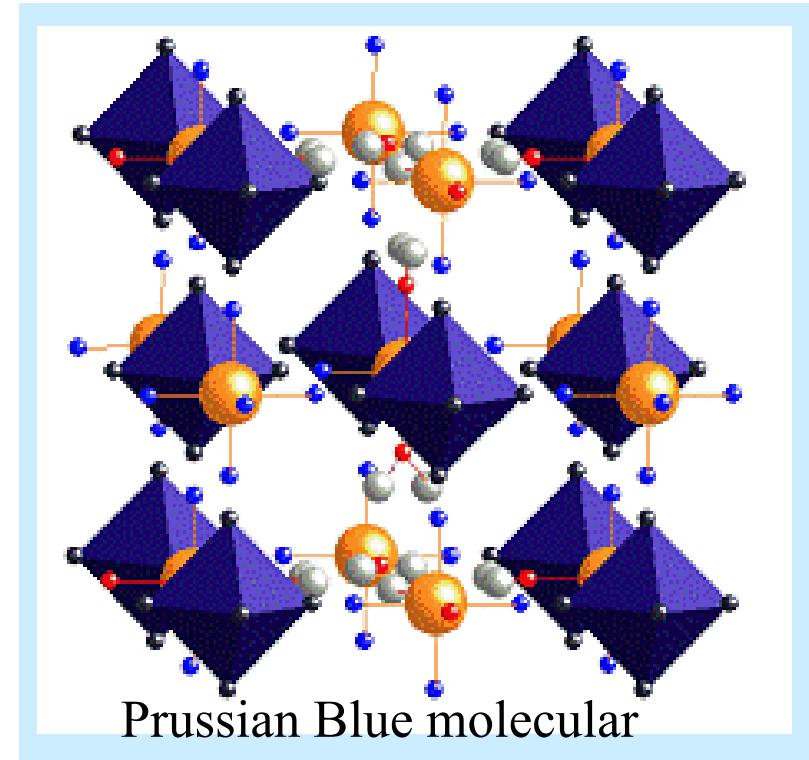
INTERMOLECULAR INTERACTIONS ARE IMPORTANT !

Non-interacting molecules:
Single Molecular Magnets (SMM)



Large relaxation times (large K)
Very low T_c
Quantum phenomena

Interacting molecules:
RT organic magnetic systems



Long magnetic order
+ new functionalities

High-temperature metal-organic magnets

Rajsapan Jain¹, Khayrul Kabir¹, Joe B. Gilroy¹, Keith A. R. Mitchell², Kin-chung Wong² & Robin G. Hicks¹

Selected metal-cyanide-based organometallic magnets order near or above RT

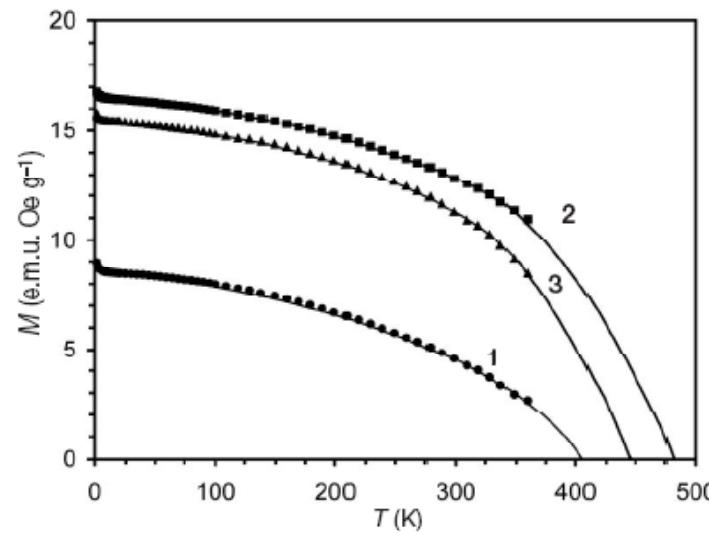
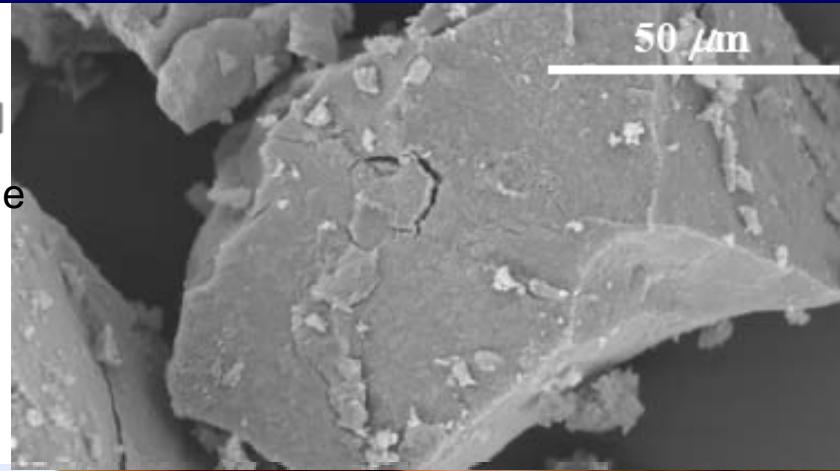
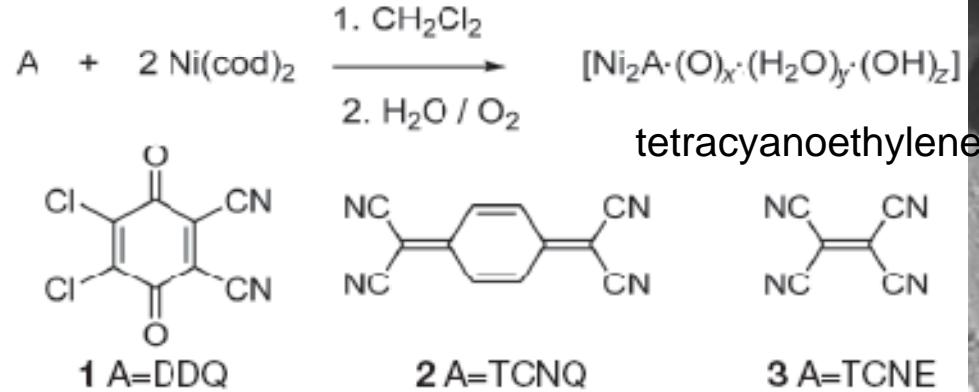


Figure 1 | Temperature dependence of field-cooled (25 Oe) magnetization for 1–3. Solid lines are extrapolations.



~350 mg of the Ni₂TCNE-based material

High-temperature metal-organic magnets

Rajsapan Jain¹, Khayrul Kabir¹, Joe B. Gilroy¹, Keith A. R. Mitchell², Kin-chung Wong² & Robin G. Hicks¹

Selected metal-cyanide-based organometallic magnets order near or above RT

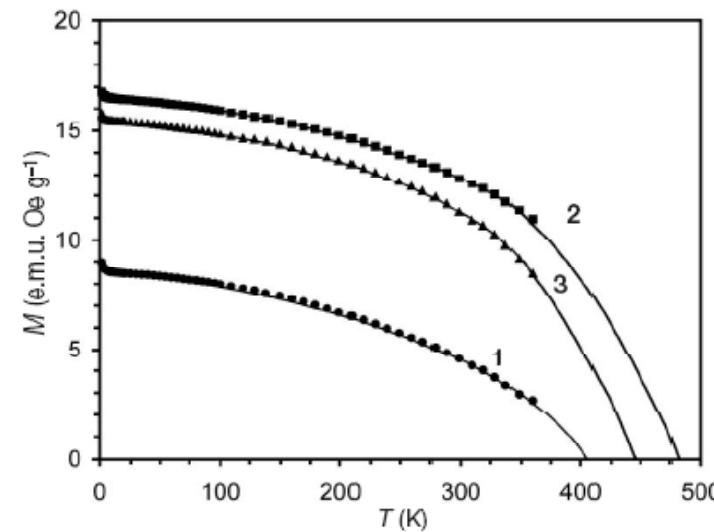
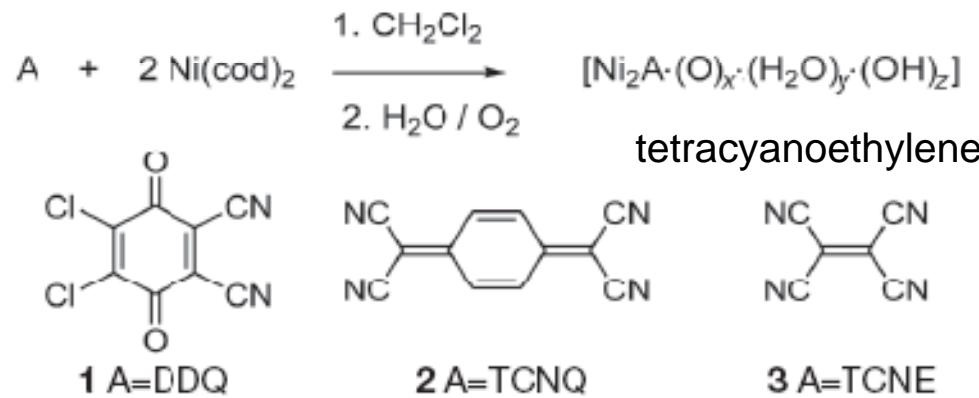


Figure 1 | Temperature dependence of field-cooled (25 Oe) magnetization for 1–3. Solid lines are extrapolations.

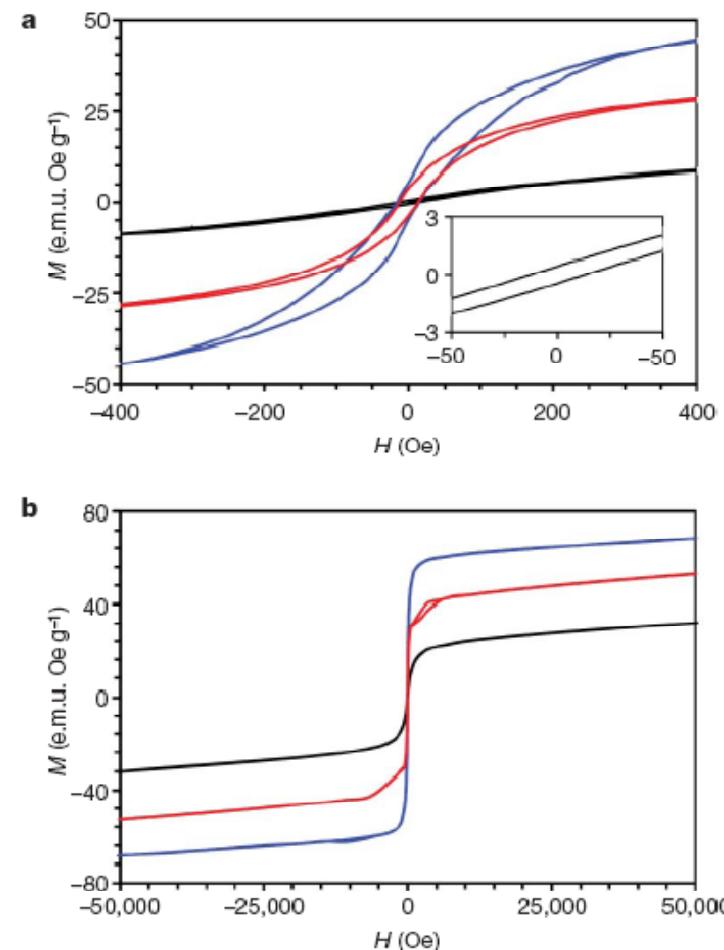


Figure 2 | Magnetic hysteresis loops for 1 (black line), 2 (blue line), and 3 (red line) at 300 K. **a**, ± 400 Oe. Inset shows expansion of the loop for 1. **b**, $\pm 50,000$ Oe.

High-temperature metal-organic magnets

Rajsapan Jain¹, Khayrul Kabir¹, Joe B. Gilroy¹, Keith A. R. Mitchell², Kin-chung Wong² & Robin G. Hicks¹

Selected metal-cyanide-based organometallic magnets order near or above RT

Chemistry World (June 2007): Magnetic dreams disputed
 The holy grail is still to make a stable, well-characterised, RT molecular magnet.

J. Miller & K. I. Pokhodnya, J. Mater. Chem. **17**, 3585 (2007)

Conclusion

Presumably the magnetic material made upon dissolution of $\text{Ni}(\text{COD})_2$ in CH_2Cl_2 consists of ‘nano’- or greater-sized particles of nickel metal. This black powder magnetic material may also have chlorine, carbon, and/or hydrogen present, but it certainly lacks the organic species used in the aforementioned paper. The

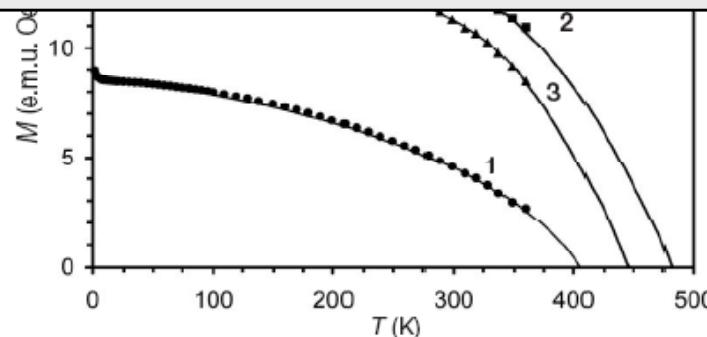


Figure 1 | Temperature dependence of field-cooled (25 Oe) magnetization for 1–3. Solid lines are extrapolations.

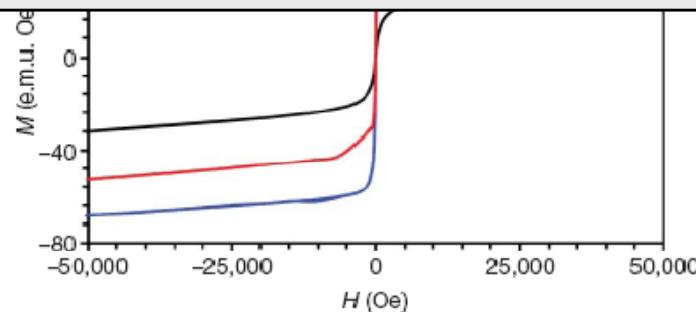


Figure 2 | Magnetic hysteresis loops for 1 (black line), 2 (blue line), and 3 (red line) at 300 K. a, ± 400 Oe. Inset shows expansion of the loop for 1. b, $\pm 50,000$ Oe.

Supramolecular control of the magnetic anisotropy in two-dimensional high-spin Fe arrays at a metal interface

Pietro Gambardella^{1,2,3*}, Sebastian Stepanow^{1,4}, Alexandre Dmitriev^{4,5}, Jan Honolka⁴, Frank M. F. de Groot⁶, Magali Lingenfelder⁴, Subhra Sen Gupta⁷, D. D. Sarma⁷, Peter Benckok⁸, Stefan Stănescu⁸, Sylvain Clair³, Stéphane Pons³, Nian Lin⁴, Ari P. Seitsonen⁹, Harald Brune³, Johannes V. Barth¹⁰ and Klaus Kern^{3,4}

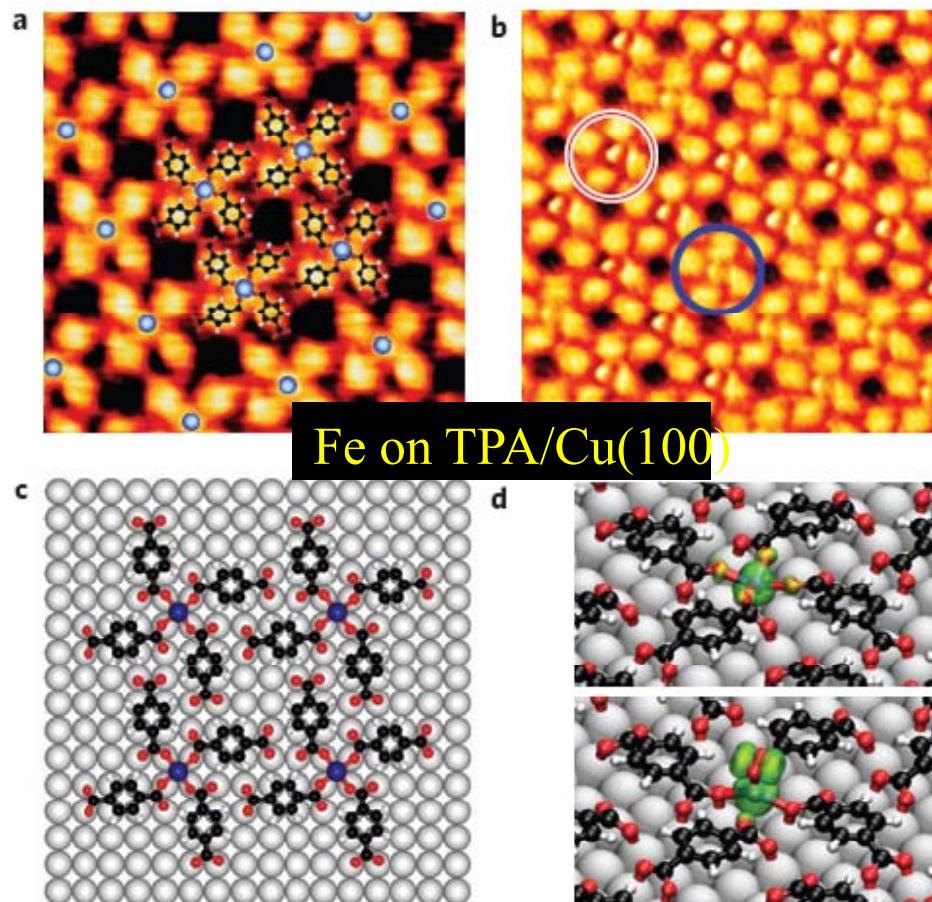
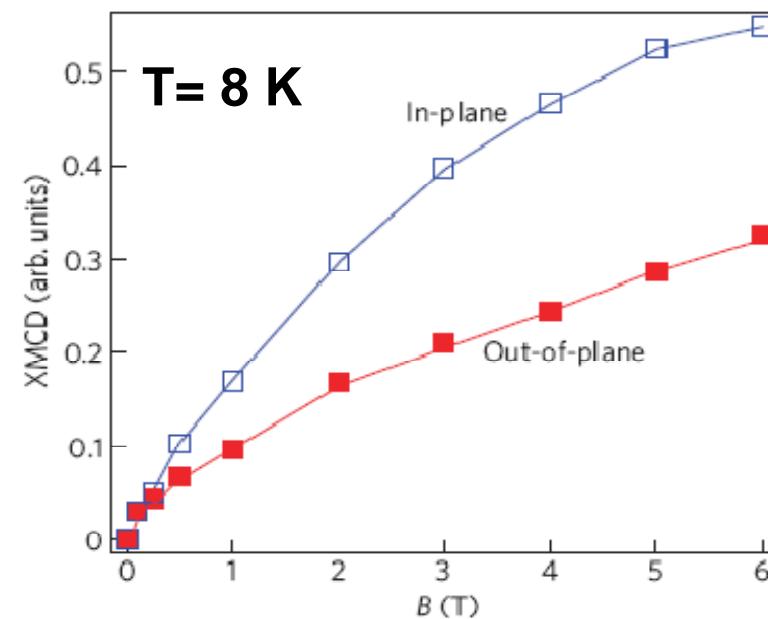
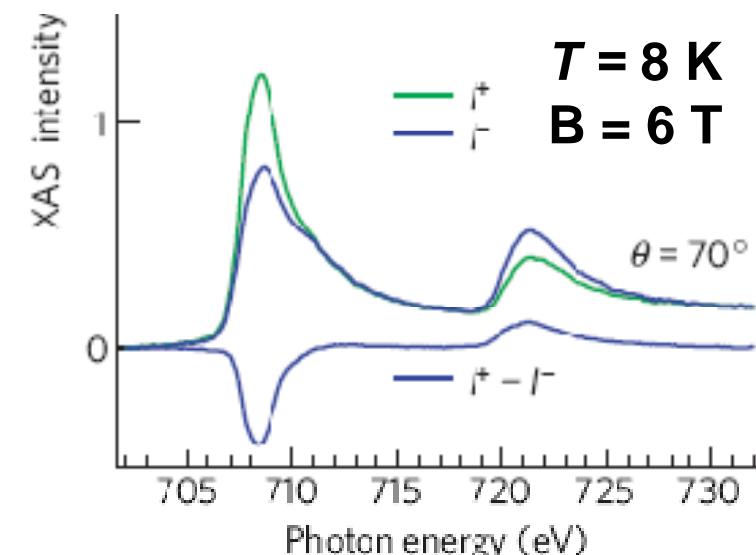
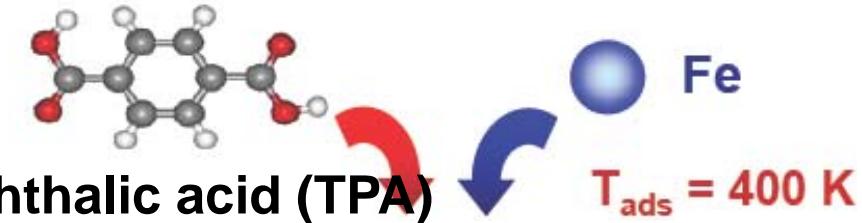


Figure 1 | Planar supramolecular layers of Fe-TPA complexes self-assembled on $\text{Cu}(100)$. **a**, $\text{Fe}(\text{TPA})_4$ array; blue dots indicate the

3d metals on supramolecular self-assembled structures



Tailoring the Nature of Magnetic Coupling of Fe-Porphyrin Molecules to Ferromagnetic Substrates

M. Bernien,^{1,*} J. Miguel,¹ C. Weis,² Md. E. Ali,³ J. Kurde,¹ B. Krumme,² P. M. Panchmatia,^{3,†} B. Sanyal,³ M. Piantek,¹ P. Srivastava,^{2,‡} K. Baberschke,¹ P. M. Oppeneer,³ O. Eriksson,³ W. Kuch,¹ and H. Wende²

¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

Antiferromagnetic coupling between paramagnetic Fe-porphyrin molecules and ultrathin Co and Ni magnetic films on Cu(100) substrates can be established by an *intermediate layer of atomic oxygen*.

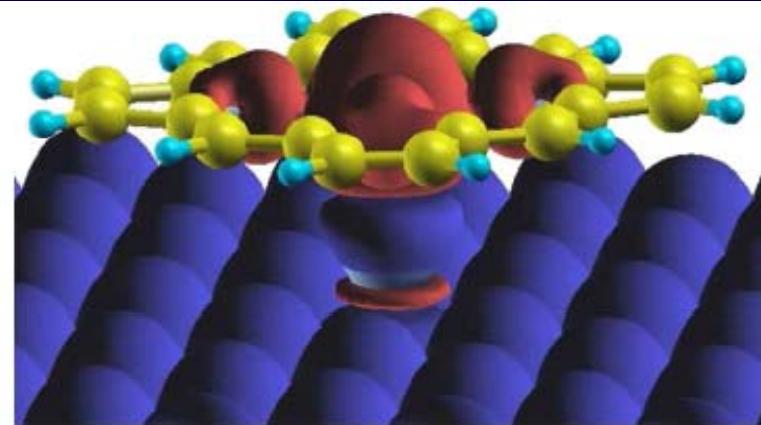
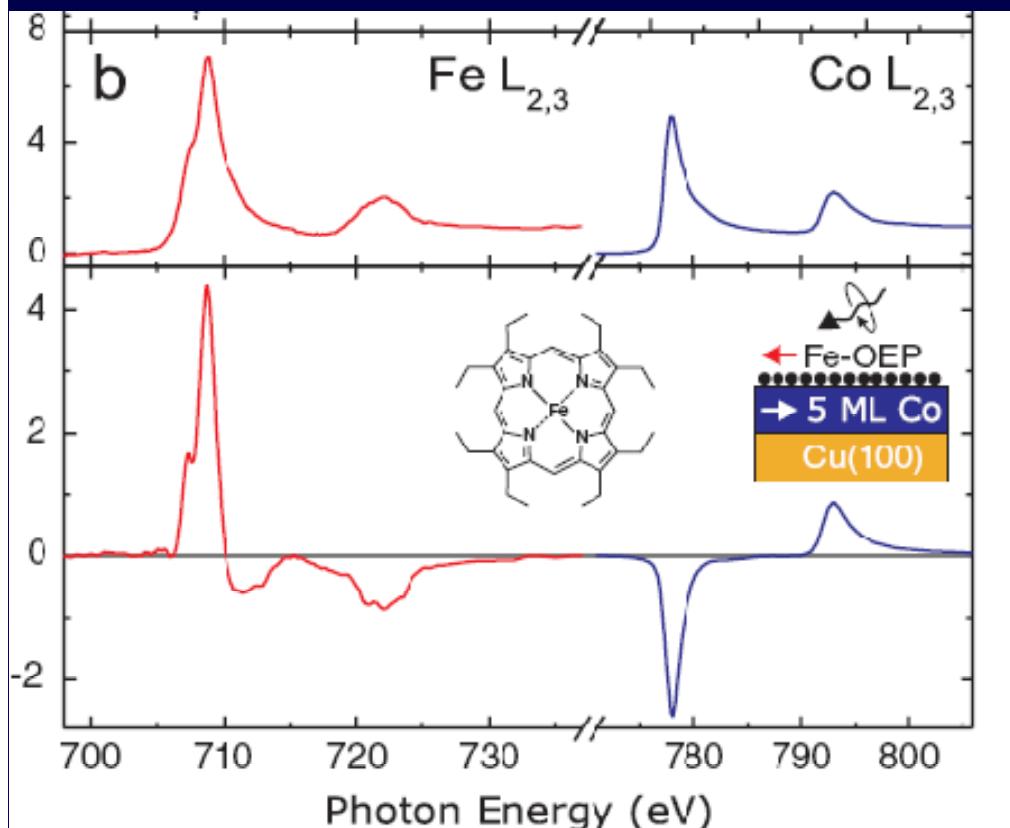


FIG. 4 (color online). *Ab initio* computed magnetization densities. Blue or dark gray color depicts majority-spin magnetiza-

the responsible coupling mechanism is **antiferromagnetic superexchange** mediated by the oxygen p_z orbitals.

Program 3. Nanomagnetism

<http://www.nanoscience.imdea.org/research/research-lines/nanomagnetism>

- Development of new hybrid (inorganic-organic) magnetic nanostructures
- Magnetization reversal and magnetoresistive studies
- Polarization dependent element-resolved x-ray spectroscopy and microscopy studies.
- Biomedical applications



- Multi-porpuise UHV growth/spectroscopy Lab.
- Advanced planetary milling Lab.
- Chemical synthesis magnetic nanoparticles Lab.
- Incubation room lab for biomedical studies / Cell Culture
- Advanced Magneto-Optics Lab.
- Magnetic microsocopy Lab.
- Magnetometry Lab.
- Magnetic Hiperthermia Lab.

NANOMAGNETISM GROUP RESEARCH

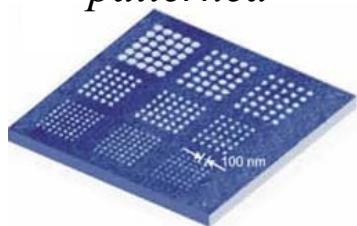
Program 3. Nanomagnetism

Artificial magnetic nanomaterials

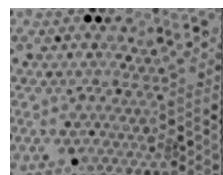
thin films



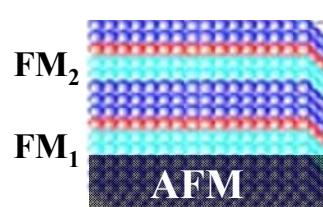
patterned



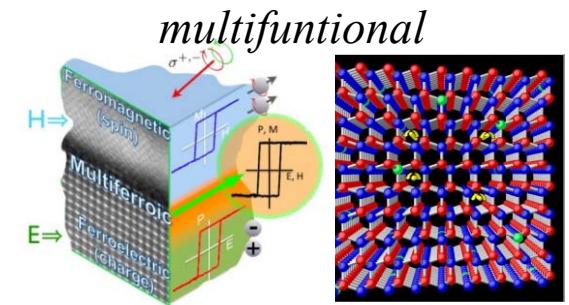
nanoparticles



multilayers

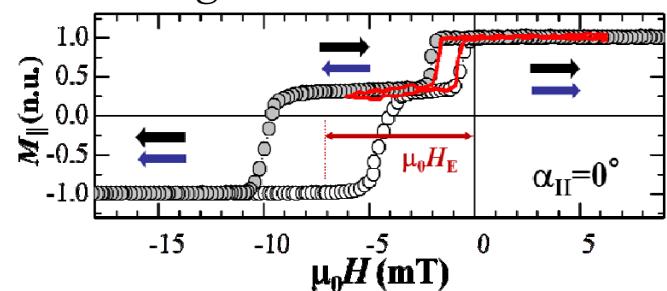


multifunctional

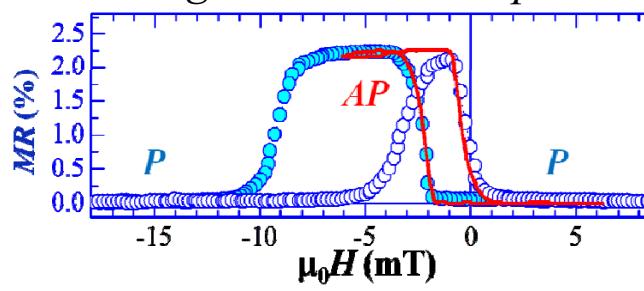


Magnetic & transport properties

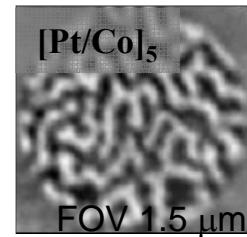
magnetization reversal



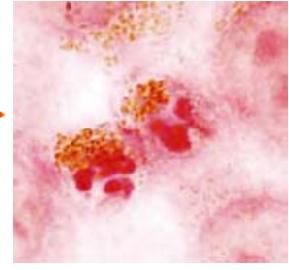
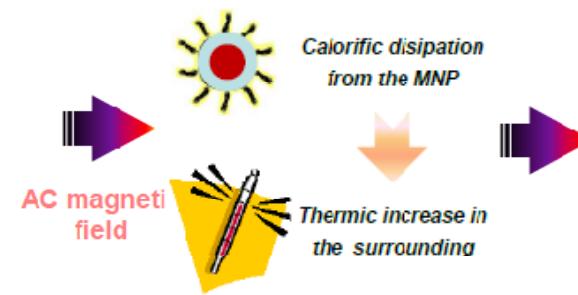
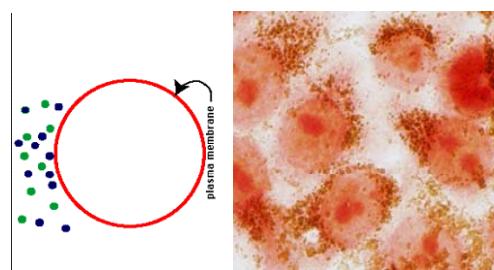
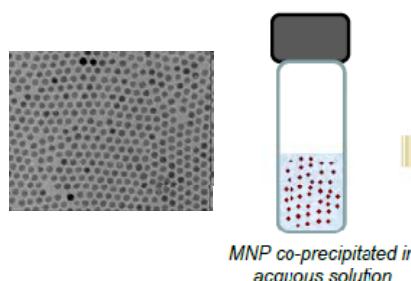
magnetoresistive response



static vs dynamics



Biomedical Applications



NANOMAGNETISM GROUP RESEARCH

Program 3. Nanomagnetism

Artificial magnetic nanomaterials

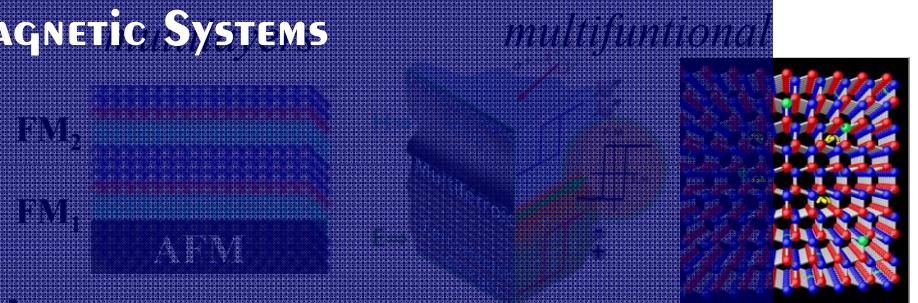
Study of Low Dimensional Artificial Magnetic Systems

thin films

patterned

nanoparticles

- Growth Modes
- Crystalline Structure
- Electronic Structure



Magnetic & transport properties

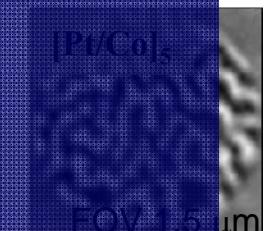
- Magnetic Properties: static vs dynamic



- Transport Properties

- Magneto-caloric Properties

static vs dynamics



Biomedical Applications

Basic understanding of the growth processes and physical properties of new materials as a first step towards the development of devices with custom-chosen properties

MNP co-precipitated in aqueous solution

