Magnetisation processes at nanoscale

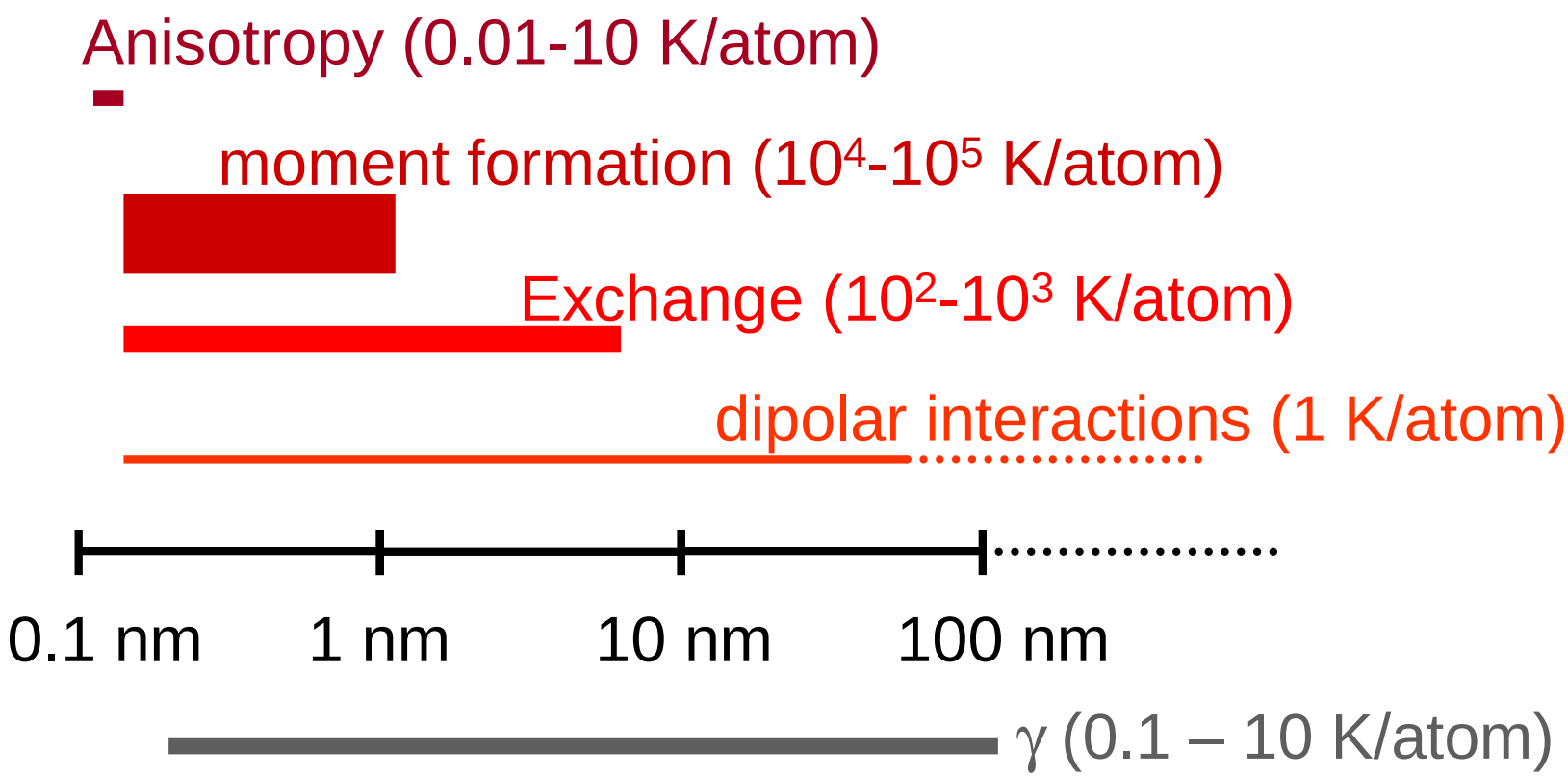
Magnetic properties of clusters
- magnetic moment
- magnetic order
- magnetocrystalline anisotropy
- finite temperature properties

Magnetization processes in exchange-coupled nanosystems
- coercivity
- ultra-soft and remanence enhancement
- exchange-spring
- nanocomposites
- magnetostrictive nanocomposites
- exchange-bias

Dipolar interactions in heterogeneous magnetic systems

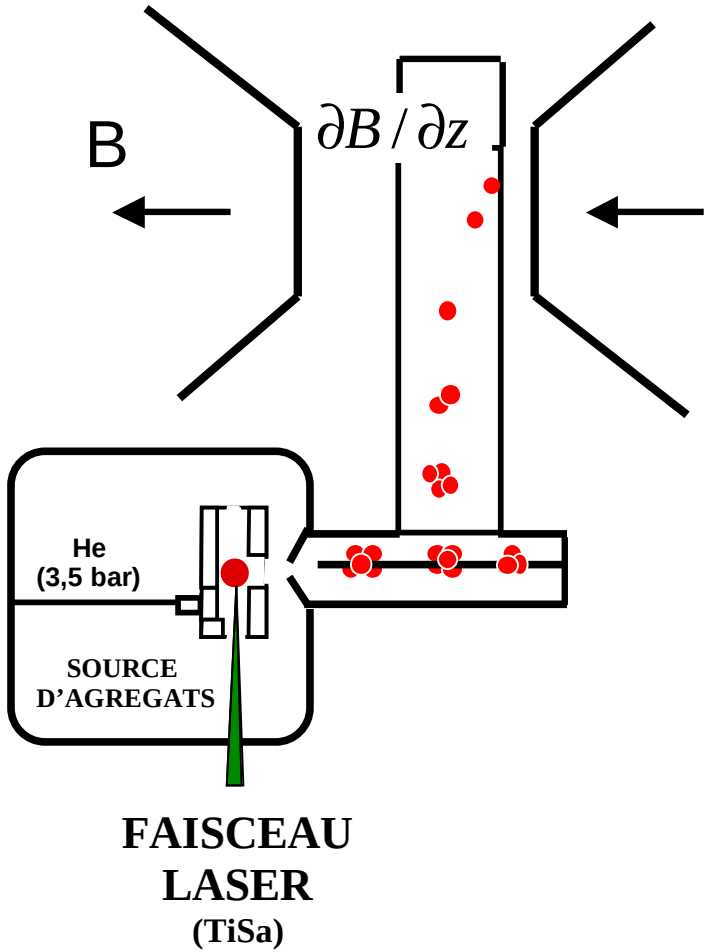
Finite-size effects in fine particles: magnetic and transport properties
X. Battle and A.Labarta, J. Phys. D: Appl. Phys. 35 (2002) R15

Strength and range of magnetic interactions

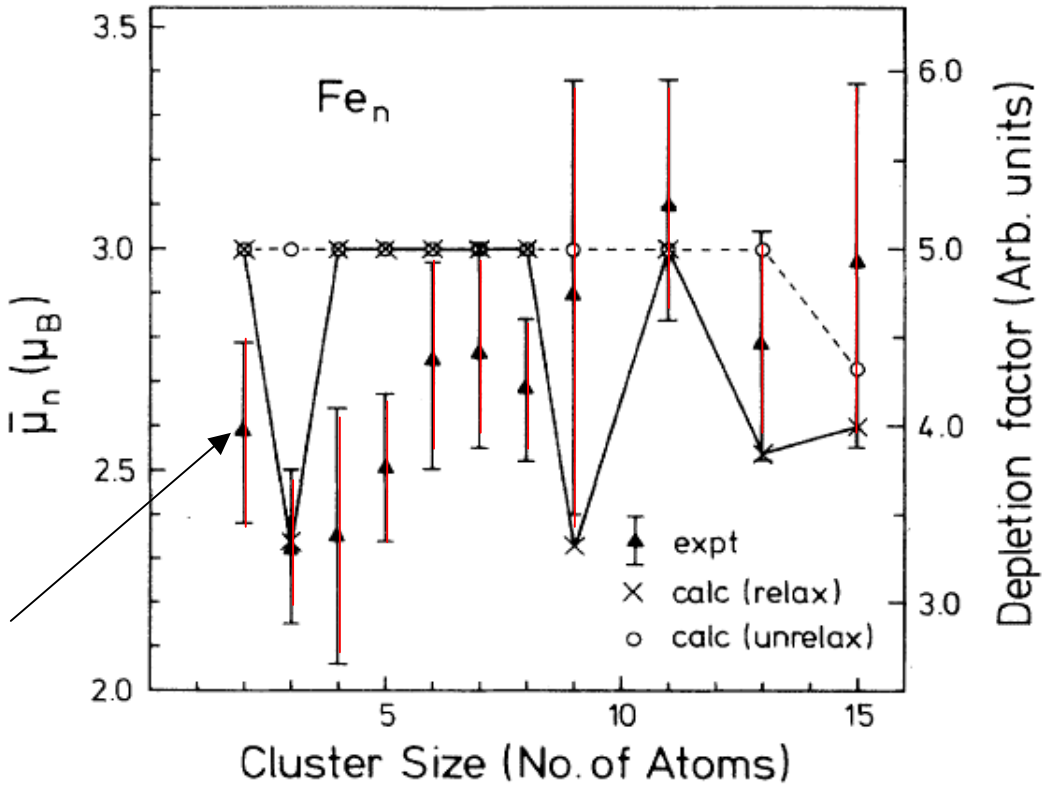


Specific properties may be predicted at the nanomater scale

Preparation and measure of the magnetic moment of free metal clusters

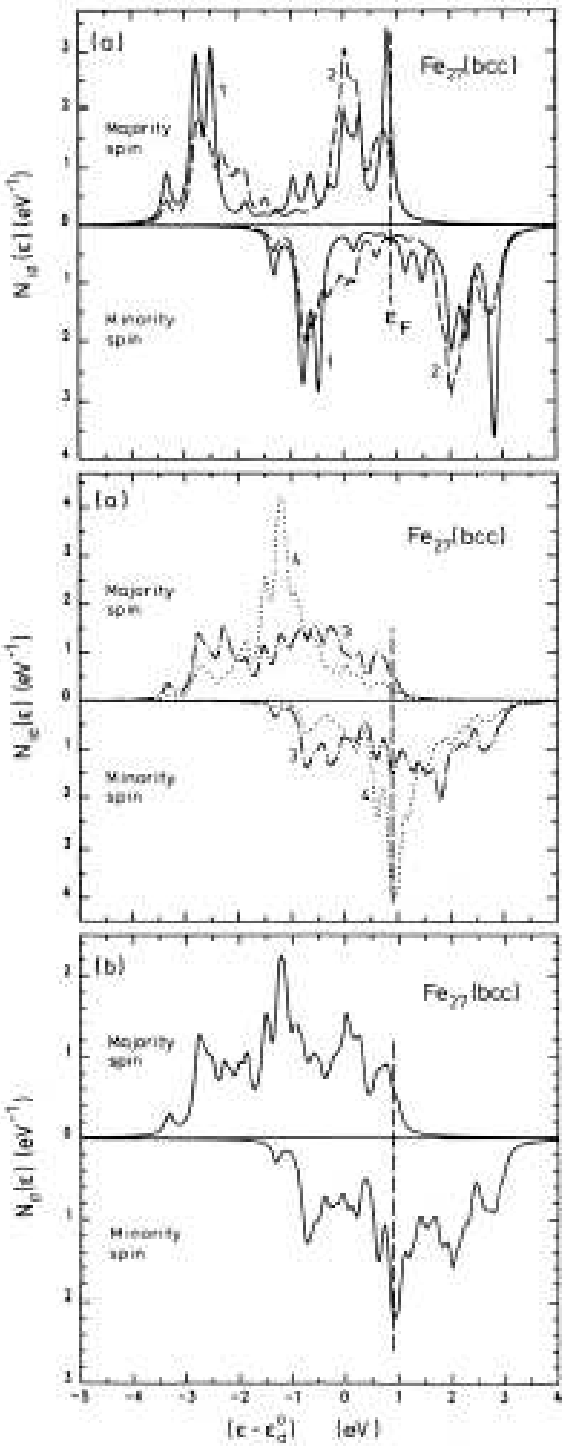


Extraction of the cluster intrinsic magnetic moment

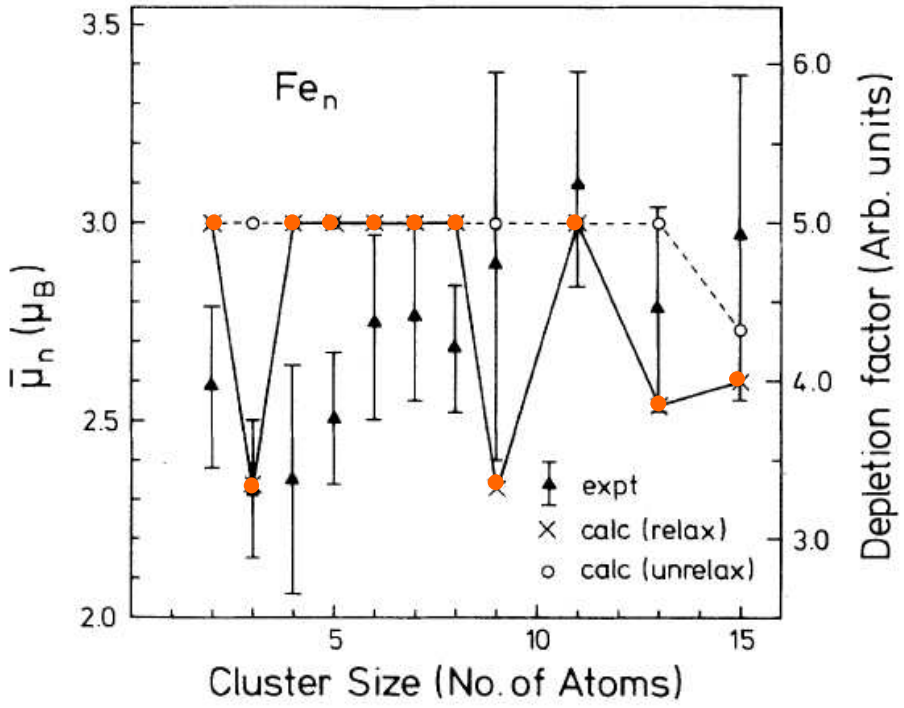


Experiment

$$\mu_{\text{eff}} = \mu \mathcal{L}\left(\frac{N\mu B}{kT}\right) = \mu\left[\coth\left(\frac{N\mu B}{kT}\right) - \frac{kT}{N\mu B}\right]$$



Magnetism of very small ferromagnetic clusters



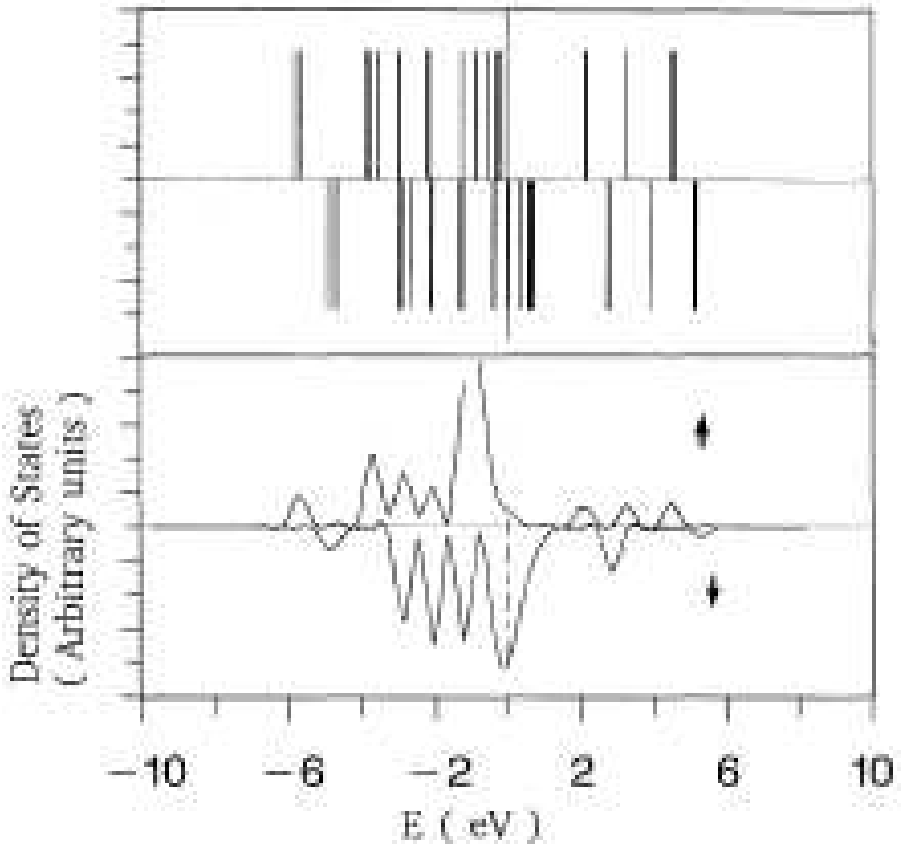
2 opposite effects :

- band narrowing for surface atoms
- contraction of the whole cluster

Onset of ferromagnetism in Rh clusters

$$\mu_{\text{eff}} = \mu\mathcal{L}\left(\frac{N\mu B}{kT}\right) = \mu\left[\coth\left(\frac{N\mu B}{kT}\right) - \frac{kT}{N\mu B}\right]$$

Cluster	μ_{expt} (μ_B)	μ (μ_B)
Rh_{12}	0.027±0.009	0.92±0.16
Rh_{13}	0.025±0.009	0.88±0.16
Rh_{14}	0.009±0.009	0.66±0.33
Rh_{15}	0.017±0.009	1.02±0.16
Rh_{16}	0.025±0.009	1.09±0.17
Rh_{17}	0.016±0.009	0.45±0.17
Rh_{18}	0.016±0.009	0.68±0.19
Rh_{19}	0.022±0.009	0.95±0.15
Rh_{20}	0.007±0.009	0.38±0.38
Rh_{21}	0.011±0.009	0.49±0.20
Rh_{22}	0.012±0.009	0.53±0.20
Rh_{23}	0.011±0.009	0.40±0.20
Rh_{24}	0.007±0.009	0.43±0.20
Rh_{25}	0.007±0.009	0.37±0.17
Rh_{26}	0.014±0.009	0.50±0.16
Rh_{27}	0.016±0.009	0.50±0.15
Rh_{28}	0.011±0.009	0.45±0.18
Rh_{29}	0.007±0.009	0.41±0.20
Rh_{30}	0.012±0.009	0.42±0.16
Rh_{31}	0.012±0.009	0.43±0.16
Rh_{32}	0.014±0.009	0.35±0.11

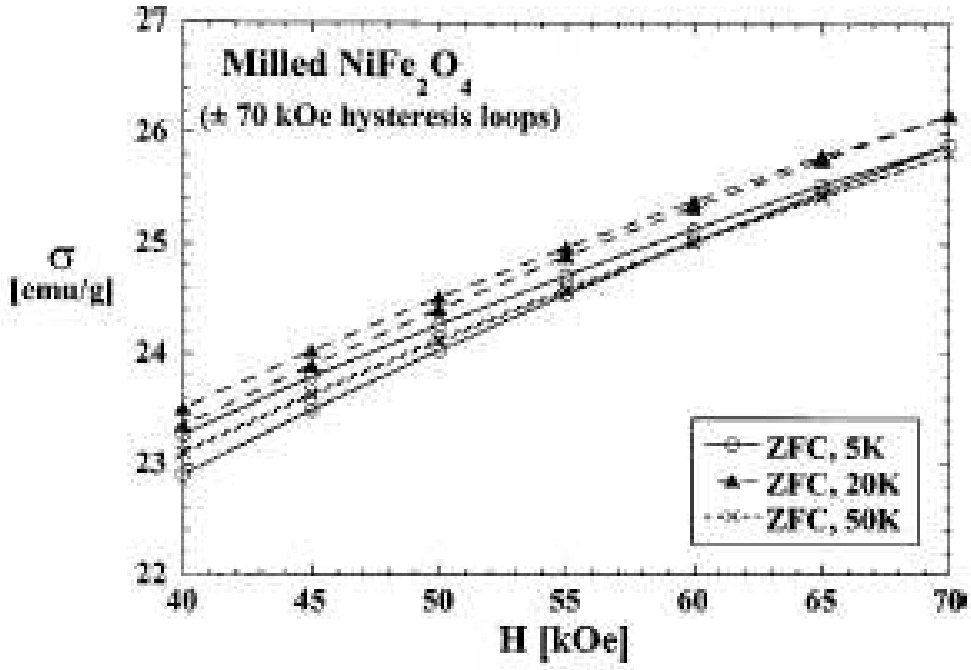


Measured on free clusters

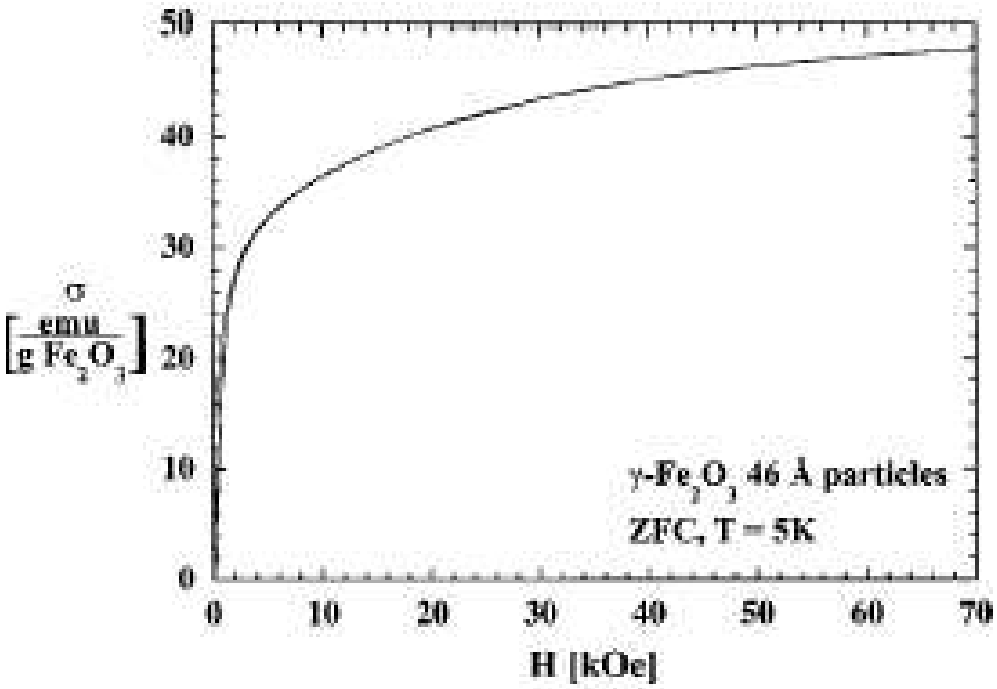
Band structure calculations

Non-saturation of magnetisation in ferrimagnetic nanoparticles

$NiFe_2O_4$

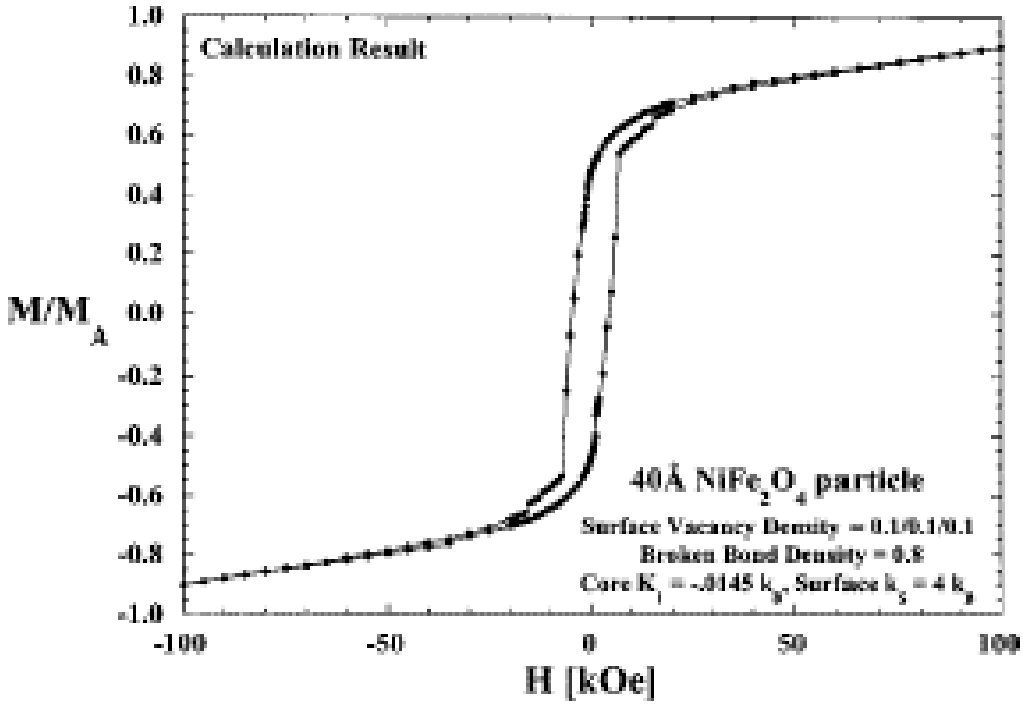


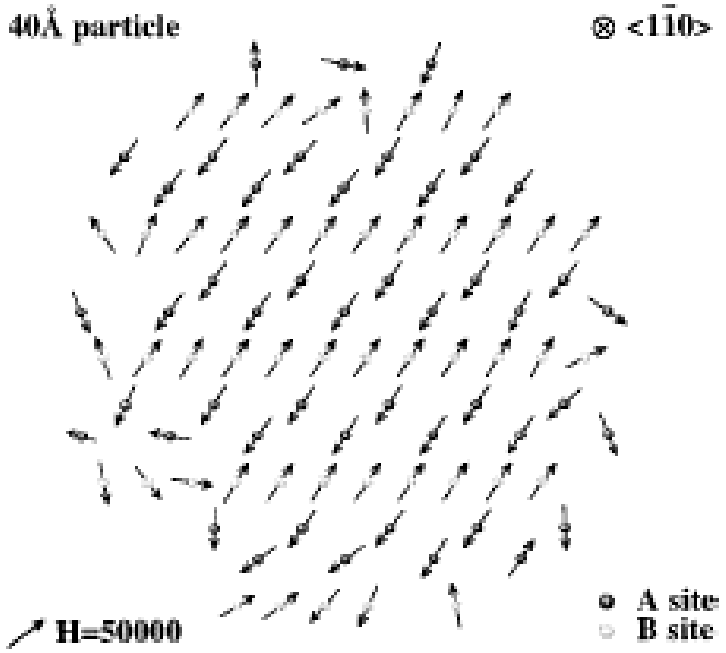
γ-Fe_2O_3



Non-saturation cannot be attributed to anisotropy would be unrealistically large

Non-collinear structure due to missing bonds in surface

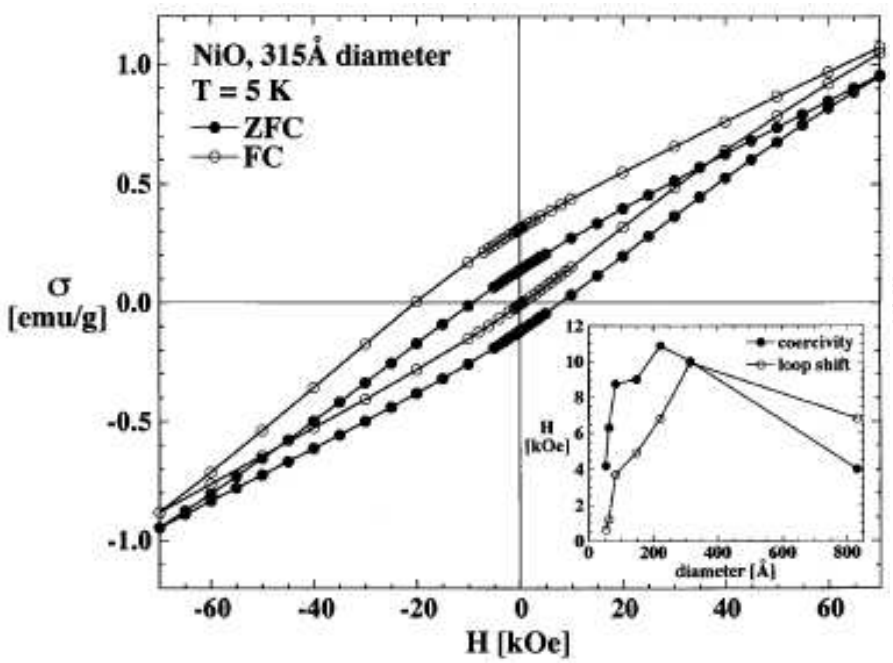


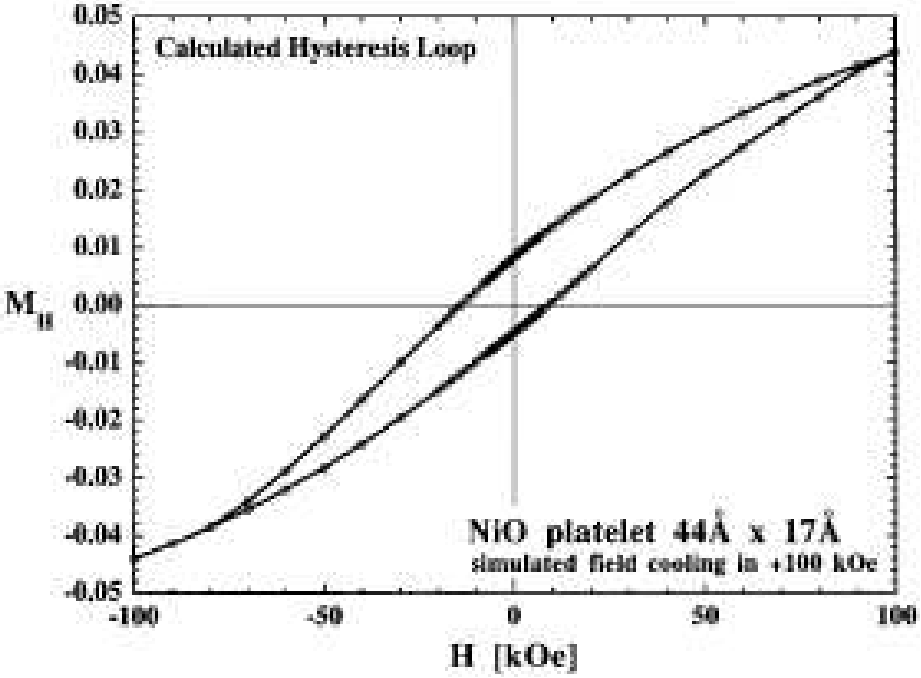


$$J_{AA} = -21.0, \quad J_{AB} = -36.0, \quad J_{AB'} = -28.1$$

$$J_{BB} = -22.0, \quad J_{BB} = +2.0, \quad J_{B'B'} = -8.6$$

Ferromagnetism of very small NiO nanoparticles

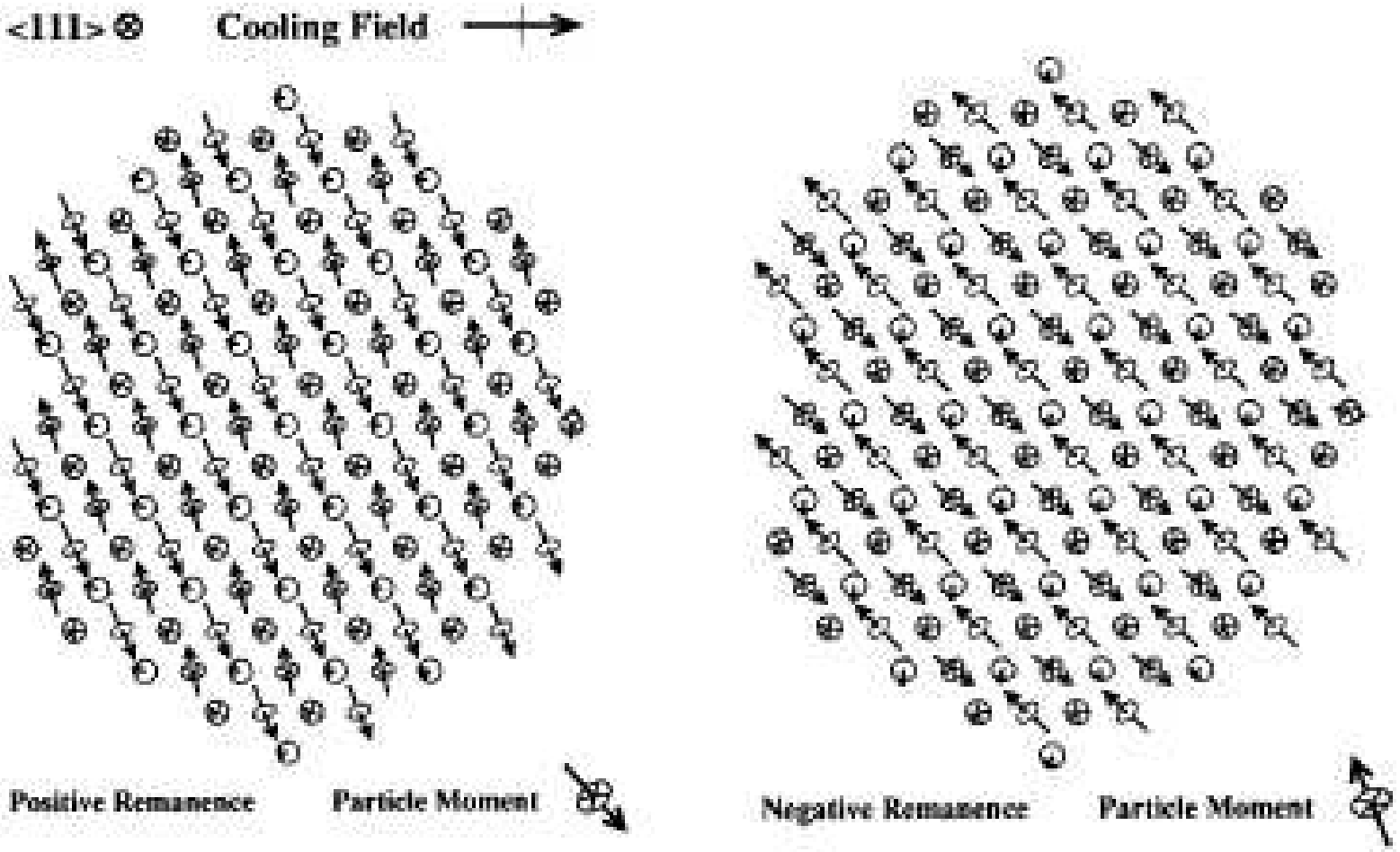




experiment

calculation

NiO nanoparticles



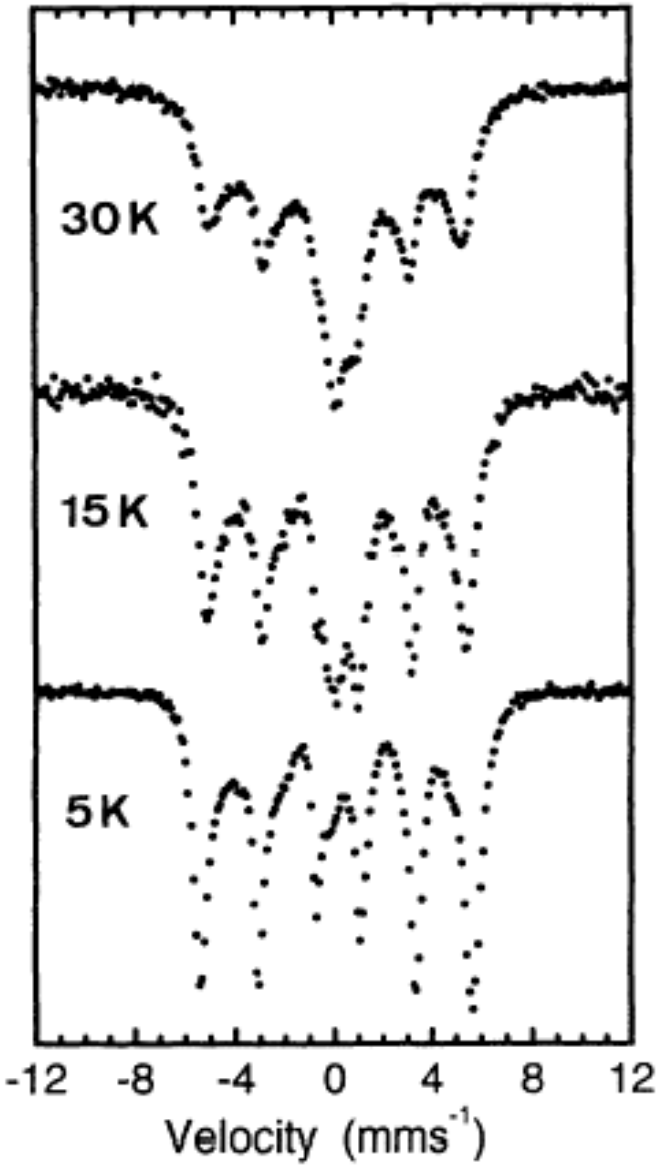
High non-collinearity due to missing bonds
+ exchange striction

Mössbauer study of very small Fe clusters

$$B_{obs} = B_0 \mathcal{L}(x) - B \qquad x = \frac{\mu B}{kT}$$

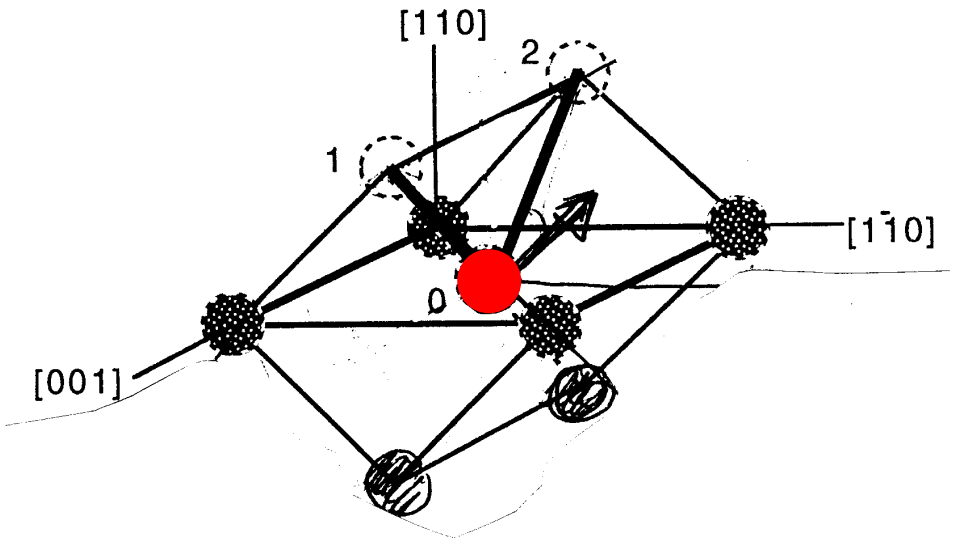
$$B_{\text{obs}} = B_0(1 - kT/\mu B) - B \,.$$

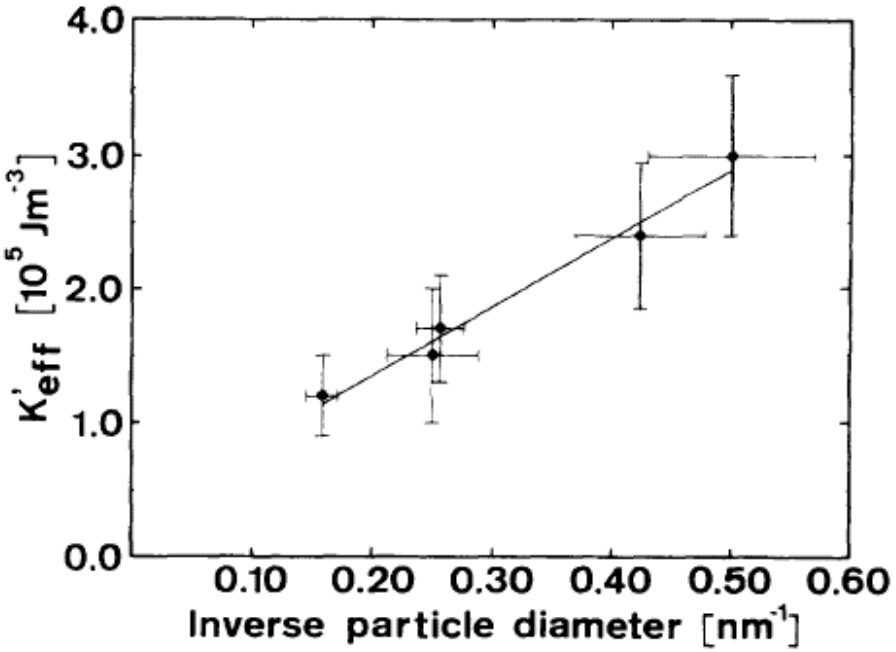
μ = cluster moment
Thus cluster volume deduced



Cluster magnetic anisotropy

$$B_{obs} = B_0(1 - kT/2K'_{eff}V)$$

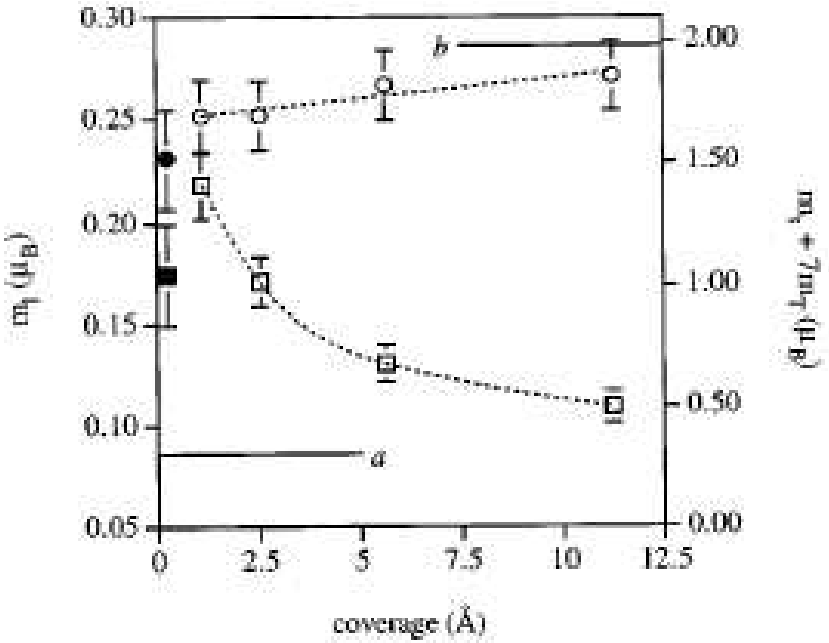


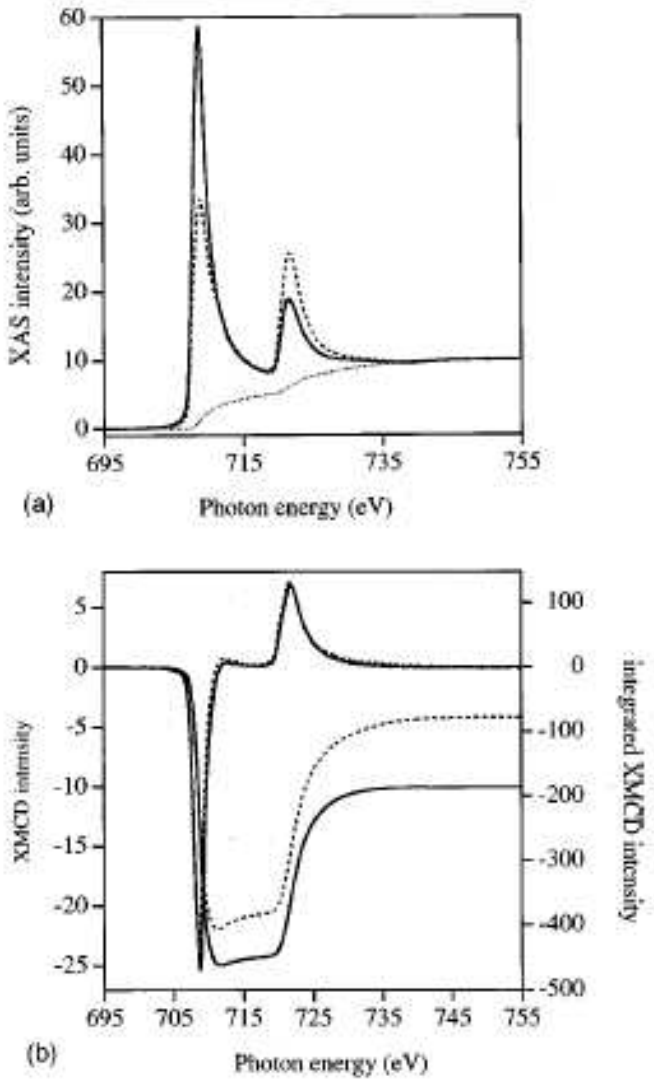


Symmetry breaking at a surface

α-Fe K = 0.5 10^5 J/m^3

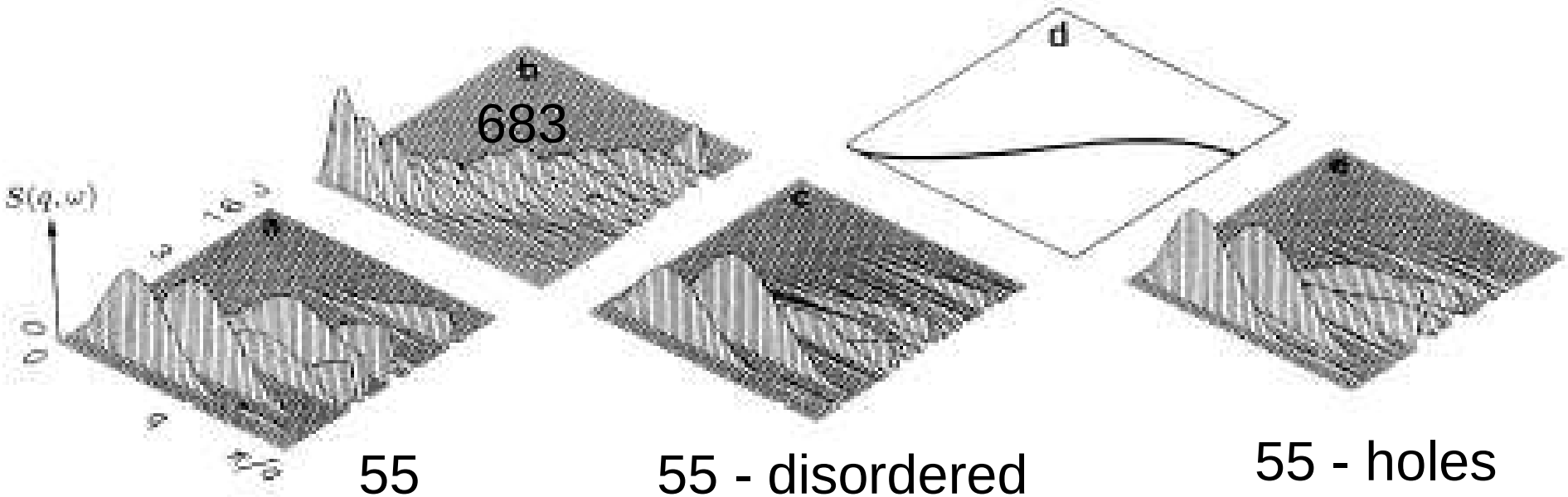
Orbital magnetic moment in Fe clusters





Spin-waves in small clusters

fcc clusters

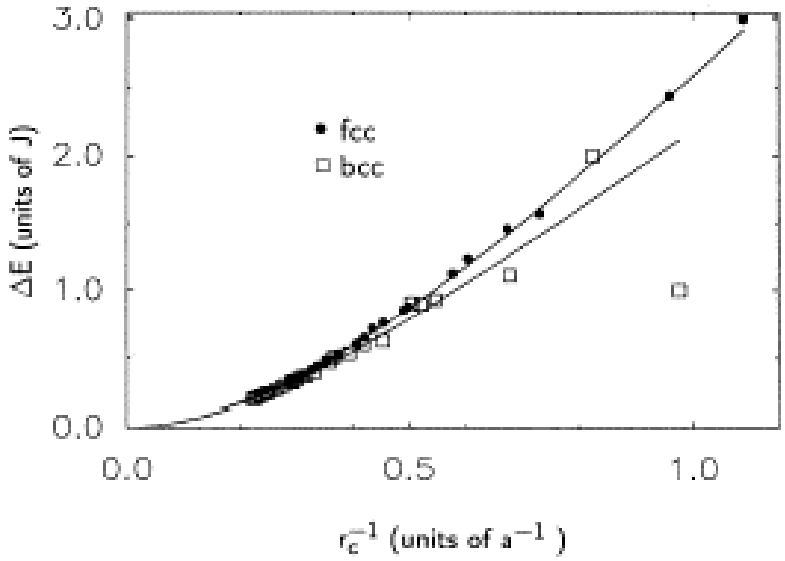


55 55 - disordered 55 - holes

bulk

$$E(k) = 2zJ\left(1-\frac{1}{2}(ka)^2\right)$$

$$\approx 2zJa^2k^2$$

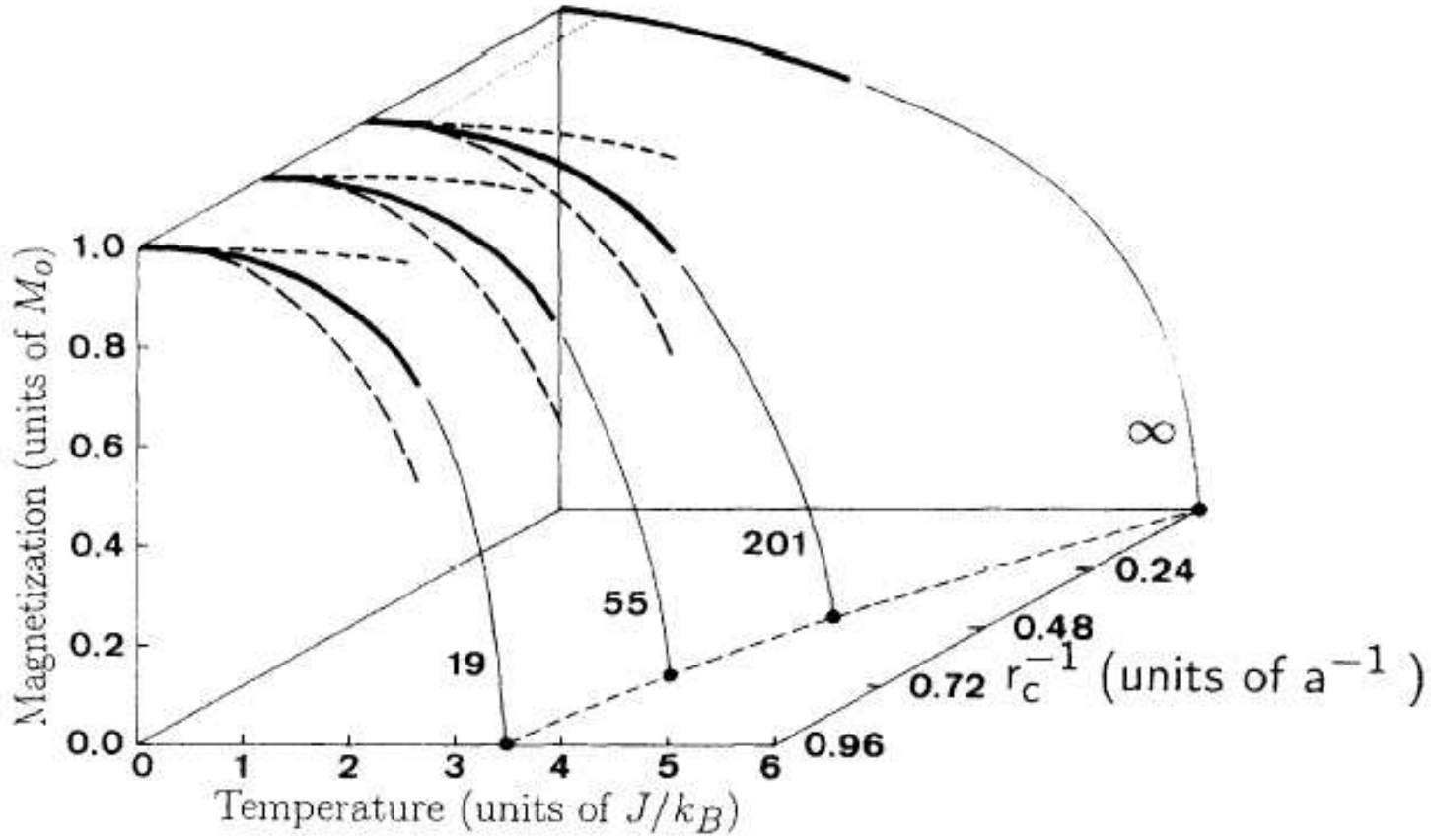


cluster

Discrete energy levels

Broadening in q

Temperature dependence of the magnetization
Curie temperature

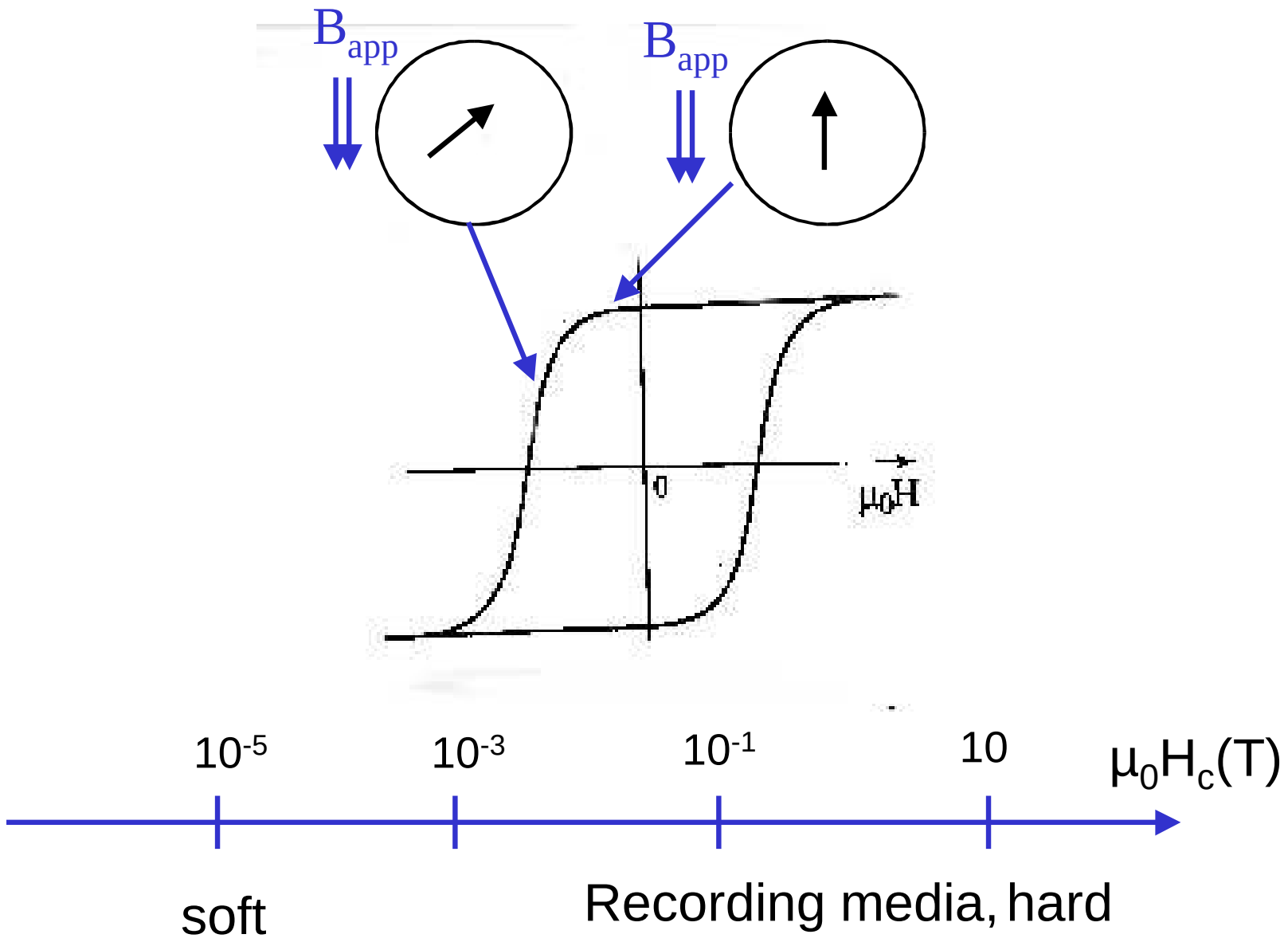


Tc reduced due to reduction in mean exchange interactions

At low T, M_s does not decrease due to the existence the energy gap

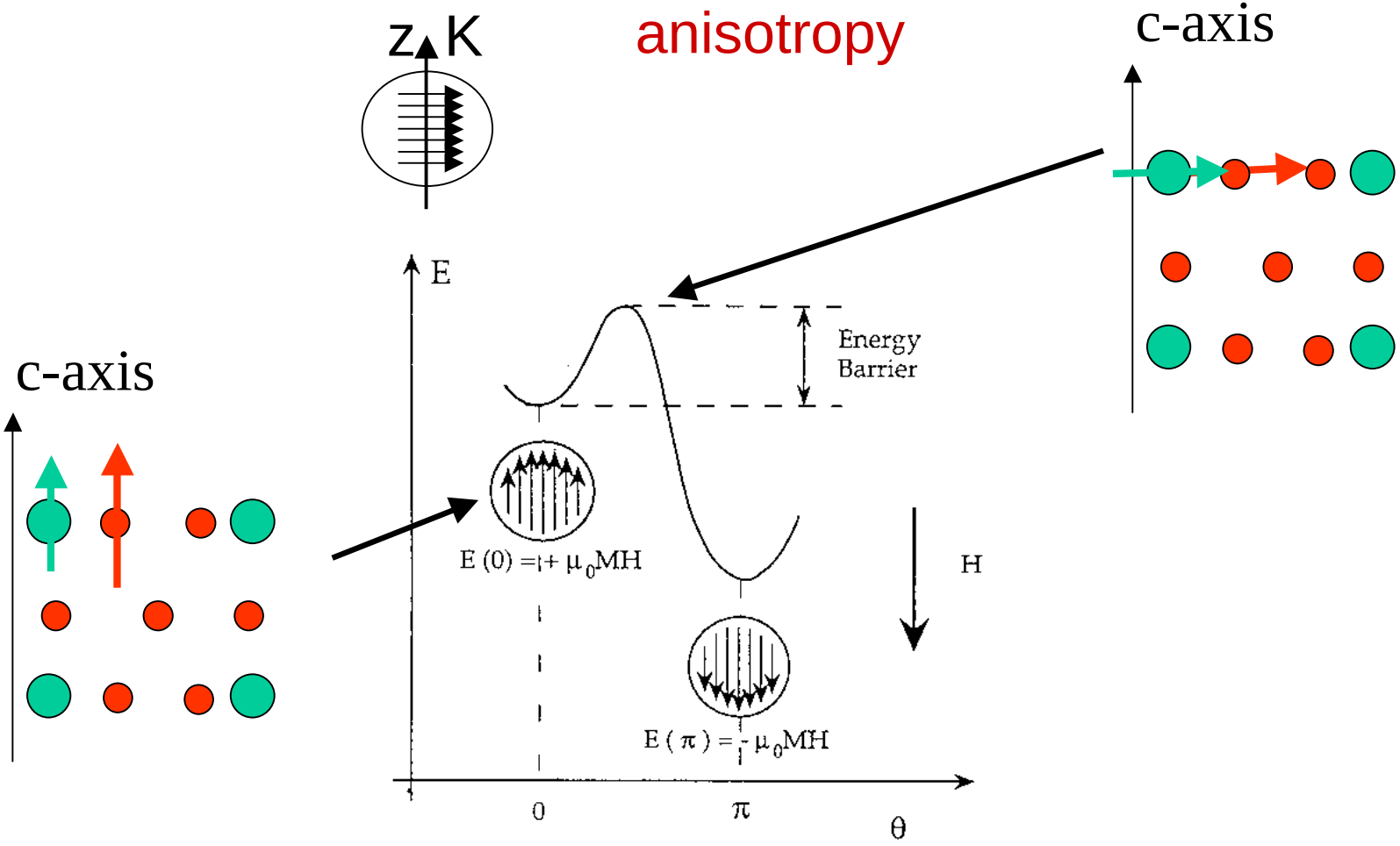
Coercivity

Main magnetic functional properties of ferromagnets



Coercivity

At the origin of coercivity : anisotropy



Coercive field for coherent rotation (Stoner-Wohlfarth)

$$E = K_1 \sin^2\theta + \mu_0 M_s H \cos\theta$$

$$\partial E / \partial\theta = K_1 \sin 2\theta - \mu_0 M_s H \sin\theta$$
$$= \sin\theta \, (2 K_1 \cos\theta - \mu_0 M_s H)$$

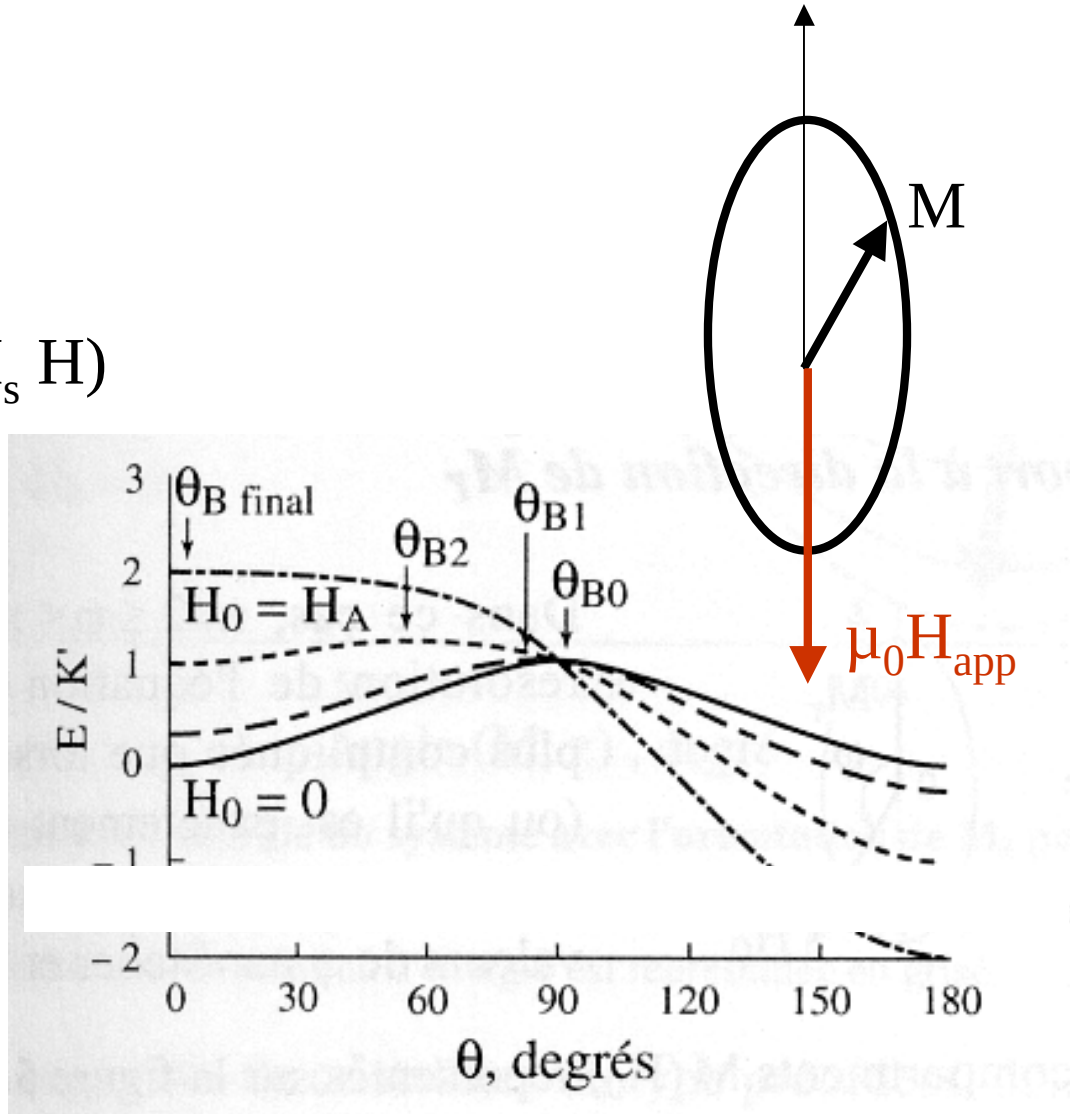
E_{min} : $\sin\theta = 0$, $\theta = 0$ or π

E_{max} : $\cos\theta = \mu_0 M_s H / 2K_1$

Coercive field :

E_{min} and E_{max} join together :

$$\mu_0 H_c = 2K_1 / \mu_0 M_s = H_A$$

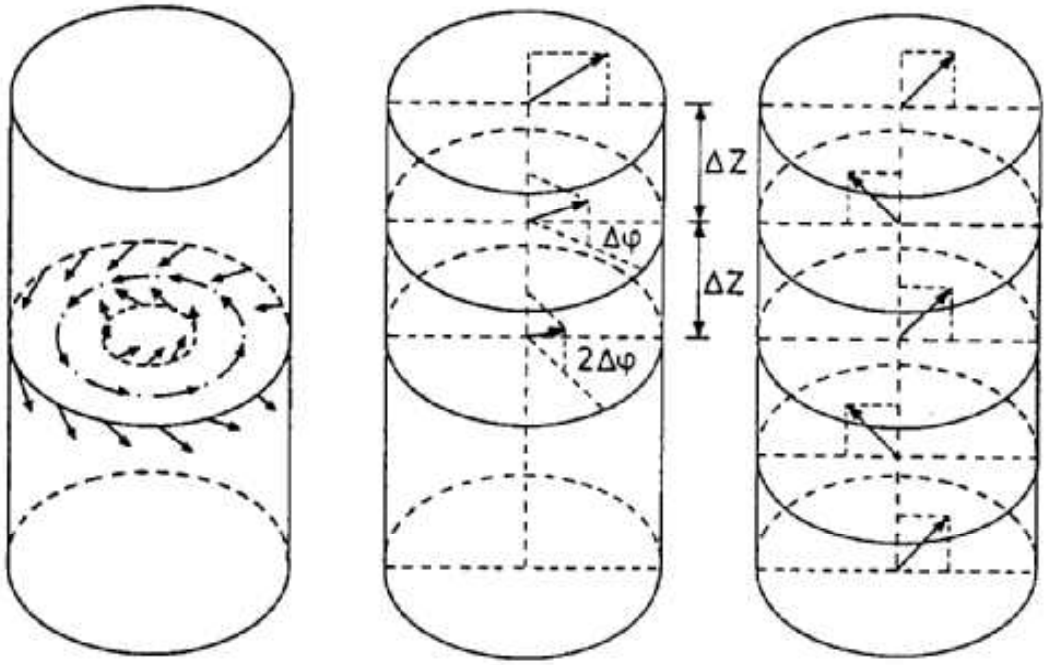


Dipolar interactions not equivalent to magnetocrystalline anisotropy

Global phenomenon

Local phenomenon

Anisotropy due to dipolar interactions
Curling

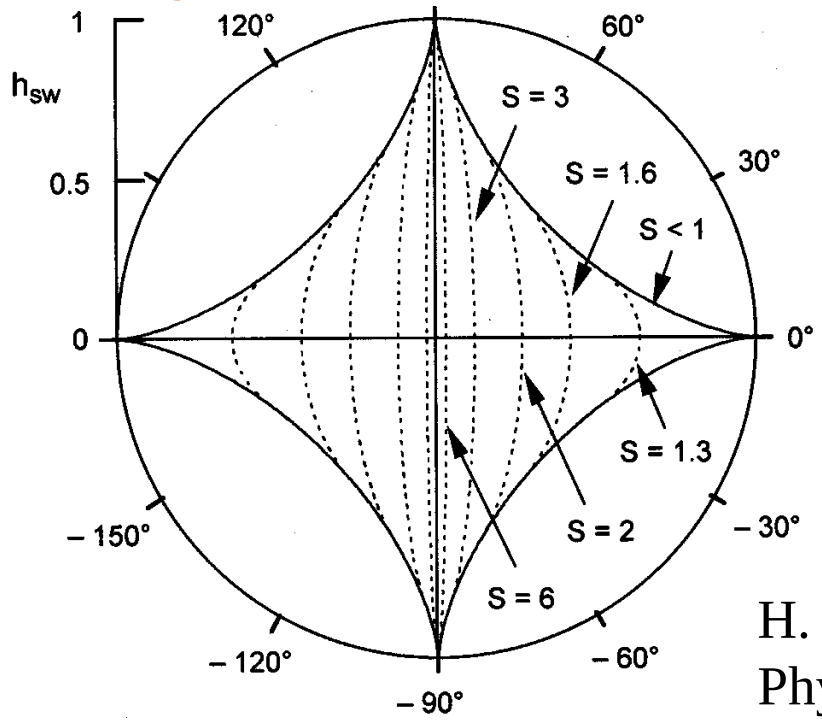


Non uniform configuration allows dipolar energy gain
at the expense of exchange

Anisotropy due to dipolar interactions

Coherent rotation : $H_c(\theta) = H_A / (\sin^{2/3}\theta + \cos^{2/3}\theta)^{3/2}$

Reversal by curling :



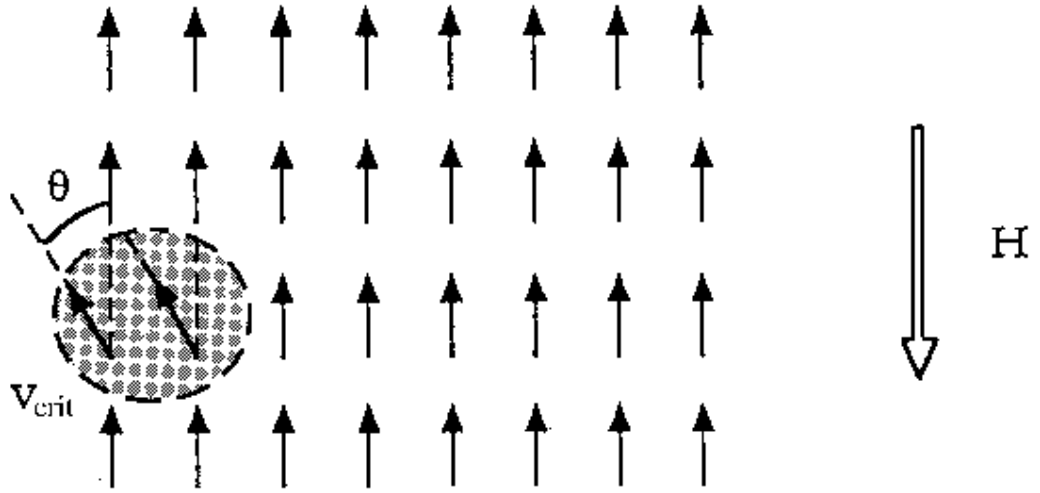
H. Frei et al.
Phys. Rev. 106 (1957) 446

$$H_{sw}^0 = \frac{M_s}{2} \frac{h_t(1+h_t)}{\sqrt{h_t^2 + (1+2h_t)\cos^2\theta}} \qquad h_t = -1.079/S^2.$$

$$H_c(\theta) \approx \frac{1}{\cos\theta}$$

Classical and quantum magnetization reversal studied
in nanometer-sized particles and clusters, W. Wernsdorfer
Adv. Chem. Phys., 118, 99 (2001)

Magnetocrystalline anisotropy : Brown paradox



$$2A_{ex}\mathrm{d}^2\theta/\mathrm{d}z^2 + K_1 \sin 2\theta - \mu_0 M_s H \sin\theta = 0$$

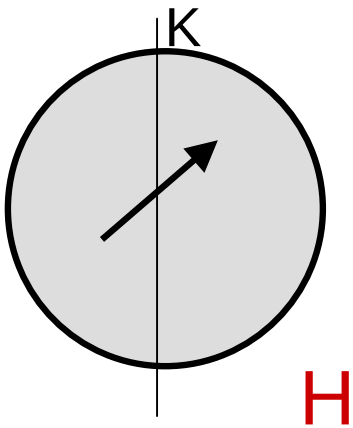
E_{min} : $\theta = 0$, $\mathrm{d}\theta/\mathrm{d}z = 0$

$$E_{max}: \ \mathrm{Cos}\theta = 1 - \frac{2A_{exch}}{\mu_0 M_s H_A}\ \frac{1}{\sin\phi}\ (\partial^2\theta/\partial z^2)$$

⟹ Reversal should occur by coherent rotation with $H_c = H_A$

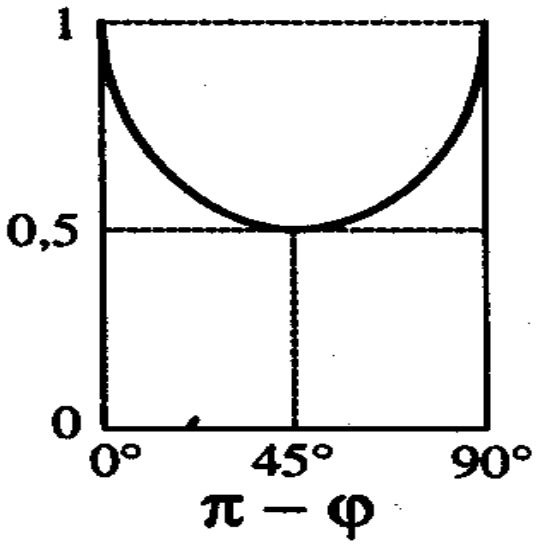
Magnetisation reversal processes

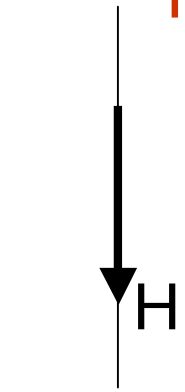
Perfect materials :
Coherent rotation

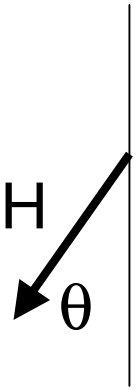


$H_c = H_A$

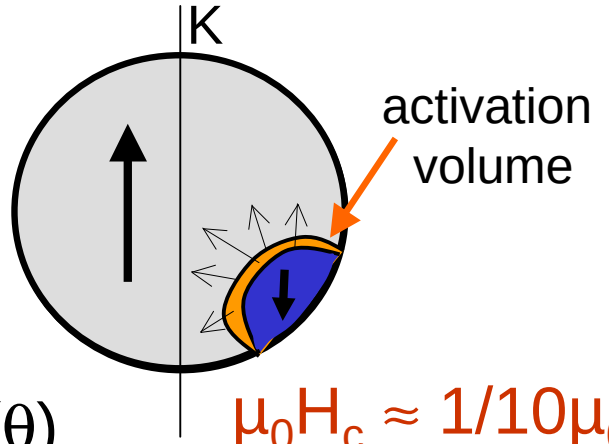
$H_c(\theta)$





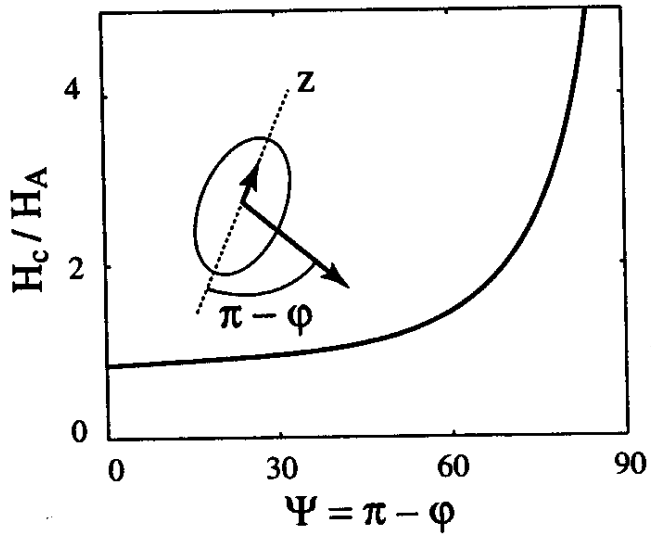


Defects :
Nucleation + propagation



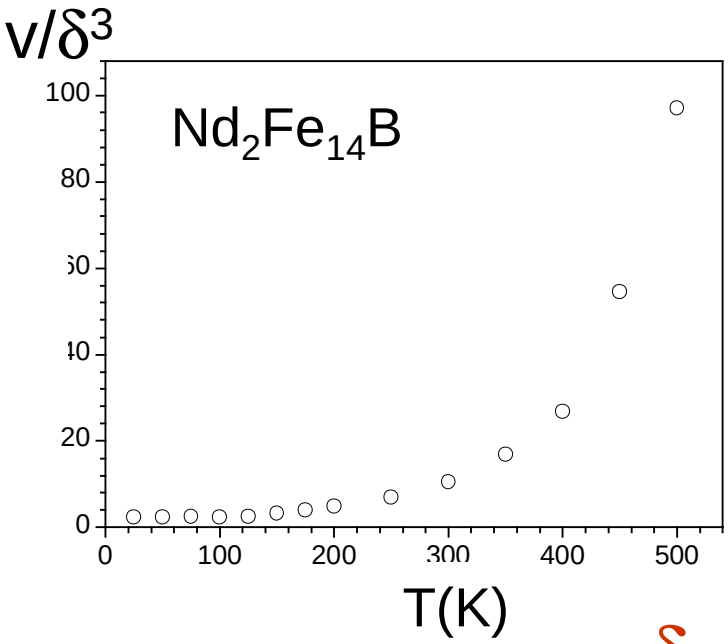
$\mu_0 H_c \approx 1/10 \mu_0 H_A$

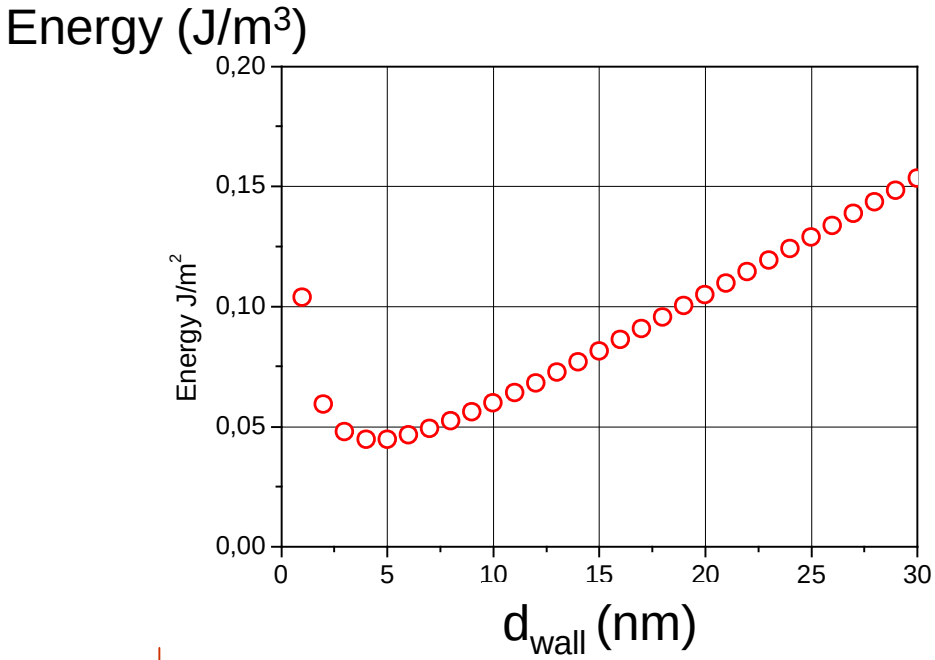
$H_c(\theta)$

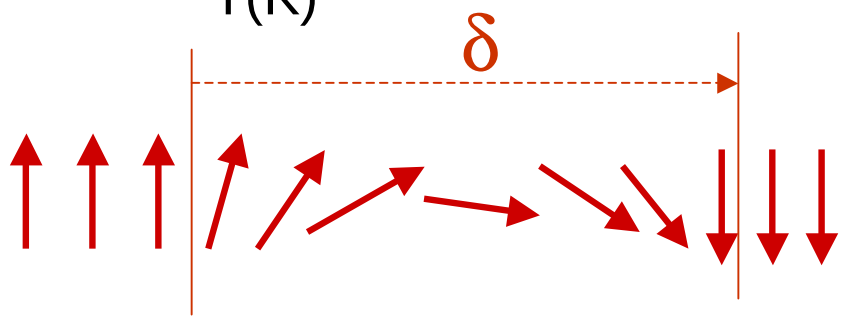


Coercivity analysis :
influence of defects on reversal

Domain wall width : Characteristic dimension for reversal







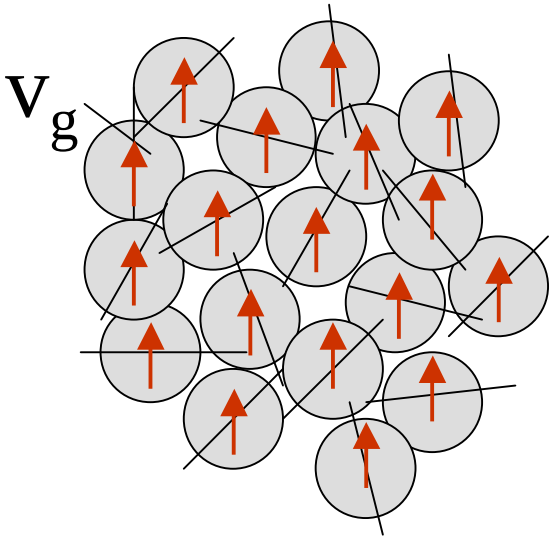
$$\delta = \pi\sqrt{\frac{A}{K}}$$

Fe : δ ~ 30 nm

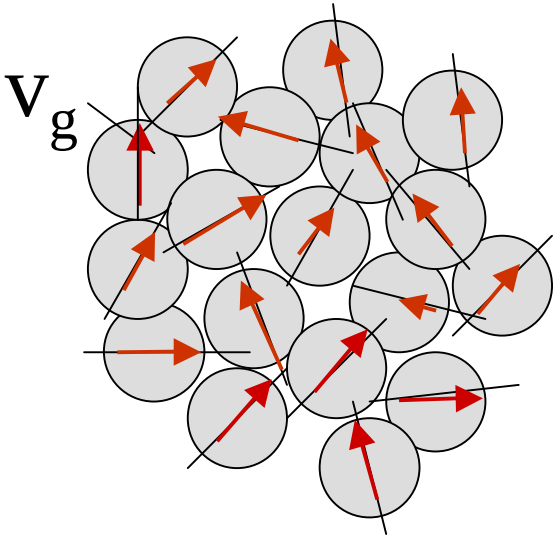
$Nd_2Fe_{14}B$: δ ~ 5 nm

what happens for D<δ ?

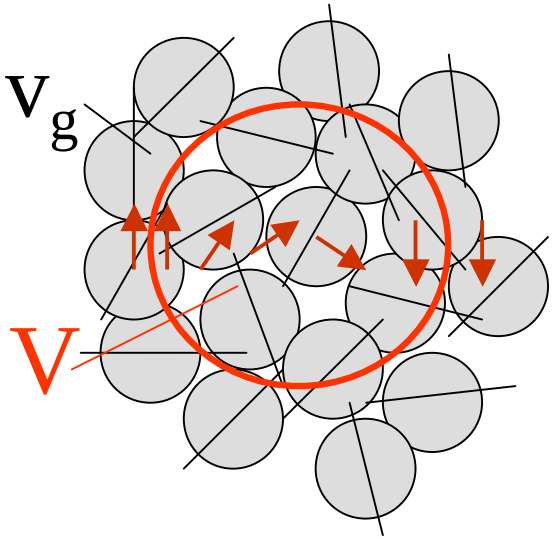
Correlation length in Exchange-coupled nanograins



Anisotropy lost : volume term



Exchange lost : surface term



$\Longrightarrow$ correlation length ξ

correlation volume $V = \xi^3$

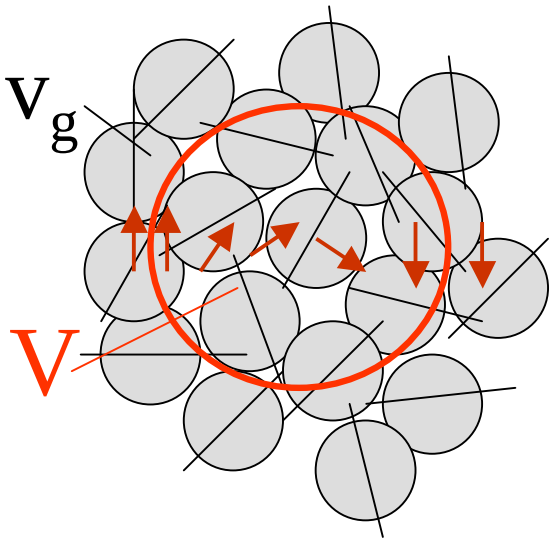
$$\xi = \pi \sqrt{\frac{A}{K}} \quad \text{with} \quad \overline{K} = K_g \sqrt{\frac{v_g}{V}}$$

$$\xi = \frac{\delta_g^4}{v_g}$$

$$\frac{1}{\sqrt{N}}$$

Correlation length and anisotropy

Herzer IEEE Trans. Mag. (1989)



$$\xi = \frac{\delta_g^4}{v_g} = \alpha^3 \delta_g \quad \text{with} \quad \alpha = \frac{\delta_g}{D}$$

$$N = \left(\frac{\delta_g}{D}\right)^{12}$$

v_g = 10 nm

soft $\delta_g \approx$ 100 nm $\xi \approx$ 100 μm

hard $\delta_g \approx$ 5 nm $\xi \approx$ 1 nm

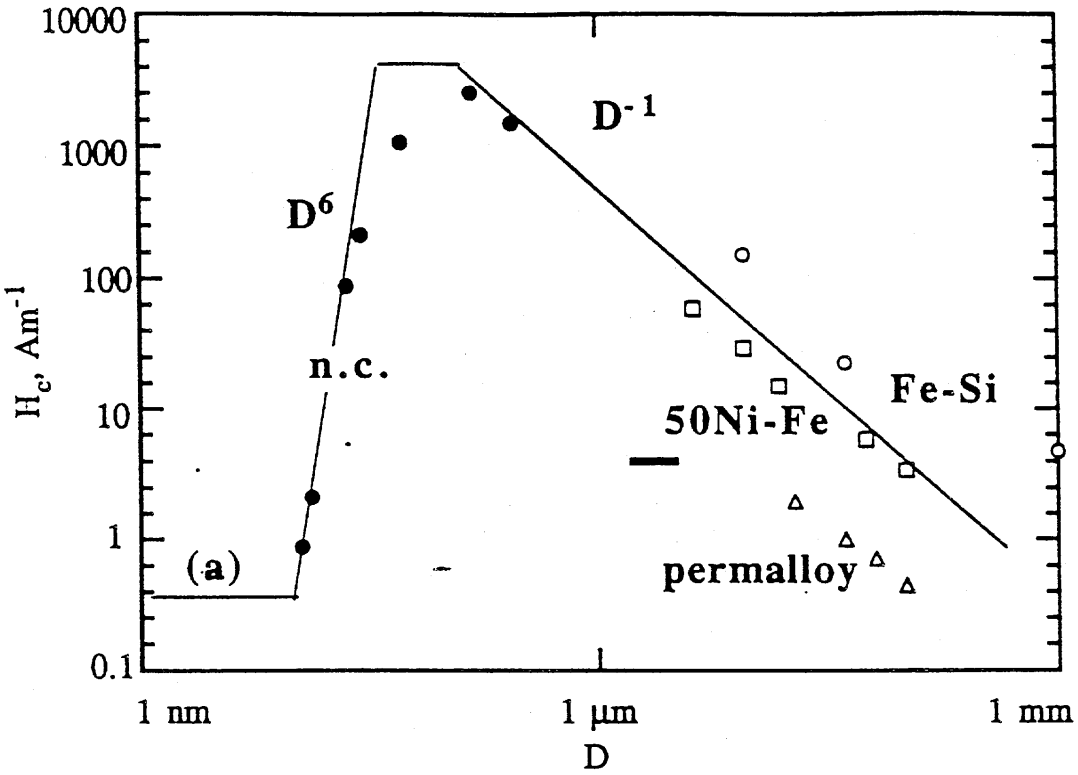
in soft materials

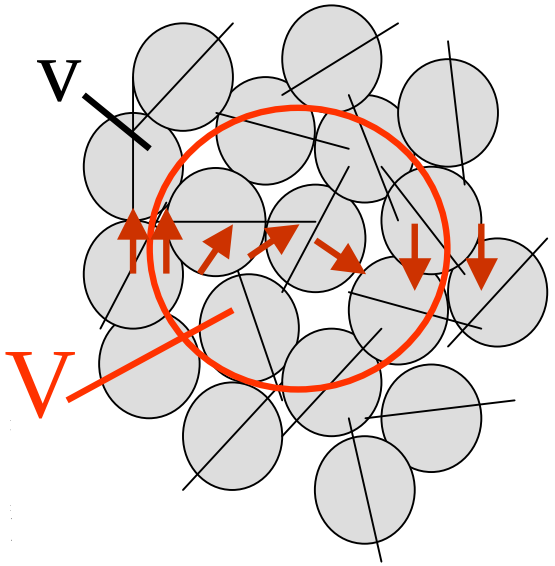
$$\overline{K} = K_g \sqrt{\frac{v_g}{V}} = K_g \frac{1}{\alpha^6}$$

Nanoscale materials development
for future magnetic applications
M.E. McHenry and D.D. Laughlin
Acta; Mater. 48 (2000) 223

ultra-soft magnetic properties expected

Exchange-coupled soft nanograins
Anisotropy and Coercivity





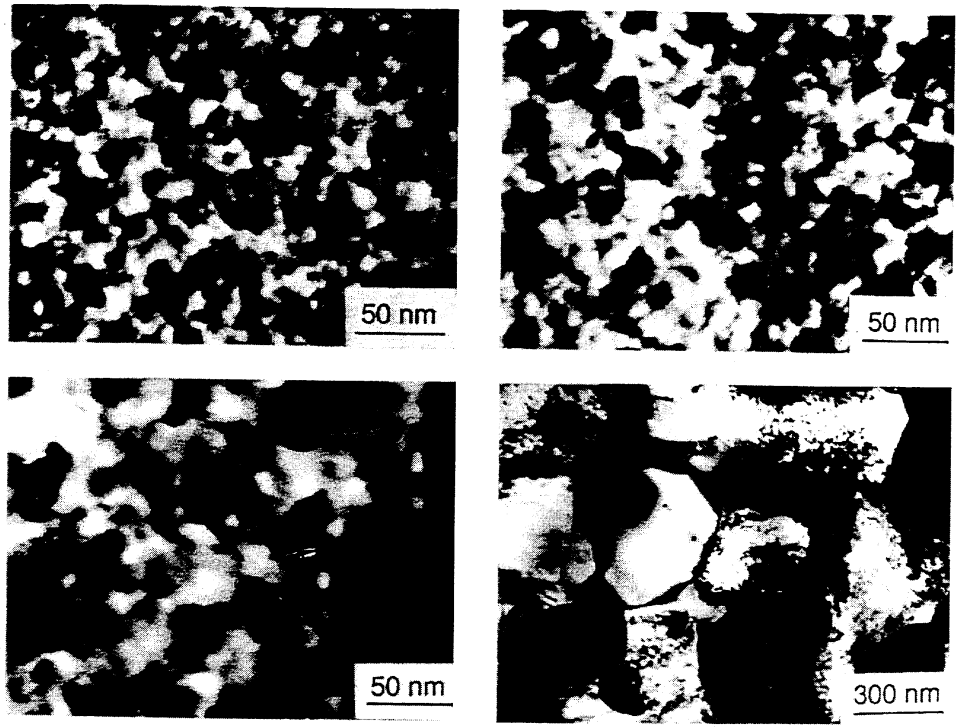
$$\overline{K} = K_g \frac{1}{\alpha^6}$$

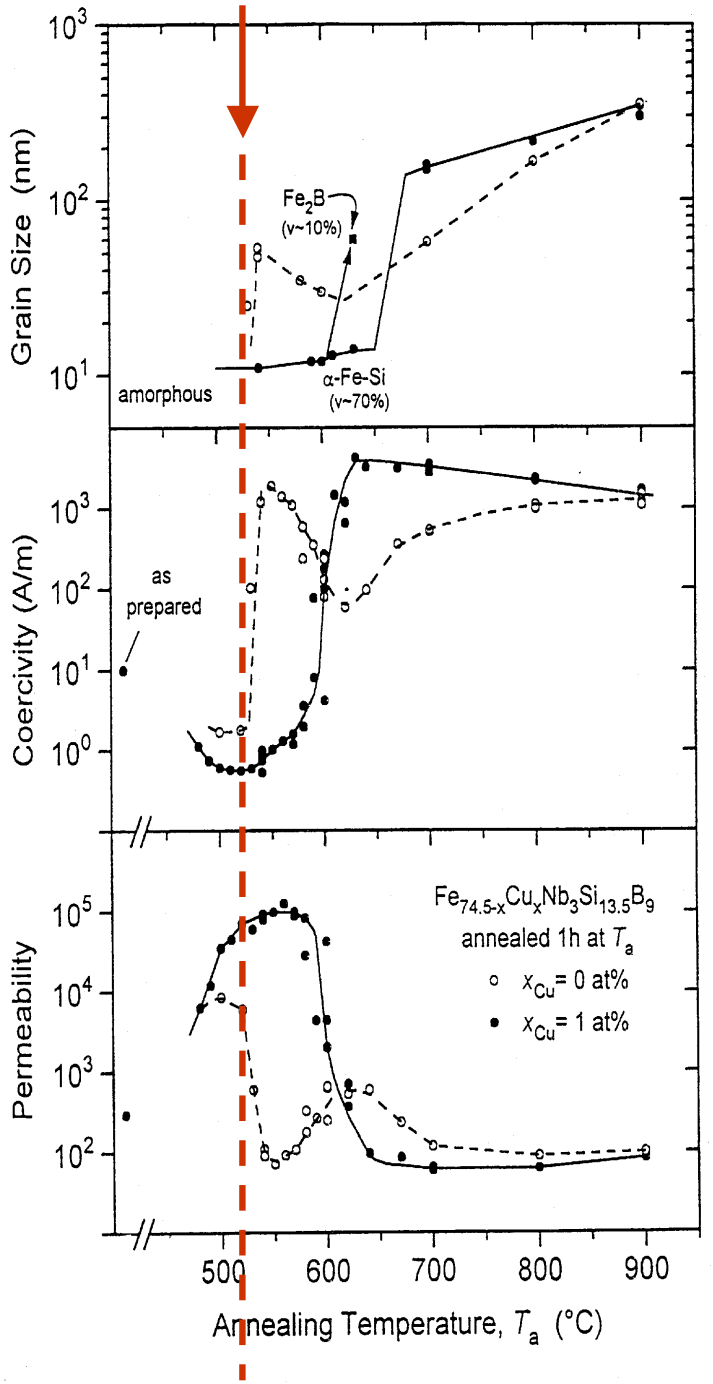
Anisotropy averaged over
many particles : extremely small

$K_g = 10^4$ J/m^3
D =10nm, δ_g = 100nm
$\alpha = 10$ $\overline{K} = 10^{-2}$ J/m^3

⇒ Ultra-soft magnetic properties

Ultra-soft Nanomaterials

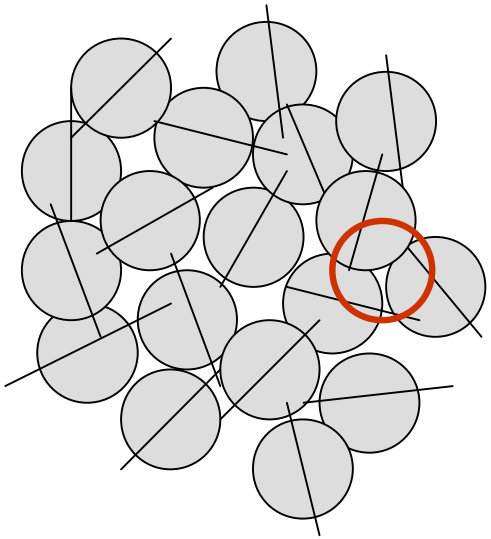




Problem :

How to combine large M_s, large χ and high resistivity ?

Exchange-coupled hard nanograins



$A \sim 10^{-11}$ J/m $K \sim 10^{7}$ J/m^3

$\delta_g \sim 5\ 10^{-9}$ m

$\Rightarrow \alpha = 0.5$

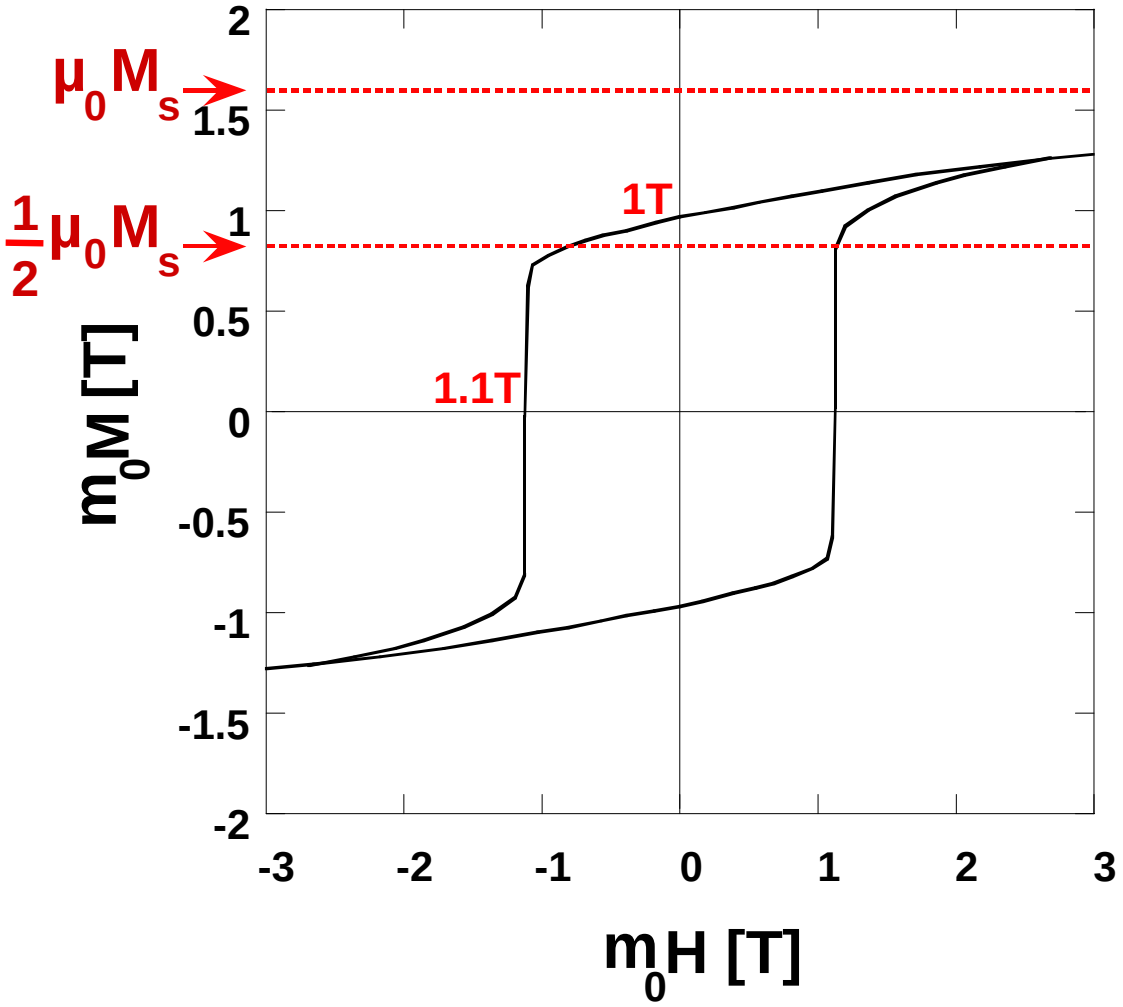
no anisotropy averaging

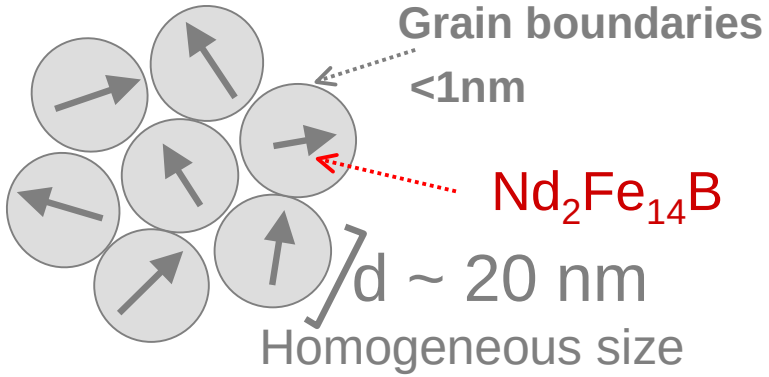
$\Rightarrow$ Anisotropy remains large

$\Rightarrow$ Hard nanomaterials

Isotropic NdFeB with enhanced remanence

(McCallum et al. (1987))



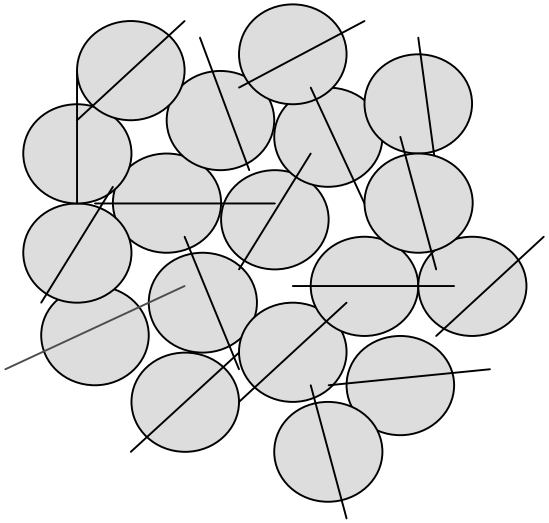


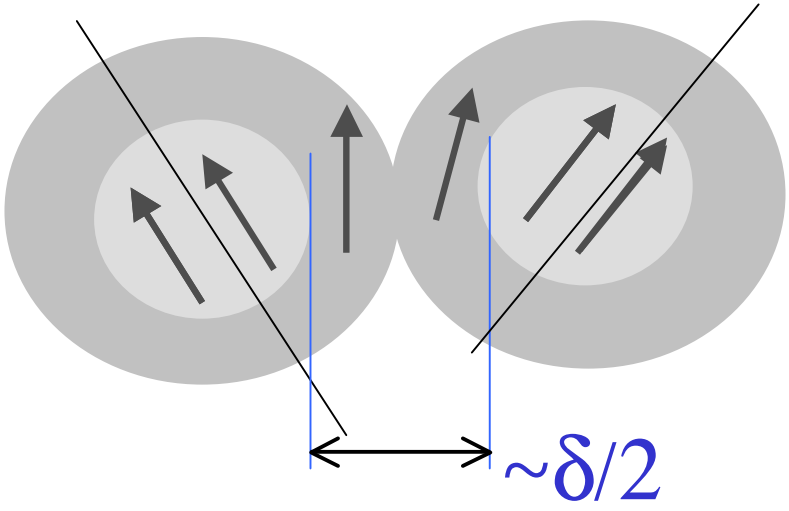
Exchange-coupled crystallites

Remanence enhancement

$M_r > 0.5M_s$

Remanence enhancement in NdFeB ribbons

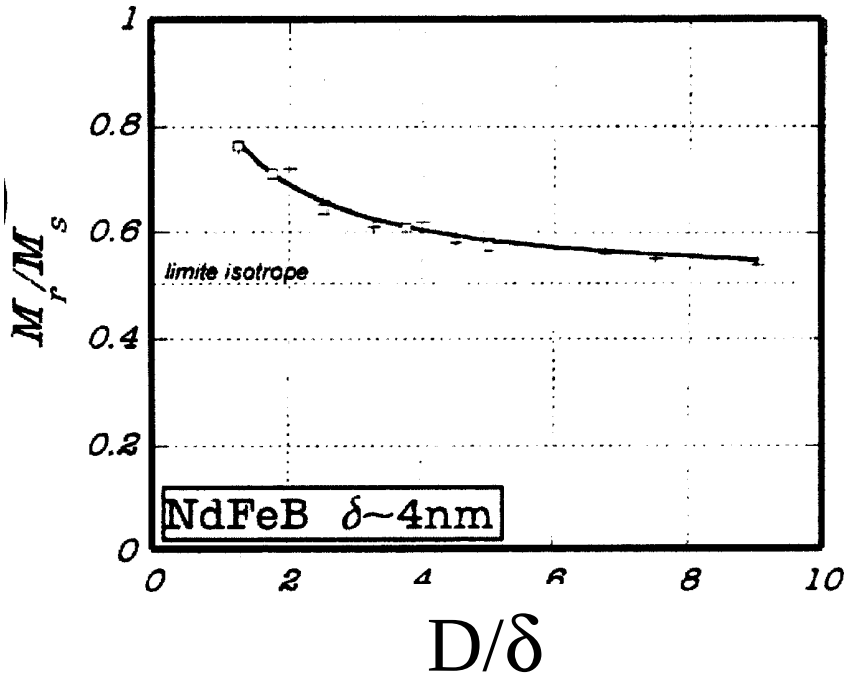




$$\alpha = D/\delta$$

$$\frac{M_r}{M_s} = 0.5\left(1-\frac{1}{2\alpha}\right)^3 + \beta\left(1-\left(1-\frac{1}{2\alpha}\right)^3\right)$$

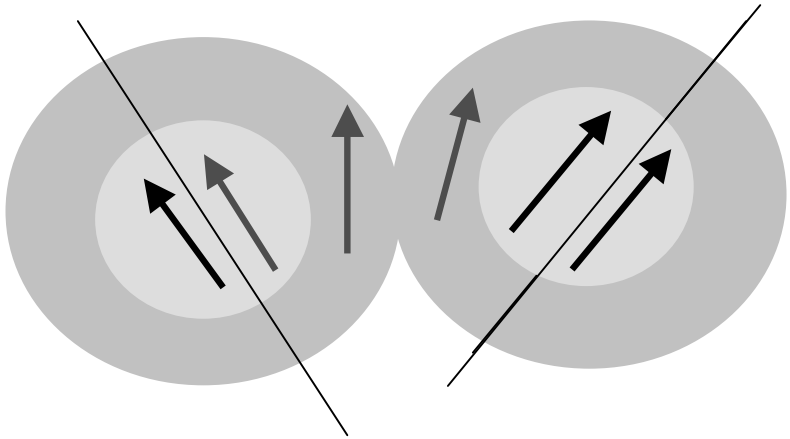
fit gives $\beta = 0.85$

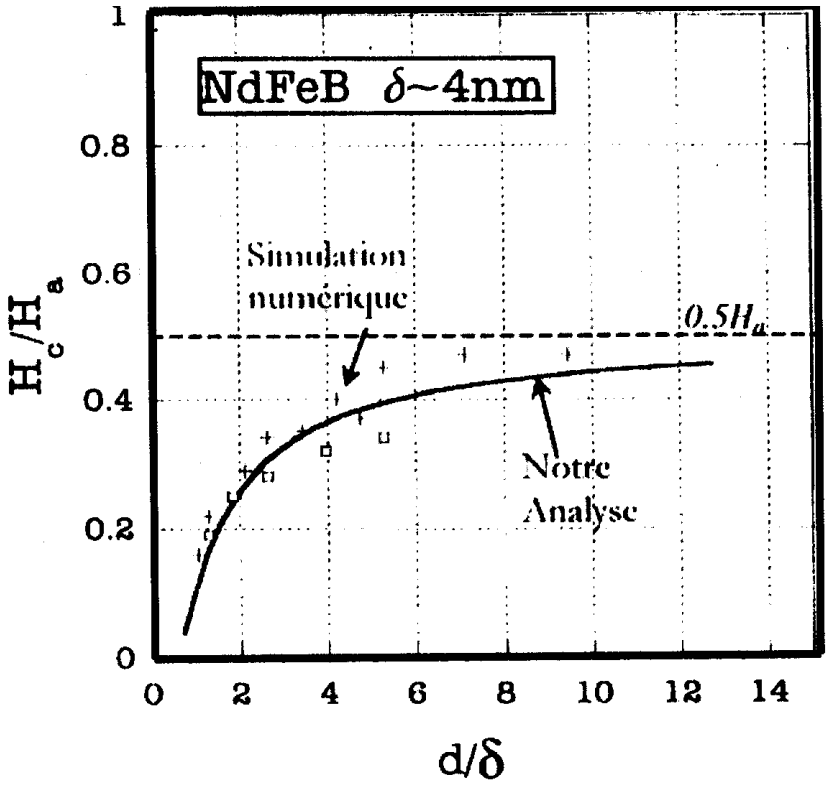


Remanence enhancement and coercivity

$$K' \sim K\left(1-\frac{1}{2\alpha}\right)^3$$

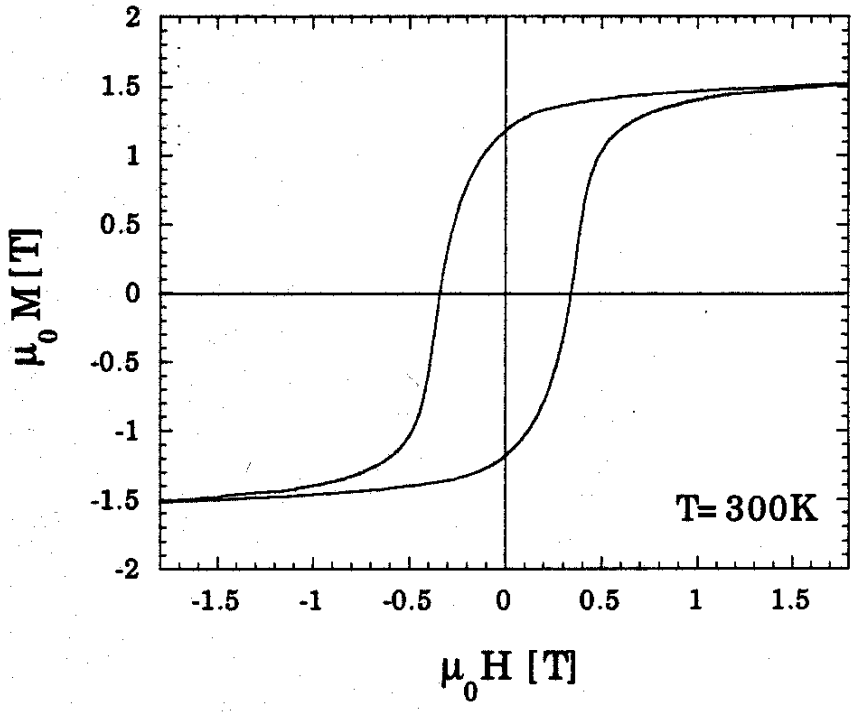
$$H_c \sim (H_A)' \left(1-\frac{1}{2\alpha}\right)^3$$

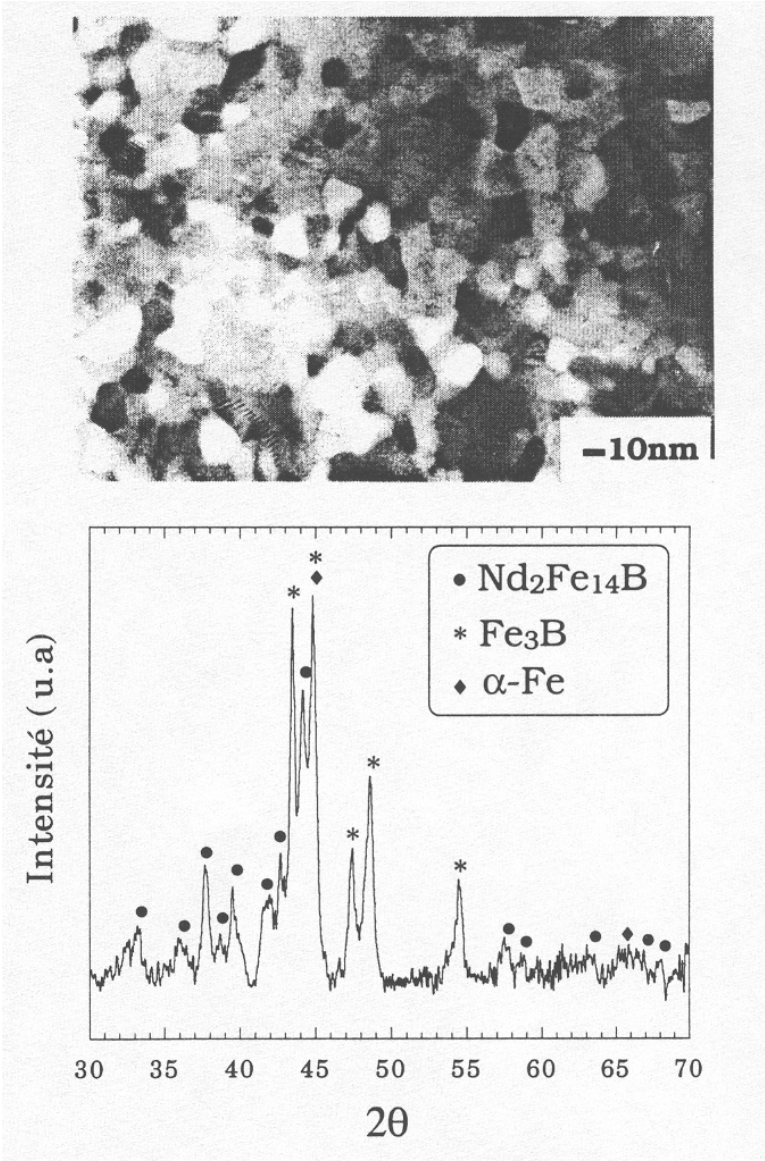




NdFeB nanocomposites

(R. Coehoorn *et al.* J. de Phys. (Paris) (1988))

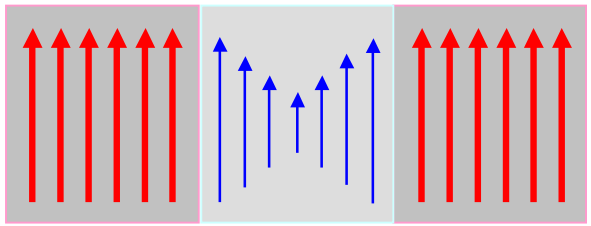




Magnetization processes in nanocomposites

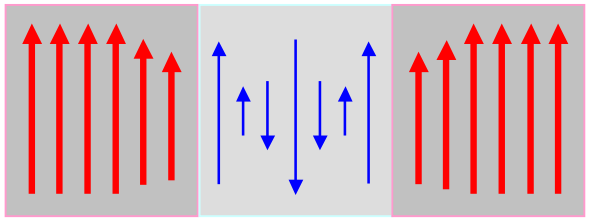
(Kneller and Hawig IEEE Trans. Mag. [1991])

❶ Nucleation : Soft



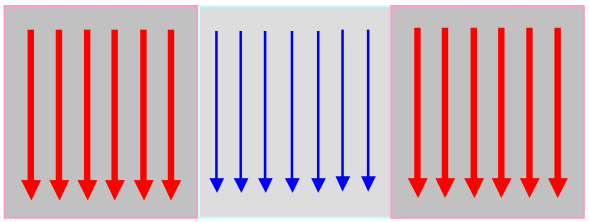
REVERSIBLE

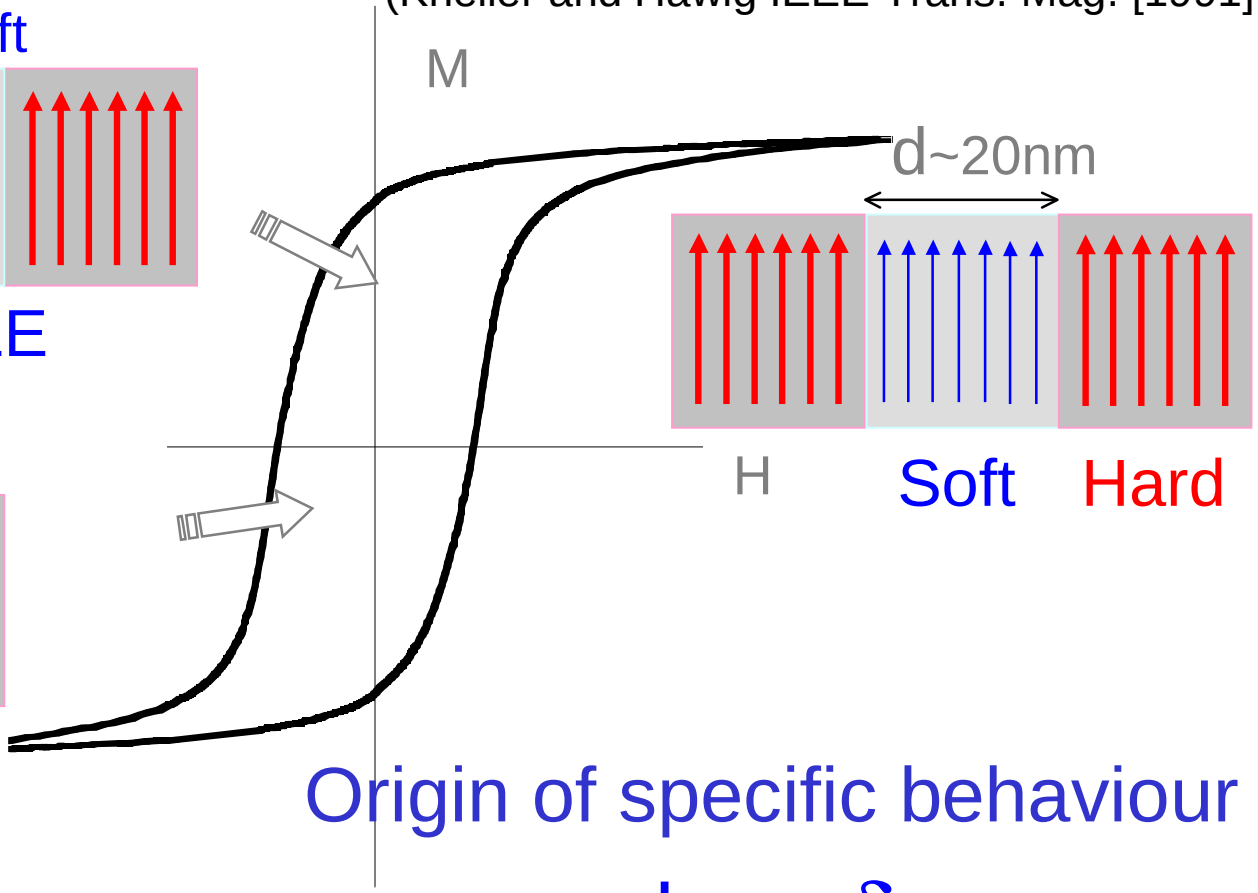
❷ Propagation: Hard



IRREVERSIBLE

Complete reversal



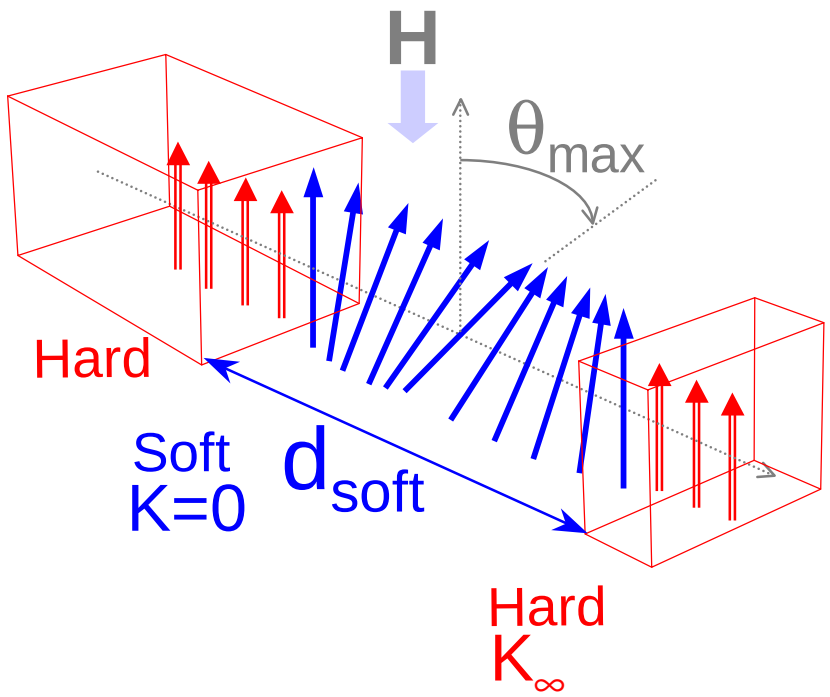


Origin of specific behaviour :

$d_{soft} < \delta_{soft}$

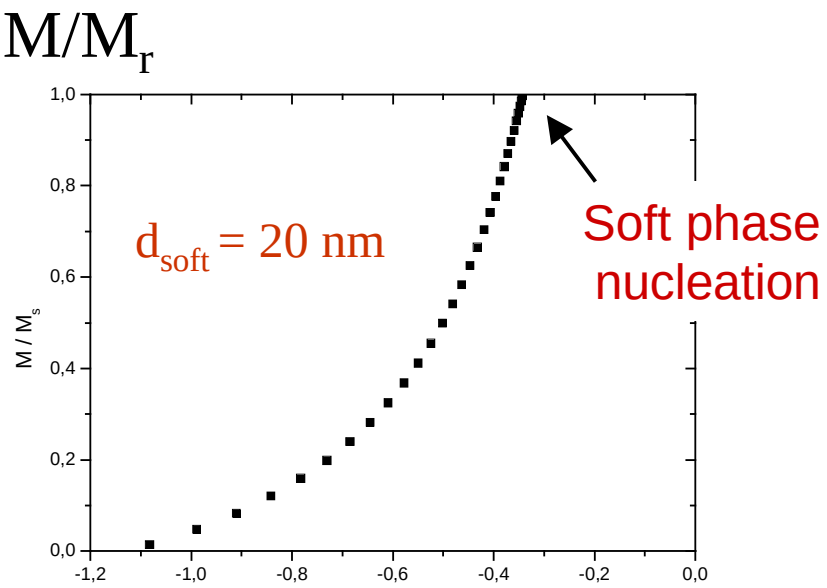
The exchange-spring magnet : a new material principle for permanent magnets,
E. Kneller and R. Hawig
IEEE Trans Mag. 27 (1991) 3588

Soft phase hardening in nanocomposites



$$E_T = \frac{4A\theta_{\max}^2}{d} + \mu_0 MHd\,\overline{\cos(\theta)}$$

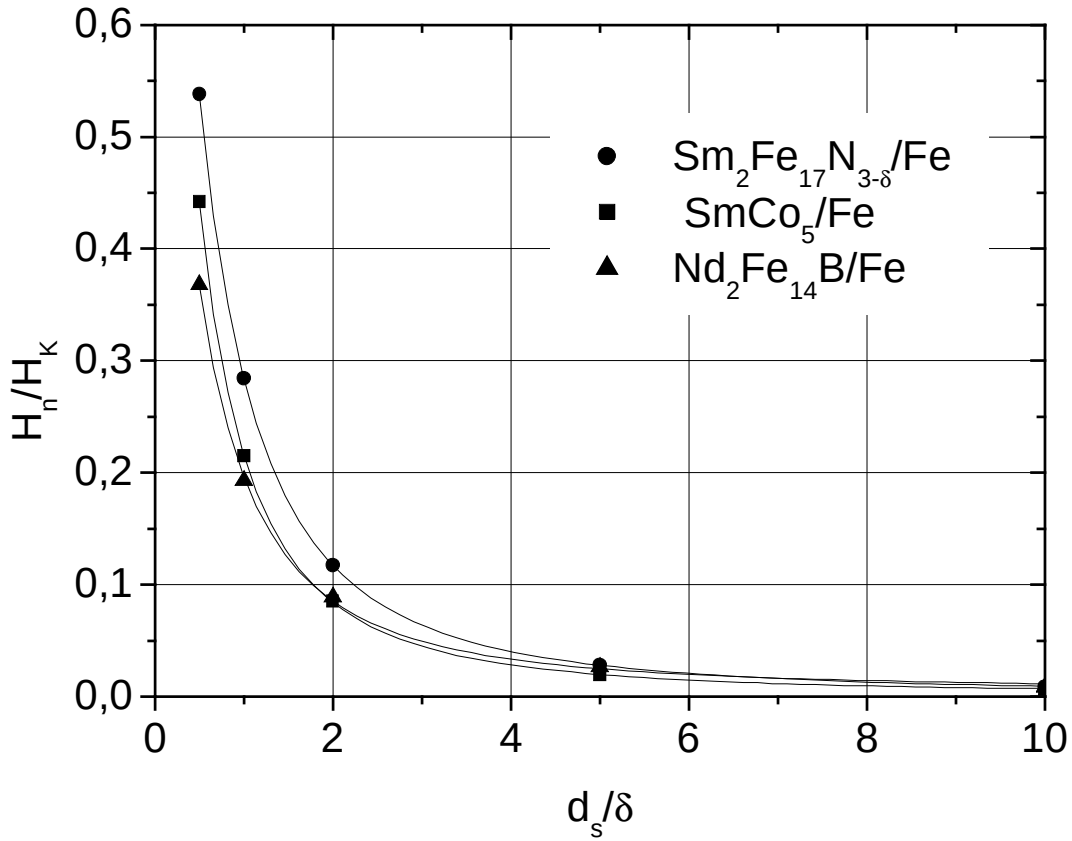
$$\mu_0 H = \frac{8A\theta_{\max}^3}{M_{soft} d^2} \frac{1}{[\theta_{\max}\cos(\theta_{\max}) - \sin(\theta_{\max})]}$$



Giant energy product in nanostructured two-phase magnets
R. Skomski and J.M.D. Coey
Phys. Rev. B48 (1993) 15812

Nucleation field in various RM/Fe multilayer nanocomposites

Skomski and Coey, Phys. Rev. B48 15812 (1993)



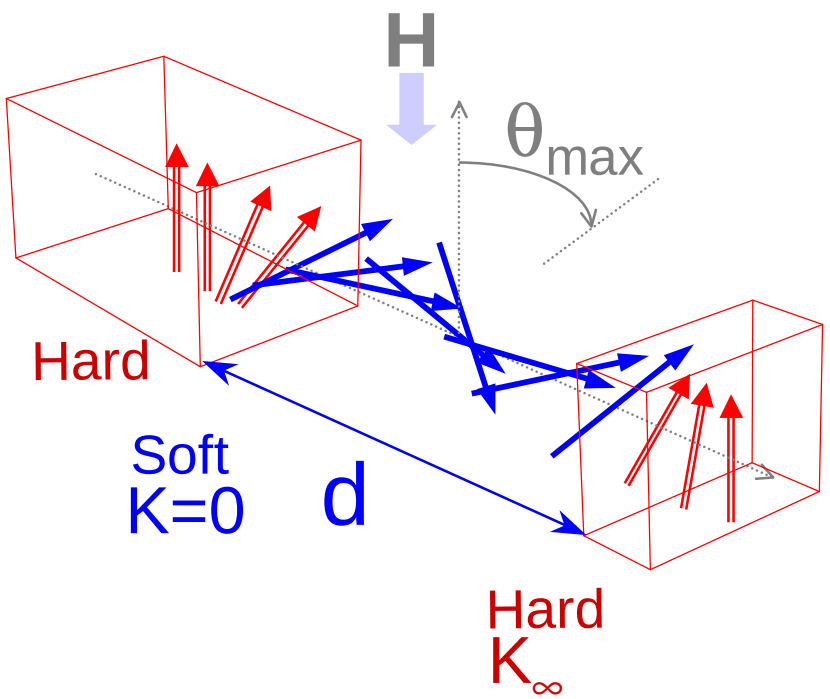
$\mu_0 H_n = 1T$

$Sm_2Fe_{17}N_{3-\delta}$ /Fe : $d_s = 10$ nm

$SmCo_5$/Fe : $d_s = 10$ nm

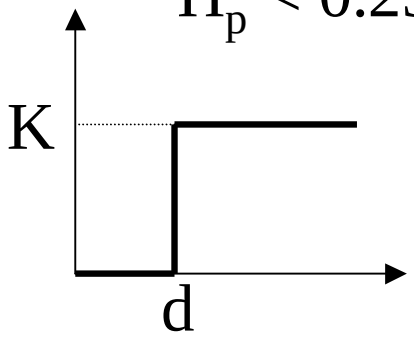
$Nd_2Fe_{14}B$/Fe : $d_s = 7.5$ nm

Propagation field



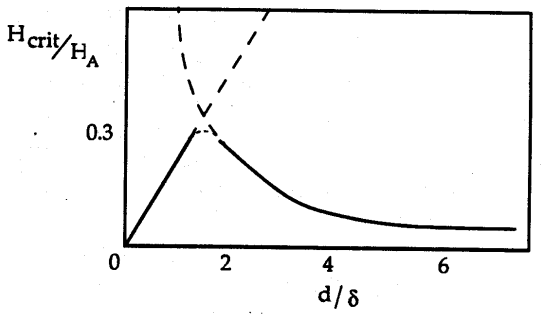
Aharoni :

$H_p < 0.25\ H_A$



Kronmüller :

$H_p < 0.3\ H_A$



Toussaint :

$$H_p = \frac{\lambda}{(1+\sqrt{\lambda})^2} H_A \quad \text{with} \quad \lambda = \frac{M_h A_h}{M_s A_s}$$

$H_p \approx 0.15\ H_A$ for perfect interface and infinite thicknesses

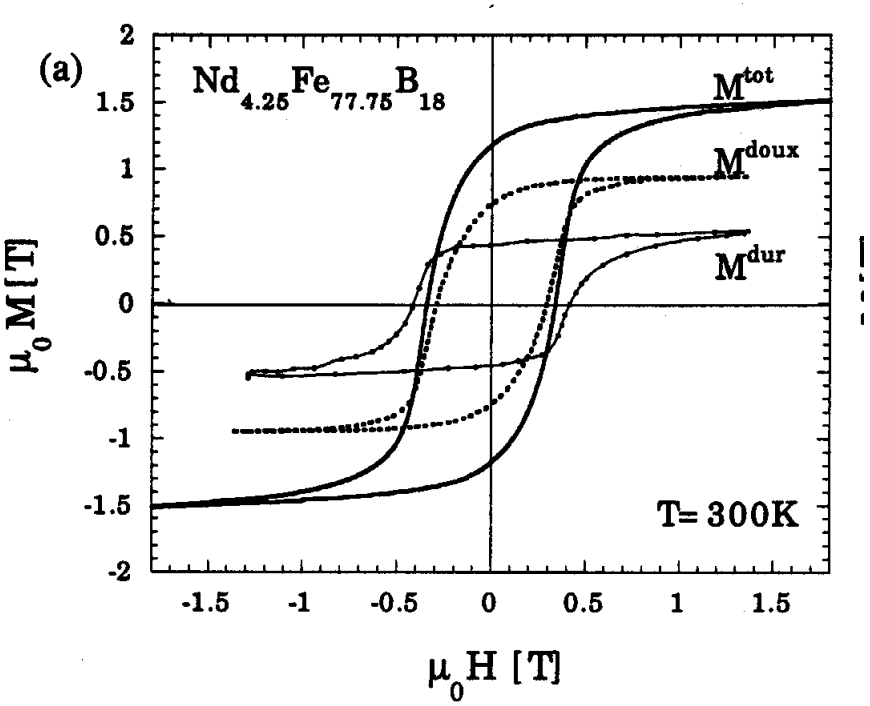
$H_p \approx 0.1\ H_A$ for $d \approx 2\delta$

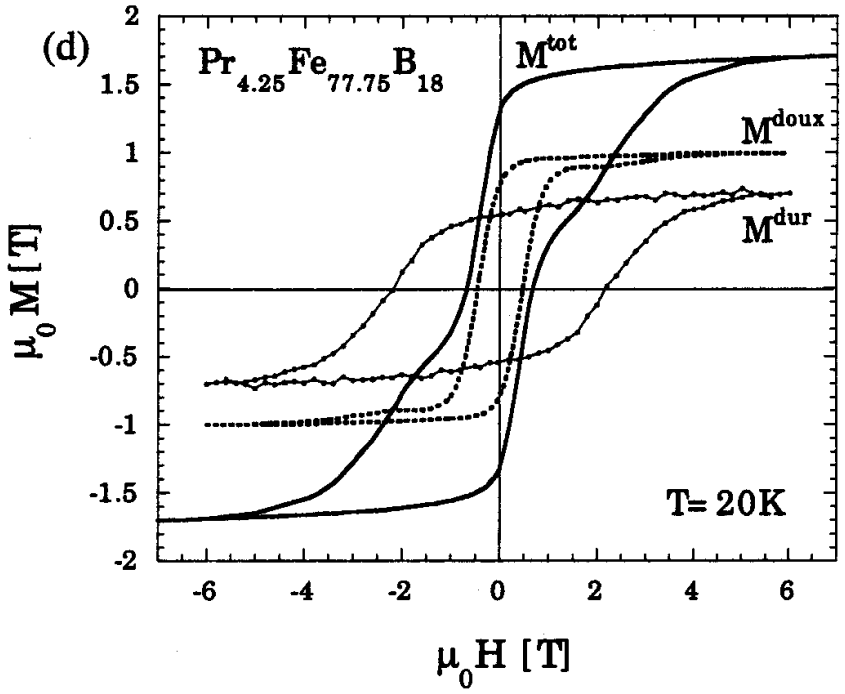
$Nd_2Fe_{14}B$

$H_p < 0.8$ T at 300 K

Propagation field in RFeB spring magnets

(S. David et al. 1999)



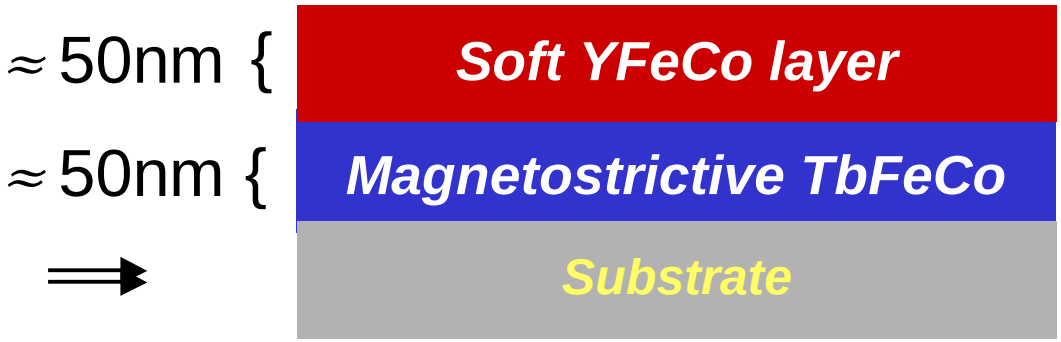


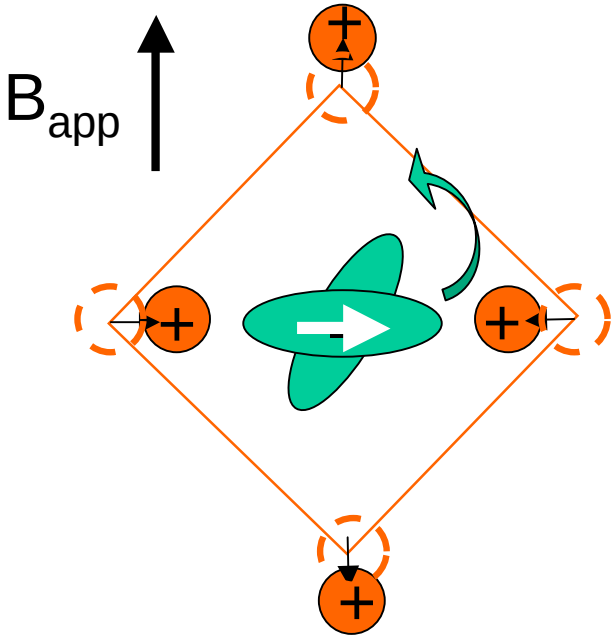
$\mu_0 H_p = 0.5$ T
$\mu_0 H_A = 8$ T
$\mu_0 H_p / \mu_0 H_A \approx 0.055$

$\mu_0 H_p = 2.4$ T
$\mu_0 H_A = 32$ T
$\mu_0 H_p / \mu_0 H_A \approx 0.075$

Conclusion : large H_c requires nanoparticle size around 10 nm
+very large anisotropy

Giant magnetostriction in multilayers



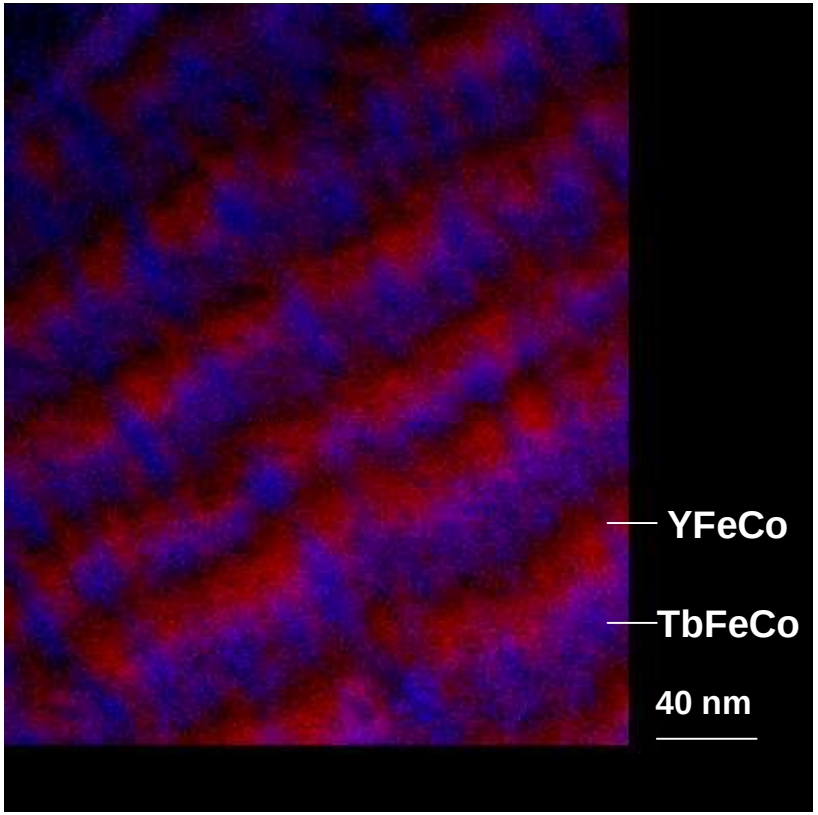


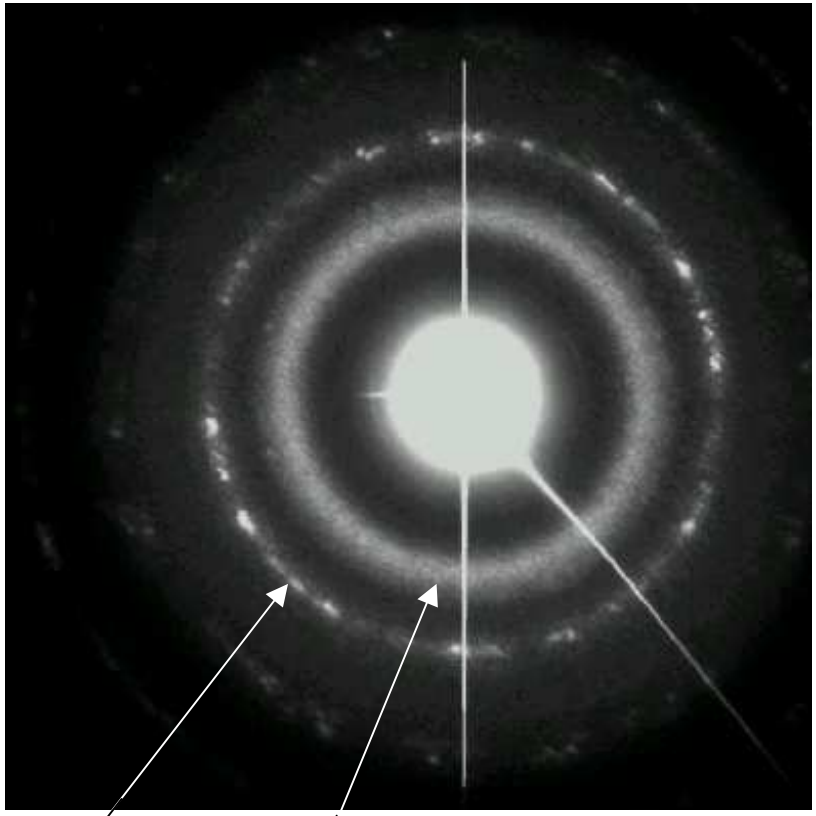
Magnetostriction :
anisotropy induced by deformation

Exploit the concept of coupled nanograins
to get low anisotropy field (large magnetization of Fe)

$\{TbFeCo/YFeCo\}_n$ multilayers

(Duc, Giang et al., JMMM, to be published)



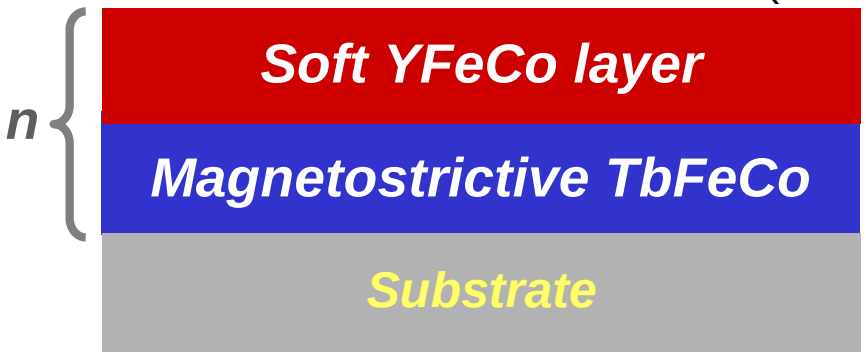


Nanocrystalline YFeCo

Amorphous TbFeCo

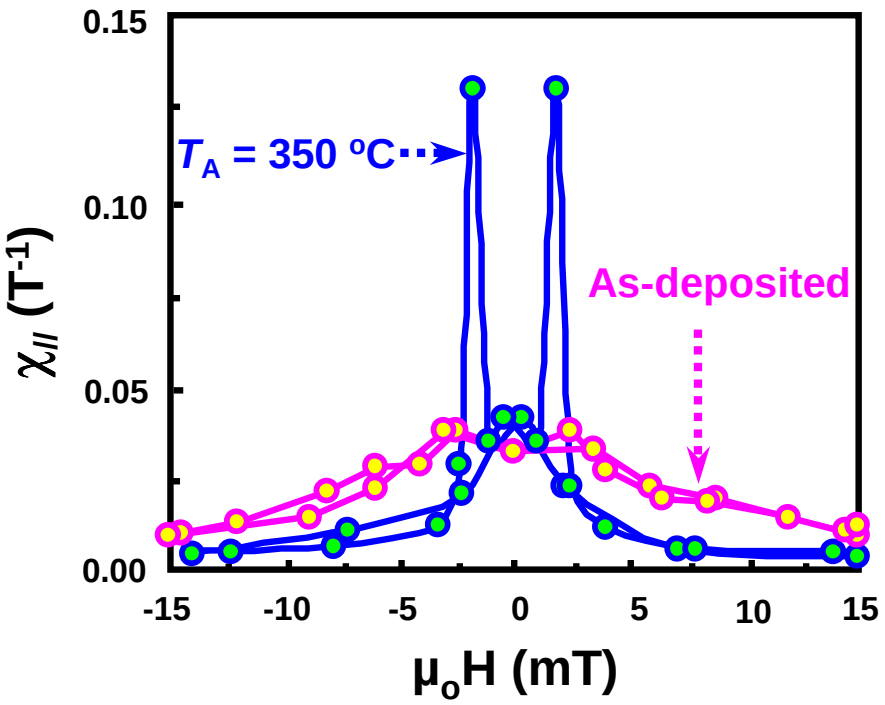
Magnetostriction in $\{TbFeCo/YFeCo\}_n$ multilayers

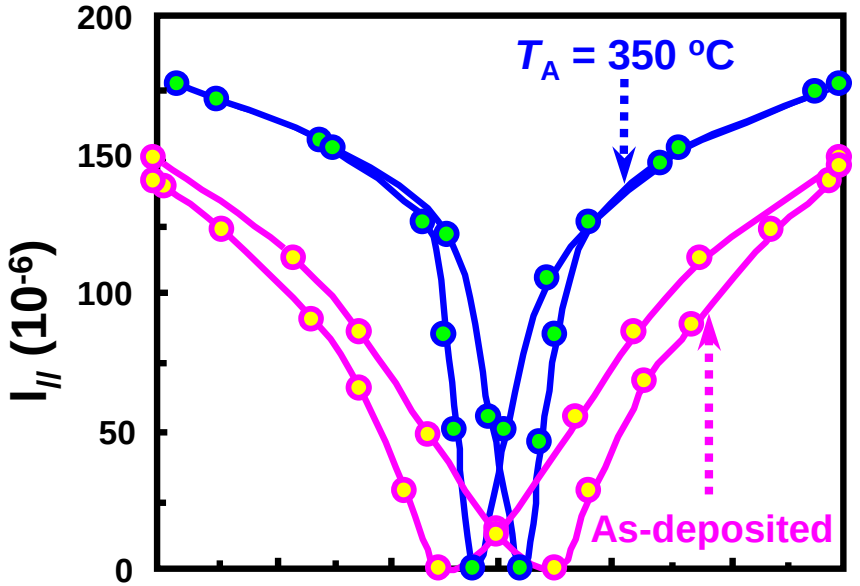
(J. Betz et al. JAP (1998), N.H. Duc et al. JMMM (2001))

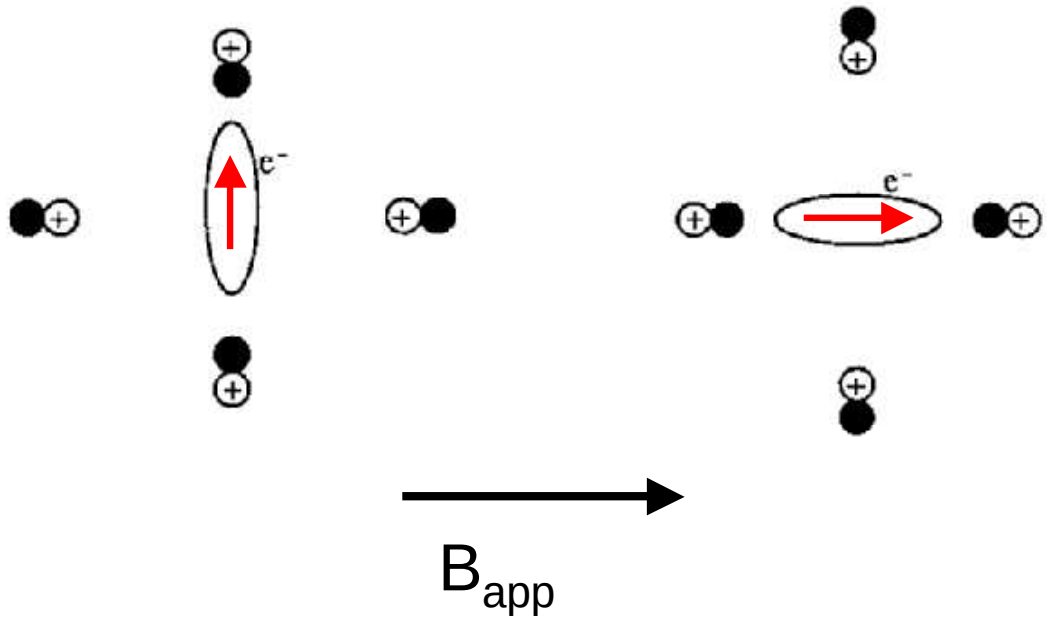


Giant magnetostrictive susceptibility

$\chi_{//} = 13\times10^{-2}\ T^{-1}$ at $\mu_o H = 1.8$ mT

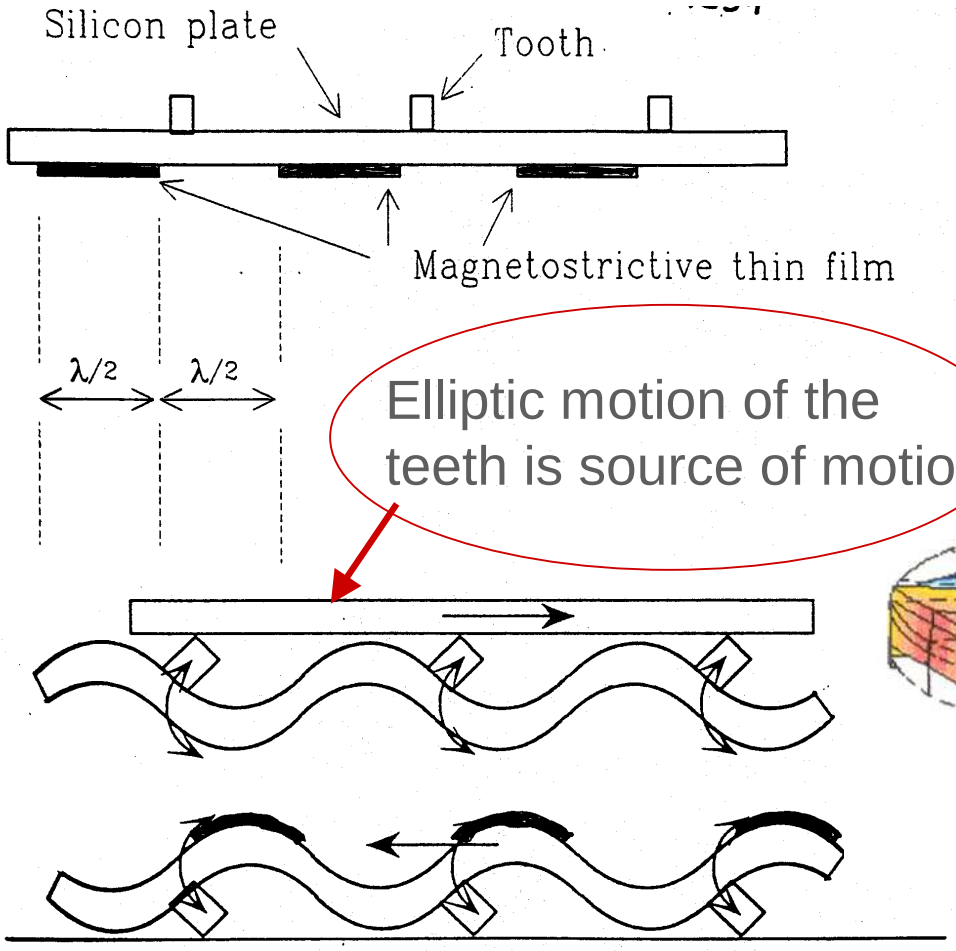






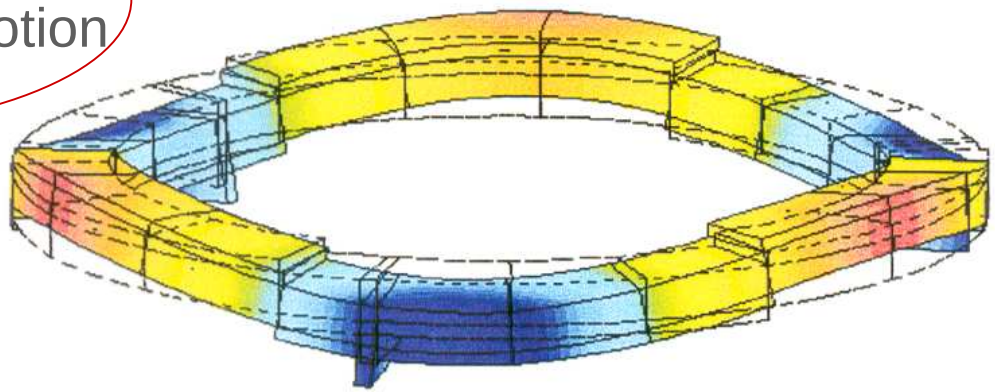
Torque due to the field is largely enhanced,
due to large magnetization of the Fe layer

Magnetostrictive micromotors



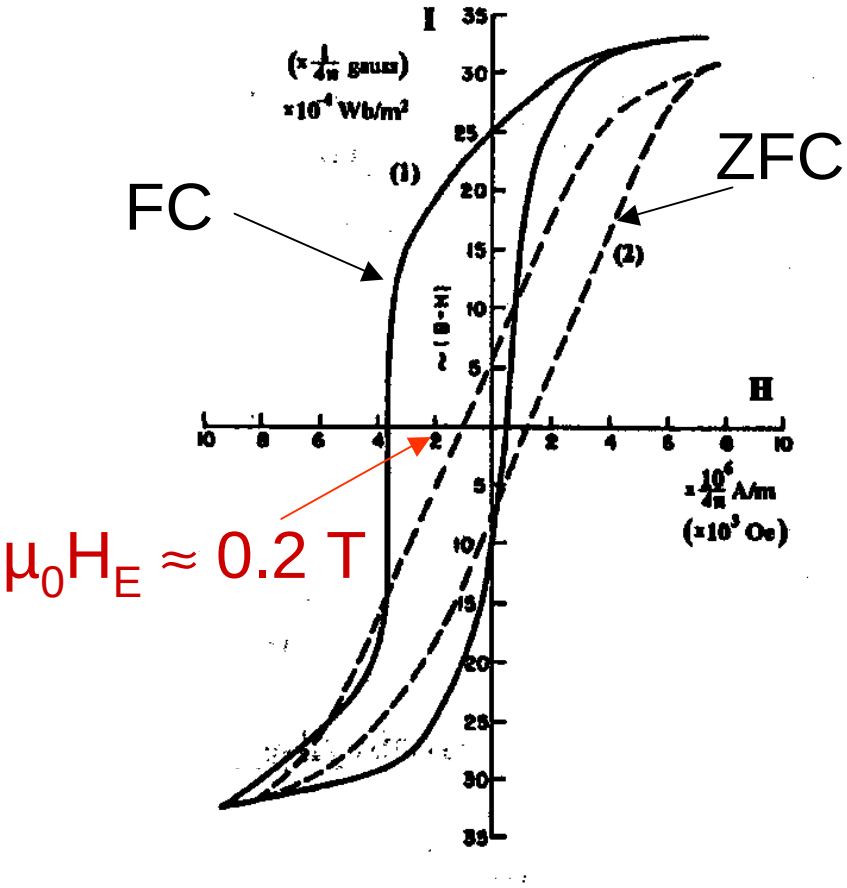
Elliptic motion of the teeth is source of motion

B_{excit} = 0.03 Tesla



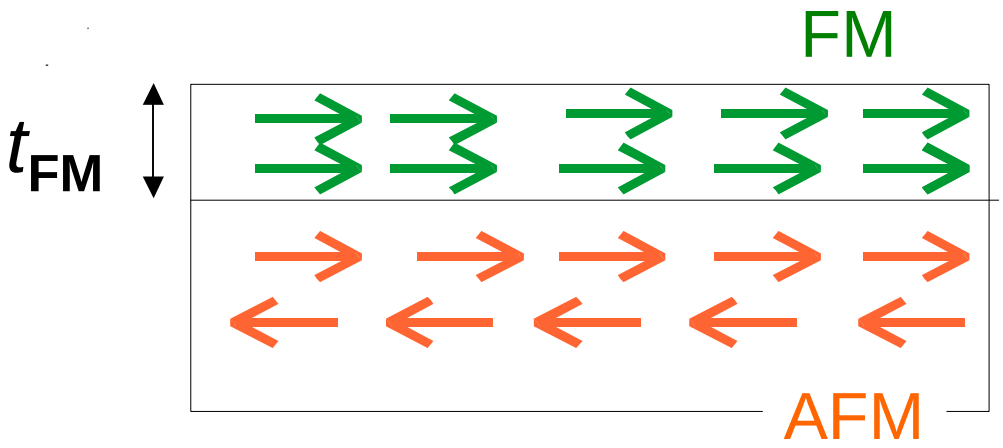
Exchange-bias

Oxidised Co nanoparticles



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

FC hysteresis loop :
-shifted with respect to M axis
- increased coercivity

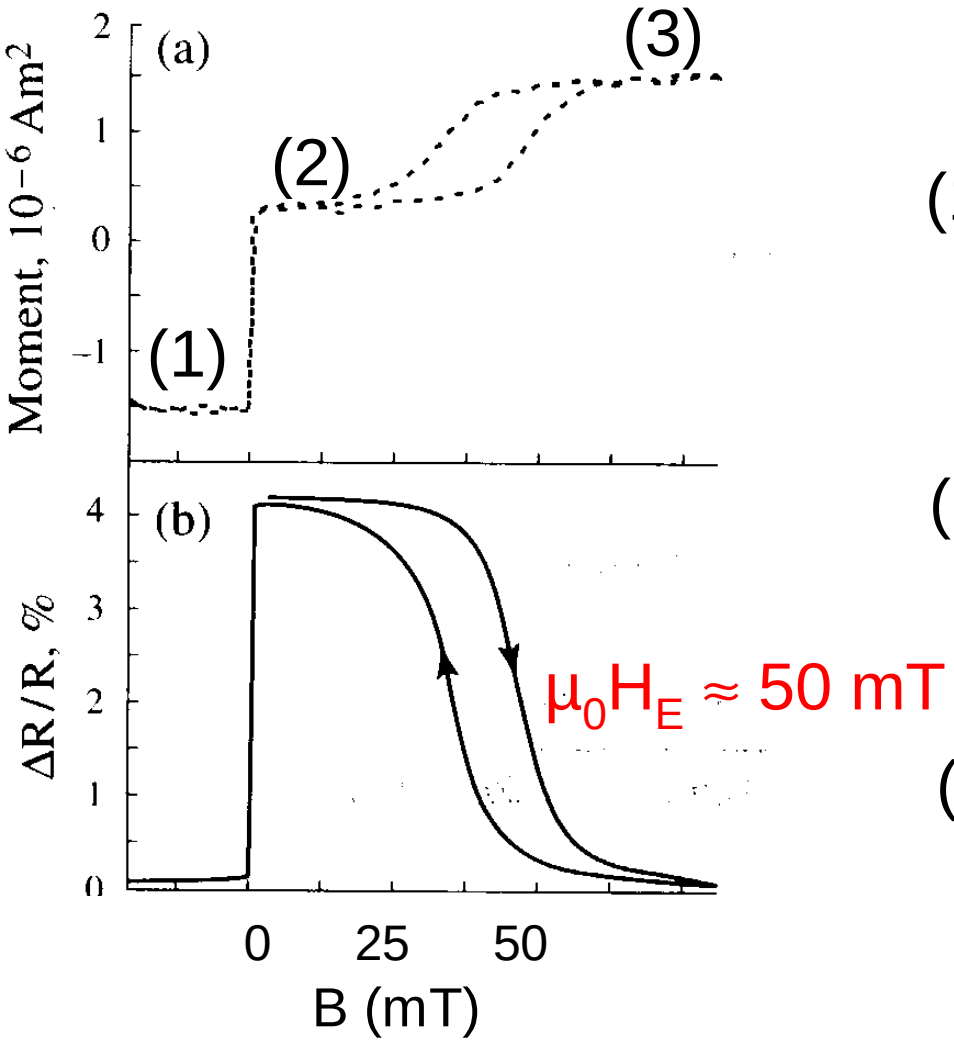


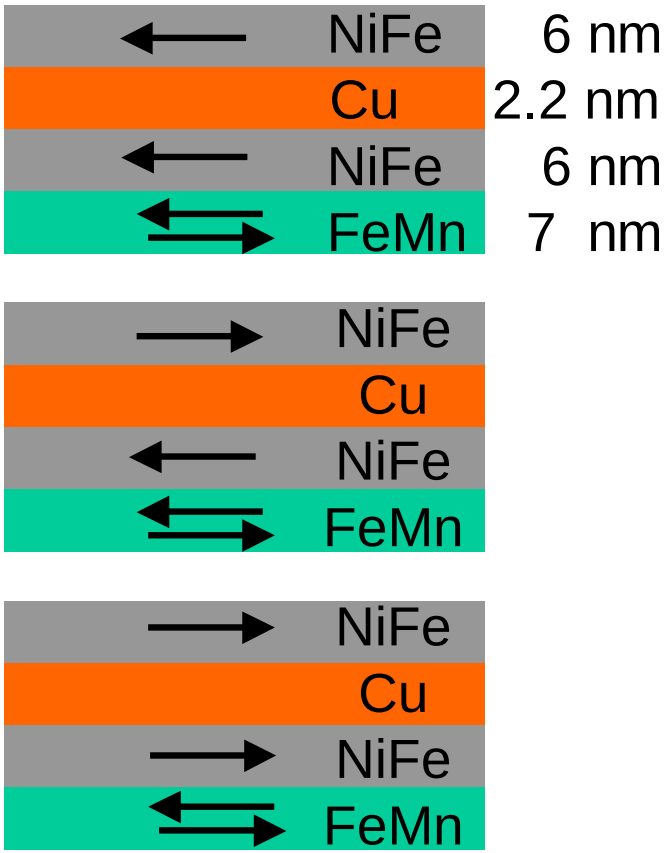
Exchange bias
J. Nogués and Ivan K. Schuller
J. Mag. Magn. Mater. 192 (1999) 203

Exchange anisotropy—a review
A E Berkowitz and K Takano
J. Magn. Magn. Mater. 200 (1999)

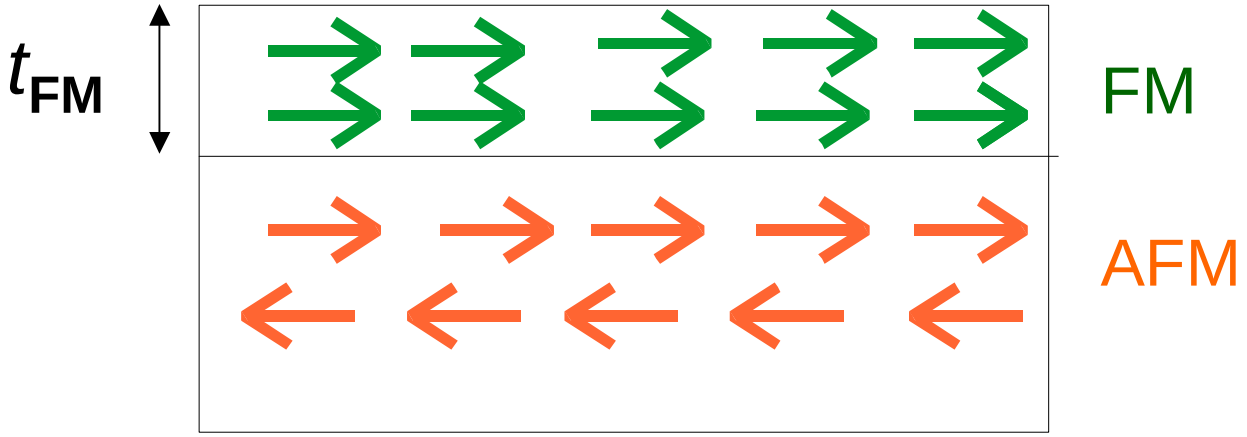
Spin valve systems

B. Dieny et al. Phys. Rev. B (1991) 43 (1297)





Evaluation of H_E



$$H_E = \frac{J_{ex}\mathbf{S}_{FM} \cdot \mathbf{S}_{AFM}}{a^2 M_{FM} t_{FM}}$$

$J_{ex}S_{FM}S_{AFM} \approx 150$ K

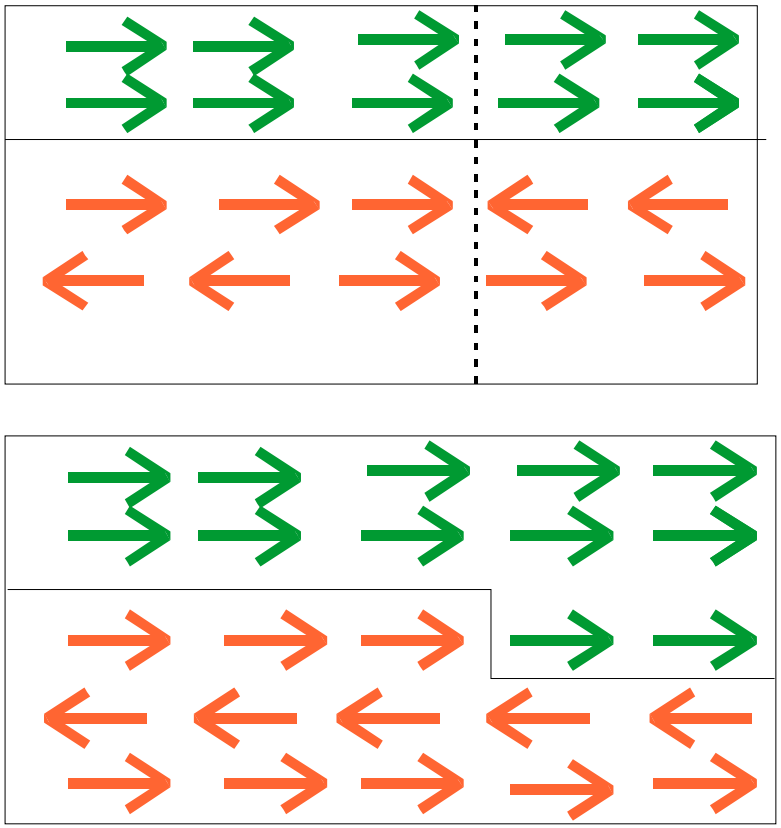
$\mu_0 M_{FM} = 1.8$ T

$t_{FM} = 10$ nm

$\Longrightarrow \mu_0 H_{E(calc)} = 2.3$ T

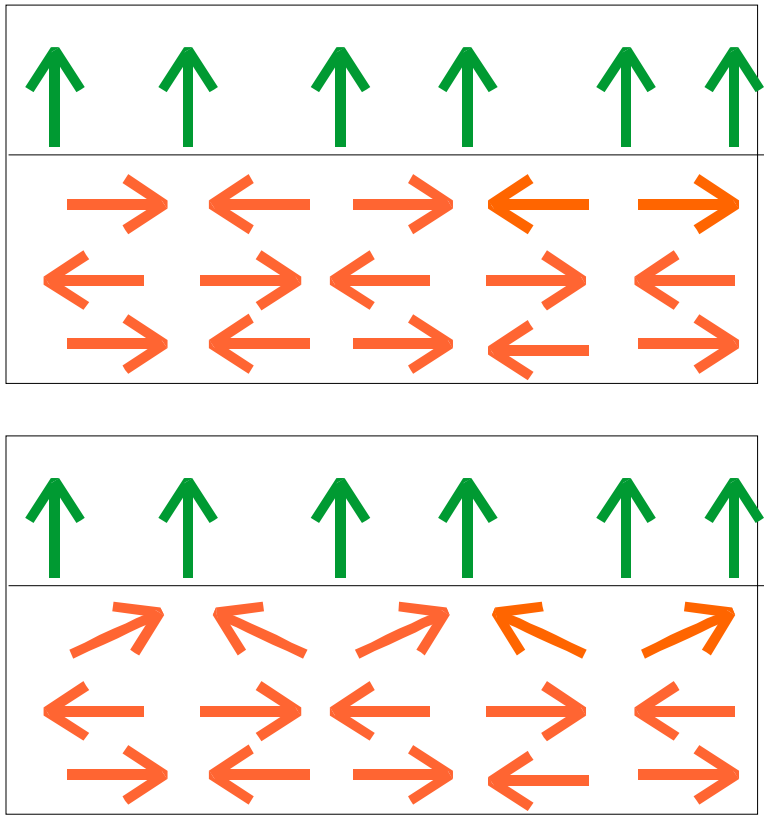
$H_{E(exp)} \approx 0.1\, H_{E(calc)}$

Coupling mechanisms in exchange-bias



Uncompensated interface

$$E = -\alpha \mu_0 \mu_{AFM} H_{exch}$$



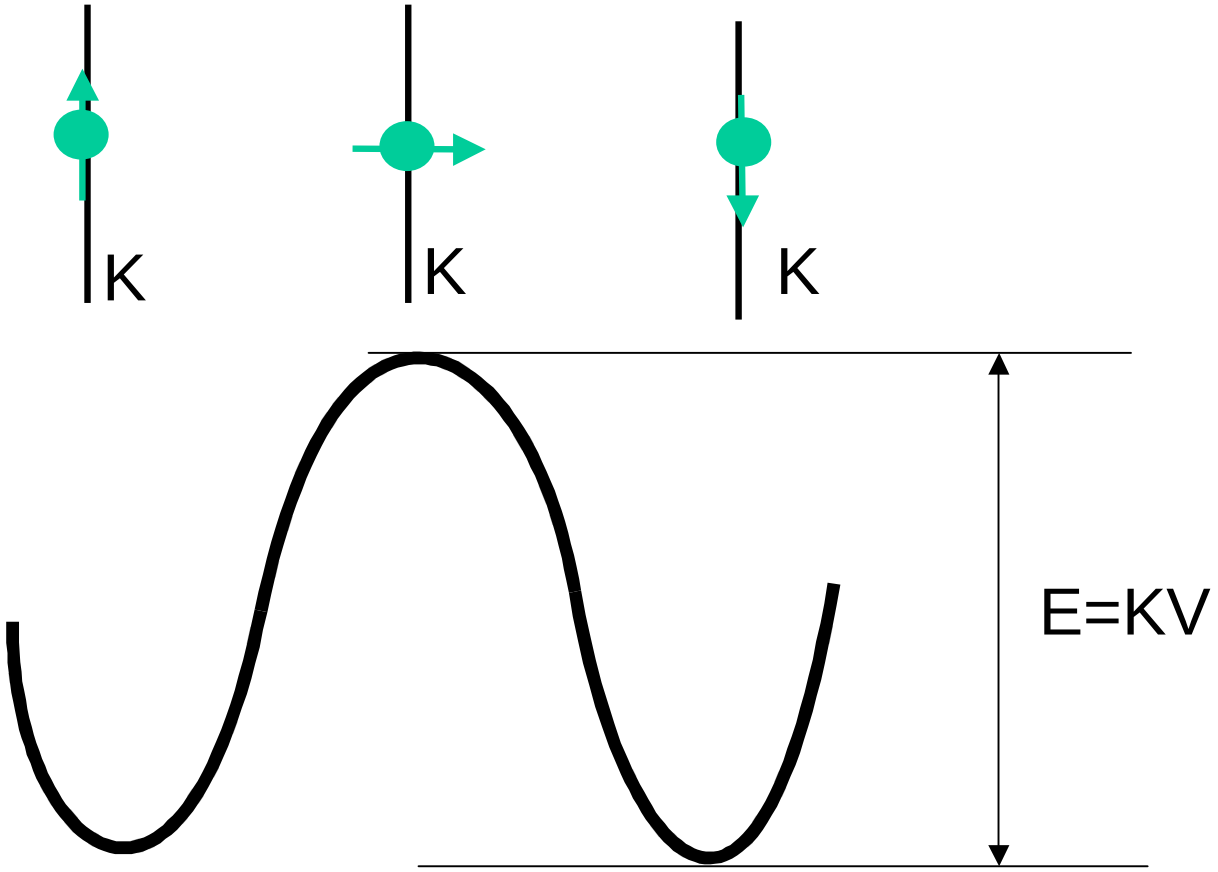
Compensated interface

$$E = -\frac{1}{2} \chi_{AFM} \mu_0 H_{exch}^2$$

with $\chi_{AFM} = 1/W$

Mechanisms for exchange bias
R.L. Stamps
J. Phys. D. : Appl. Phys., 33 (2000) R247

Nanoparticles and the so-called superparamagnetic limit



$$\tau = \tau_0 e^{\frac{E}{k_B T}}$$

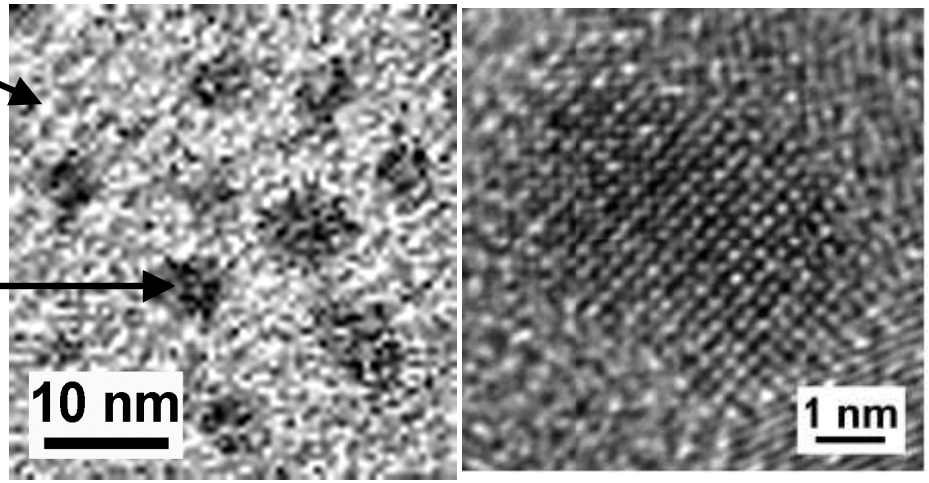
Limit reached for E ≈ 25 kT

Co : V ≈ 100 nm^3

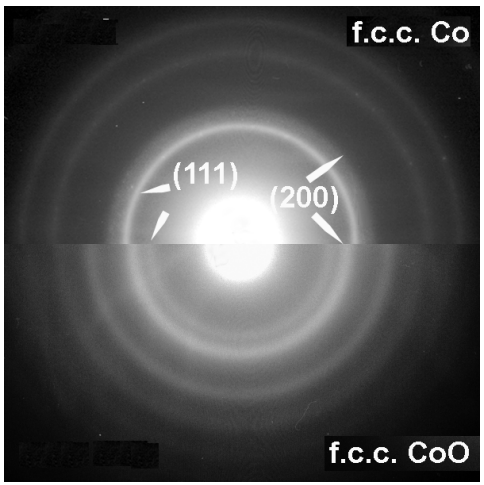
Ferromagnetic nanoparticles in a non-magnetic or antiferromagnetic matrix

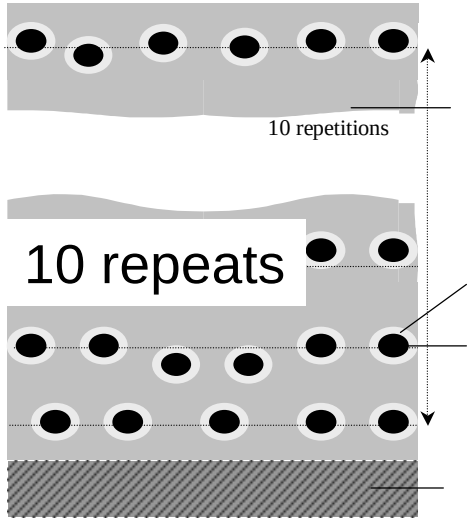
Matrix
(C, Al_2O_3, CoO)

Co nanoparticles



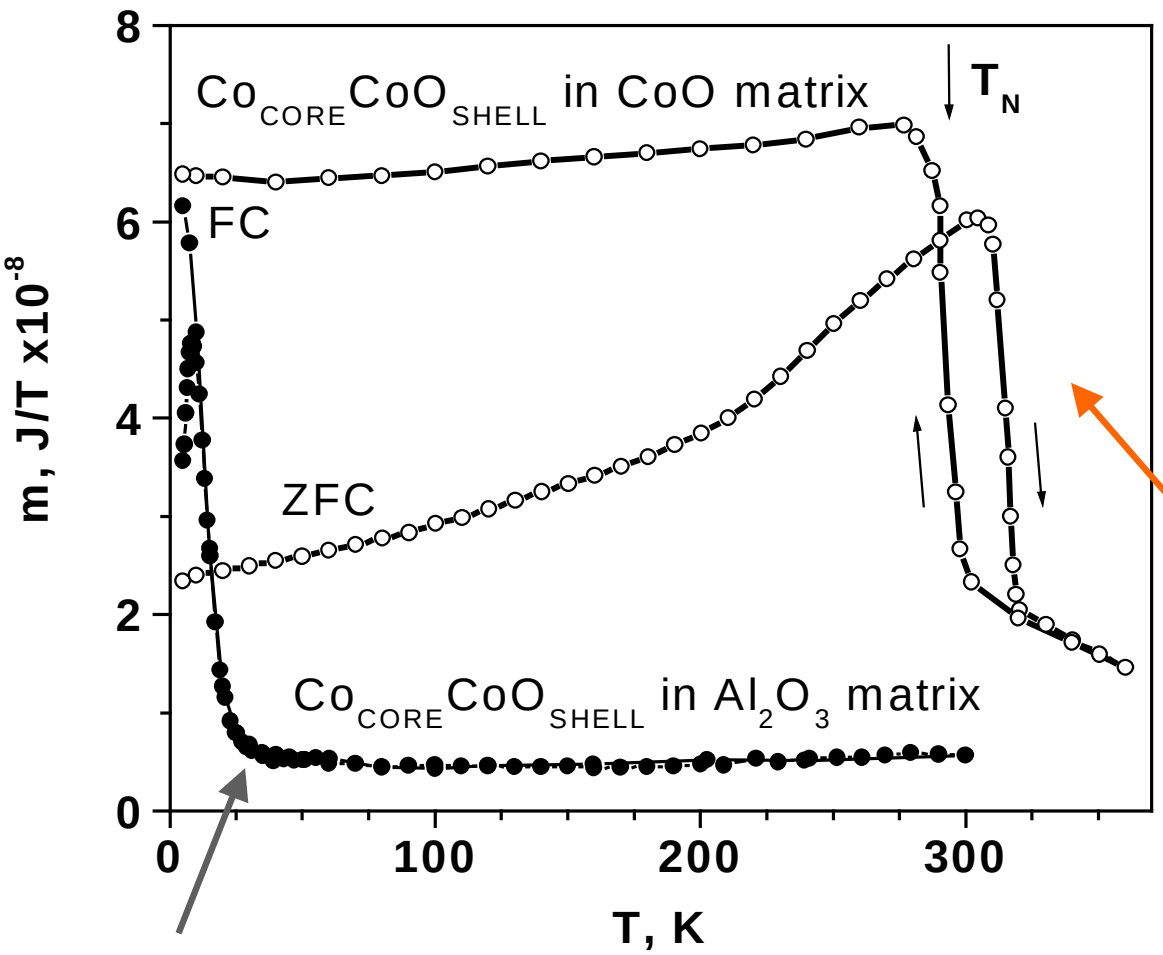
Average particle size
3-4 nm

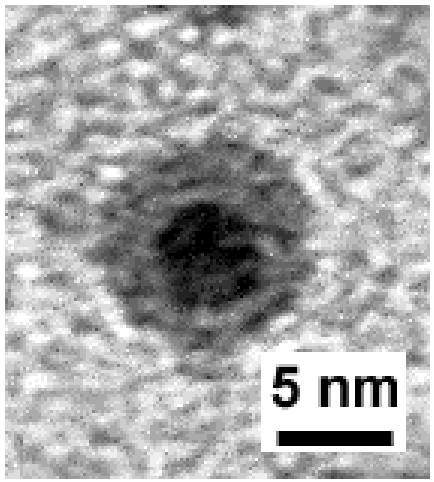




"cluster gun" + conventional sputtering

Dependence of the blocking temperature on the nature of the matrix





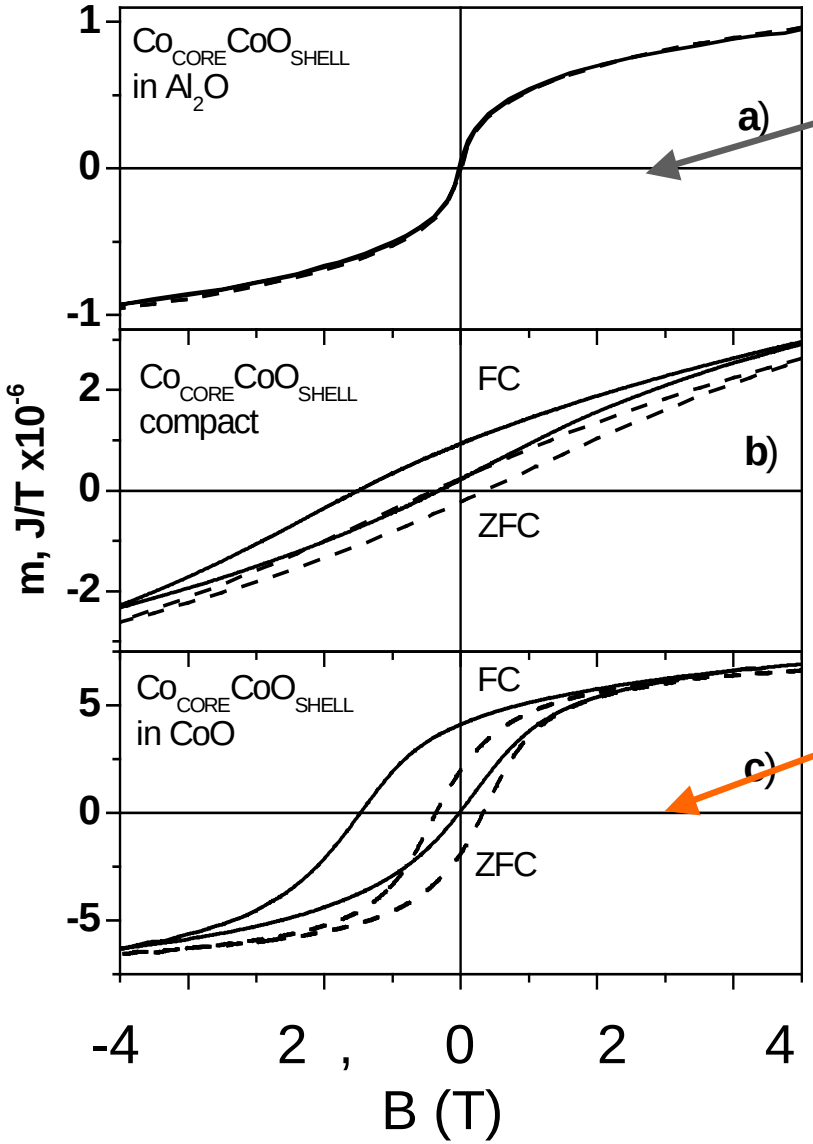
AFM matrix
$T_B \approx T_N$ CoO

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

Beating the superparamagnetic limit with exchange-biasV. Skumryev, S.Stoyanov, Y. Zhang, G. Hadjipanayis, D. Givord et J. NoguèsNature, 423 (2003) 850

Dependence of the hysteresis cycles on the nature of the matrix

T = 4.2 K



Non-magnetic matrix

Shifted cycle + hysteresis

AFM matrix

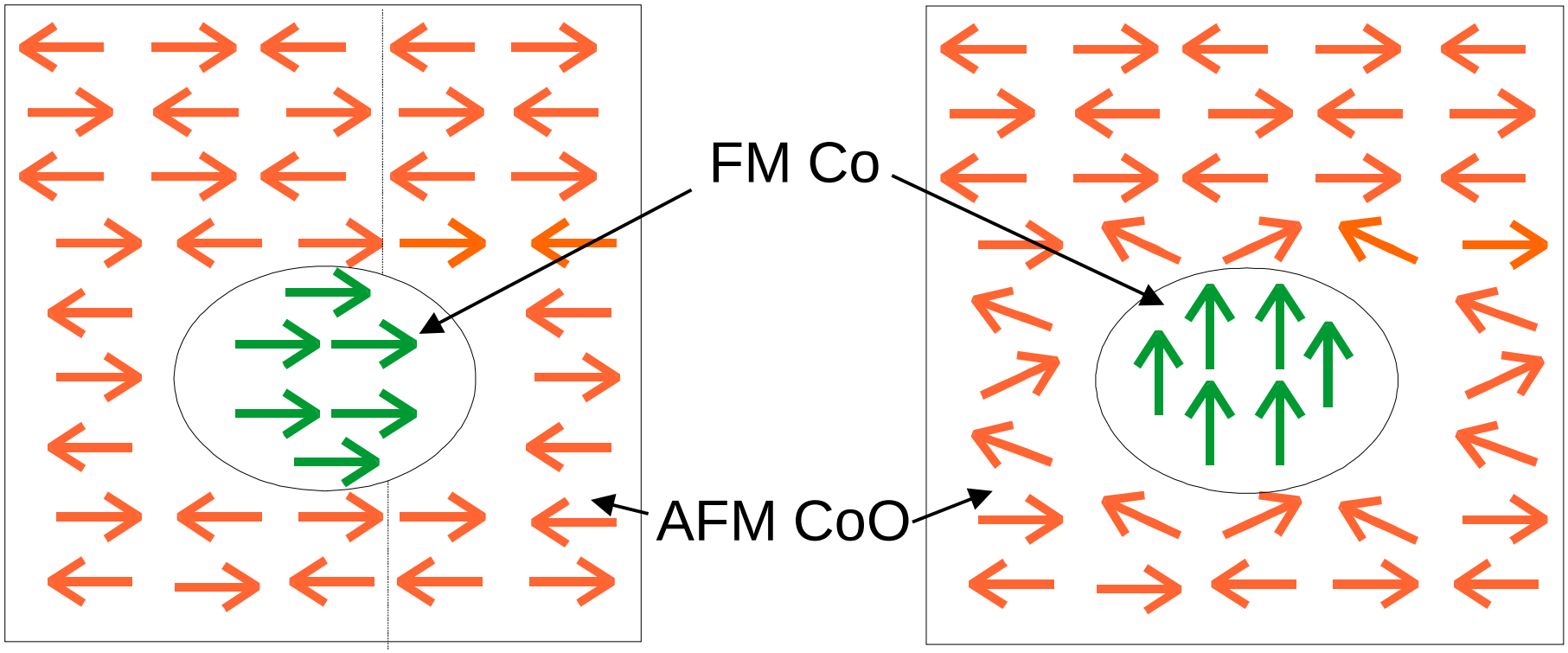
$\mu_0 H_c = 0.76$ T

$\mu_0 H_E = 0.74$ T

Possible coupling schemes for Co/CoO

Uncompensated case

Compensated case



$\sqrt{N}/N = 27/750 = 4\%$

$$E = \frac{4}{100}\mu_0 \mu_{AFM} H_{exch}$$

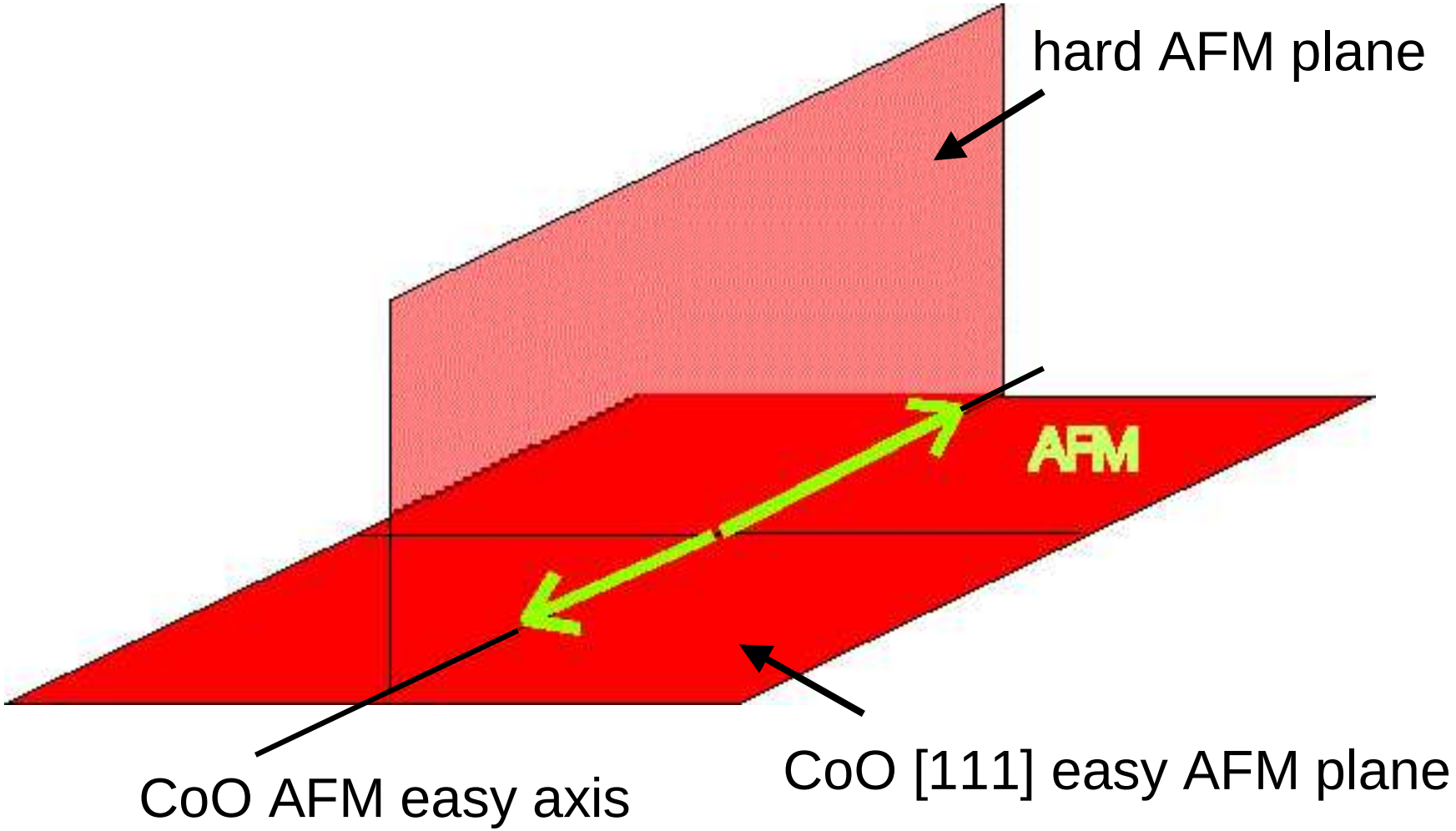
$\mu_0 H_{exch} = 84T$

$$E = -\frac{1}{2}\chi_{AFM}\mu_0 H_{exch}^2$$

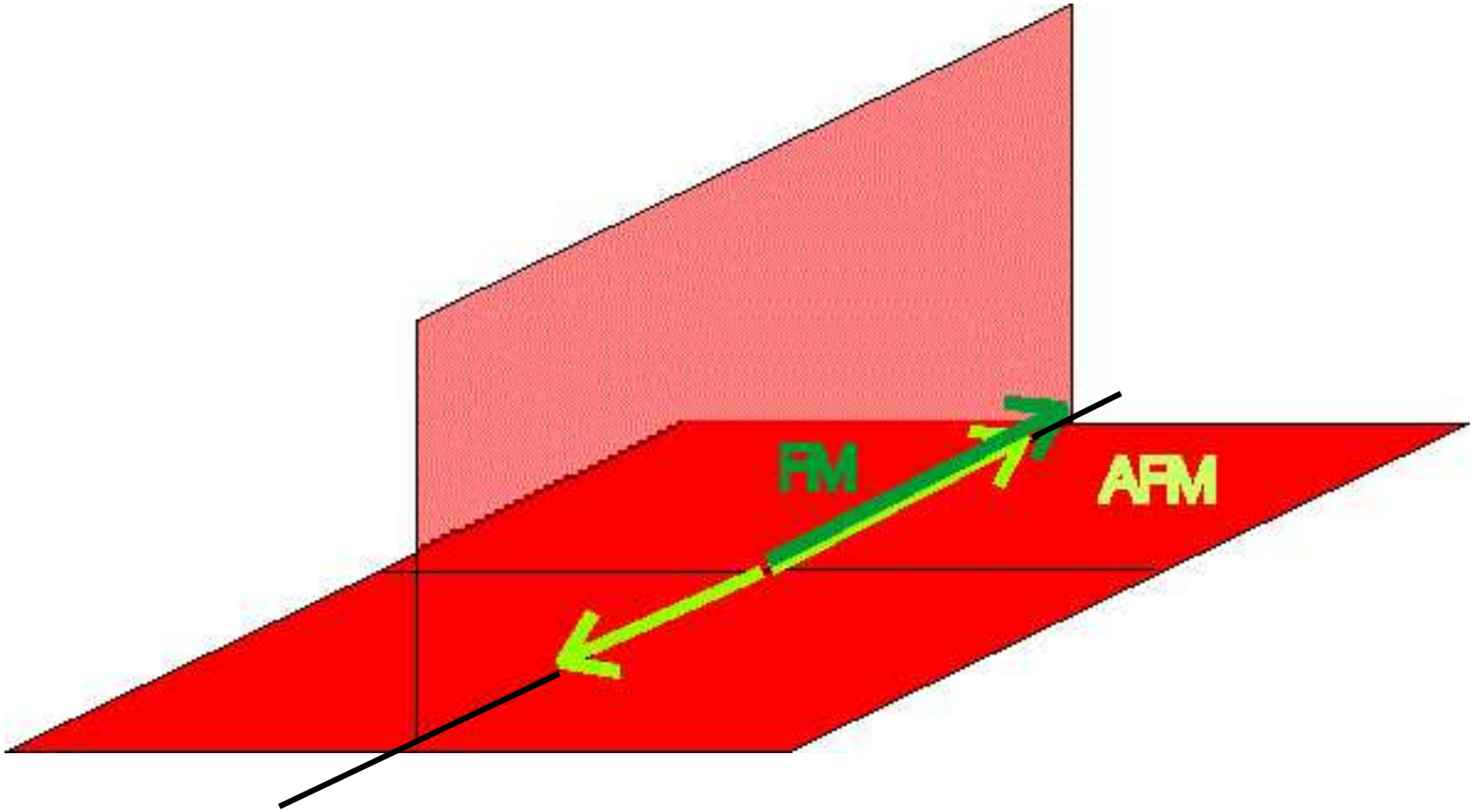
$E_{coupling} \approx - 10^{-22}$ J

$E_{coupling} \approx - 10^{-21}$ J

Uncompensated AFM interface

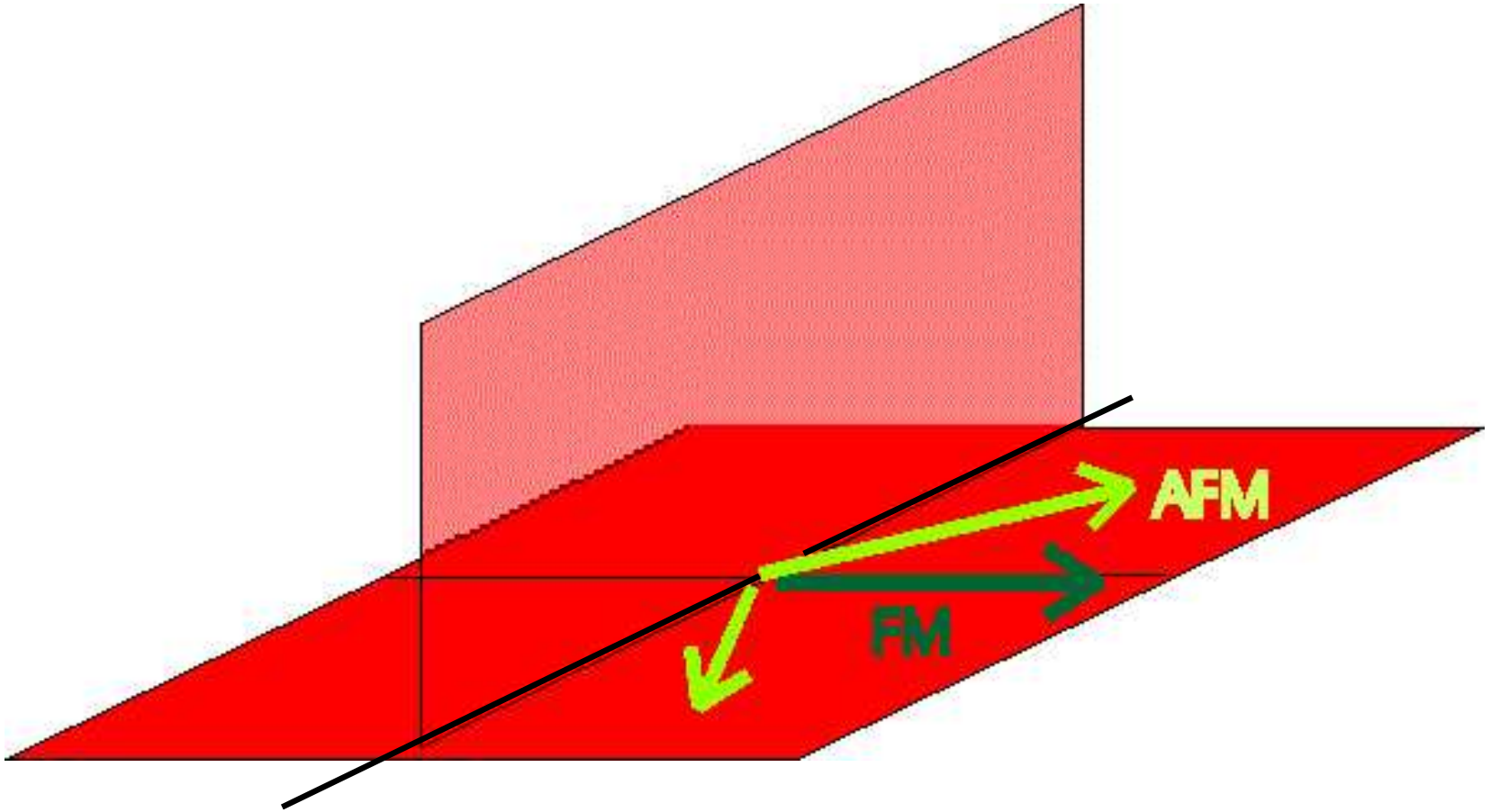


Uncompensated AFM interface



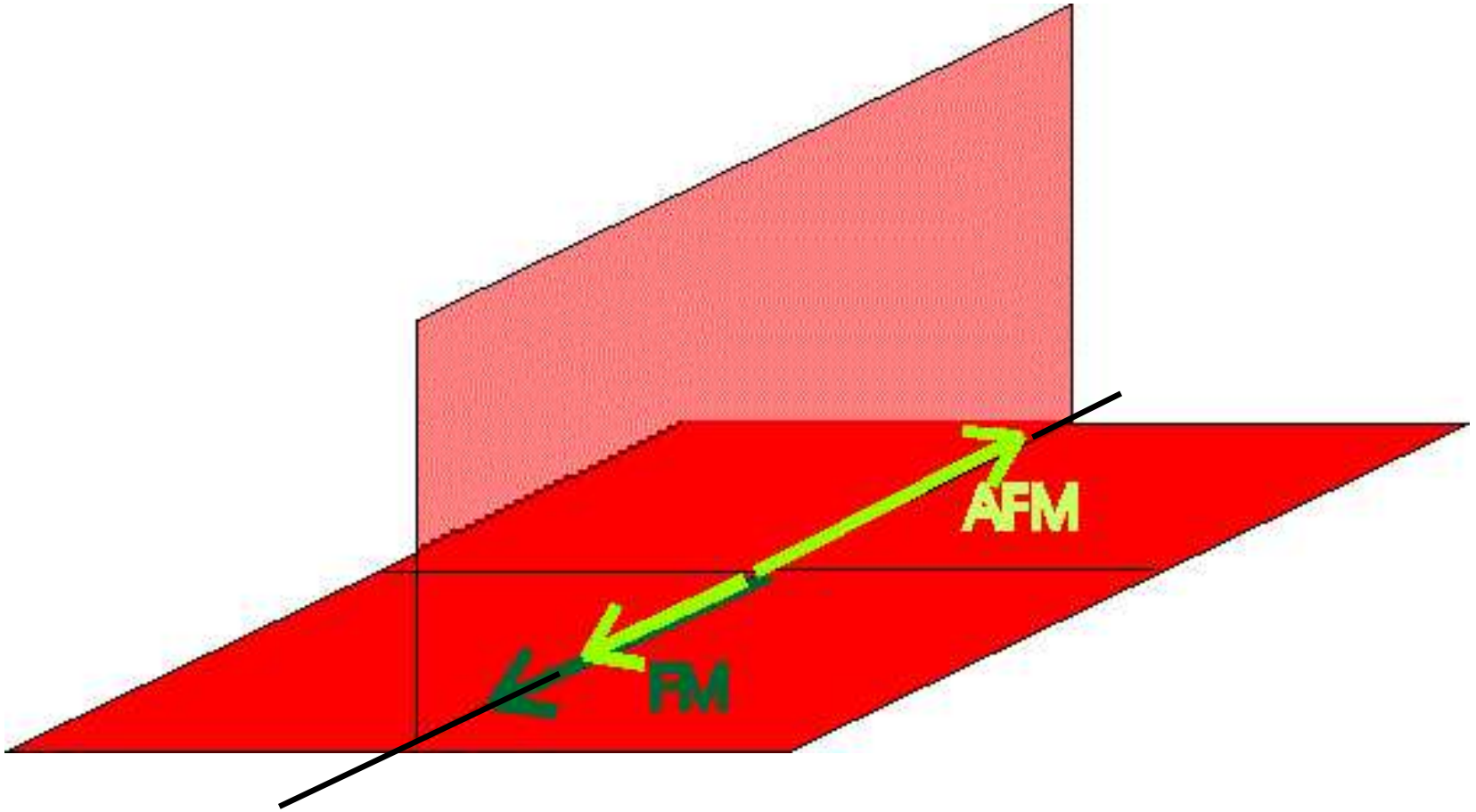
Co FM moment aligns along the dominant AFM sublattice

Uncompensated AFM interface



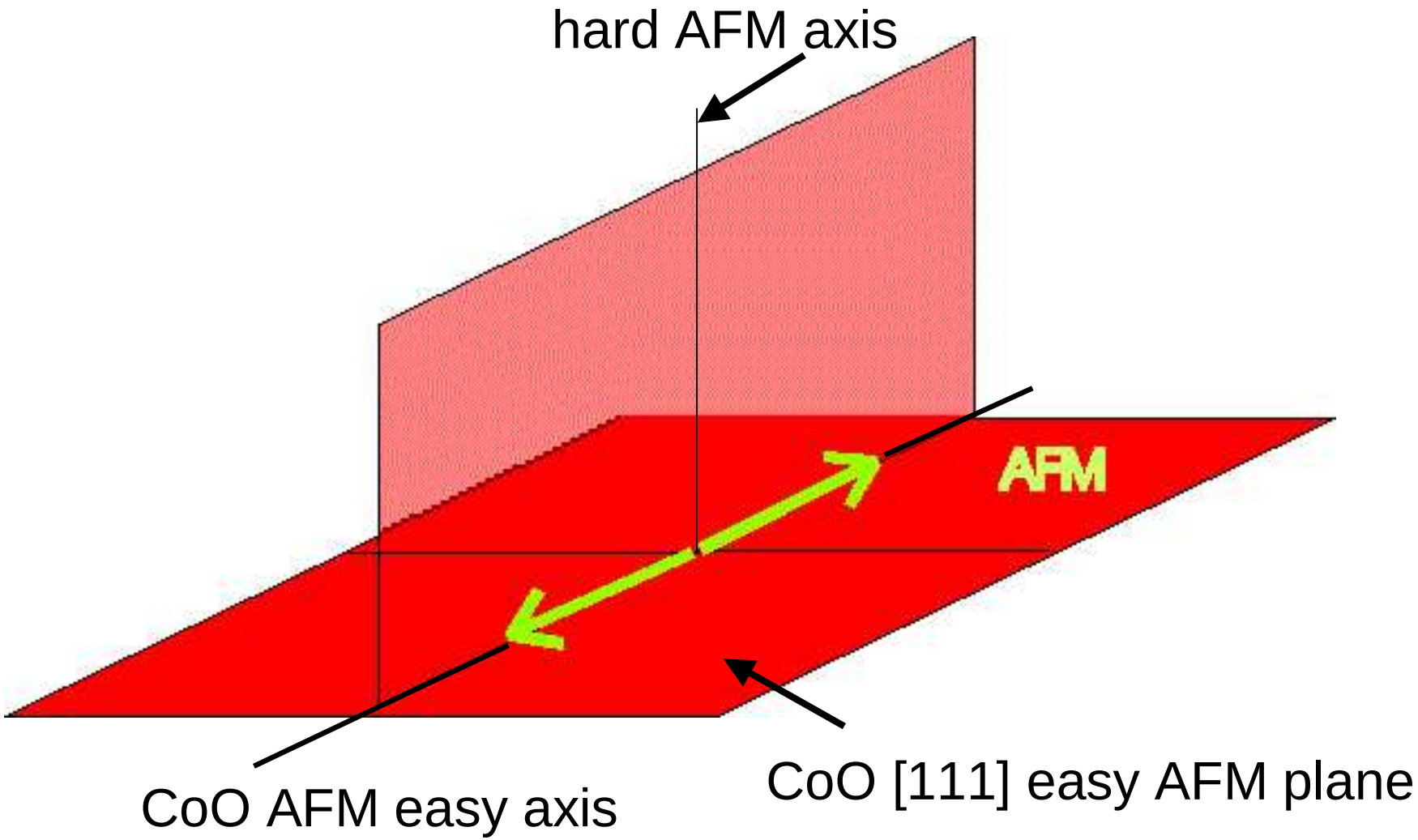
FM rotation within the AFM easy plane

Uncompensated AFM interface

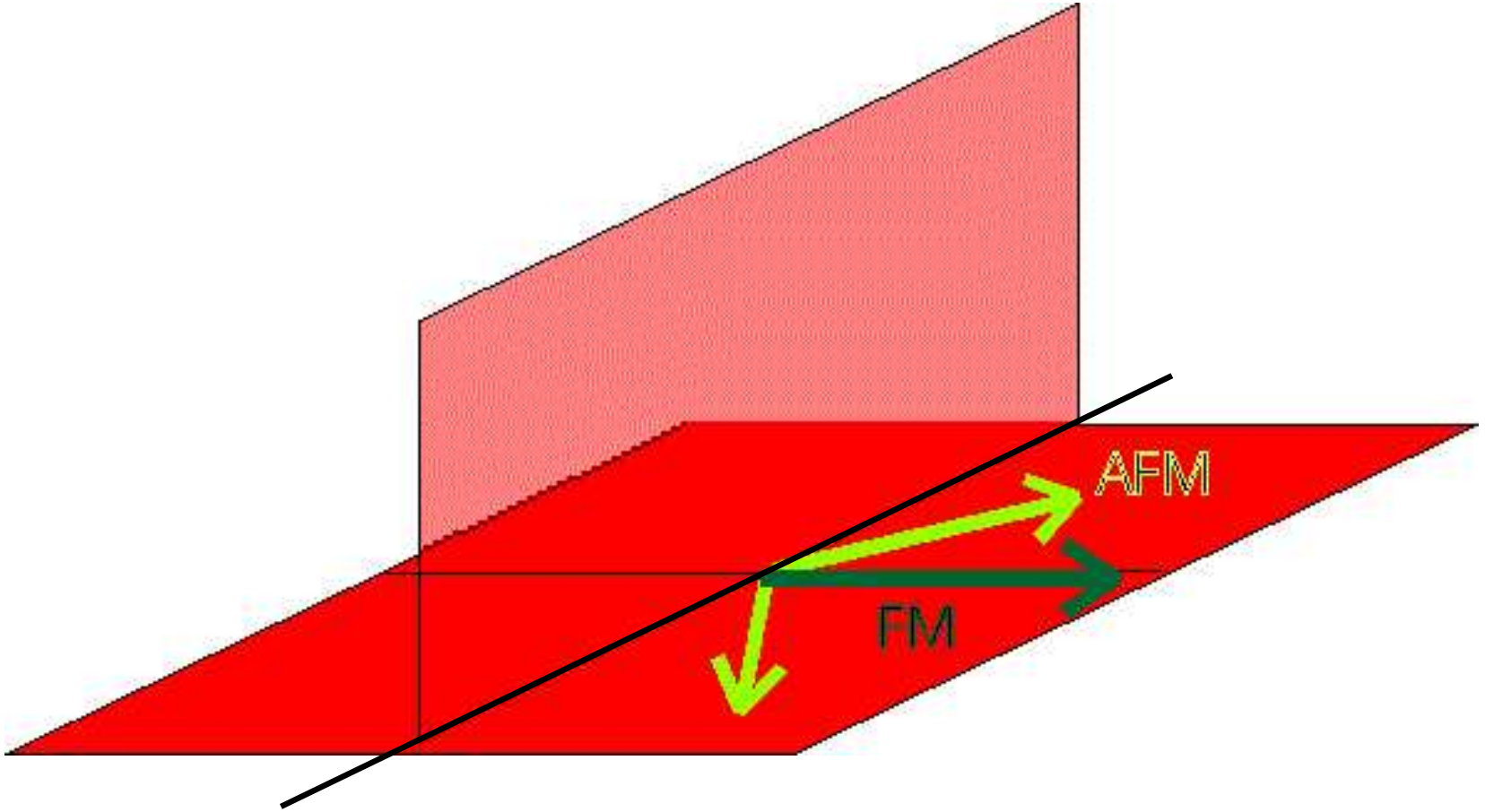


Moment configuration after reversal

Compensated AFM interface

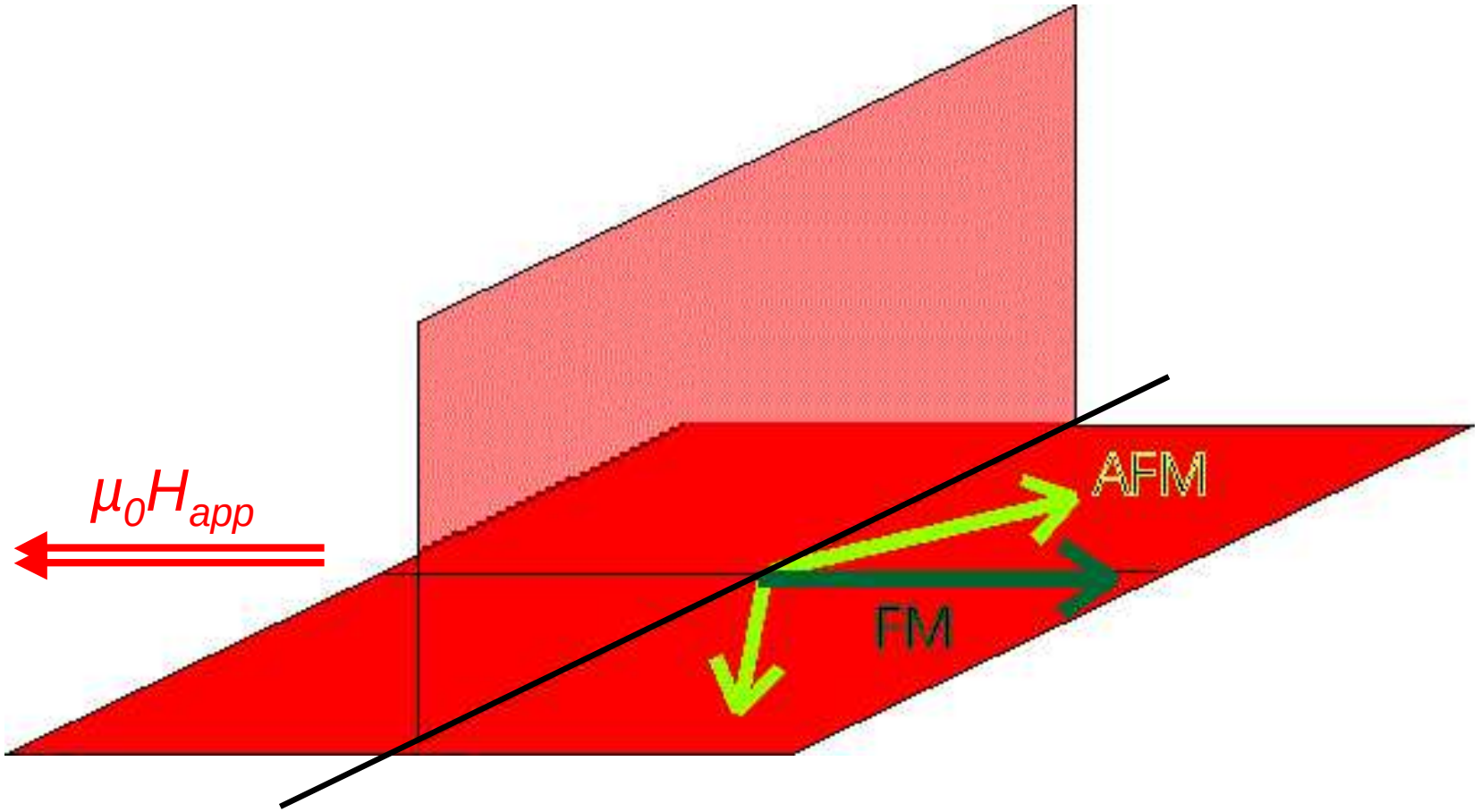


Compensated AFM interface



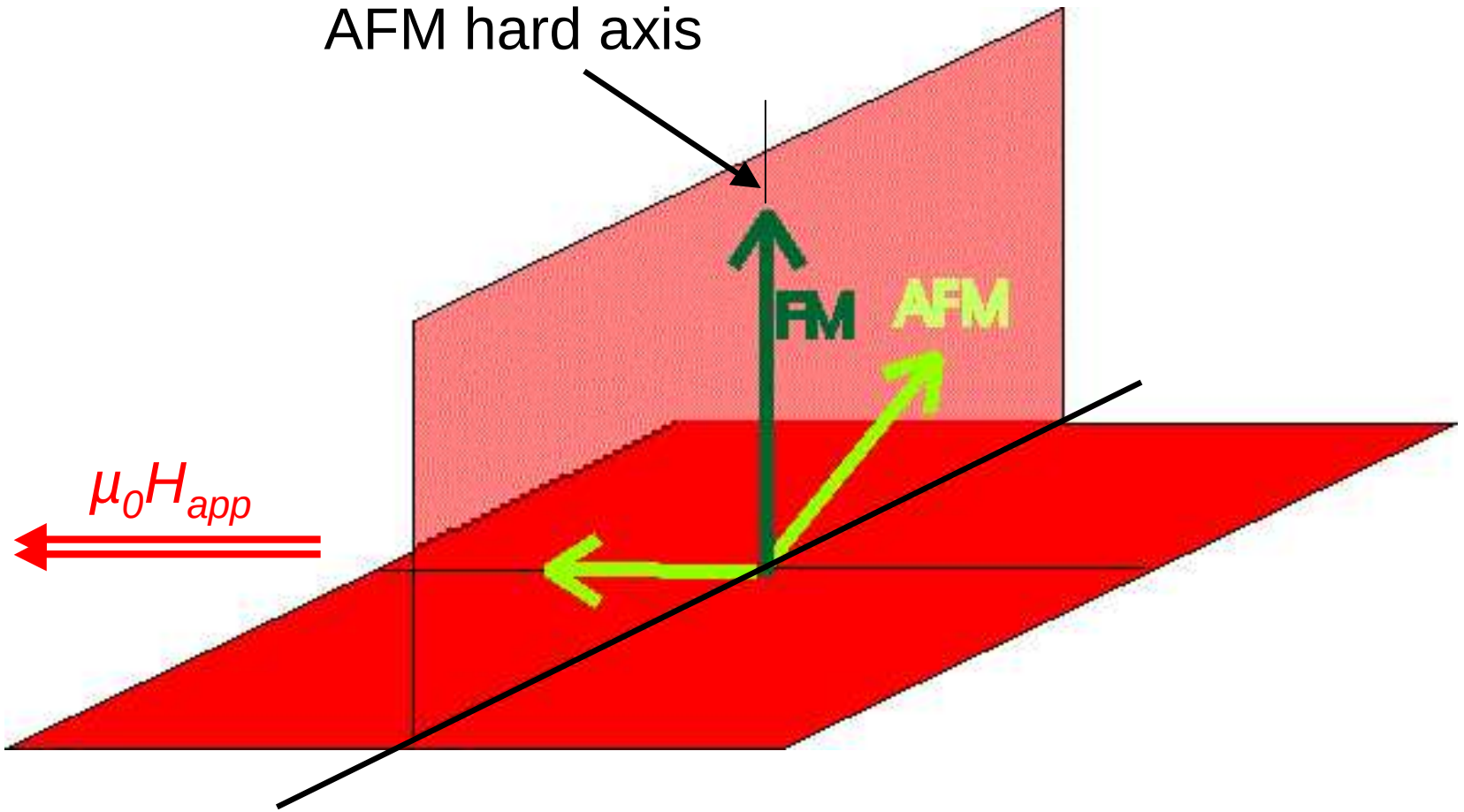
FM moments align perpendicularly to the AFM moments
and induce canting of the AFM moments

Compensated AFM interface



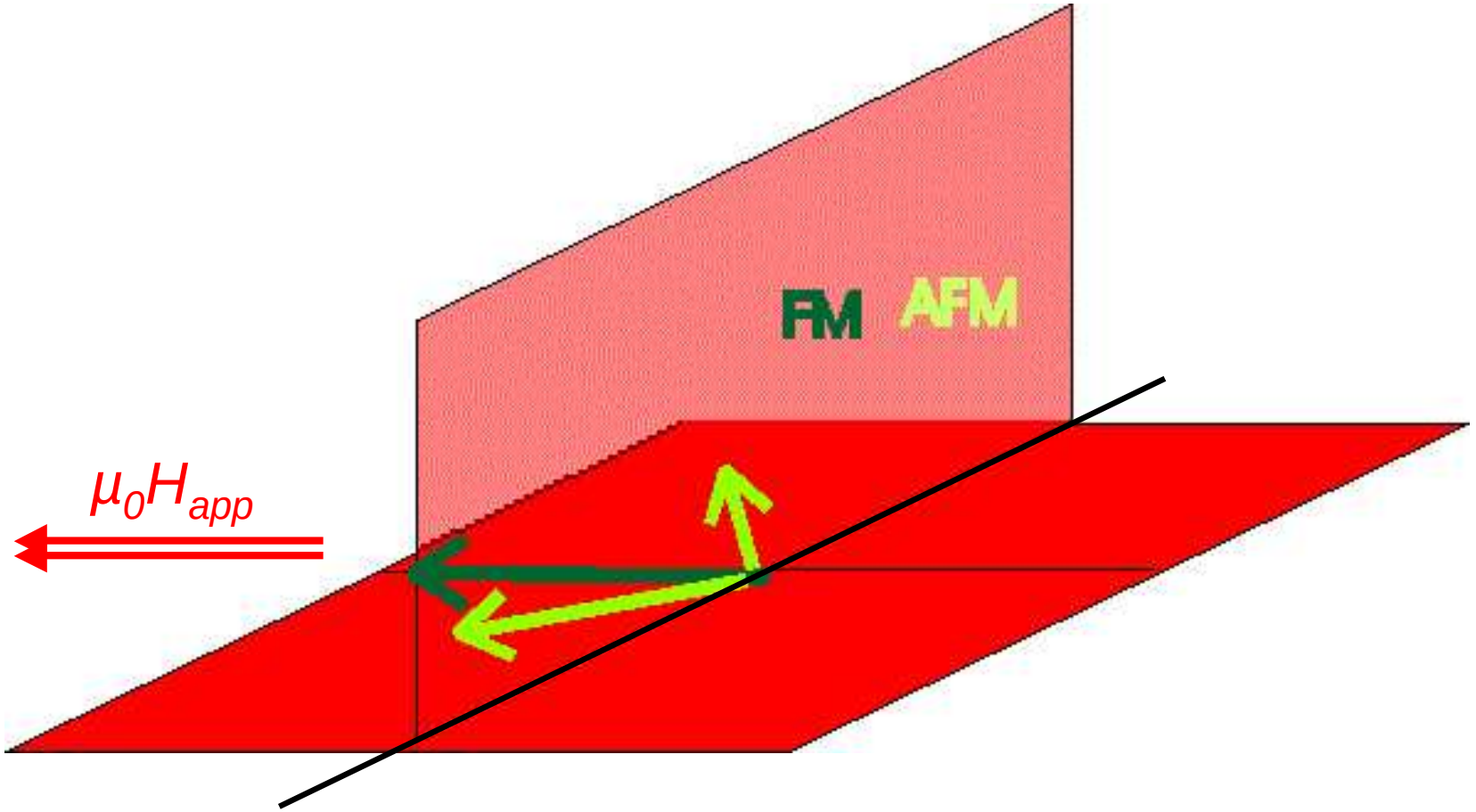
Magnetisation reversal under field

Compensated AFM interface



FM moment rotation occurs
in the plane perpendicular to the AFM easy axis

Compensated AFM interface

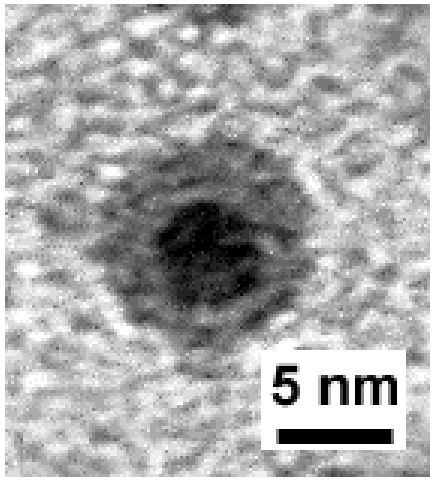


To this approximation, the final state is identical to the initial one

Co/CoO coercive field

$E = -1/2\ \Delta\chi_{\perp}\ \mu_0 H_{exch}^2$ with $\chi_{\perp} = \frac{1}{w(1+\alpha)}$

$$\alpha = \frac{K_1}{2w\mu_0 M_{AFM}^2}$$



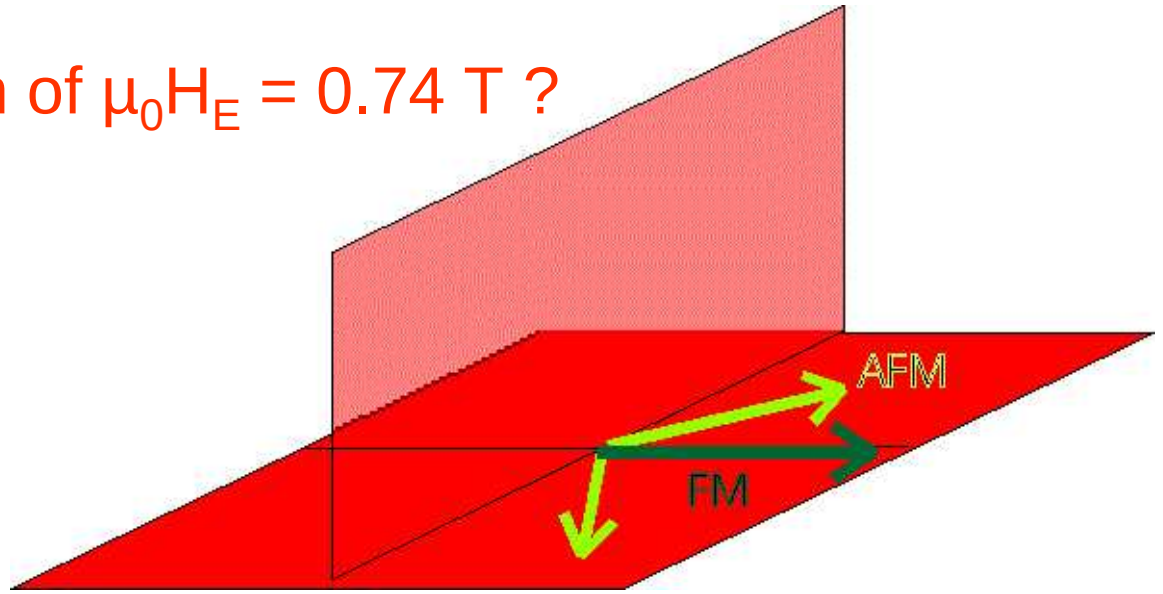
$K_1 = 2.7\ 10^7\ J/m^3$

Calculated $\mu_0 H_c = 1.3$ T
Experimental $\mu_0 H_c = 0.76$ T

Co/CoO bias-field

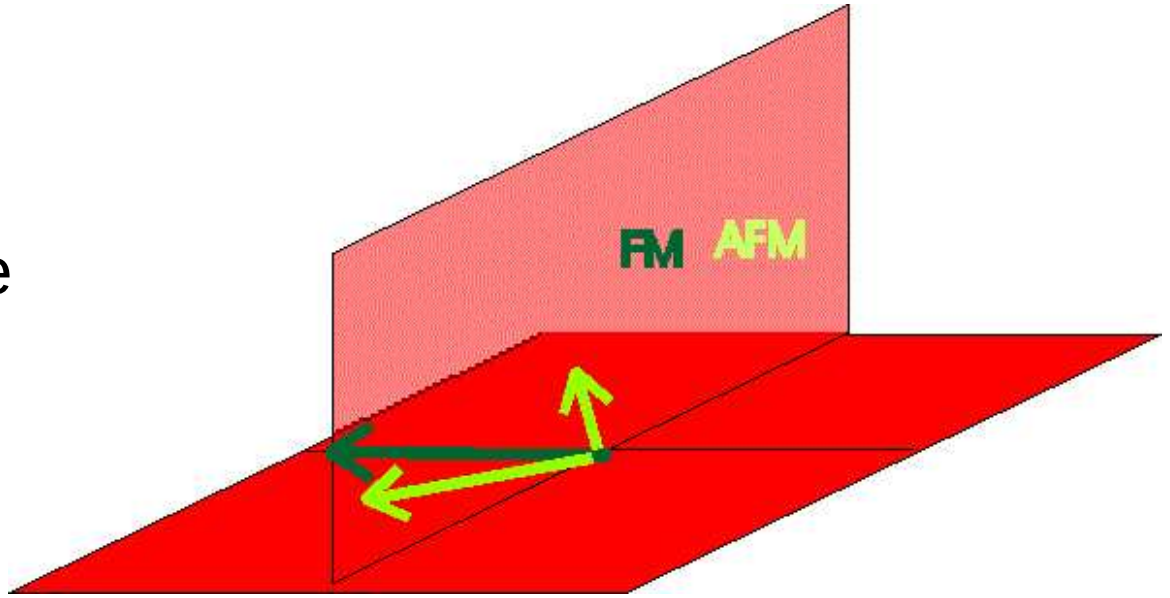
Origin of $\mu_0 H_E = 0.74$ T ?

Initial state



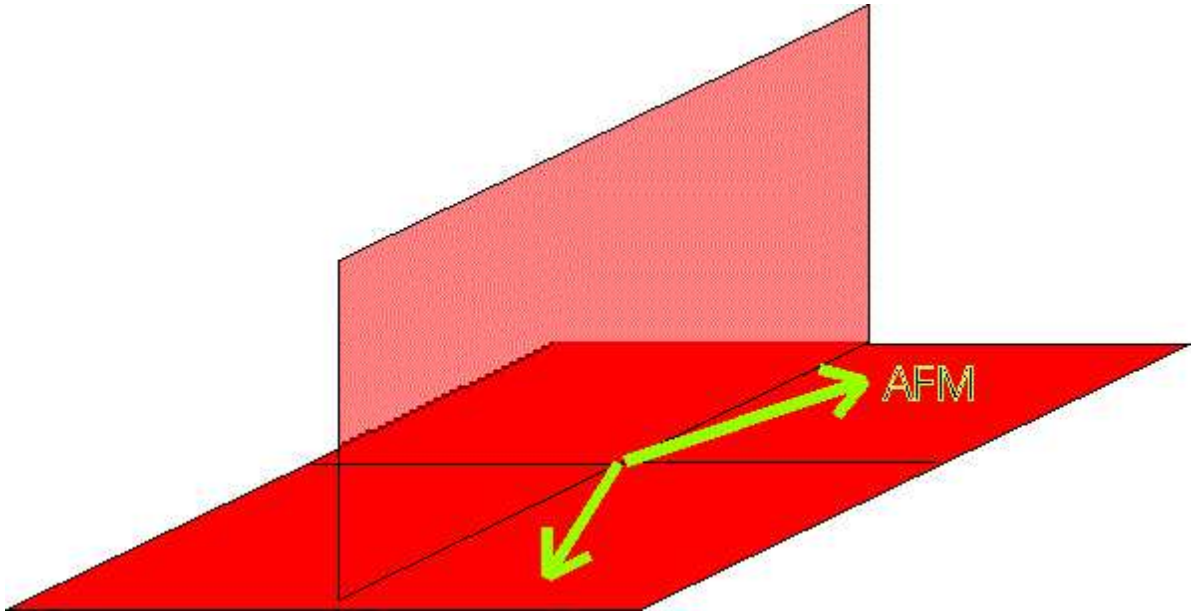
Identical to

Final state



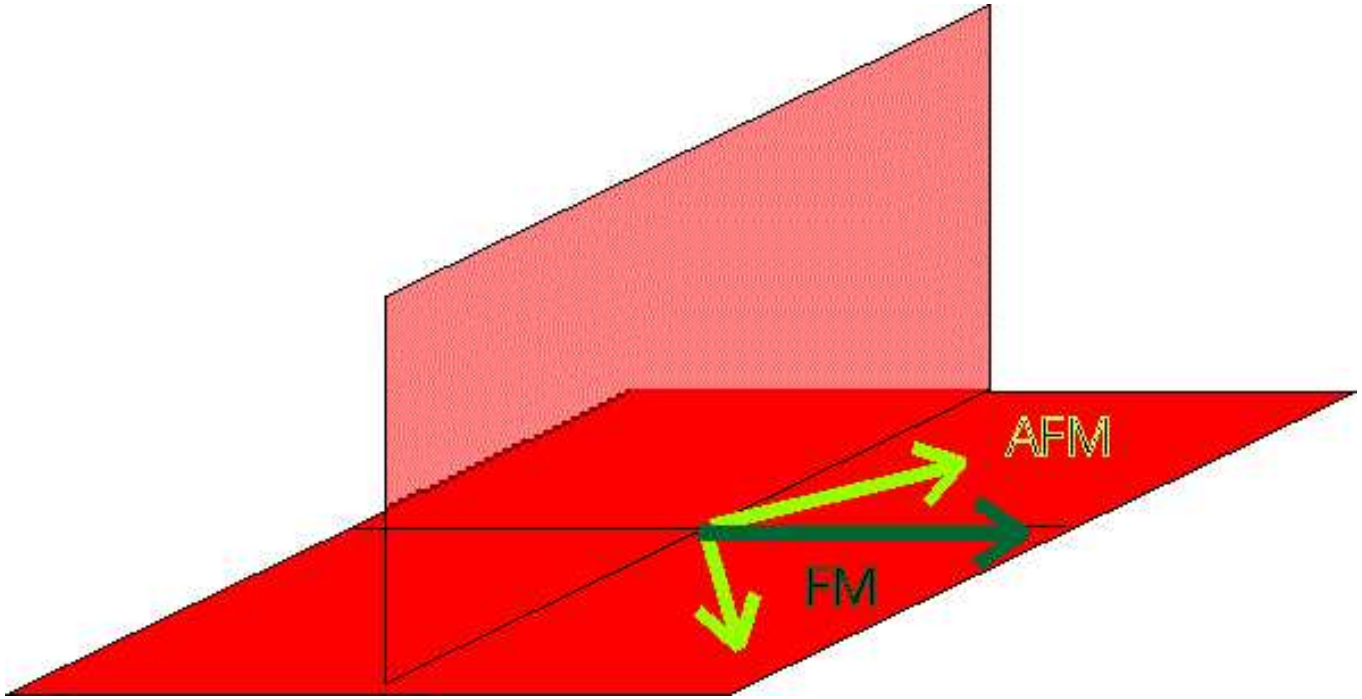
Other mechanism required to explain exchange-bias

Origin of exchange bias in Co/CoO



Pre-existing canting at the CoO interface

Exchange bias at Co/CoO interface



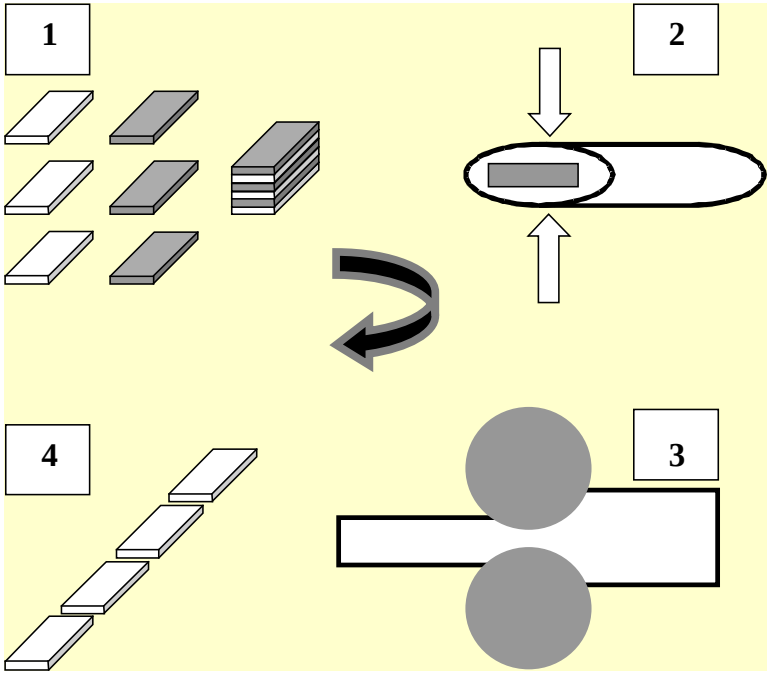
Average canting angle to account for $\mu_0 H_E = 0.74$ T
$\approx 20°$

usual value for oxide nanoparticles

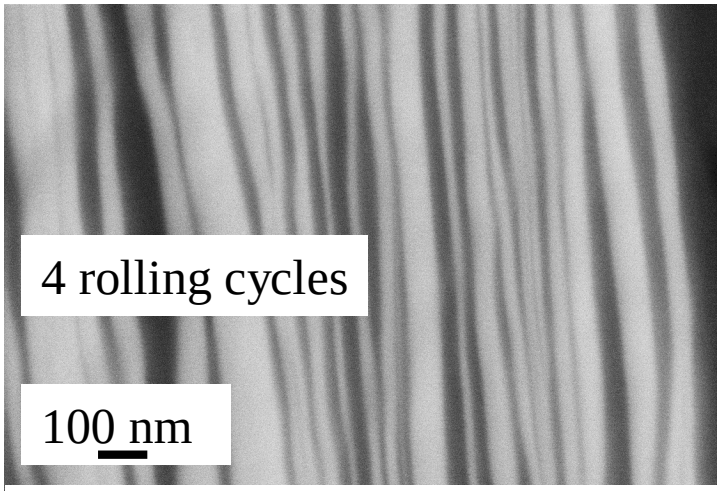
Hard FePt prepared by sheath rolling

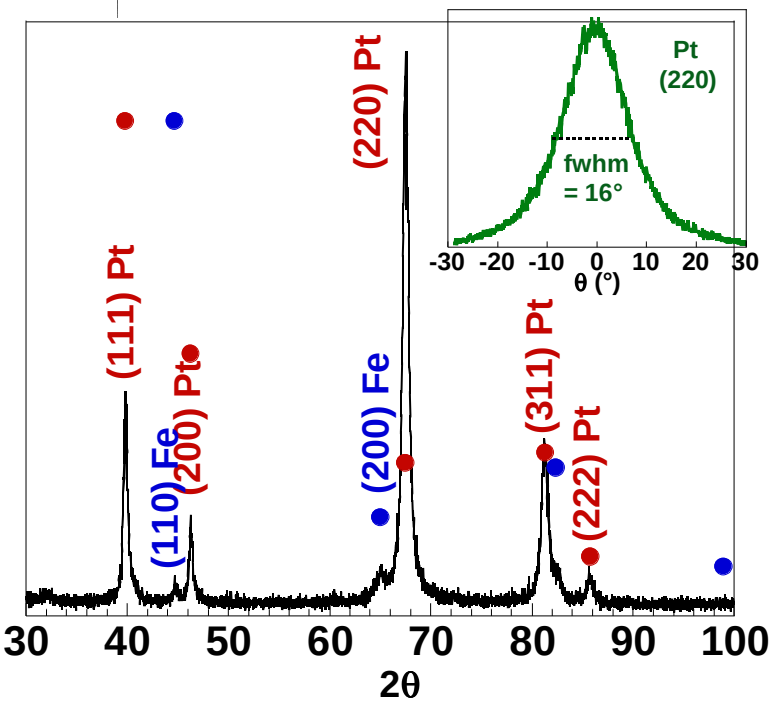
Hard-Magnetic FePt alloys prepared by cold-deformation
N.H. Haï, N.M. Dempsey, D. GivordJ. Magn. Magn. Mater. 262 (2003) 353

{Fe(75µm)/Pt(100µm)}$_{10}$
- 49 at% Fe
- stack dimensions: 1.8×4.5×15 mm^3

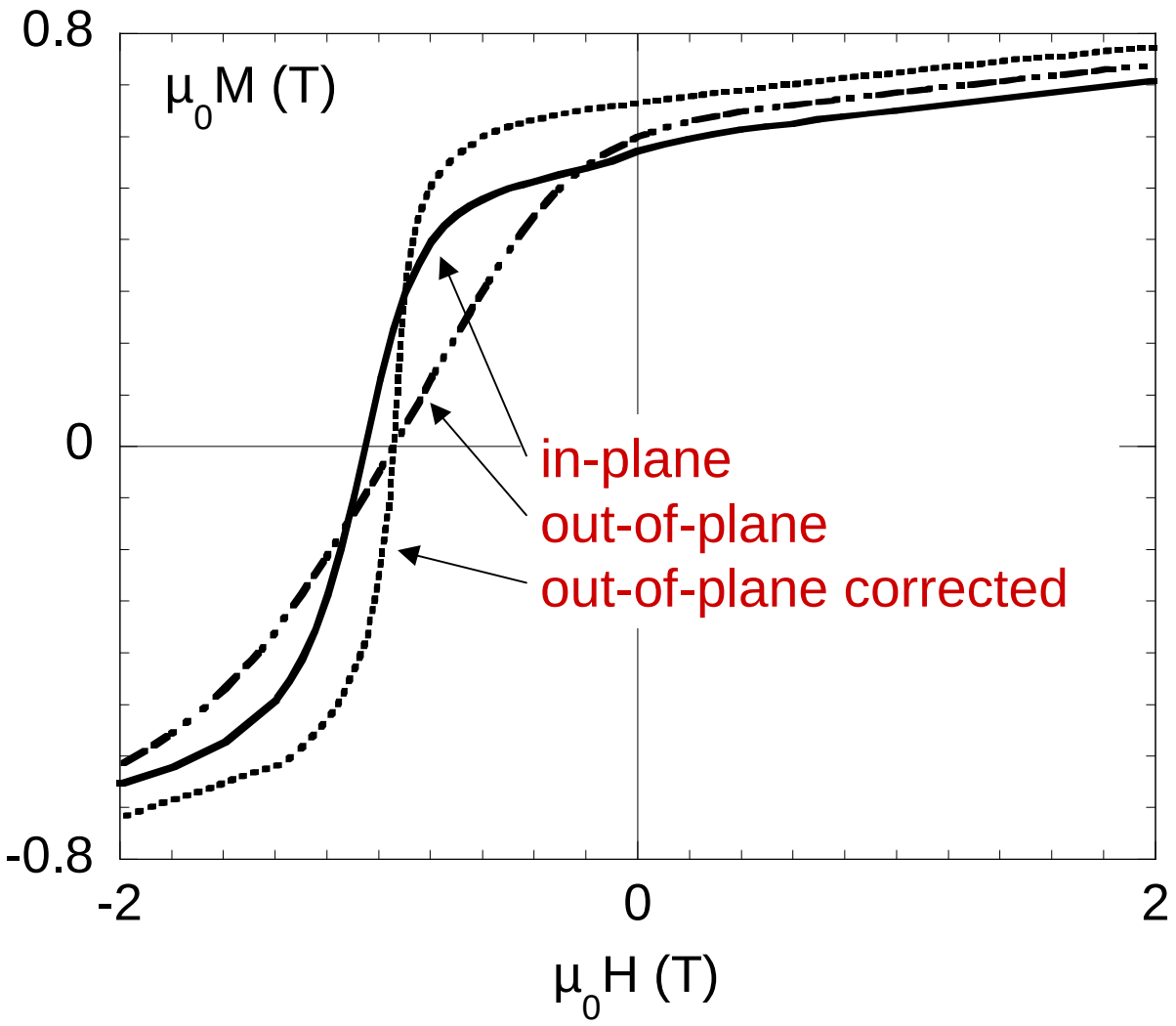


≈ 100 passes per cycle ; t_{init}/t_{final} ≈10
No stress-relieving heat treatment

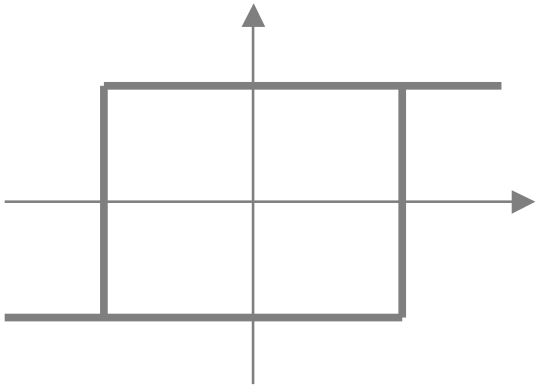




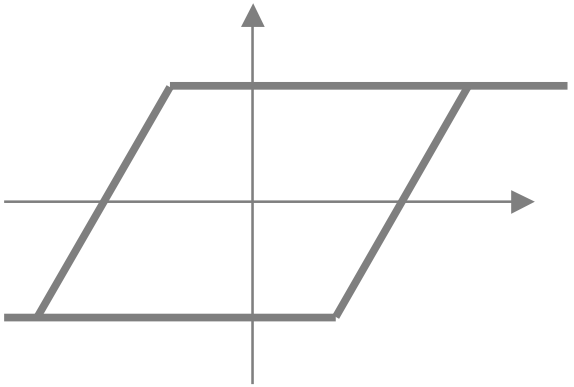
FePt : in-plane versus out-of-plane magnetisationmeasurements



Demagnetising field corrections in a coercive system



$H_D = 0$



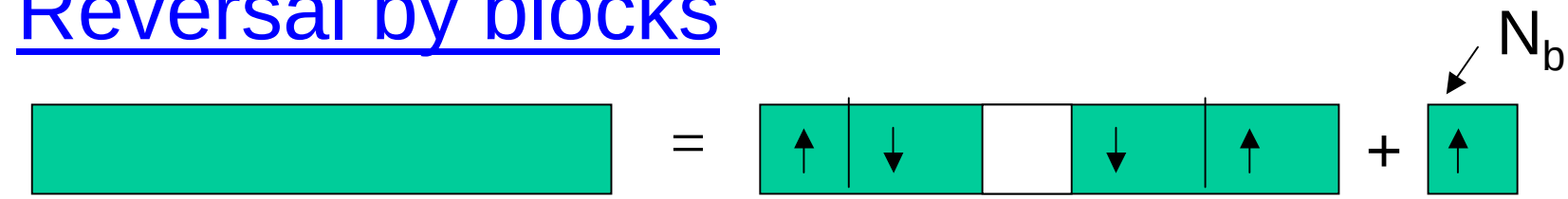
$H_D \neq 0$

Implicit assumption : Magnetisation is homogeneous
Internal field is constant

In particular : $M = 0 \Rightarrow H_D = O$

Demagnetising field in a heterogeneous system

Reversal by blocks

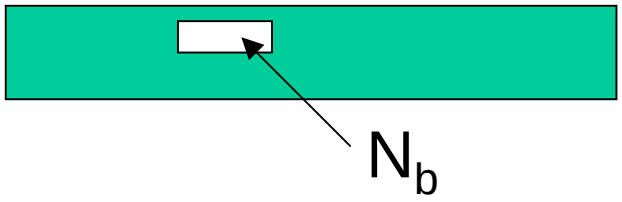


$$H_D = (N_M - N_b)\langle M\rangle + N_b M$$

$\langle M\rangle = 0$; => $H_D = N_b M \neq 0$ => difference in H_c for OP and IP

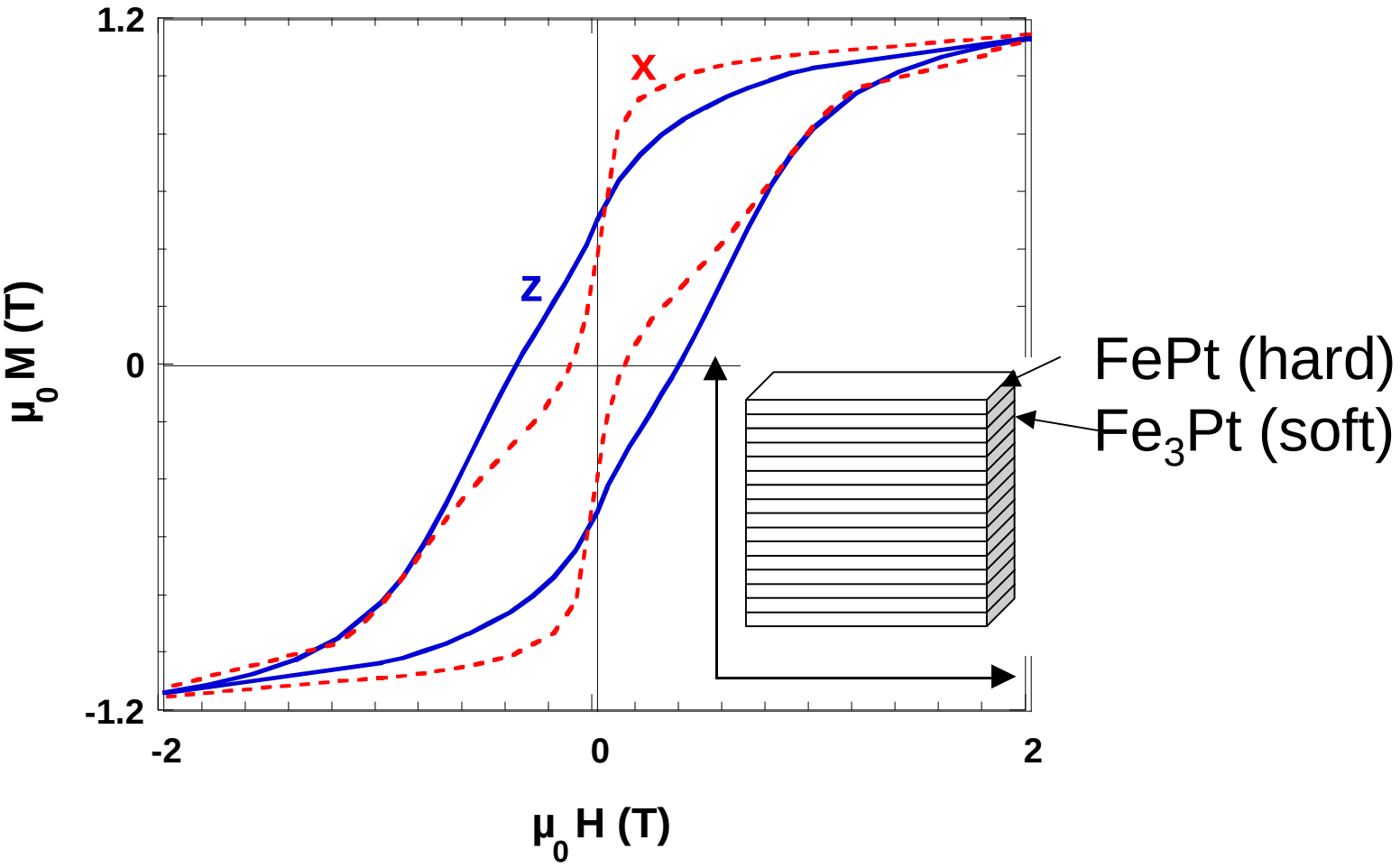
$(N_M - N_b)^{\perp} \neq (N_M - N_b)^{//}$ => difference in slope of OP and IP

Heterogeneous nanostructure

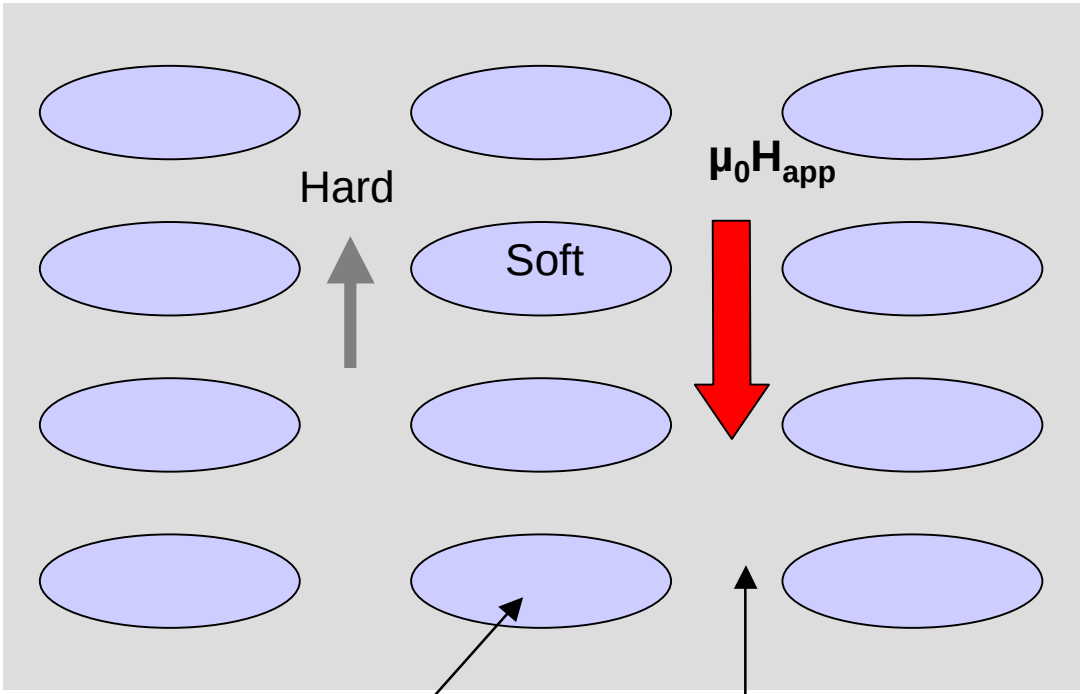


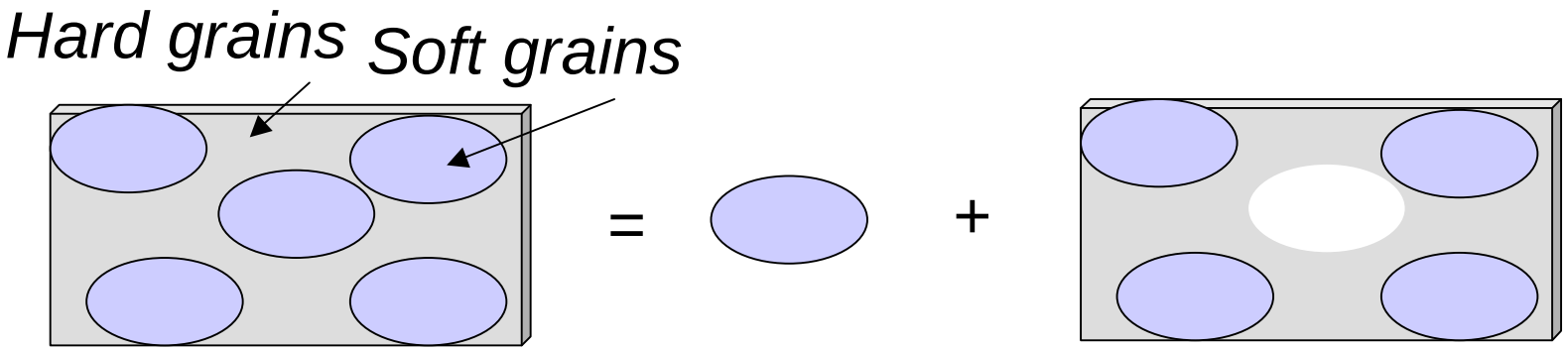
Identical expressions as for reversal by blocks

$FePt/Fe_3Pt$ composites

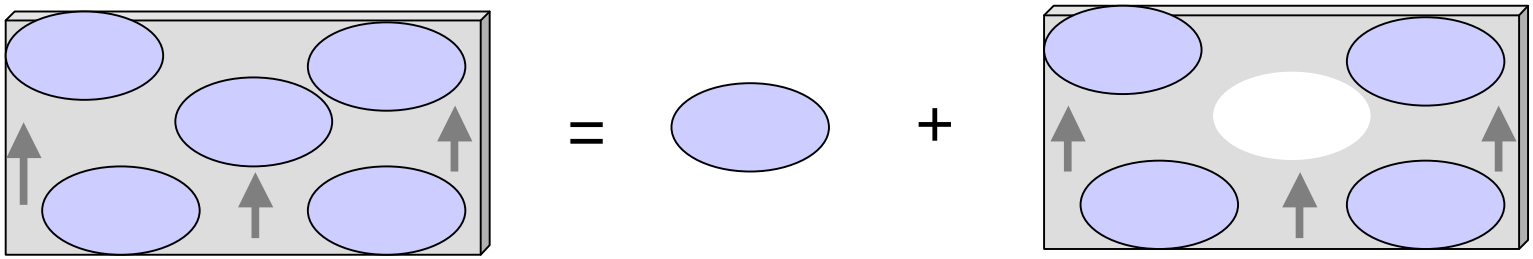


Dipolar interactions in a heterogeneous system





Dipolar interactions in nanocomposites



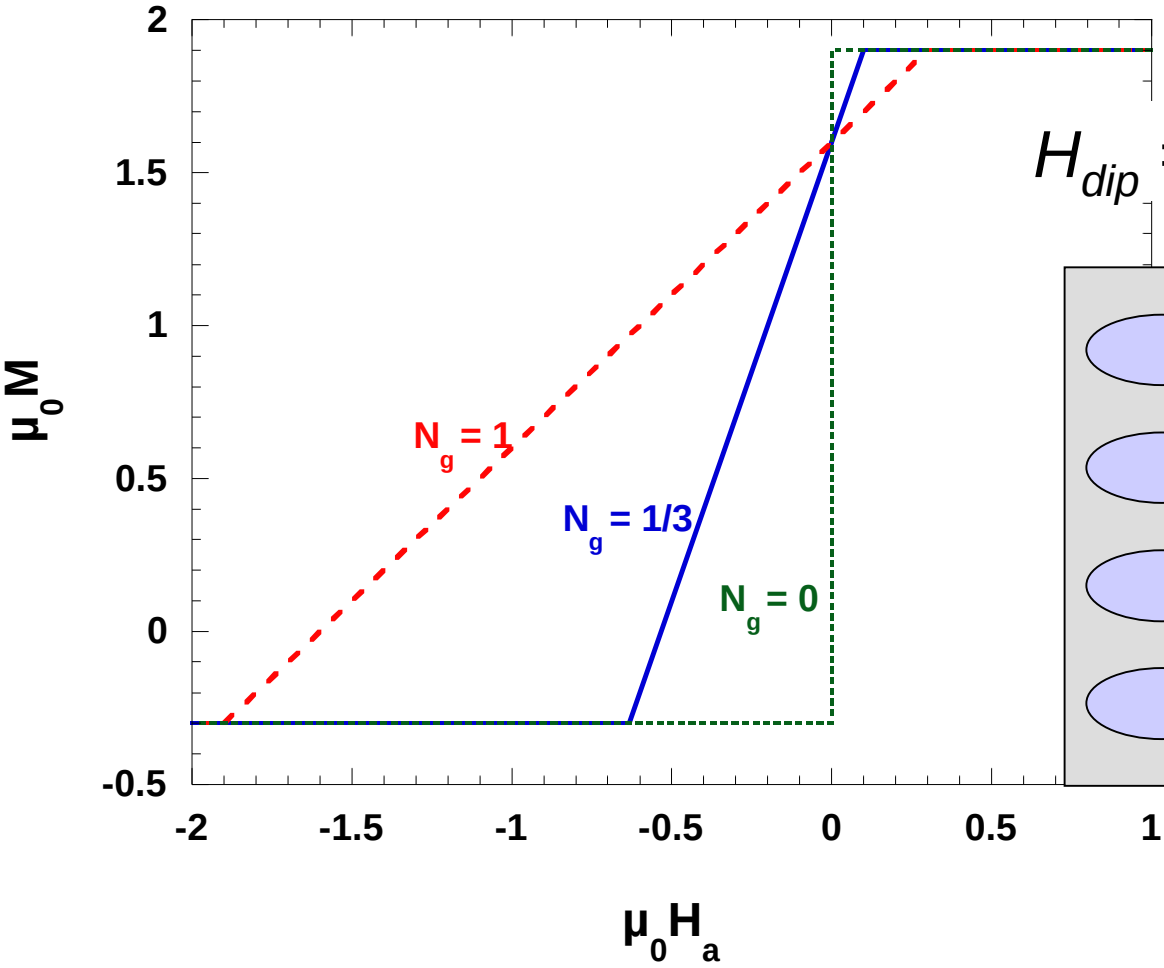
Created by hard and soft grains in the environment

Dipolar field = H_d + H_c

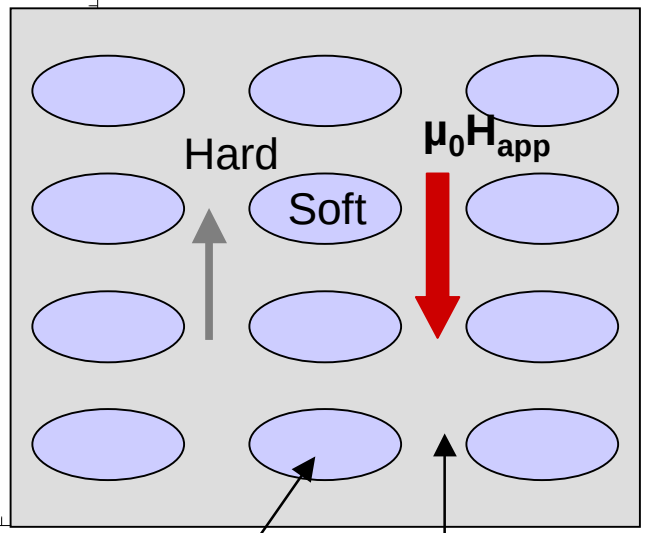
$$E_{soft}^{dip} = -\frac{1}{2} N_g \mu_0 M_{soft}^2 - \frac{1}{2} N_g \mu_0 \alpha M_{soft}^2 + N_g \mu_0 (1-\alpha) M_{soft} M_{hard}$$

$$E_{soft}^{tot} = E_{soft}^{dip} - \mu_0 M_{soft} H_{app}$$

Magnetisation reversal in a system of dipolar-coupled grains



$$H_{dip} = N_g (1-\alpha) (M^{s}_{hard} - M_{soft})$$



N_g $N_b = 0$

$$M_{soft} = \frac{[(N_g - N_b)(1-\alpha) M^{s}_{hard} + H_{app}]}{\alpha N_b + (1-\alpha) N_g}$$

$N_g = 1/3$ 1

$FePt/Fe_3Pt$ calculated versus experimental M(H)