



NanoMaterials

Nanometer-(nm)-The unit

$$1\text{nm} = 1\mu \text{ m}/10^3 = 10^{-9} \text{ m.}$$

Nano-materials: At least, one dimension of object on the nanometer size scale 1-100nm.

**Nanoparticle (0D), Nanowire (1D),
Nanofilm (2D), Nanocrystallite(3D)**
**Composites : At least one composition is
nanomaterial. Nanoarchitectonics**

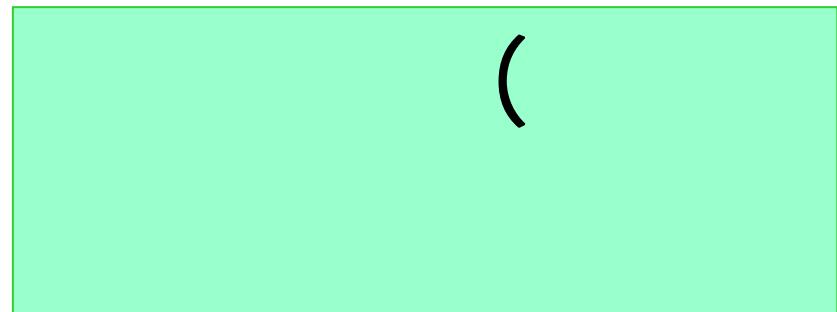
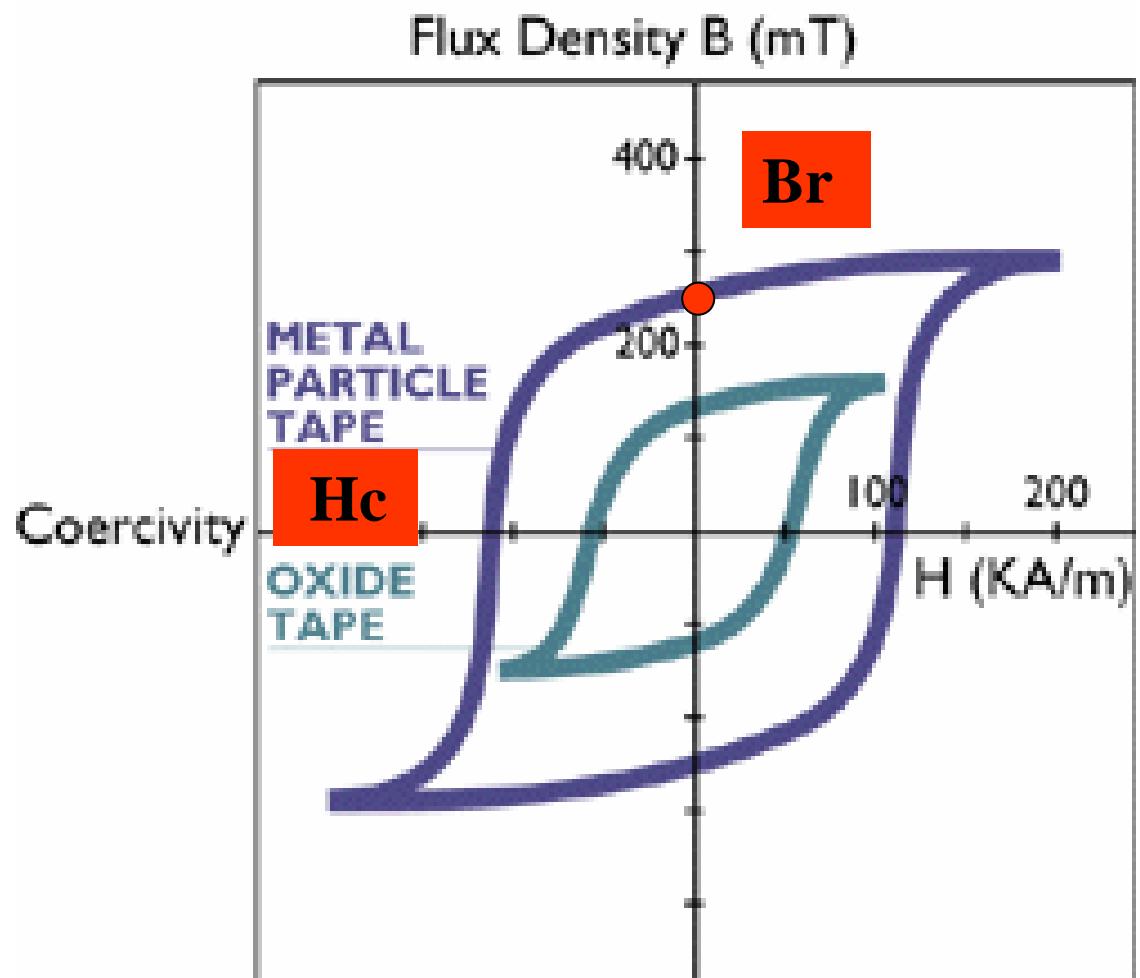
Characteristic Physical Length-L_{ch}

Magnetic single domain	10nm	1μ
Superparamagnetic	1	10nm
Exchange correlation length	10-40nm	
Mean free path of electron	1	10nm
Spin diffusion length	10nm-	1μ
Wave length of light	400/700nm	

Small size effect; Quantum size effect;

MQT (Macroscopic quantum tunneling)

Surface effect $S_V = S/V \sim 1/d$



().Magnetic Nano particles & Applications

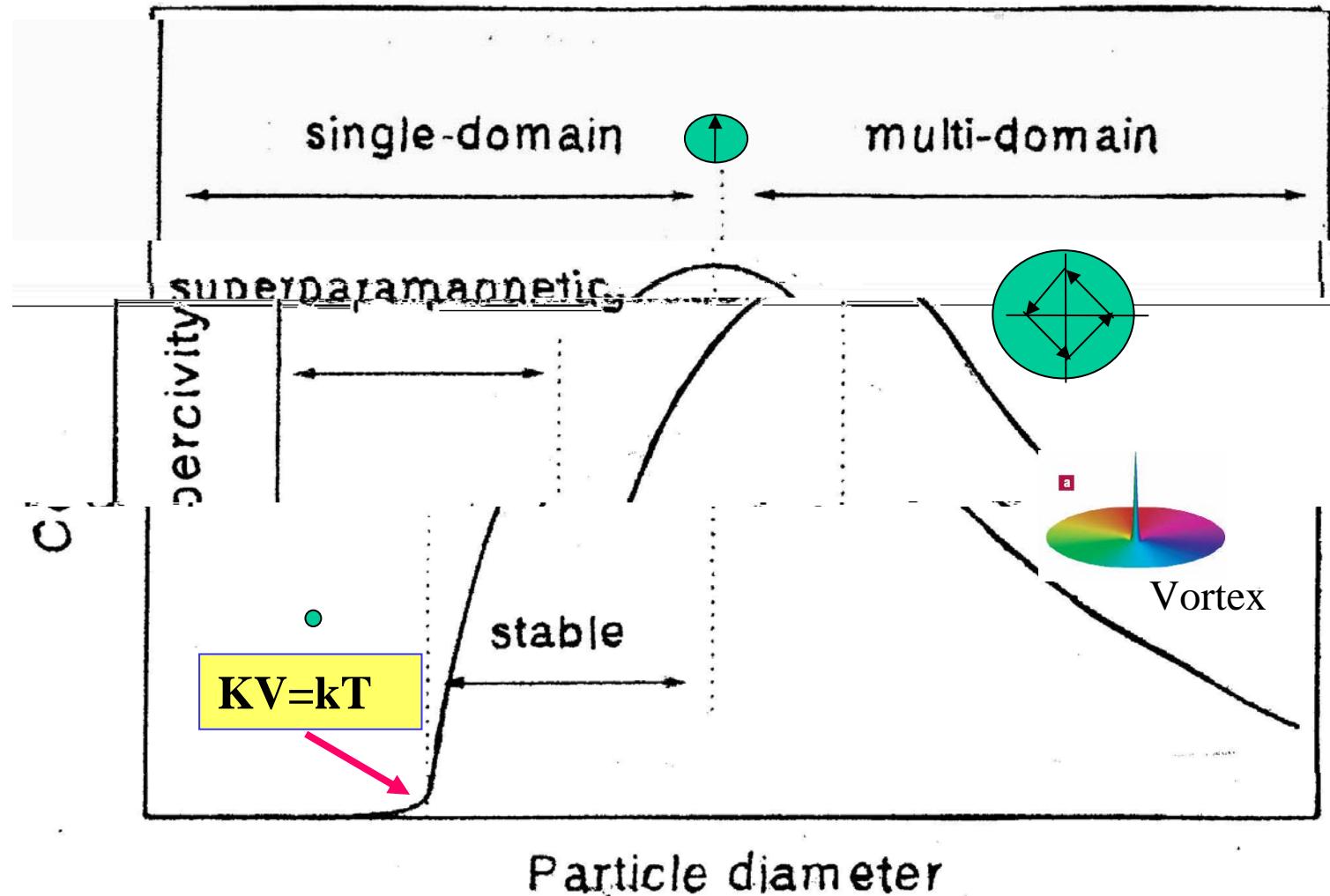


Fig. 1. Size dependence of coercivity.

The characteristic physical length

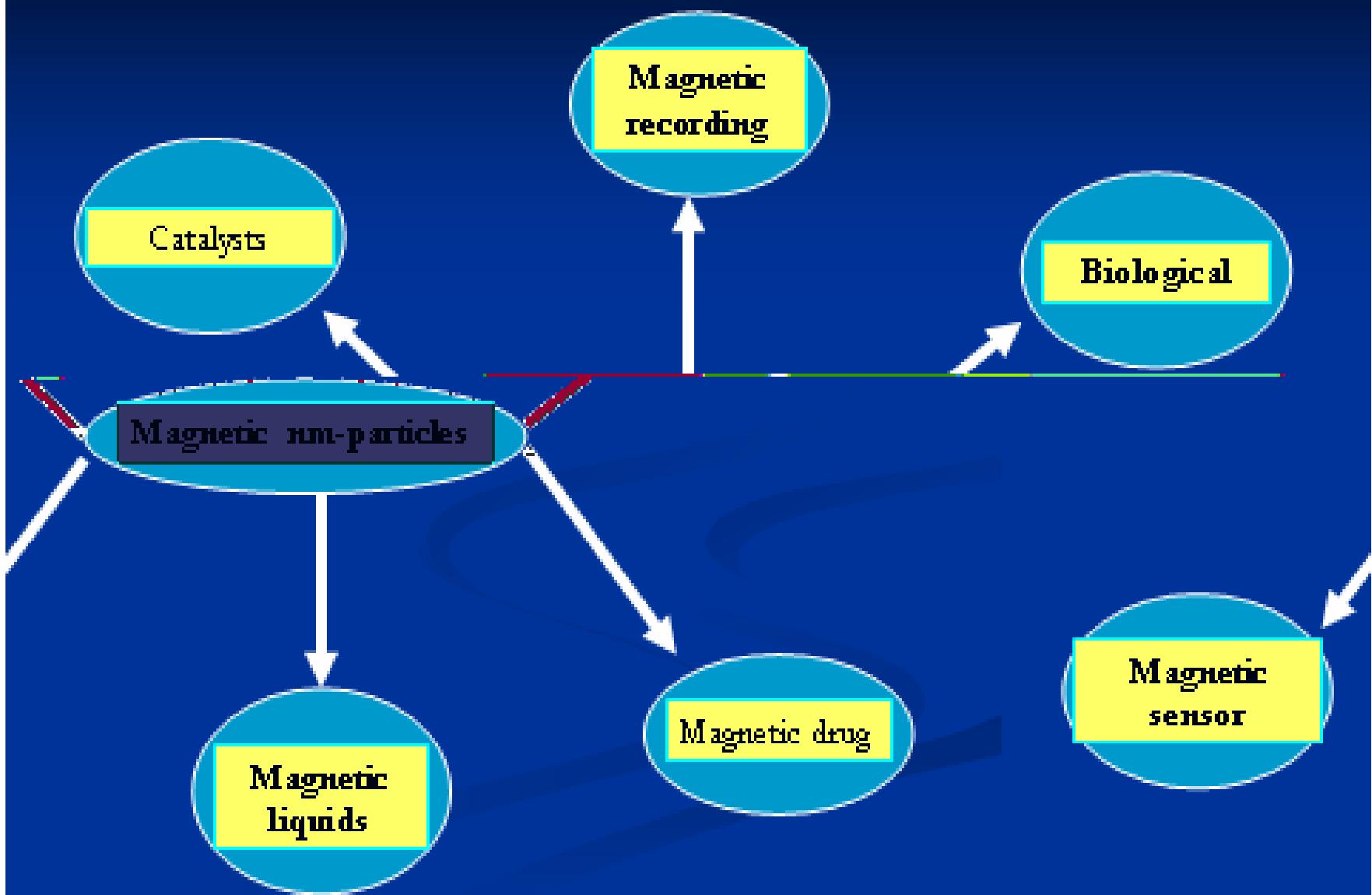
$$* \text{ Single domain : } R_c \propto (AK)^{1/2}$$

M	Fe	Co	Ni	BaM	Nb ₂ Fe ₁₄ B	SmCo ₅	Sm ₂ Co ₁₇ N _{2.3}
Rc (nm)	8.0	11.4	21.2	450	125	400	180

$$* \text{Superparamagnetism: } KV = 25k_B T_B$$

M	Fe ₃ O ₄	Ni	Fe	Co
D(nm)	10	4.0	6.3	5
T _B (K)	300	25	78	55

The Applications of Magnetic Nano-Particles



Nanomedicine

Targeted drugs for lung cancer

The aerosols containing magnetic nanoparticles with drugs can be guided to specific regions in the lung of mice with an external magnetic field. With this technique, higher doses of drugs can be delivered to the cancerous region without increasing side effects.

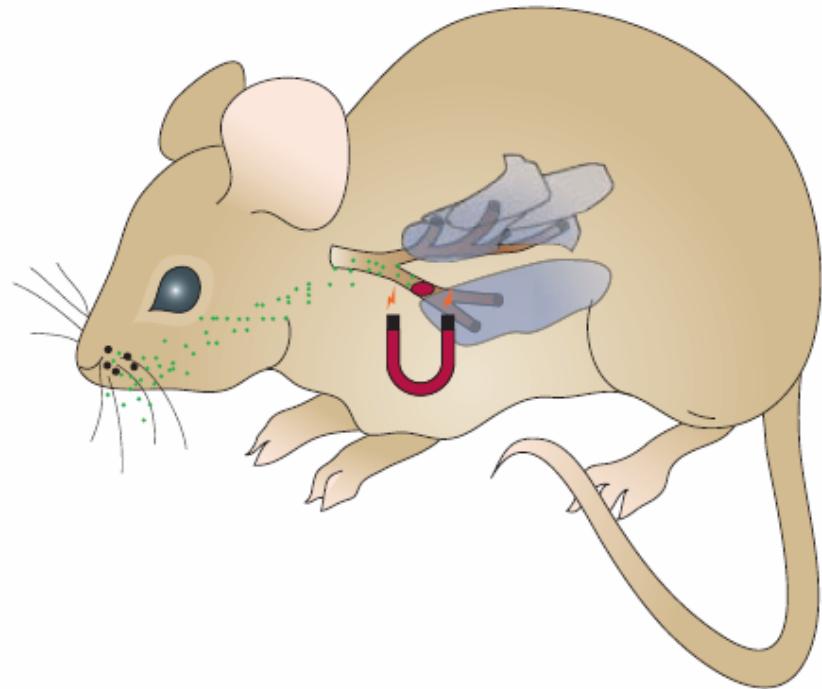
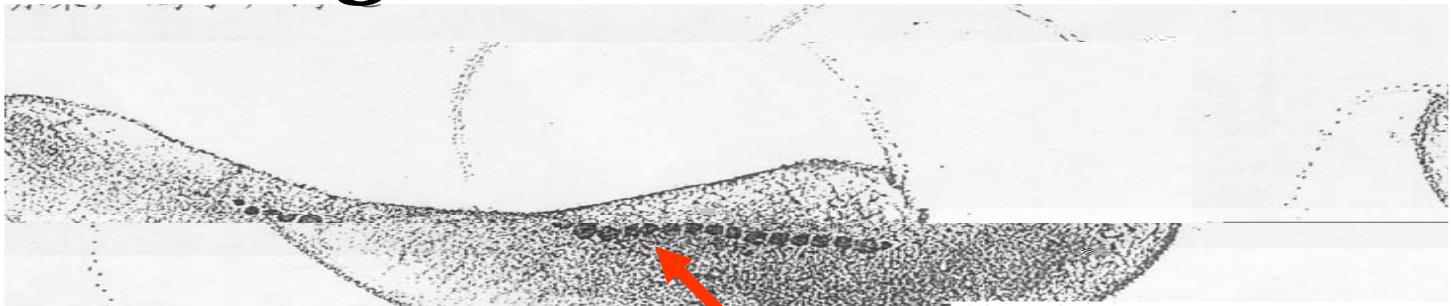
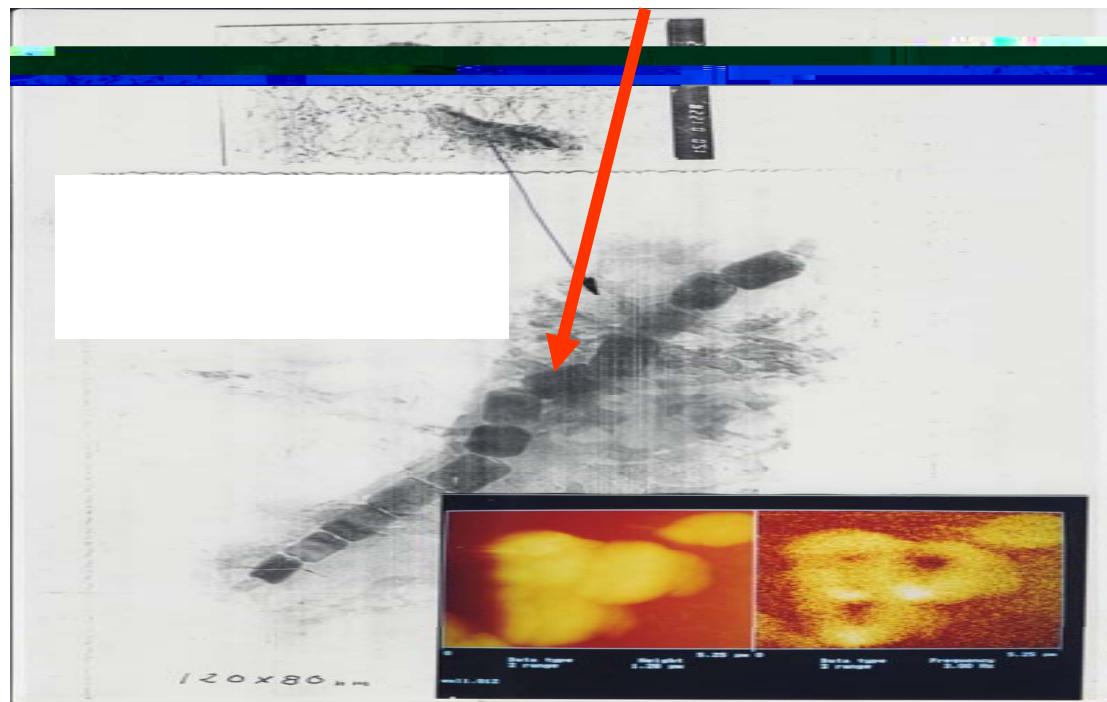


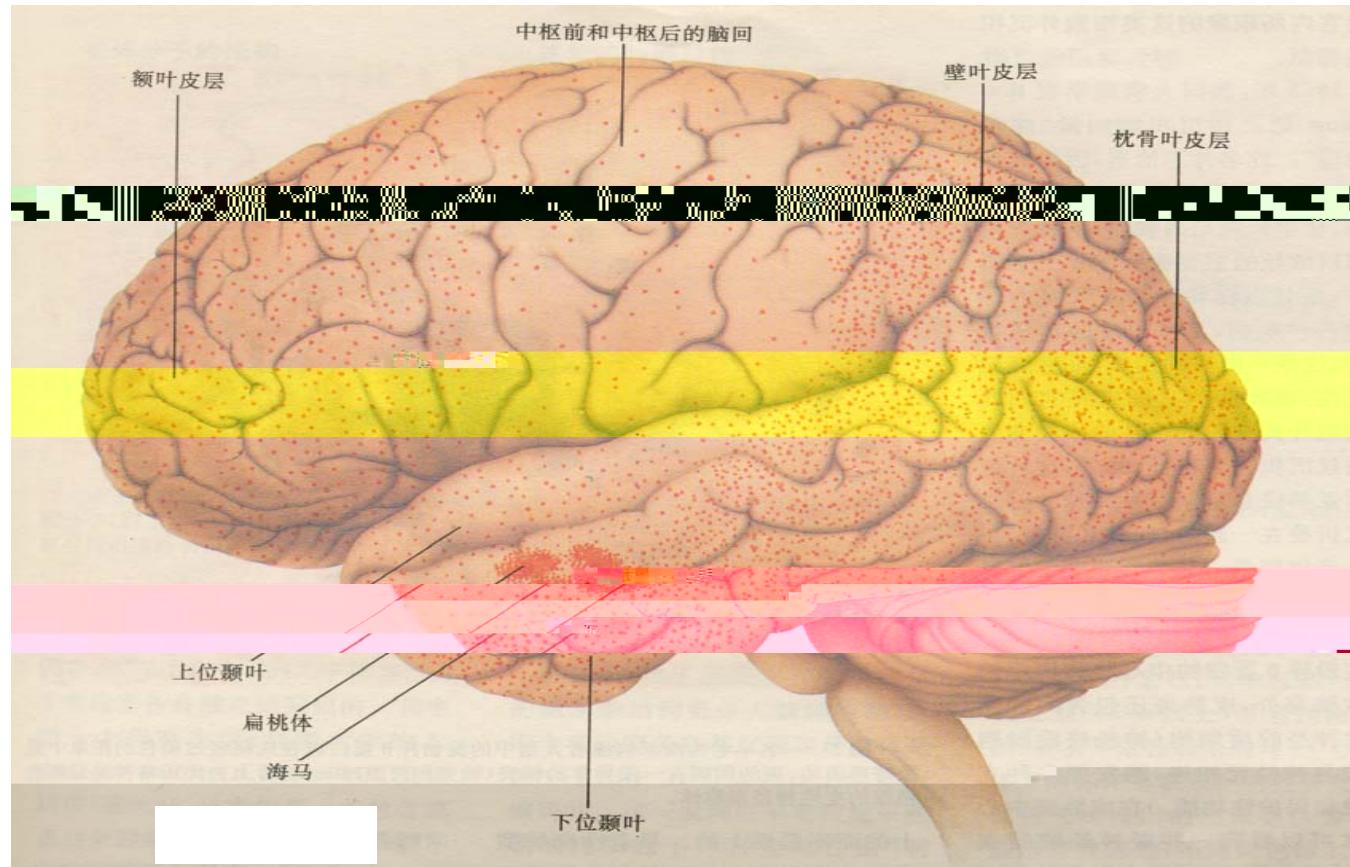
Figure 1 Magnetic-field guided drug delivery with magnetic aerosols. Superparamagnetic nanoparticles are placed in microdroplet aerosols (green) and delivered along the airways (brown) toward the lungs (grey). A localized magnetic field causes large numbers of nanoparticles to accumulate in a specific region, shown here in red.

Magnetotactic bacteria



Magnetic nanochain assembled by magnetosome





500

**The first product in nano-materials is
“Ferrofluid” in 1965.**



Magnetic liquid(Fe_3O_4)

Interface for magnetic particles with Core/shell structure

- **Antiferromagnet (AFM) / Magnetic particle**
- **Ferromagnet (FM) or Ferrimagnet (FIM)/
Magnetic particle**
- **Nonmagnetic organic, Inorganic or metal
/Magnetic particle**

The functions of the shell

- 1. To control the magnetic properties**
- 2. To prevent grain growth and agglomeration**
- 3. To enhance chemical stability**
- 4. To get some exchange couple effect**

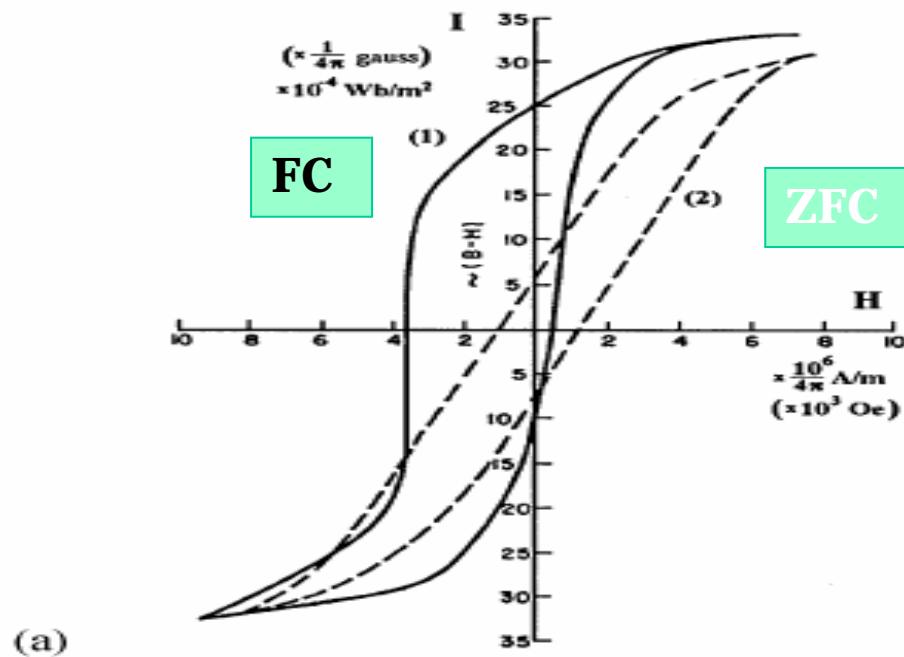
Exchange couple in (Co/CoO) nanoparticles

a). Hysteresis loops at 77K of CoO/Co particles.

(1). After cooling the sample in a 10kOe field. (2).ZFC

$$F = HM_S \cos - K_U \cos + K_1 \sin^2 ,$$

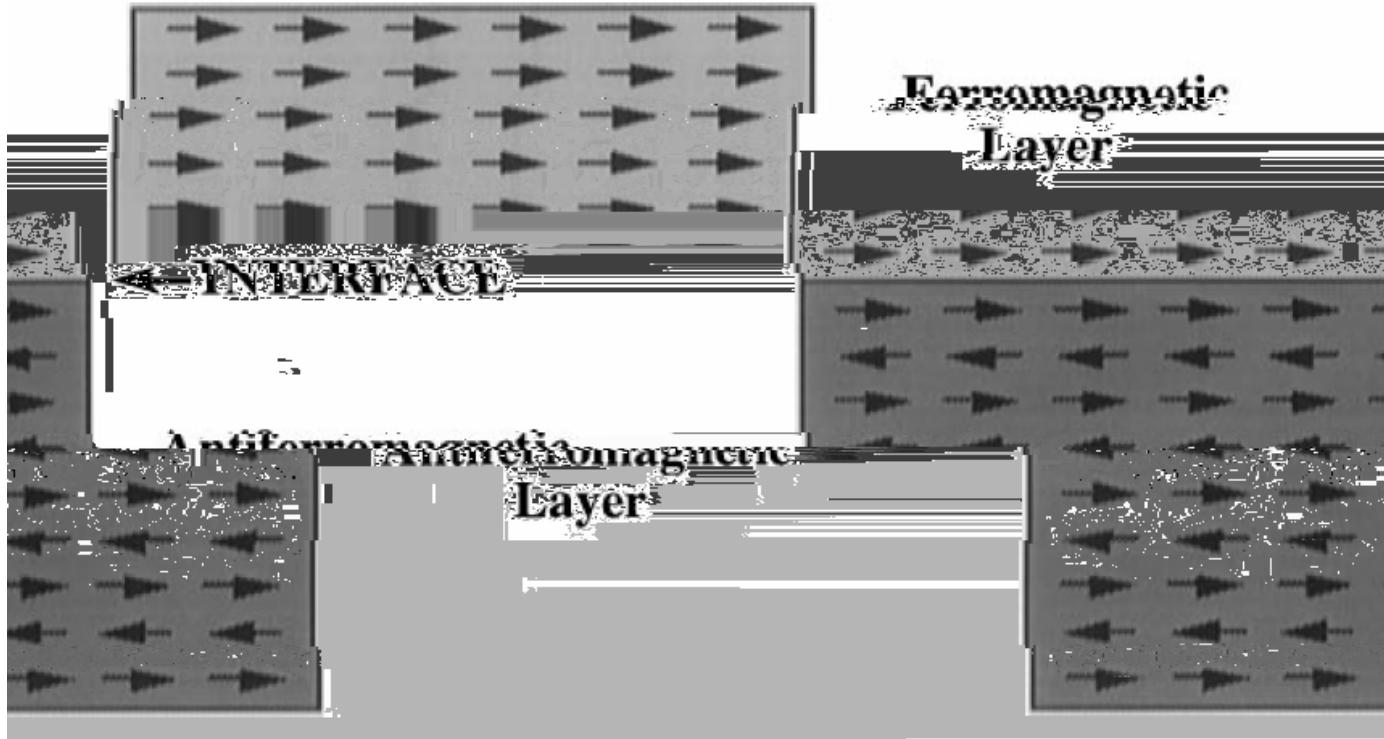
K_U unidirectional anisotropy energy constants.



FM/AFM

Co/CoO

T_N=293K



Schematic of the ideal FM/AFM interface

$$H_E = \frac{\Delta\sigma}{M_{FM}t_{FM}} = \frac{2J_{ex}S_{FM} \cdot S_{AFM}}{a^2 M_{FM} t_{FM}},$$

	CoO	NiO	CuO	Ir-Mn	Pt-Mn	Rh-Mn	Fe-Mn
T _N (K)	293	525	453	600-750	485-975	850	425-525

The surface spin of antiferromagnet can either be compensated (the magnetic moments with the atomic surface layer cancel out) or uncompensated

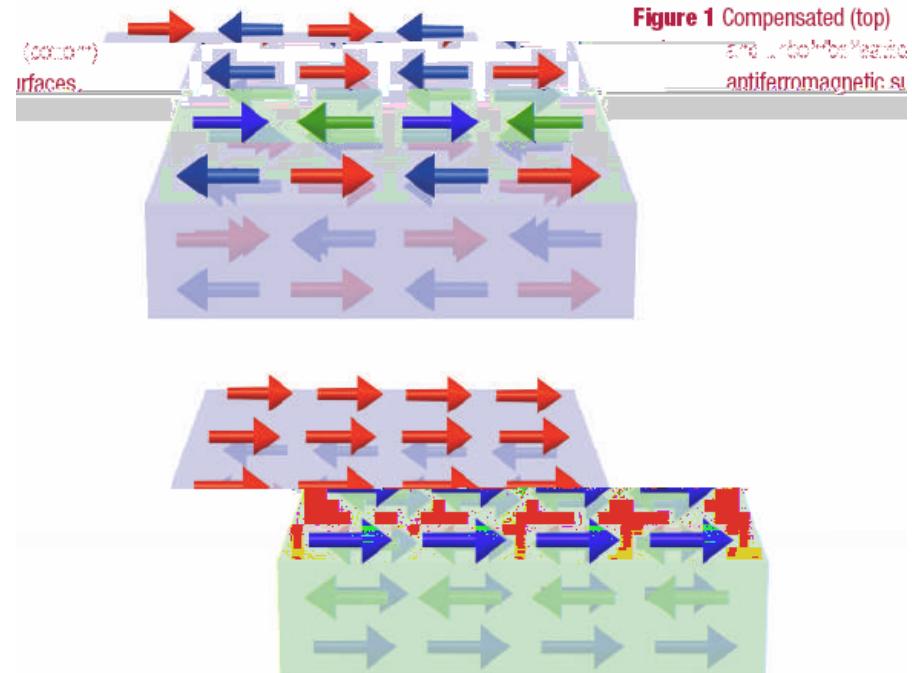
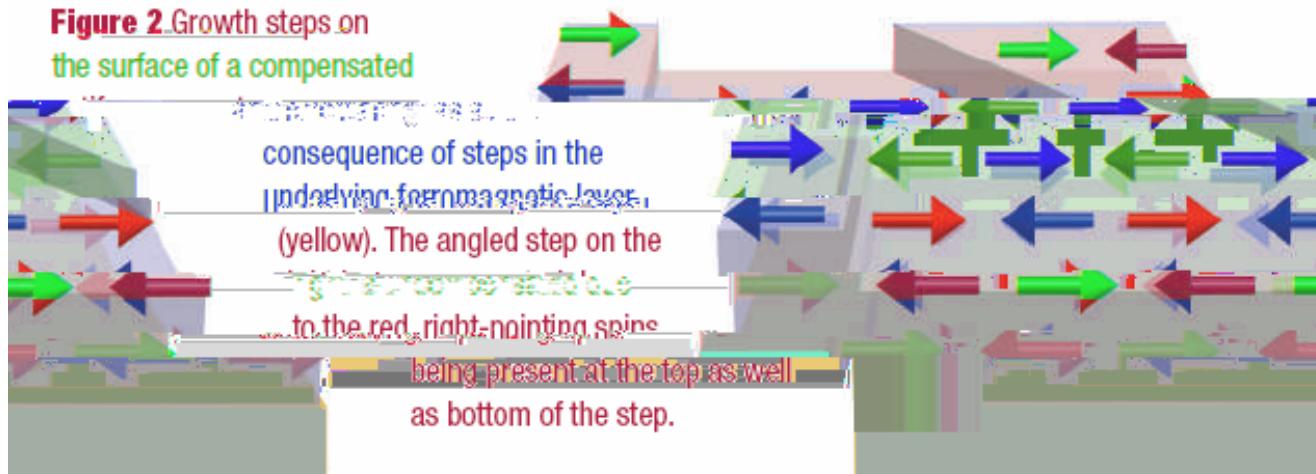


Figure 2 Growth steps on the surface of a compensated



Beating the superparamagnetic limit with exchange bias

The blocking temperature , T_B , increases almost two orders magnitude for 4nm Co/CoO nano particles in the CoO matrix. This leads to a marked improvement in thermal stability. This mechanism provides a way to beat the superparamagnetic limit in isolated particles.

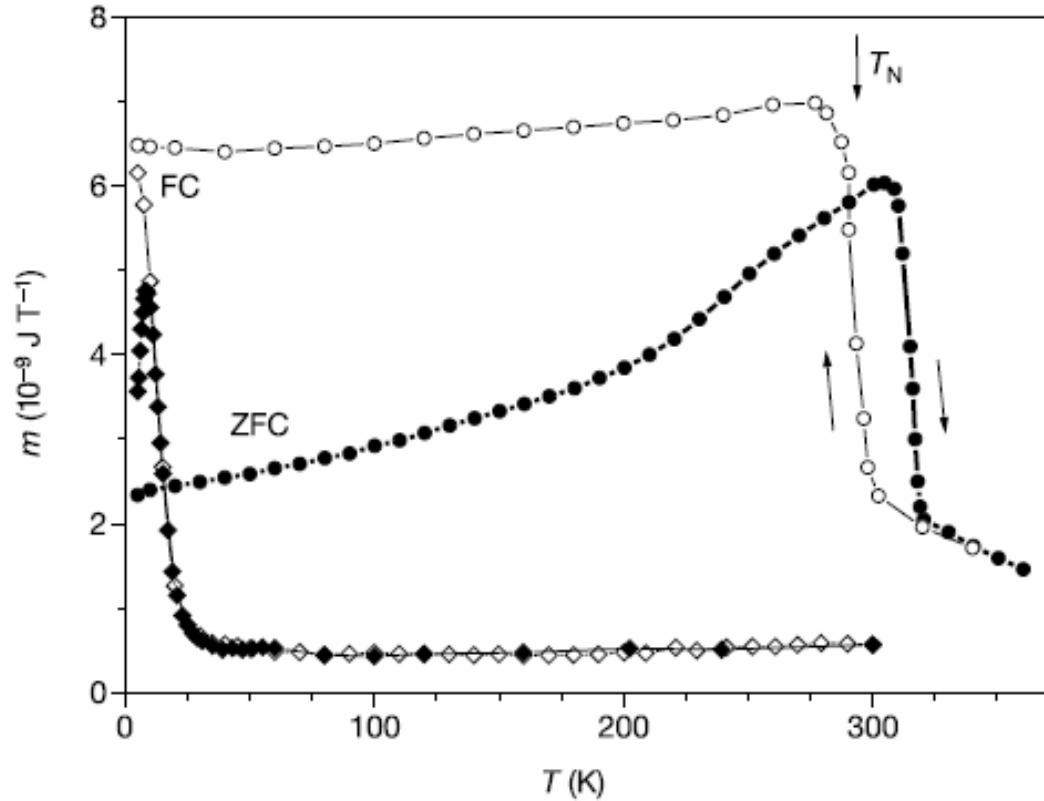
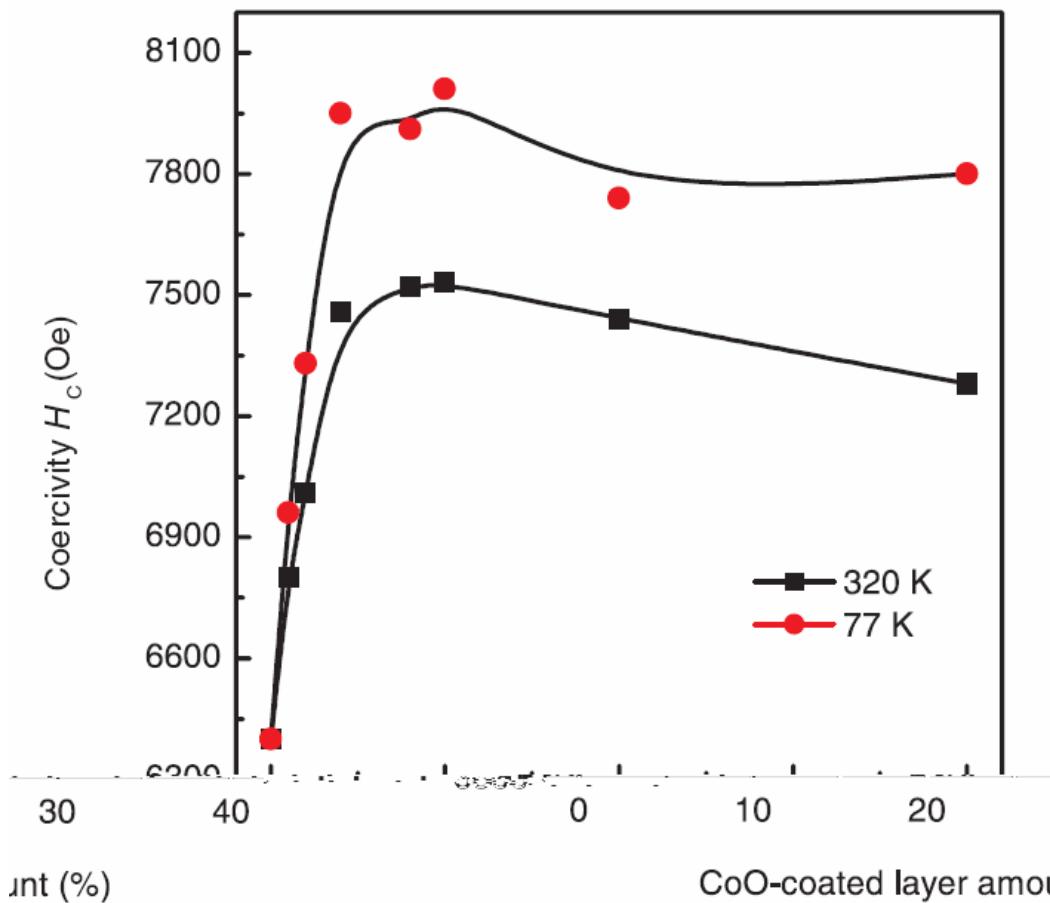


Figure 2 Magnetic moments of 4-nm $\text{Co}_{\text{core}}\text{CoO}_{\text{shell}}$ particles. Shown is the temperature dependence of the zero-field cooled (ZFC; filled symbols) and field-cooled (FC; $\mu_0 H_{\text{FC}} = 0.01 \text{ T}$, open symbols) magnetic moment (m) of 4-nm $\text{Co}_{\text{core}}\text{CoO}_{\text{shell}}$ particles. m decreases from a paramagnetic (Al_2O_3) matrix (diamonds), or in an AFM (CoO) matrix (circles). The measuring field is $\mu_0 H = 0.01 \text{ T}$. The Néel temperature of CoO is indicated by an arrow. The lines are guides to the eye.

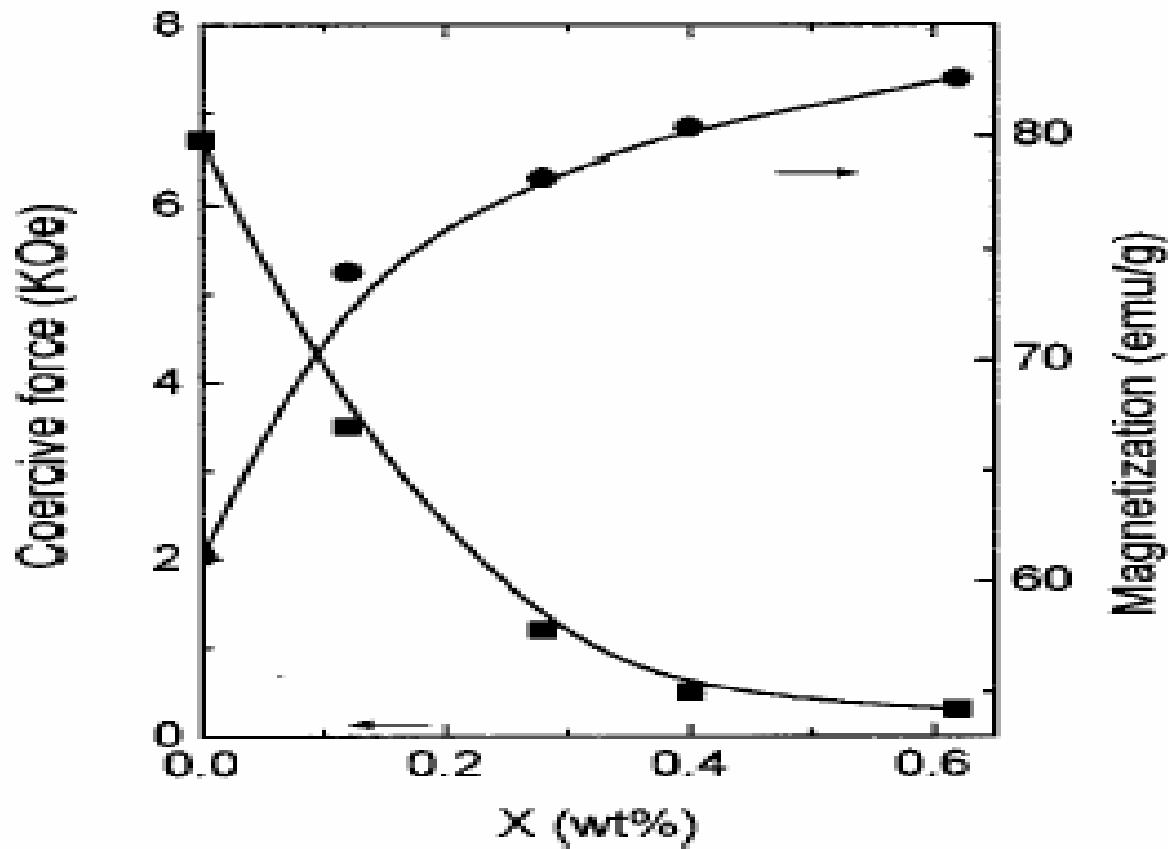


1. $\text{SrFe}_{12}\text{O}_{19} / \text{CoO}$

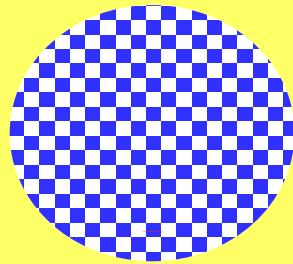


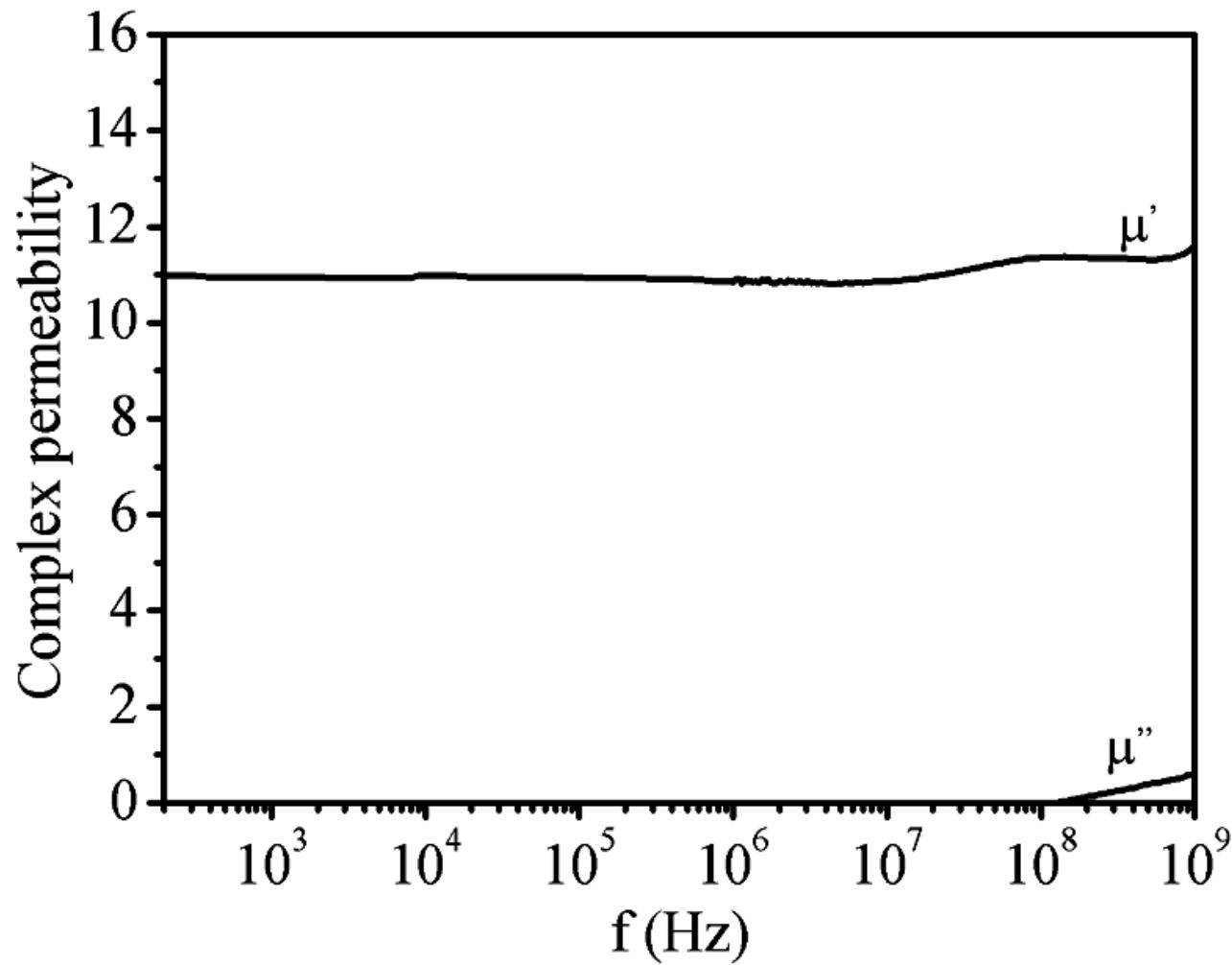
H_c sharply increases for small CoO content, then reaches a maximum at 10% of the coating amount

2. SrM / Fe₃O₄



SrM particles coated with soft magnetic materials Fe₃O₄ , Ms increases and Hc decreases very obviously with the rise of Fe₃O₄ coating . The Hc can be controlled by coated quantity.





The permeability spectra of $\text{Fe}/\text{SiO}_2/\text{C}$ particles sample at room temperature

). Magnetic Nanocrystalline Materials

- The nanocrystalline material is composed of nanocrystallines. It may be considered as a densely assembly of nano-particles which are interacted through interface.
- Huge interface
- Interaction
 - Exchange interaction
 - Magnetic interaction

Exchange length , $L_{ex} = (A/Ms^2)^{1/2}$. (within L_{ex} the spins of ferromagnet remain parallel, $L_{ex} 1-6$ nm)

Domain wall width, σ ,

$\sigma = (A/K)^{1/2}$. (exchange correlation length or domain wall parameter, the distance over which the variations of the spin orientation are correlated)

σ **L_{ex} (for hard magnets, while , $\sigma \gg L_{ex}$ for soft magnetic materials)**

Single domain size for a sphere, $R_{SD} = (AK)^{1/2}$

	L_{ex} (nm)	σ (nm)	D_{SD} (nm)	J. Nogués et al., Physics Reports, 422(2005)65-117
Fe	1.5	40	18	
Co(hcp)	2.0	12	70	
Ni	3.4	80	60	
$Ni_{80}Fe_{20}$	4.0	100	22	
$SmCo_5$	4.9	4.0	764	

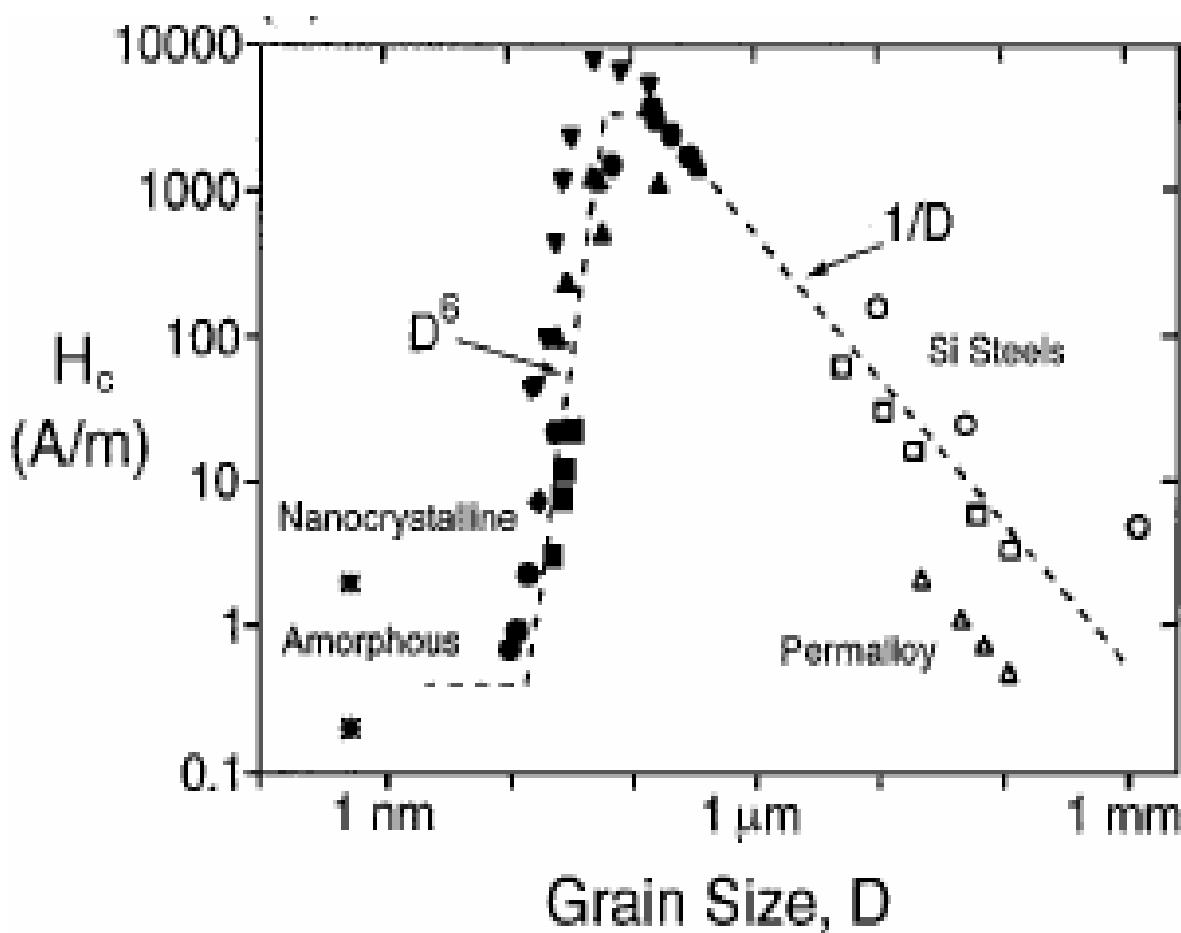
(2.1). Nano-Crystalline Soft Magnetic Materials

- The progress of soft magnetic materials
- Fe
- FeSi(1900)
- FeNi(1920)
- Ferrites (1935-1946)
- Amorphous (1970)
- Nano-Crystalline Soft Materials

Magnetic nanocrystalline system. FM/FM interface

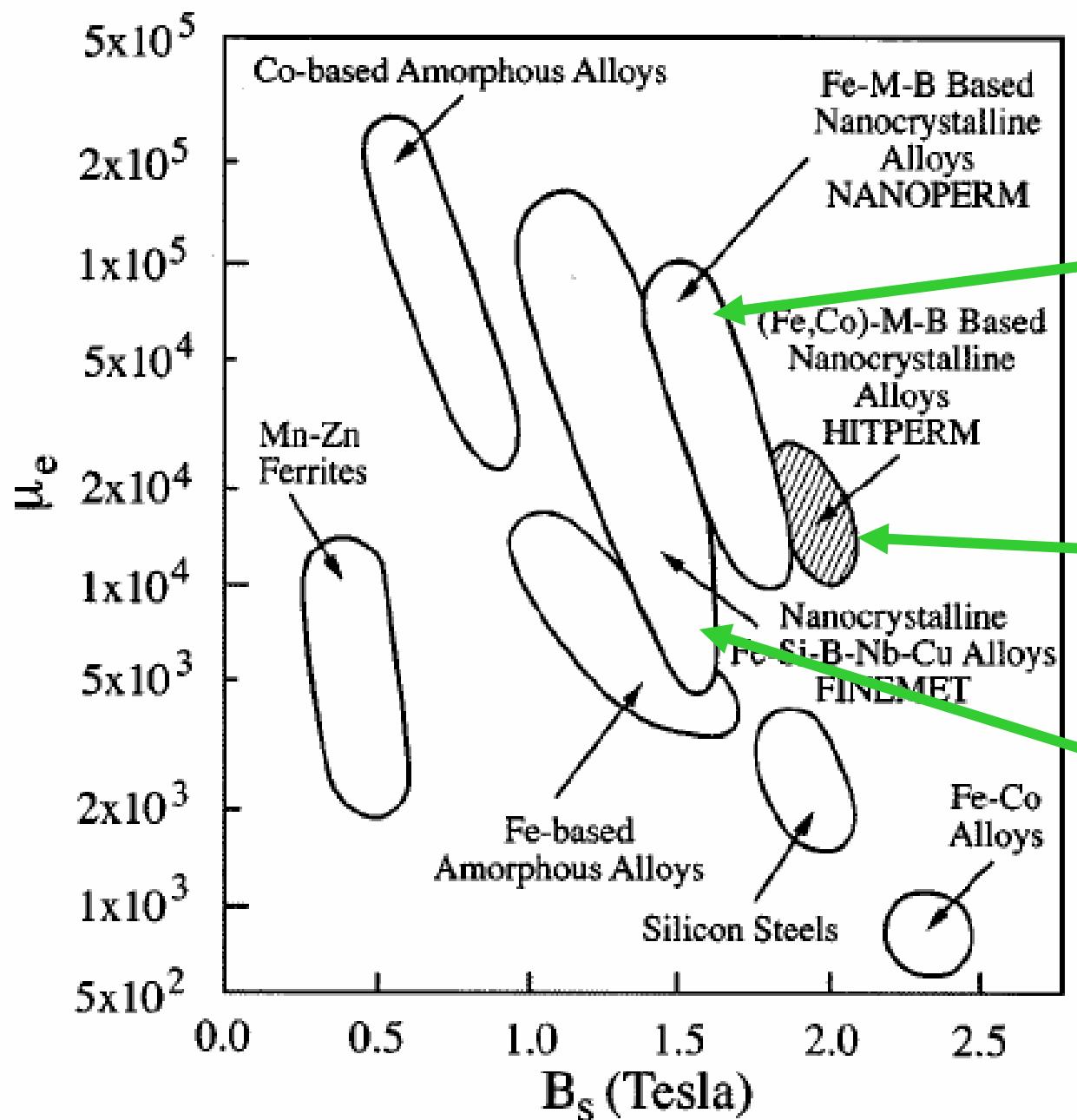
Random anisotropy theory---Herzer
JMMM.294(2005)99

$$L_o = (A/K)^{1/2}, \text{ If } D < L_o,$$
$$K_e = K/N^{1/2},$$
$$N = (L_o/D)^3$$
$$H_c \sim D^6$$



M	-Fe	-Fe _{amr}	Nd ₂ Fe ₁₄ B	SmCo ₅	Sm ₂ Fe ₁₇ N
L _o (nm)	23	35	2.1	5.2	2.6

Commercial Nanocrystalline Alloy

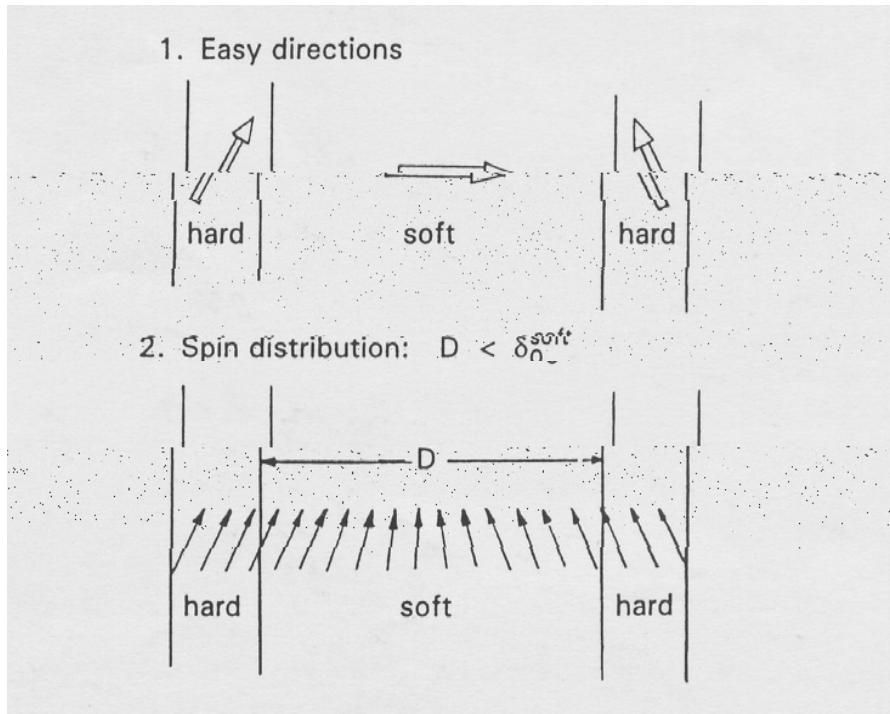


2. NANOPERM
Fe-M-B-Cu
(M=Zr,Nb,Hf--)

3. HITPERM
(FeCo)-M-B-Cu

1. Finemet (1988)
Fe_{73.5}Si_{13.5}B₉Nb₃Cu₁

(2.2). Nanocomposite exchange coupled magnets



Remanence:

$$M_r/M_s > 1/2$$

Reduced the quantity of rare earth element

Ms;Tc;K for some soft and hard magnetic materials

	Fe	Ni	Co	Fe ₂ Co	SrM	NdFeB
Ms(kA/m)	1714	484	1422	1933	370	1281
Tc (K)	1043	631	1404		733	585
K(kj/m ³)	42	-51	530		370	4400

- ♠ Saturation magnetization Ms Hard < soft
- ♠ Anisotropy K : Hard > Soft
- ♠ Nanocomposite exchange coupled of hard and soft phases
maybe have both high Ms and Hc
- ♠ **(BH)m=1 MJ/m³ (120 MG Oe), RE 5 wt % . for
2.4 nm (Sm₂Fe₁₇N)₃ / 9 nm (Fe₆₅Co)₃₅**

The best magnetic properties for
 $(Nd,Pr,Dy)2Fe14B/ -Fe$

$Br = 1.438T (14.38kG)$

$Hcj = 995KA/m (12.5kOe)$

$(BH)m = 405KJ/m^3 (50.97MG Oe)$

DAYTON University

Lee D et al., Proc. Of 18th International Workshop on HPMA(Annecy, france, August-September, 2004). Vol. 2, 667-9\678

Nanocomposite exchange coupled is diffusing to other applications

- 1 Magnetic recording : FePt/FeRh reduced reversely field
- 2 Magnetostriction : TbFe/Fe (FeCo) multilayer reduced Hc

Magnetic Nanowire & Nanotube

- Magnetic nanowires have various applications such as: perpendicular magnetic recording media for high density magnetic recording.
- Sensor in MEMS
- Magnetic multilayered nanowires for CPP-GMR
- The spin diffusion length can be determined.

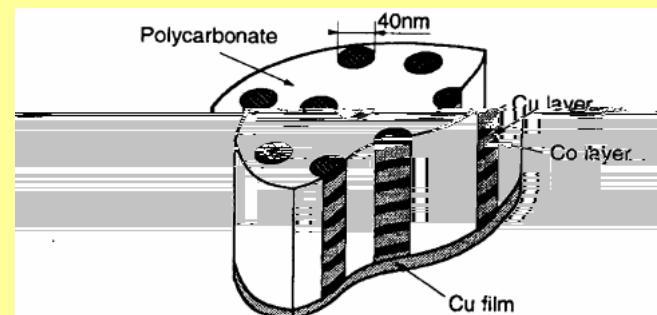
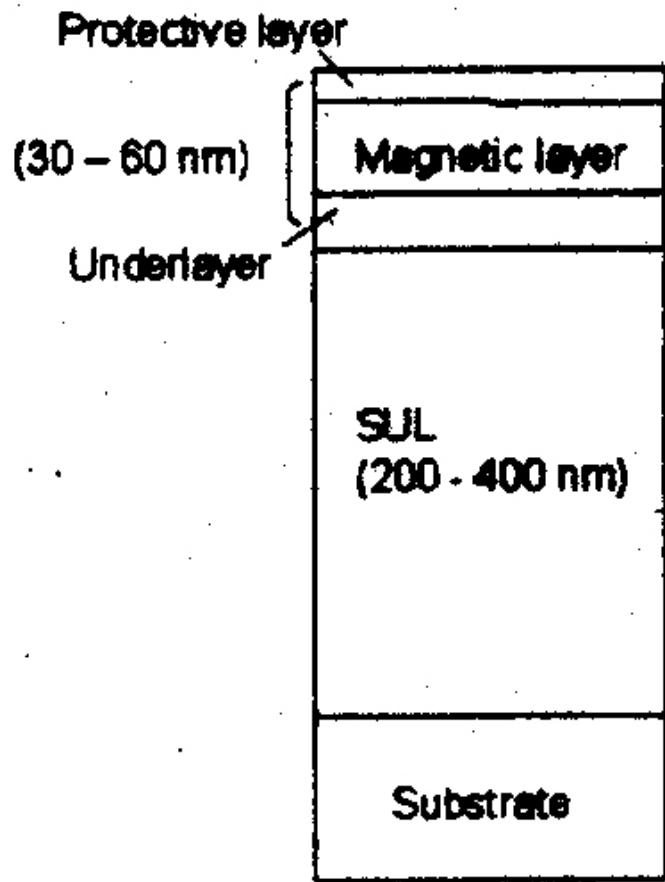
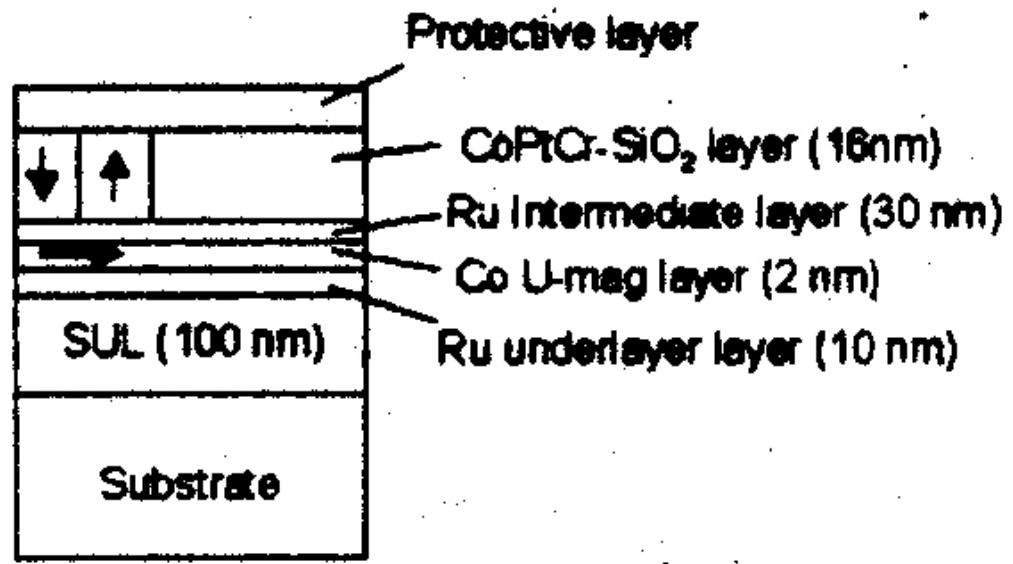


Fig. 1. Schematic of an array of multilayered nanowire nanoporous track-etched polymer membrane.



(a)

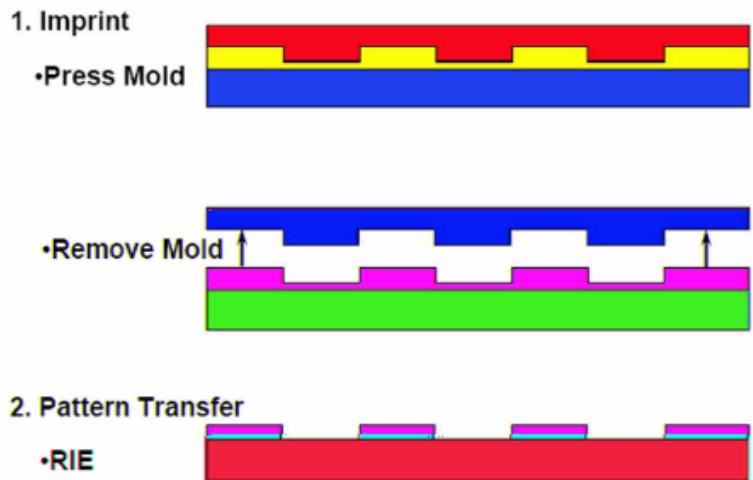


(b)

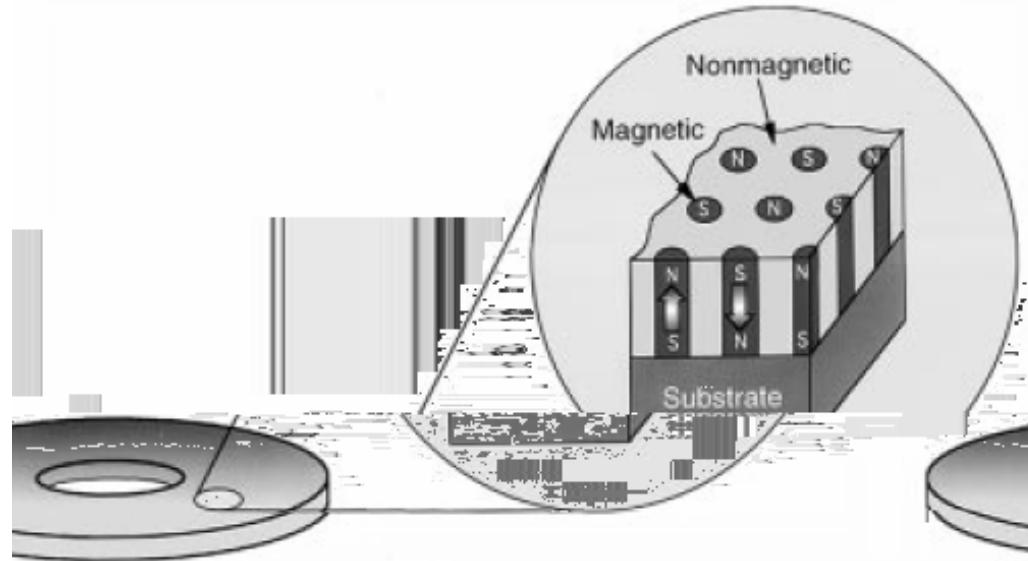
SUL-Soft magnetic underlayer

Fig. 1. Cross-sectional structures of (a) a conventional perpendicular recording and (b) the U-mag media.

Longitudinal to Perpendicular Magnetic Recording model.

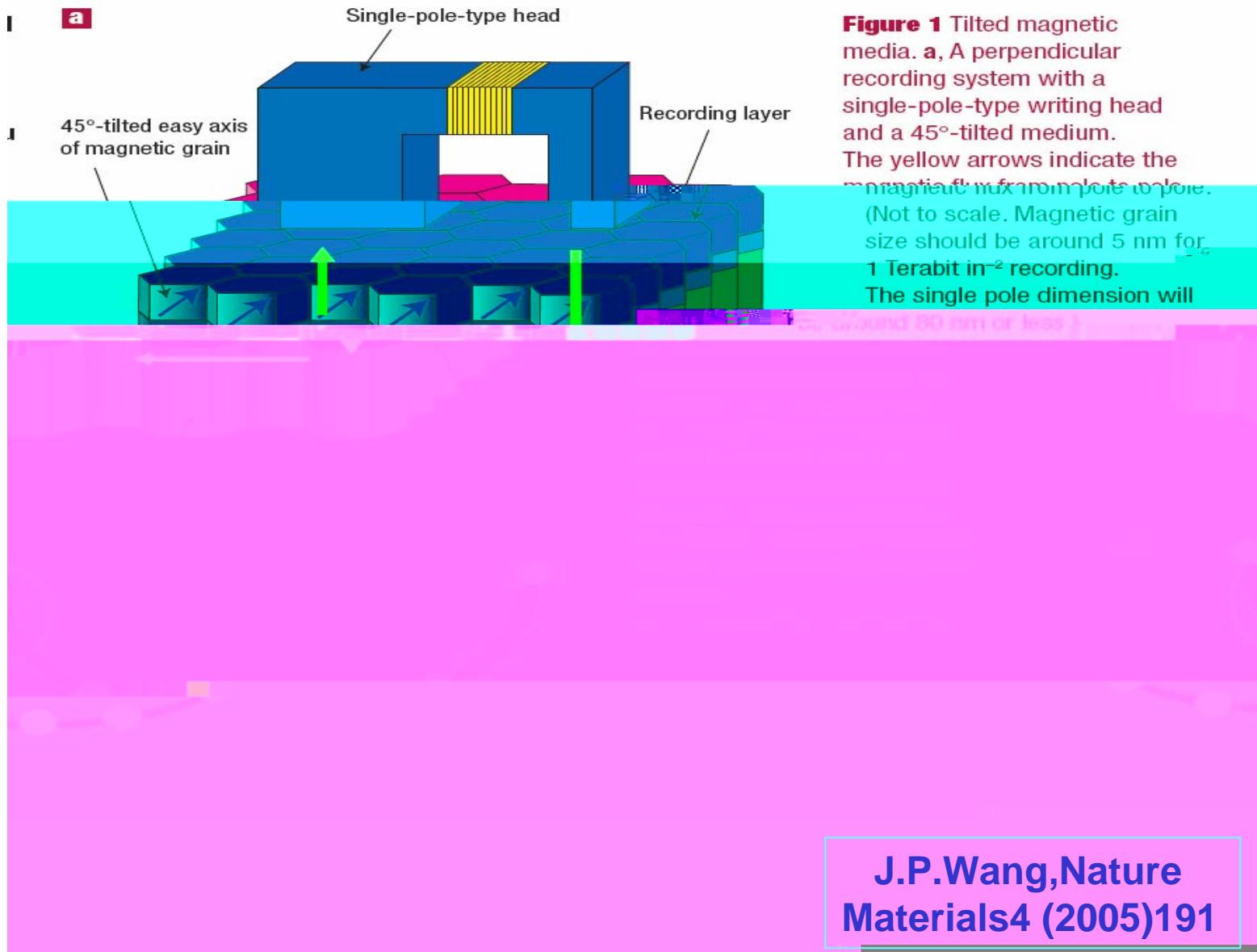


Schematic of nanoimprint lithography consisting of 1).imprint and 2). pattern transfer
For mass production



**Bit –Patterned media
(Quantized magnetic disk)**

Patterned magnetic nanostructures give us new freedom in controlling magnetic material properties.





Fe₄₈C0₅₂ nmwires

**Porous alumina
template**

D~22nm

**Interpore distance~
50nm**

Hc=3.89 kOe

Mr/Ms=0.954

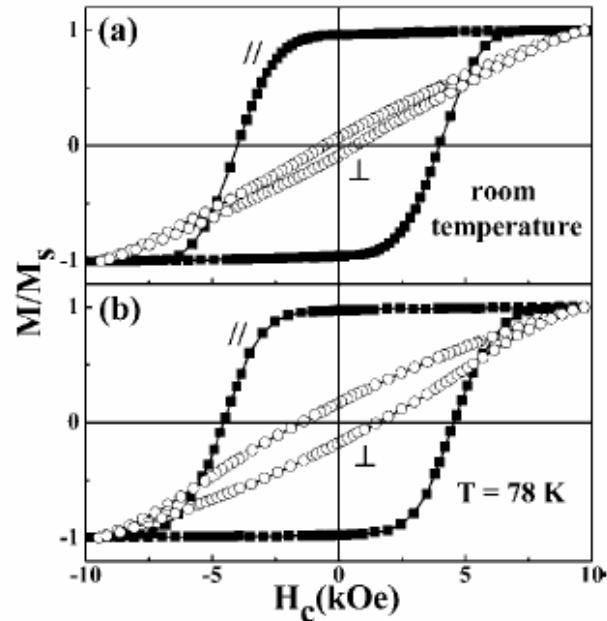
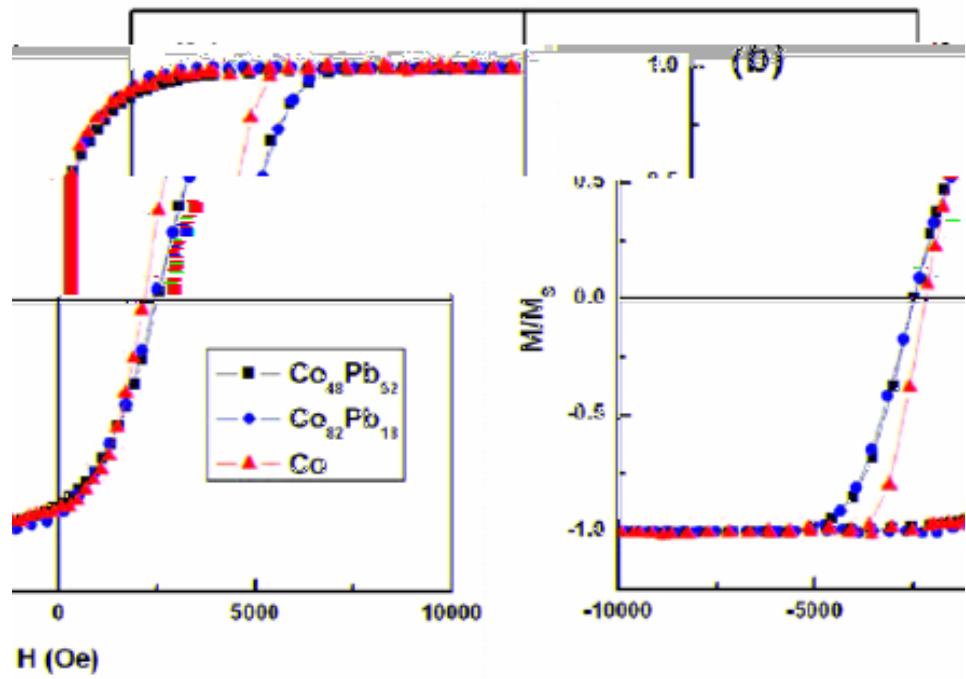


Figure 5. Hysteresis loops of the arrays with a diameter of about 22 nm and an interpore distance of about 50 nm measured at room temperature and 78 K (51).

Co-Pb heterogeneous alloy nanowire arrays



Annealing at 700 with the applied field of 10kOe. D~20nm

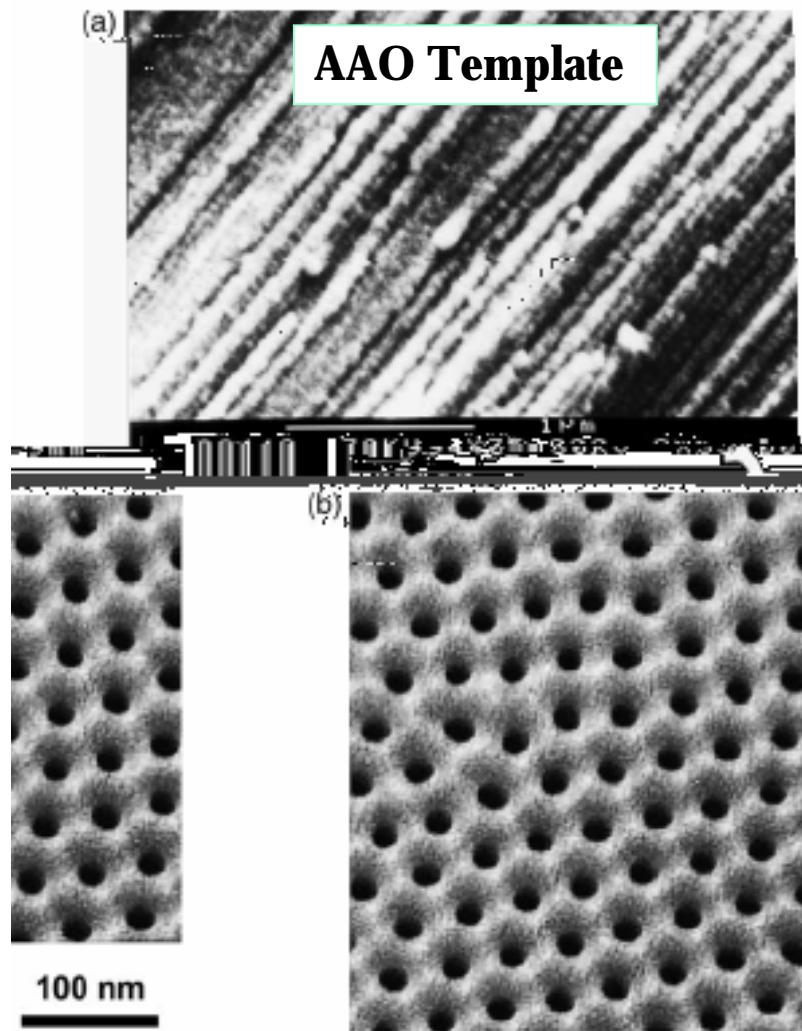


Fig. 1. SEM images of the anodic alumina oxide template with pores of 20 nm in diameter: (a) The cross section view; (b) the top view.

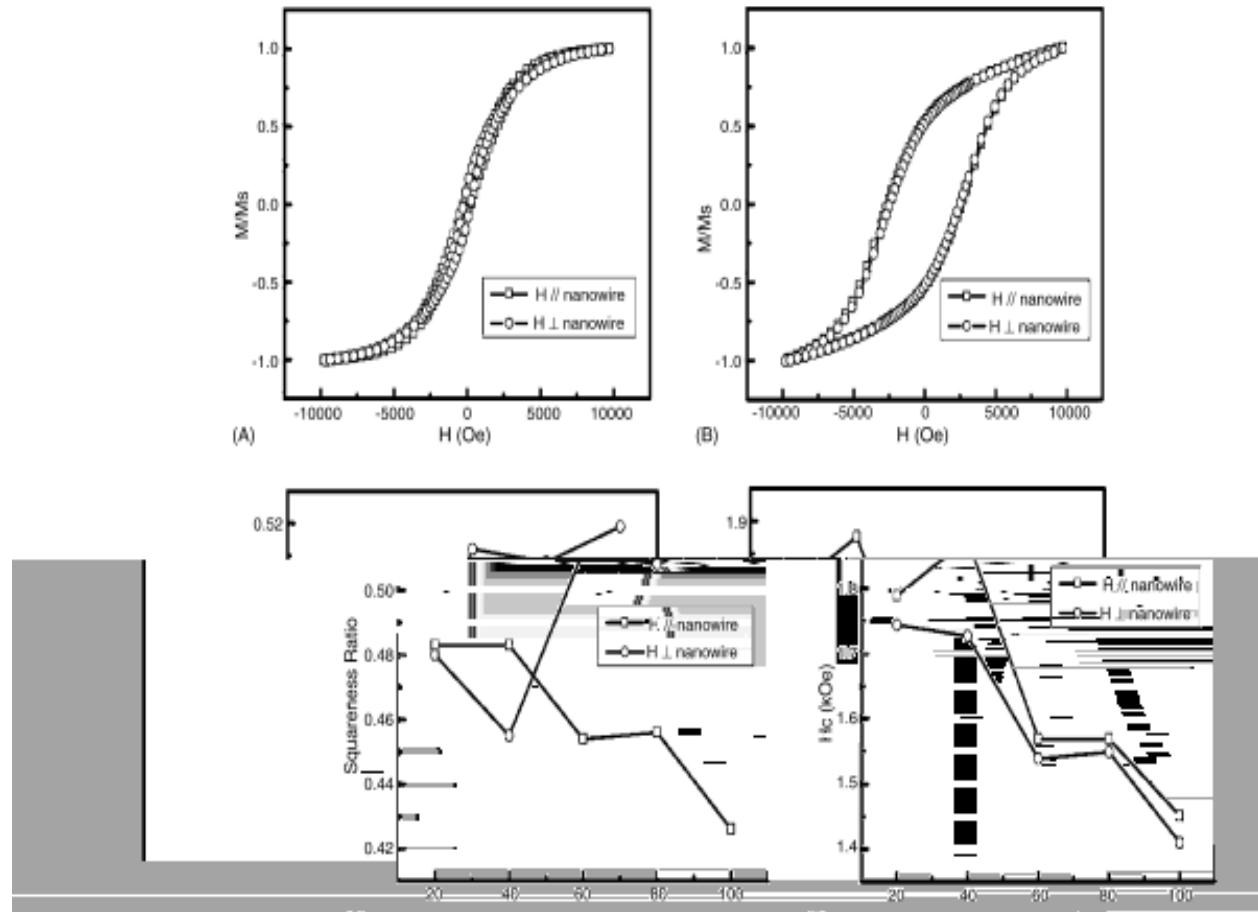
$H_c = 2500\text{Oe}$; $M_r/M_s = 0.9$ for $\text{Co}_{36}\text{-Pb}_{64}$, $T_a = 700$

CoFe_2O_4 nanowire

CoFe_2

nanowire array
prepared by
AAO template-
electrodepositio-
n method and
further
oxidation

CoFe_2O_4 nanowire



function of
widening time
at room
temperature

Fig. 3: Hysteresis loops of nanowire arrays widened for 40 min (c) CoFe_2 and (d) CoFe_2O_4 ; (e) Squareness ratio of CoFe_2O_4 nanowire arrays as a pore widening time; (f) I_c of CoFe_2O_4 nanowire arrays as a function of pore widening time. All templates were dc anodized for 8 h and deposited for CoFe_2O_4 nanowires were annealed at 620 °C for 30 h. The magnetic properties were measured with the applied field parallel and vertical to the nanowire axis.

Magnetic Nano-film, Multlayer

- Films have been an important subject in basic and applied science.
- Thin film
- Granular film
- Multlayer

Spintronics()

- Electrons have both charge and spin two degree of freedom.
- Microelectronic industry is solely based on the charge degree of freedom of electrons.
- Spintronics is a spin- based electrons .
- From physical point if enhance spin degree to the electronic devices, marvelous new devices based on the spintronics should be produced.
- The charge currents may be replaced by the spin currents in the future electronic devices.

2007



Peter Grünberg
(1939- 5-18)

Albert Fert
(1938-3-7)

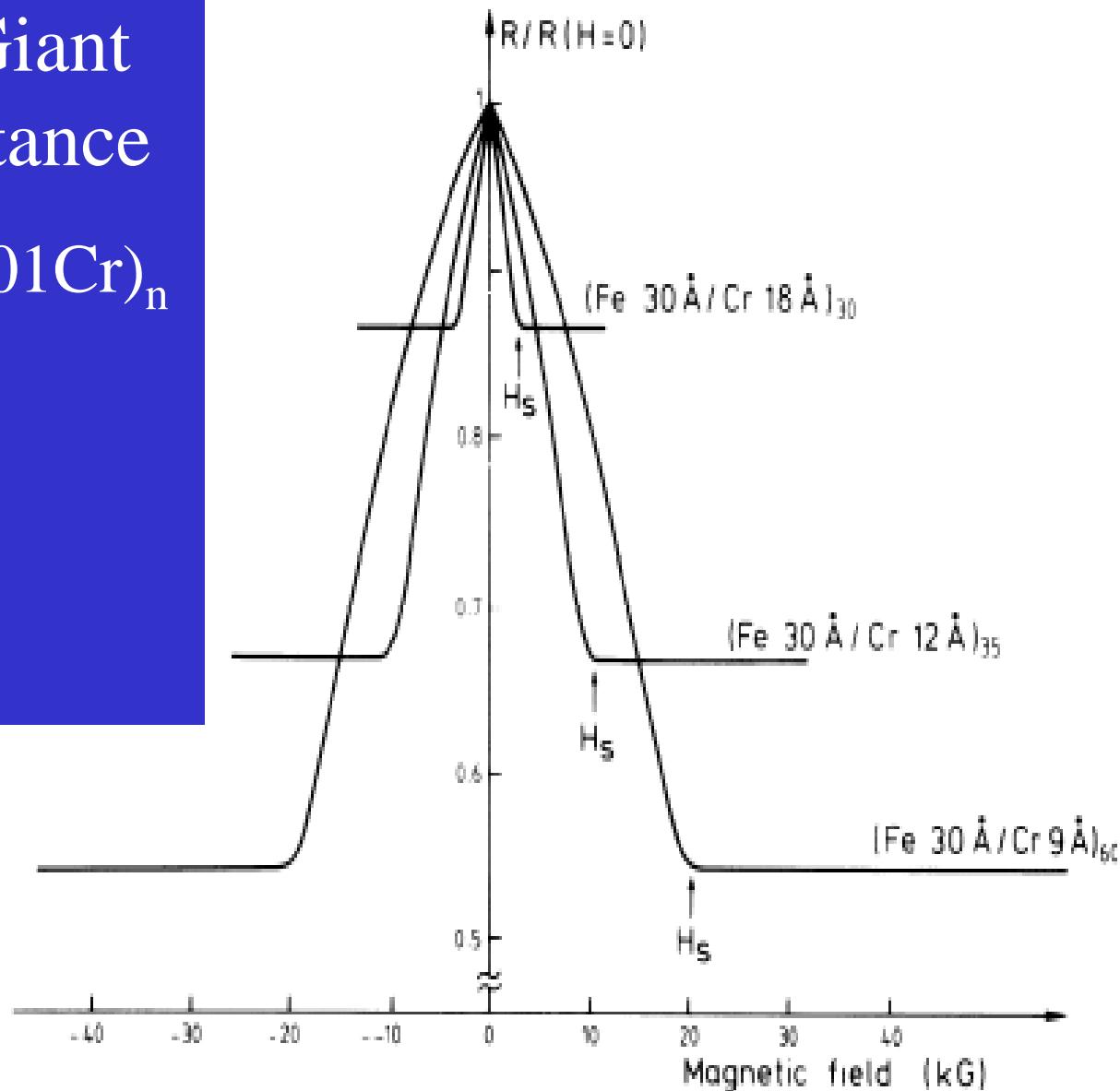
GMR—Giant Magnetoresistance

(GaAs/001Fe/001Cr)_n

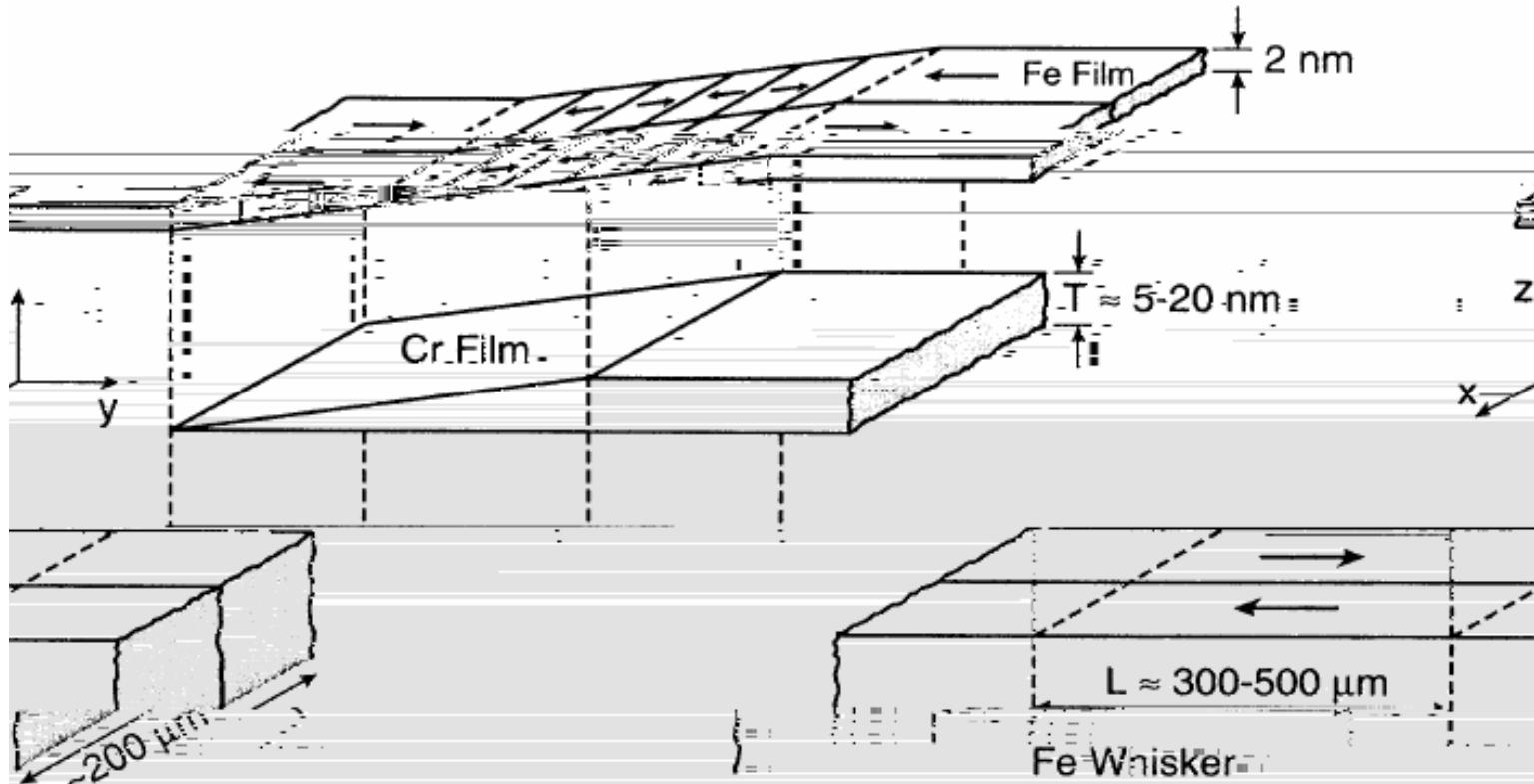
MBE

Fe-

Cr-



$(\text{Fe/Cr})_n$

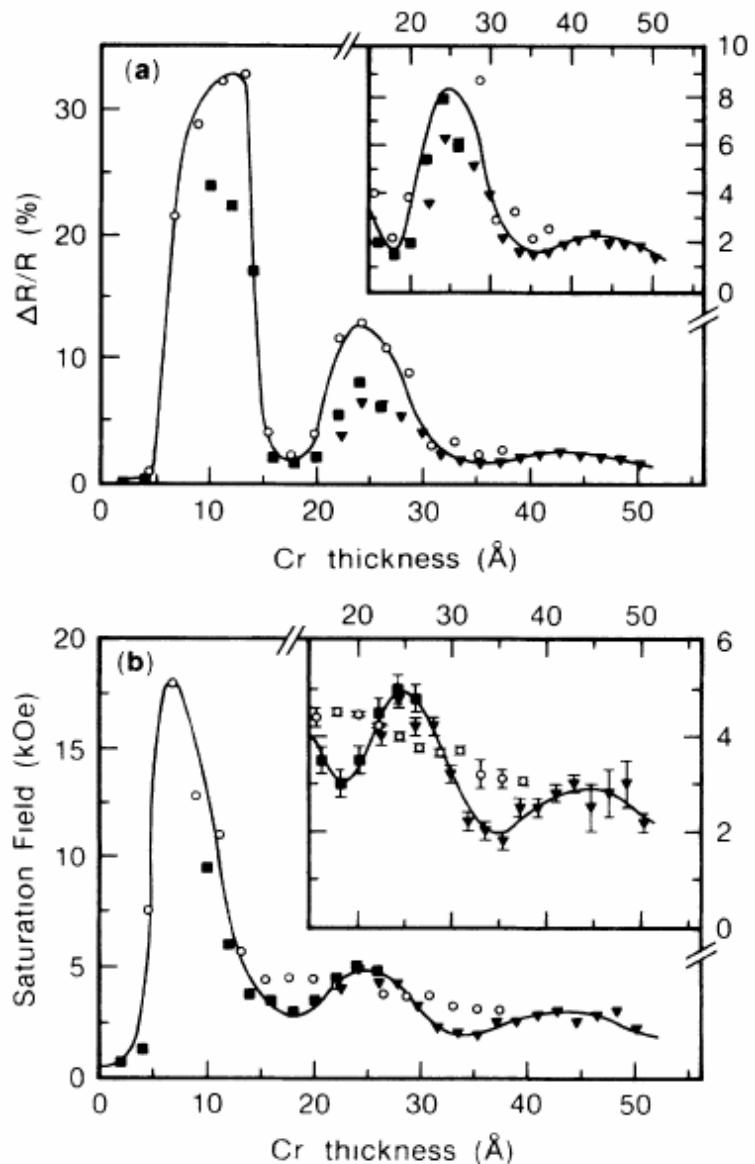


of the sample structure isker substrate, the eva- r. The arrows in the Fe in each domain. The z times; the actual wedge

FIG. 1. A schematic exploded view showing the Fe(100) single-crystal wh isker substrate, the eva- r. The arrows in the Fe in each domain. The z times; the actual wedge scale is expanded approximately 5000 angle is of order 10^{-3} deg.

Parkin
GMR
RKKY

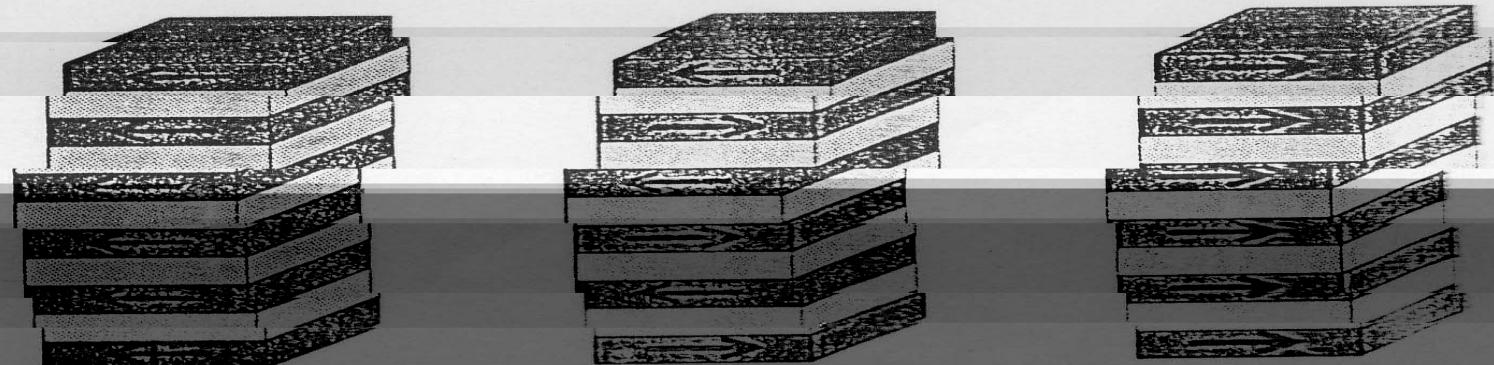
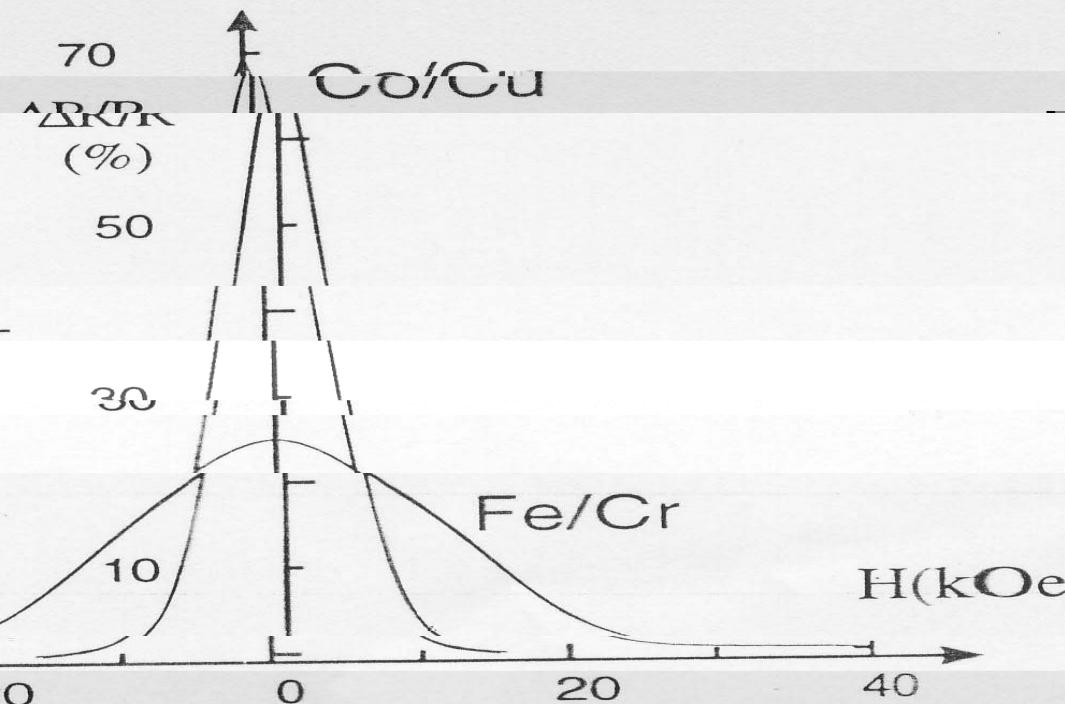
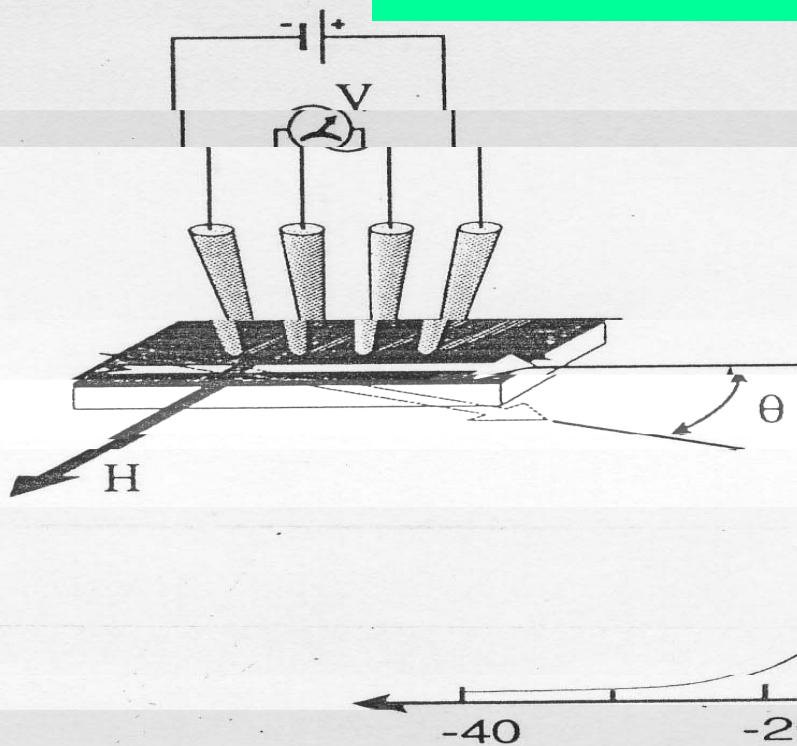
Fe/Cr;
Co/Cr
Co/Ru



Giant Magnetoresistance

3

GMR

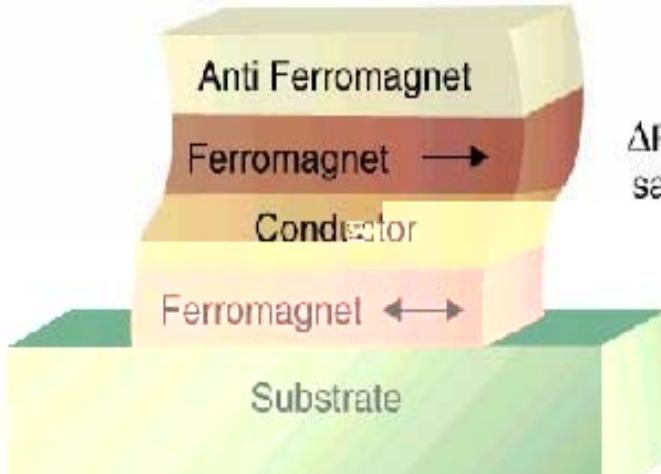


(Spin valve)

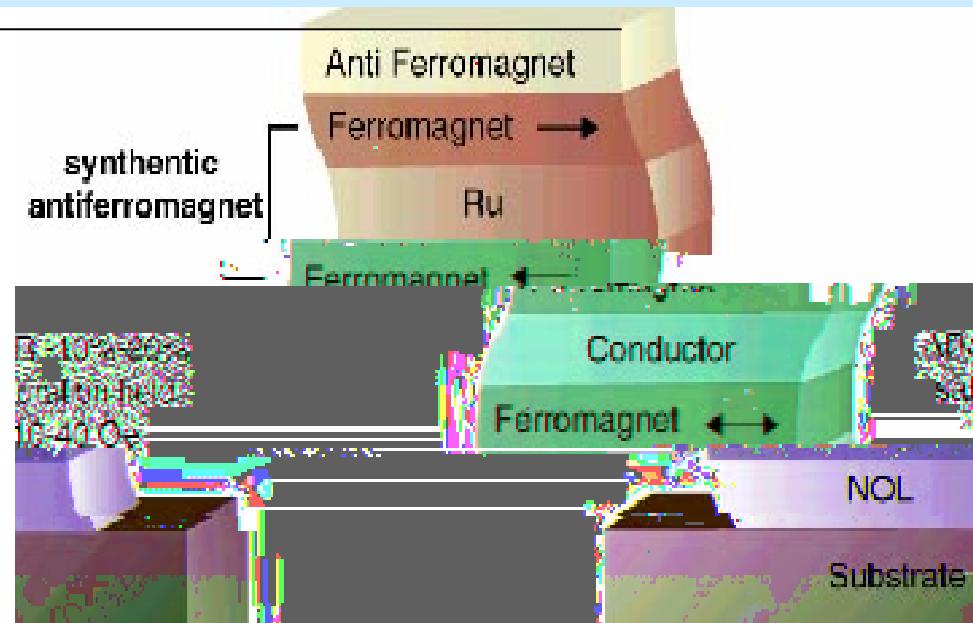
$\text{Ni}_{80}\text{Fe}_{20}$

, NiFe; FeCo)

FeMn; MnIr)



$\Delta R/R$ -5%-10%
saturation field
10-30 Oe



$$\lambda^{\uparrow} \quad \lambda^{\downarrow}$$

λ (nm)	Fe	Co	NiFe	Cu
λ^{\uparrow}	1.5 ± 0.2	5.5 ± 0.4	4.6 ± 0.3	20.5
λ^{\downarrow}	2.1 ± 0.5	1.0	0.6	20.5

Cu : $\lambda^{\uparrow} \quad \lambda^{\downarrow} \quad 20.5$ nm.

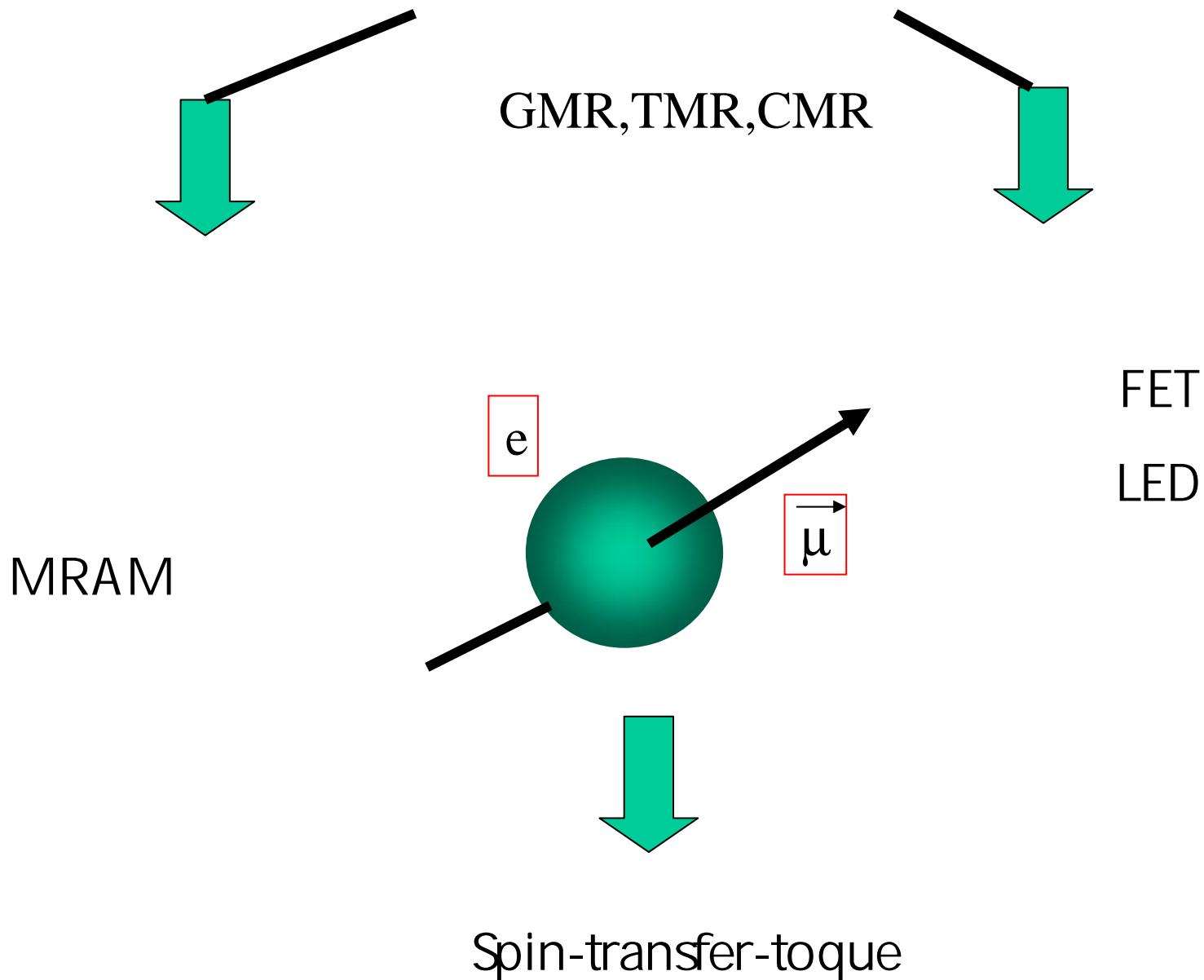
(Ls= D τ s) 50-100nm

(Cu, Au, Ag, Al etc.). Ls 1-10

P

Metals						
Materials	Ni	Co	Fe	$\text{Ni}_{80}\text{Fe}_{20}$	$\text{Co}_{50}\text{Fe}_{50}$	$\text{Co}_{84}\text{Fe}_{16}$
P (%)	33	45	44	48	51	49
J.S.Moodera, G.Mathon, <i>J.M.M.M.</i> ,200(1999)248-273						

Oxide Compounds			
Materials	CrO_2	Fe_3O_4	$\text{La}_{0.61}\text{Sr}_{0.23}\text{MnO}_3$
P (%)	$90 \pm 3.6\%$ [a]	40 [b]	72 [c]



- -
- AMR,GMR,**TMR**,CMR----
-

MRAM

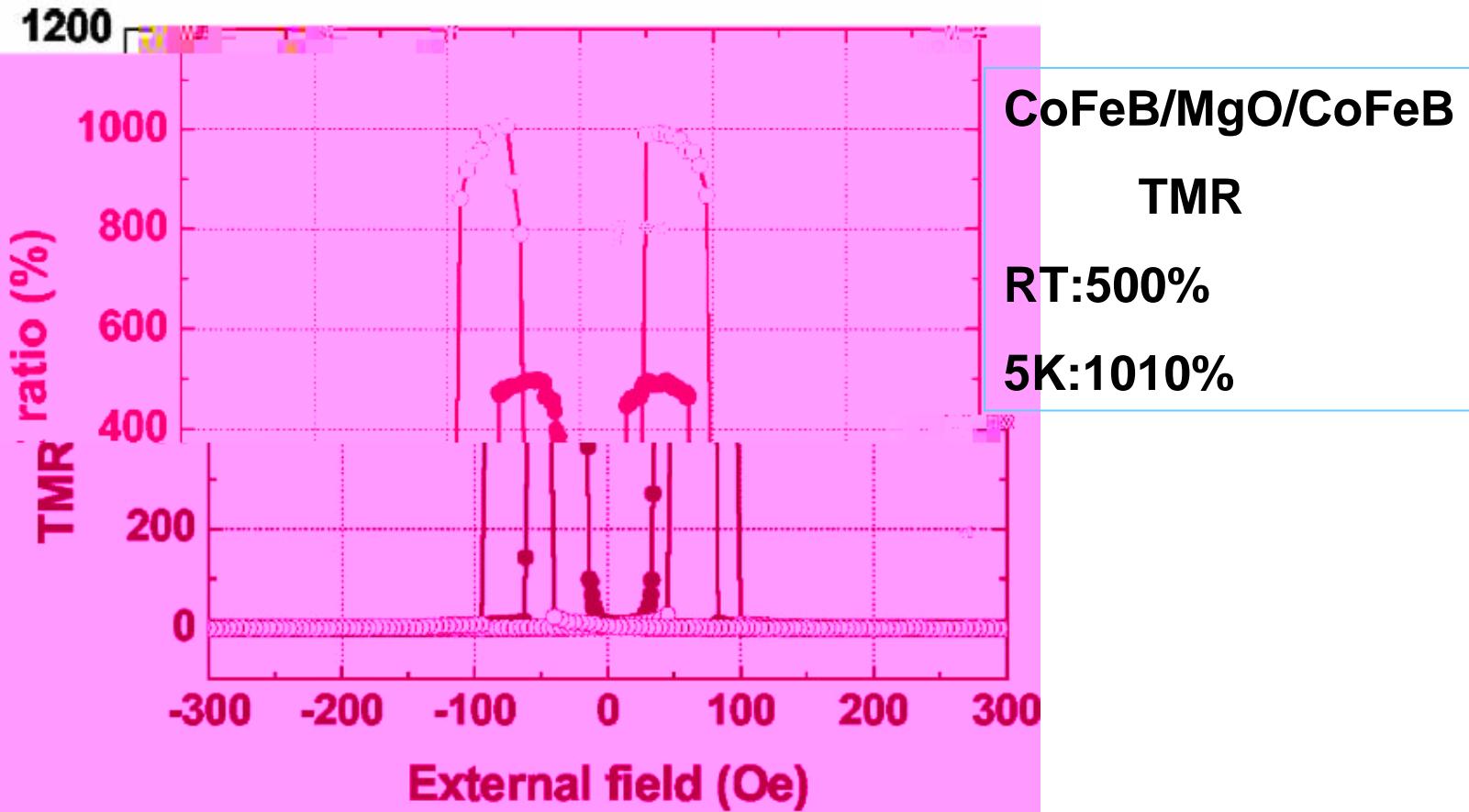
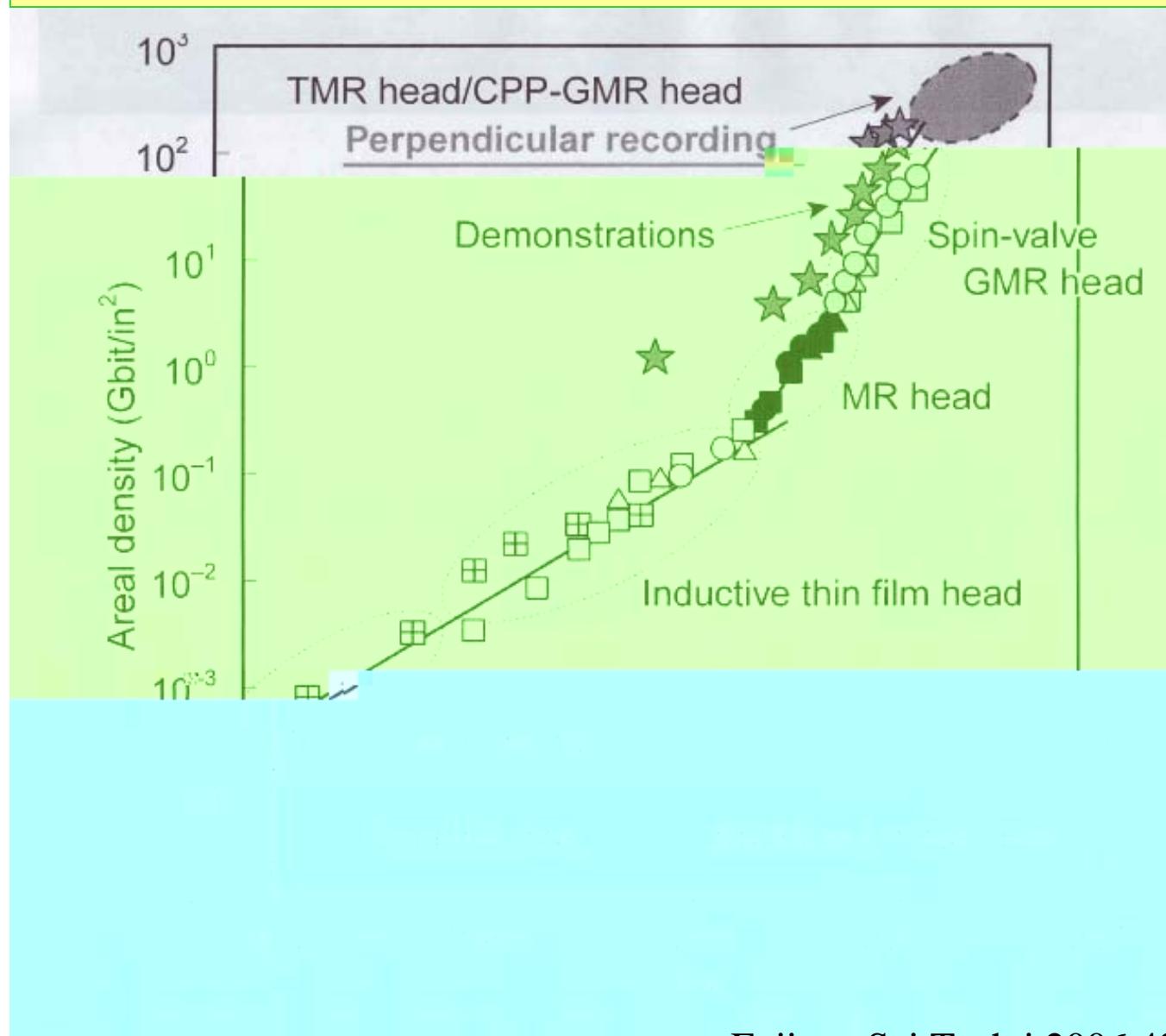
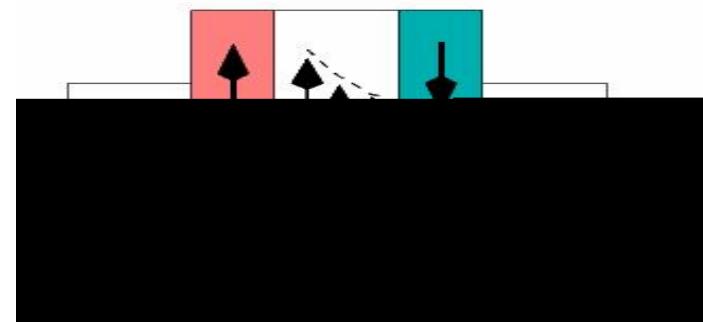
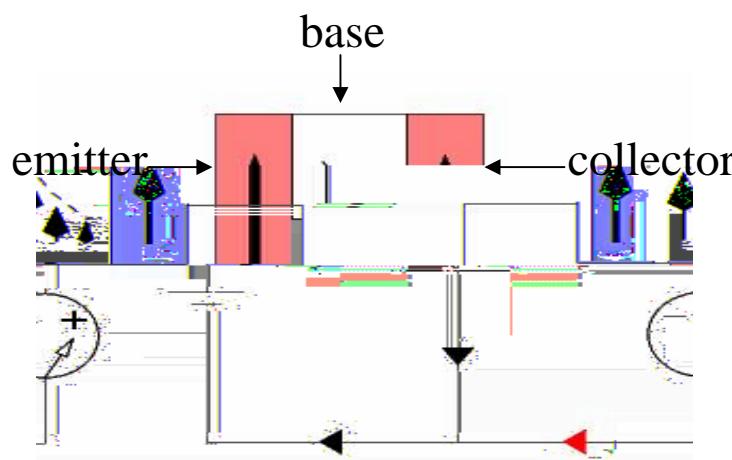
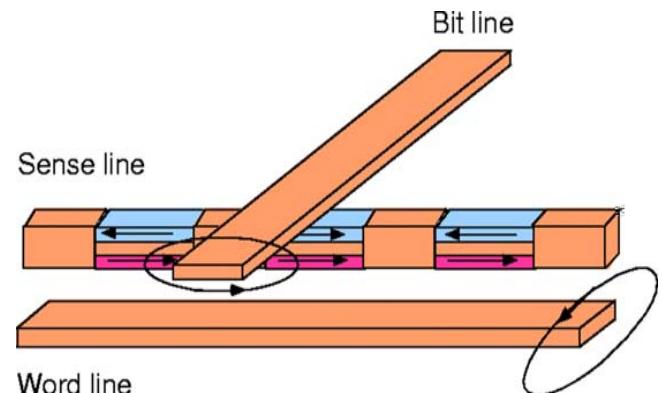
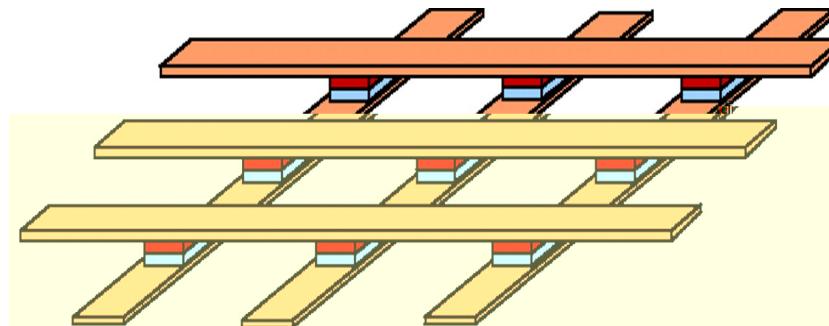


FIG. 2. TMR loops of a MTI having 4 and 4 3 nm. $(\text{Co}_{0.7}\text{Fe}_{0.3})_{57}\text{B}_{42}$ trôdes and a 2.1-nm-thick MgO annealed at 475 °C measured at RT (solid black circles) and 5 K (open circles).



😊MRAM ; Spin Transistor

Nonvolatility, increased data processing speed, decreased electric power consumption, increased integration densities , and anti-irradiation



Spin transistor: three-terminal,bipolar device

MRAM



♥ DRAM

♥ Flash

Flash

♥ MRAM

♥ MgO
transfer torque)

Spin-
MRAM

industrial production.

In July 2006, Freescale started selling the first commercial MRAM module, with 4Mbit of memory, for 25\$ a piece.

2008: Freescale launches independent company-EverSpin to accelerate MRAM business

Toshiba - advances in 1Gb MRAM. Expects MRAM to take over DRAM in 2015

Samsung and Hynix to launch STT-MRAM JV in September, expect the chip to mature around 2012

1

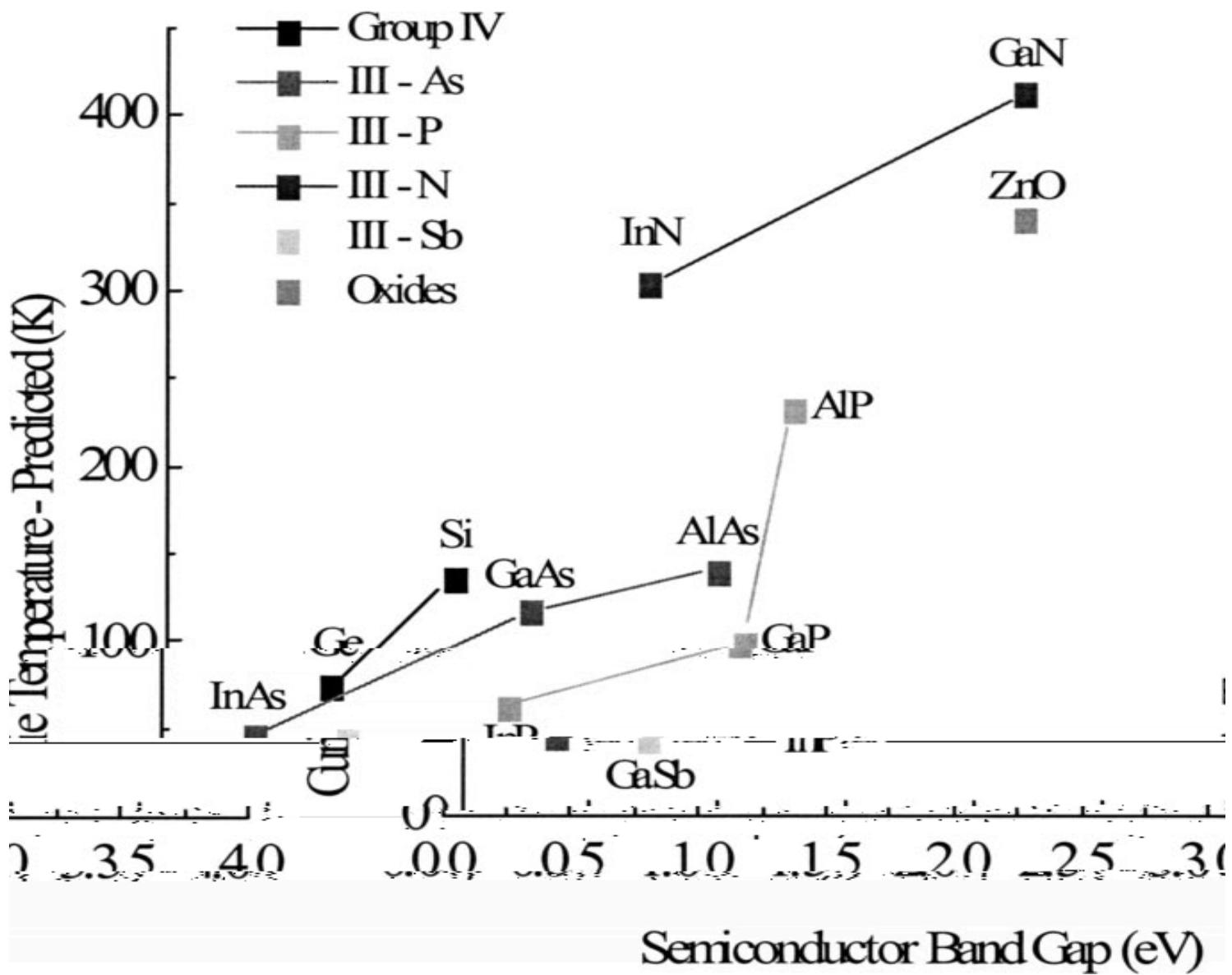
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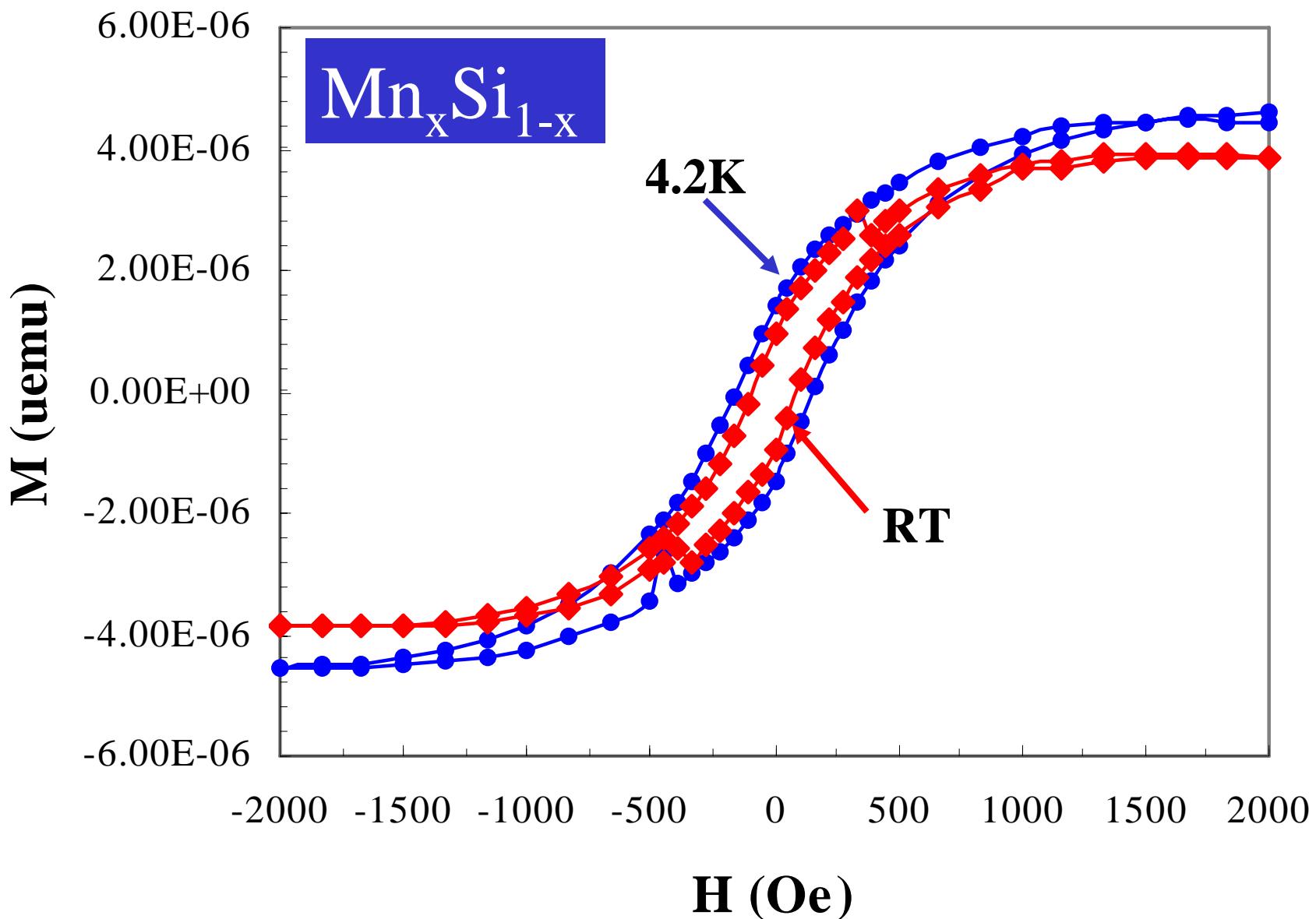
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4.

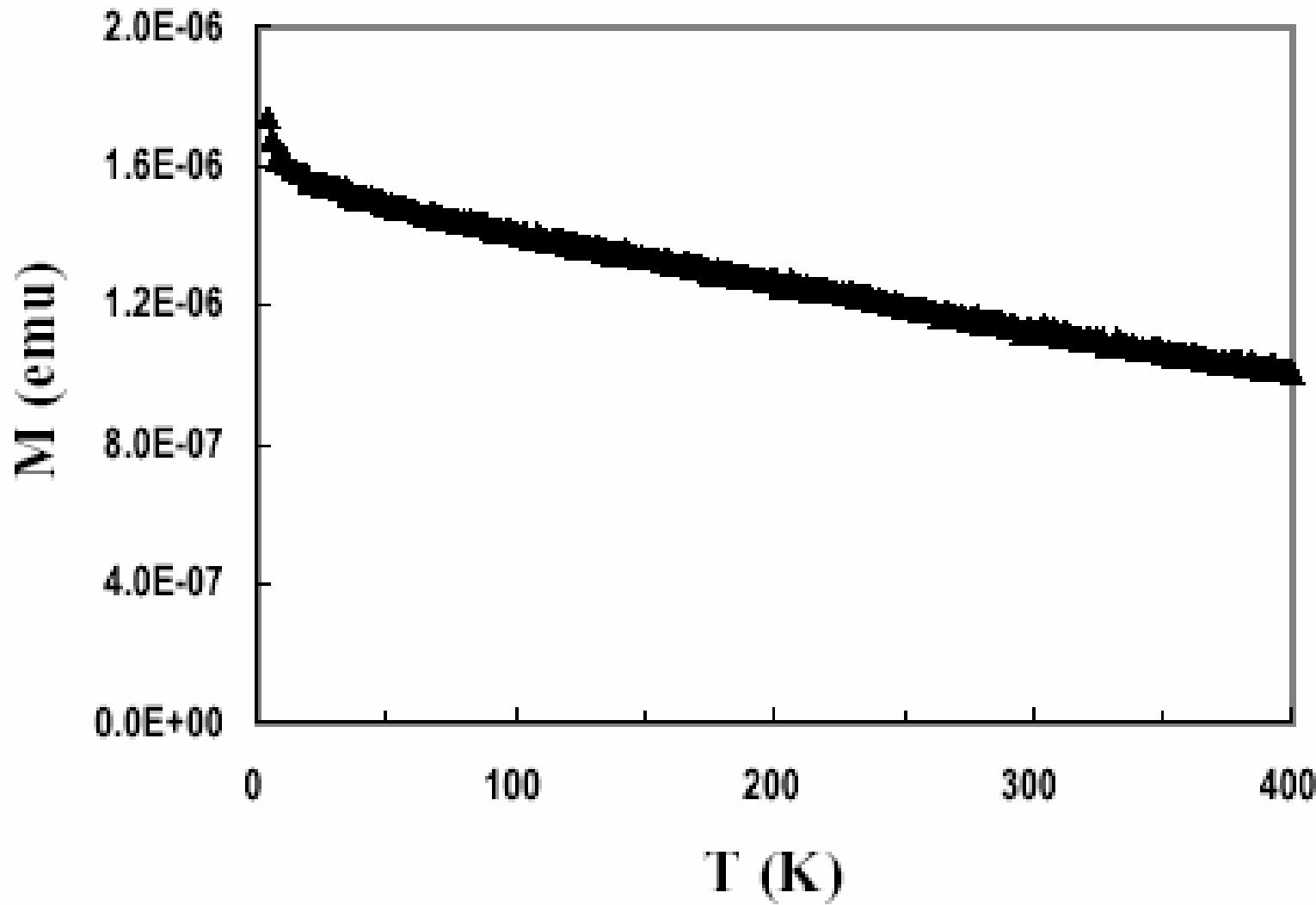
5. TMR,



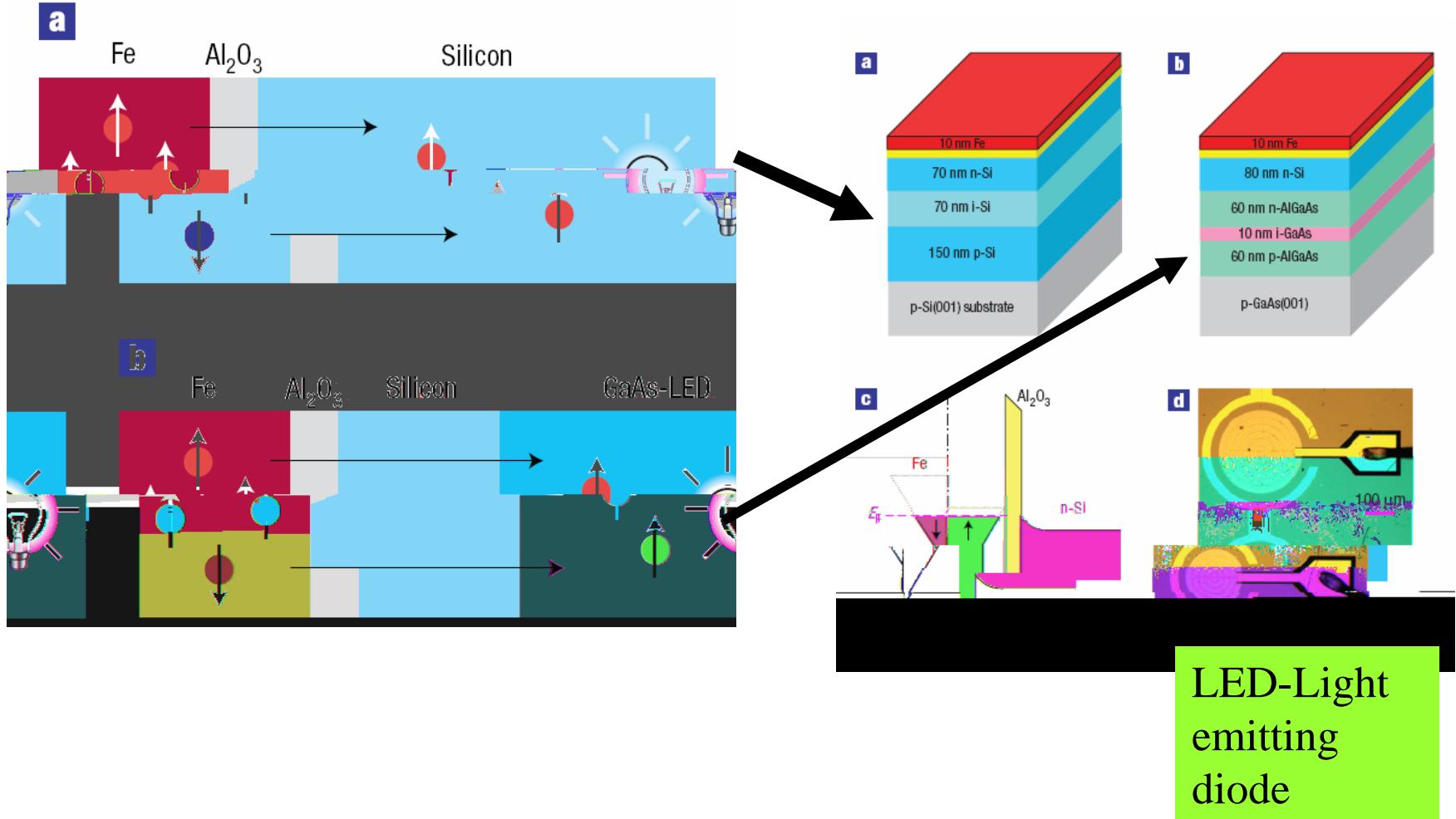
The predicted Curie temperatures as a function of the band gap



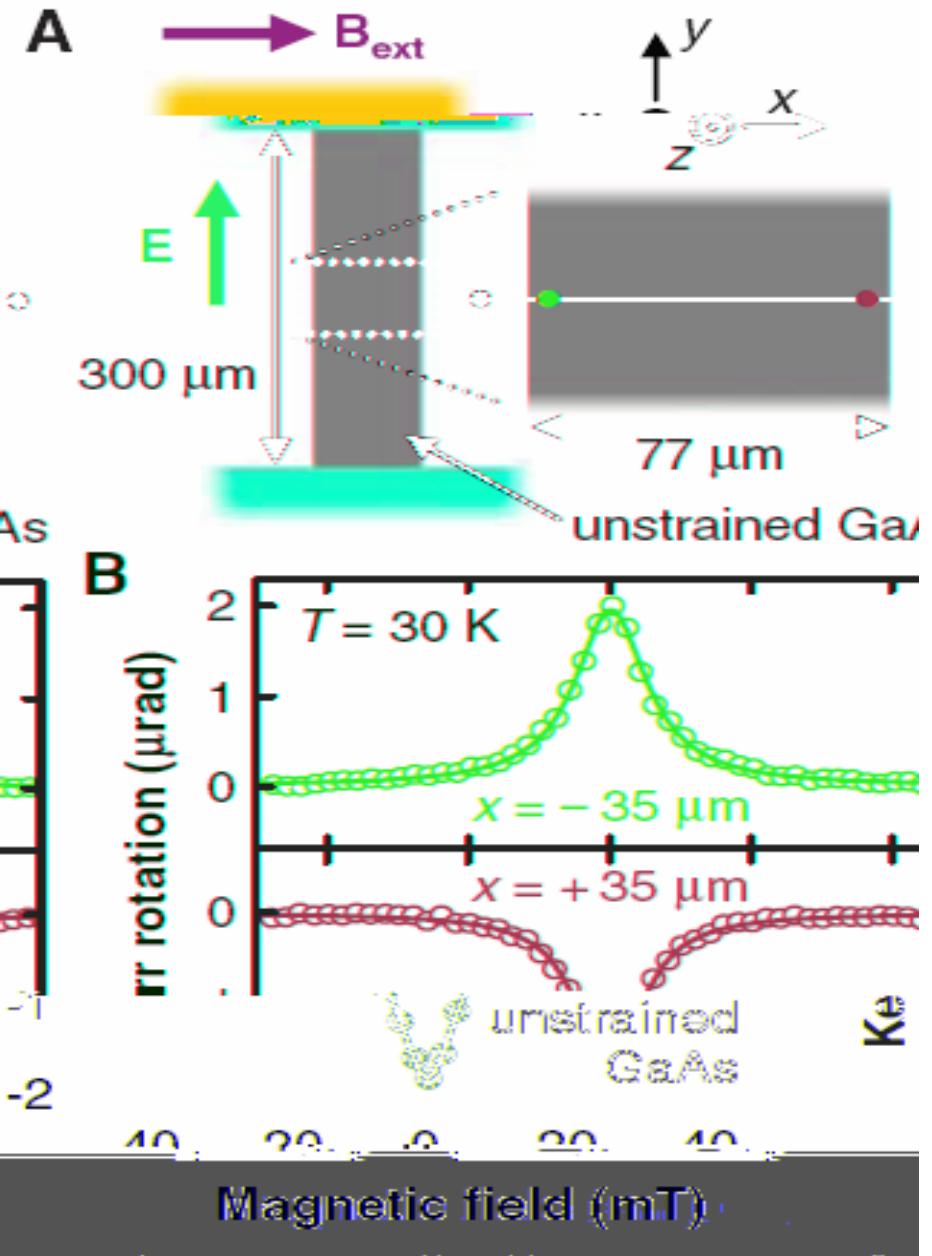
Magnetic hysteresis loops for MnSi alloy



Demonstration of the injection of spin into silicon



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GaAs Spin Hall Effect

GaAs

Kerr

Kato Y.K. et al., Science
306(2004) 1910

Rashba spin-orbit

J. Sinova et al.,

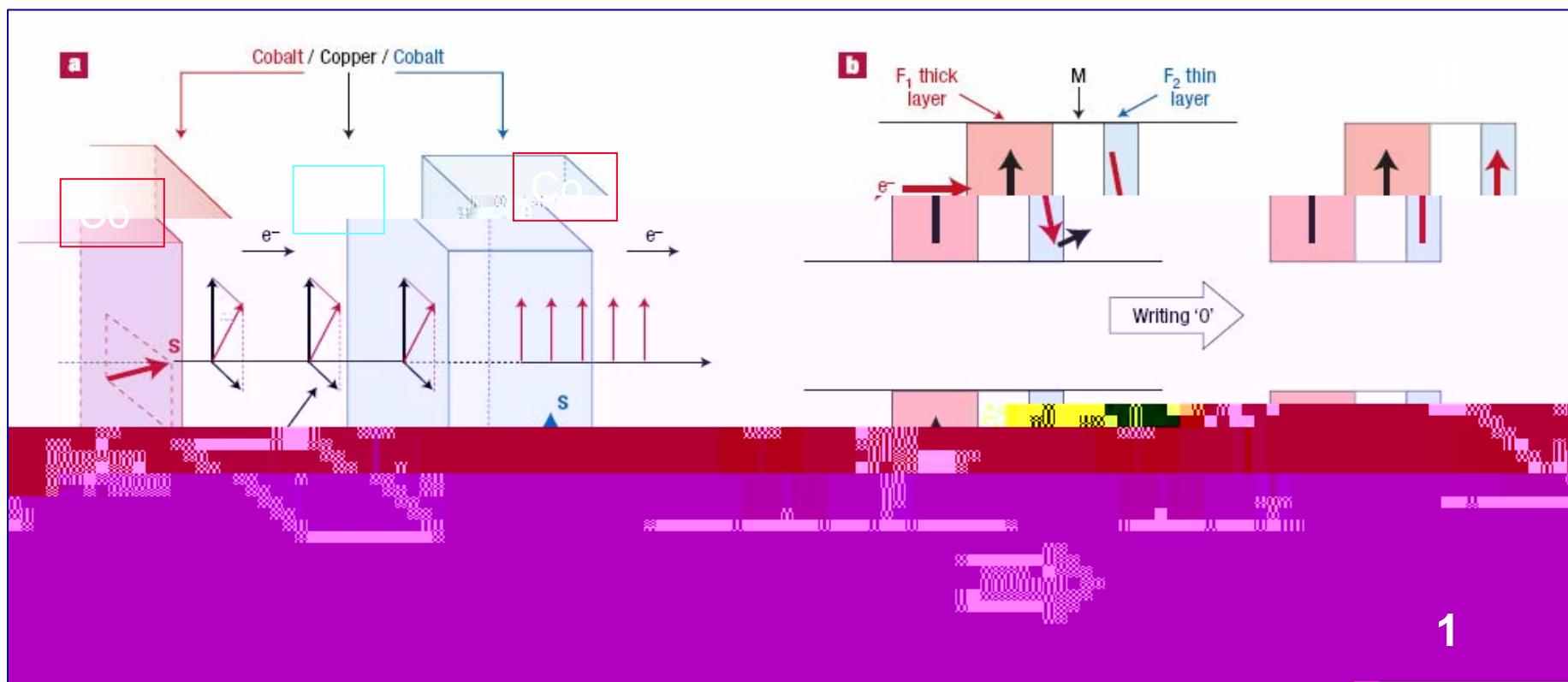
PRL 92(2004) 126603

GMR TMR

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Principle of Spin Transfer Torque (STT)

STT-RAM



$$\frac{\partial \vec{M}(\vec{r}, t)}{\partial t} = -|\gamma| \vec{M} \times \vec{H}_{\text{eff}} + \frac{\alpha}{M_s} \vec{M} \times \frac{\partial \vec{M}}{\partial t} + \frac{\sigma I}{M_s} \vec{M} \times (\vec{M} \times \vec{P})$$

PRECSSION DAMPING SPIN TRANSFER

The magnetization direction in the centre of a submicrometre magnetic disk can now be switched by an electrical current. This discovery demonstrates the potential of realizing all-electrically controlled magnetic memory devices.

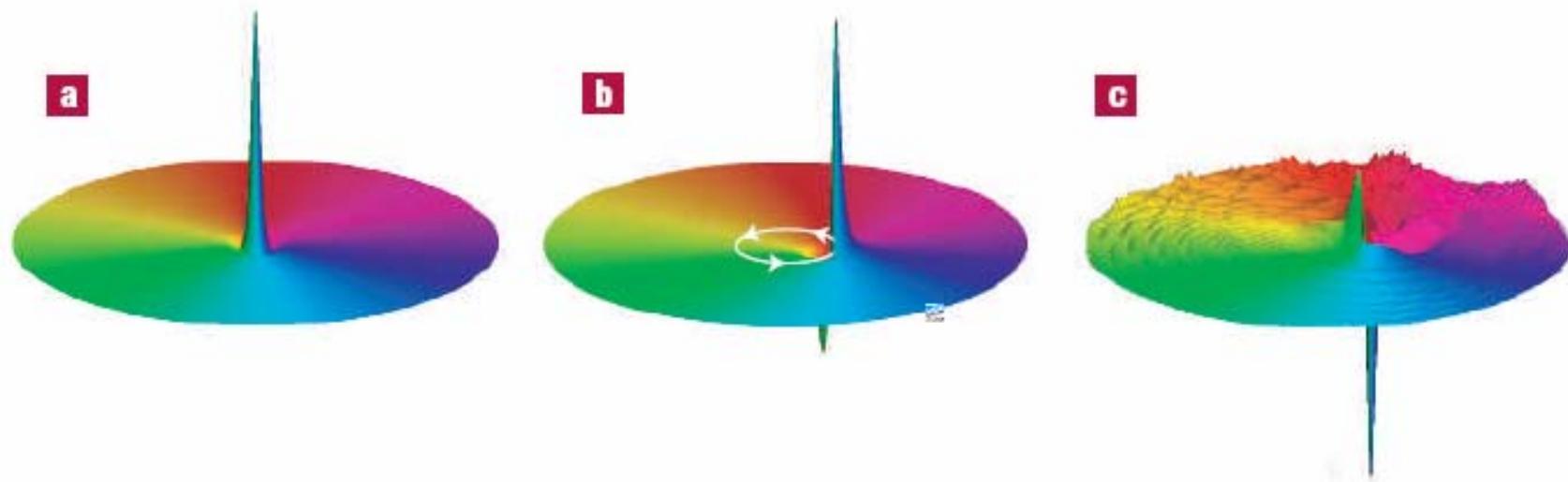
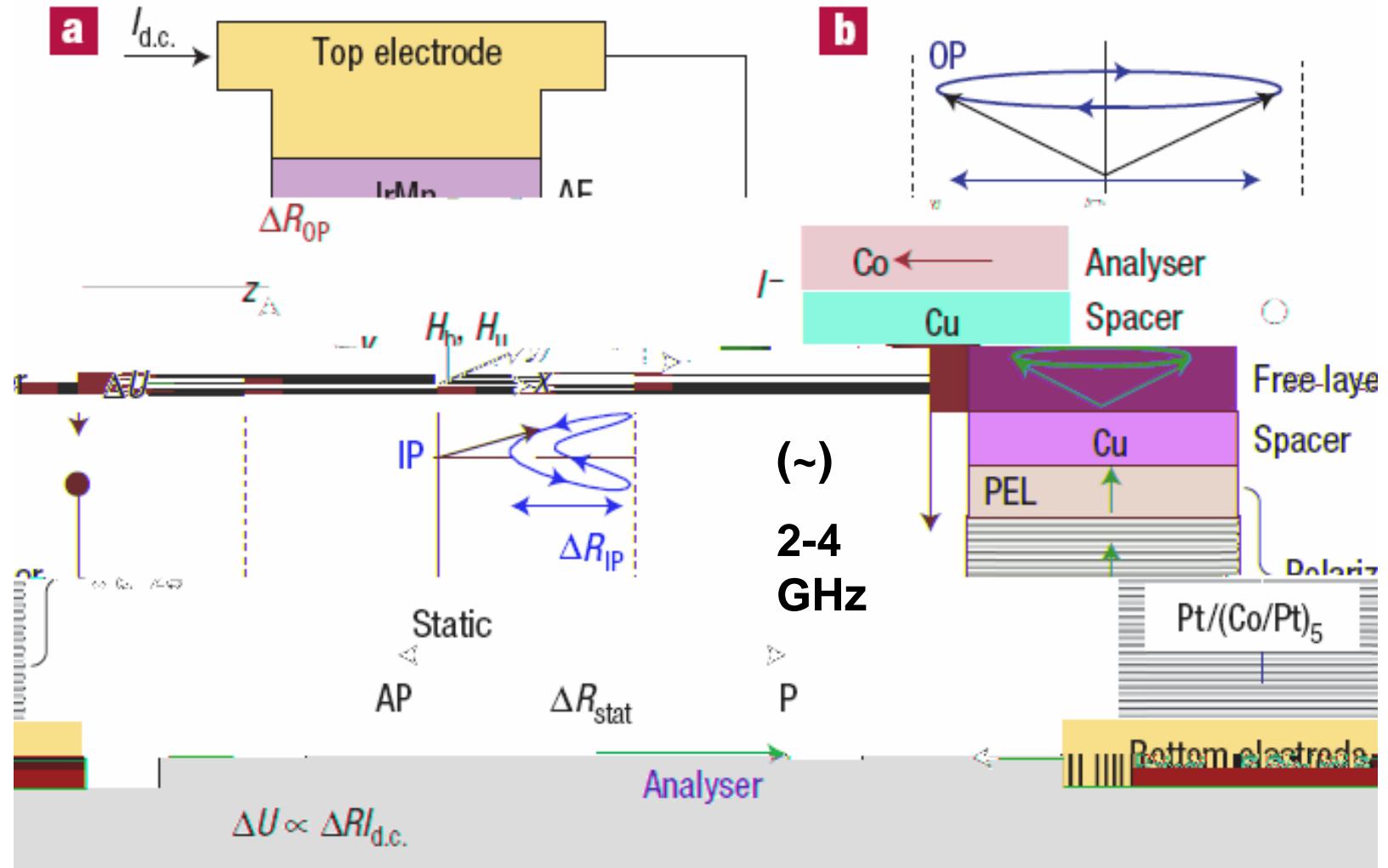


Figure 1 Magnetic vortex-core reversal. **a**, A magnetization vortex with its core shown in the centre. The height...
in proportionality to the out-of-plane component (see text). **b**, When an oscillating electric current is applied, the
core begins to orbit the centre (**b**), and eventually switches to its other bistable state (**c**).

Spin-torque oscillator-RF Device





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