Influence of Size on the Properties of Materials

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1. General Introduction to finite size

Why make things small?

Physics reasons:

1) -finite size (electrons confined),
   -domain formation inhibited.
2) -more interface.

Economic reasons –
more devices on a chip
or more magnetic storage
density

Why Make Things Small?

1) Modify/create new materials properties

i) Finite size effects

Quantization of energy levels (confinement)

$$k_F = (3\pi^2 n)^{1/3}$$

$$\lambda_F \sim 1/n^{1/3}$$

Reduced ordering temperatures

Melting point

Magnetic ordering

Increased coercivity (single magnetic domains)

ii) Surface/Interface effects. Layers, particles, < 10nm.

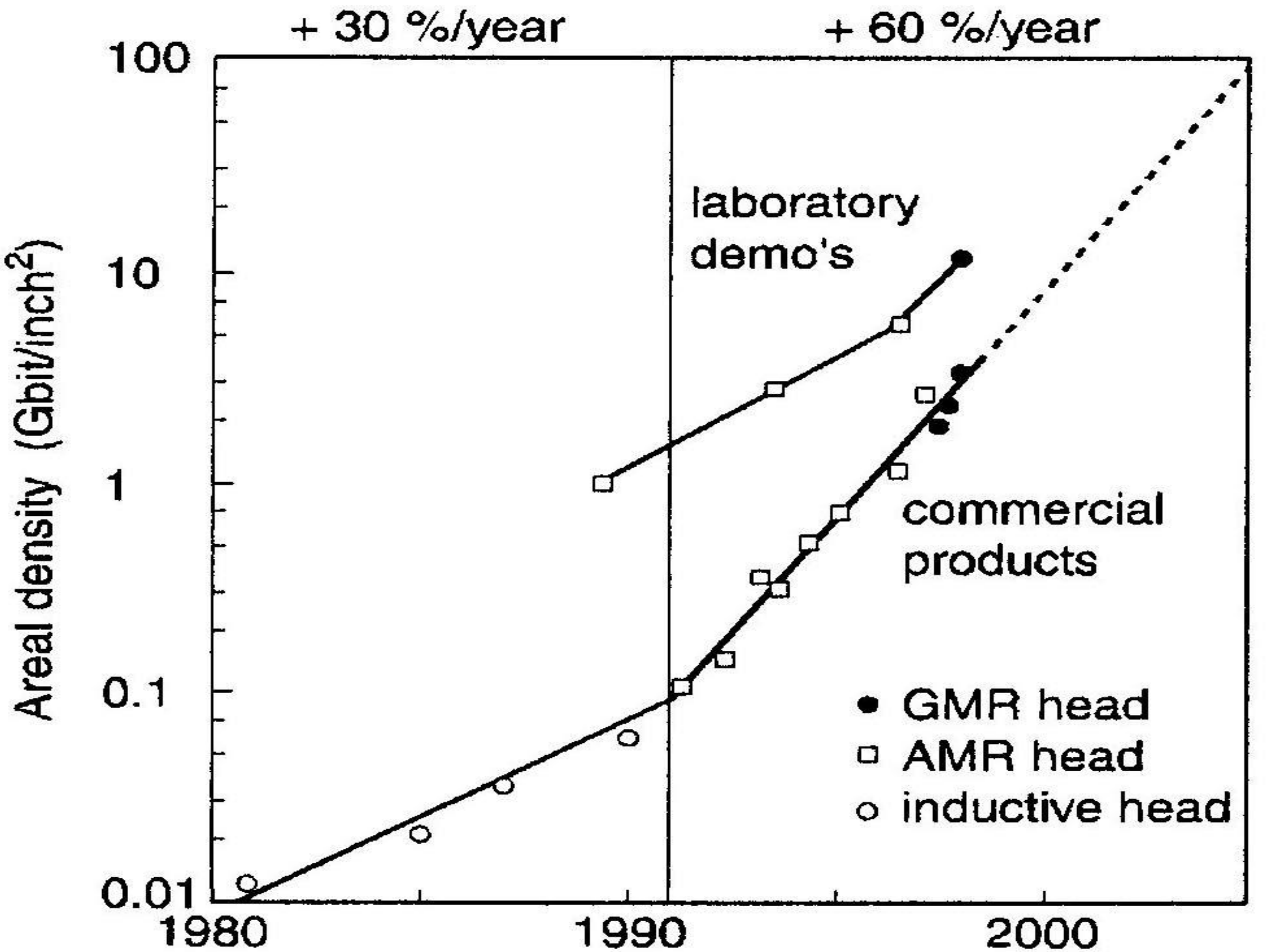
Interface Anisotropy

Interface Exchange

Giant magnetoresistance in magnetic nanostructures

Economical to make current devices smaller.

e.g. magnetic storage media (Himpsel, Adv. Phys. 47, 511 (1998))



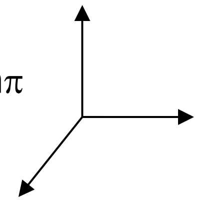
Bit density for a hard disk

Electron density and size effects- general

Finite size effects - Quantization of energy levels (confinement)
Allowed states:

$-h^2/2m\,(d^2/dx^2+\ldots)\,\psi = E_k\,\psi \qquad \psi(x+L,y,z)= \psi(x,y,z)$

From SE $E = h^2k^2/2m$



Boundary condition $\psi = e^{ikr} \qquad e^{ik_xL} = 1$ or $k_xL = 2n\pi$

$k_x=2\pi/L,\ 4\pi/L,\ldots\ldots$
$E_k = h^2/2m(k_x^2+k_y^2 + k_z^2)$

Max $k = kF \qquad 2\,(4/3)\,\pi\,k_F^3\,/(2\,\pi/L)^3 = N \qquad k_f = (3\,\pi^2N/V)^{1/3}$

$E_f = h^2/2m\ \ k_f^2$
$k_F = (3\pi^2n)^{1/3}$
$\lambda_F \sim 1/n^{1/3}$

Semiconductor n << metal n

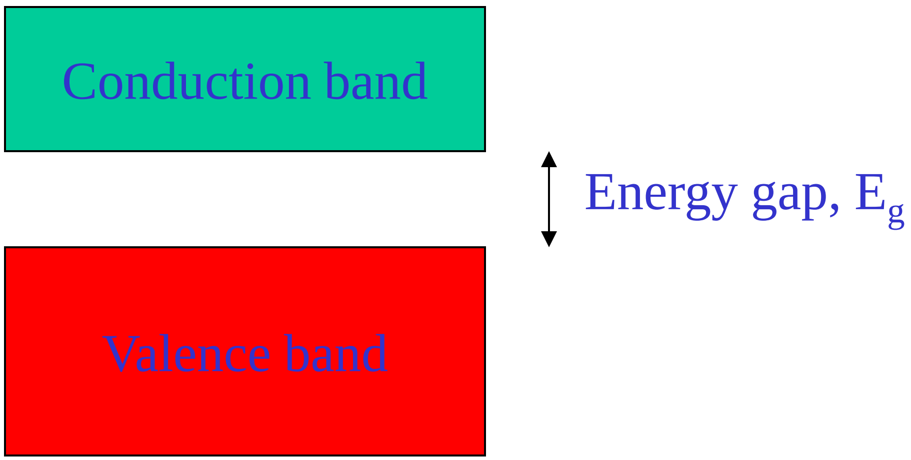
L large – energy levels closely spaces – continuum
L small Energy levels not closely spaced
Semiconductor n small, λ_F is large. There size effects more important for semiconductors at large size than for metals.

Electrons (and holes) in ‘quantum wells’

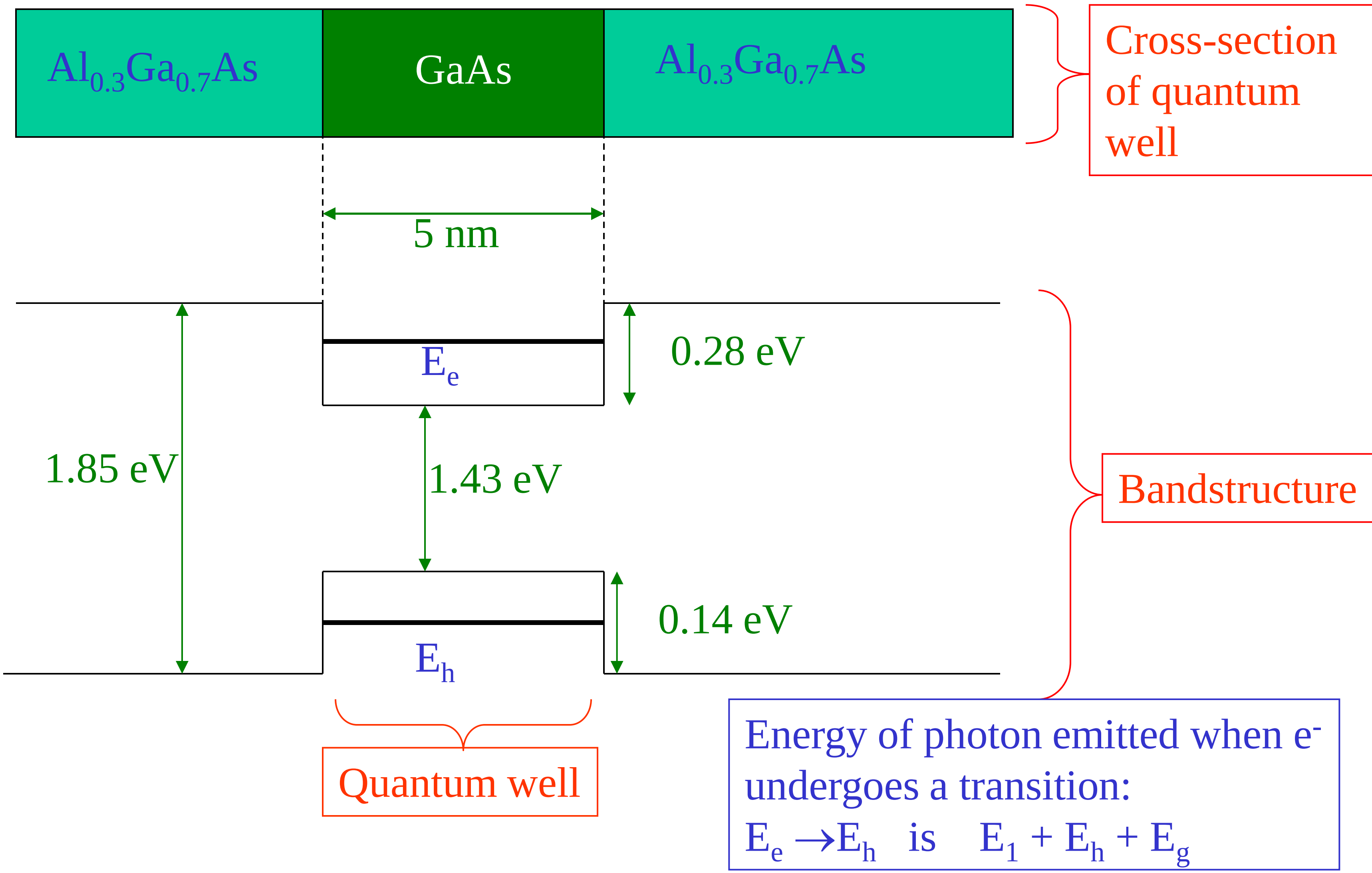
Discuss the differences between a conductor, semiconductor, insulator

Energy levels and bandgaps in bulk materials

Room temp about 1/40 eV



Band structure of a quantum well



Semiconductor preparation

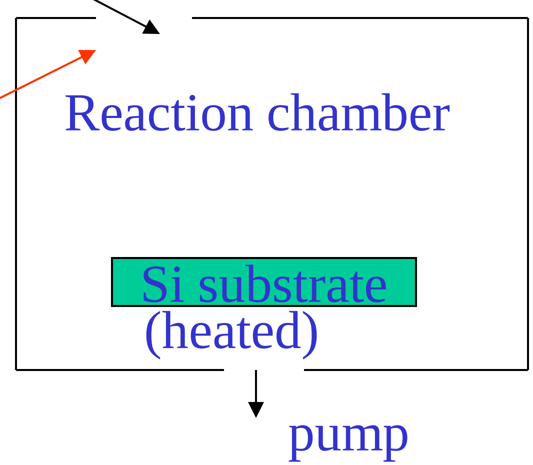
Starting materials must be very pure – then use a well defined amount of doping

<u>Vapor phase epitaxy</u>

$$SiCl_4 + 2H_2 \rightarrow Si + 4HCL$$

Si(As)

Add dopant gas e.g. one containing As (column 5), donates electron.



Silicon tetrachloride reacts with H to give elemental Si.

Occurs at surface – deposit Si (+ any impurities).

HCl does not disturb surface

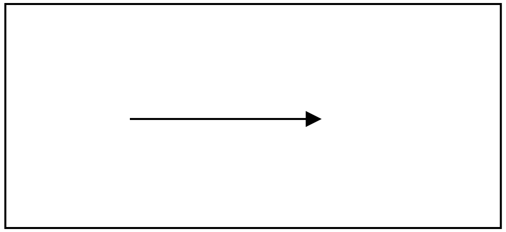
Reaction is reversible – etch Si surface

Can use other gases such as Silane (SiH_4)

2. Finite size in magnetic systems

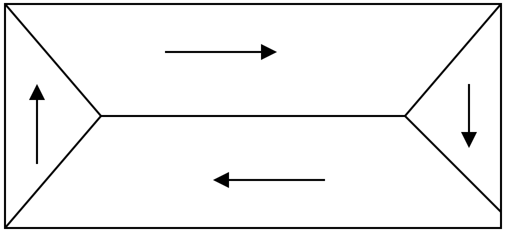
Single magnetic domains

Bulk material – in the form of a single magnetic domain



B outside is large so
$\int(B^2/2\mu_o)\, dV$ is small

Bulk material – breaks up into magnetic domains to reduce magnetostatic energy



B outside is small so
$\int(B^2/2\mu_o)\, dV$ is small

Energetics of magnetic domains

Magnetostatic energy $E_m = \int(B^2/2\mu_o)\,dV \propto$ volume V of magnetic domain.

$\varepsilon_w \equiv E_m/V = \{\int(B^2/2\mu_o)\,dV\}V \approx$ constant

Domain wall energy, E_w (J/m^2) $\propto$ surface area of wall $\propto V^{2/3}$

$\varepsilon_w = E_w$ (J/m2)/V $\propto$ surface area of wall/V $\propto V^{-1/3}$

Bulk: $V^{-1/3}$ smaller than V, easier for domain walls to form

Nanoscale: $V^{-1/3}$ larger than V, difficult for domain walls to form

So expect that for sufficiently small V, the sample should be a single magnetic domain.

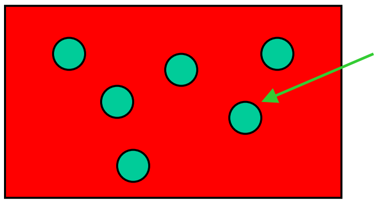
Important because domain walls no longer present $\rightarrow$ coercivity is very high

Coercivity

1) Particles – 3 dimensions in the nm range

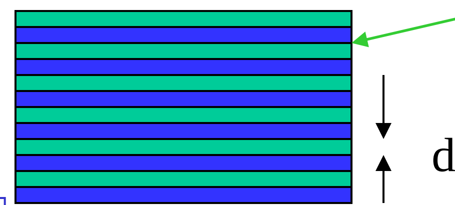
2) layers – 1 dimension in the nm range

Isolated particles:



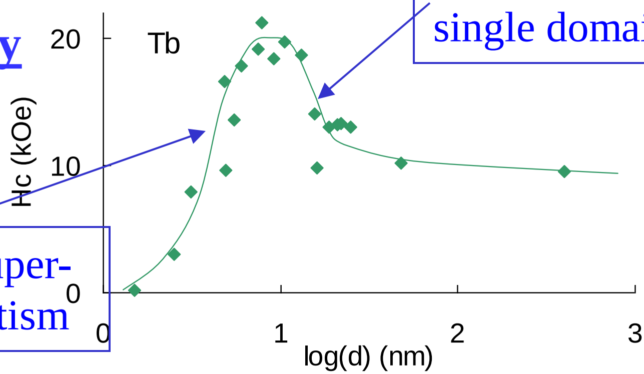
Rare-earth/Ti matrix

Multilayers:



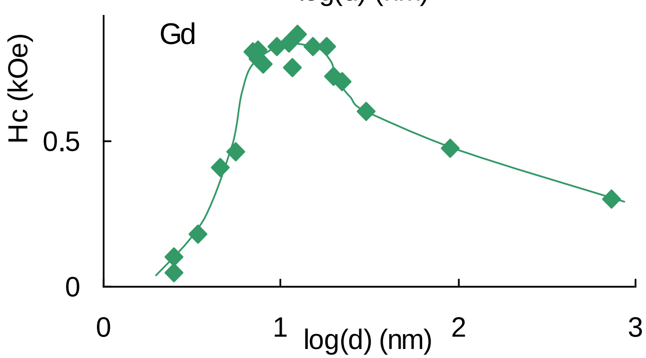
Rare-earth/Mo layers

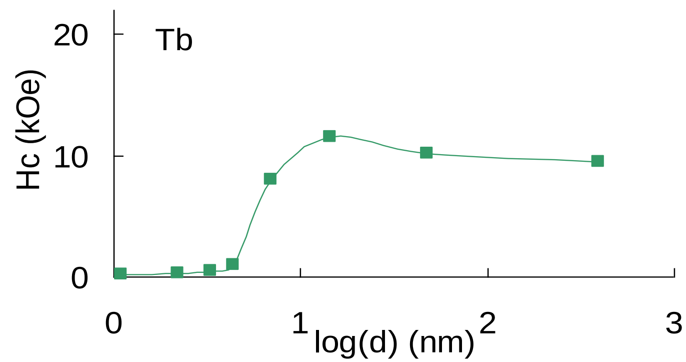
Coercivity

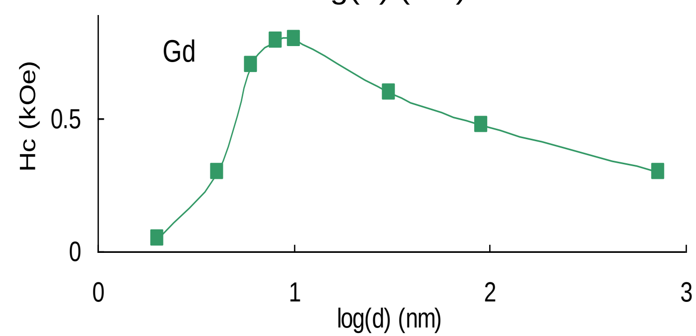


Particles become single domain

Onset of super-paramagnetism



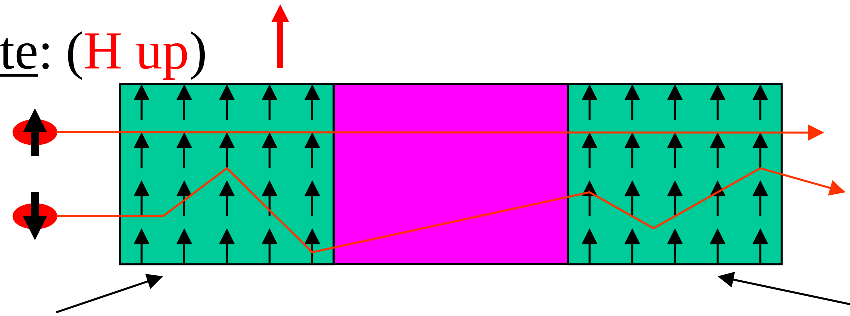




Why make things small?

3) New devices: Spin Valve

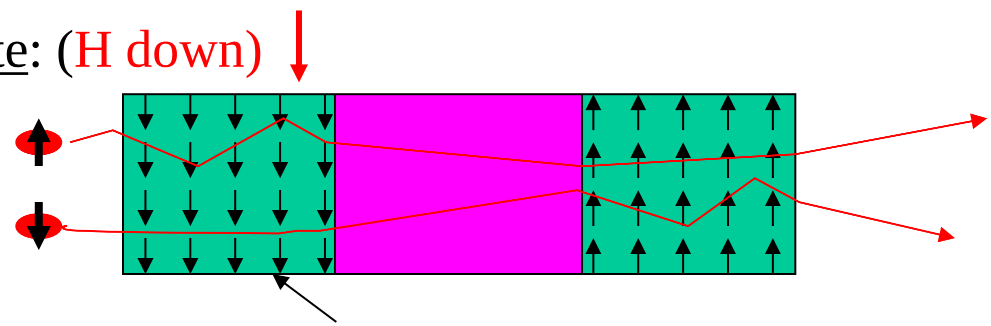
Low resistance state: (H up)



Soft magnetic layer

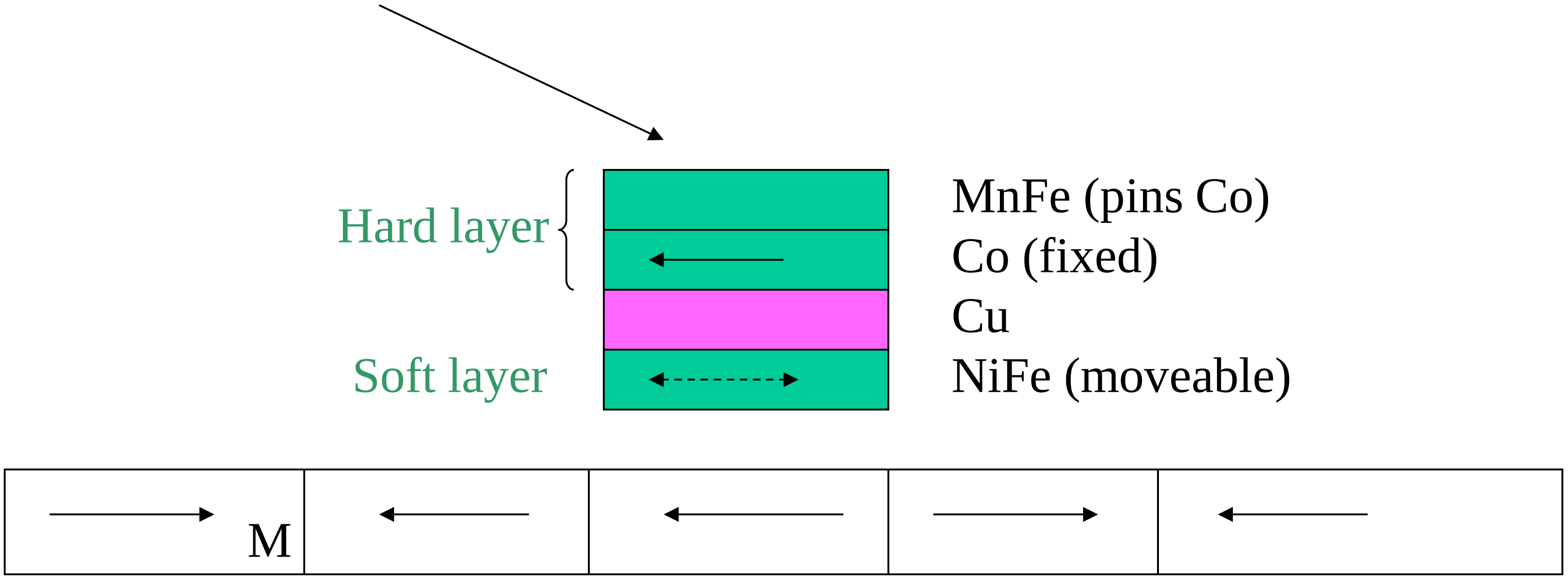
Hard magnetic layer

High resistance state: (H down)



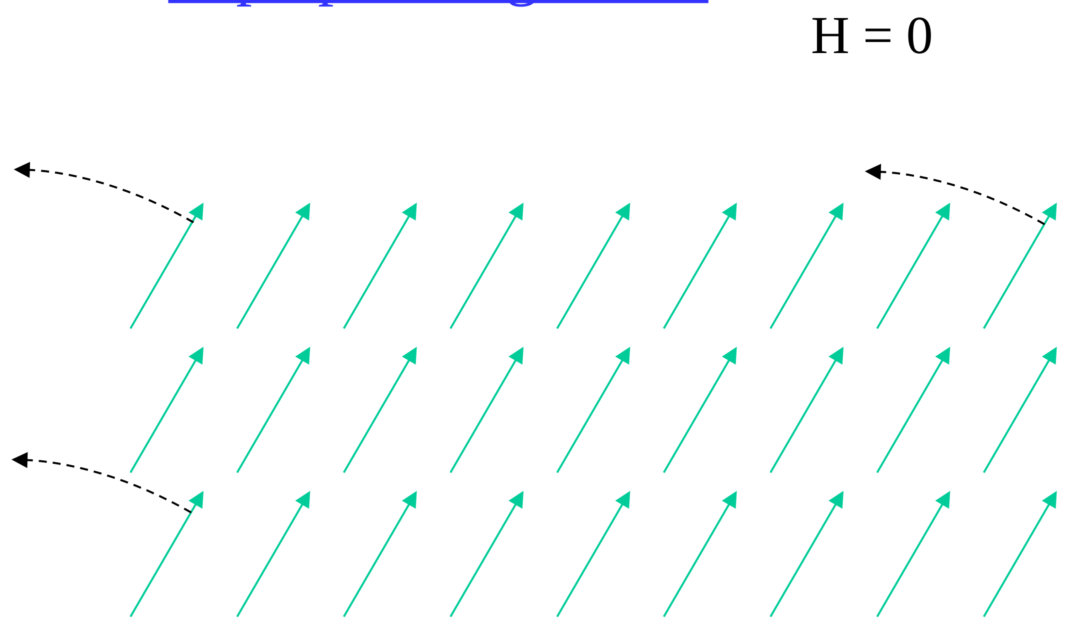
soft layer reverses

Spin Valve Read Head



Recording medium.

Superparamagnetism



kT (thermal energy) > KV (anisotropy energy), moments not pinned to lattice.

When H = 0, M = 0 so $H_c = 0$.

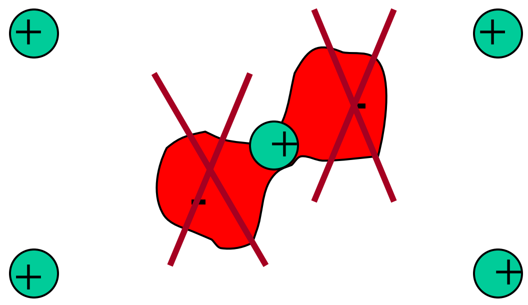
Magnetic Anisotropy

Origin of Magnetic anisotropy

1) Interaction between a local quadrupole moment (L) and electric field gradients.

2) $\mu = \mu(L, S)$

$\Rightarrow$ Magnetic anisotropy



Strength of Magnetic anisotropy

Rare-Earths ✸ large L ✸ strong magnetocrystalline anisotropy
Transition metals ✸ small L ✸ weak magnetocrystalline anisotropy

Metal	K_1 (J/m^3)
Co	7×10^5
Tb	-5.6×10^7
Dy	-5.5×10^7
Gd	-1.2×10^5

All hexagonal : $E_A = K_1 \sin^2\theta + K_2 \sin^4\theta$ ……….

Note that for Fe, Ni: E_A = (expression with cubic symmetry)

A Problem: Superparamagnetism

Smaller bit size $\rightarrow$ higher density magnetic recording (Co-Pt-Cr)

Currently bit size is ~ 0.25 μm, Density = 10 Gigabit/in^2

Superparamagnetism

Flip rate due to thermal fluctuations:

$$1/\tau = \nu \exp(-\Delta E/k_B T)$$

ν: $2.4\times10^9\ s^{-1}$

ΔE: Depends on size of particle (KV)

size (nm)	τ
10	1 week
20	10^{104} years

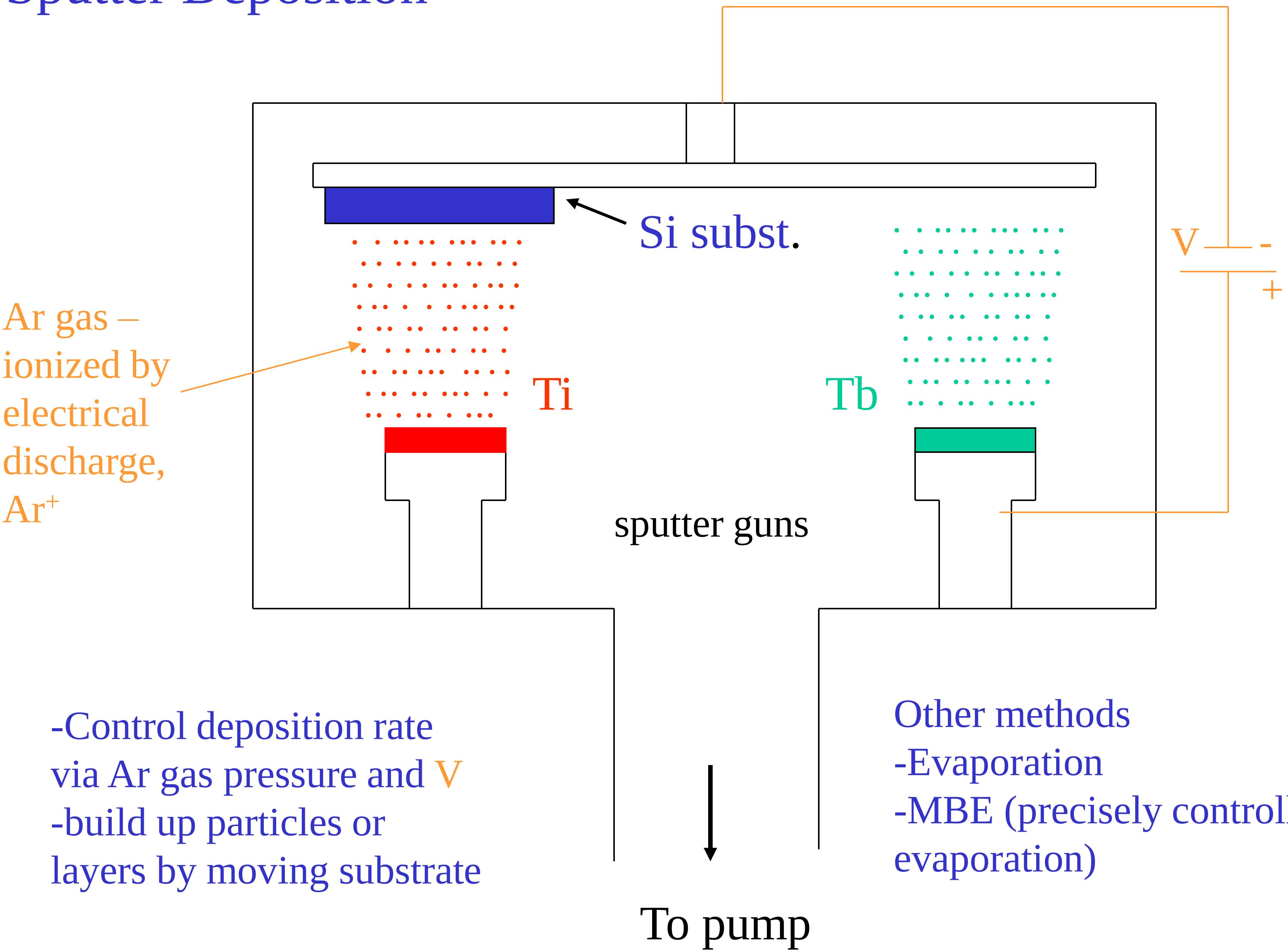
Lower limit $\rightarrow$ bit size 20 nm, Density = 1 Terabit/ in^2

Superparamagnetism $\rightarrow$ ultimate limit for storage density

3. Tb (and other elemental rare-earth) particles in a Ti matrix

– fundamental studies

Sputter Deposition



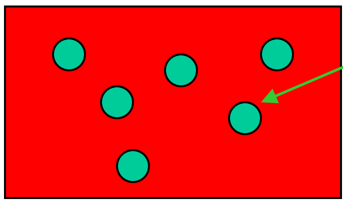
-Control deposition rate via Ar gas pressure and V
-build up particles or layers by moving substrate

Other methods
-Evaporation
-MBE (precisely controlled evaporation)

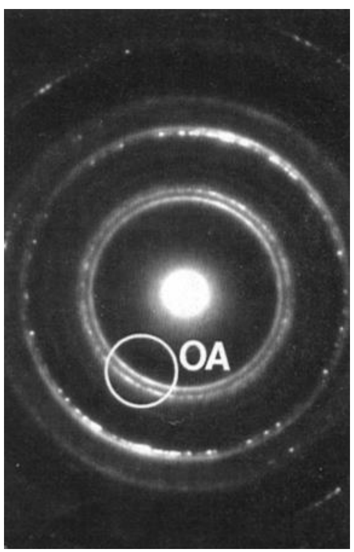
Structure

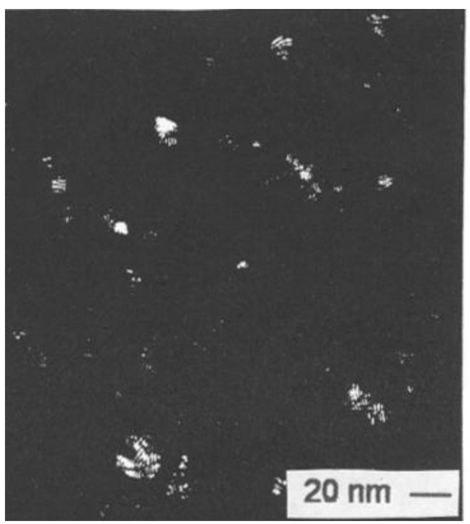
1) Particles – 3 dimensions in the nm range

Isolated particles (Tb):



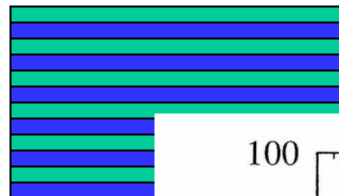
Tb/Ti matrix



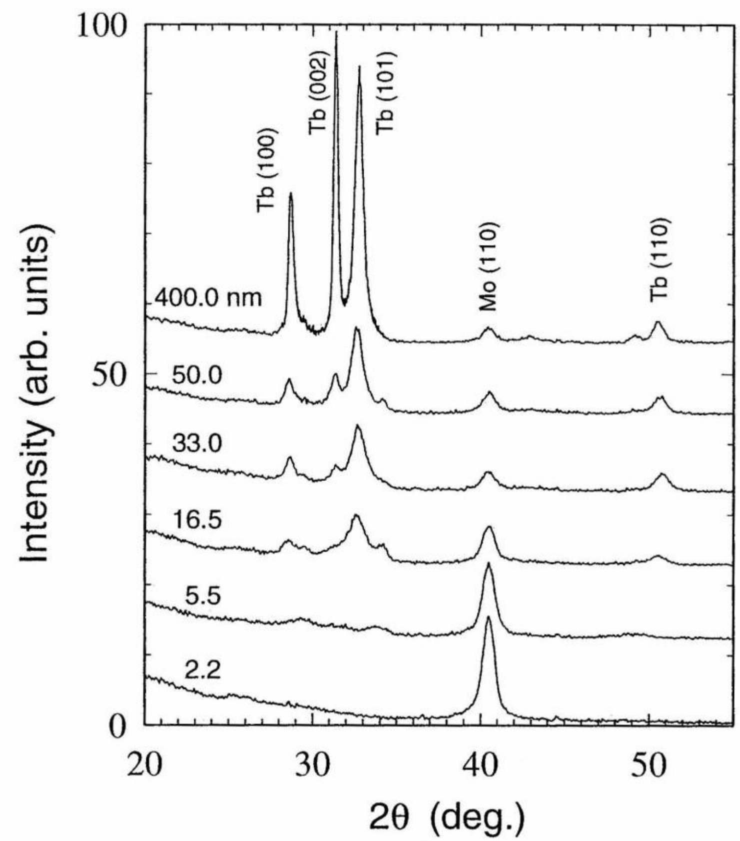


2) layers – 1 dimension in the nm range

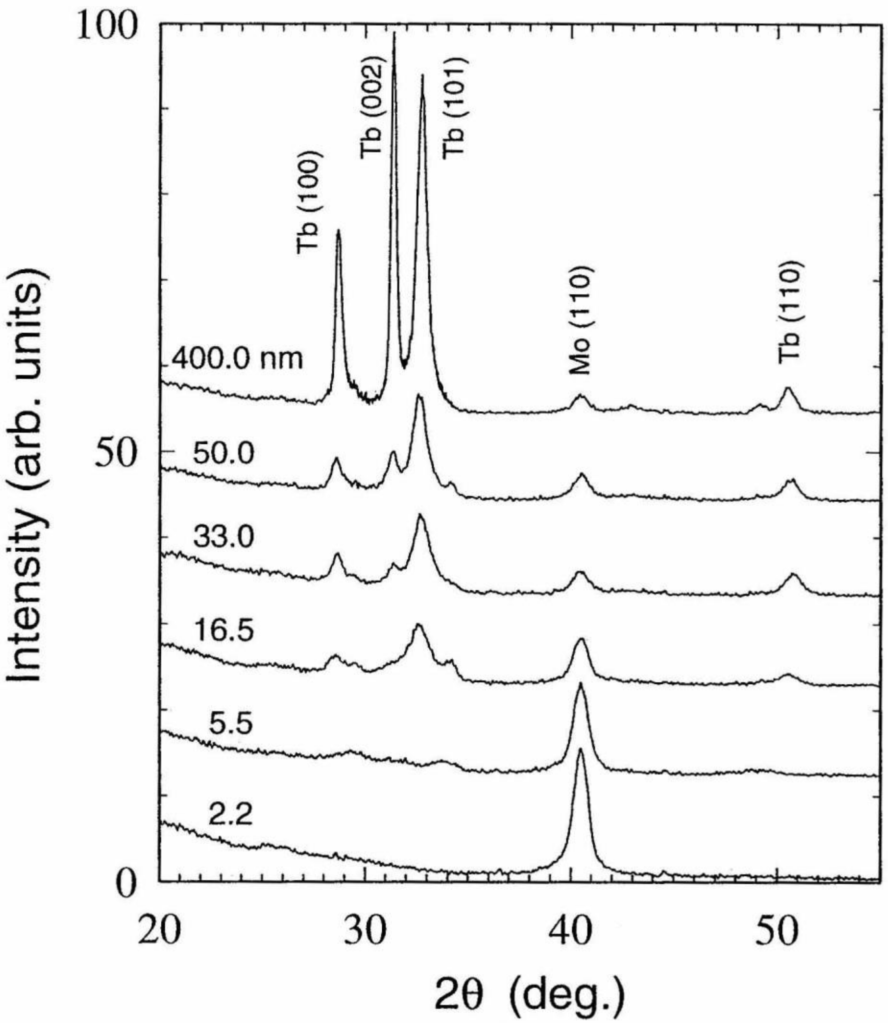
Multilayers:

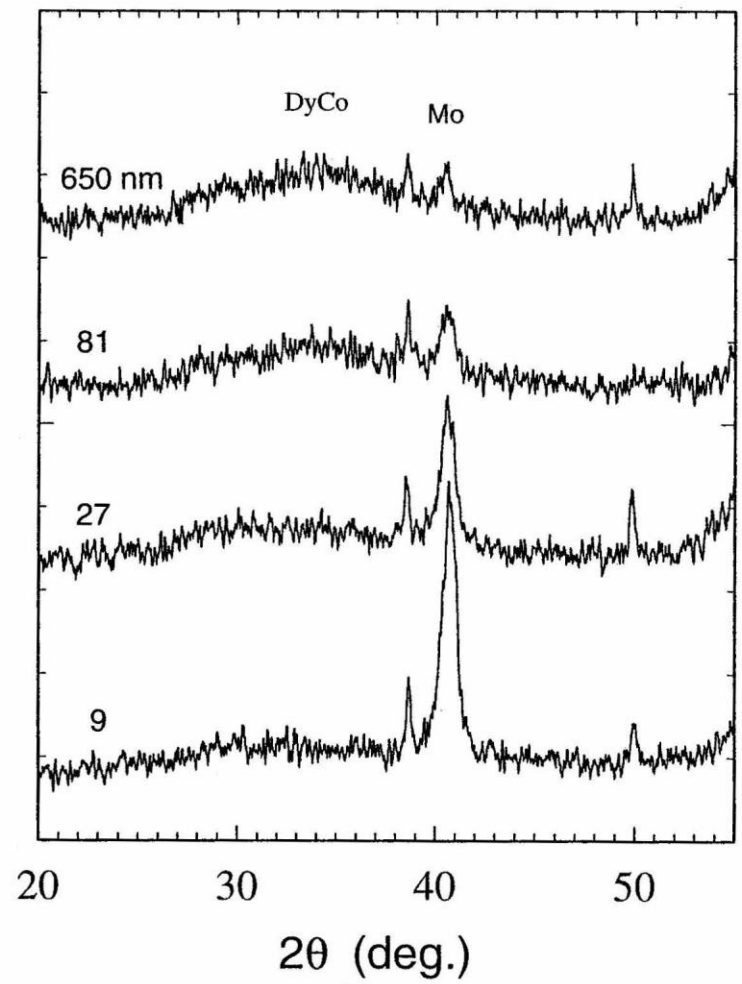


Tb/Mo layers

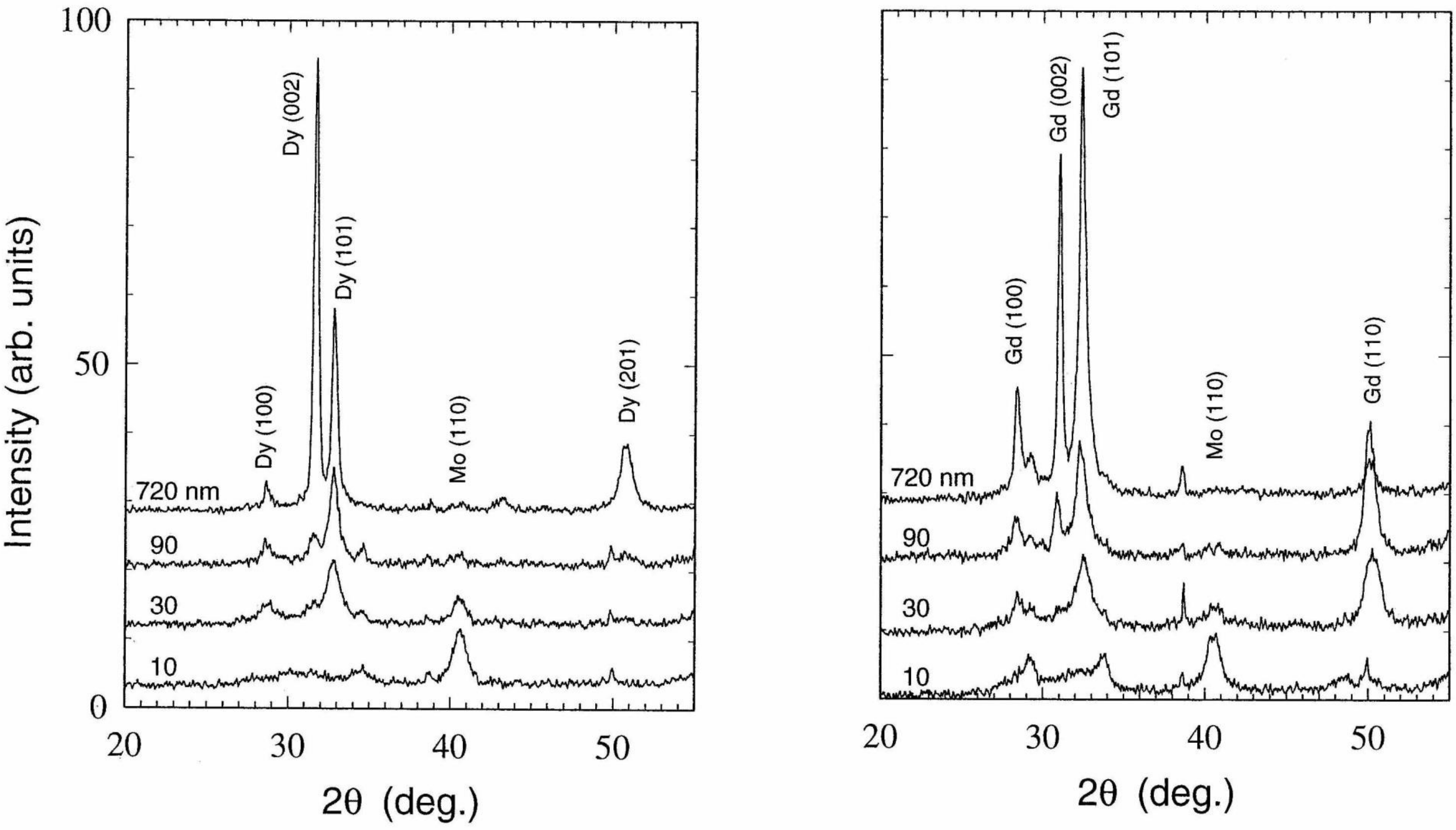


X-ray diffraction of R/Mo multilayers





X-ray diffraction of R/Mo multilayers



As size changes for particles or layers, look at:

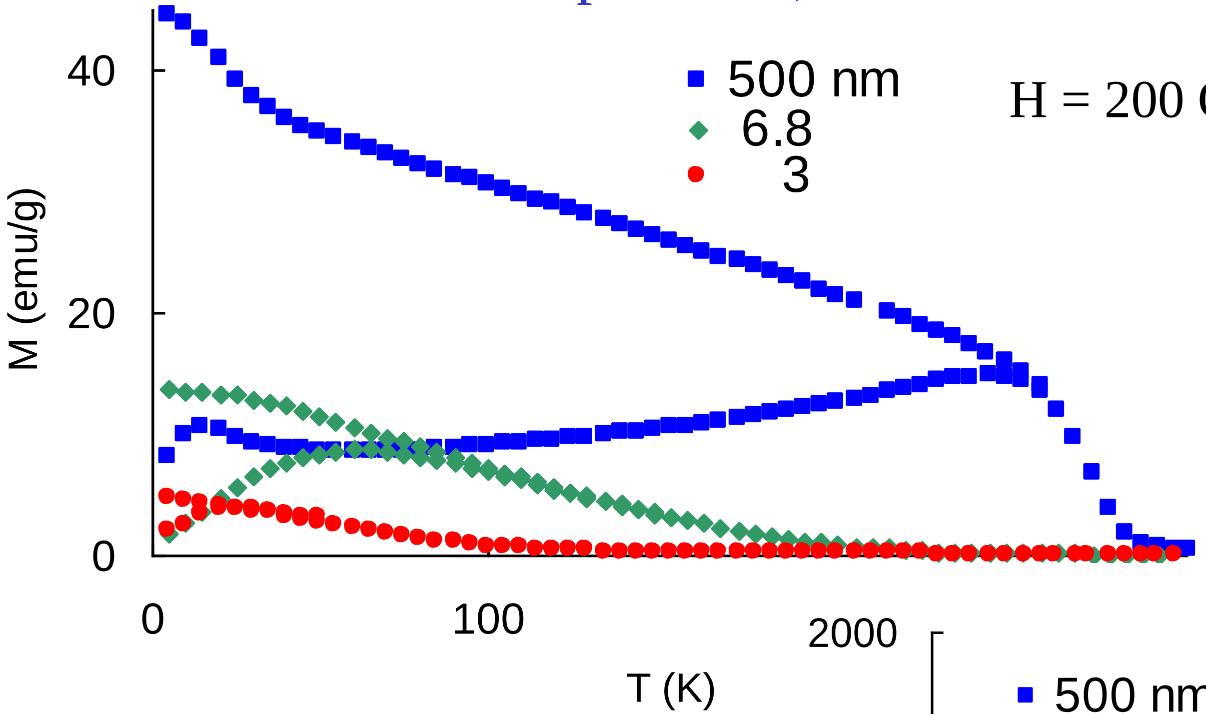
Magnetic ordering temperature

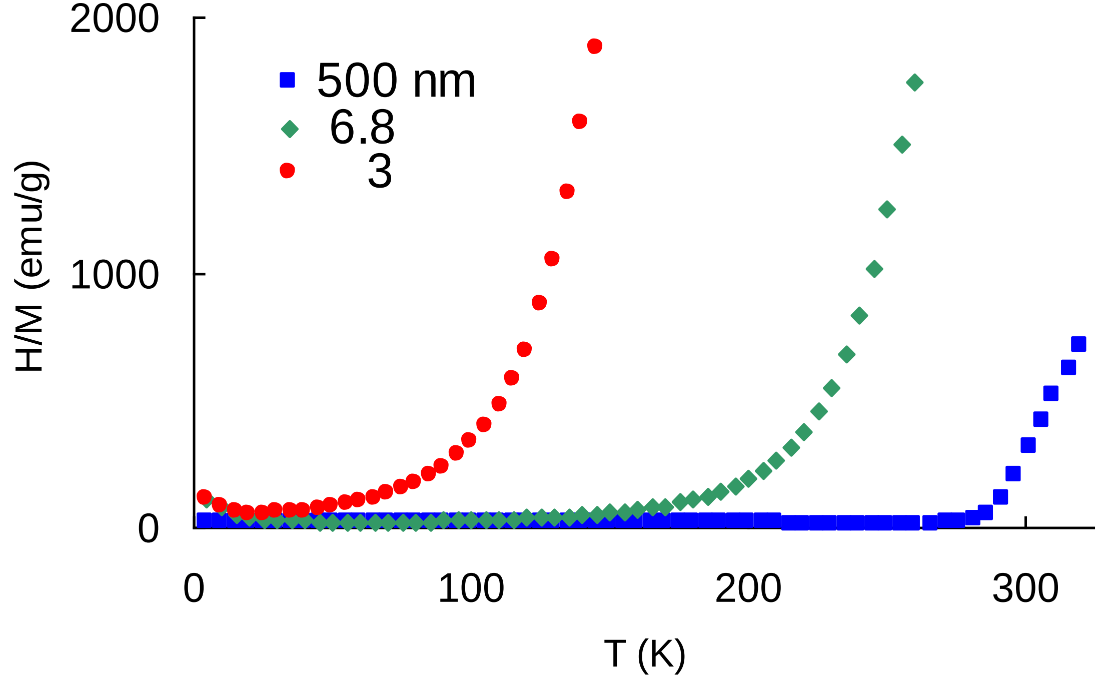
Coercivity

Magnetic Anisotropy

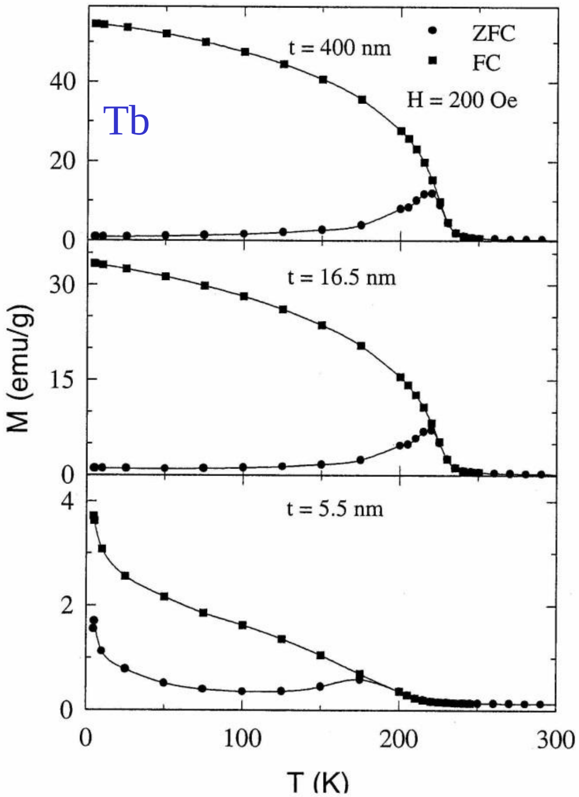
Time dependent magnetization

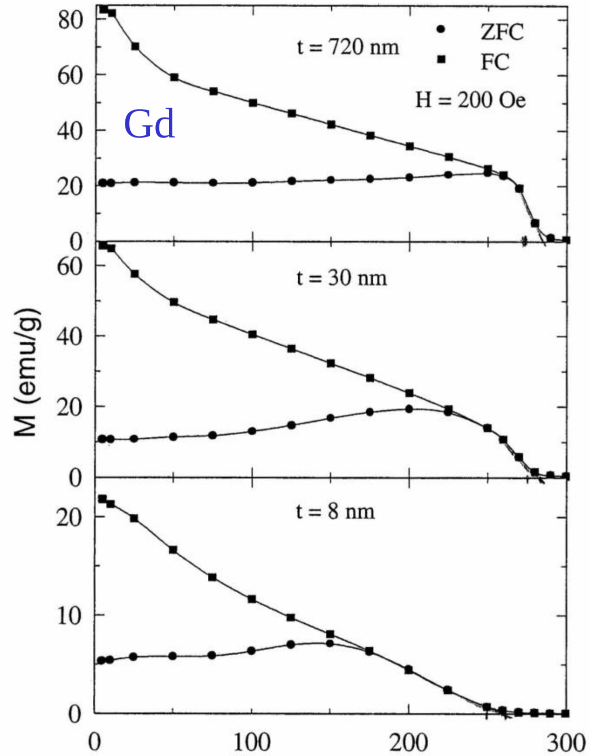
Gd particles, finite size and T_c

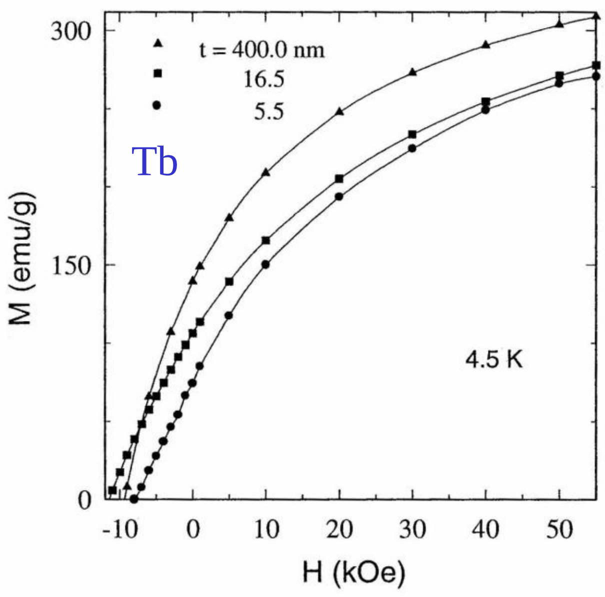


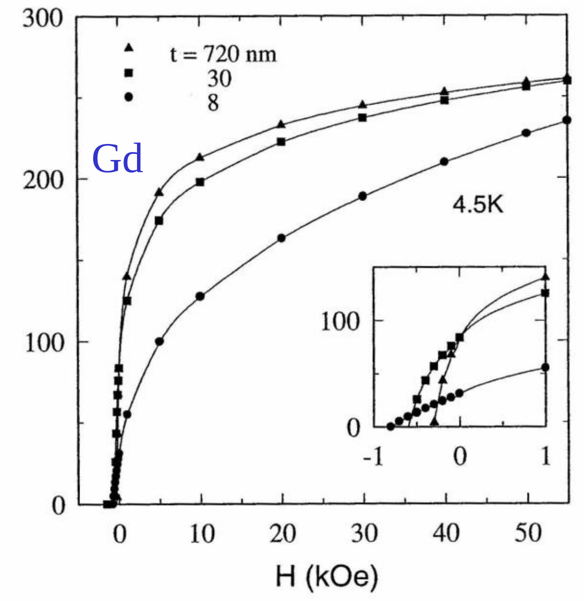


Magnetic layers:
R(t nm)/Mo(18 nn







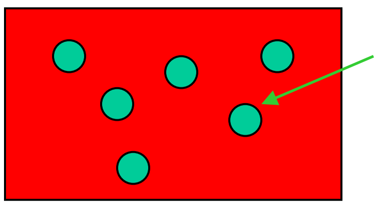


T_c and finite size

1) Particles – 3 dimensions in the nm range

2) layers – 1 dimension in the nm range

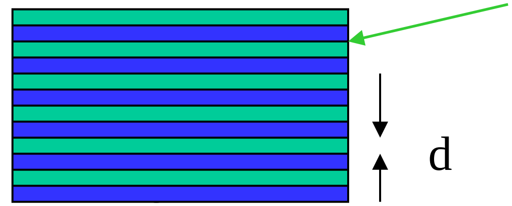
Isolated particles:



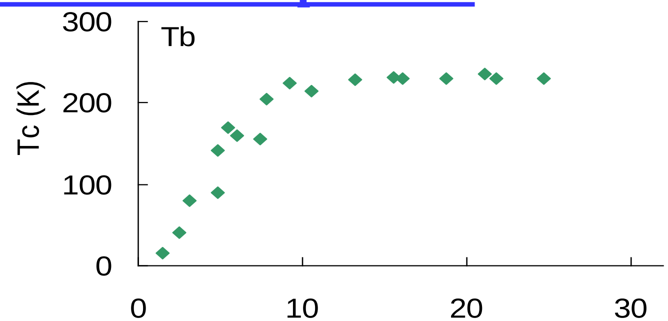
Rare-earth/Ti matrix

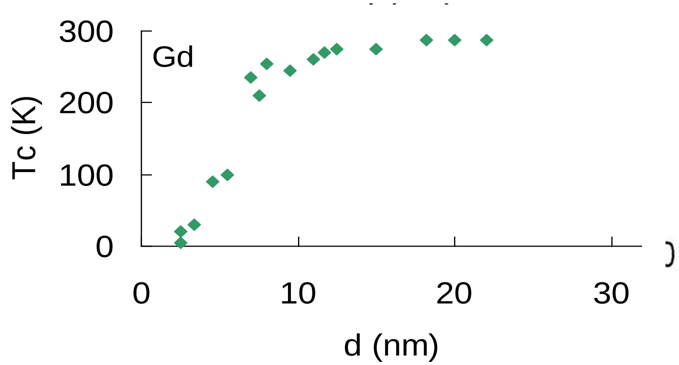
Multilayers:

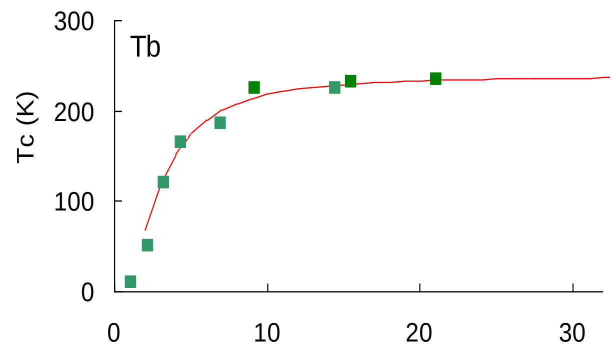
Rare-earth/Mo layers

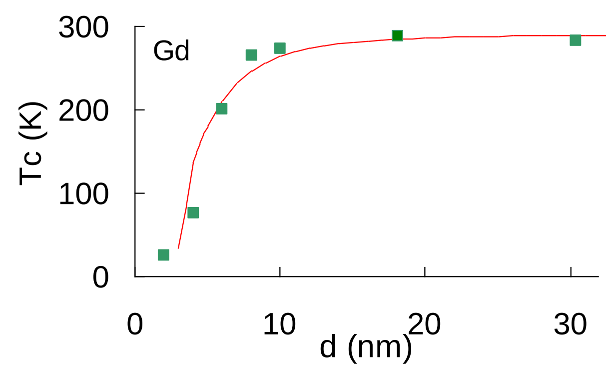


Transition Temperature









Reduction of T_C and Finite Size Scaling

Reduction of T_C with layer thickness described by:

$(T_{bulk} - T_C)/T_C = ((d – d')/t_0)^{-B}$

where:

T_{bulk} - bulk transition temperature

B - exponent to be determined

d' - about thickness of one monolayer

t_0 - constant to be determined

System	B(exponent)	Ref
Gd	2.6 ± 0.4	O'Shea (1998)
Tb	1.9 ± 0.2	"
Dy	1.5 ± 0.2	"
Ni	1.25± 0.07	F. Huang (1993)
$CoNi_9$	1.39± 0.08	"
Co	1.34±	C. Schneider (1990)

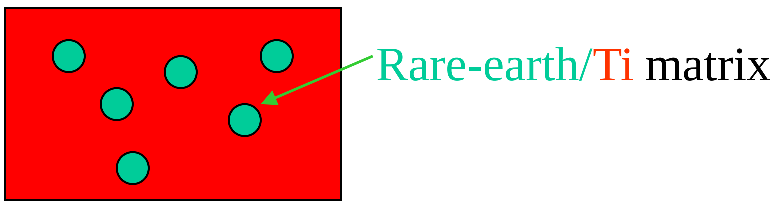
B is expected to be 1.33 ± 0.15 from theory. [Ritchie et al., Phys. Rev. B7, 480 (1973)]

Coercivity

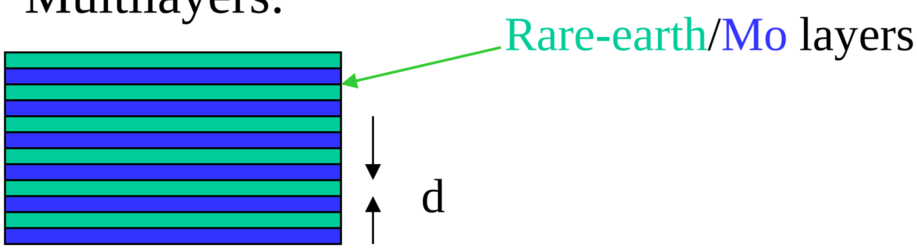
1) Particles – 3 dimensions in the nm range

2) layers – 1 dimension in the nm range

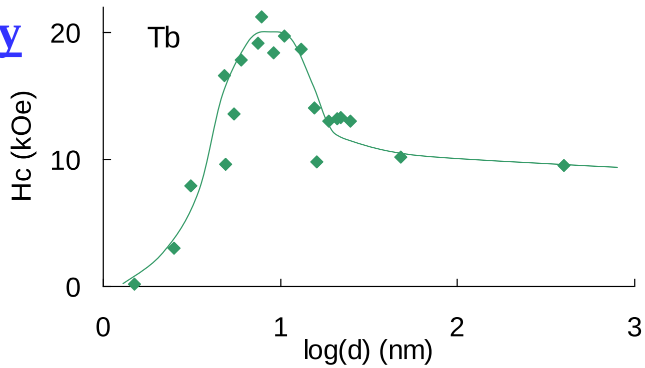
Isolated particles:

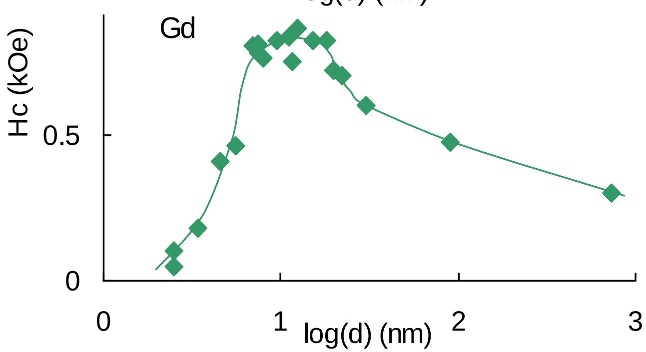


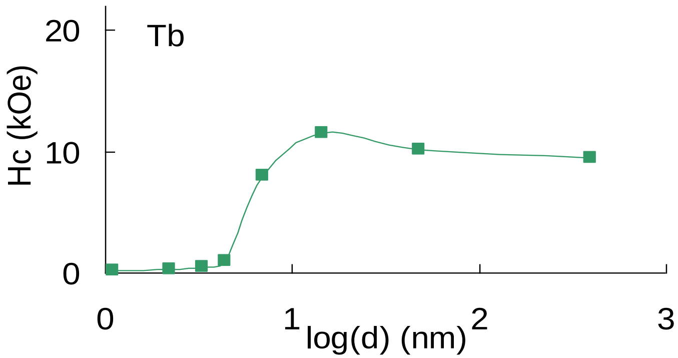
Multilayers:

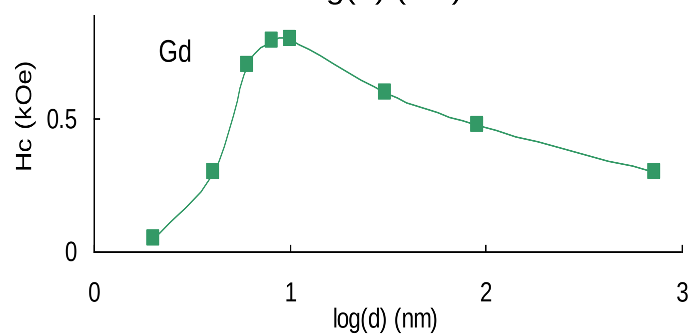


Coercivity









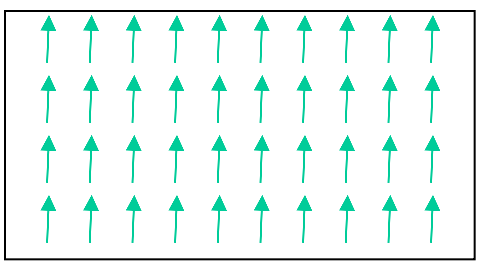
Magnetic Domains

$$\Delta F = + E(\text{domain wall}) + \text{dipolar energy}$$

$\sim V^{2/3}$ $\sim V$

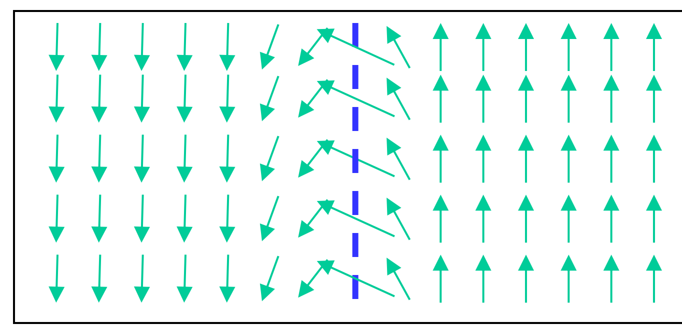
<u>Small particle</u>

single domain

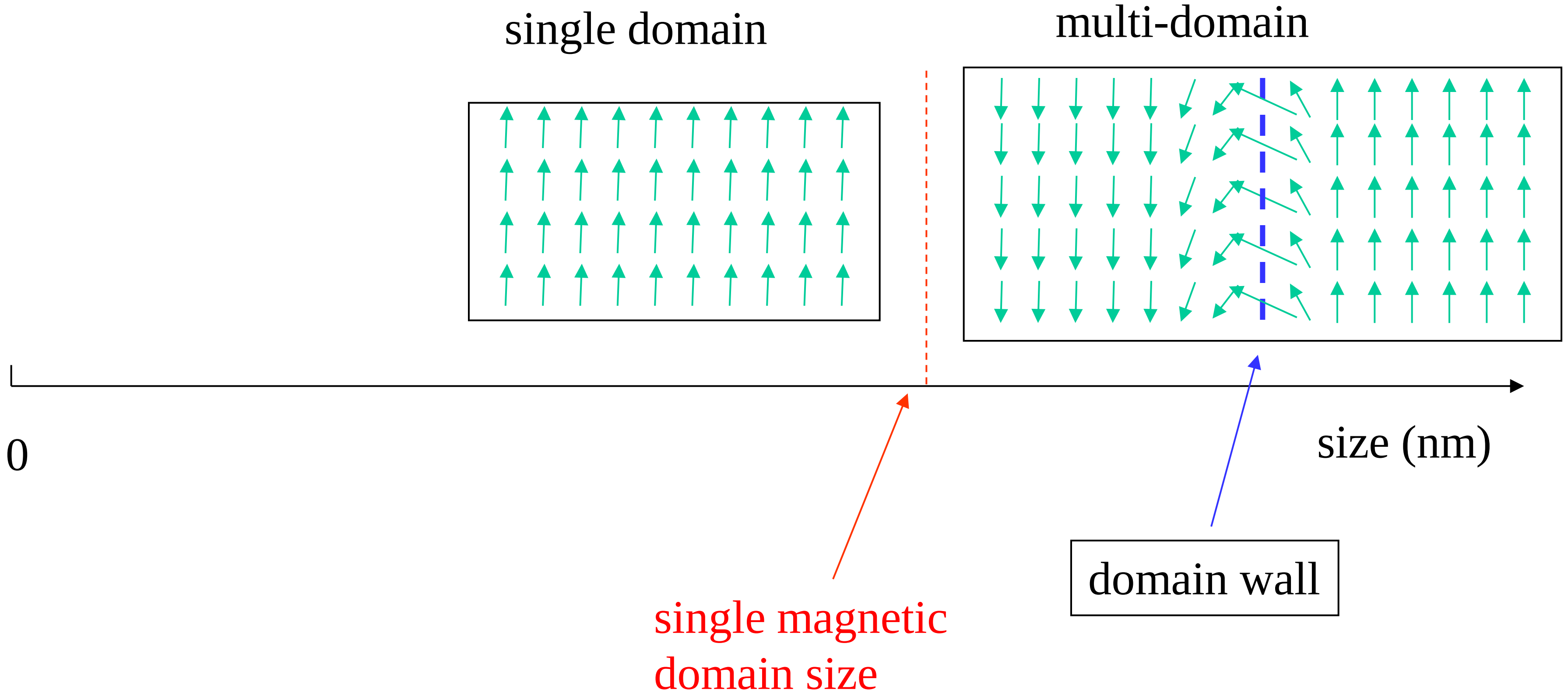


<u>Larger particle</u>

multi-domain



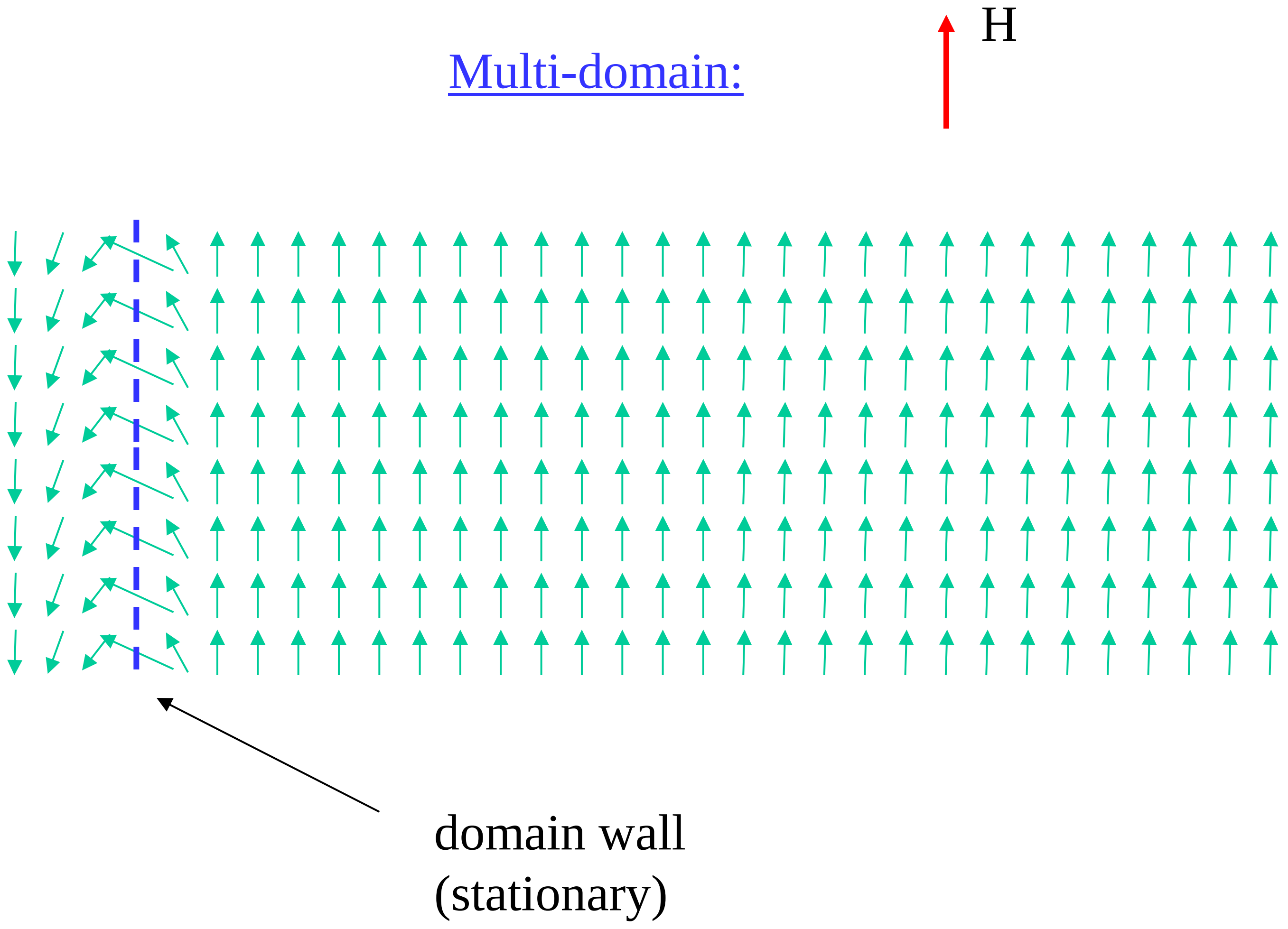
domain wall

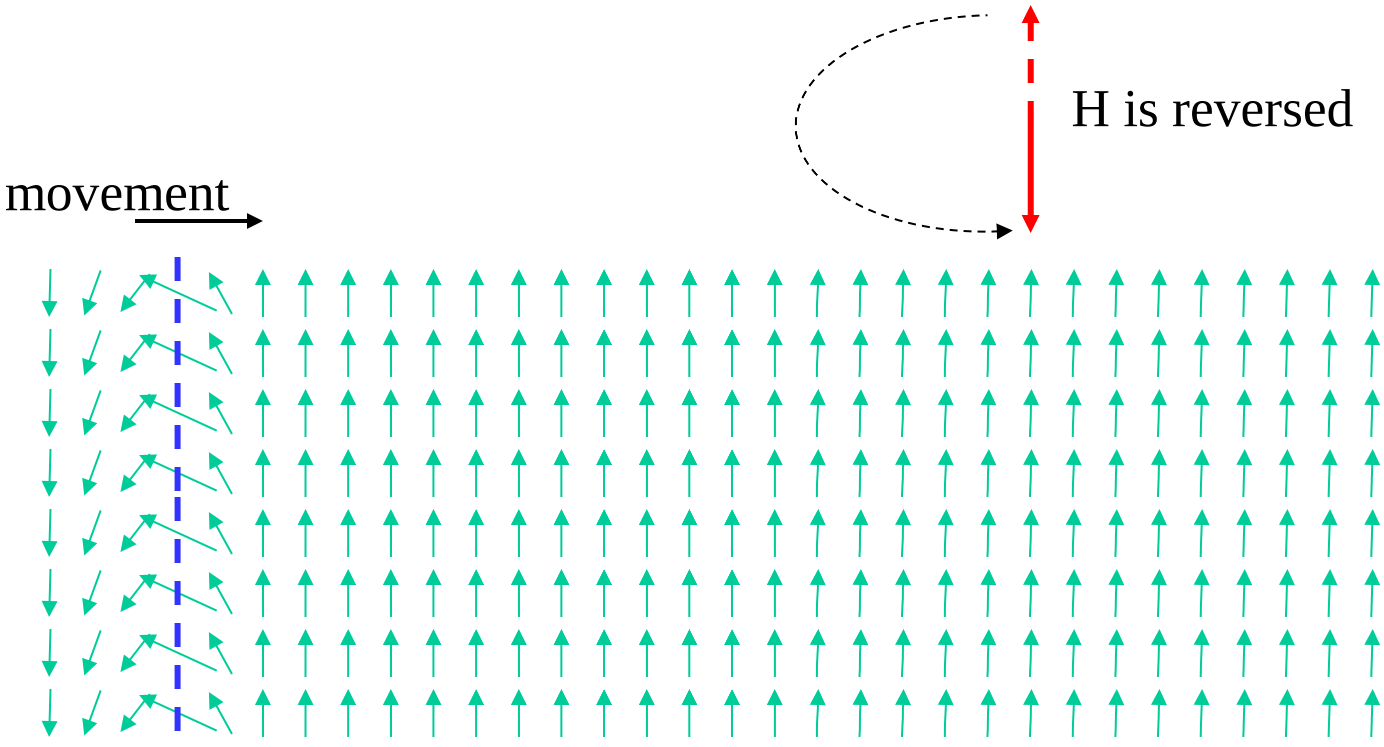


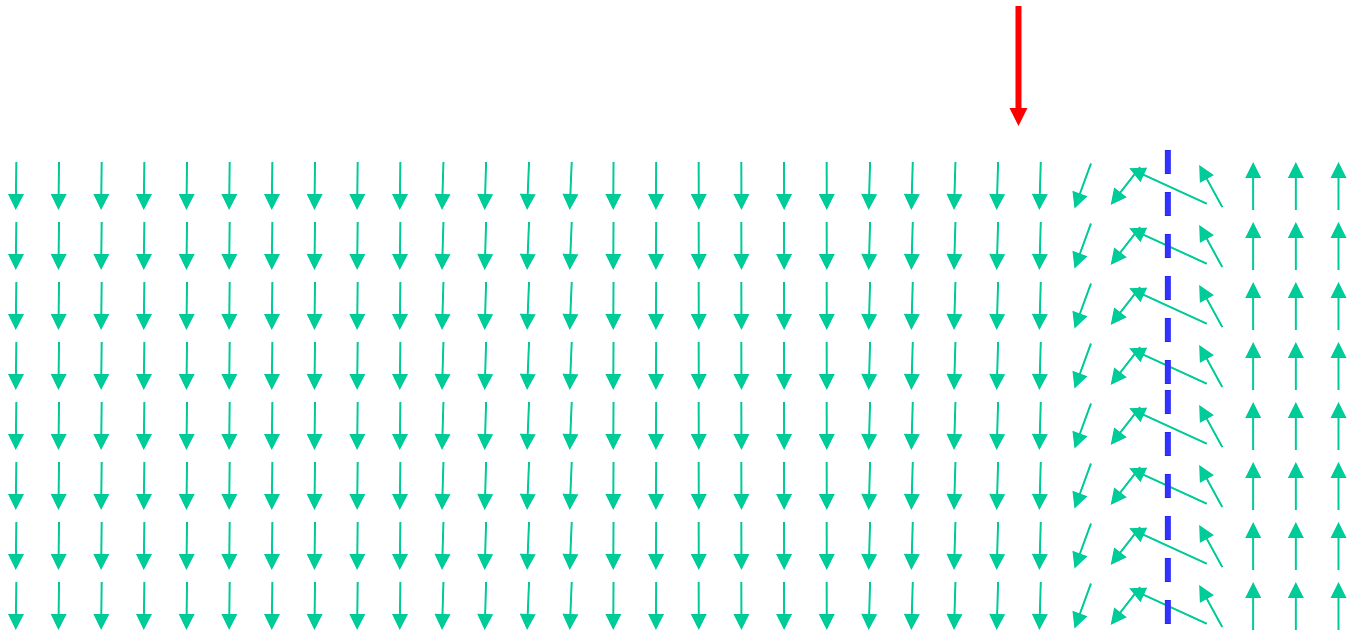
single domain
multi-domain
0
size (nm)
domain wall
single magnetic
domain size

Domain wall motion

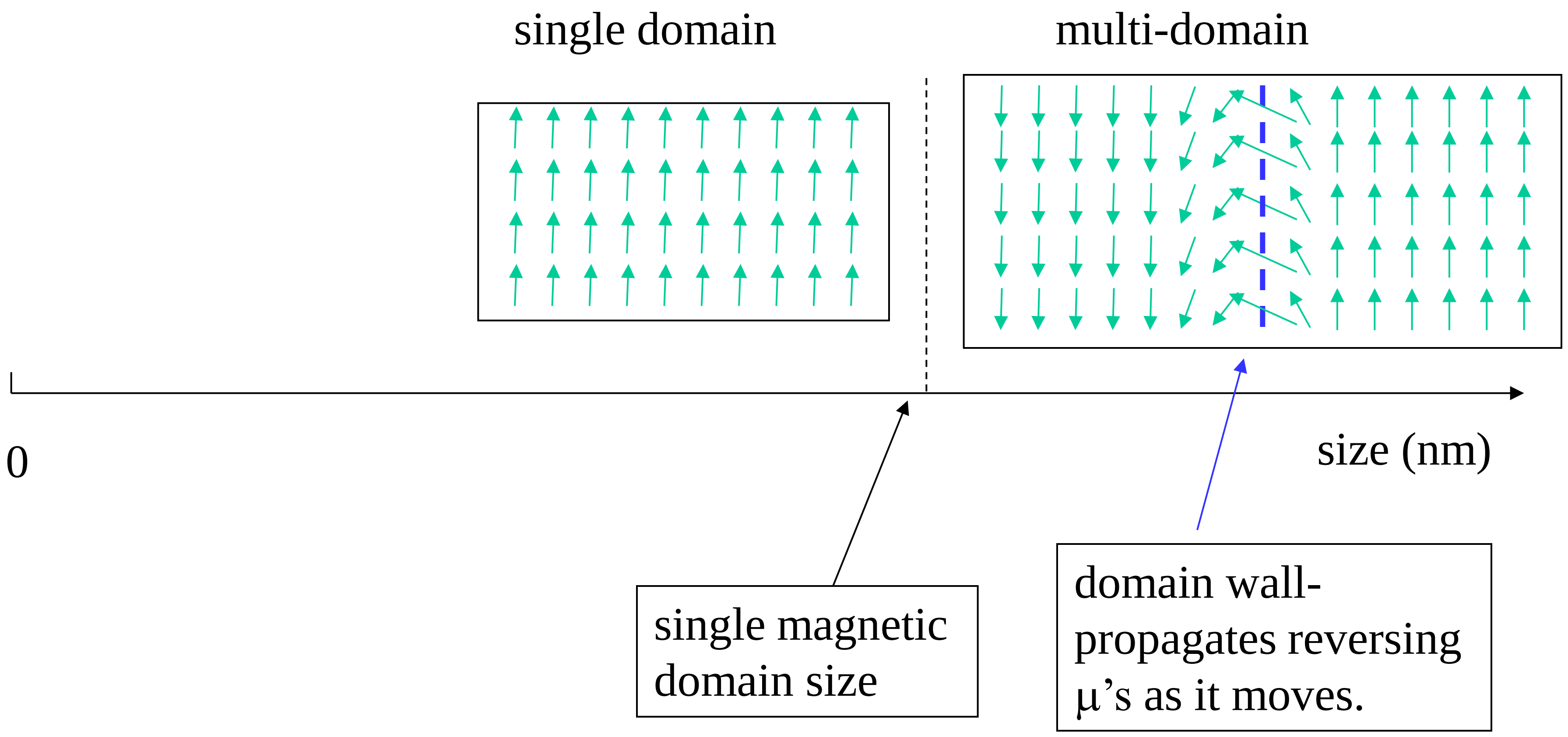
Multi-domain:



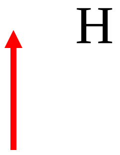

H is reversed
movement

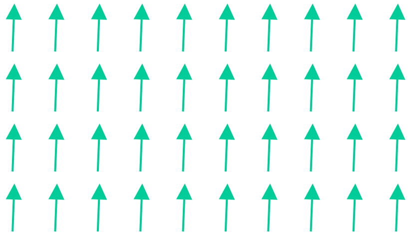


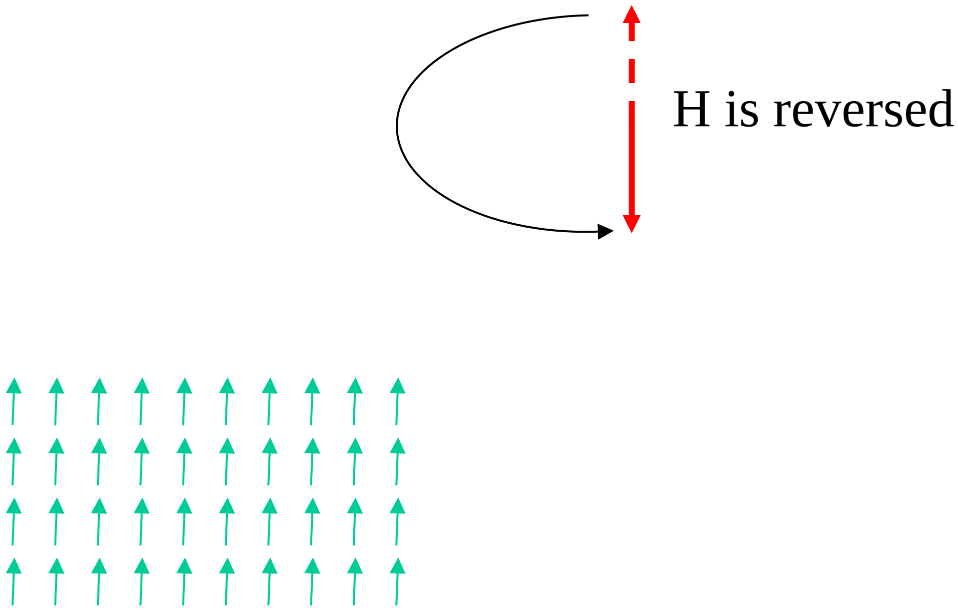
Magnetic Domains

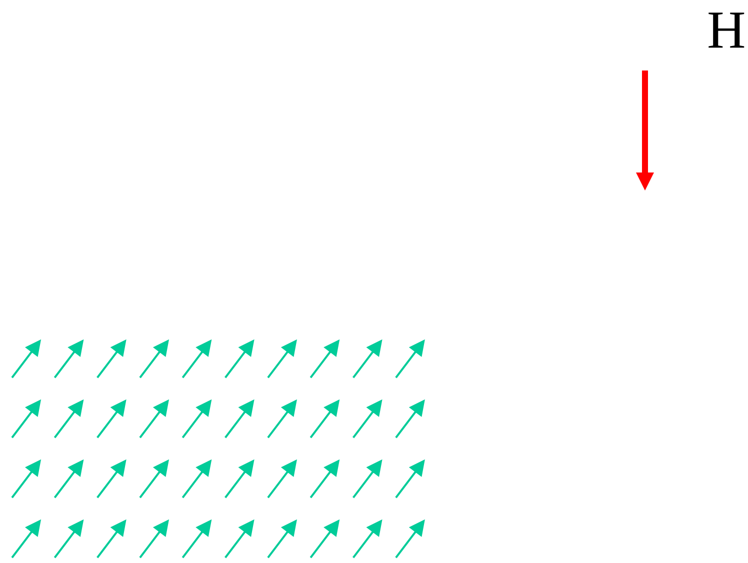


Single domain: coherent rotation

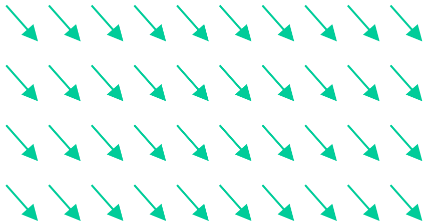


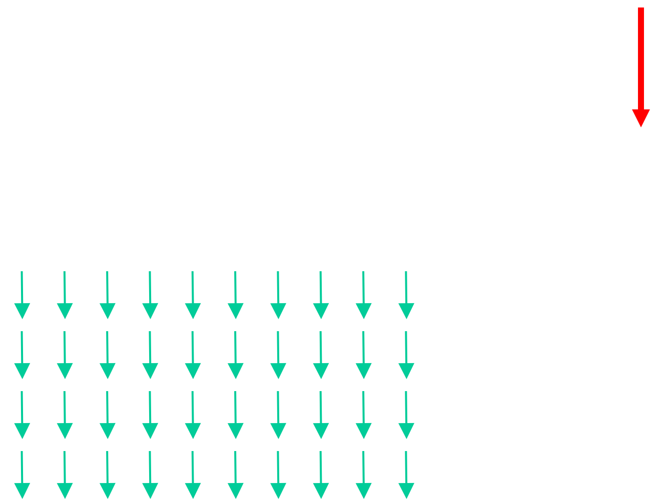



H is reversed

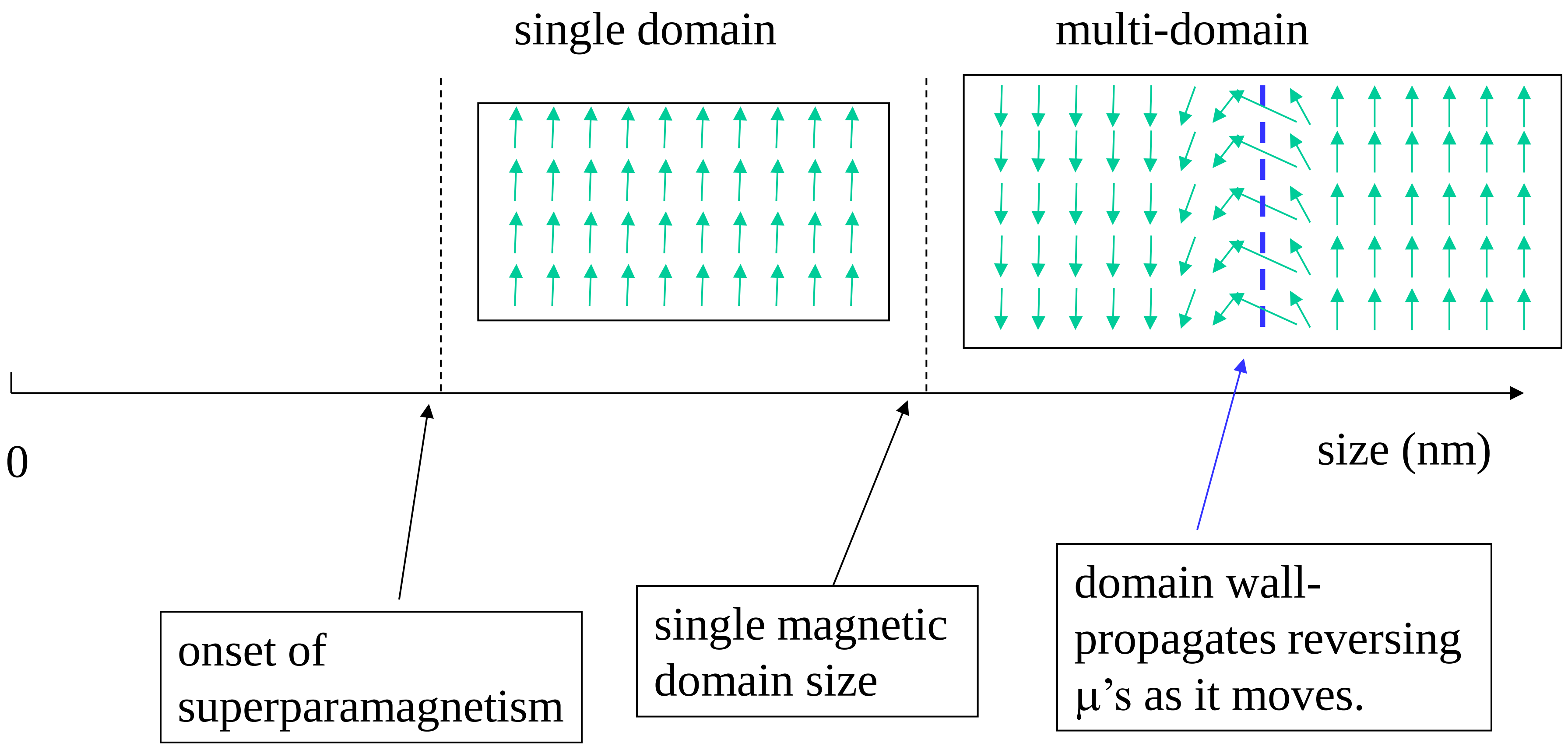


Step-by-step



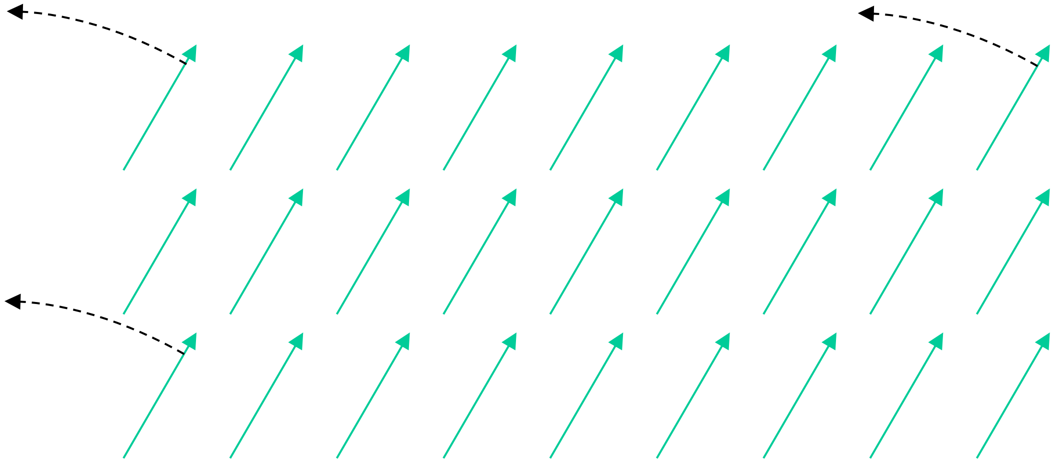


Magnetic Domains



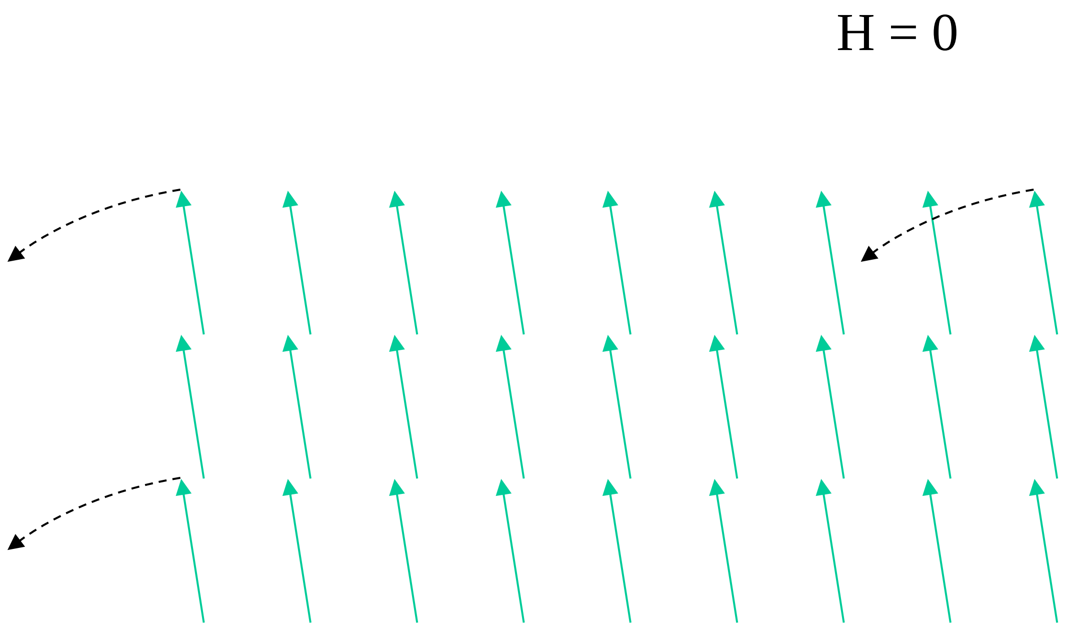
Superparamagnetism

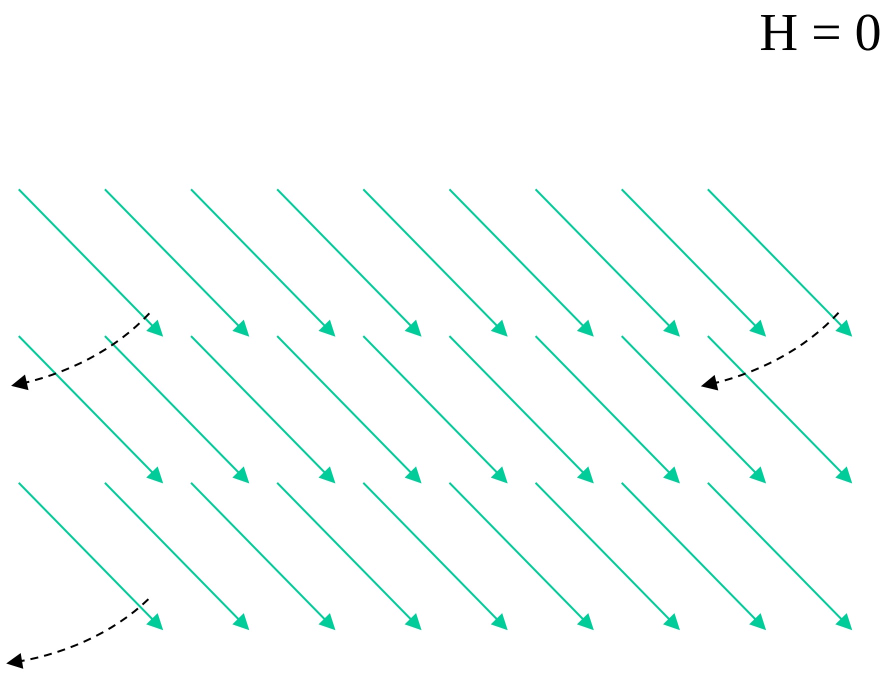
H = 0

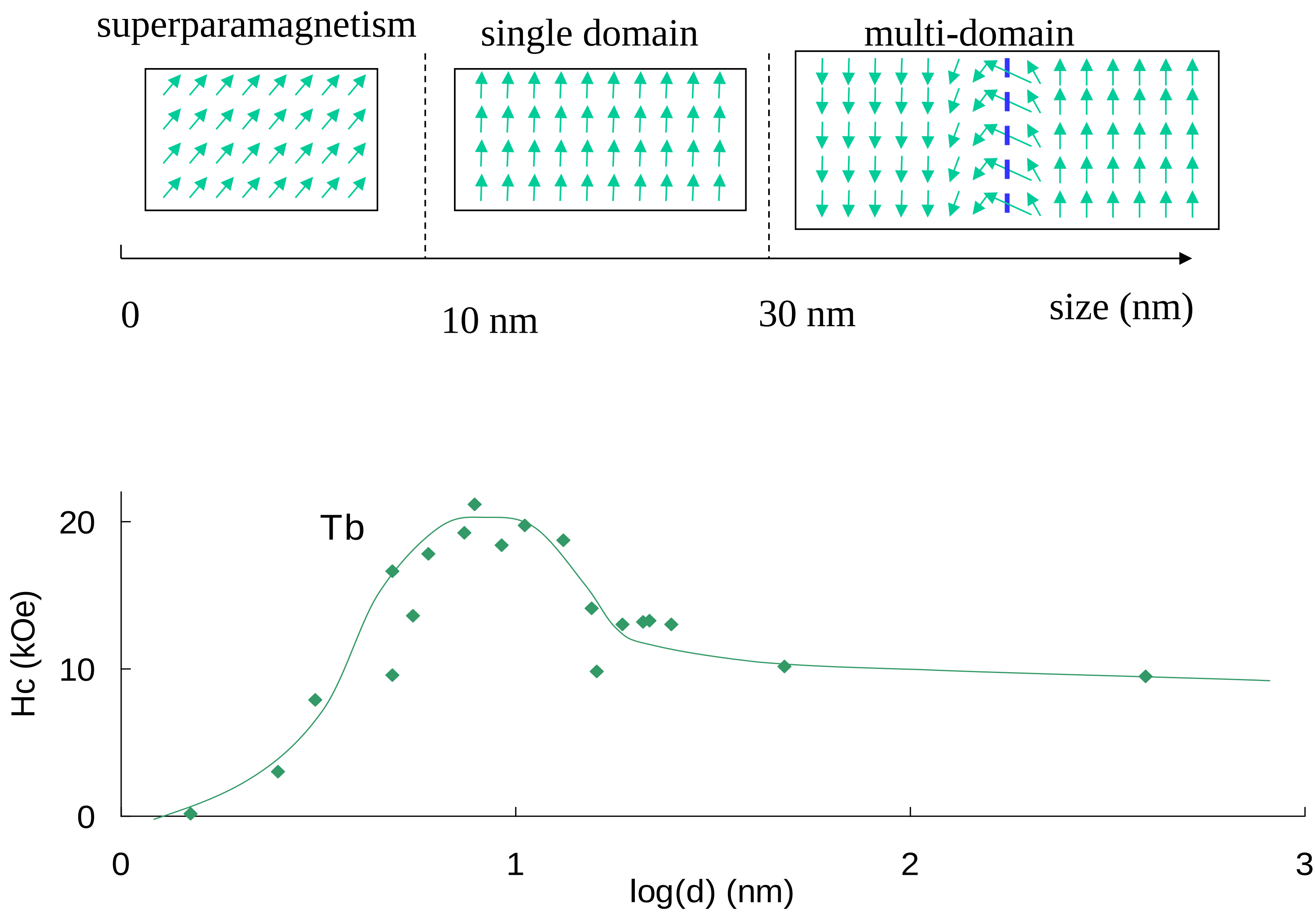


kT (thermal energy) > KV (anisotropy energy), moments not pinned to lattice.

When H = 0, M = 0 so $H_c = 0$.


H = 0


H = 0


superparamagnetism
single domain
multi-domain
0
10 nm
30 nm
size (nm)
Tb
Hc (kOe)
20
10
0
0
1
2
3
log(d) (nm)

4. Rare-earth layers and interface anisotropy

Anisotropy and Interfaces

Contributions to anisotropy(per unit area):

Bulk: $K_V t$

Demagnetization: $(-2\pi M_s^2)t$

Interface: $2K_s$

Two interfaces/bilayer

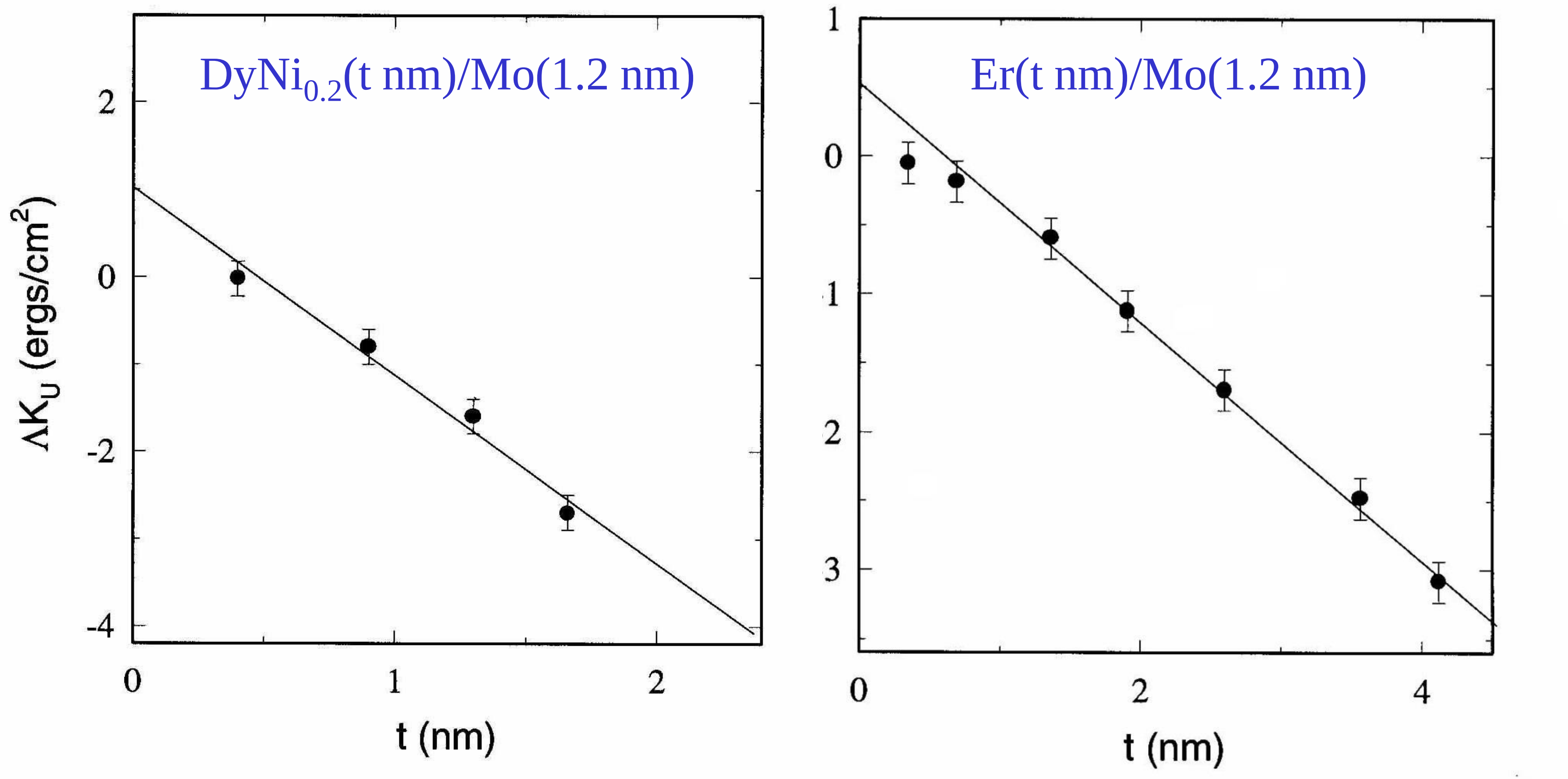
Interface anisotropy/area

Anisotropy/volume $\equiv K_u$ = (Bulk + Demag + Interface)/Λ

$$K_u = 2K_s/\Lambda + (K_V - 2\pi M_s^2)t/\Lambda$$

Experiment: measure total anisotropy K_u as a function of Λ

Experimental Results



[Perera, O'Shea, J. Appl. Phys. 70, 6212 (1991)]

Interface anisotropy discussion

R	M_O (emu/cm^3)	M_S (emu/cm^3)	$K_V \times 10^6$ (ergs/cm^3)	K_S (ergs/cm^2)	$K_V/n^{1/3}$ (ergs/cm^2)
$Dy_{80}Ni_{20}$	2260	860	-14(3)	0.50(10)	0.44(10)
Er	2250	1080	-2.57(20)	0.25(3)	0.08(1)

Note: $K_s > 0$ favors perpendicular anisotropy

Estimated enhancement of magnetic anisotropy using a point charge model, larger for Dy than Er.

A. Fert, Magnetic and Transport Properties of Metallic Multilayers, Summer School on Metallic Multilayers, aussois, France (1989)

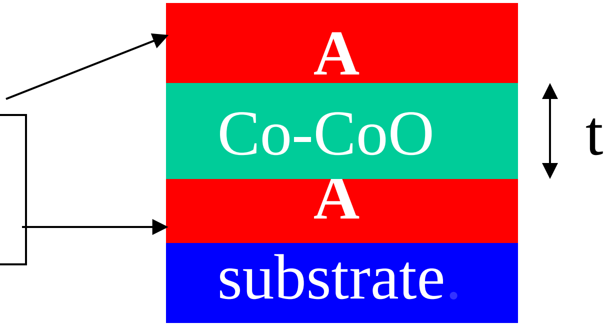
Interface anisotropy discussion

Estimated enhancement of magnetic anisotropy using a point charge model, larger for Dy than Er.

A. Fert, Magnetic and Transport Properties of Metallic Multilayers, Summer School on Metallic Multilayers, aussois, France (1989)

5. Co/CoO thin layers and inverted hysteresis

Interface Exchange



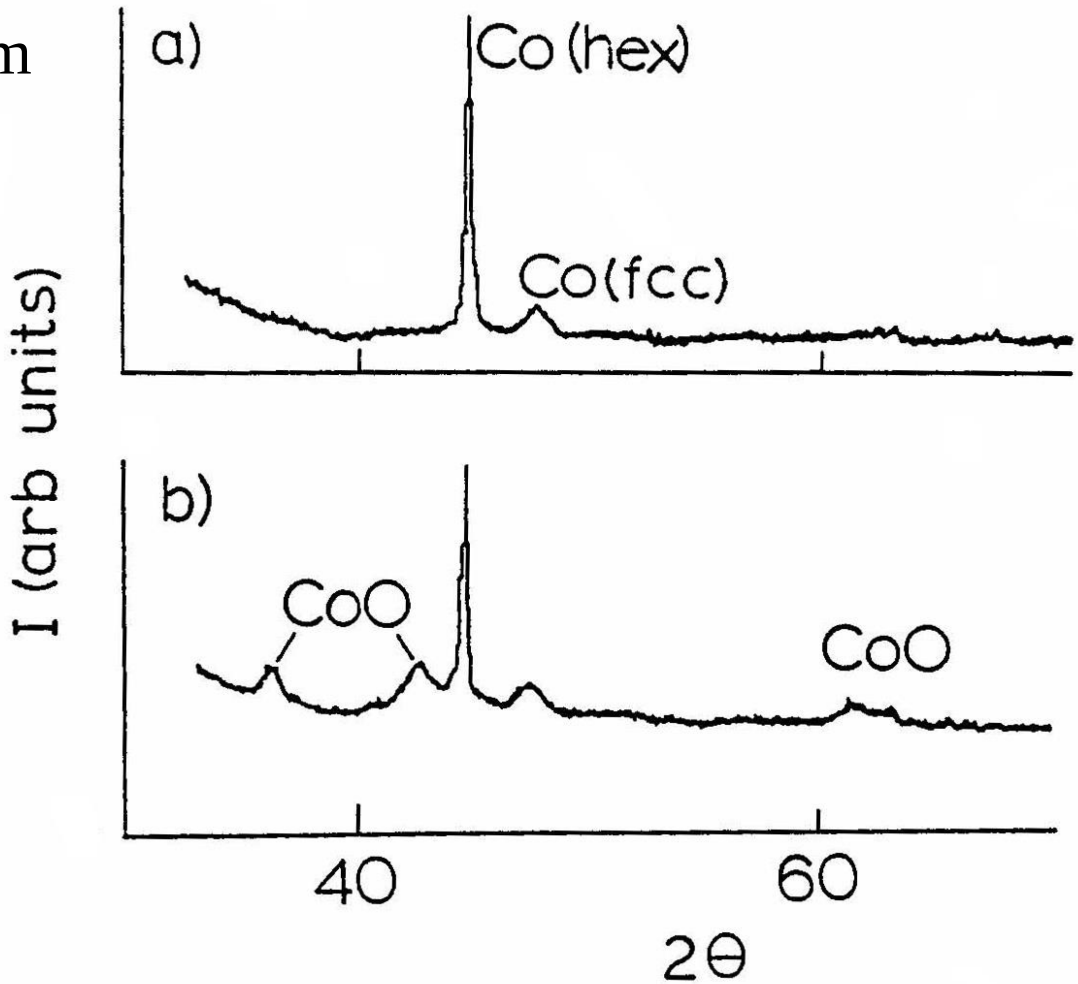
Buffer layer (Al or Cu) provides protection

Gao, O'Shea, J. Magn. Magn. Mater. 127, 181 (1993)
O'Shea, Al-sharif, J. appl. Phys. 75, 6673 (1994)

X-ray diffraction

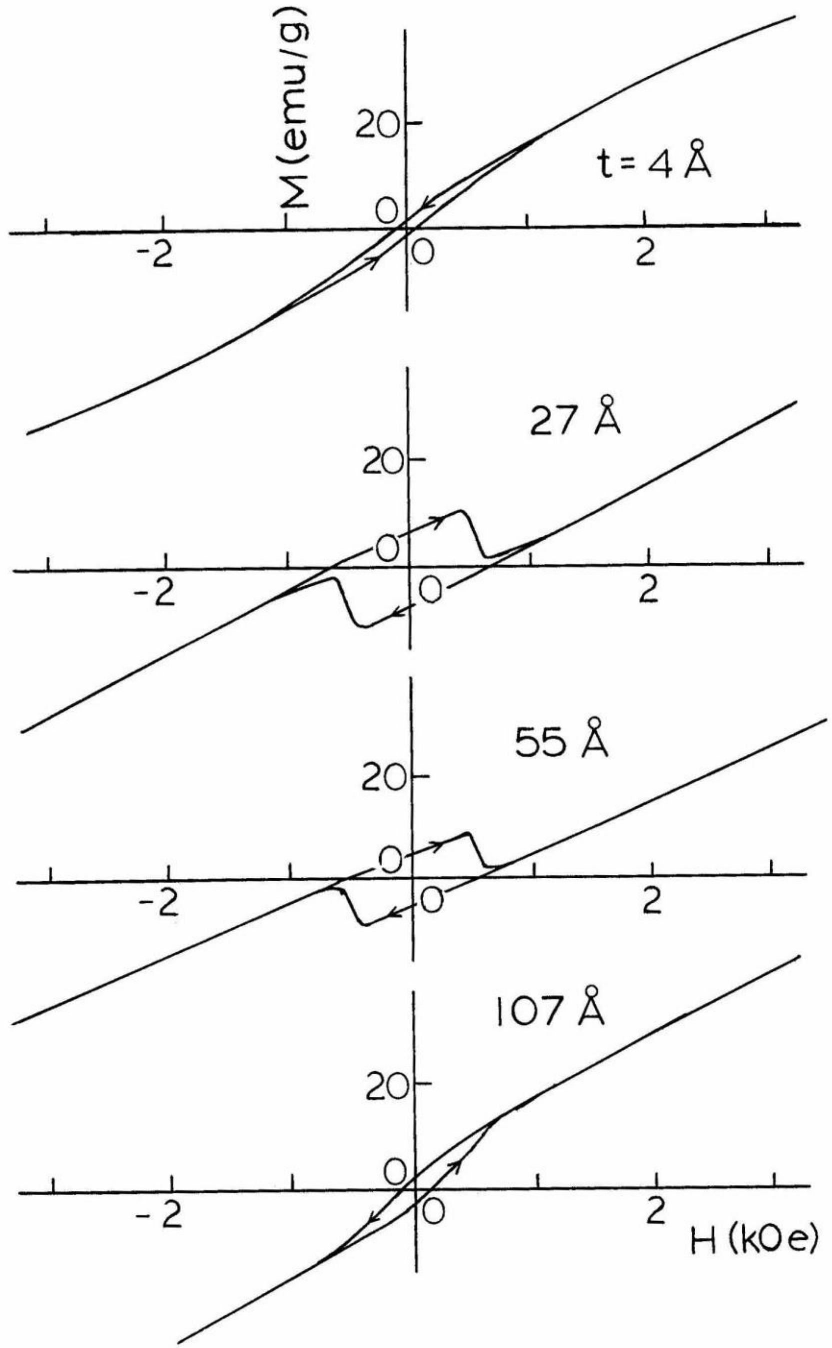
Homogeneous Co film

Co-O film



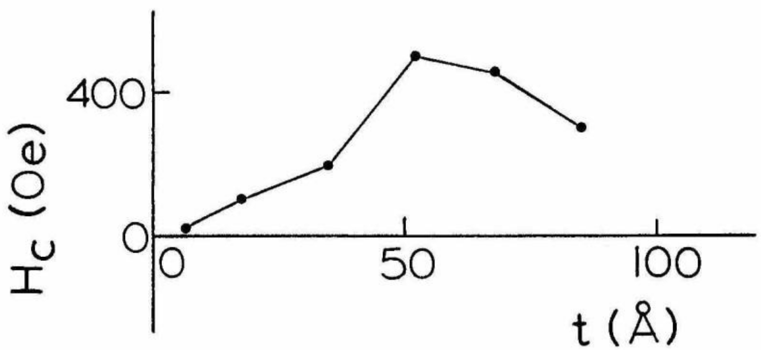
Hysteresis loops

[CoO-Co](t A)/Al(10 A)



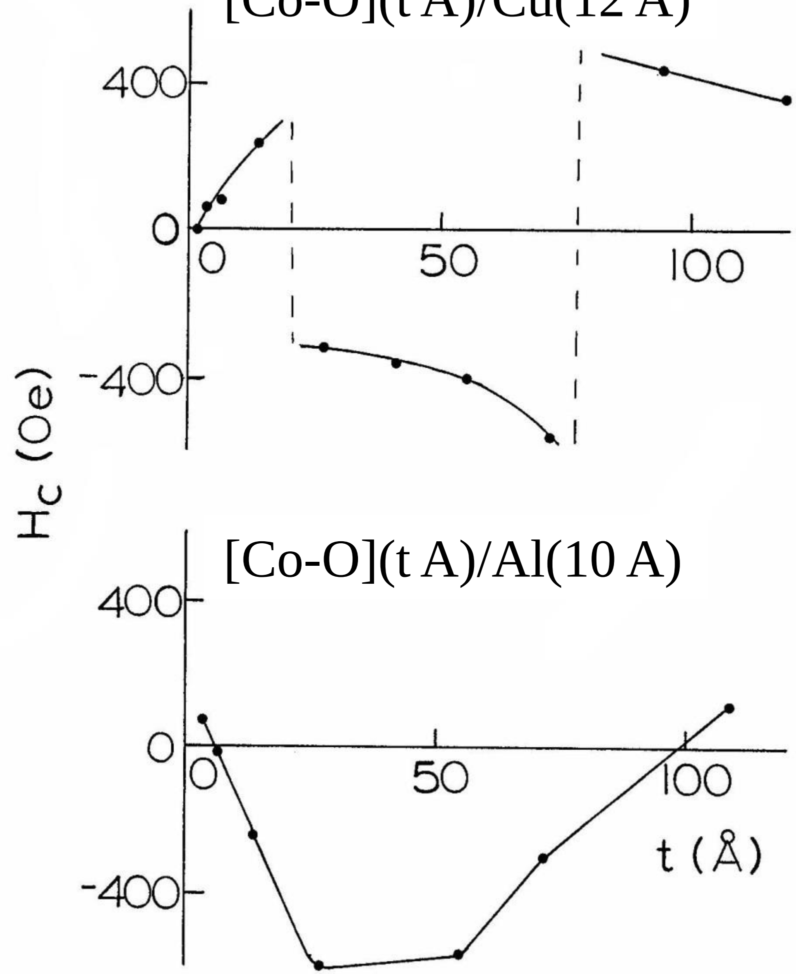
H_c vs t

Co(t A)/Cu (34 A)



[Co-O](t A)/Cu(12 A)

[Co-O](t A)/Al(10 A)



Model of two-phase system

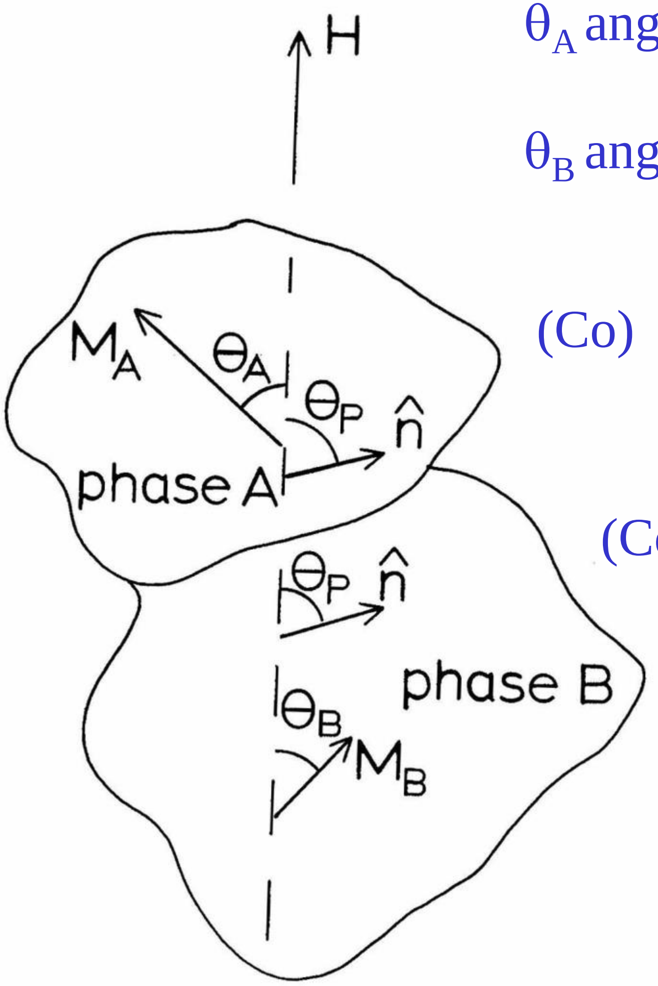
$$E = -M_A H \cos\theta_A - M_B H \cos\theta_B$$
$$-J_i \cos(\theta_B - \theta_A)$$
$$-K_A \sin^2(\theta_A - \theta_P)$$
$$-K_B \sin^2(\theta_B - \theta_P)$$

$$M = M_A \cos\theta_A - M_A \cos\theta_A$$

θ_P angle between anisotropy axes and H

θ_A angle between M_A and H

θ_B angle between M_A and H

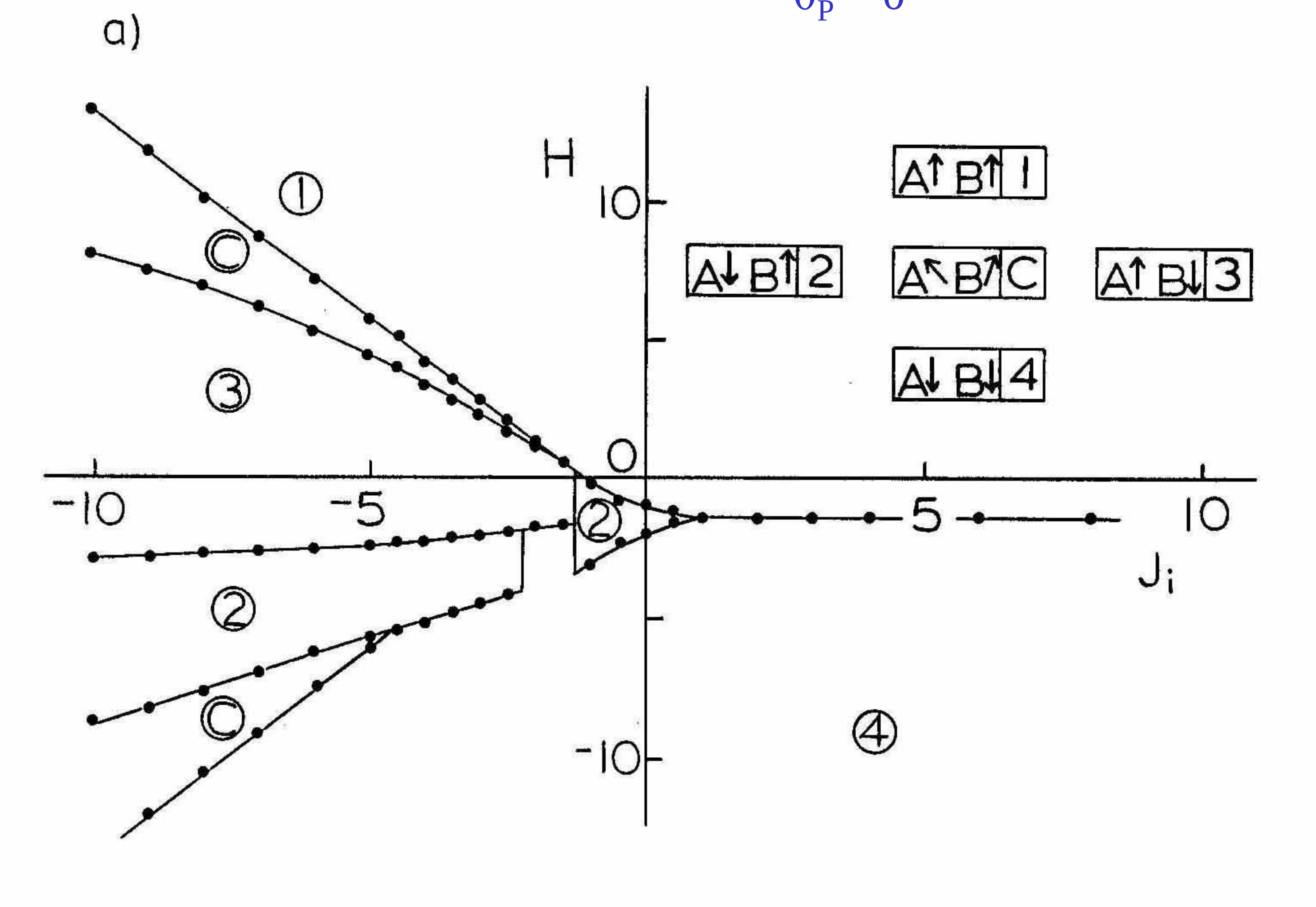


(Co)

(CoO)

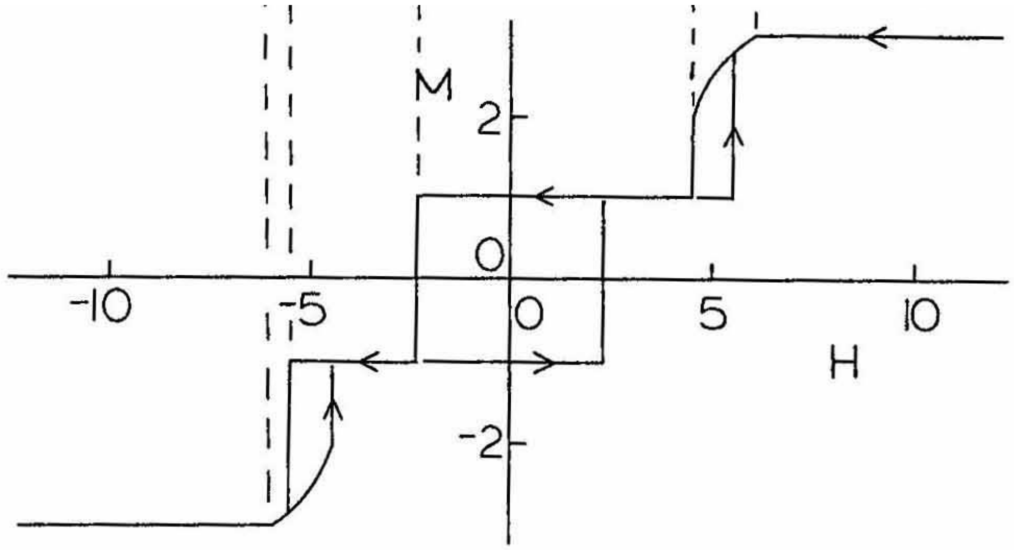
Calculated magnetic phase diagrams

$M_A = 2$, $M_B = 1$,
$K_A = 1$, $K_B = 1$,
$\theta_P = 0$



Hysteresis Loop (not inverted)

Hysteresis loop



Co-CoO Results

Can obtain inverted behavior in hysteresis with right choice of M's and K's

Appear to correspond to phases with large M and small K (pure Co) and a second phase with small M and larger K (CoO).

Final comments

Finite size effects exist in many nanostructured rare-earth based magnetic systems. These effects appear in the

- Magnetic ordering temperature
- Magnetic anisotropy
- Coercivity

New physics at the interface also emerges with an interfacial contribution to magnetic anisotropy that can be measured multilayers.