MAGNETISM in the Nano World

Robert D. Shull

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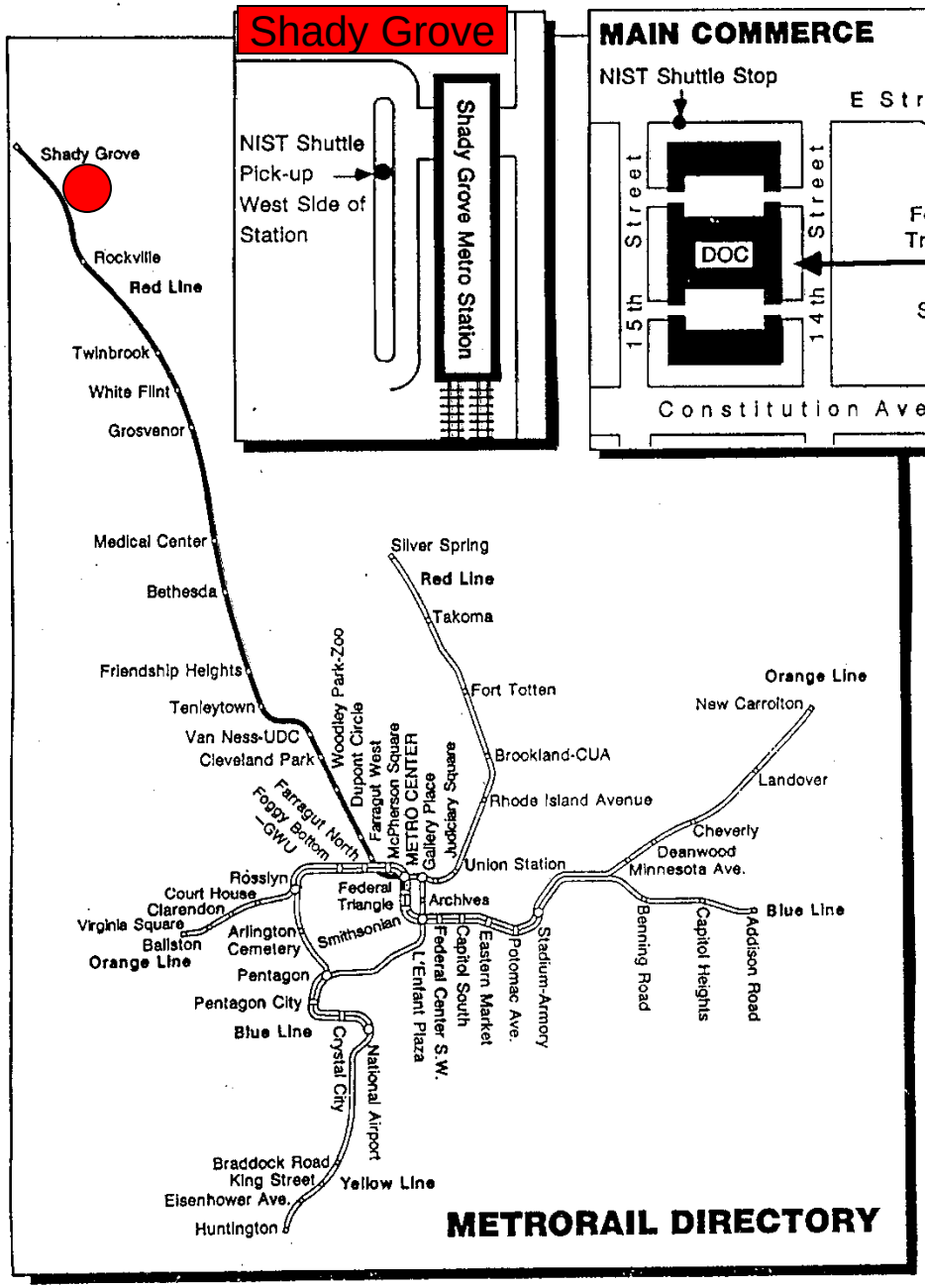
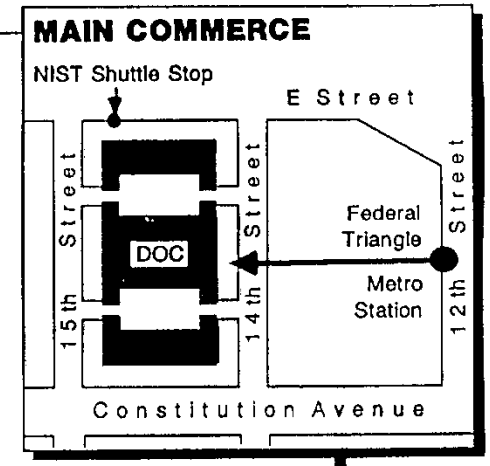
National Institute of Standards and Technology
Gaithersburg, Maryland, USA

Founding Member: OSTP Nanoscale Science, Engineering and Technology Subcommittee, NSET

NBS

NIST





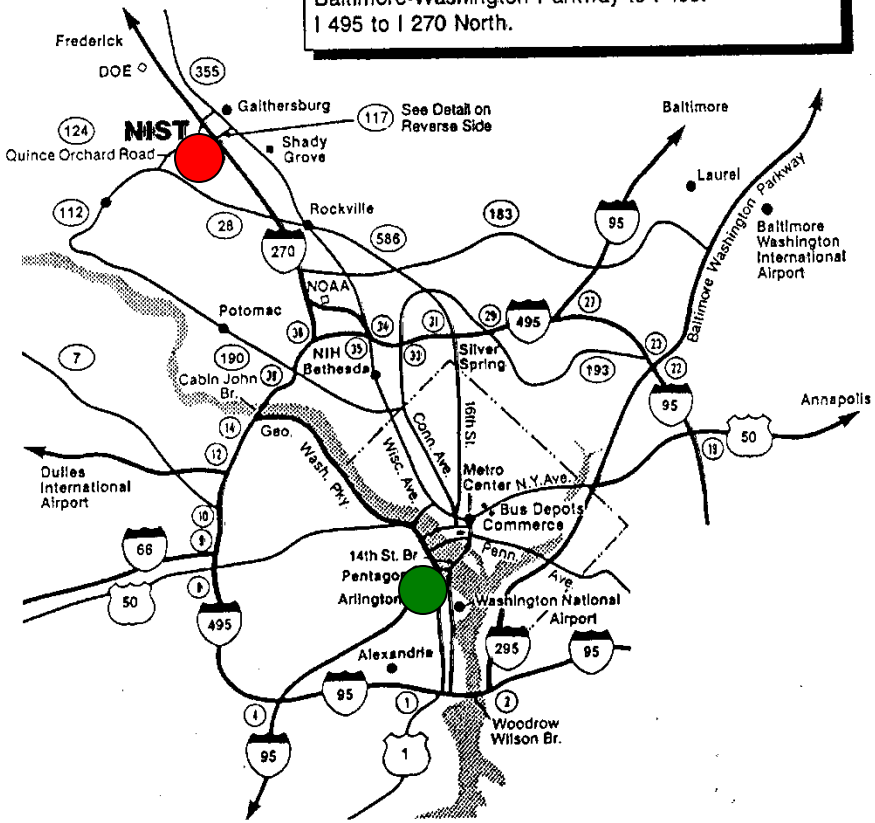
DRIVING INSTRUCTIONS

From Downtown Washington --
Connecticut Avenue to I 495 and I 270 North
or
River Road (Route 190) to I 495, or
Geo. Washington Memorial Pkwy. (Va. side) to I 495
I 495, follow signs to I 270 North.

From Dulles Airport --
Dulles Access Road to I 495
I 495 to I 270 North.

From National Airport --
Geo. Washington Memorial Pkwy. (Va. side) to I 495.
I 495 to I 270 North.

From Baltimore-Washington International Airport --
Baltimore-Washington Parkway to I 495.
I 495 to I 270 North.



Washington D.C.

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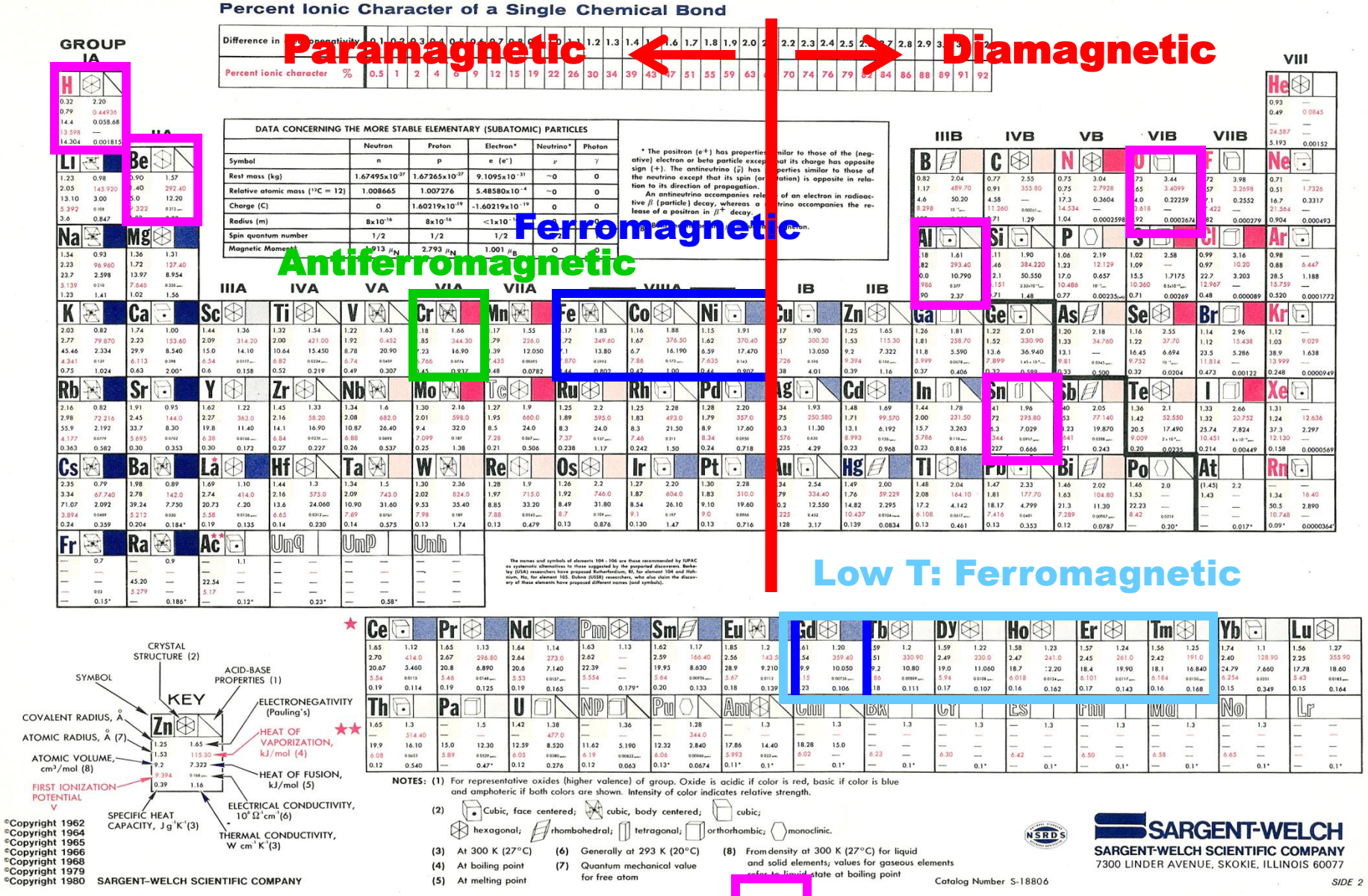
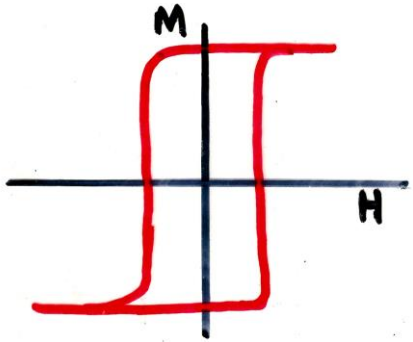
Room Temperature Magnetic Properties

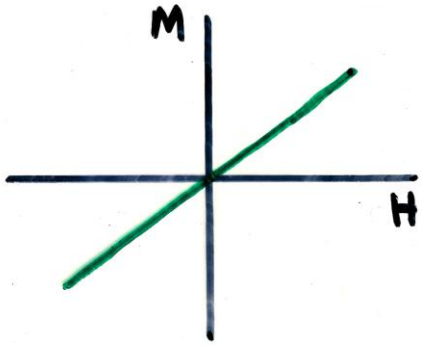


COMMON TYPES OF MAGNETISM

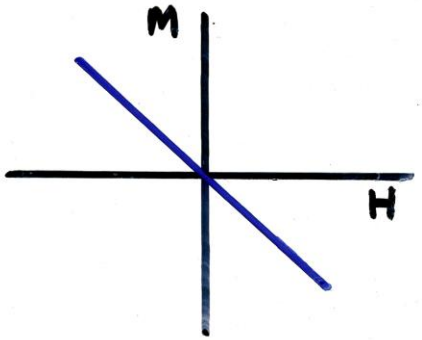
Ferromagnetism



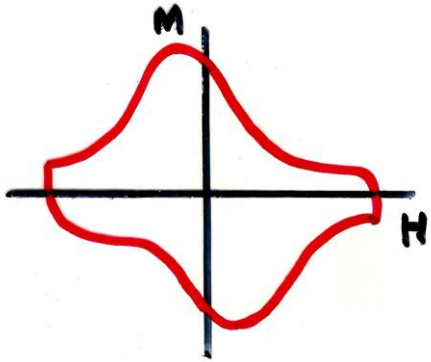
Paramagnetism



Diamagnetism



Superconductivity



MAGNETIC MATERIALS ARE EVERYWHERE!!!

- Magnetic Recording Media, Magnetic Reading and Writing Devices
- ALL Motors
- ALL Transformers
- ALL Generators
- Credit Cards
- Cellular Phones
- Auto & Engine Timing
- Radios & Televisions
- Microwave Devices
- Xerographic Copiers
- Magnetic Separation (Biological Analysis, and Scrap Sorting)
- Magnetic Refrigerators
- Theft Control Devices
- Airport Security
- Permanent Magnets
- Magnetic Fluids
- MRI Contrast Agents
- MF Microscopes
- Motion Control Devices
- Doorbells
- Charging Units
- Fluorescent Lighting

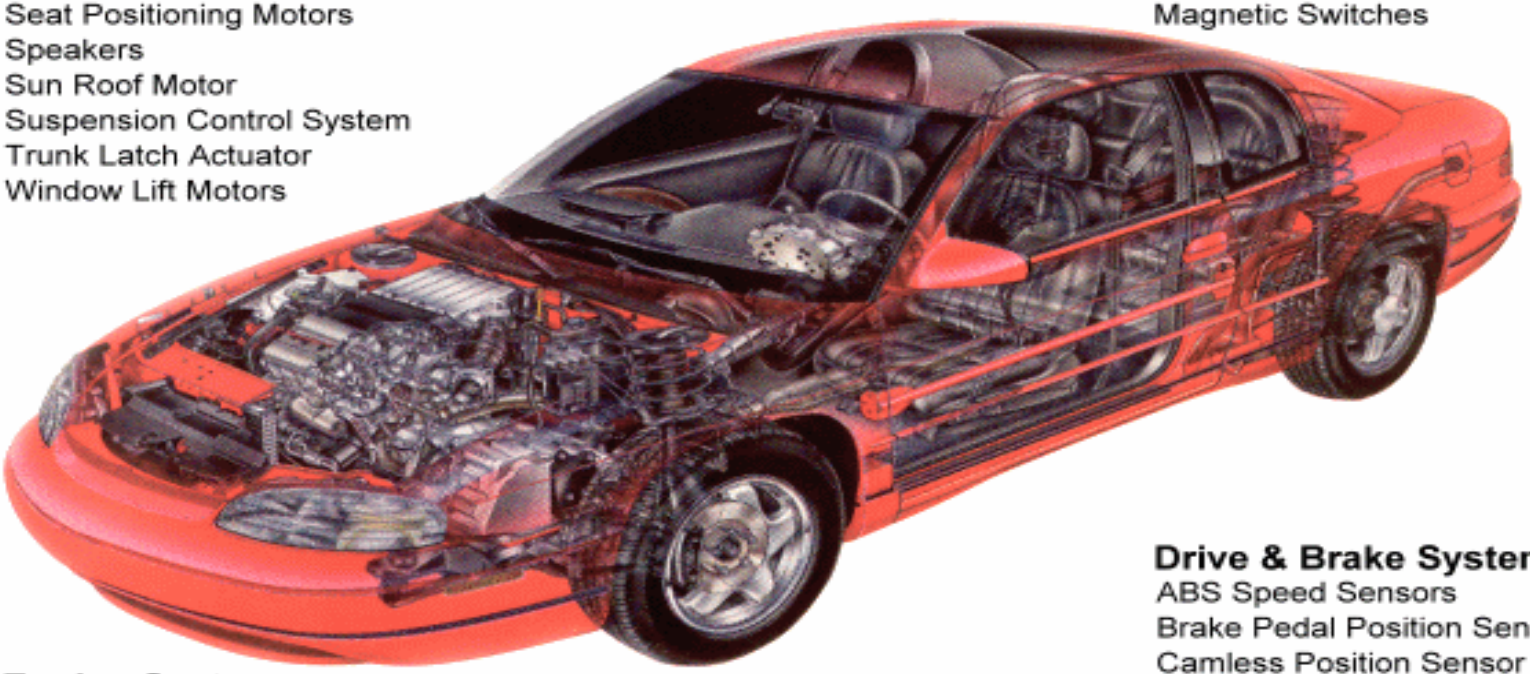
Magnetic Characters are ALL DIFFERENT!!! How do you Measure them???

Magnets in a Modern Automobile

Comfort and Convenience
Compass
Door Lock Actuators
Entertainment System Drives & Controls
HVAC Fan Motor
Seat Position Sensors
Seat Positioning Motors
Speakers
Sun Roof Motor
Suspension Control System
Trunk Latch Actuator
Window Lift Motors

Passenger Safety
Air Bag Sensor
Seat Belt Sensors

Cockpit Controls
Cruise Control
Electric Power Steering
Electronic Key Sensor
Instrumentation Gauges
Liquid Level Sensors
Magnetic Switches

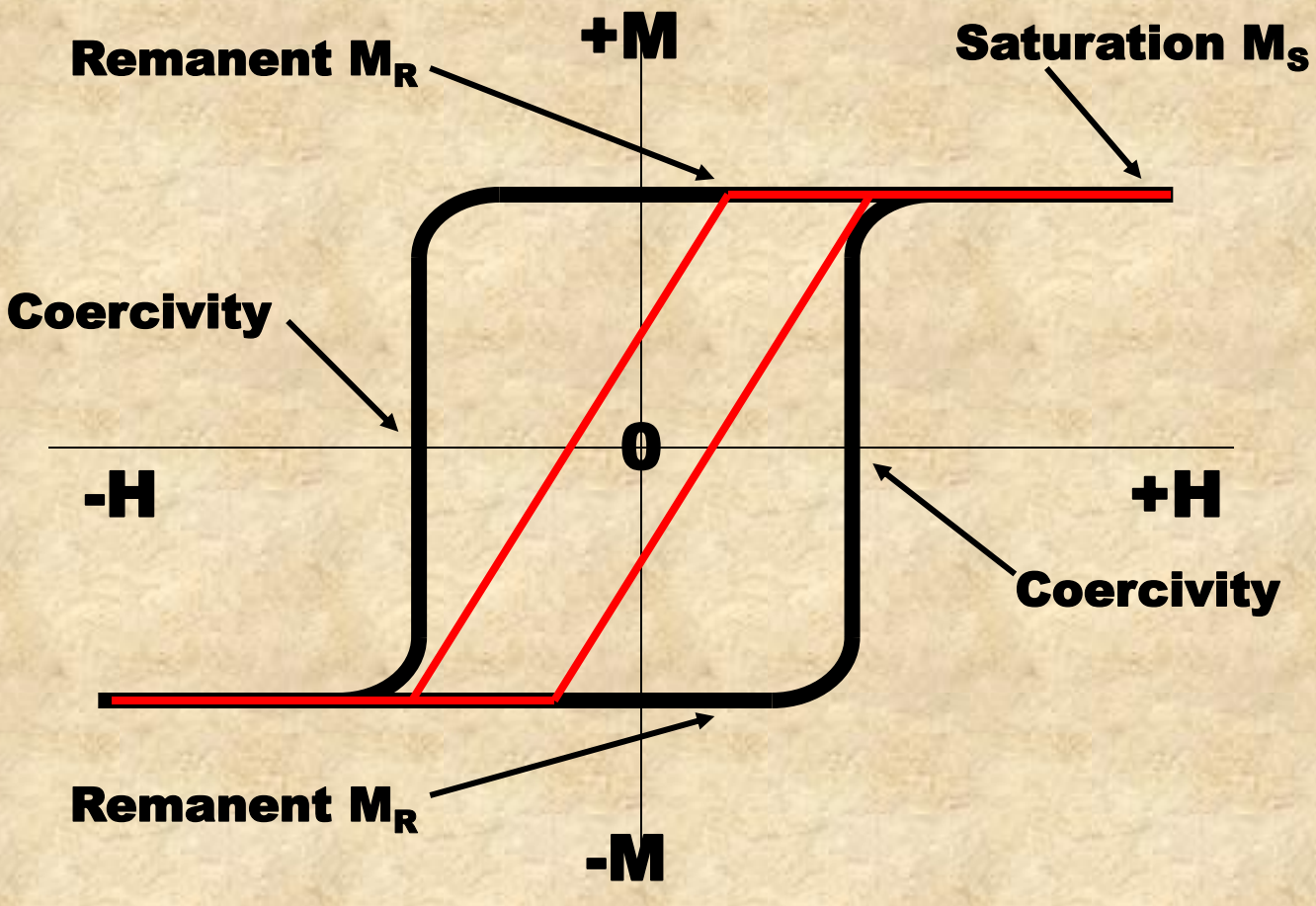


Drive & Brake Systems
ABS Speed Sensors
Brake Pedal Position Sensor
Camless Position Sensor
Electric Brake Actuators
Transmission Chip Collector
Transmission Shift Sensor

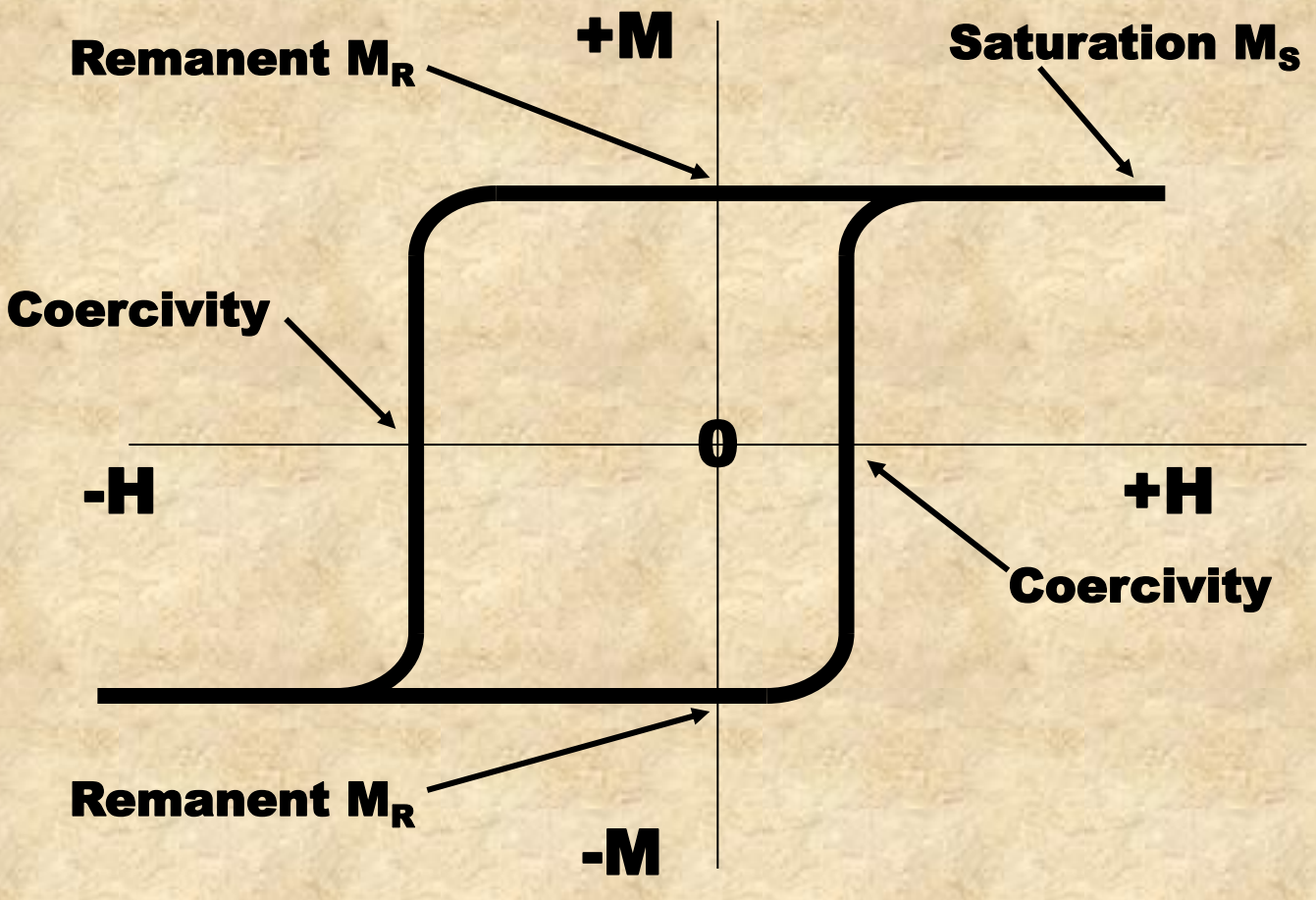
Engine System
Alternator
Cooling Fan Motor
Crankshaft Position Sensor
Emission Control Vent Motors
Fuel Pump Motor
Idle Speed Control
Starter Motor
Throttle Position Sensor

External Systems
Antenna Lift Motor
Headlight Door Motors
Headlight Aiming Motors
Mirror Positioning Motos
Windshield Wash Pump Motor
Windshield Wiper Motor

Hysteresis Loop for a Ferromagnet



Exchange Bias Hysteresis Loops



OUTLINE

(I). Why is NANO any different???

(II). Nano - Magnetic Phase Diagram

(IV). Magnetic Application Areas

- Small Size
  - High Density Recording Media
  - Bio Applications (MRI Imaging; Hyperthermia)
  - Transformers (Lower Coercivity)
  - Permanent Magnets (Strong Exchange)
- New Magnetic Phenomena
  - Superparamagnetism (Enhanced Mag. Cooling, Inks)
  - Spin Dependent Scattering (GMR Effects)
  - Spin Torques & Forces (Switches & Memory)
- Special Domain Walls & Dynamics (Biased Devices)

(V). Summary

THREE REASONS

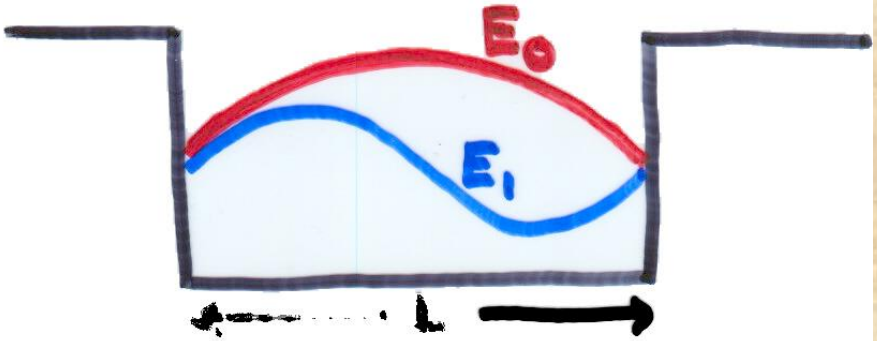
WHY PROPERTIES ARE DIFFERENT

WHEN MATERIALS POSSESS

SOME NANOSCALE DIMENSION

(1)

Quantization of Energy States

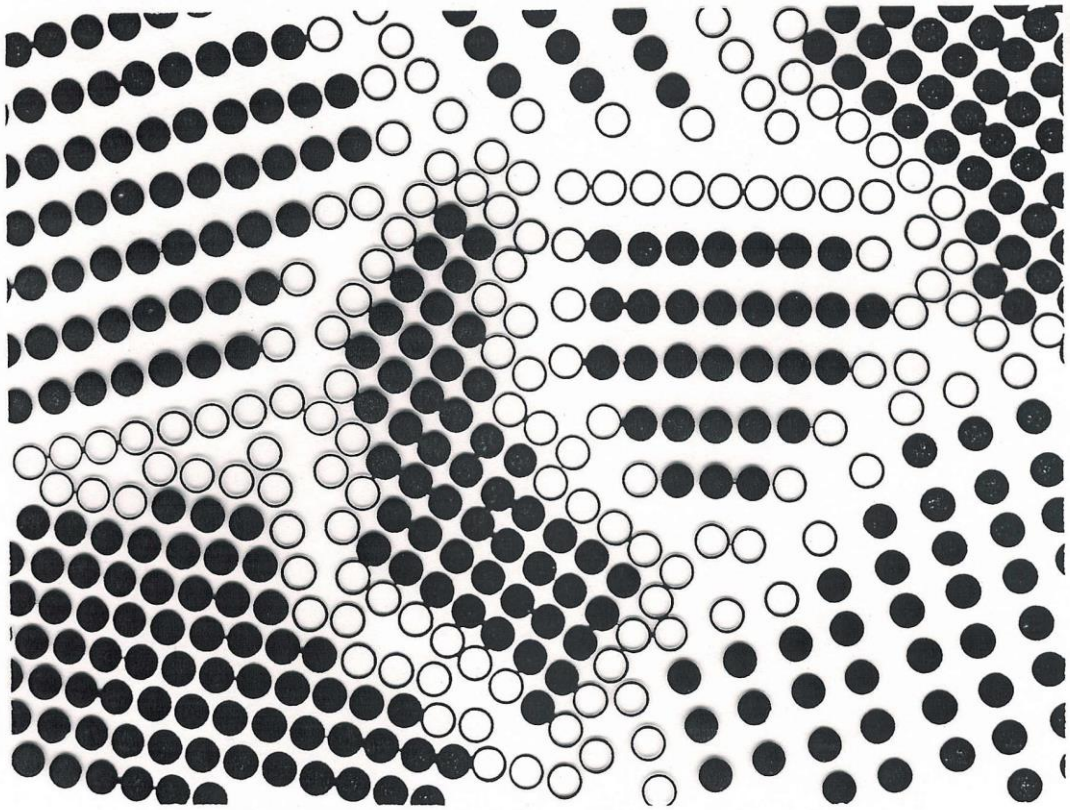


$$E_n = \frac{n^2 C}{L^2}$$

"Confinement" Effects

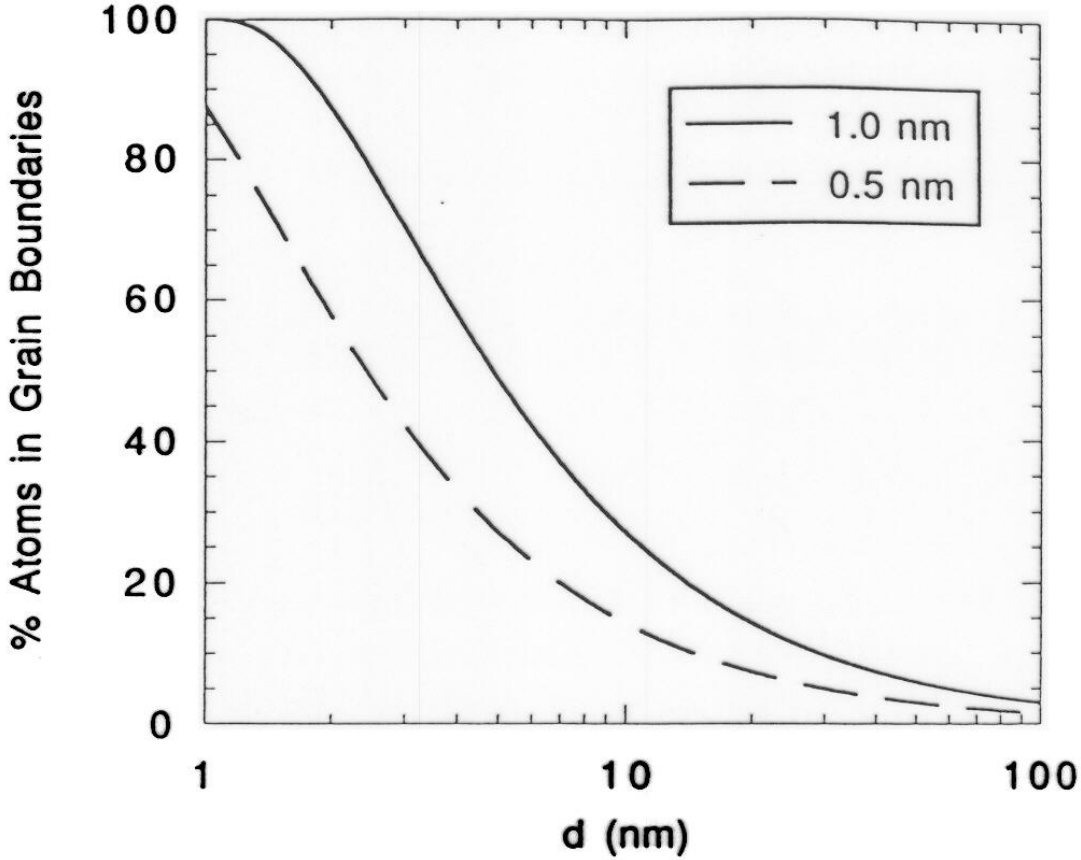
(2)

STRUCTURE SCHEMATIC:
-NANOPHASE MATERIAL-



Schematic of an equiaxed nanocrystalline metal showing atoms associated with individual grains (filled circles) and those constituting the grain boundaries (open circles). [H. Gleiter, Prog. Mater. Sci. 89, 223 (1989)]

HIGH INTERFACE VOLUME
-NANOPHASE MATERIALS-



Percentage of atoms in grain boundaries of a nanophase material as a function of grain diameter, with grain boundary thickness of 0.5 and 1.0 nm (i.e., 2 or 4 atomic planes). [R.W. Siegel, Annu. Rev. Mater. Sci. 21, 559 (1991)]

(3)

CRITICAL LENGTH SCALES

Resistivity – mean free path

Thermal Conductivity – mean free path

Strength – dislocation Burgers vector

Transmission & Reflection - wavelength

Diffraction & Scattering - wavelength

Absorption – penetration depth

Atomic Transport – diffusion length

Superconductivity – coherence length

Elasticity – bond & chain lengths

Reaction Rate – diffusion length

Boundary Motion – radius of curvature

Fluid Flow – boundary layer thickness

Magnetism – exchange length, domain wall width

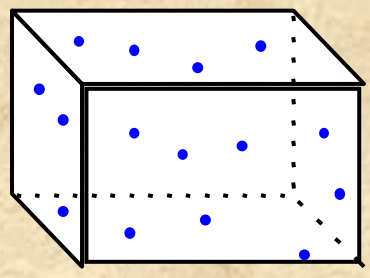
Intercellular Migration – cell diameter

MAGNETIC LENGTH SCALES
(IN NANOMETERS)

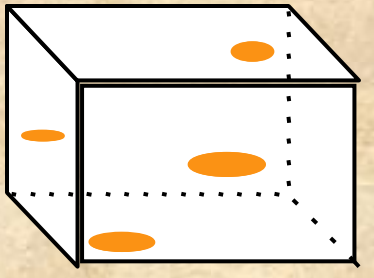
LENGTH	SYMBOL	DEFINITION	Fe	$Nd_2Fe_{14}B$
Exchange Length	l_{ex}	$\sqrt{(\mu_o A/J_s^2)}$	1.5	1.9
Coherence Radius	R_{coh}	$(\sqrt{24})l_{ex}$	7	9
Domain Wall Width	δ_W	$\pi l_{ex}/\kappa$	40	3.9
Single-Domain Size	R_{SD}	$36\kappa l_{ex}$	6	107
Superparamagnetic Blocking Radius (at 300 K)	R_B	$(6k_BT/K_1)^{1/3}$	8	1.7

(Calculated by Michael Coey, Univ. of Dublin)

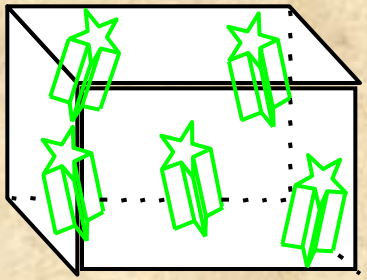
NANOCOMPOSITE MORPHOLOGIES



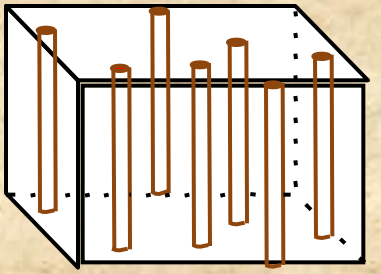
Spherical Particle



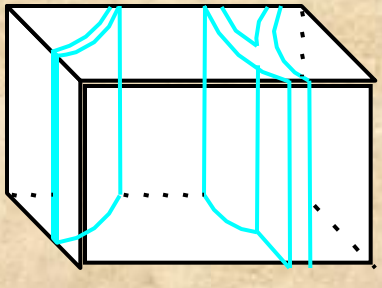
Disc-Shaped Particle



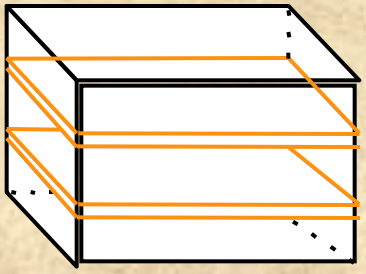
Rod-Shaped Particle



Fiber



Intergranular Film



Layered

Critical Dimensions:

Particle Diameter, Separation Distance, Aspect Ratio, Fiber Diameter, Layer Thickness, Grain Diameter, ...

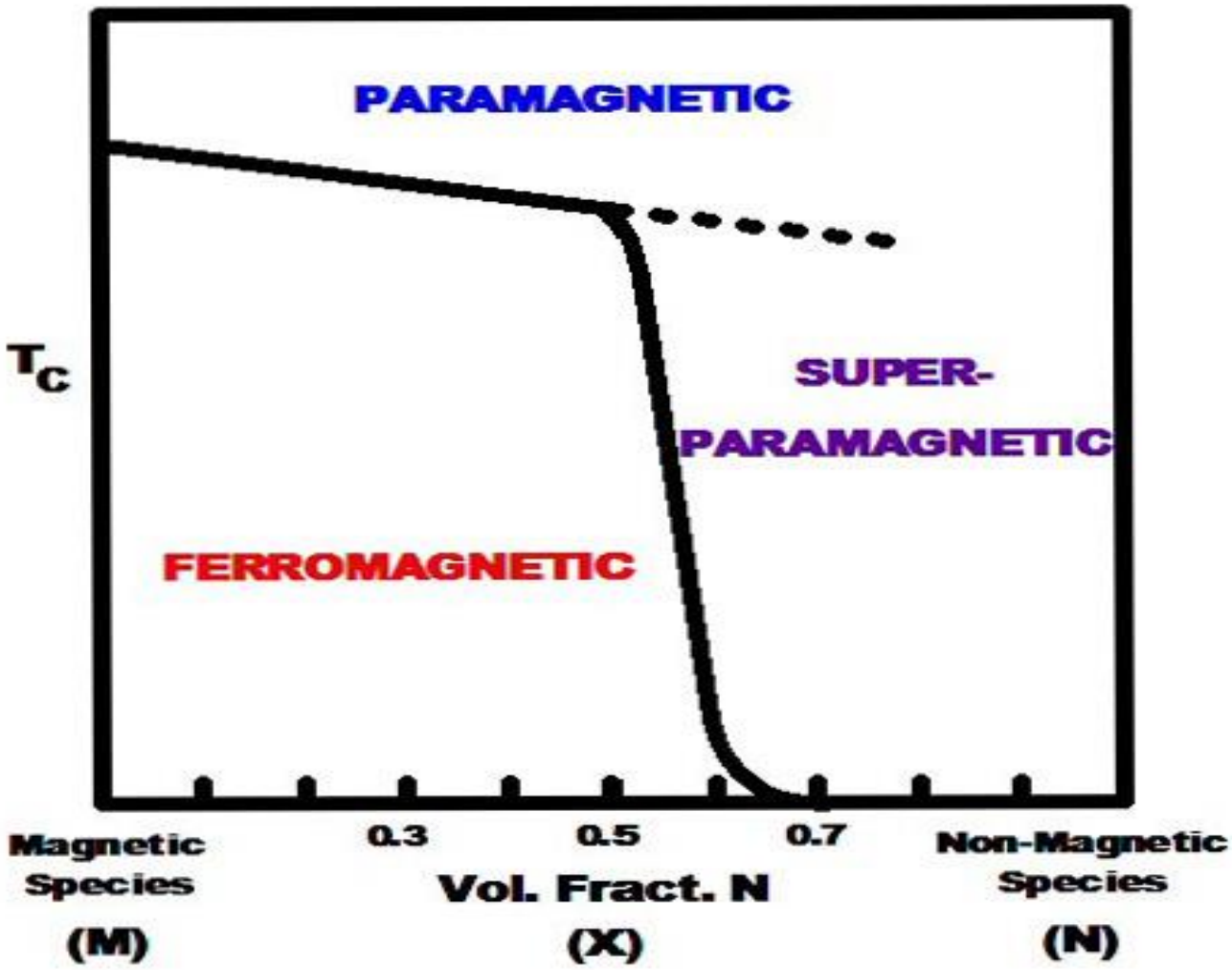
NOVEL TYPES

OF MAGNETISM

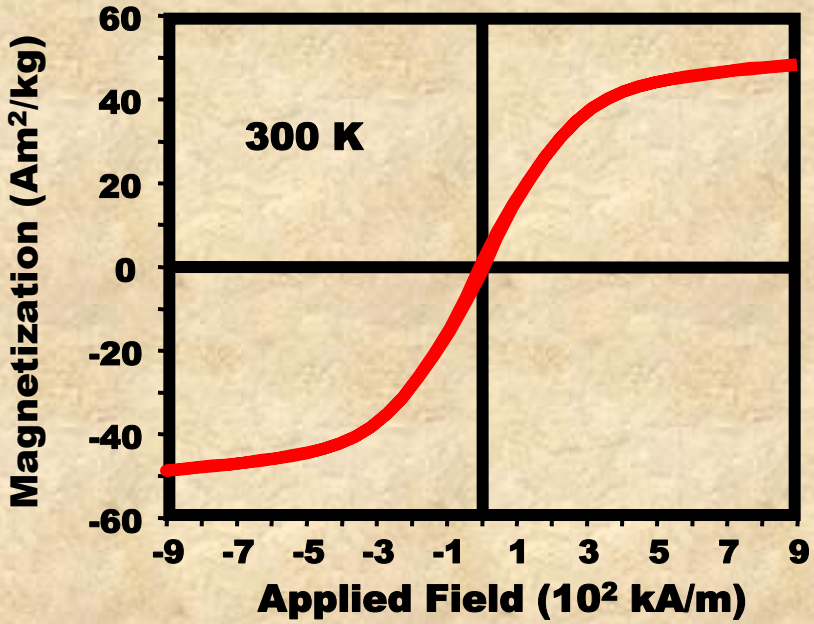
NANOCOMPOSITE

$(M_{1-x}N_x)$

MAGNETIC PHASE DIAGRAM



SUPERPARAMAGNETISM



Applications:

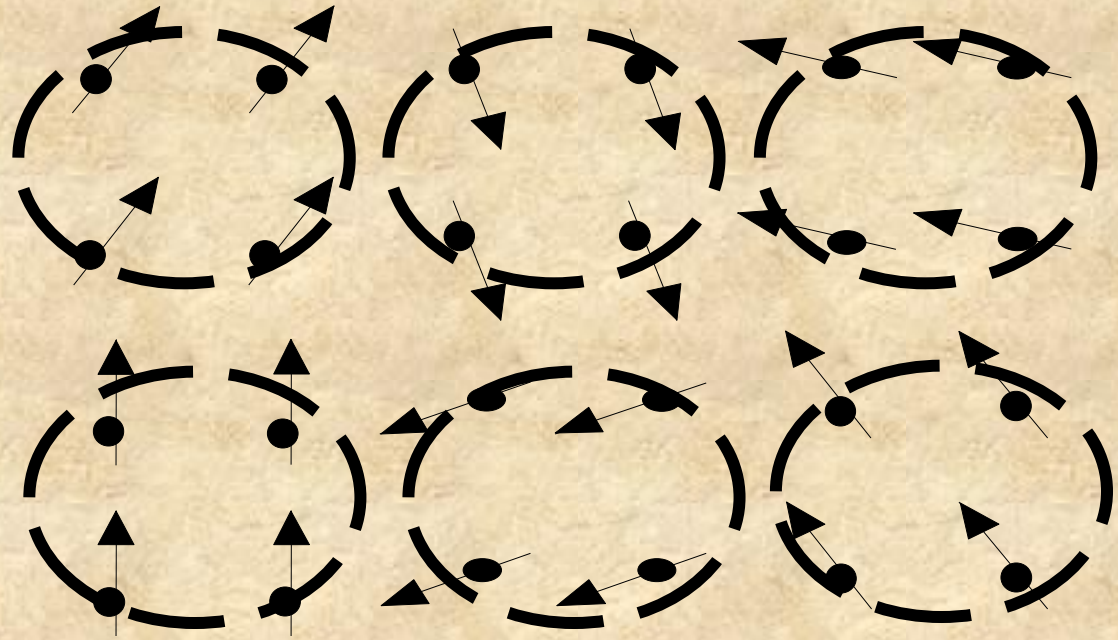
Magnetic Inks
Magnetic Separation
Vacuum Sealing
Magnetic Marking
Magnetic Refrigeration
Magnetic Resonance Imaging

No Remaining Magnetism Upon Field Removal!!!

(Occurs when Particles are Very Small and Decoupled)

Demonstration: Superparamagnetism

SMALL PARTICLE BEHAVIOR



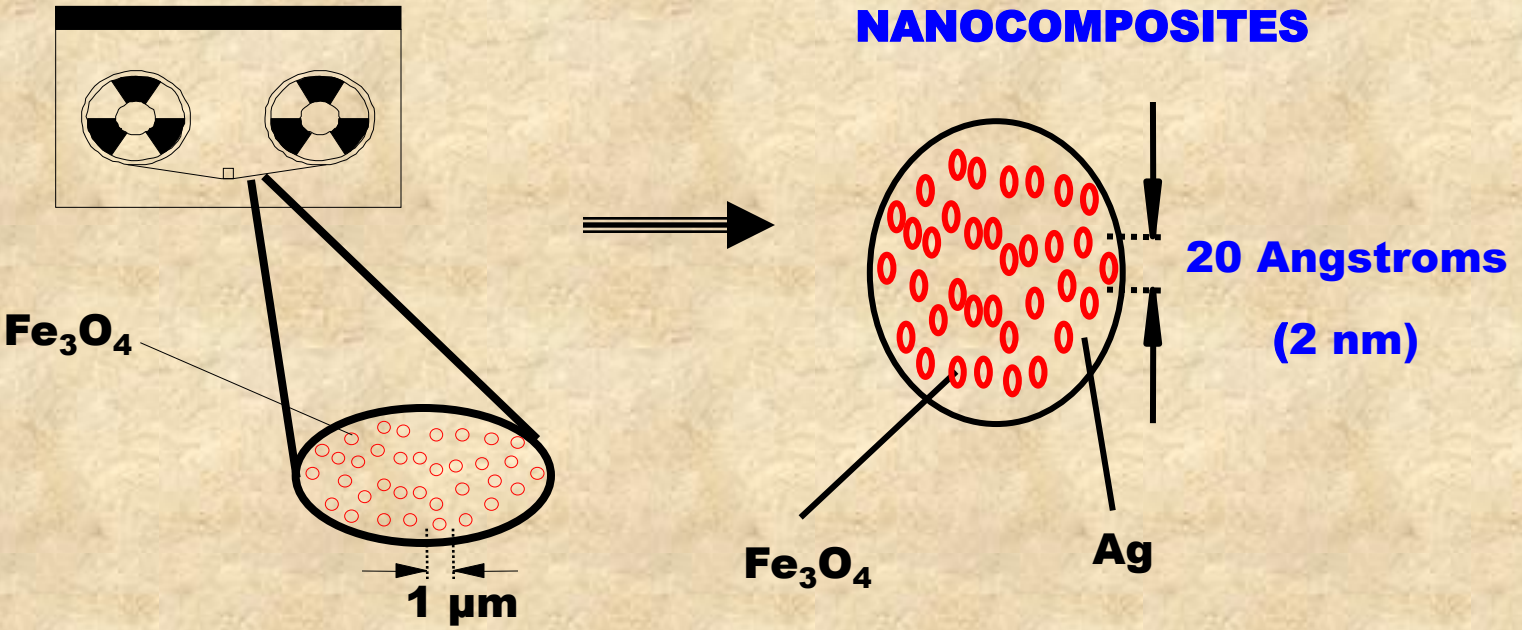
Assembly of magnetic clusters (each comprised of many ferromagnetically-aligned elemental moments of magnitude) μ acting independently.

= Superparamagnetic Material:

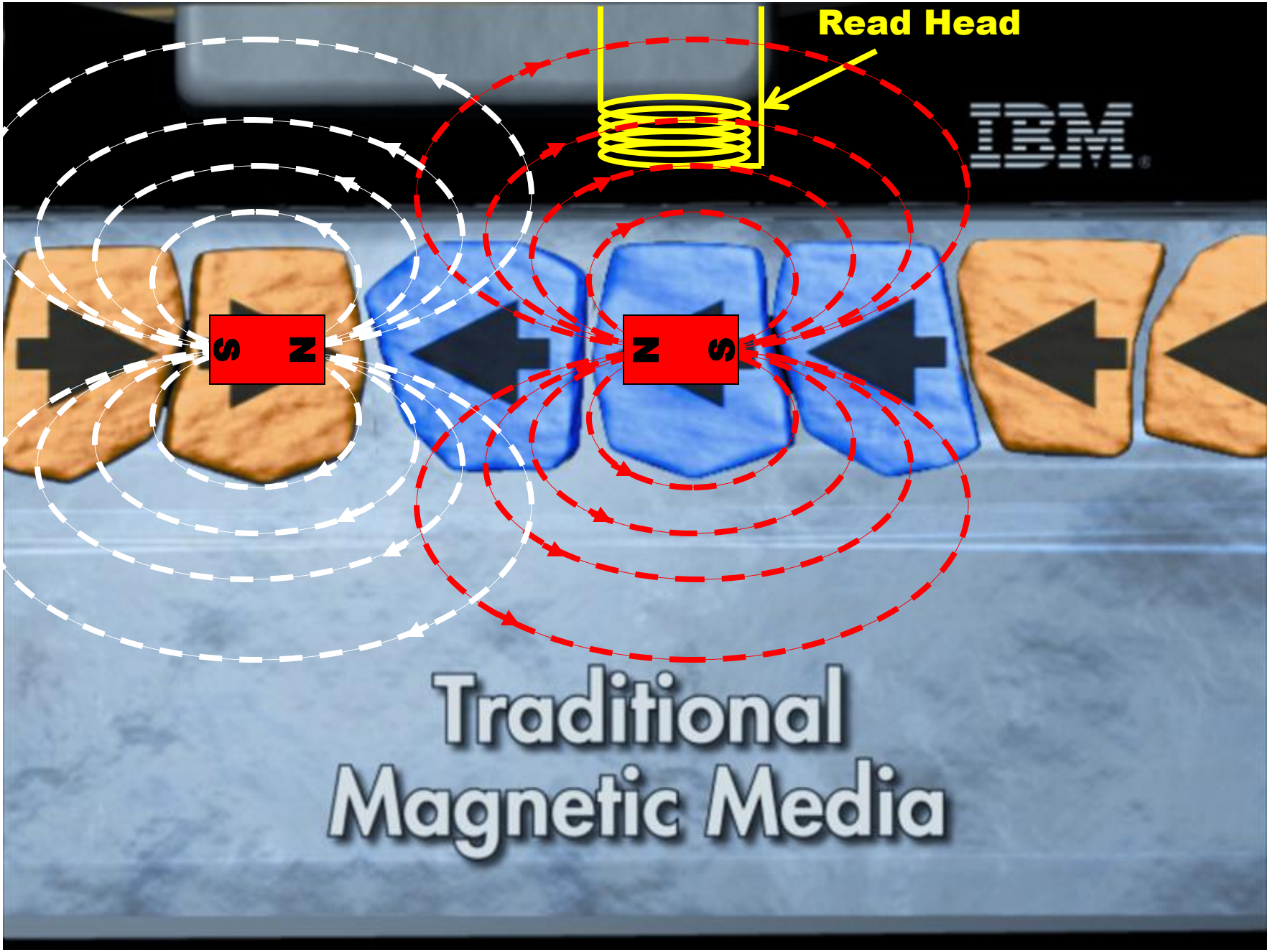
HIGHER DENSITY MAGNETIC RECORDING MEDIA

IMPROVED MAGNETIC RECORDING MEDIA

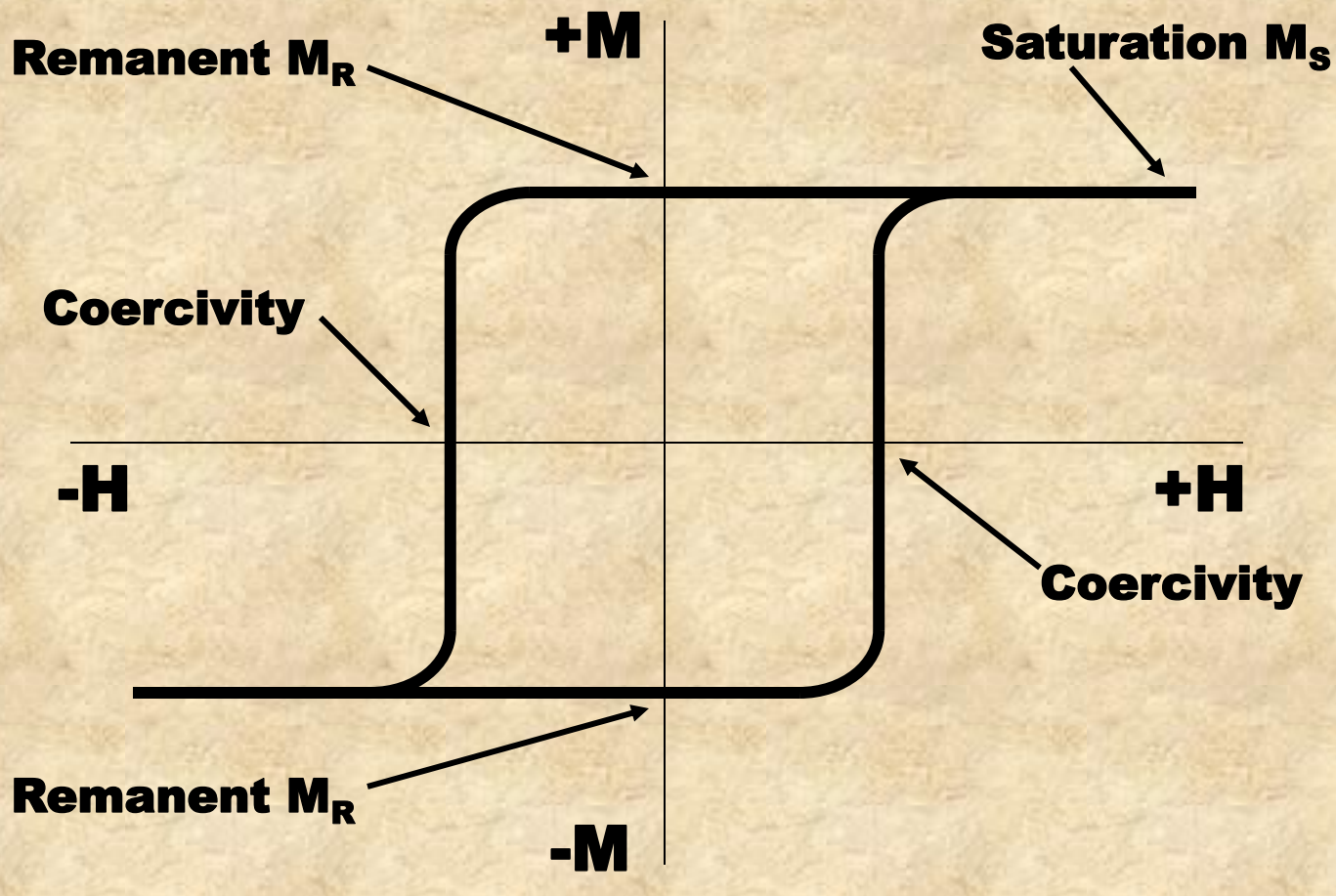
Conventional Media | **High Density Media**

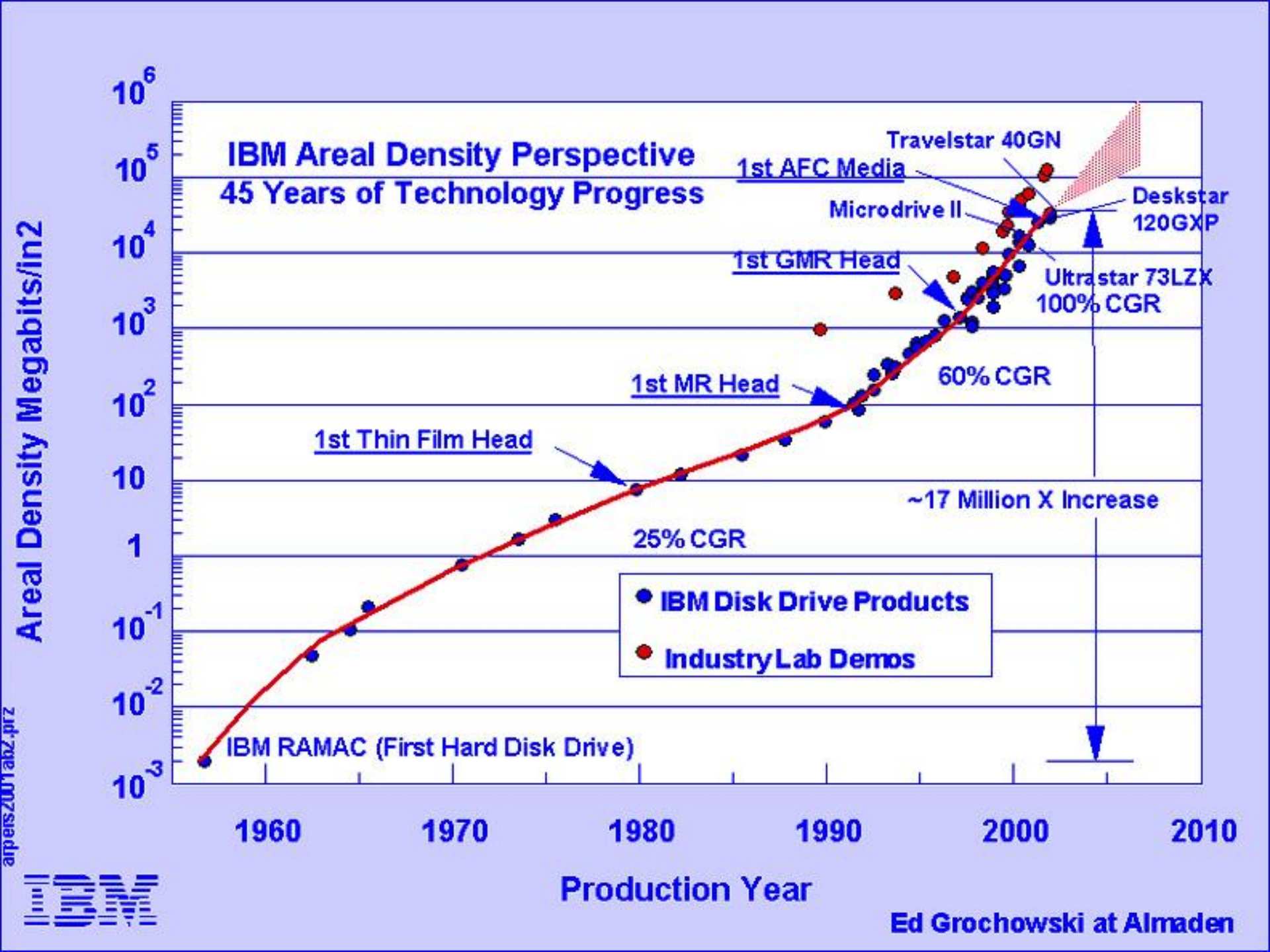


Higher Density Achieved by Reduction of "Bit" Size so there are More Bits/Unit Area


Read Head
IBM
S
N
N
S
Traditional
Magnetic Media

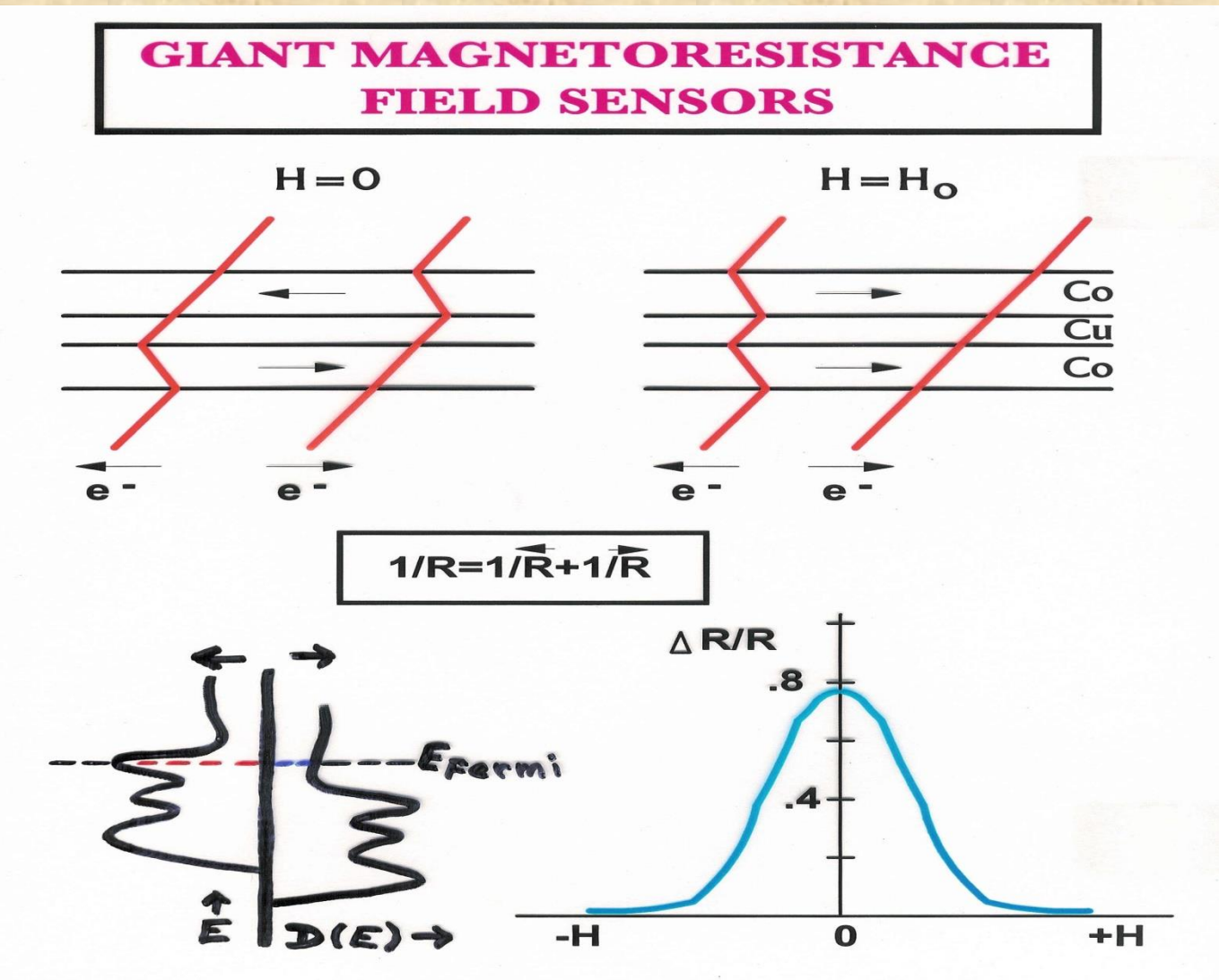
HYSTERESIS LOOP OF A FERROMAGNET



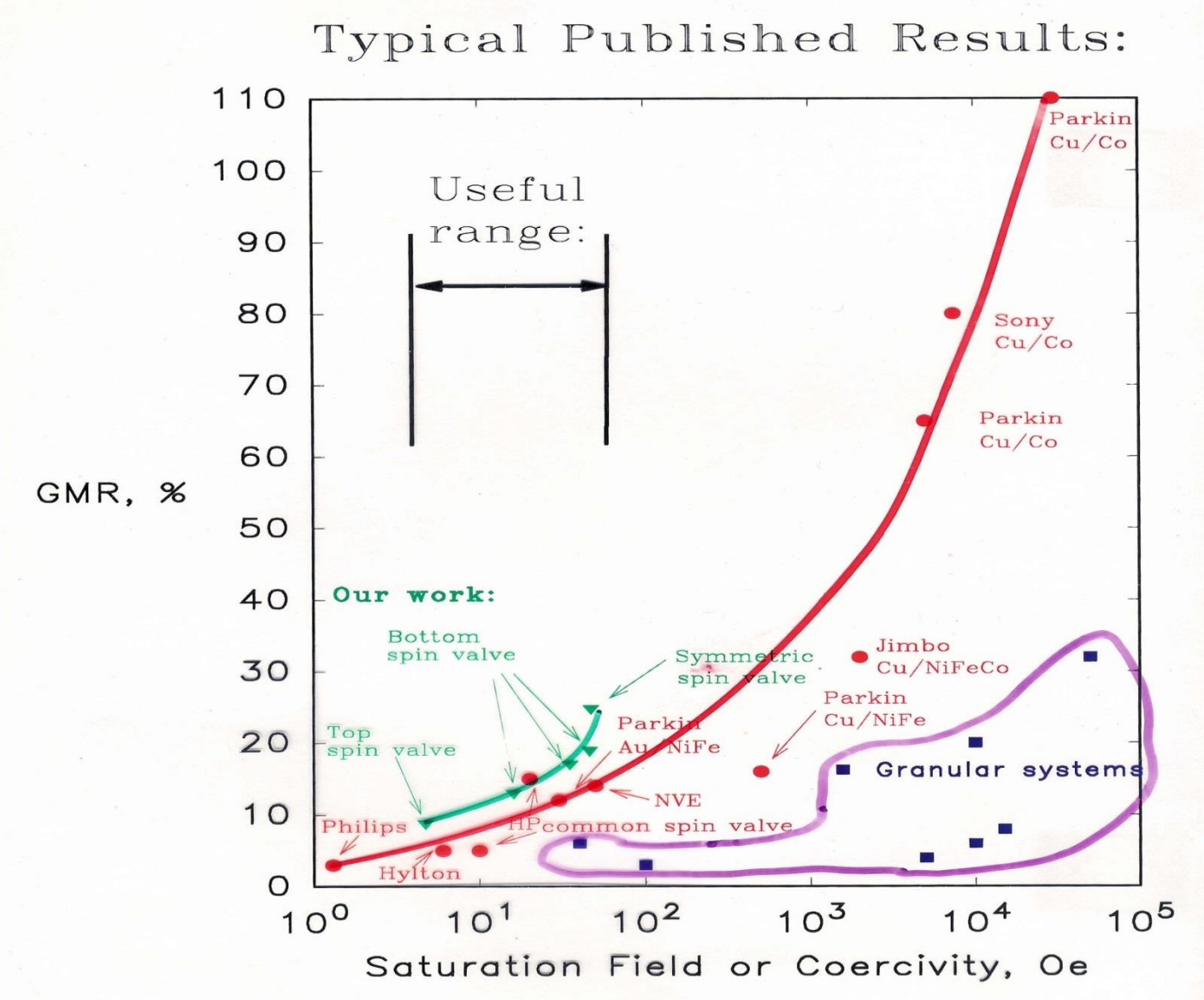


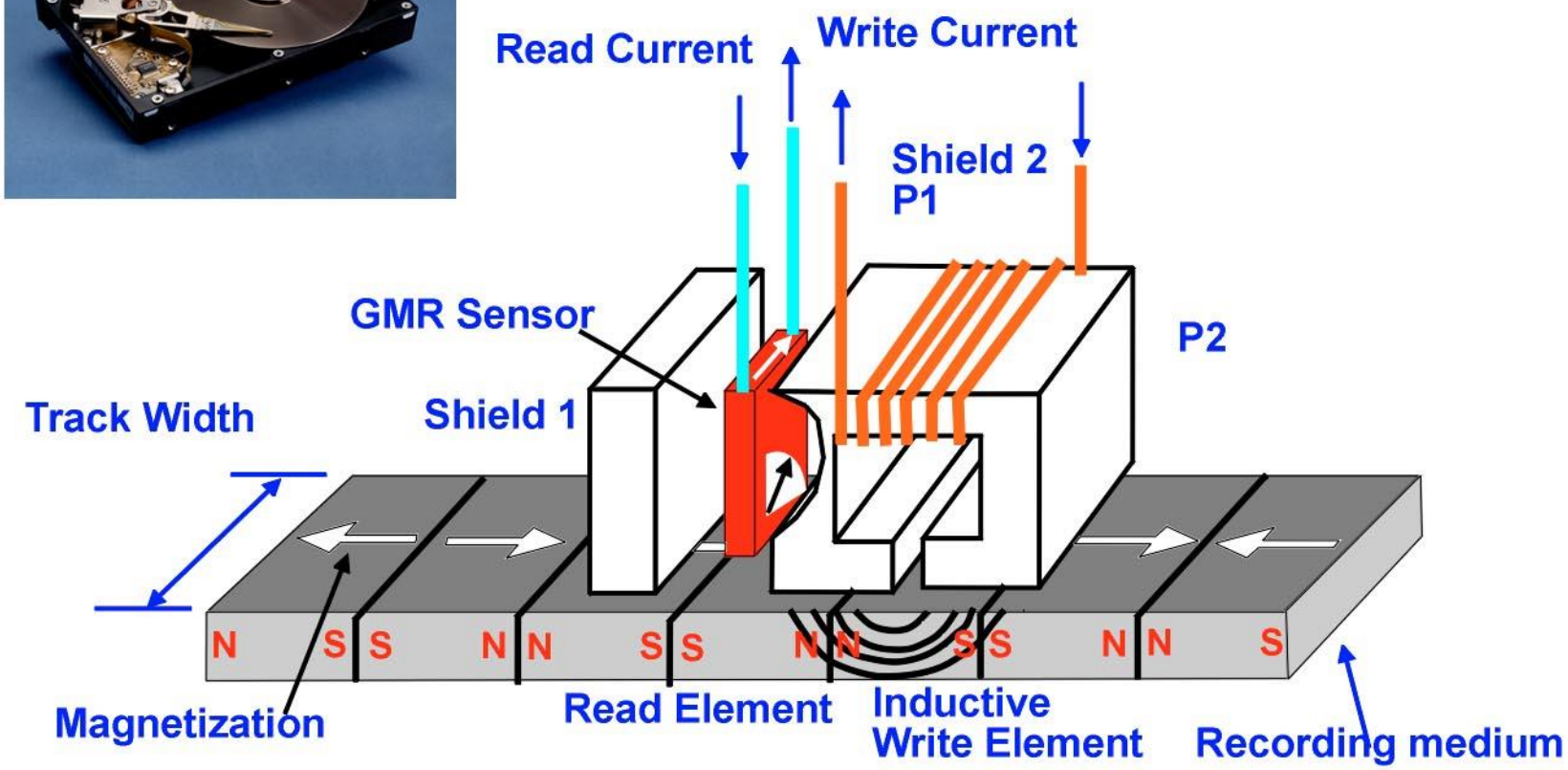
IBM Areal Density Perspective
45 Years of Technology Progress
Areal Density Megabits/in2
Production Year
Travelstar 40GN
1st AFC Media
Microdrive II
Deskstar 120GXP
1st GMR Head
Ultrastar 73LZX
100% CGR
60% CGR
1st MR Head
1st Thin Film Head
~17 Million X Increase
25% CGR
IBM Disk Drive Products
Industry Lab Demos
IBM RAMAC (First Hard Disk Drive)
Ed Grochowski at Almaden
arpers2001ab2.prz

COUPLED ELECTRICAL AND MAGNETIC DEVICES IN NANOCOMPOSITE SYSTEMS



[Baibich, et. al., Phys. Rev. Lett. 61, 2472 (1988).]


Typical Published Results:
GMR, %
Saturation Field or Coercivity, Oe
Useful range:
Our work:
Bottom spin valve
Top spin valve
Symmetric spin valve
Parkin Au/NiFe
NVE
Philips
HP
common spin valve
Hylton
Parkin Cu/Co
Sony Cu/Co
Parkin Cu/Co
Jimbo Cu/NiFeCo
Parkin Cu/NiFe
Granular systems



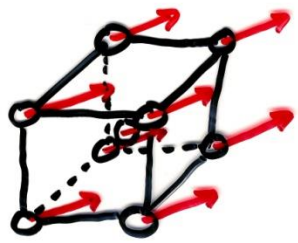
Magnetic recording process.

Ed Grochowski
IBM Almaden Research Center

TIME DEPENDENCE

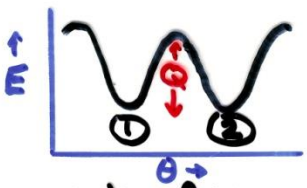
IN NANOMAGNETIC THINGS

Kinetically Frozen Nanoparticle Moments



Magnetocrystalline Anisotropy

- forces spins to lie along certain crystal directions



Rotation of Cluster Spins face an Energy Barrier $Q = KV$

Anisotropy Constant — Volume

rate of jumping from 1 → 2 $= \nu \exp\left[-\frac{KV}{k_B T}\right] = 1/\tau$

For experimental time $\tau = 100$ sec.

$$10^{-2} = 10^{9} \exp\left[-KV/k_B T\right]$$

$\therefore$ for $V \geq 25\, k_B T / K$

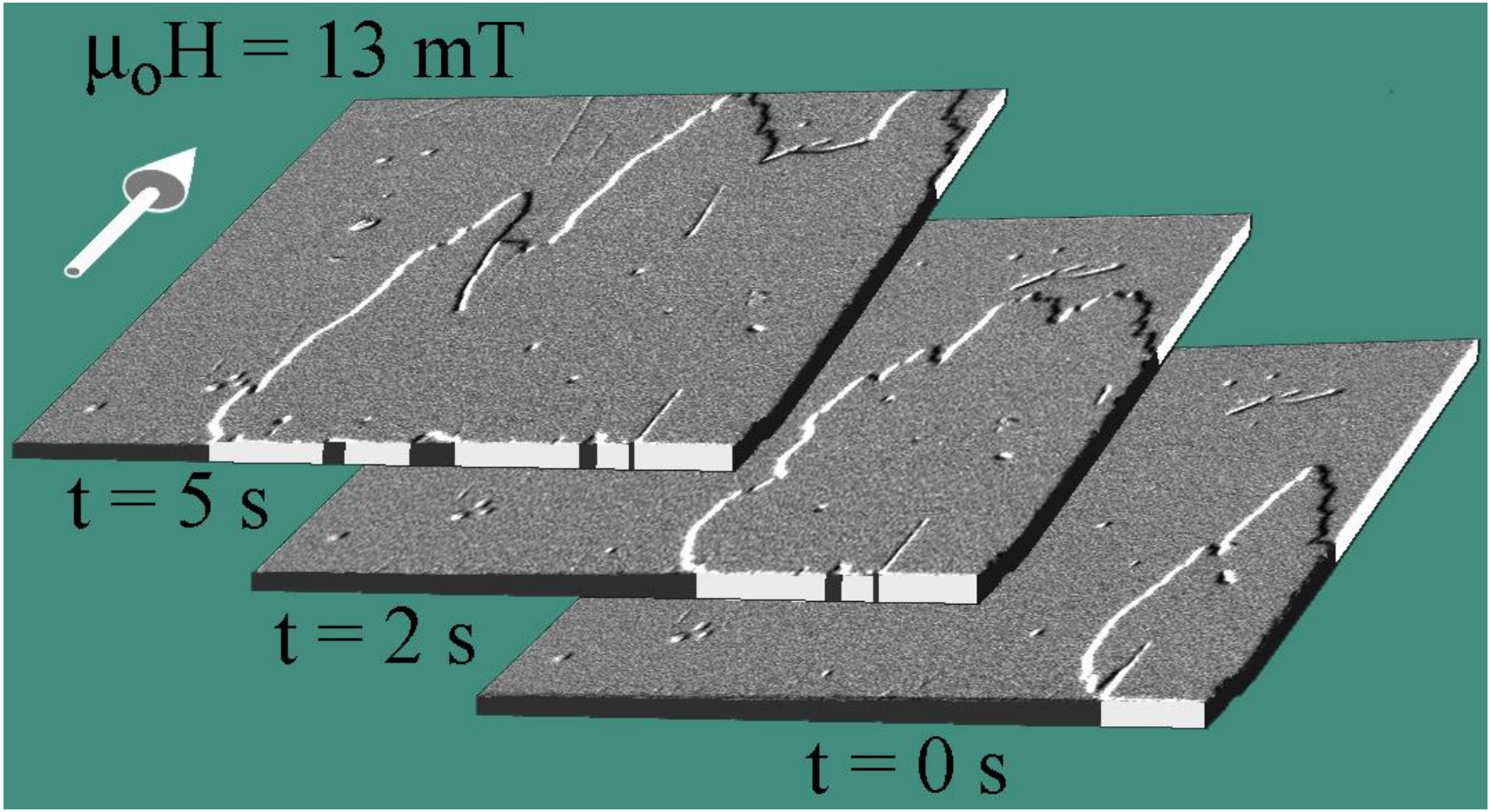
or

$$T \equiv T_B \leq KV/25 k_B$$

the spins are kinetically frozen or "Blocked"

In nanoparticles, the Magnetic Moments (e.g., Spins) can be kinetically frozen if the temperature is low enough. That temperature is called the "blocking" temperature: T_B . That temperature depends slightly upon how it is measured. It also depends on the Volume of the material and the Magnetic Anisotropy of that material.

Time Dependent Domain Activity



Co(2.5 nm)/Ru(0.5 nm)/Co(2.1 nm) Synthetic AF Media
- The New Type of High Density Recording Media

SOFT MAGNETIC

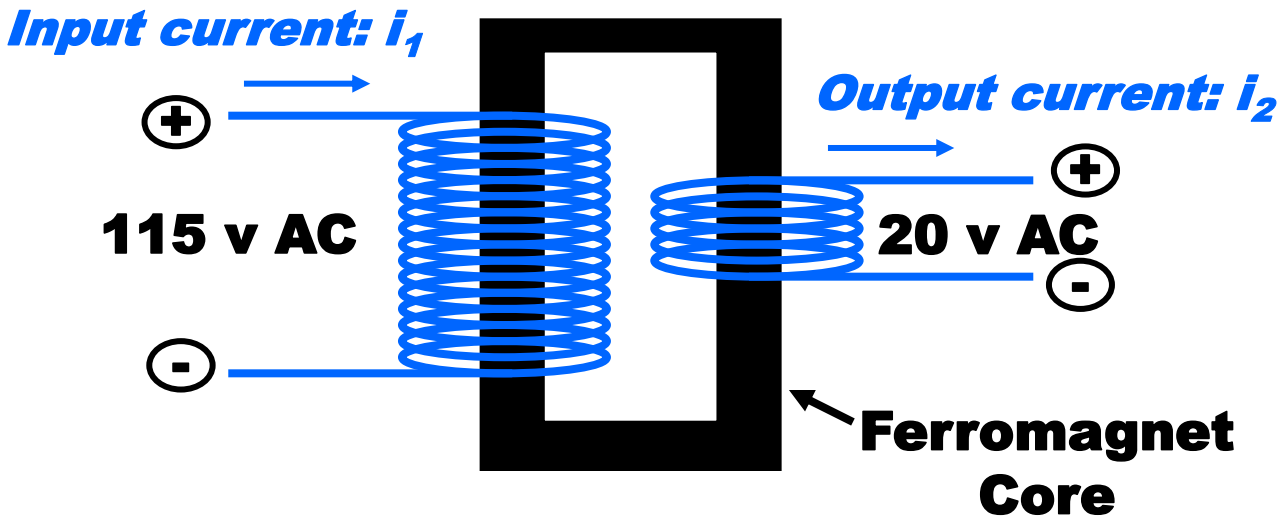
PROPERTIES ARE DIFFERENT

WHEN MATERIALS POSSESS

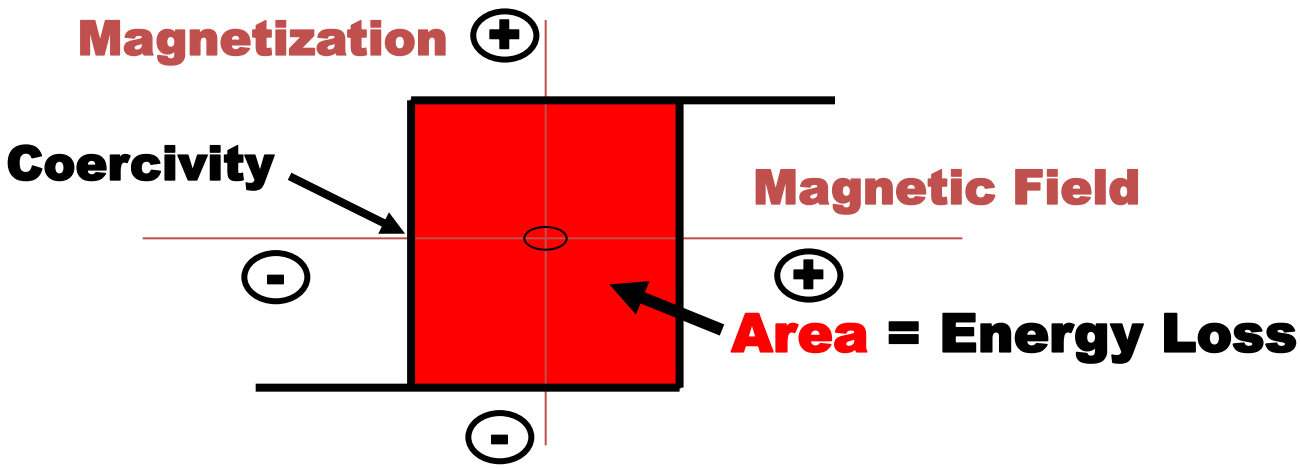
SOME NANOSCALE DIMENSION

TRANSFORMER

An AC current creates an alternating magnetic field in a coil of wire

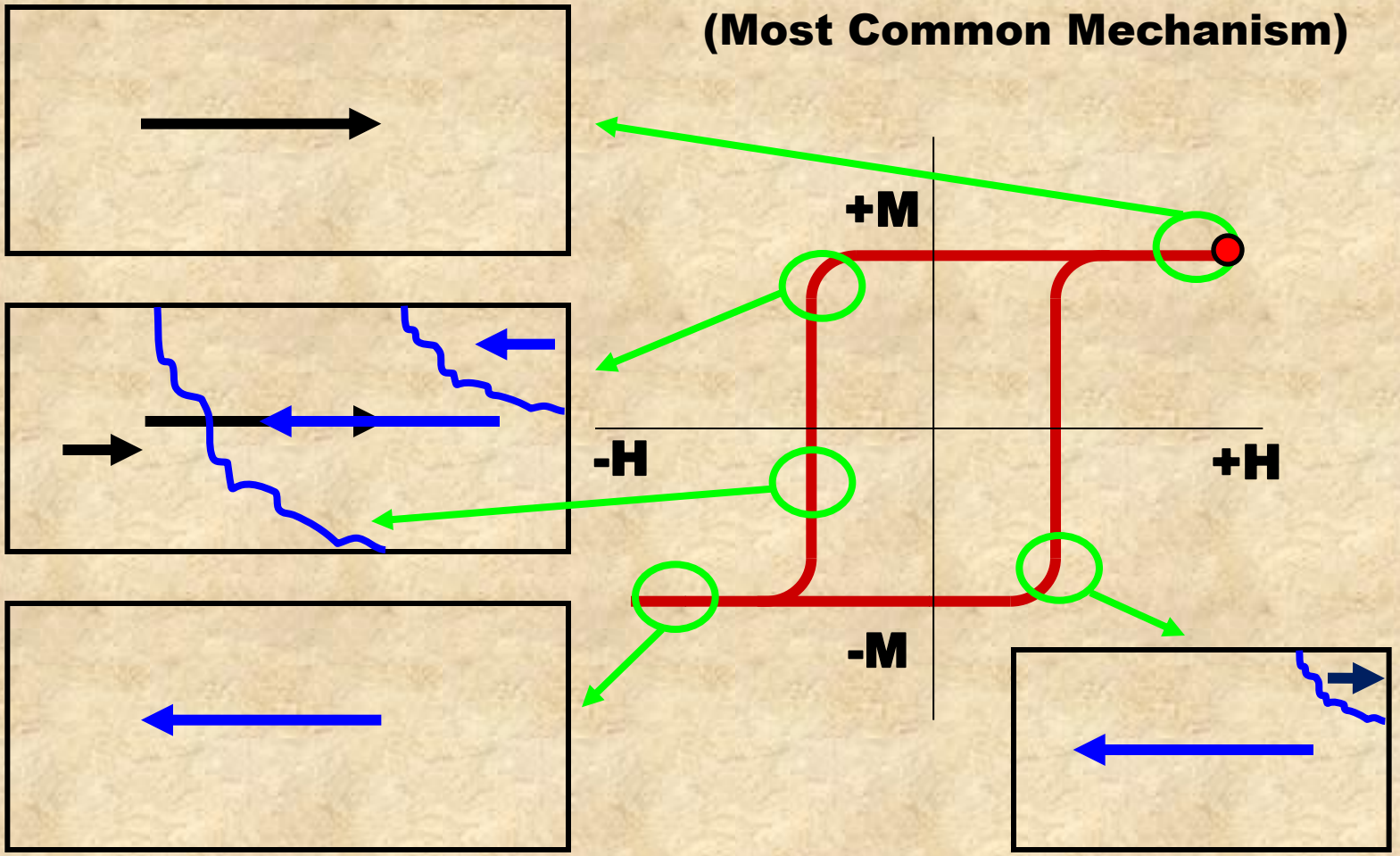


"Hysteresis Loop" of a Ferromagnet

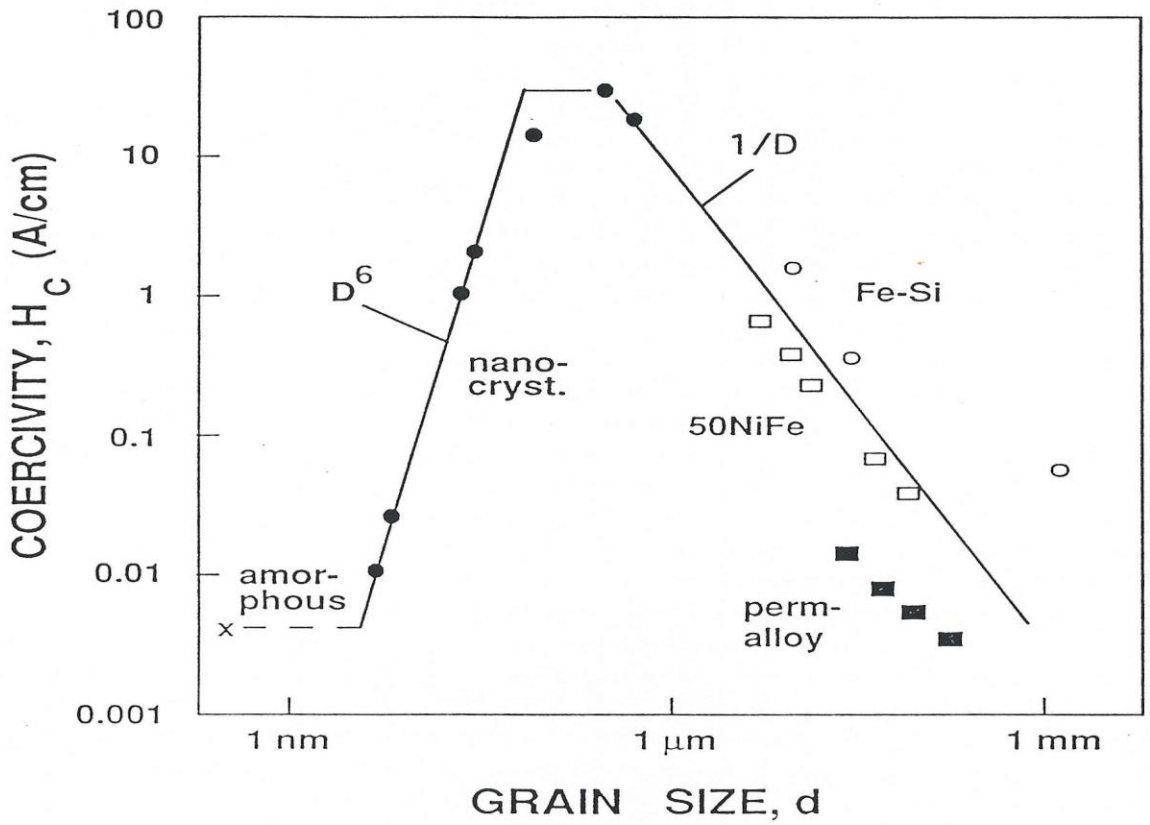


Magnetization Reversal by Domain Nucleation & Growth

(Most Common Mechanism)

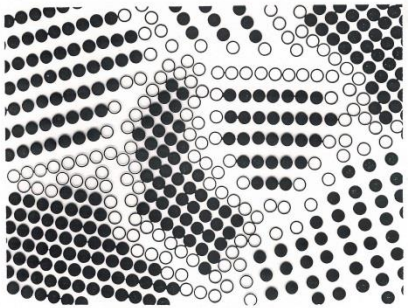


ENHANCED (AND REDUCED) MAGNETIC COERCIVITY



Magnetic coercivity vs. grain size for several soft ferromagnetic materials. [G. Herzer, IEEE Trans. MAG26, 1397 (1990)]

STRUCTURE SCHEMATIC:
-NANOPHASE MATERIAL-



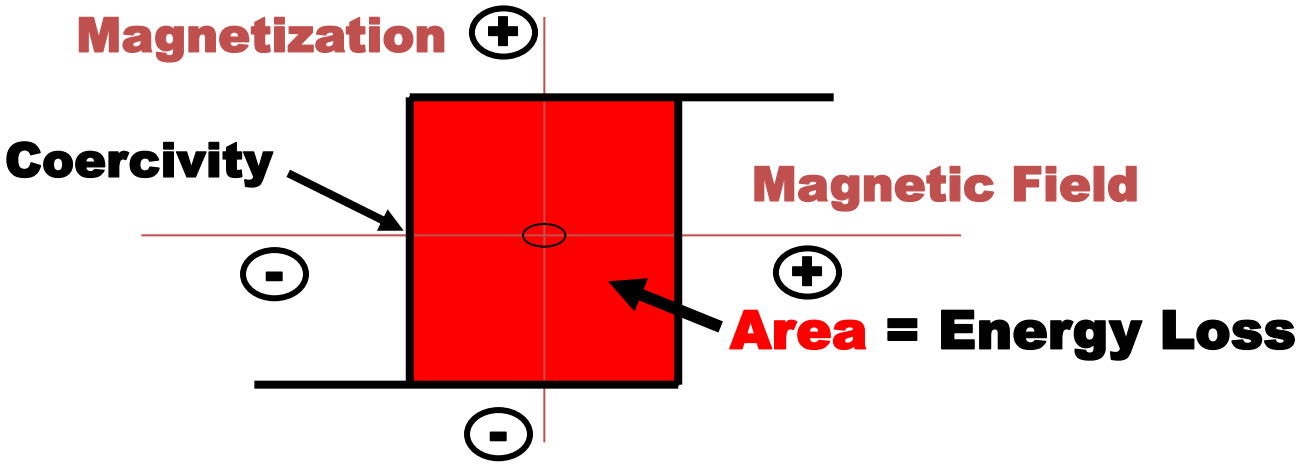
Schematic of an equiaxed nanocrystalline metal showing atoms associated with individual grains (filled circles) and those constituting the grain boundaries (open circles). [H. Gleiter, Prog. Mater. Sci. 89, 223 (1989)]

Grain Boundaries are very effective "pinning sites" of magnetic domain walls, thereby impeding their motion

But when "d" is less than a domain wall width, the walls can then move through the grain boundaries

TRANSFORMER

"Hysteresis Loop" of a Ferromagnet



For each cycle of the field (which happens 60 times a second from US electrical outlets) the energy expended by the Red Area in the above diagram goes into heating the transformer. Either the transformer core heats to above its Curie temperature (thereby becoming a useless paramagnet) or it melts and destroys the transformer, or the heat must be extracted. Reducing the coercivity of the core reduces significantly the heat created and saves a lot of wasted energy.

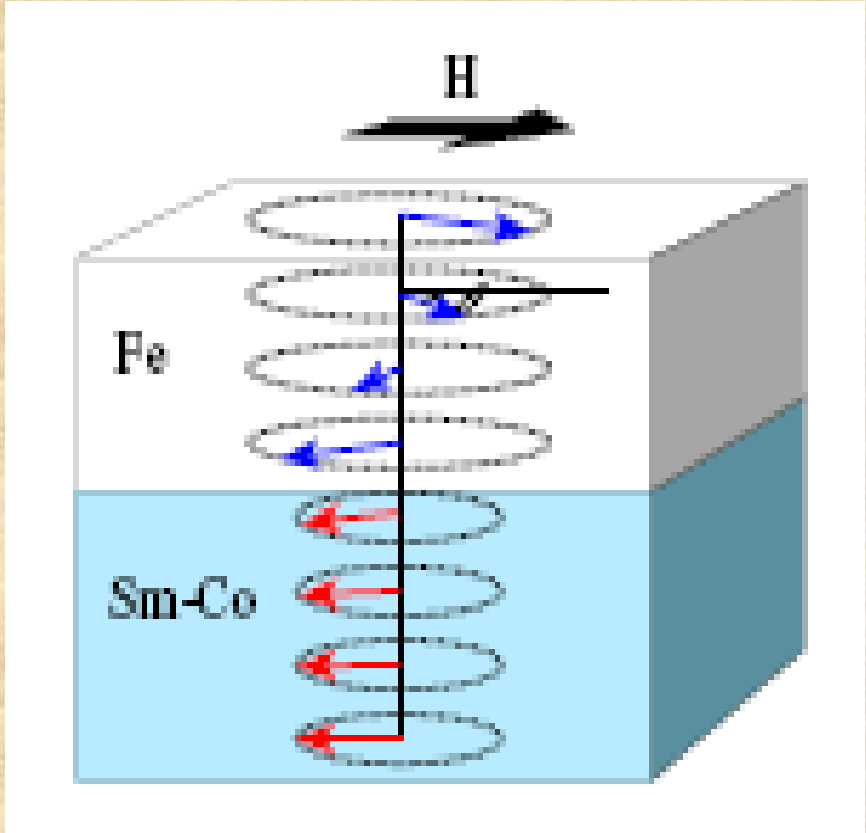
CHANGE IN DOMAIN DYNAMICS

IN A HARD FM/SOFT FM

NANOCOMPOSITE

= AN IMPROVED PERMANENT MAGNET

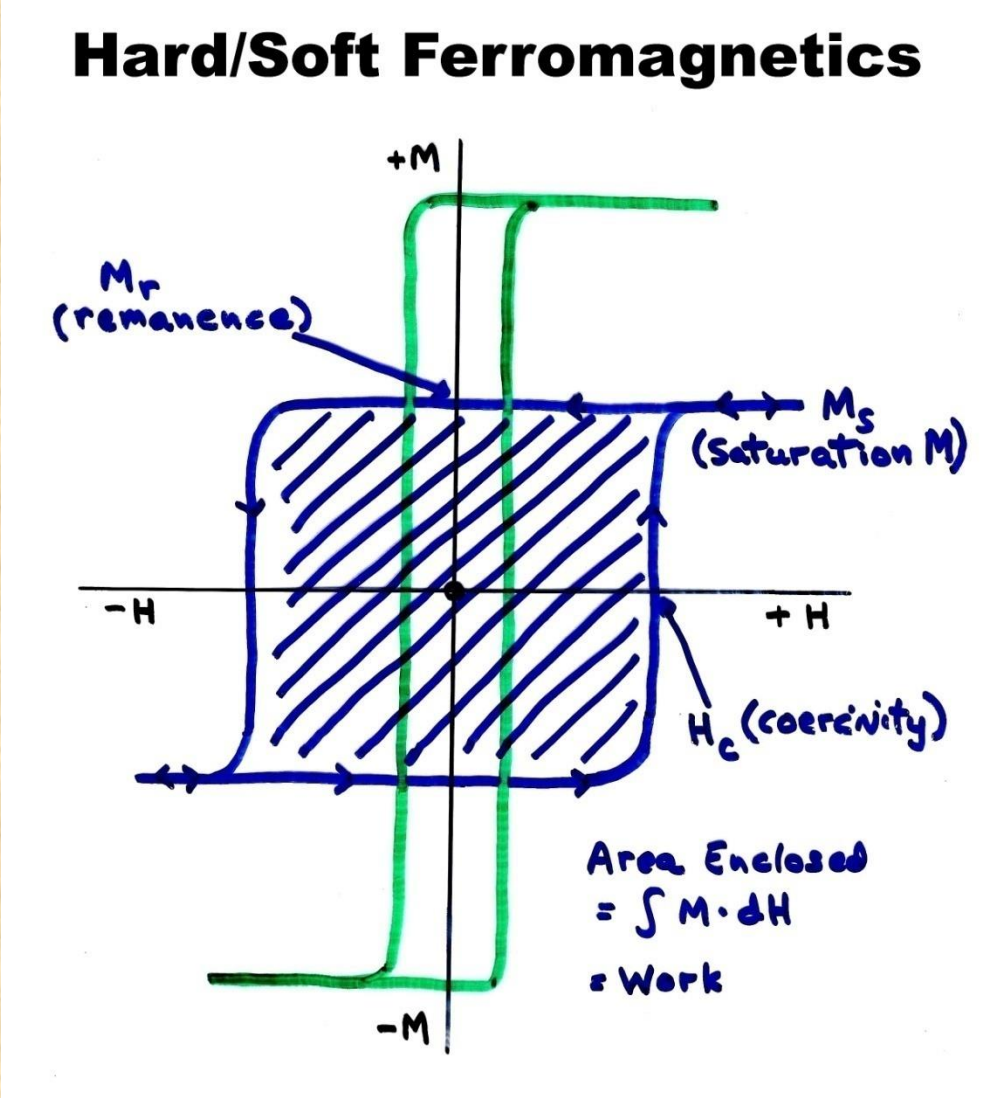
Origin of High Coercivity in Hard/Soft Ferromagnetic Bilayer



[E. Kneller & R. Hawig, IEEE Trans. Mag. 27, 3588 (1991).]

Bottom Layer of the Soft Ferromagnet (Fe) is pinned by the top layer of the Hard Ferromagnet (SmCo).

Each successive layer in the Soft FM is bound to the layer below it causing its magnetic moment to be closely aligned to it. The further away each Soft FM layer is from the AF interface, the easier it is to align with the external field, thereby creating a "spin spiral". This keeps domain walls perpendicular to the interface from forming.



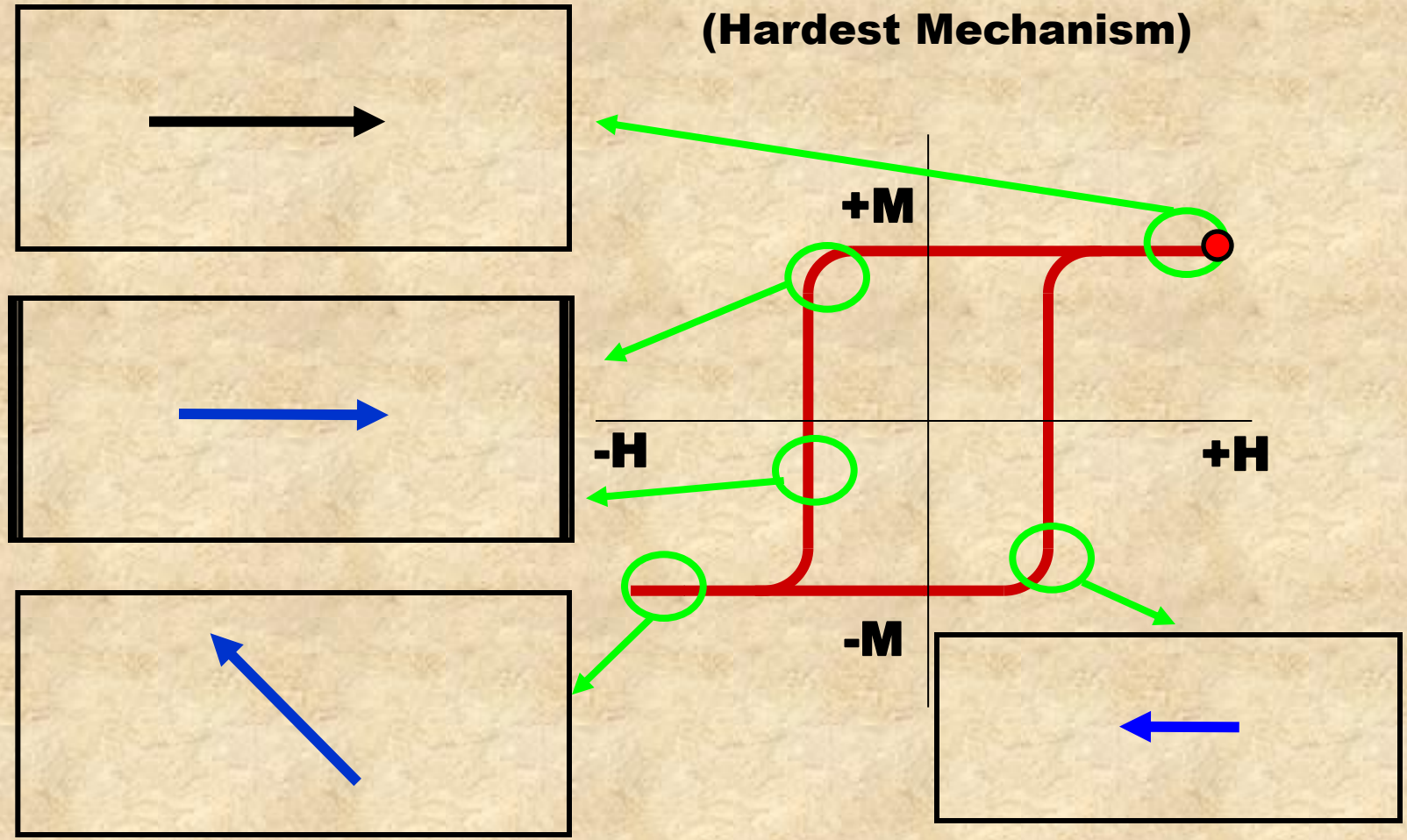
Composites of nm thick Hard & Soft Ferromagnets are thought to be the way to the future "Hardest" Ferromagnets.

This is because the magnetic Exchange interaction at the interface causes the Magnetization to change by the more difficult process of the coherent rotation of all the spins at one time, rather than by the nucleation & growth of domains. This results in a larger coercivity.

Substitution of Soft FMs Increase the saturation M, resulting in an increase in hysteresis loop area.

Magnetization Reversal by Coherent Rotation

(Hardest Mechanism)



HARD MAGNETIC MATERIALS

"Magnequench" Magnets

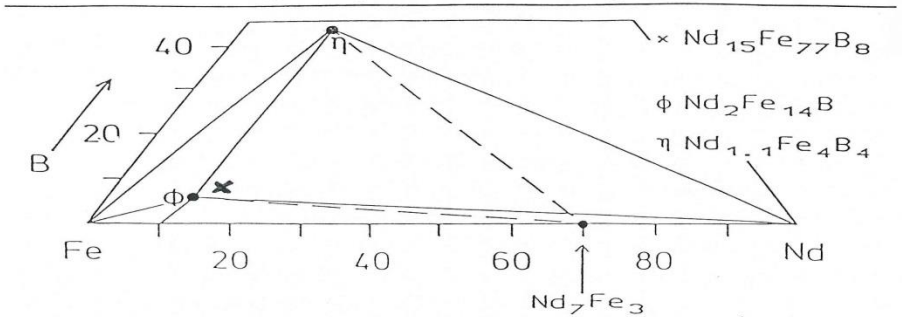


Figure 7. A comparison of the phase relations in the equilibrium phase diagram (solid line) and in the metastable phase diagram (dashed line).

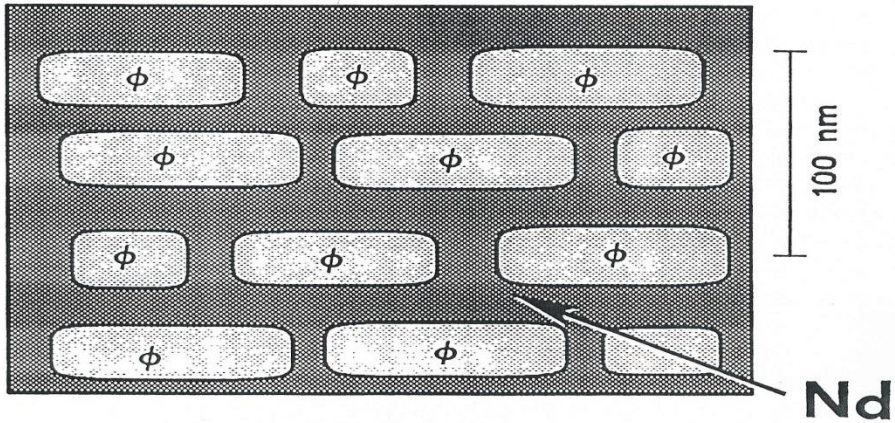


Figure 8. The ideal microstructure of a sintered magnet. The hard magnetic grains (ϕ) are decoupled by neodymium-rich nonmagnetic grain boundary phase.

A. Hutten, JOM (March, 1992) p. 11.

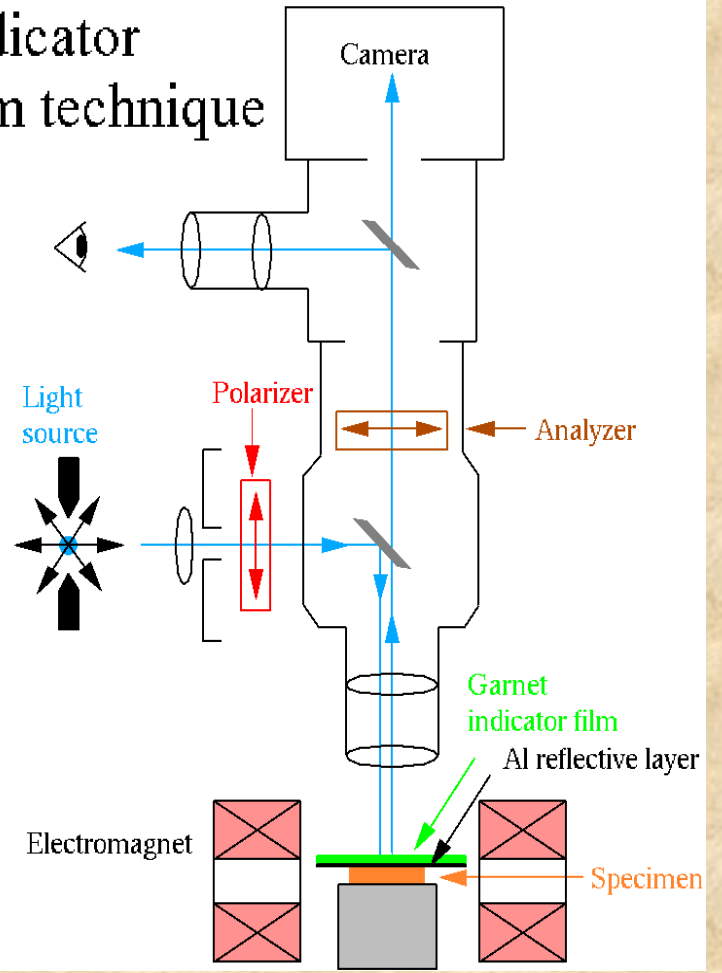
The make the "Hardest" Ferromagnetic materials (i.e., for the strongest permanent magnets), advantage is taken of the Interface effects.

The best Nd-Fe-B magnets are intentionally made off-stoichiometry in order to make them multiple phase so there are many interfaces.

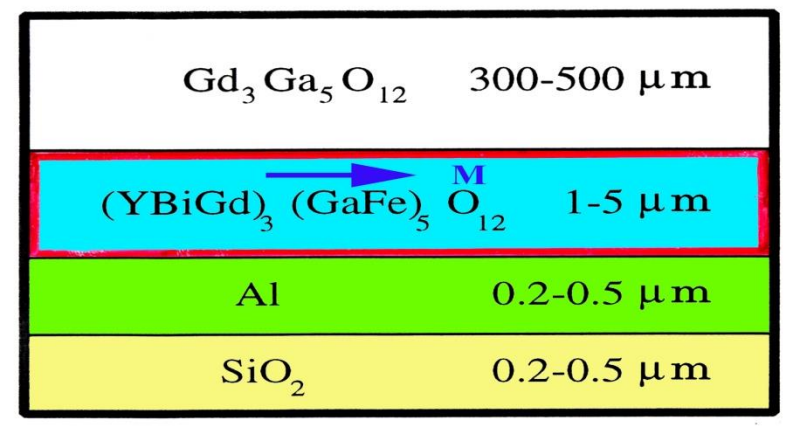
The "Hard" phase is also made nanometer in size in order to increase the interface area.

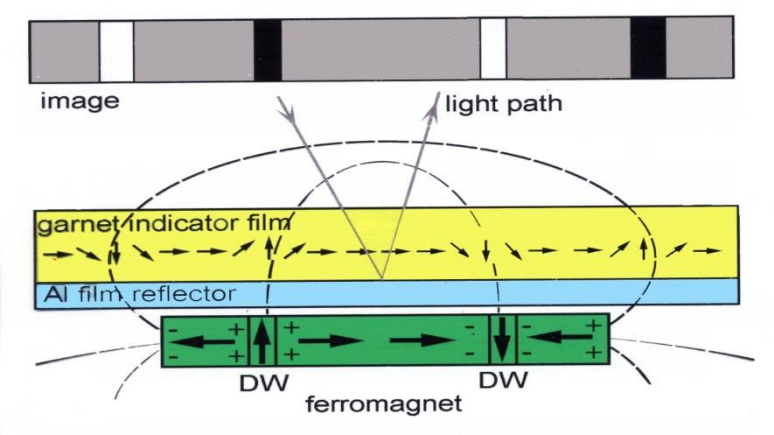
PROOF OF MAGNETIZATION IN A HARD FM/SOFT FM EXCHANGE SPRING

Magneto–Optical Indicator Film technique



Indicator Film

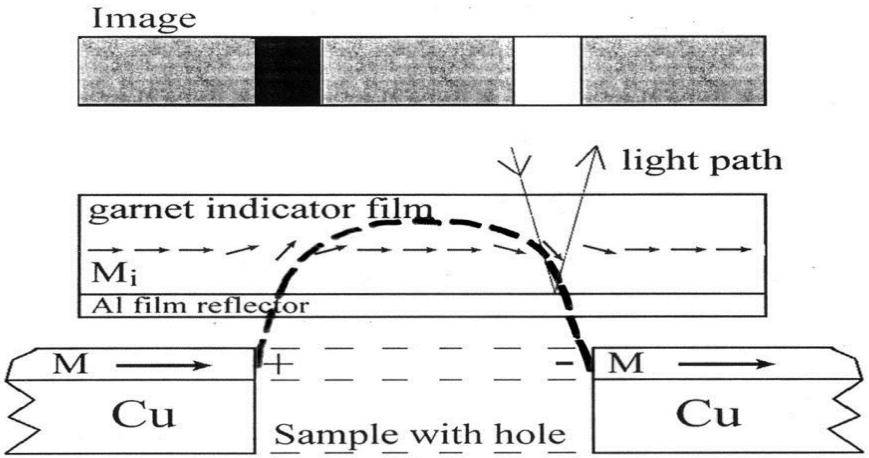




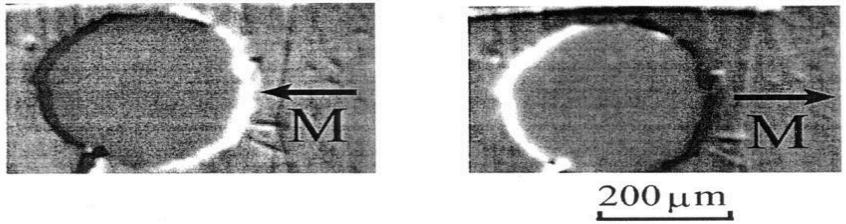
Domain Imaging Of a SmCo/Fe Hard/Soft FM Bilayer

Since No MOIF image contrast was observed on the top of the soft FM (Fe) in a SmCo/Fe Bilayer During field reversal, a Trick was employed. A small hole was drilled through the bilayer, and the magnetization in the area was determined by the magnetic poles of opposite sign which formed on the opposite inside edges of the hole.

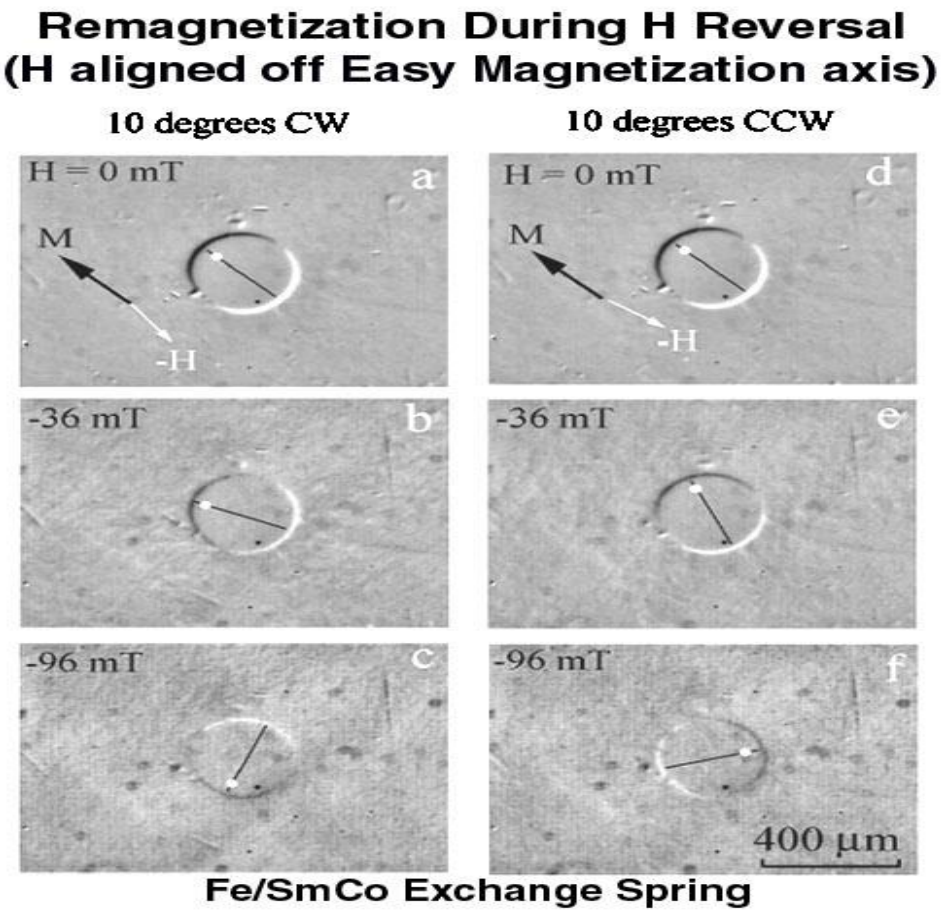
Schematic Illustrating the MOIF Technique for Investigation of Stray Magnetic Fields Around a Hole in a Multilayer Sample.



Magneto-Optical Image of Stray Fields Around a Hole in a 1 nm Multilayer Sample with Opposite Magnetization Directions.



Proof of Rotation Reversal Process in SmCo/Fe Bilayer



Fe/SmCo Exchange Spring

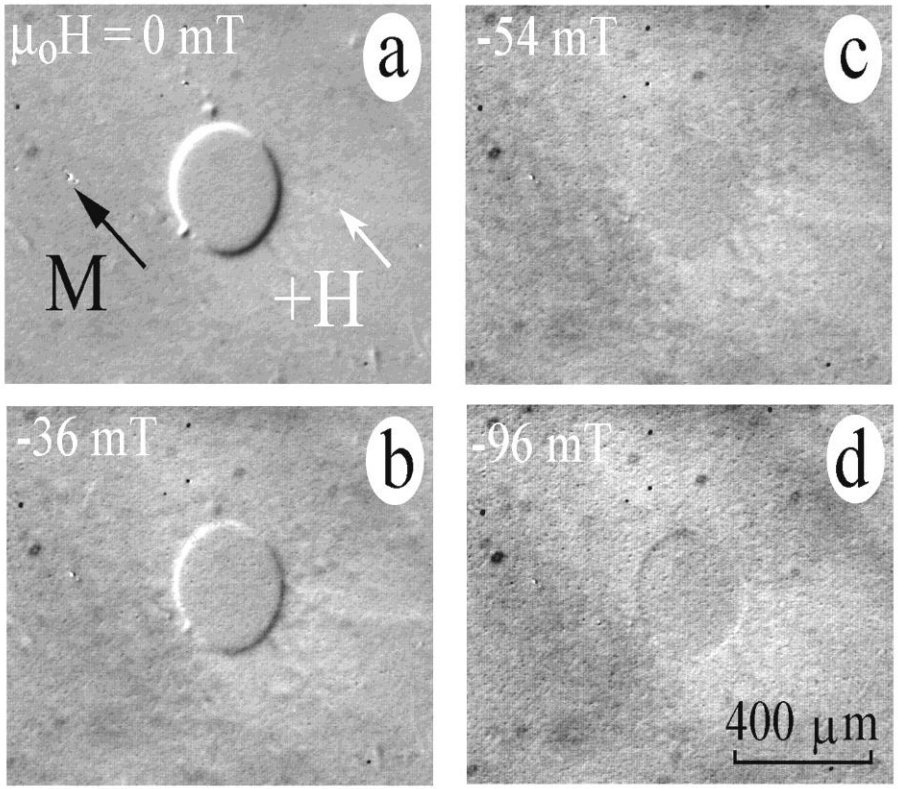
R.D. Shull, A.J. Shapiro, V.S. Gornakov, V.I. Nikitenko, J.S. Jiang, H. Kaper, G. Leaf, S.D. Bader, IEEE Trans. Magn. *37*, 2576 (2001).

Application of a reversed field is shown by the rotation of the MOIF image contrast at the hole edges to be accompanied by a rotation of M, when H is aligned just slightly off the easy axis of Magnetization of the Fe.

MOIF images with no hole present showed no contrast, indicating no domain walls perpendicular to the surface as would be expected for a normal FM.

New Feature in the Reversal Process in SmCo/Fe Bilayer

H Aligned Along Easy Magnetization Direction



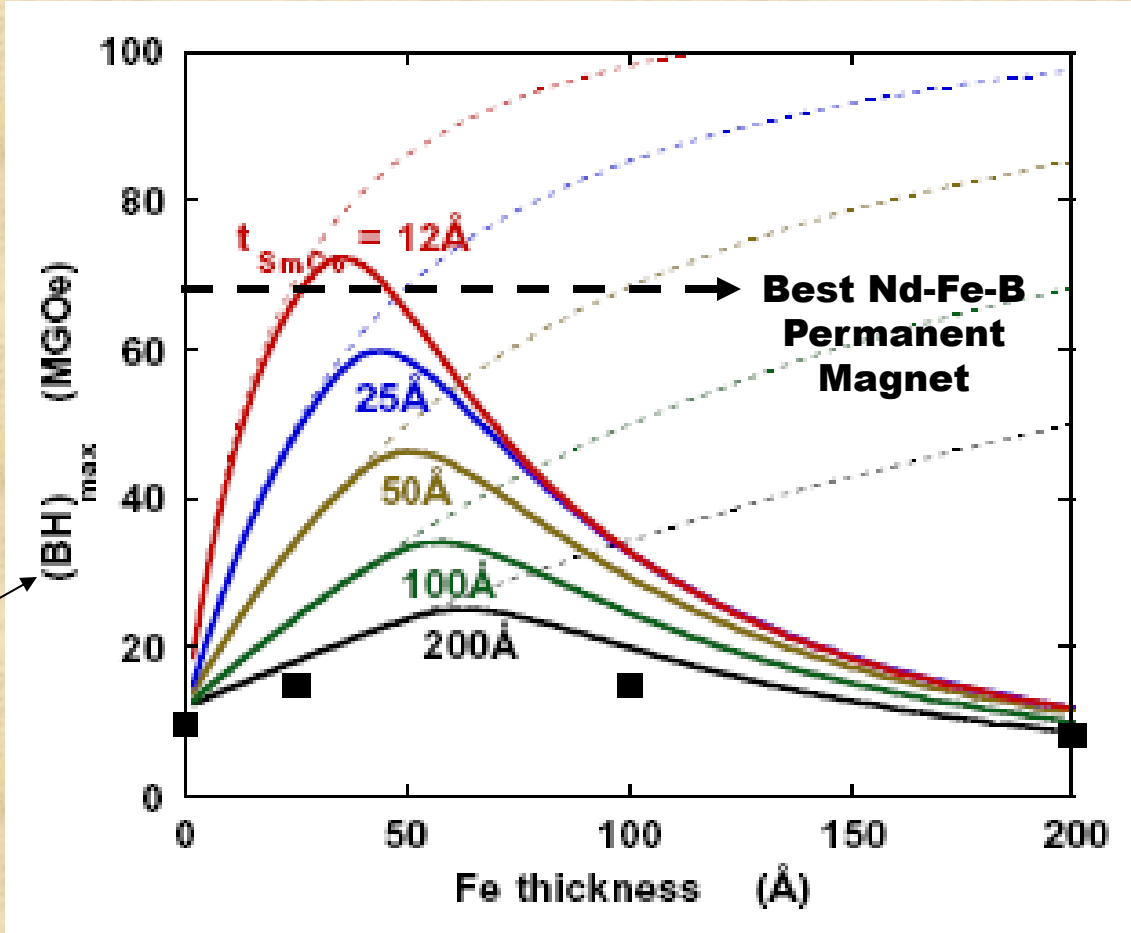
Fe/SmCo Exchange Spring

R.D. Shull, A.J. Shapiro, V.S. Gornakov, V.I. Nikitenko, J.S. Jiang, H. Kaper, G. Leaf, S.D. Bader, IEEE Trans. Magn. *37*, 2576 (2001).

When H is aligned along the easy axis of magnetization of the Fe, reversal of H does not result in a rotation in the contrast at the hole edge, but it is accompanied by an overall reduction in image contrast.

This effect is caused by a distribution in directions of the easy axes of magnetization in the small grains of the material: some rotating clockwise & some rotating CCW in response to H.

Improved Permanent Magnet By Multilayers of nm-thick SmCo & Fe



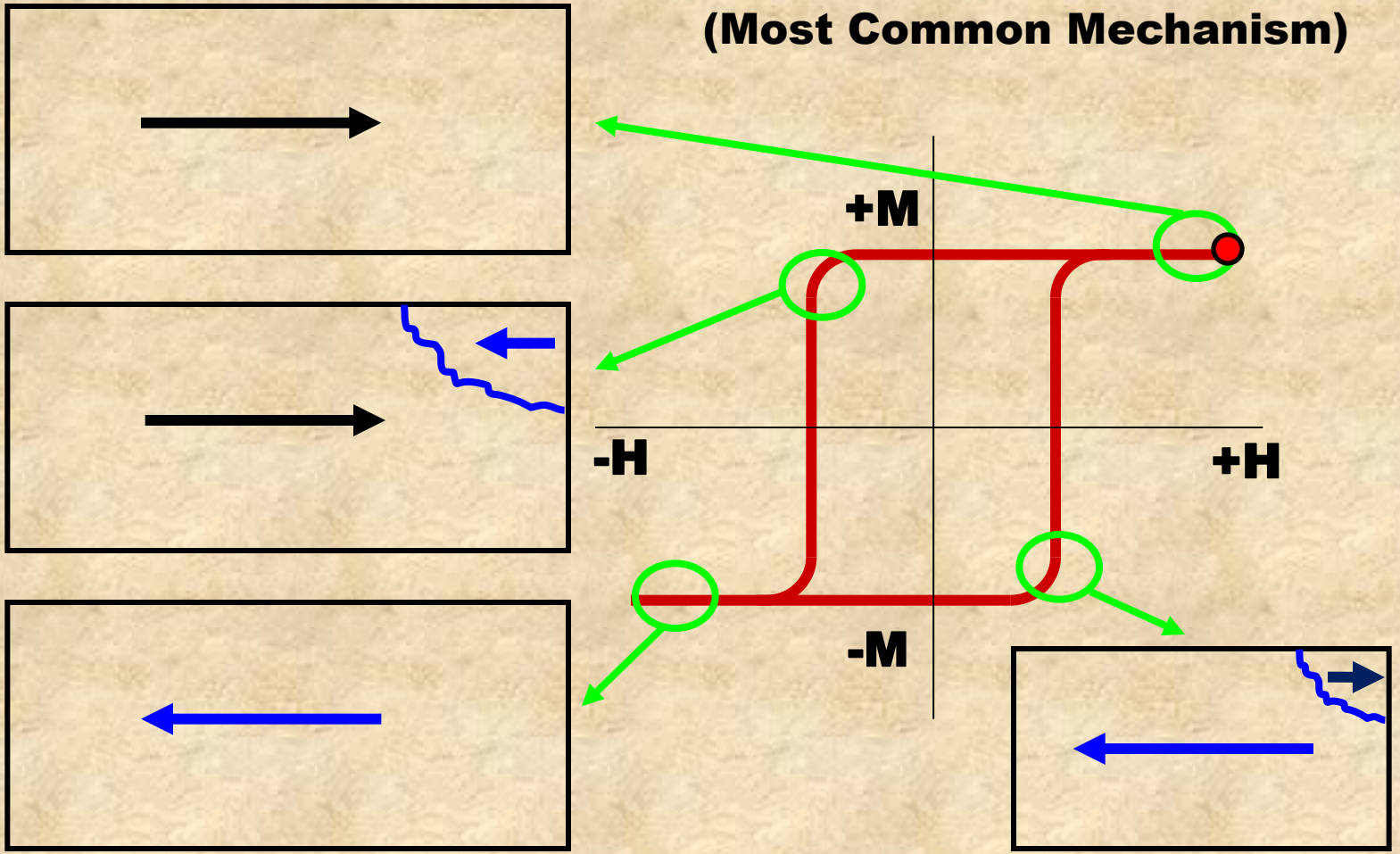
Hysteresis Loop Area

[J. Jiang, E. Fullerton, C. Sowers, I. Inomata, S. Bader, A. Shapiro, R. Shull, V. Gornakov, V. Nikitenko, IEEE Trans. Magnetics 35, 3229 (1999).]

MAGNETIZATION-DIRECTION DEPENDENT NUCLEATION

Magnetization Reversal by Domain Nucleation & Growth

(Most Common Mechanism)

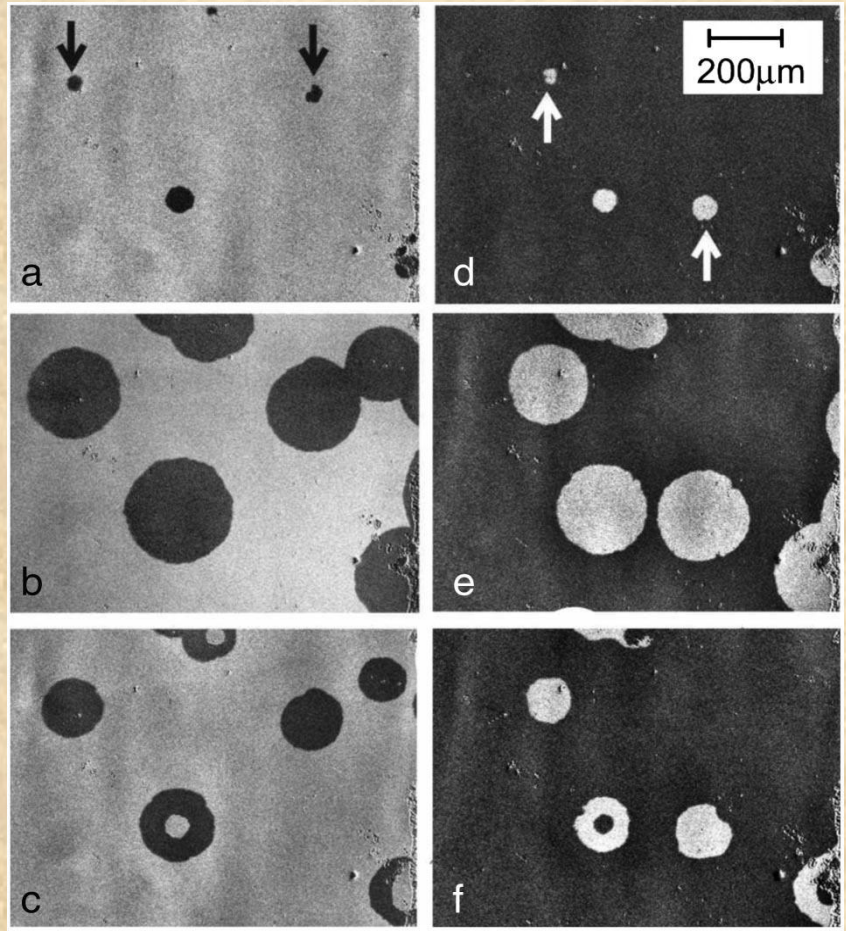


Anomalous Field Dependent Nucleation in [Co(0.4 nm)/Pt(3 nm)]$_2$ Multilayers

μ_0H = -17.3 mT
t = 0 s

μ_0H = -17.3 mT
t = 2 s

μ_0H = +17.3 mT
after -17.3 mT
t = 0 s



μ_0H = +17.3 mT
t = 0 s

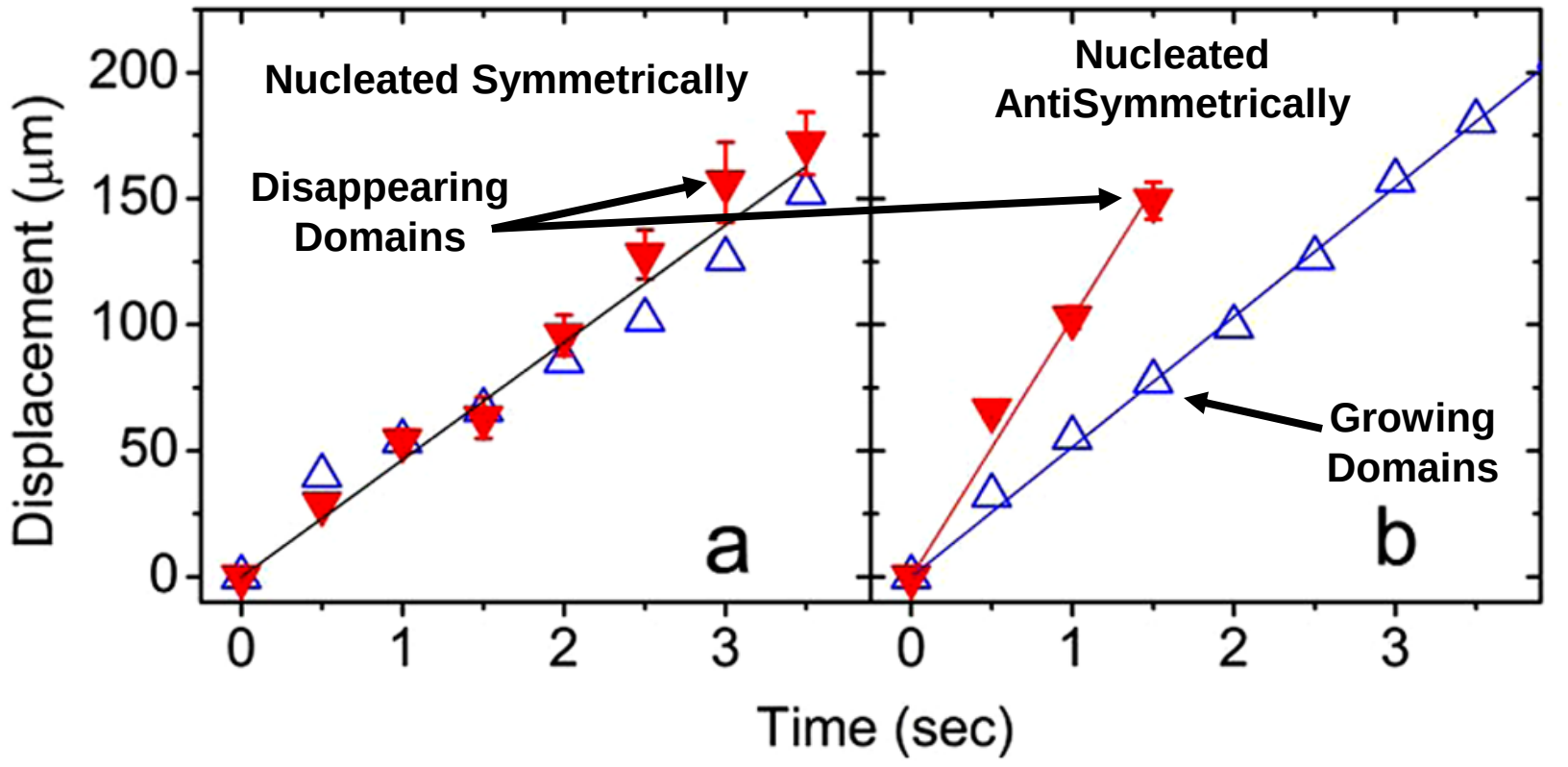
μ_0H = +17.3 mT
t = 2 s

μ_0H = -17.3 mT
after +17.3 mT
t = 0 s

Arrows indicate Field-Direction-Dependent Nucleation Sites!!!

[L. Iunin, et.al. Phys. Rev. Letters 98, 117204 (2007)]

Growth Rate of Magnetic Domains in [Co(0.4 nm)/Pt(3.0 nm)]$_2$ Multilayers



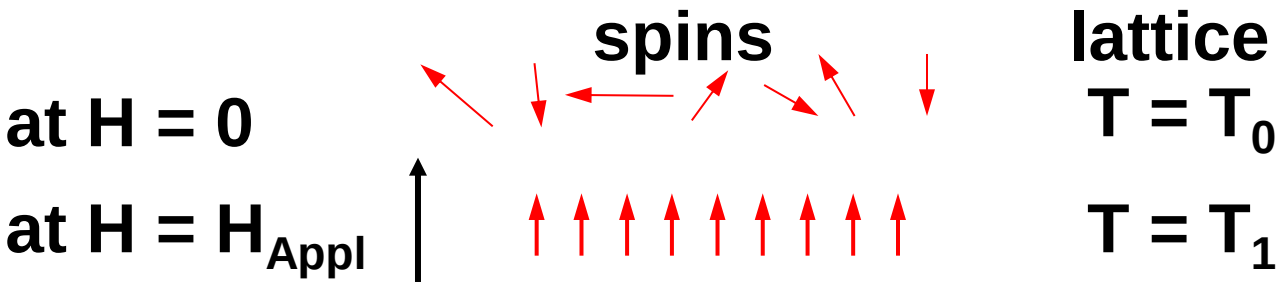
$\mu_0 H = \geq 1.52$ mT ($\mu_0 H_C = 2.3$ mT)

ENHANCED MAGNETOCALORIC EFFECTS IN NANOCOMPOSITE SYSTEMS

- FOR AN IMPROVED REFRIGERATOR

MAGNETOCALORIC EFFECT

SYSTEM = SPIN + LATTICE



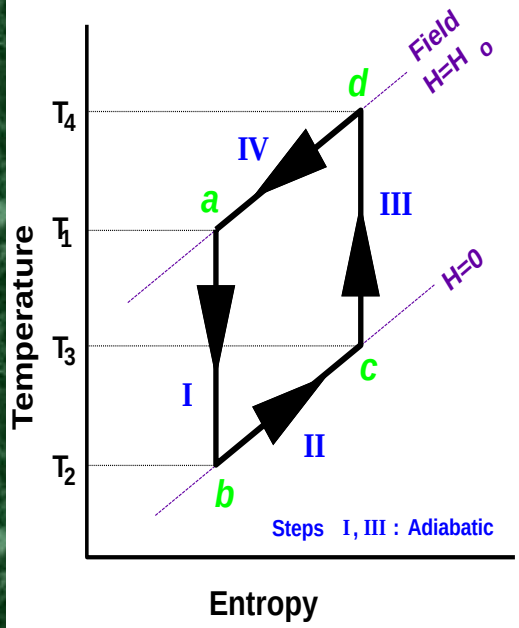
Total entropy change of the (Spin+Lattice) system upon application of a magnetic field, H_{Appl}, (reversibly) is ZERO.

Decrease in spin entropy causes an increase in lattice entropy, $C_H dT/T$.

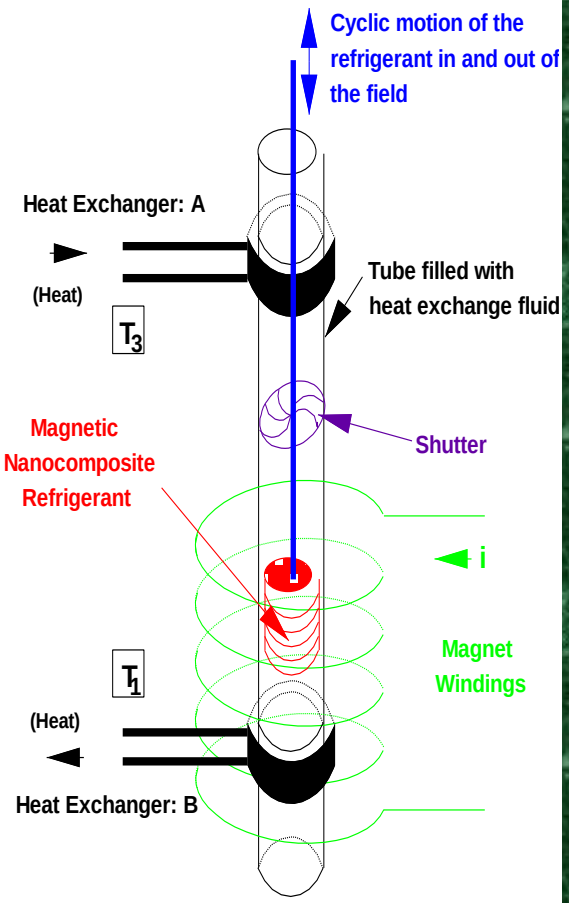
Magnetocaloric effect = $dT = (T_1 - T_0)$.

MAGNETIC REFRIGERATION

Refrigeration Cycle



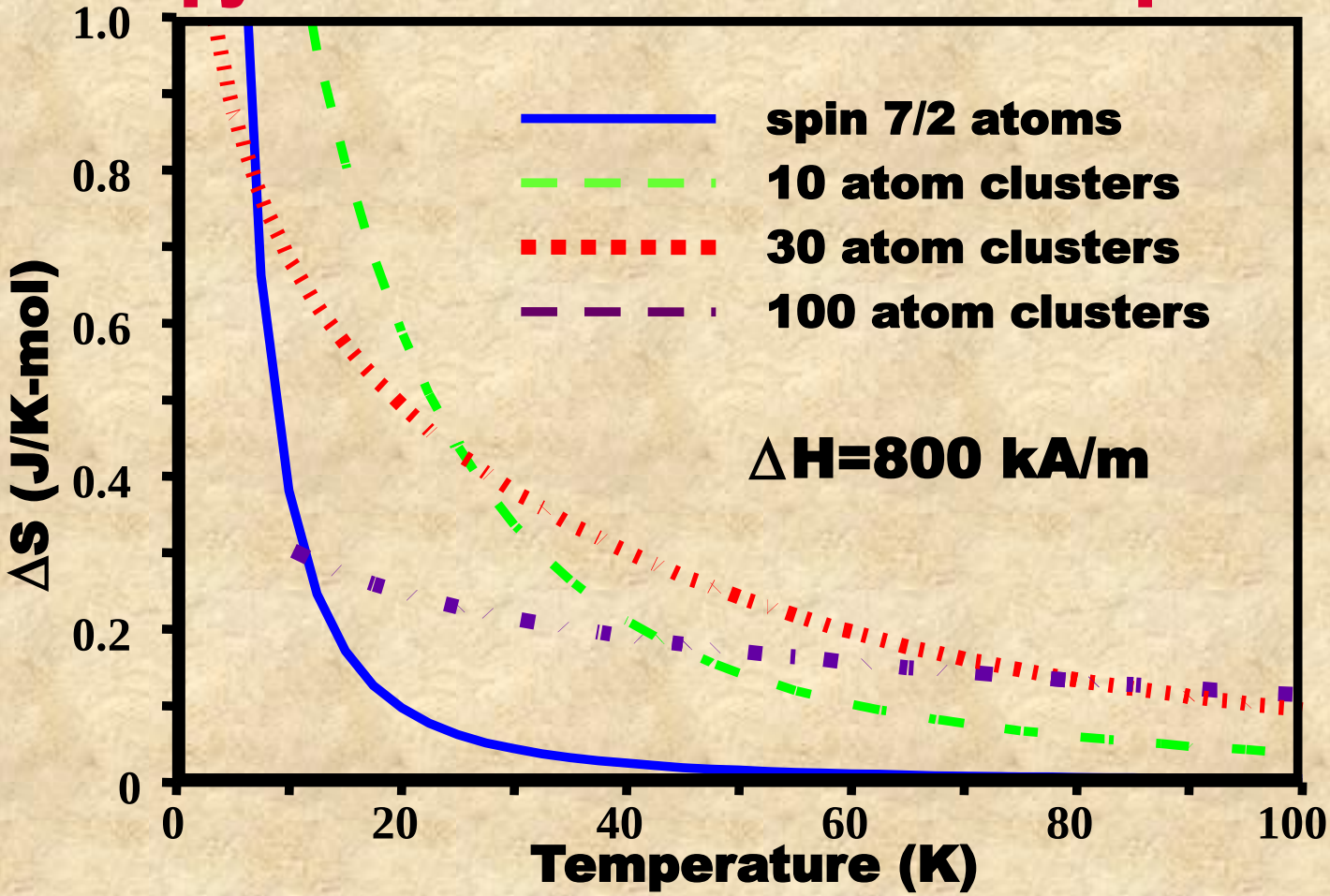
Refrigerator



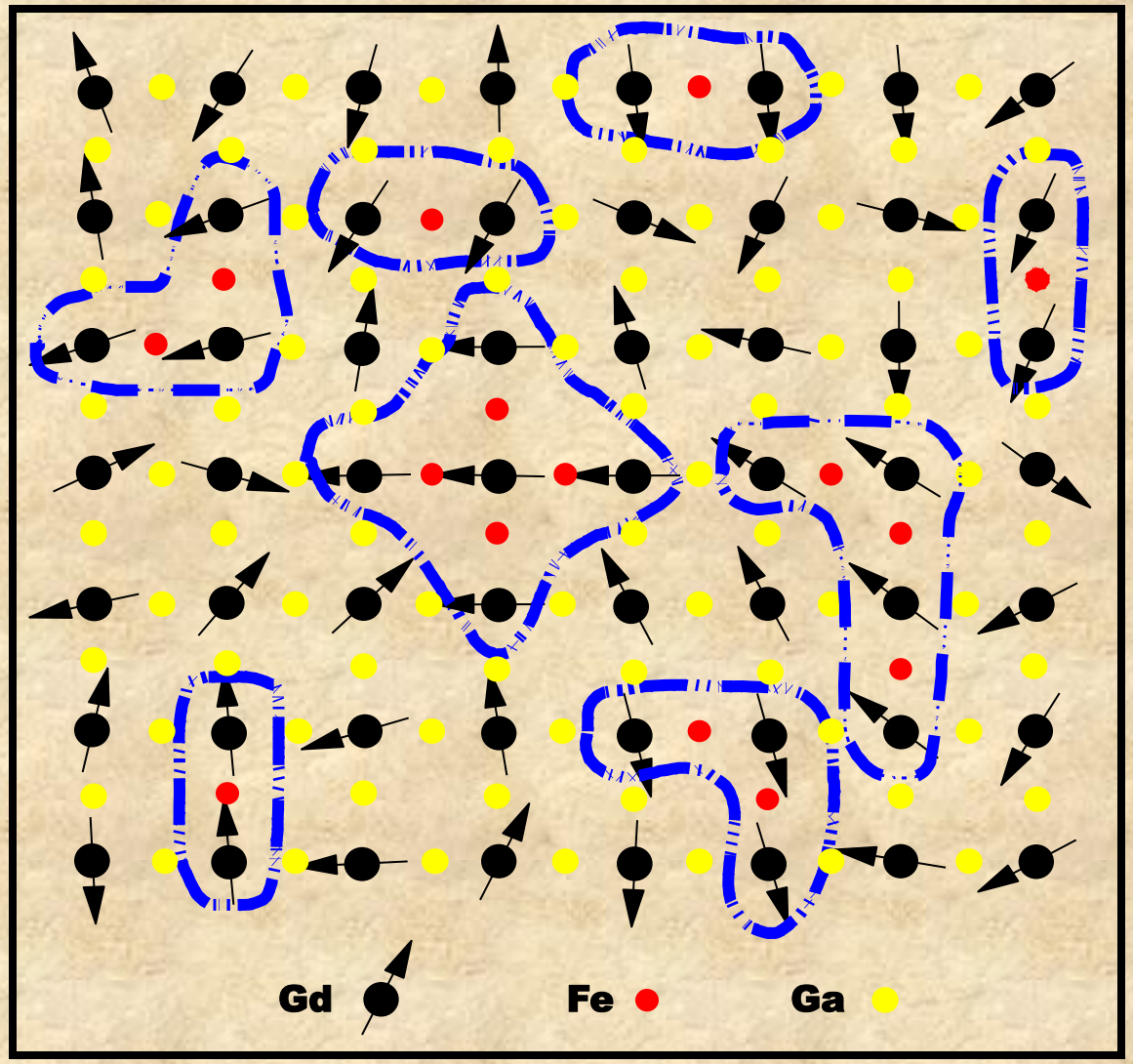
WHY MAGNETIC REFRIGERATORS ???

- Large Entropy Change on Ordering
  (40-200 times that of a gas)
- Based on a REVERSIBLE Process
  (Carnot efficiencies conceivable)
- Refrigerant and Heat Transfer Media are
  DIFFERENT (No chlorofluorocarbons, CFCs)
- No Compressor & Few Moving Parts
  (Low vibration, High durability)

Entropy Enhancement in Nanocomposites



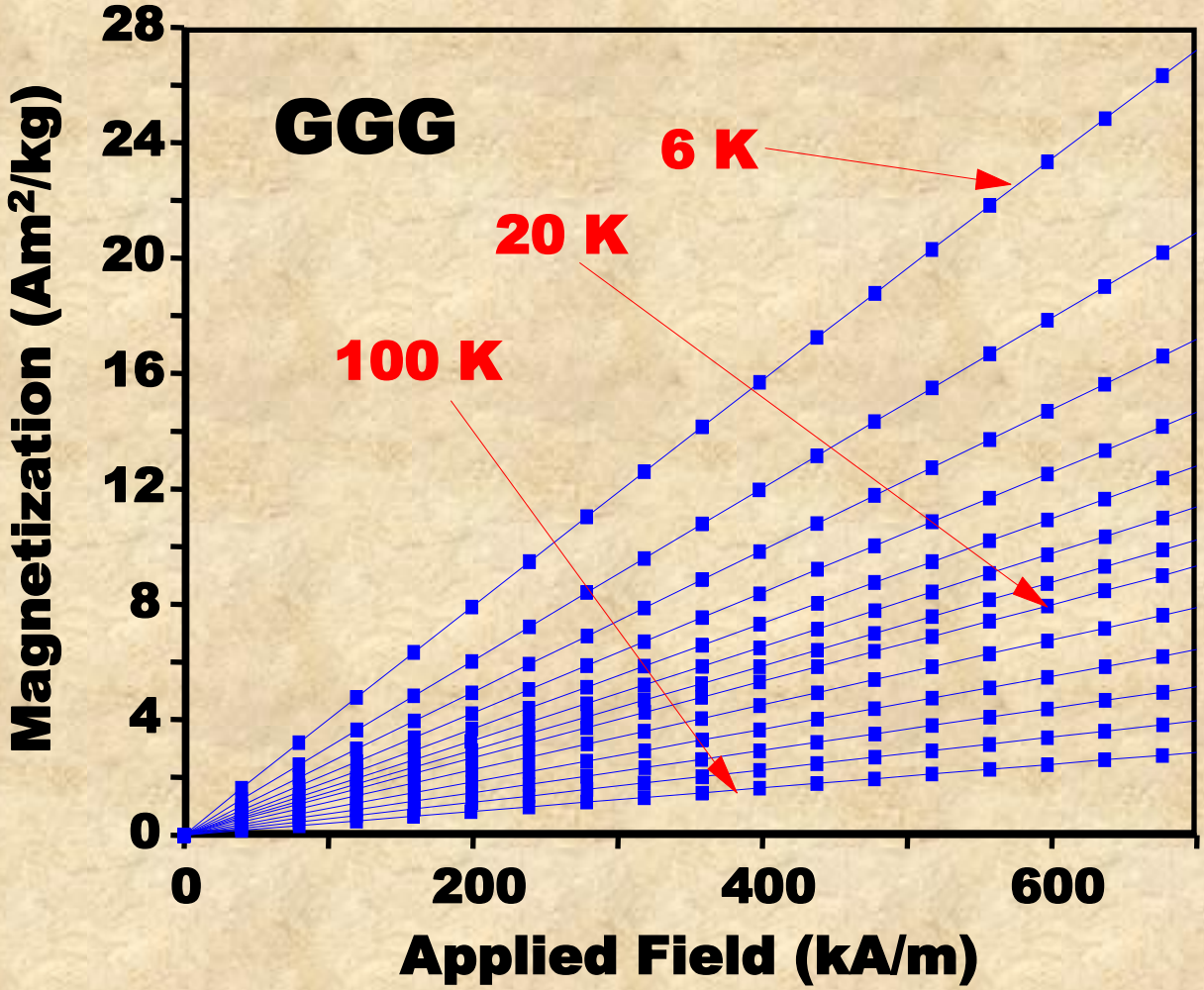
Grouping the atoms together in clusters gives larger entropy changes than single atoms in the ∆H,T regiemes accessible by refrigerators.



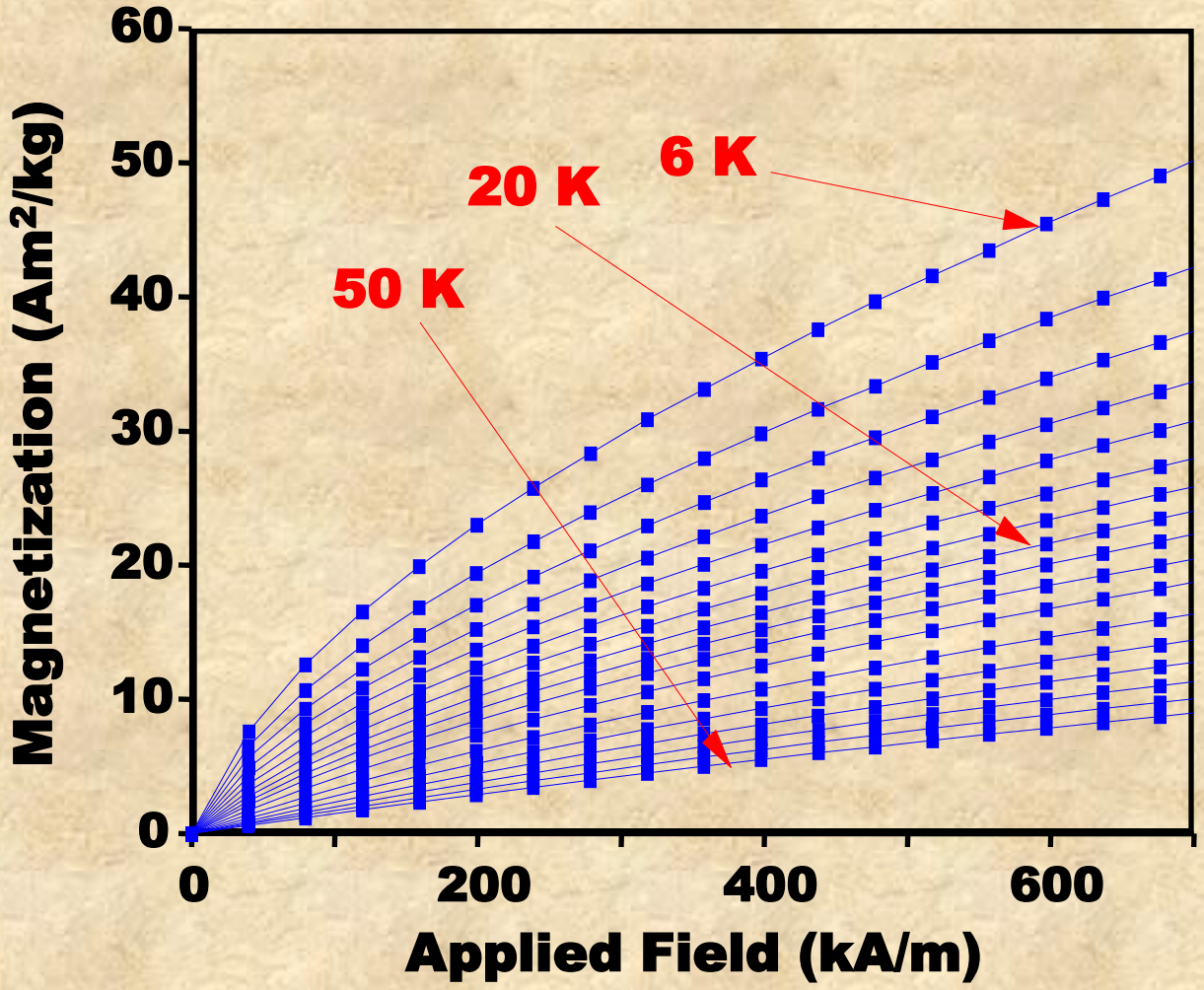
Fe spins create Magnetic Clusters

Schematic Picture of $Gd_3Ga_{5-x}Fe_xO_{12}$ Magnetic Nanocomposites

$Gd_3Ga_5O_{12}$ Magnetization Isotherms

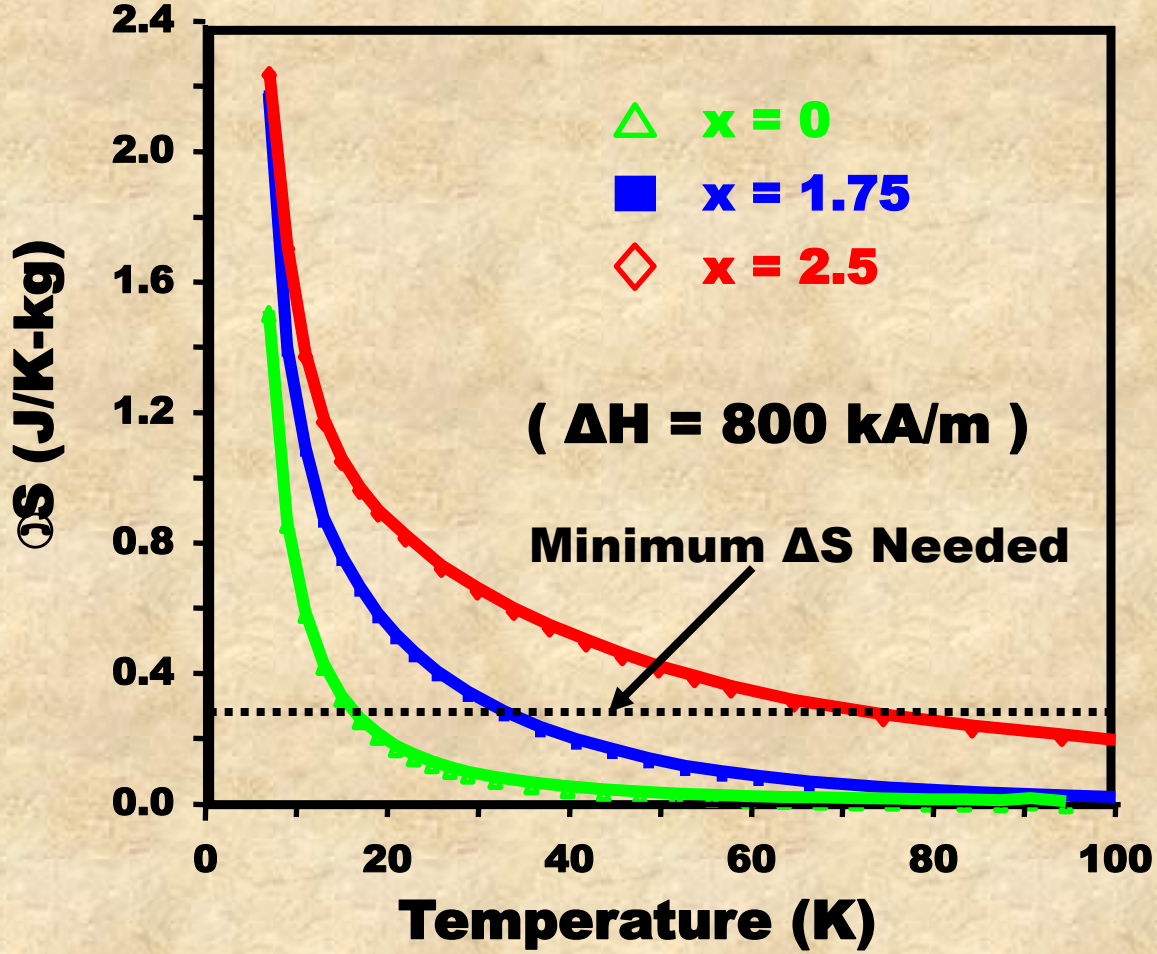


$Gd_3Ga_{3.25}Fe_{1.75}O_{12}$ Magnetization Isotherms



Curvature shows the material has nanometer-sized clusters, thereby possessing super-paramagnetism

Magnetocaloric Effect Entropy Changes for $Gd_3Ga_{5-x}Fe_xO_{12}$ Nanocomposites



And you Don't need to worry about magnetic Hysteresis Effects!!!

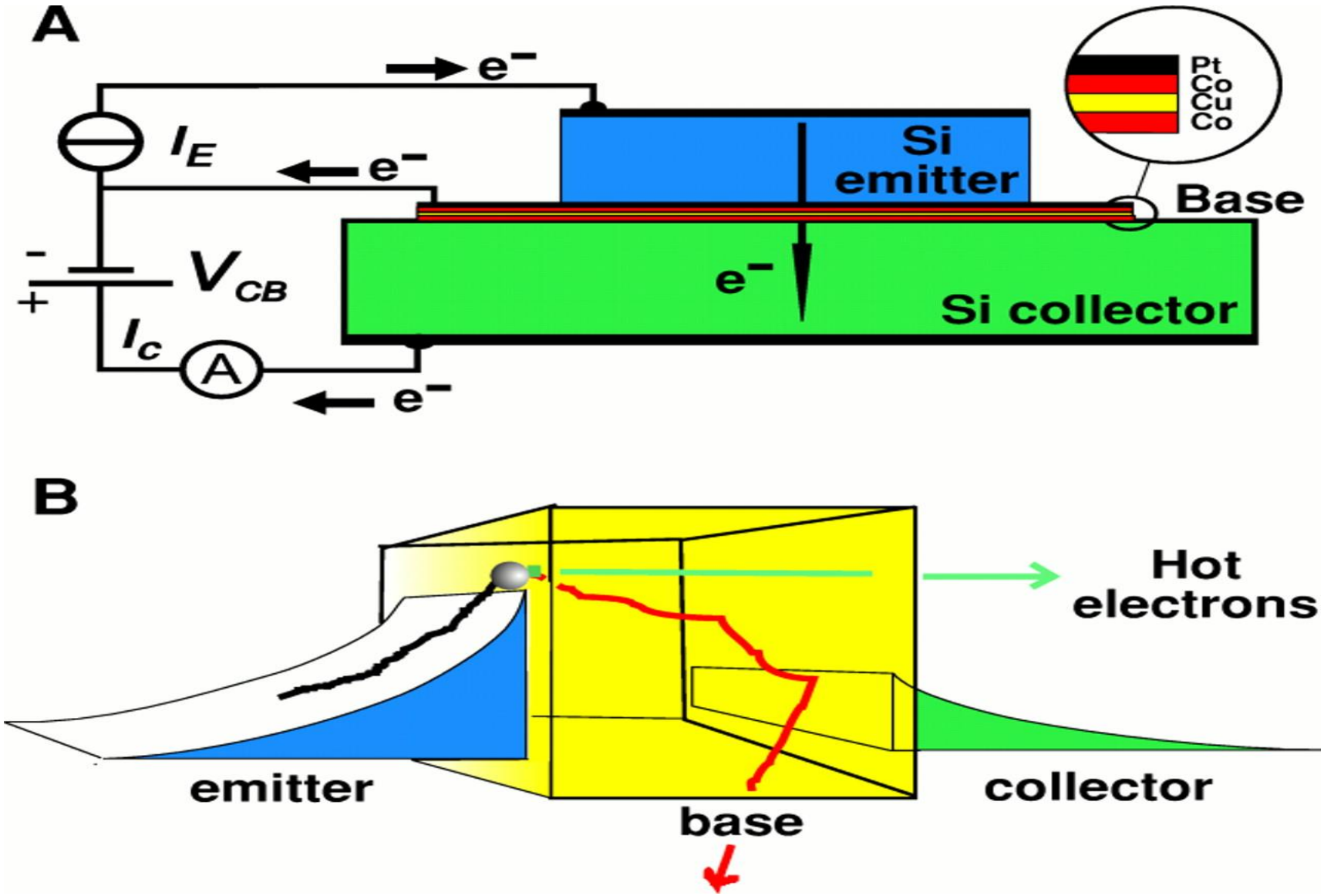
US Patent No. 5,381,664 Jan 17, 1995

R. McMichael, J. Ritter, R. Shull, J. Appl. Phys. 73, 6946 (1993).

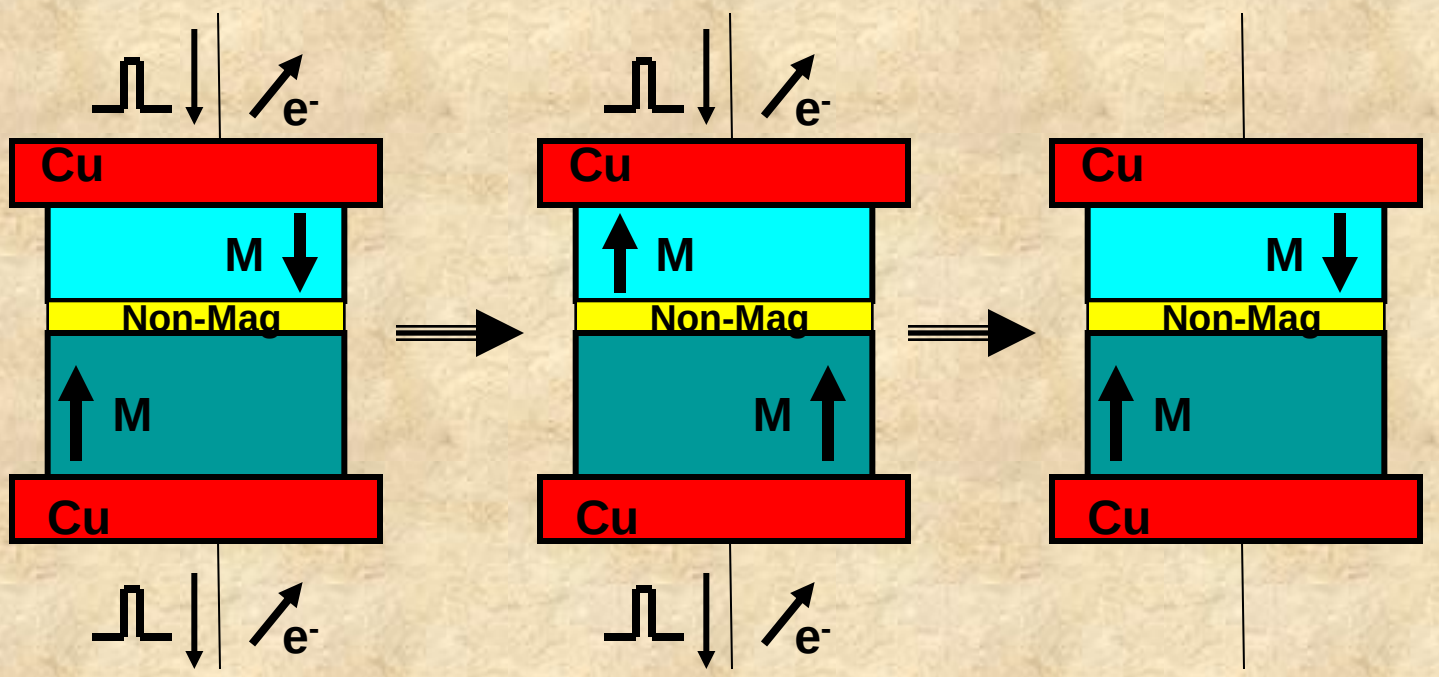
NEW ELECTRONICS PARADIGM

(USE OF THE SPIN ON AN ELECTRON
RATHER THAN ITS CHARGE
AROUND WHICH TO DESIGN
NOVEL ELECTRONIC DEVICES)

SPIN TRANSISTOR



SPIN – TORQUE SWITCHING



- Use of an electric current pulse to switch the magnetization direction of a thin ferromagnetic (FM) film
- Electron spin must be not be collinear with M
- Lateral size of the FM must be less than 50 nm so current H is small
- Lateral size of the FM can be easily scaled down for higher density

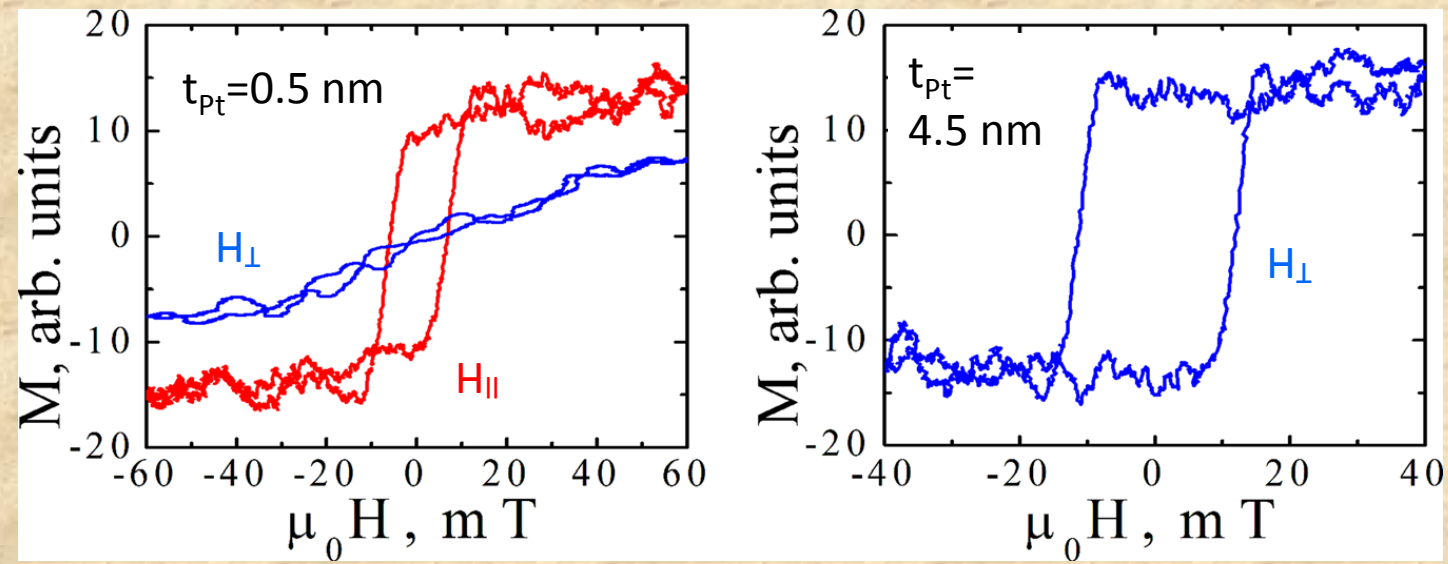
FUTURE DIRECTIONS

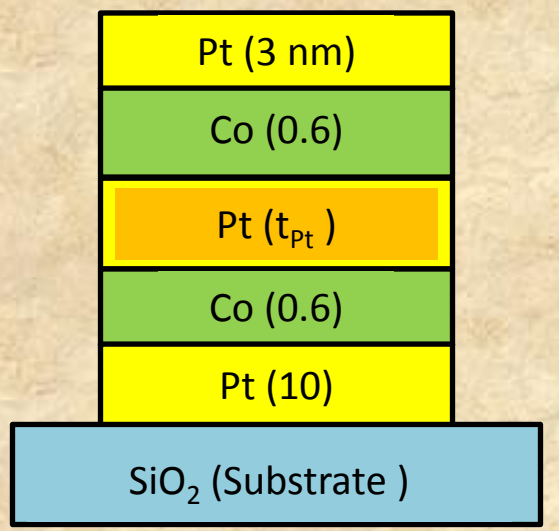
USE OF INTERFACES

TO CONTROL

MAGNETIC ANISOTROPY

Nanofunctional Materials





Shows variation in the Pt layer thickness can change the in-plane magnetic anisotropy to perpendicular as that layer becomes thicker.

R. Shull, Y. Iunin, Y. Kabanov, V. Nikitenko, O. Skryabina, & C. Chien, J. Appl. Phys. 113, 17C101 (2013).

NIST
National Institute of Standards and Technology

FUTURE DIRECTIONS

CREATION OF SPIN CURRENTS

(WHERE ONLY SPIN IS CONDUCTED;

NO CHARGE IS CONDUCTED)

SUMMARY

- Increased surface/volume ratio of nanomagnets makes them more susceptible to interaction effects with neighboring magnetic materials.
- "Nanostructuring" a material can result in the creation of new magnetic states, like superparamagnetism.
- "Nanostructuring" can also affect Domain motion, making it surprisingly easier & resulting in very Soft ferromagnets
- Nanocomposites provide a means for designing better Hard ferromagnets (i.e., permanent magnets)
- Nanocomposites provide a means for moving Magnetic Refrigeration to Higher Temperatures and Lower Fields
- "Nanostructuring" can enable control of magnetic anisotropy
- Small sizes allow flow through the body, enabling targeted drug delivery, treatment, and improved imaging
- Spintronic Devices may revolutionize electronic devices

1994 Nobel Prize in Physics

-Pioneer of Neutron Diffraction-

Clifford G. Shull
1915-2001

Swedish King
Carl XVI Gustav