NANOMAGNETISM (I)

WHAT IS IT????

SO WHAT????

Robert D. Shull

Leader: Magnetic Materials Group, National Institute of Standards and Technology

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

V. President: The Minerals, Metals, & Materials Society (TMS)

OUTLINE

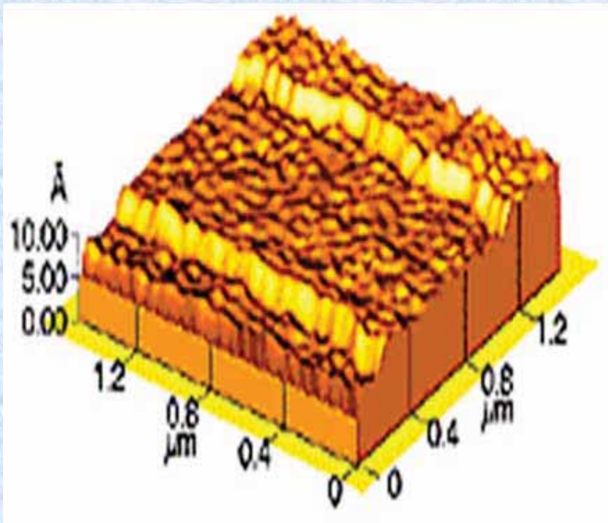
(I). What is Nanotechnology??

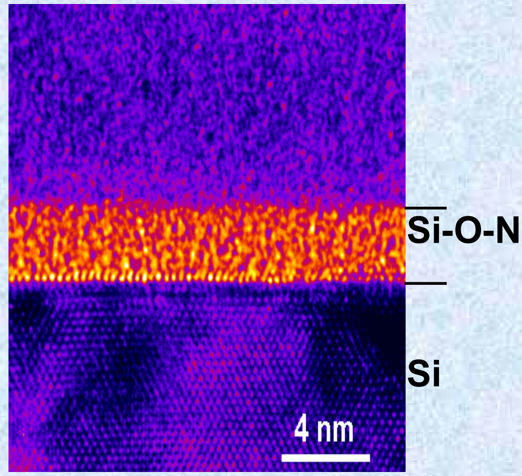
(II). Why is it Different???

(III). Nanomagnetism Changes
- -New Magnetic States
- -Time Dependence
- -Soft Magnetic Behavior

(IV). Summary

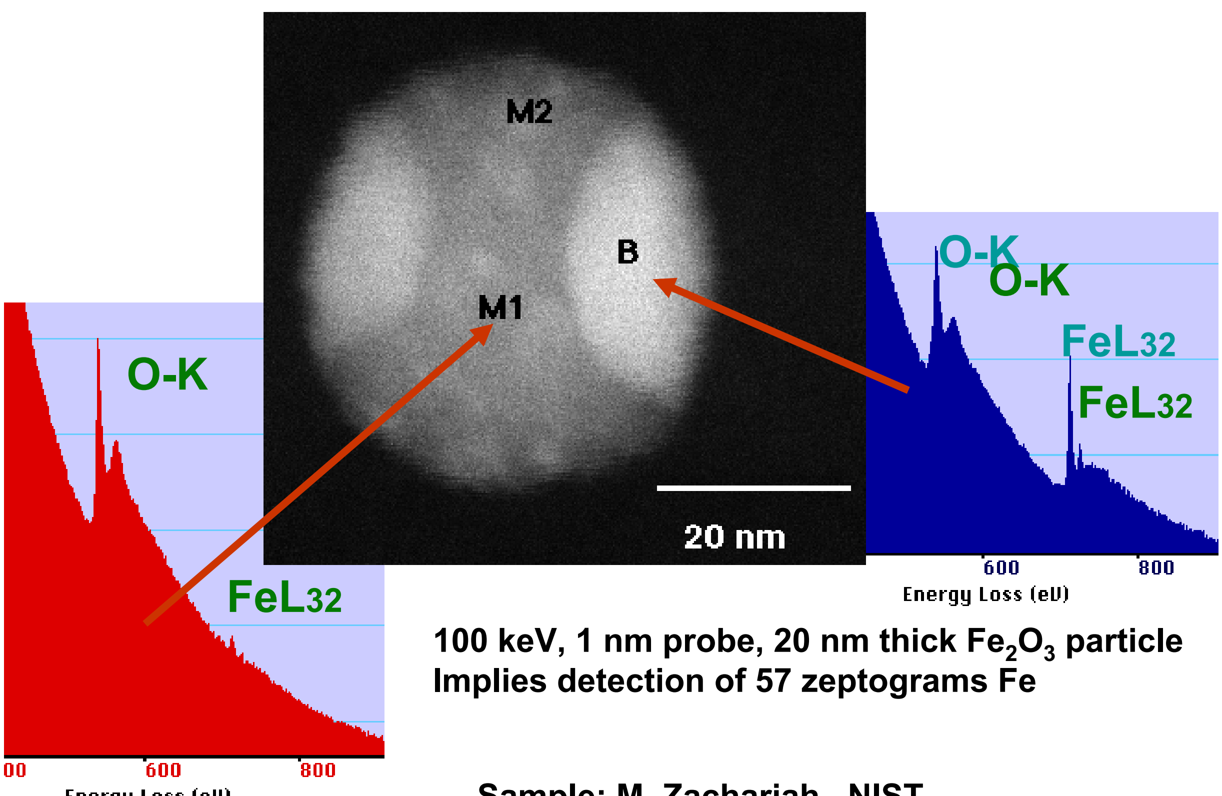
NANOTECHNOLOGY IS THE ABILITY TO CONSTRUCT STRUCTURES WITH ATOMIC LEVEL CONTROL





Silicon Oxynitride
On Silicon
(J.H. Scott, NIST)

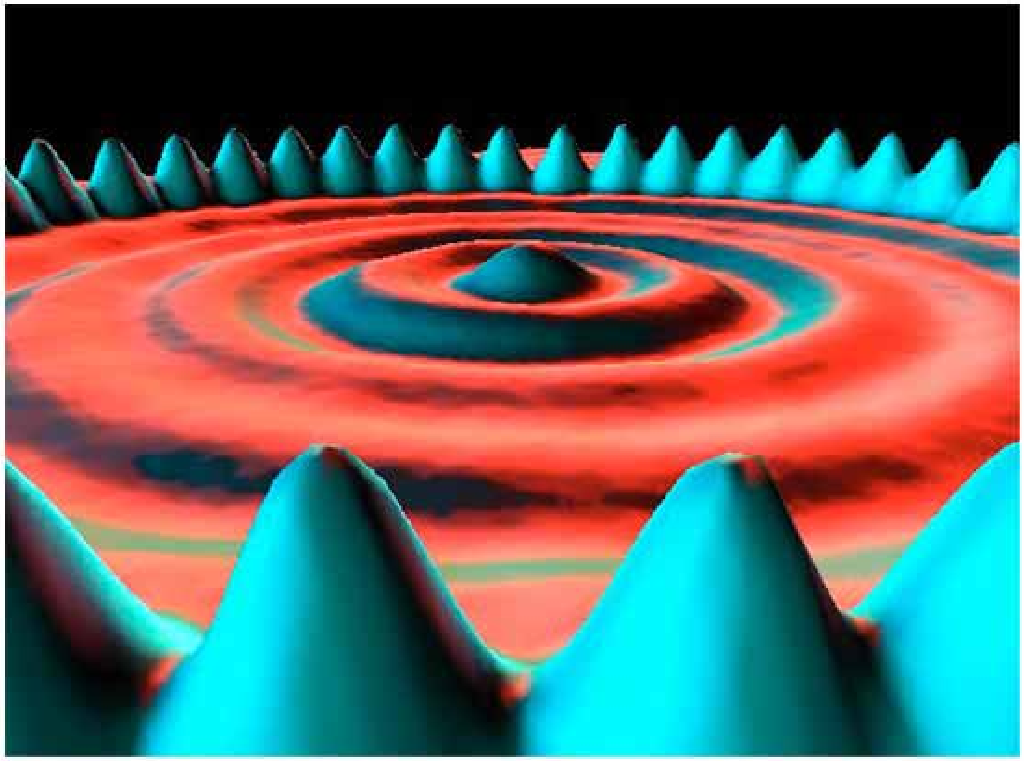
Flame Synthesized SiO_2-Fe_2O_3



100 keV, 1 nm probe, 20 nm thick Fe_2O_3 particle
Implies detection of 57 zeptograms Fe

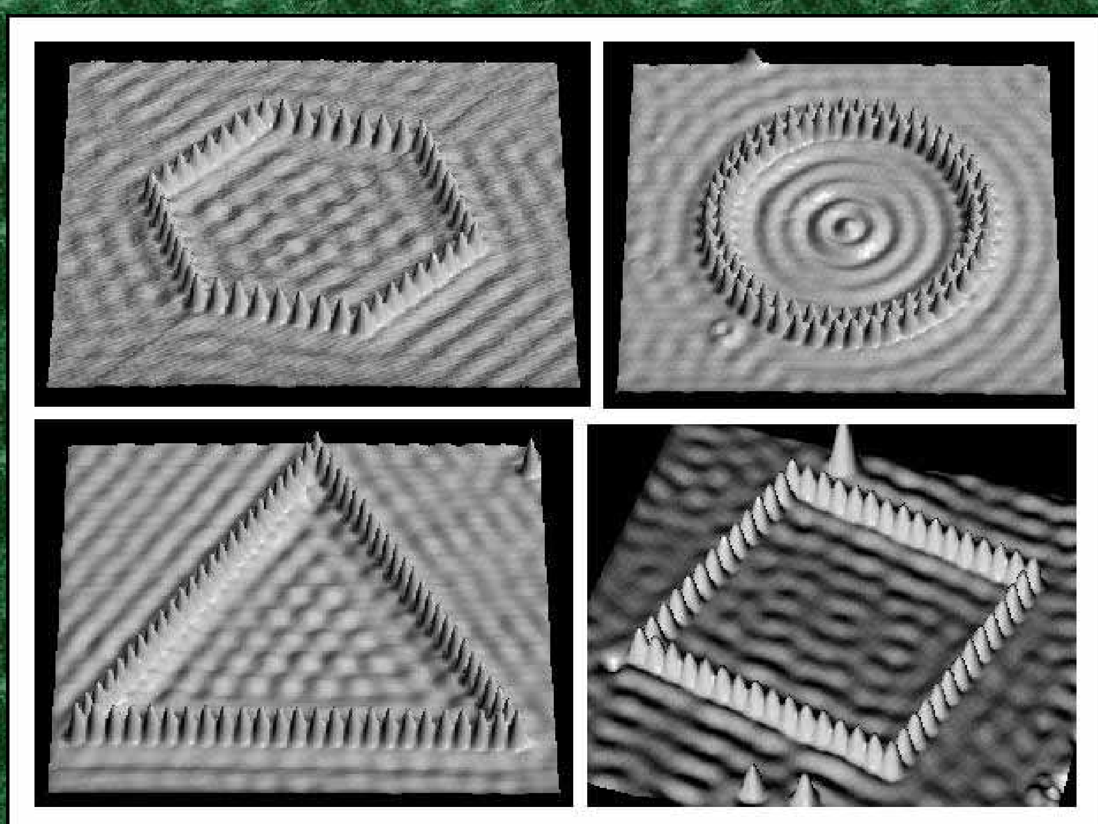
Sample: M. Zachariah, NIST
Analysis: D. Newbury, NIST

QUANTUM CORRAL (Fe atoms on Cu)



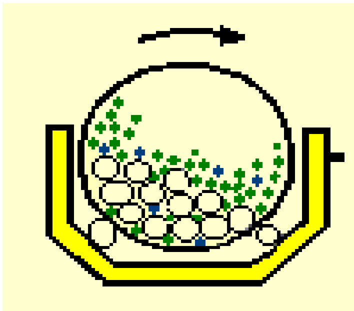
(Don Eigler, IBM-Almaden)

QUANTUM CORRALS (Fe on Cu)

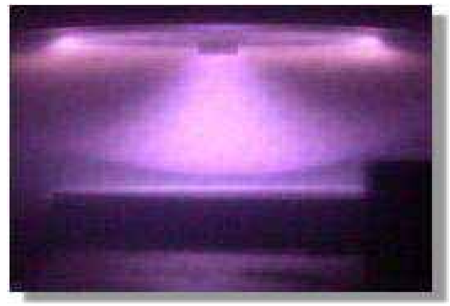


(Don Eigler, IBM Almaden)

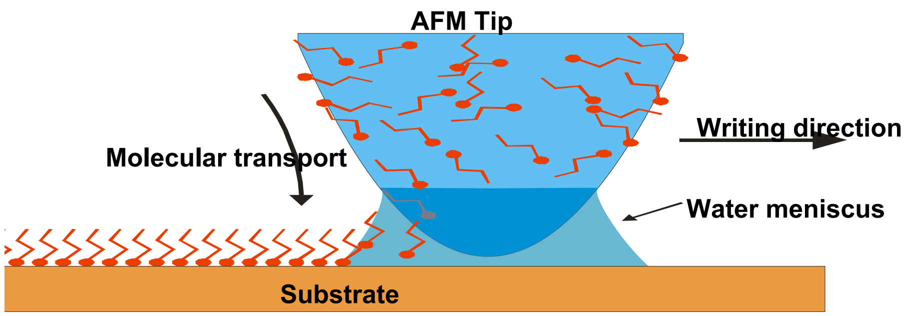
PRODUCTION METHODS



Mechanical Alloying



Plasma or Vapor Deposition



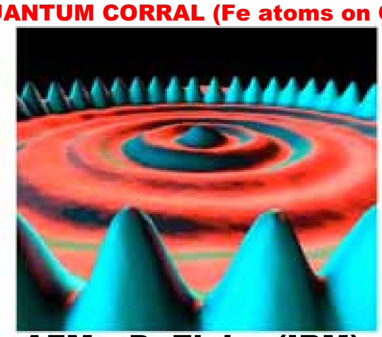
Dip Pen Lithography: Chad Mirkin (Northwestern Univ.)

PRODUCTION METHODS

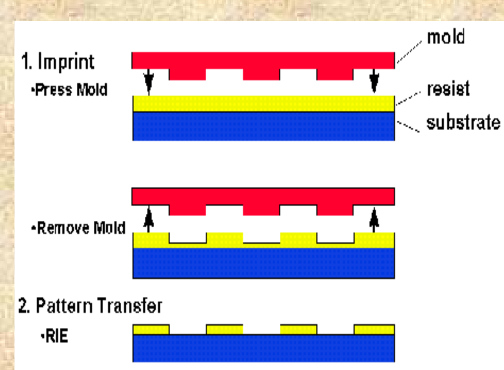
- Sputtering
- Inert Gas Condensation (IGC)
- Plasma Vapor Deposition (PVD)
- Condensed Vapor Deposition (CVD)
- Pulsed Laser Deposition (PLD)
- Chemical Precipitation from Solution
- Ion Replacement & Reduction
- Sol Gel Chemistry
- Solid Solution Precipitation
- Rapid Solidification (RSP)
- Mechanical Alloying (MA)
- Electrodeposition
- Filling of Nanopores
- Dip Pen Lithography
- Nanoimprint Lithography (NIL)
- Atomic Force Microscope
- Self Assembled Monolayers (SAMs)

⋮

QUANTUM CORRAL (Fe atoms on Cu)



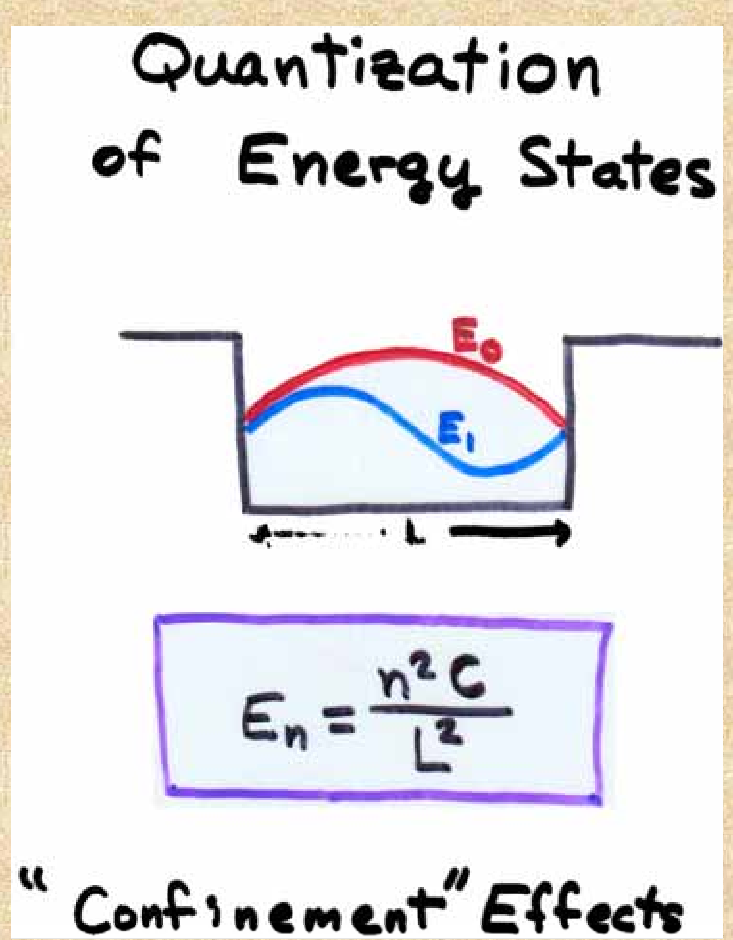
AFM – D. Eigler (IBM)



NIL – S. Chou (Princeton)

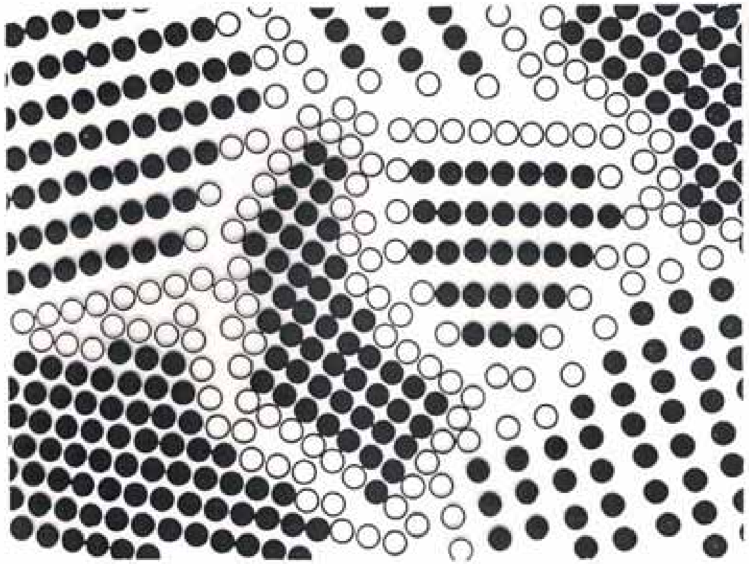
THREE REASONS WHY PROPERTIES ARE DIFFERENT WHEN MATERIALS POSSESS SOME NANOSCALE DIMENSION

(1)



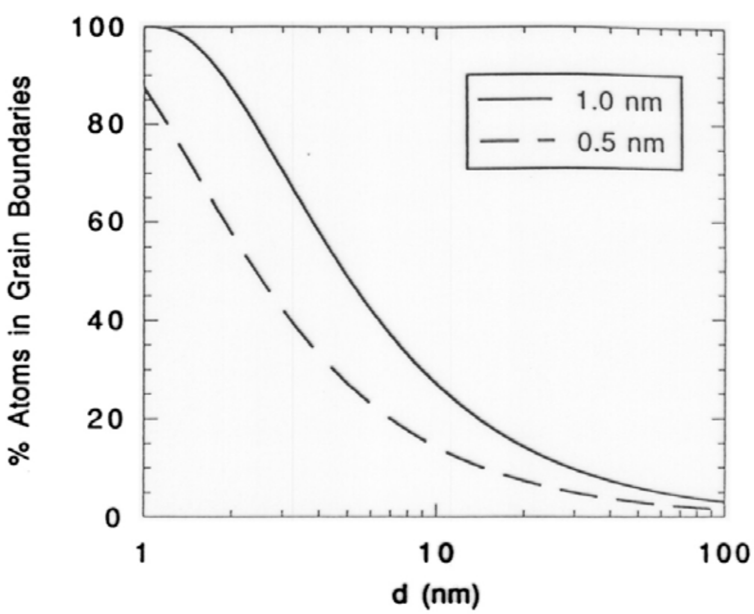
(2)

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**

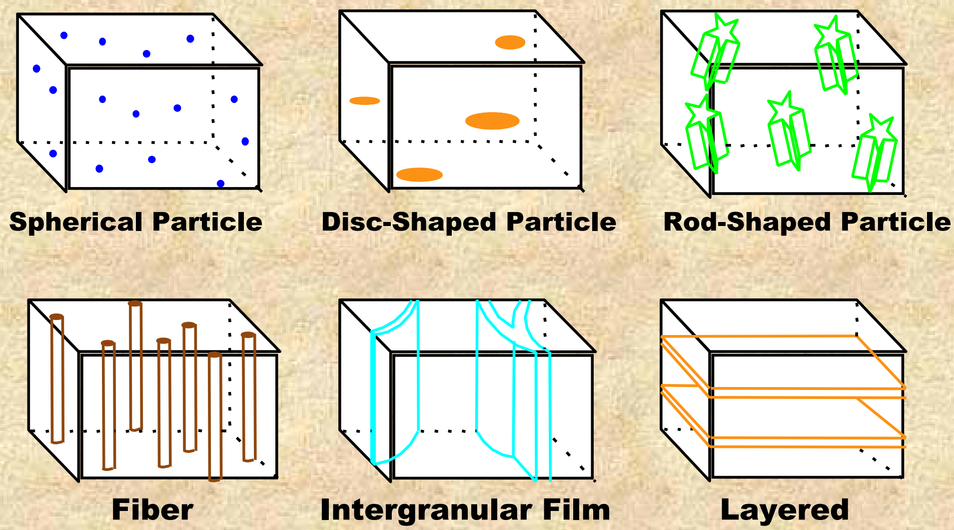
Resistivity – mean free path
Thermal Conductivity – mean free path
Strength – dislocation Burgers vector
Transmission & Reflection - wavelength
Diffraction & Scattering - wavelength
Absorption – penetration depth
Atomic Transport – diffusion length
Superconductivity – coherence length
Elasticity – bond & chain lengths
Reaction Rate – diffusion length
Boundary Motion – radius of curvature
Fluid Flow – boundary layer thickness
Magnetism – exchange length, domain wall width

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

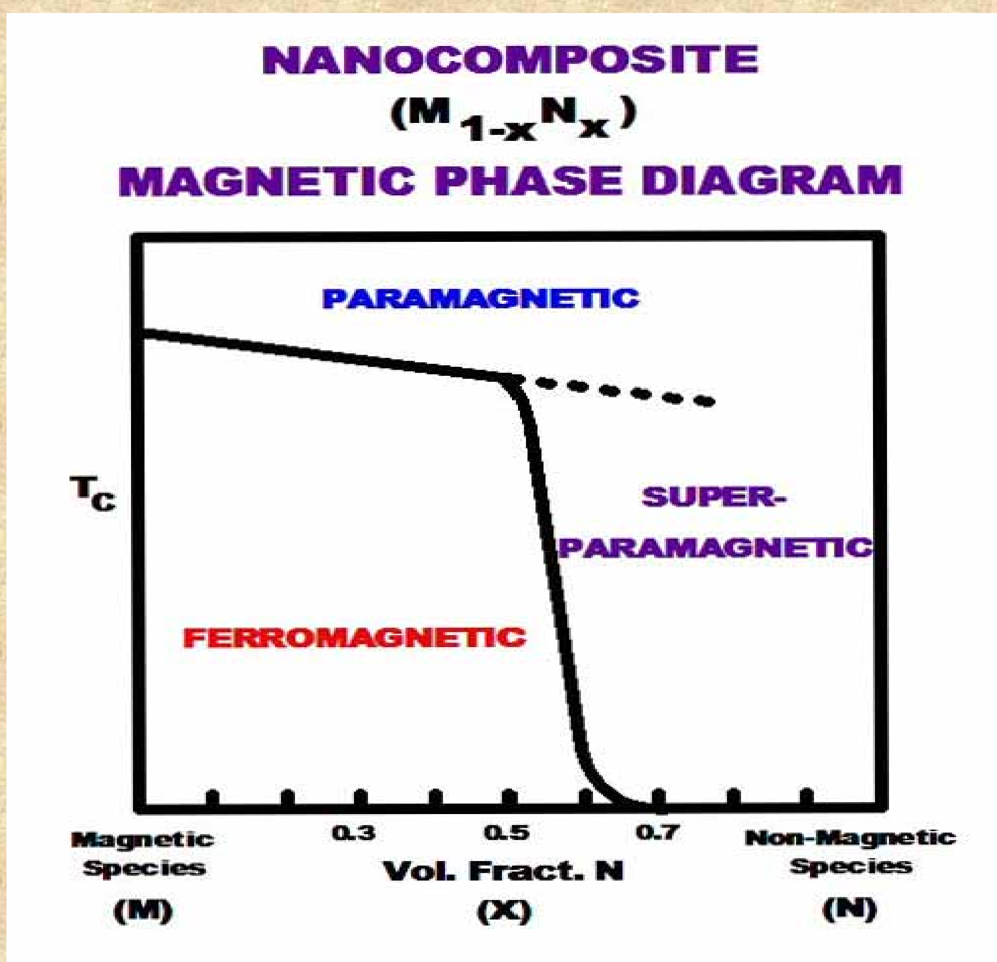
(Calculated by Michael Coey, Univ. of Dublin)

NANOCOMPOSITE MORPHOLOGIES

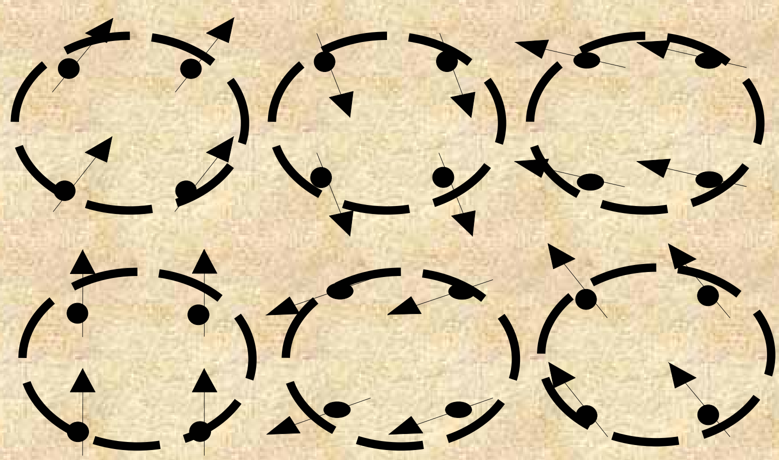


Critical Dimensions:

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



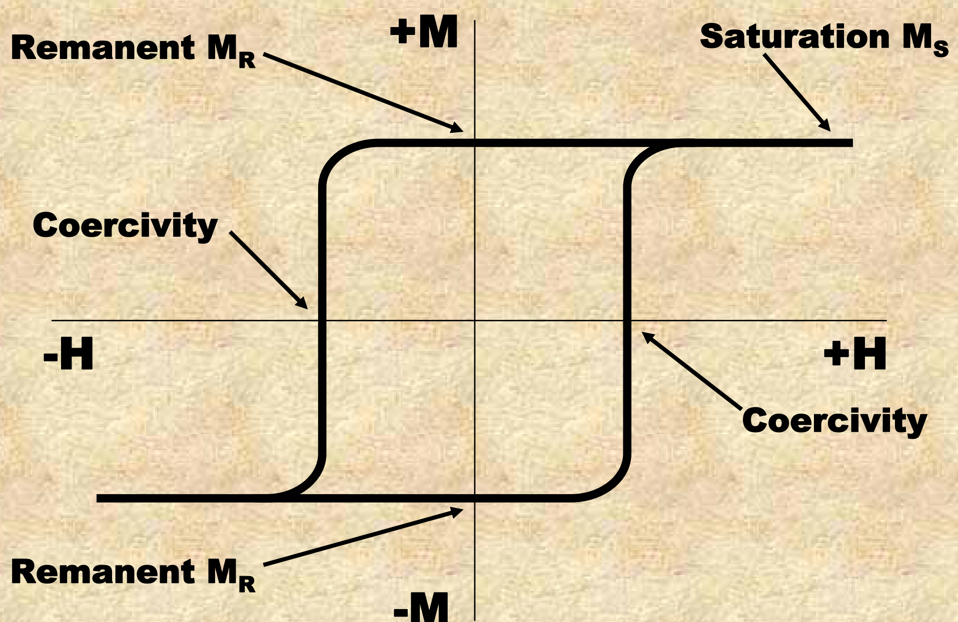
SMALL PARTICLE BEHAVIOR



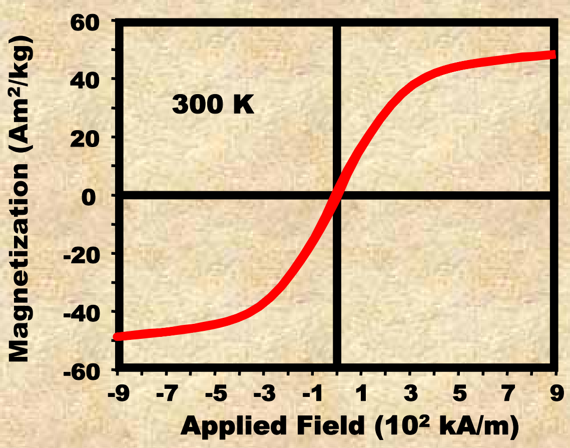
Assembly of magnetic clusters (each comprised of many ferromagnetically-aligned elemental moments of magnitude μ) acting independently.

= Superparamagnetic Material:

HYSTERESIS LOOP OF A FERROMAGNET



SUPERPARAMAGNETISM

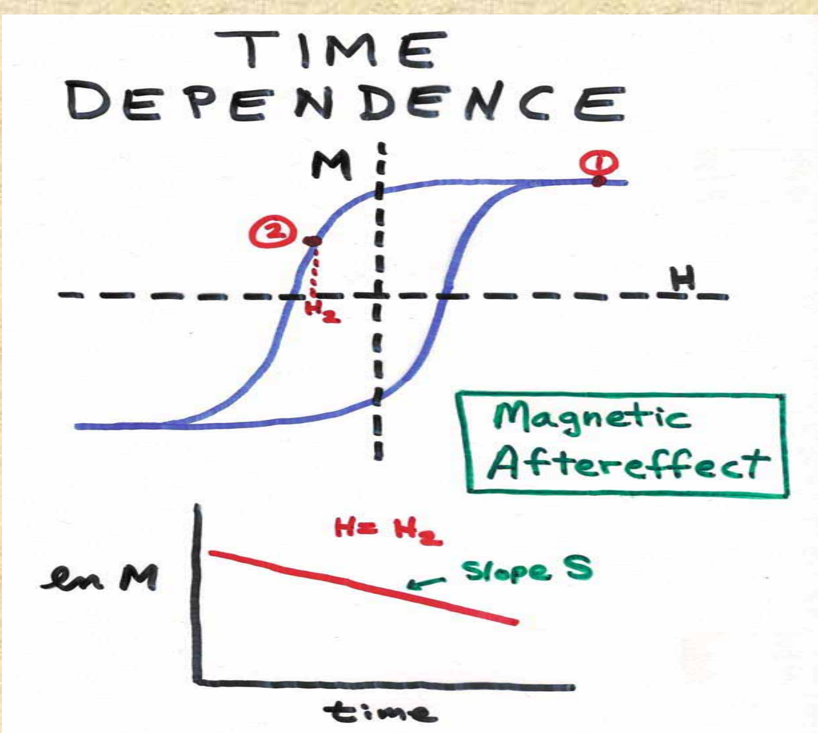


Applications:

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

No Remaining Magnetism Upon Field Removal!!!

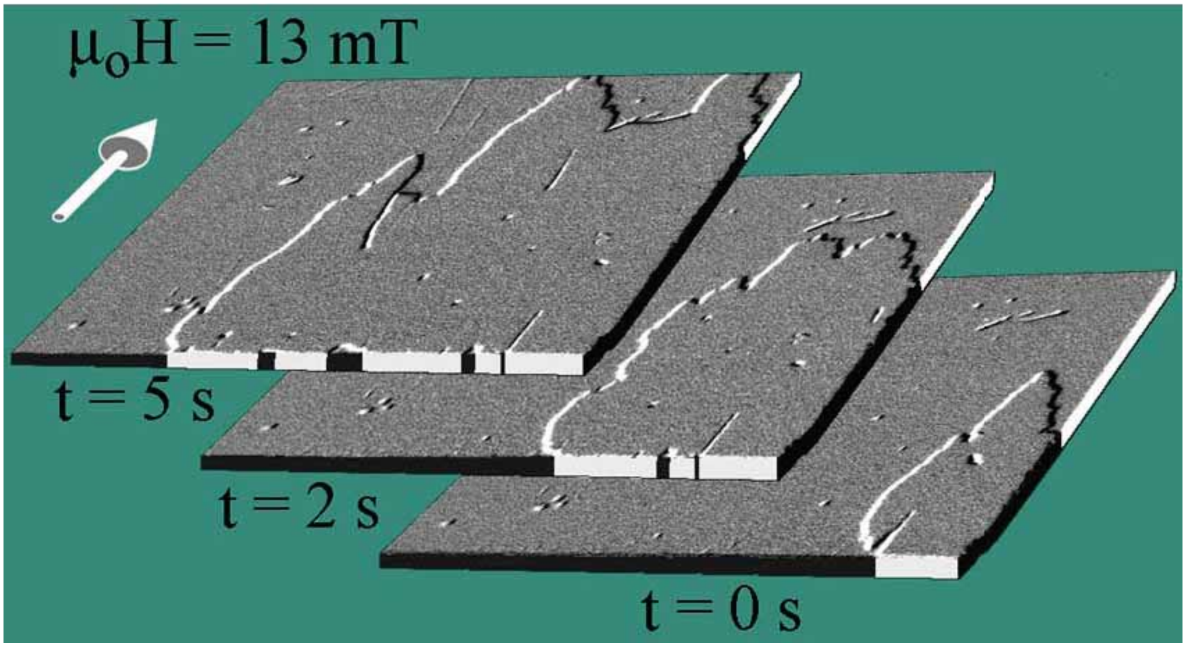
(Occurs when Particles are Very Small and Decoupled)



A New Concern for Nano-Magnetic Materials

For conventional Ferromagnets, there is no time dependence, so this is a new constraint on the application of Nanomagnets.

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

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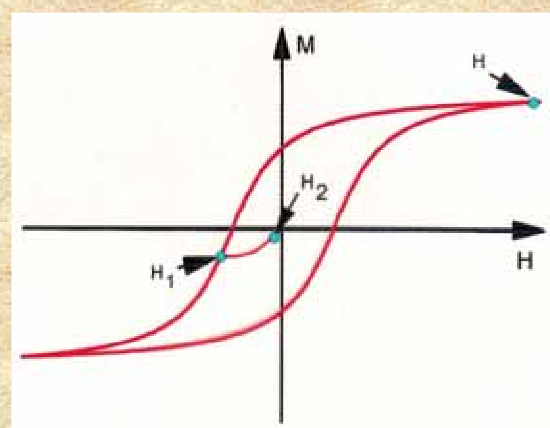
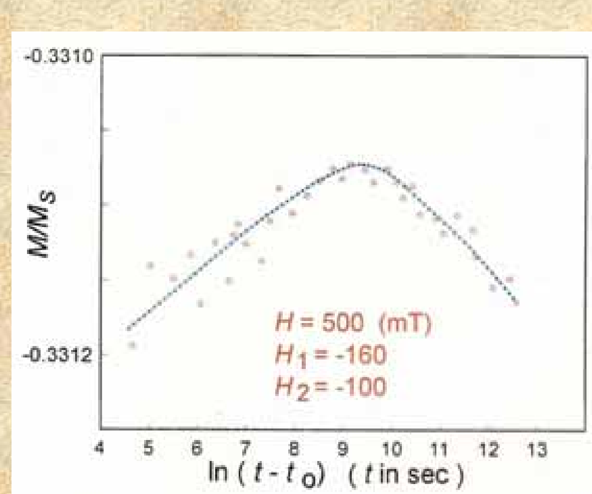
TIME DEPENDENCE



Results in
2 Time Constants!



Two-Step Field-Change Method

Which Method is Best???

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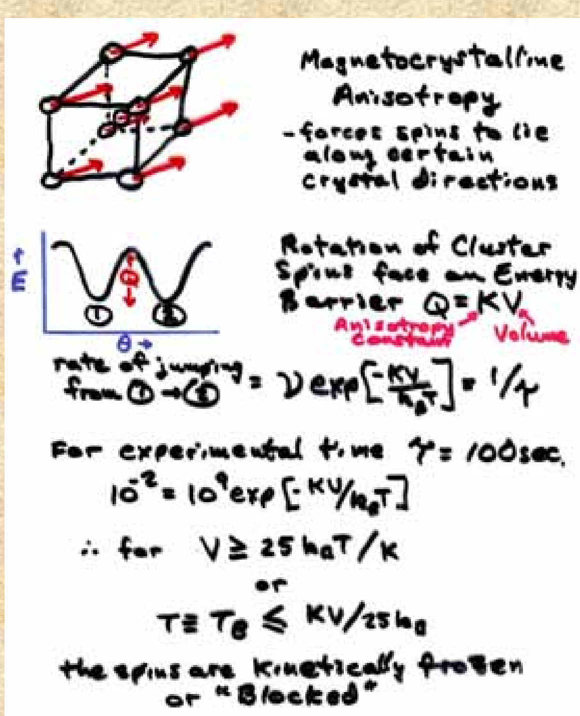
Kinetically Frozen Nanoparticle Moments



In nanoparticles, the Magnetic moments 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.

HIGHER DENSITY

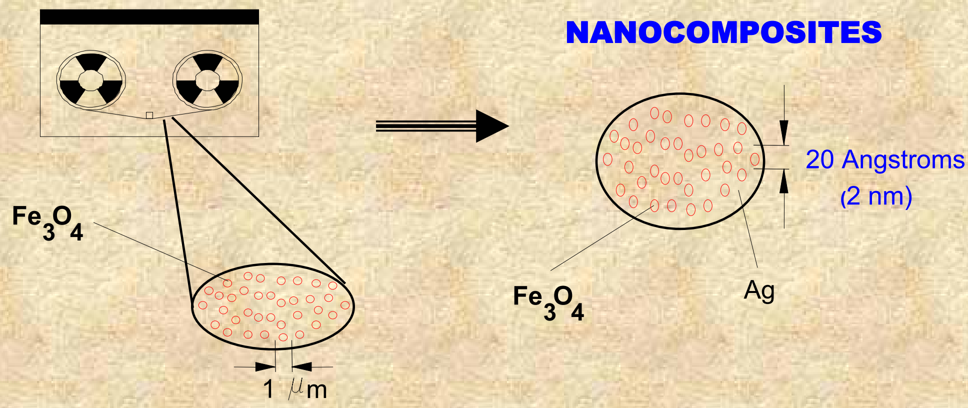
MAGNETIC RECORDING MEDIA

CHANGES WITH SIZE REDUCTION

(BOTH THICKNESS & LATERAL SIZE)

IMPROVED MAGNETIC RECORDING MEDIA

Conventional Media | **High Density Media**



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

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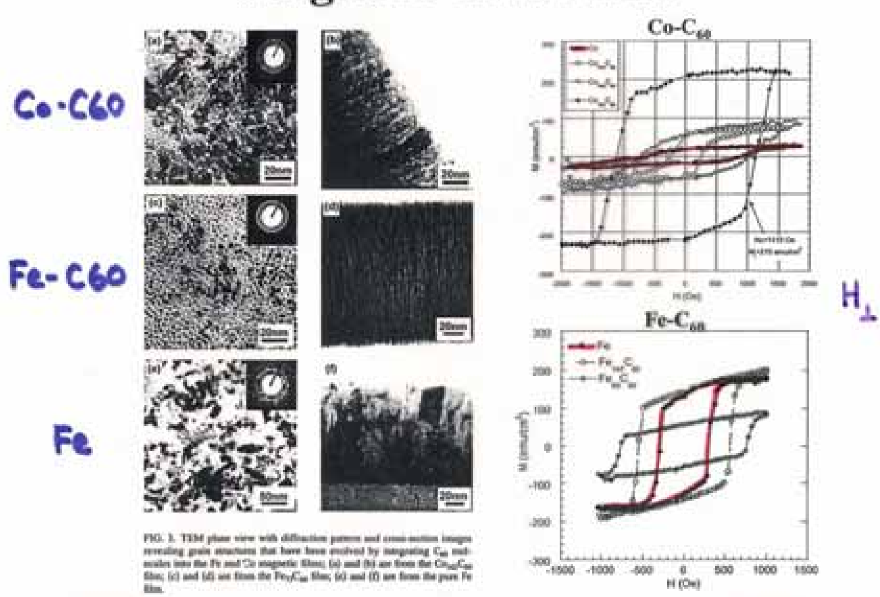
NOVEL Metal-C60 Nanocrystalline Magnetic Thin Films



L.A. Zheng, B.M. Lairson, E.V. Barrera, R.D. Shull, APL 77, 3242 (2000)

NIST
National Institute of Standards and Technology

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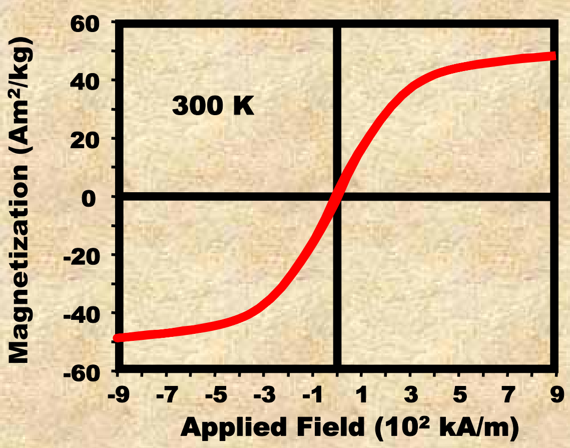
SUPERPARAMAGNETISM SETS A LIMIT TO PARTICLE (“BIT”) SIZE REDUCTION!!!



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)

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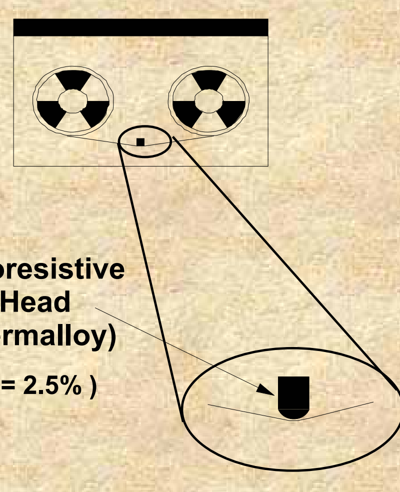
NEED FOR HIGHER SENSITIVITY MAGNETIC FIELD SENSORS WITH PARTICLE SIZE REDUCTION

(Also true for Biological Applications of Small Magnetic Particles)

MAGNETORESISTANCE

Recorder Heads



Giant Magnetoresistance (GMR) Heads

($\Delta\rho/\rho$ > 50%)

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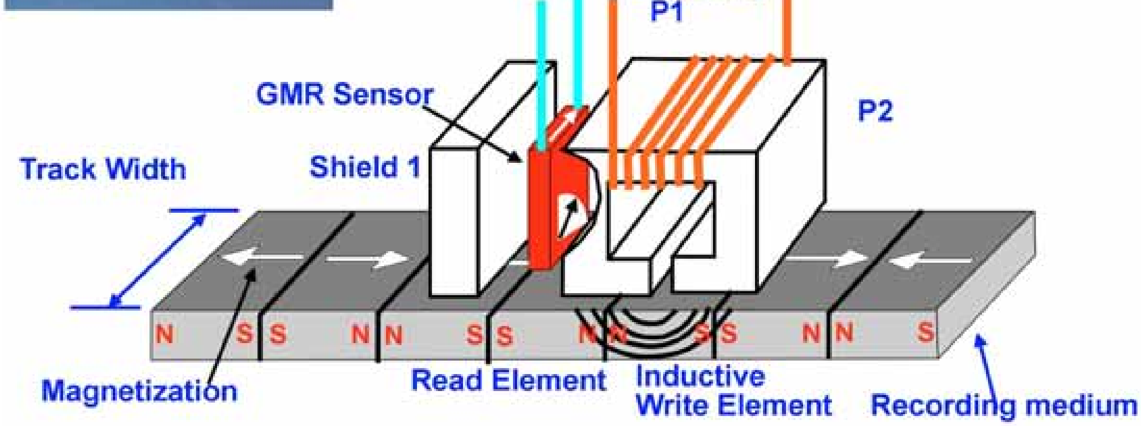
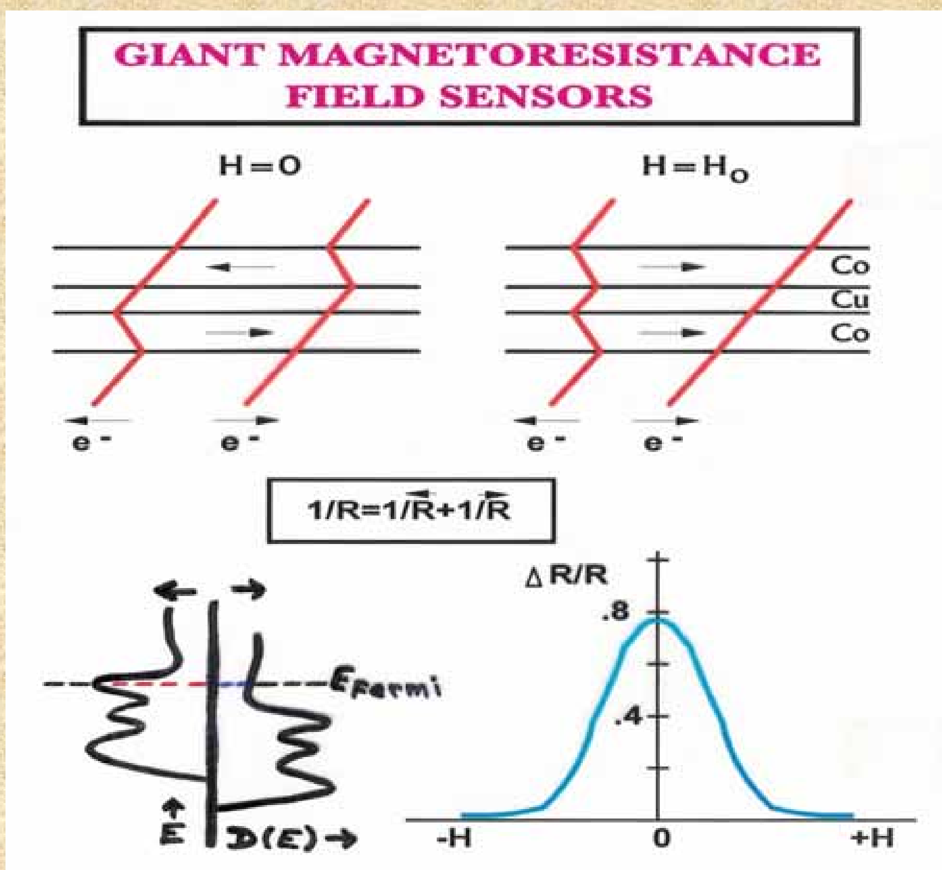
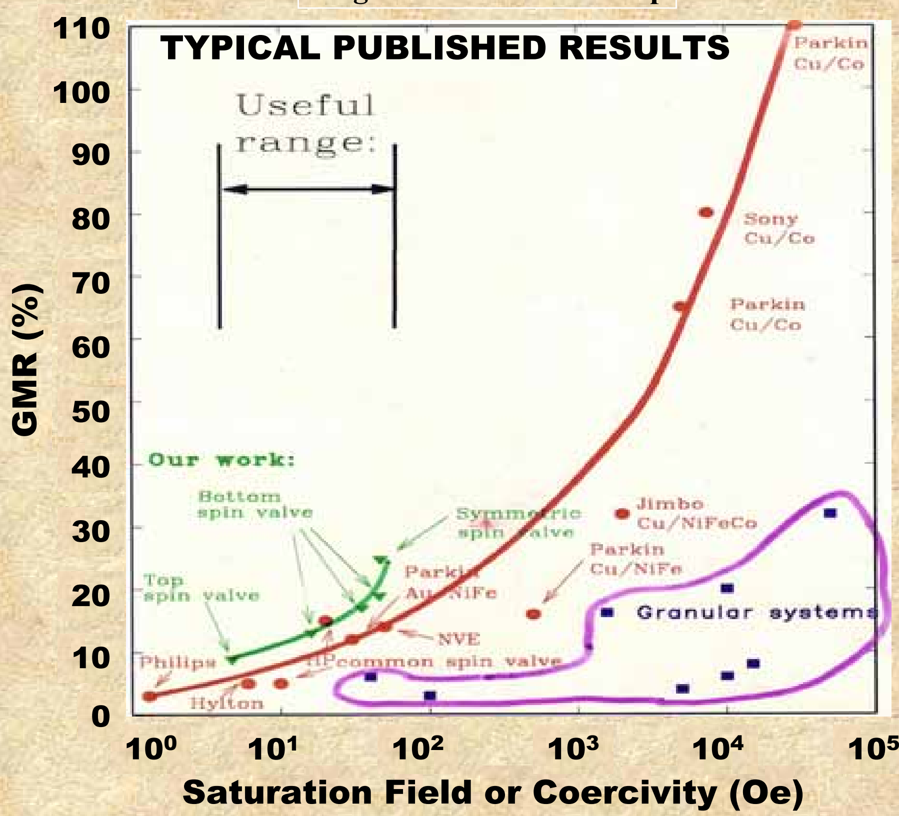


Magnetic recording process.

Ed Grochowski
IBM Almaden Research Center

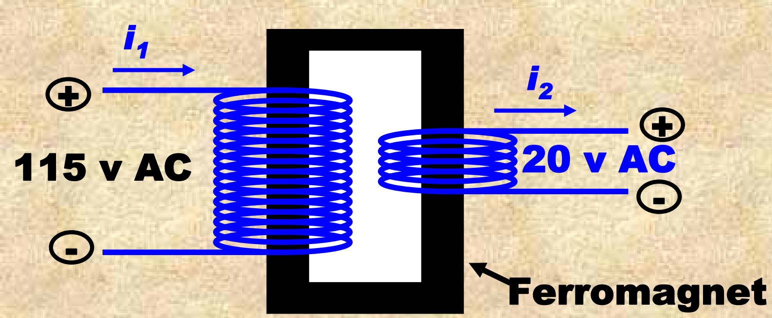


[Baibich, et. al., Phys. Rev. Lett. 61, 2472 (1988).]

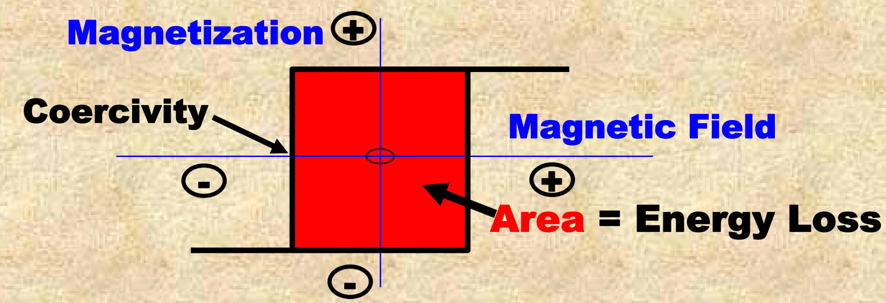


SOFT MAGNETIC PROPERTIES ARE DIFFERENT WHEN MATERIALS POSSESS SOME NANOSCALE DIMENSION

TRANSFORMER



“Hysteresis Loop” of Ferromagnet



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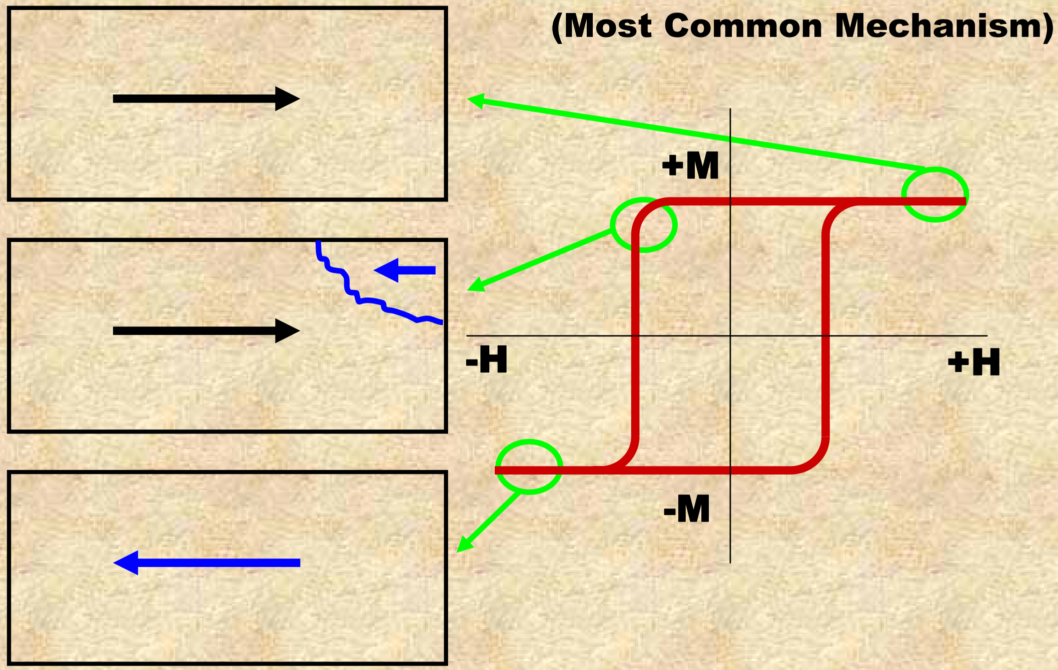
Magnetization Reversal by Domain Nucleation & Growth

(Most Common Mechanism)



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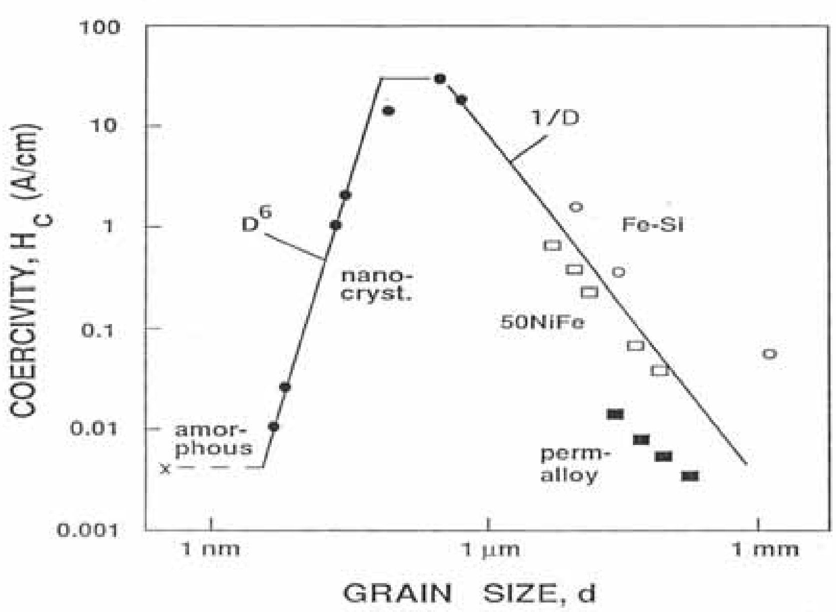
ENHANCED (AND REDUCED) MAGNETIC COERCIVITY



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

- **Normally, coercivity increases with decreasing grain size.**
- **But, when the grain size becomes comparable to the domain wall width, magnetic coercivity begins dropping with the grain size and magnetic hysteresis decreases!!!**

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" a material can also result in a Time dependence in the magnetization.**
- **Improved magnetic field sensors (using the GMR effect and resonance techniques) are now enabling e more applications, including biomedical.**
- **"Nanostructuring" can also affect Domain motion, making it surprisingly easier & resulting in the best transformers**

NANOMAGNETISM (II)

DOMAINS IN NANO-FERROMAGNETS???

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

V. President: The Minerals, Metals, & Materials Society (TMS)

OUTLINE

(I). **Domains in Nanomaterials?**

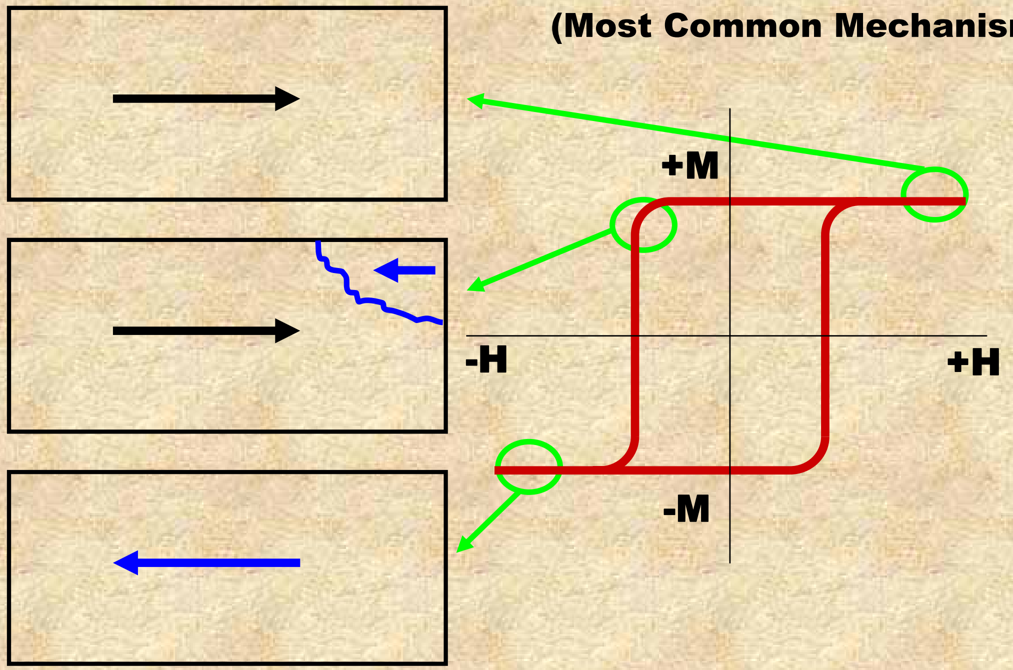
(II). **Size Dependence**

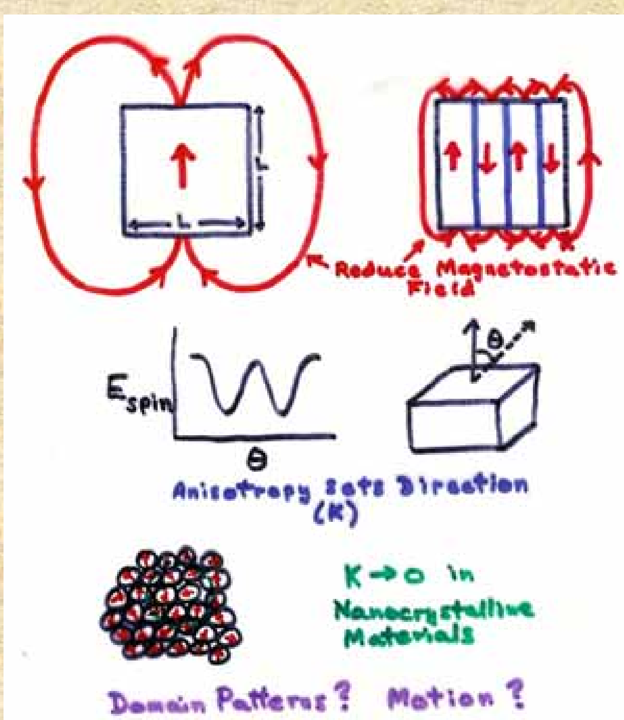
(III). **Domains in Thin Film Nanocomposites**
- **-AF/FM Bilayers**
- **-AF/FM Bilayers (AC-Demagnetized)**
- **-Hard/Soft FM Bilayers**

(IV). **Summary**

Magnetization Reversal by Domain Nucleation & Growth

(Most Common Mechanism)

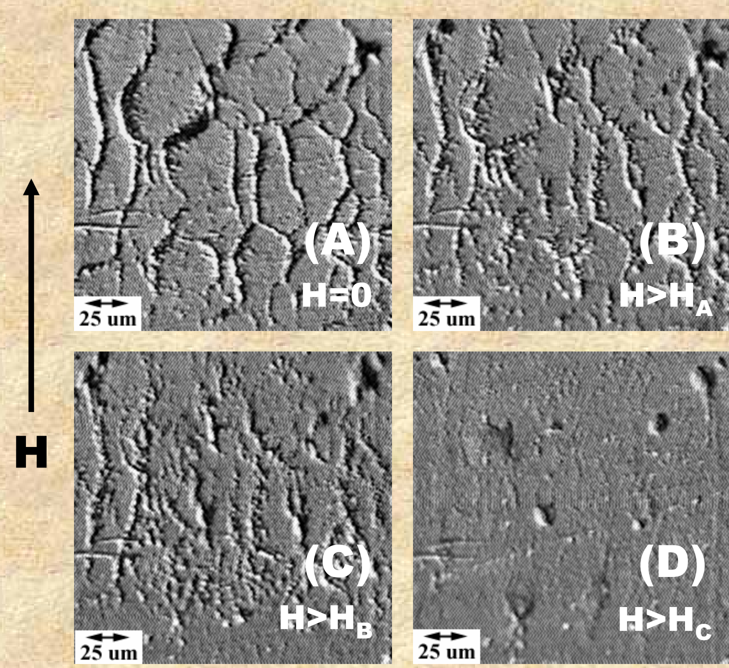




DO DOMAINS EXITS IN NANOCRYSTALLINE FERROMAGNETS???

Domains require an anisotropy to exist. Since the magnetocrystalline anisotropy is thought to go to zero in nanocrystalline materials, do magnetic domains actually exist in these materials???

Domain Patterns in Nanocrystalline (d=18 nm) Ni (Imaged by Magnetic Fluid Method)



Field dependent patterns in a magnetic fluid on top of Nano-Ni shows domains exist and grow with the field.

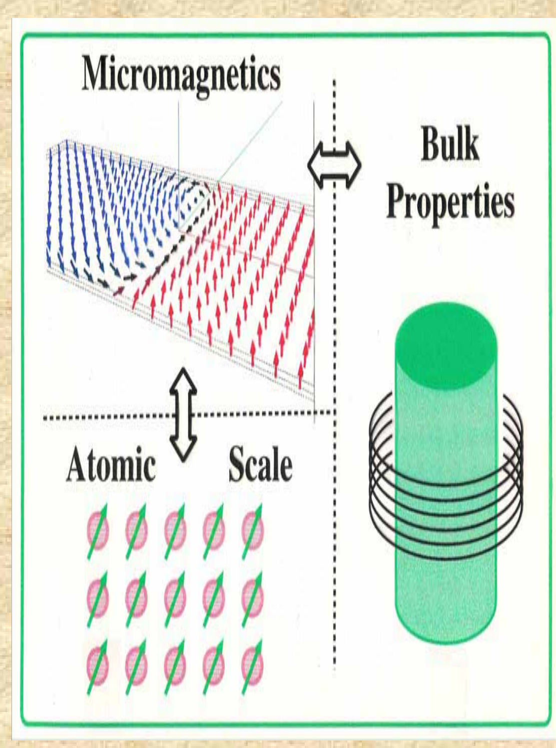
The patterns also show the domains are much larger than the grains at H=0.

DOMAIN WALLS

ARE ALSO A FUNCTION OF

SIZE

Computational Standards



Micromagnetic Equations

$$(1+\alpha^2)\frac{\partial \mathbf{M}}{\partial t} = -\gamma\, \mathbf{M}\times\mathbf{H}_{\rm eff} - \frac{\gamma\alpha}{M_s}\mathbf{M}\times(\mathbf{M}\times\mathbf{H}_{\rm eff})$$

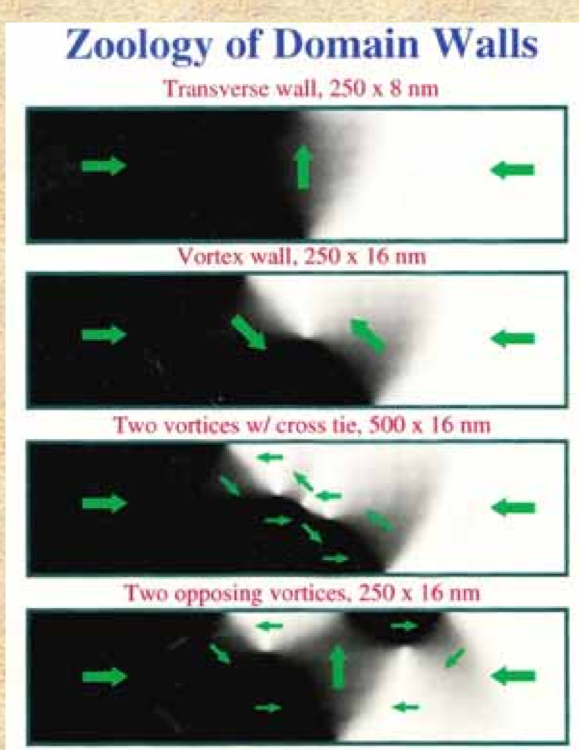
$$\mathbf{H}_{\rm eff} = -\partial\mathcal{E}_{\rm tot}/\partial\mathbf{M}$$

$$\mathcal{E}_{\rm tot} = \mathcal{E}_{\rm ex} + \mathcal{E}_{\rm K} + \mathcal{E}_{\rm s} + \cdots$$

$$\mathcal{E}_{\rm ex} = \frac{A}{M_s^2}\left[(\nabla M_x)^2 + (\nabla M_y)^2 + (\nabla M_z)^2\right]$$

$$\mathcal{E}_{\rm K} = \frac{K_c}{M_s^4}(M_x^2M_y^2 + M_y^2M_z^2 + M_z^2M_x^2)$$

$$\mathcal{E}_{\rm s} = -\frac{1}{2}\mathbf{M}\cdot\int_V(\nabla\cdot\mathbf{M})G\,dv + \int_S \mathbf{M}\cdot\mathbf{n}G\,ds$$

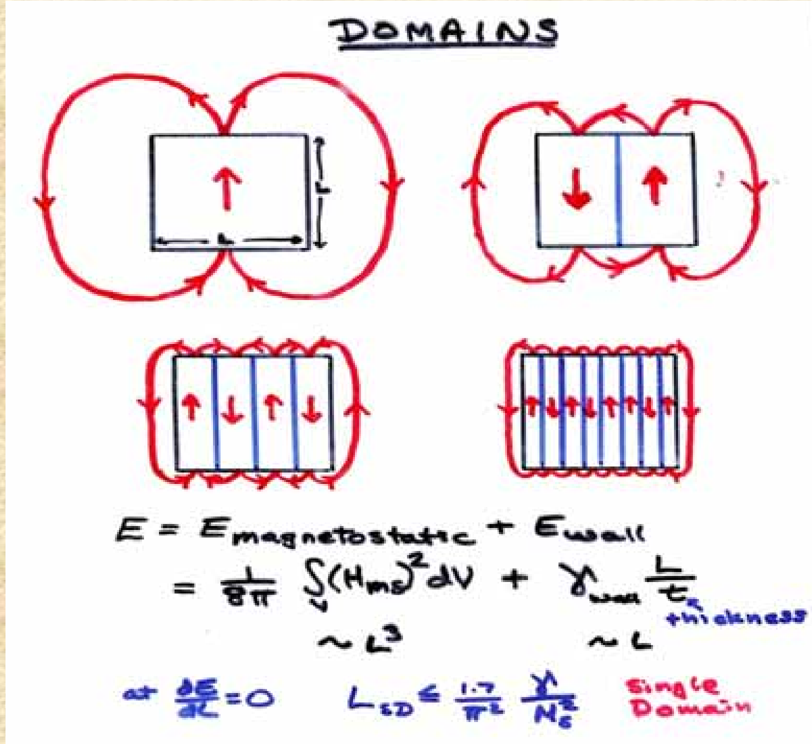


Walls Separating Magnetic Domains Change as the Domain Dimensions Change

This Changes the Way Domains Grow in Response to a Magnetic Field Application.

This Affects the Shape, Width, and Area Enclosed In the Hysteresis Loop of that Material.

R.D. McMichael & M.J. Donahue, IEEE Trans. Magnetics 33, 4167 (1997).



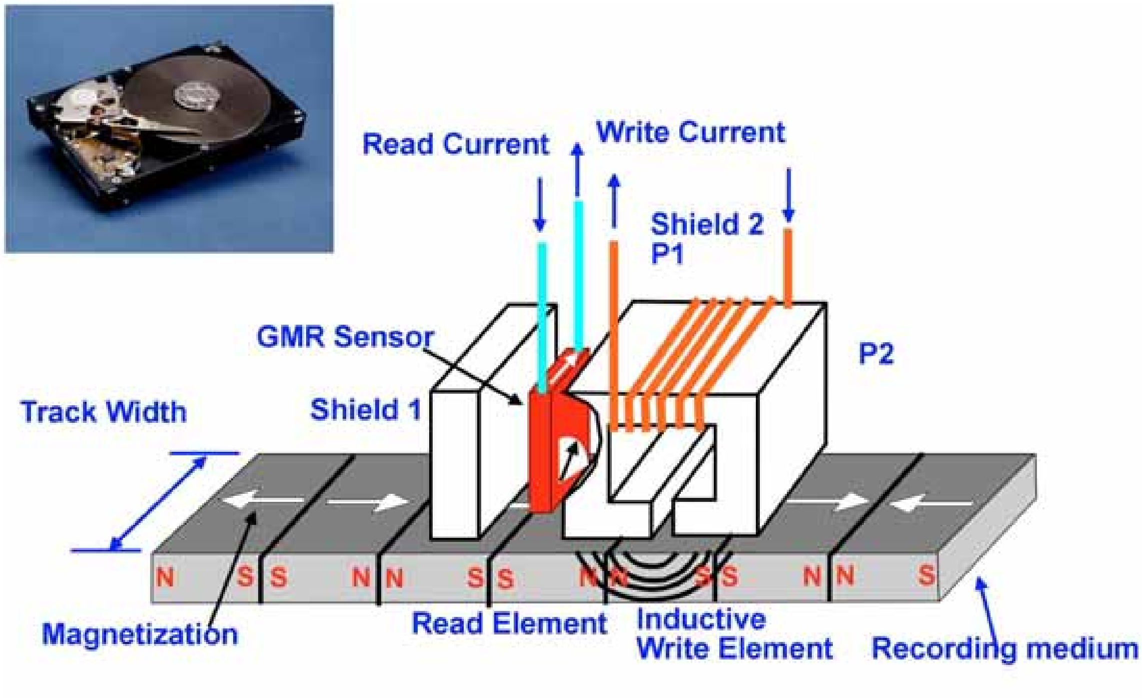
In a Ferromagnet, domains are a way to reduce the magnetostatic energy of the material.

Sooner or later, it costs too much energy to Create a wall.

Particles less than this minimum size are a single magnetic domain.

EXAMPLE:

CHANGE IN DOMAIN DYNAMICS IN NANOCOMPOSITE SYSTEMS - IN A SPIN VALVE READ HEAD



Magnetic recording process.

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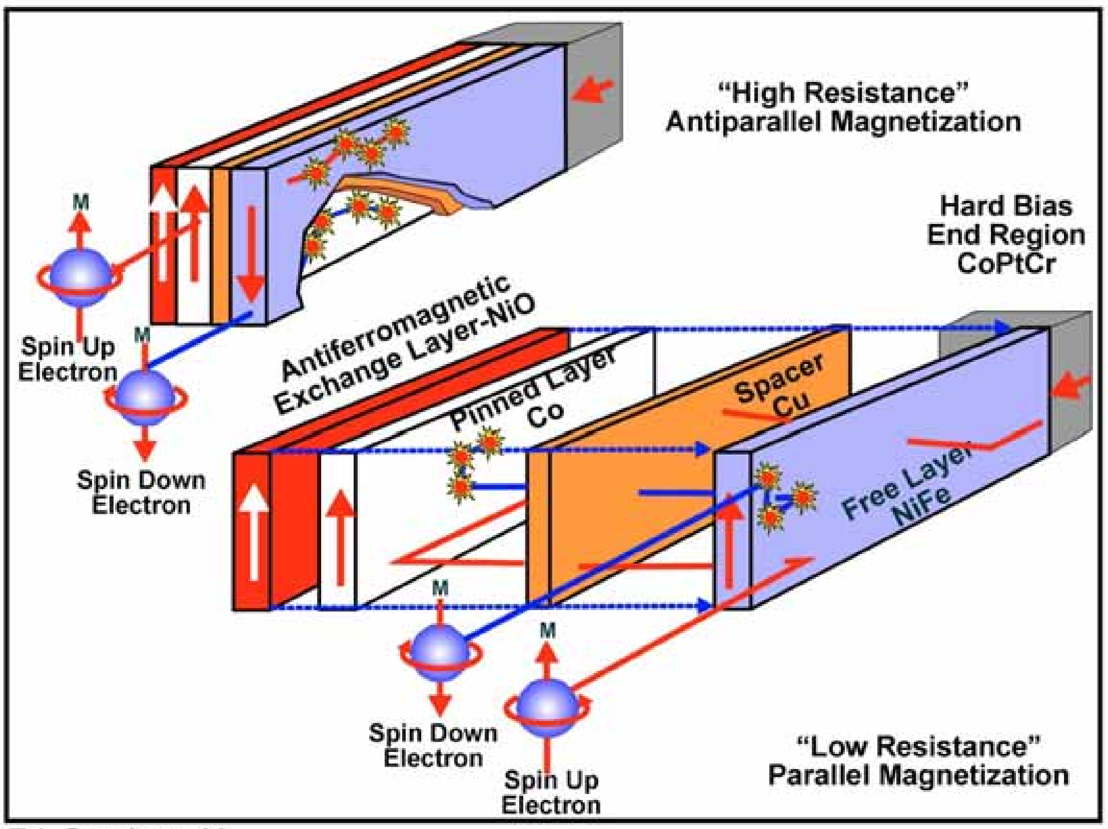
IBM Almaden Research Center

GMR/ Spin valve operation



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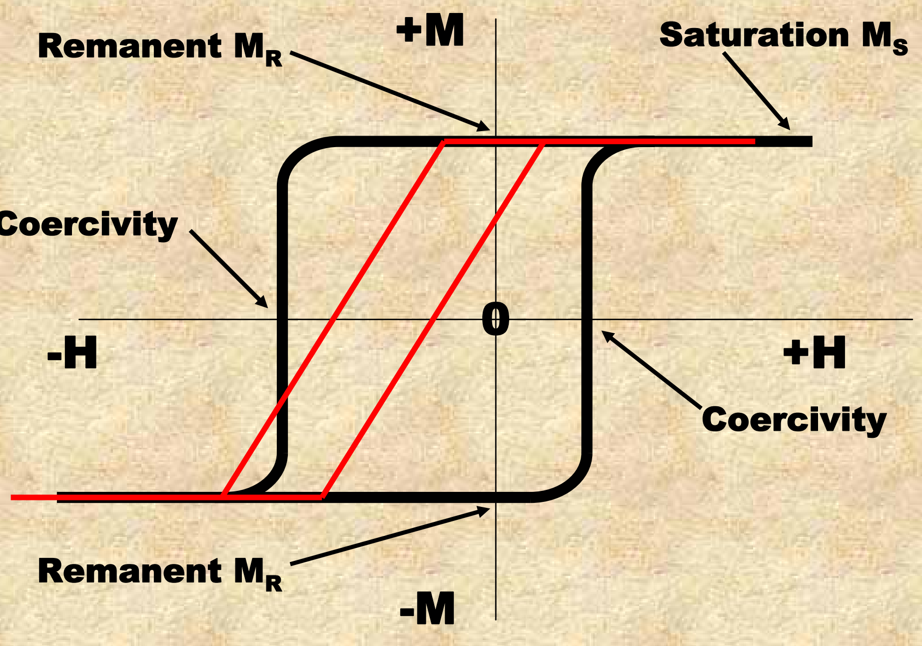
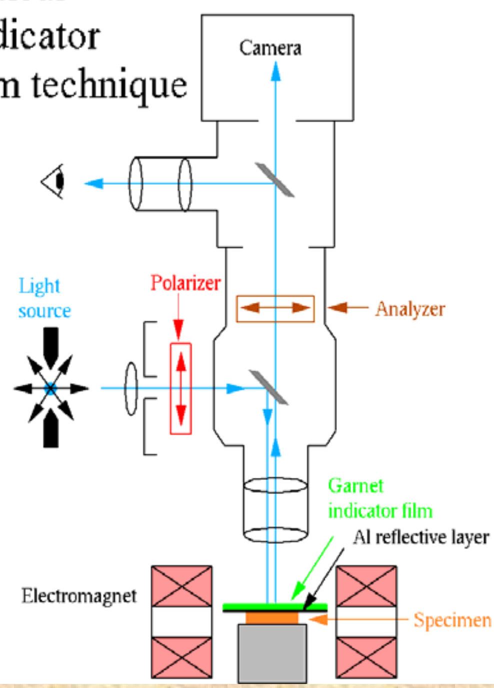
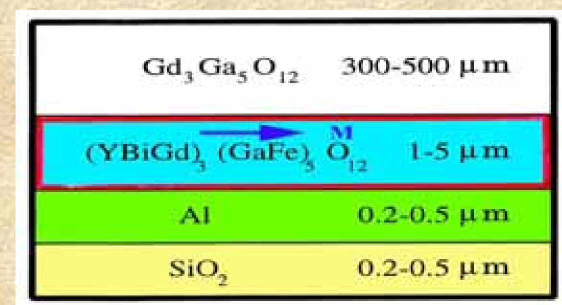
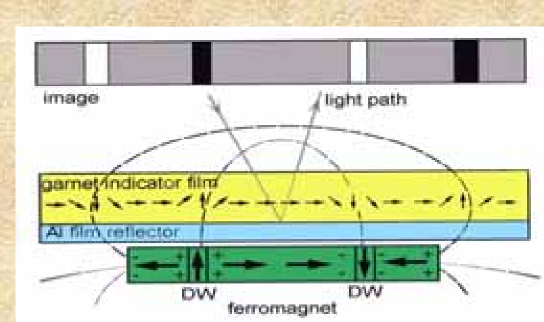
Exchange Bias Hysteresis Loops



Magneto–
Optical
Indicator
Film technique







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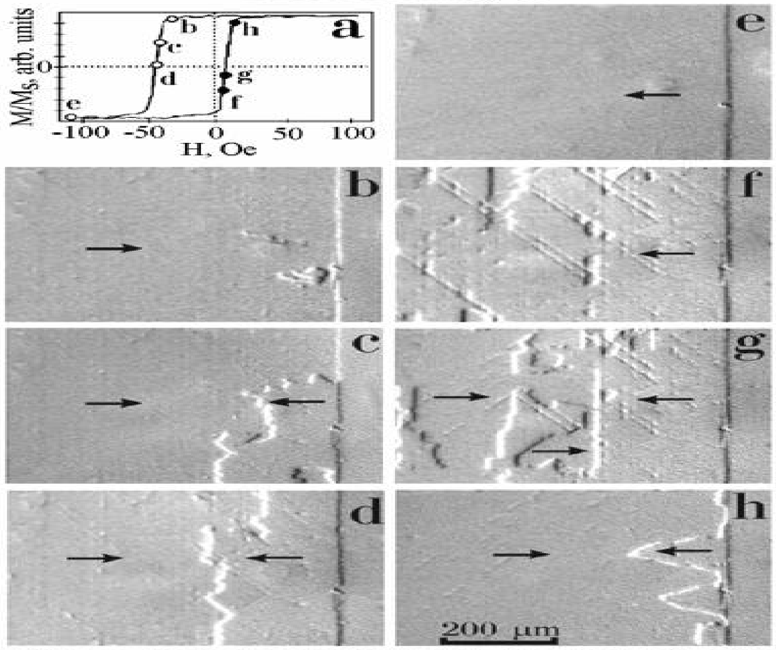
MOIF Images of the Remagnetization Process in an Exchange-Biased NiO/NiFe AF/FM Bilayer



Nikitenko, Gornakov, Dedukh, Yu, Kabanov, Khapikov, Shapiro, Shull, Chaiken, Michel, PRB *57*, R8111 (1998).

National Institute of Standards and Technology

When layers become nanometer-thick, interface interactions become predominant.

- **In Antiferromagnetic/Ferromagnetic (AF/FM) bilayers:**

  Domain nucleation is controlled by Magnetostatic Energy minimization during the application of a negative field.

  But, Exchange Energy minimization controls the nucleation during field reduction!!!

- **In Normal Ferromagnets, domain nucleation occurs in the same place during forward and reverse cycles.**

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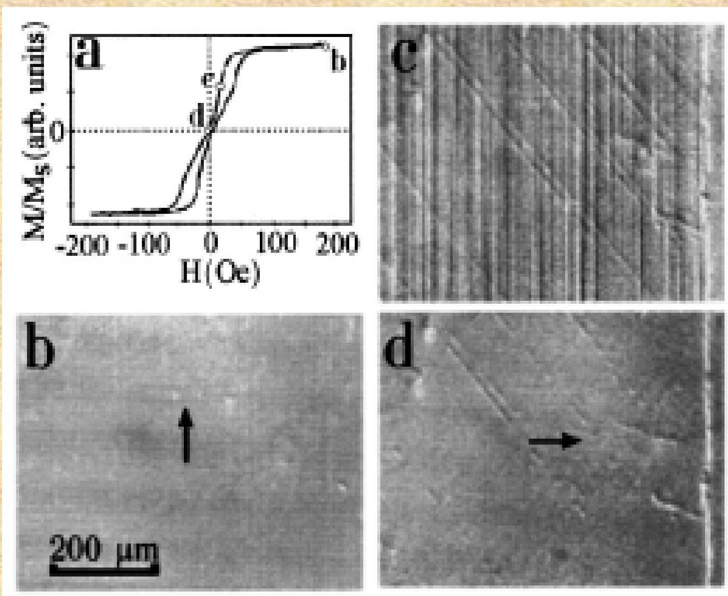
Remagnetization with H Oriented Perpendicular to Exchange Bias In Epitaxial NiO/NiFe AF/FM Bilayer



Now, no wall Motion is observed while MOIF contrast appears & disappears as H is reduced and Reversed.

This indicates M reversal occurs by spin rotation and not by domain nucleation & growth.

[V. Nikitenko, V. Gornakov, L. Dedukh, Yu Kabanov, A. Khapikov, A. Shapiro, R. Shull, A. Chaiken, E. Michel, Phys. Rev. B 57, No. 14, R8111 (1998).]

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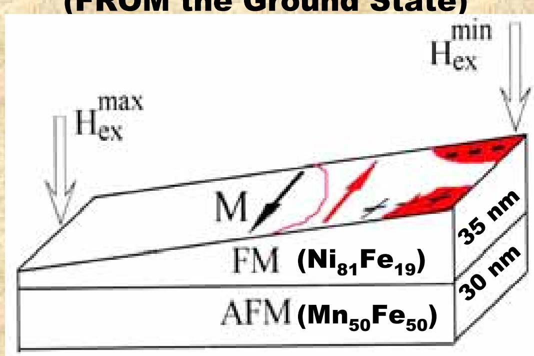
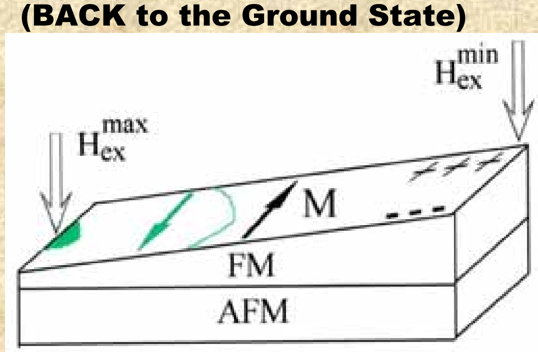
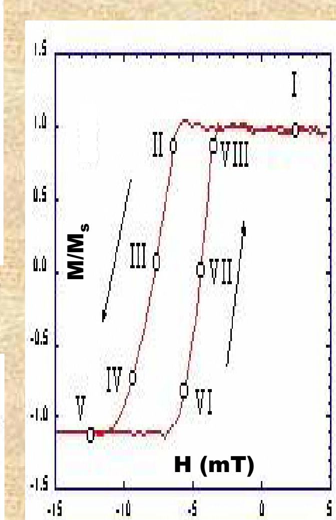
Asymmetry in Domain Nucleation in AF/FM Bilayer

1st Reversal of M (FROM the Ground State)

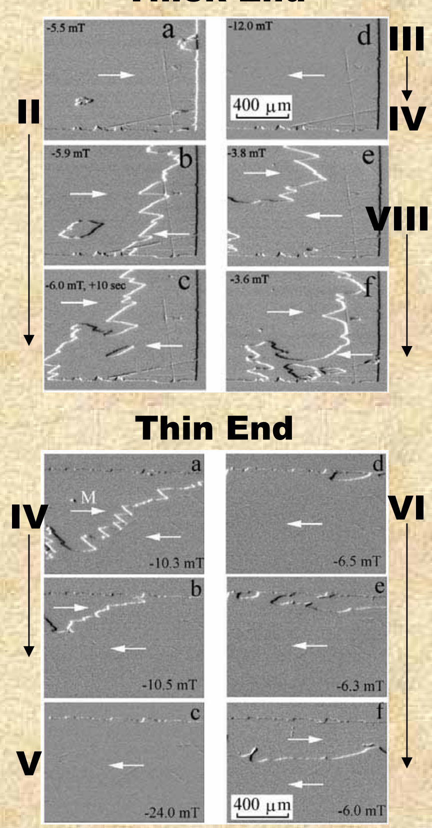


2nd Reversal of M (BACK to the Ground State)





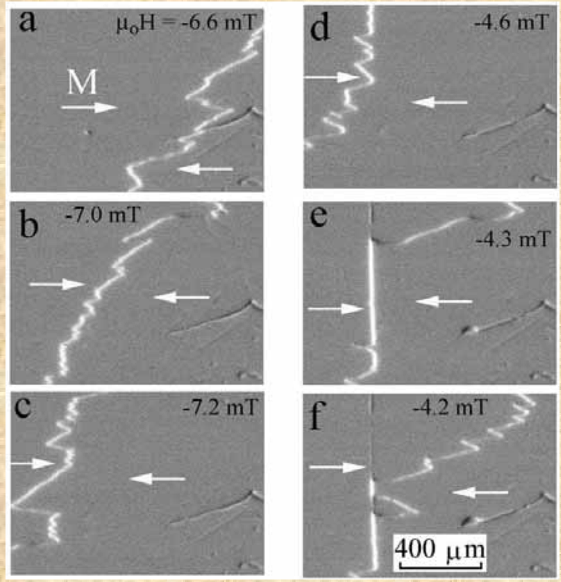
Thick End



[V. Nikitenko, et. al., Phys. Rev. Lett. 84, 765 (2000).]

Asymmetry in Domain Dynamics in AF/FM Bilayer

1st Reversal of M (FROM the Ground State)



H

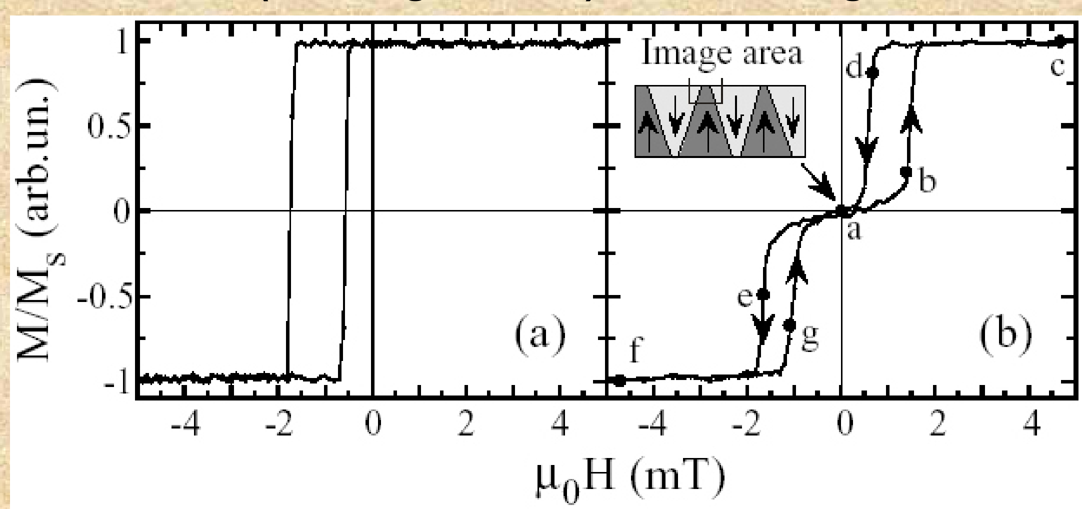
2nd Reversal of M (BACK to the Ground State)

Note the Vertical Defect does NOT affect the domain motion during the 1st Reversal, but DOES affect the Motion during the 2nd reversal.

[V. Nikitenko, V. Gornakov, A. Shapiro, R. Shull, K. Liu, S. Zhou, C. Chien, Phys. Rev. Lett. 84, 765 (2000).]

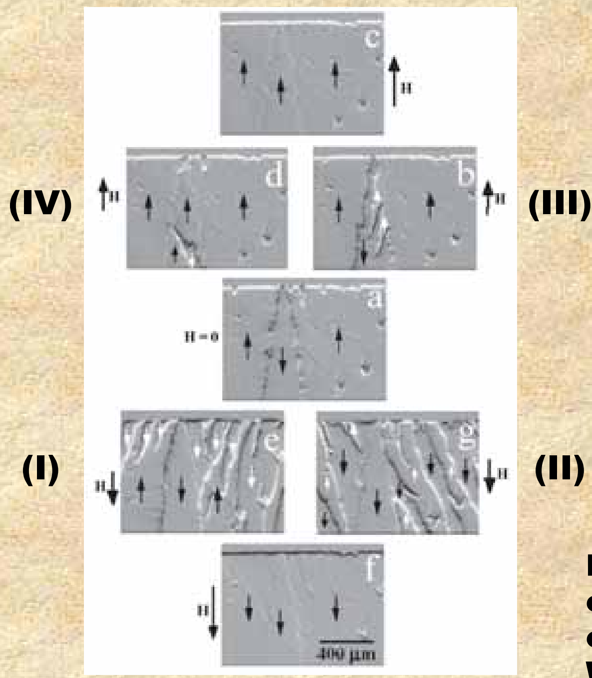
Domain Dynamics in FeMn/NiFe AF/FM Bilayer (AC Demagnetized at $T>T_{Neel}$ of AF)

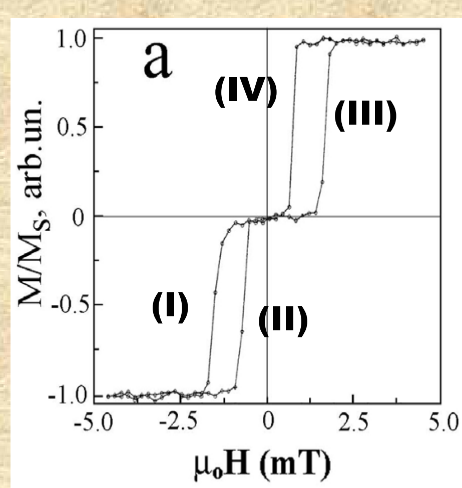
Field Cooled (Exchange Biased) **AC-Demagnetized**



C. Chien, V. Gornakov, V. Nikitenko, A. Shapiro, R. Shull, IEEE Trans. Magnetics 38, No. 5, 2736 (20002).]

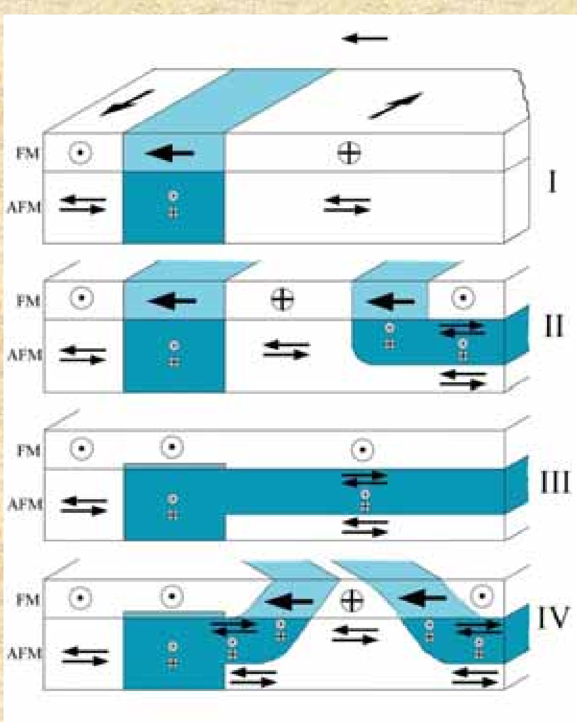
Domain Motion in AC Demagnetized FeMn/NiFe AF/FM Bilayer





Residual Image at top and bottom of original domain structure show original AF domains have not moved While the FM domains changed.

[Chien, Gornakov, Nikitenko, Shapiro, Shull, IEEE Trans. Magnetics 38, No. 5, 2736 (20002).]



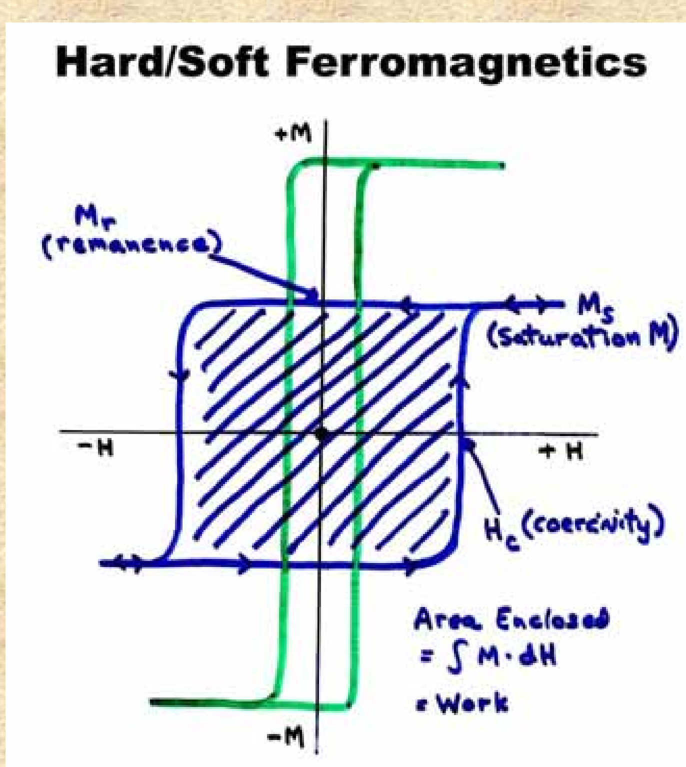
Domain motion in AC-Demagnetized AF/FM Bilayer can be explained By the formation of an Exchange spring parallel To the AF/FM interface, Pinned at one end by the AF and at the other end by the FM

EXAMPLE:

CHANGE IN DOMAIN DYNAMICS

IN NANOCOMPOSITE SYSTEMS

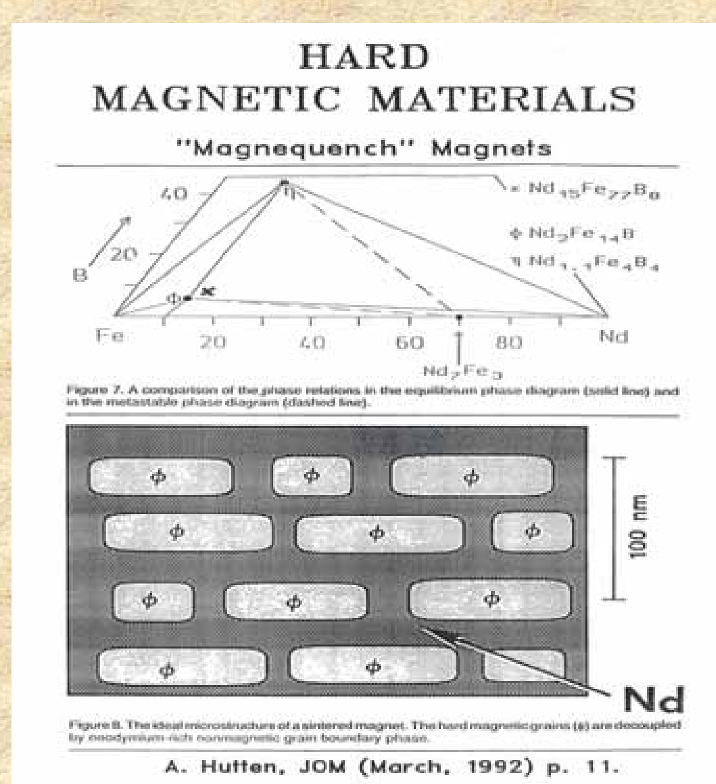
- IN AN IMPROVED PERMANENT MAGNET



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.



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.

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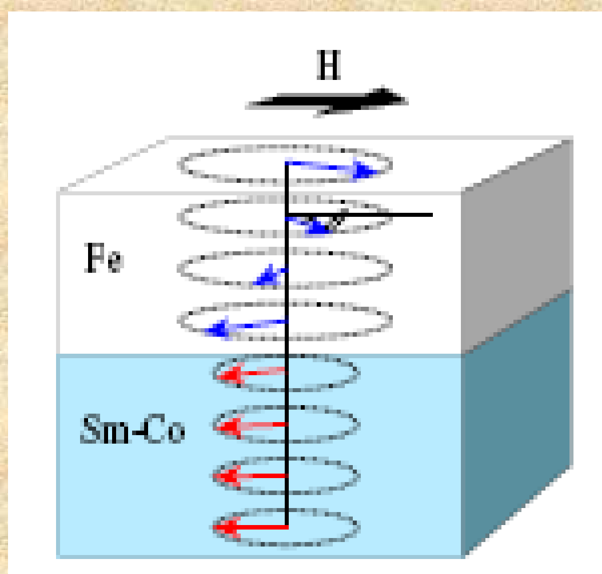
Origin of High Coercivity in Hard/Soft Ferromagnetic Bilayer



[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.

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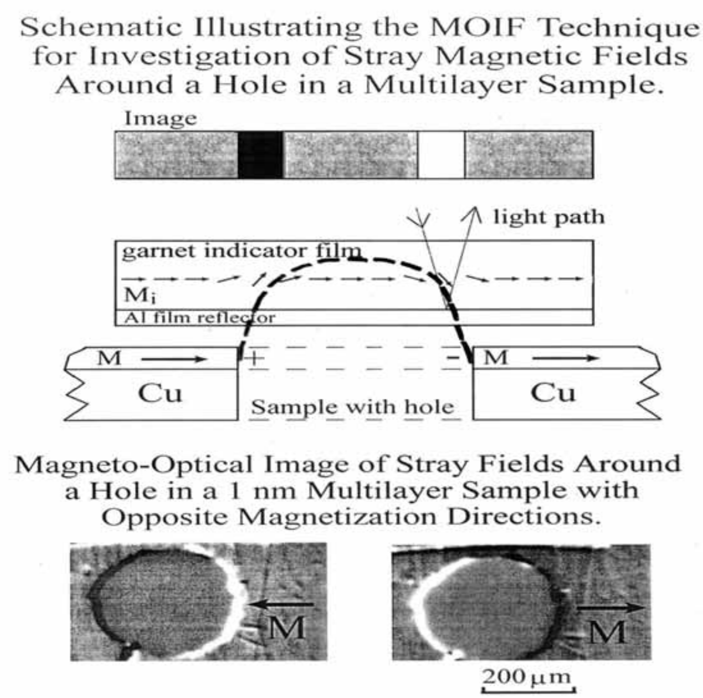
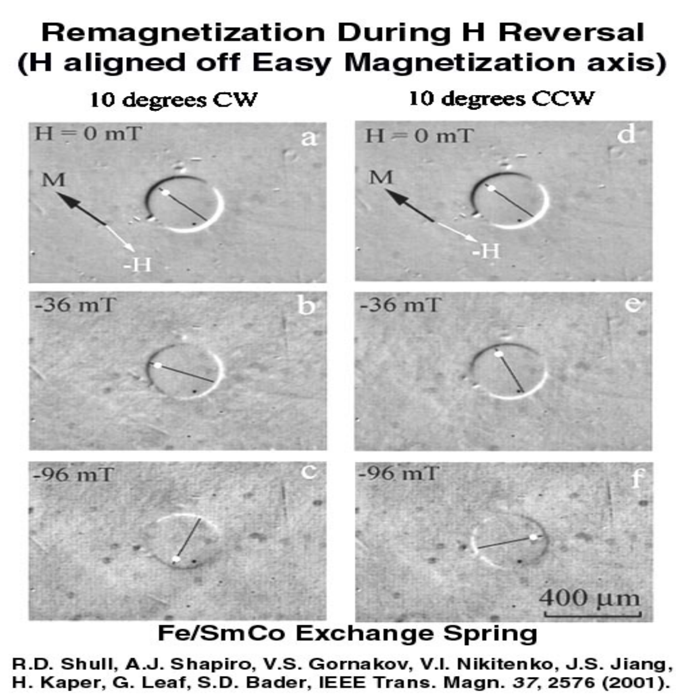
Domain Imaging Of a SmCo/Fe Hard/Soft FM Bilayer

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.



Proof of Rotation Reversal Process in SmCo/Fe Bilayer

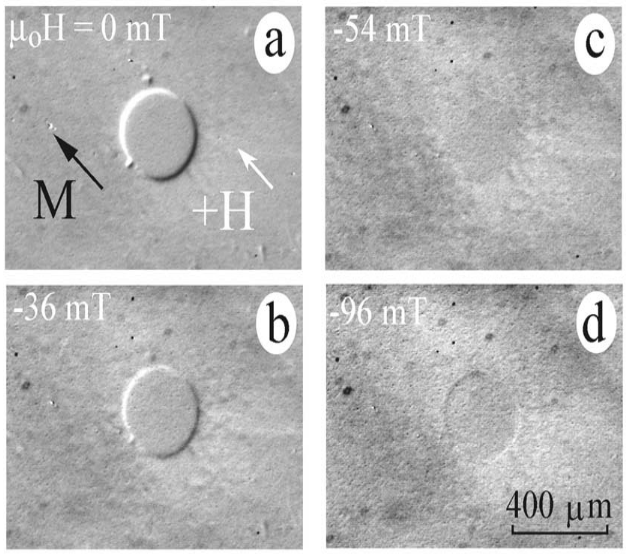


Application of a reversed field is shown by the rotation of the MOIF image contrast at the hole edges to be accompanied by a rotation of M, when H is aligned just slightly off the easy axis of Magnetization of the Fe.

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

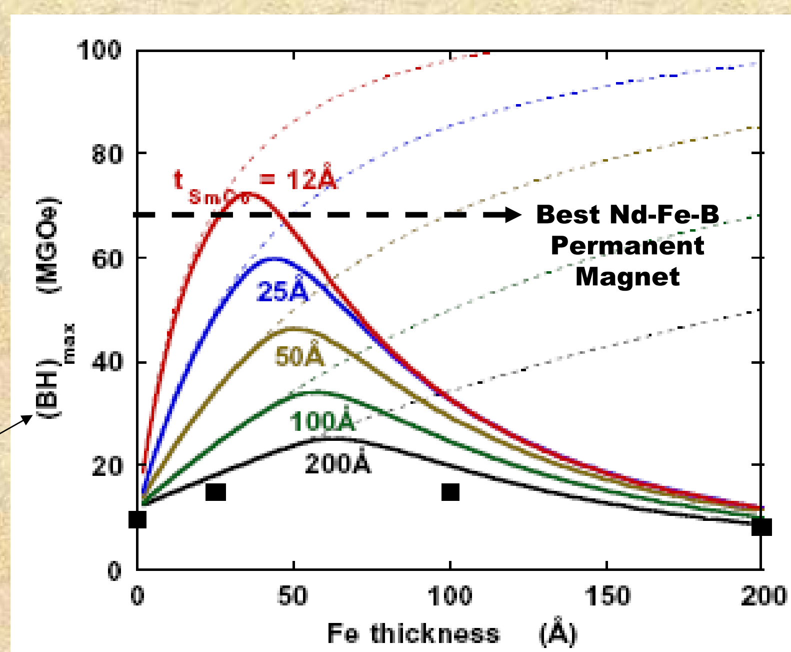
R.D. Shull, A.J. Shapiro, V.S. Gornakov, V.I. Nikitenko, J.S. Jiang, H. Kaper, G. Leaf, S.D. Bader, IEEE Trans. Magn. *37*, 2576 (2001).

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).]

Summary

- The usefulness of a material for a particular application depends on how easily or hard it is to change its magnetization.
- Observation of Domain patterns is critical to understanding how a material changes its magnetization.
- Increased surface/volume ratio of nanomagnets makes domain motion more susceptible to interaction effects with neighboring magnetic materials.
- AF/FM Exchange Biased films possess a novel asymmetry in their reversal behavior
- Nanocomposites provide a means for designing better Hard ferromagnets (i.e., permanent magnets)

OUTLINE

- (I). Magnetocaloric Effect (dT)
  - Definition
- (II). Basic dT and dS Equations
- (III). Dependence on Magnetic State
  - In Paramagnets
  - In Ferromagnets
  - In Magnetic Nanocomposites
- (IV). Measurement Methods
  - Direct Method
  - Indirect Method
- (V). dT and dS Data
  - 11%Fe+Silica Gel Nanocomposite
  - Garnet Nanocomposites
- (VI). Summary

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NANOMAGNETISM (III)

MAGNETIC REFRIGERATION

Robert D. Shull
(Group Leader:
Magnetic Materials Group)

National Institute
of Standards and Technology
Gaithersburg, Maryland
USA

Member: OSTP Nanoscale Science, Engineering, and Technology Subcommittee (NSET)

V. President: The Minerals, Metals, & Materials Society (TMS) of AIME

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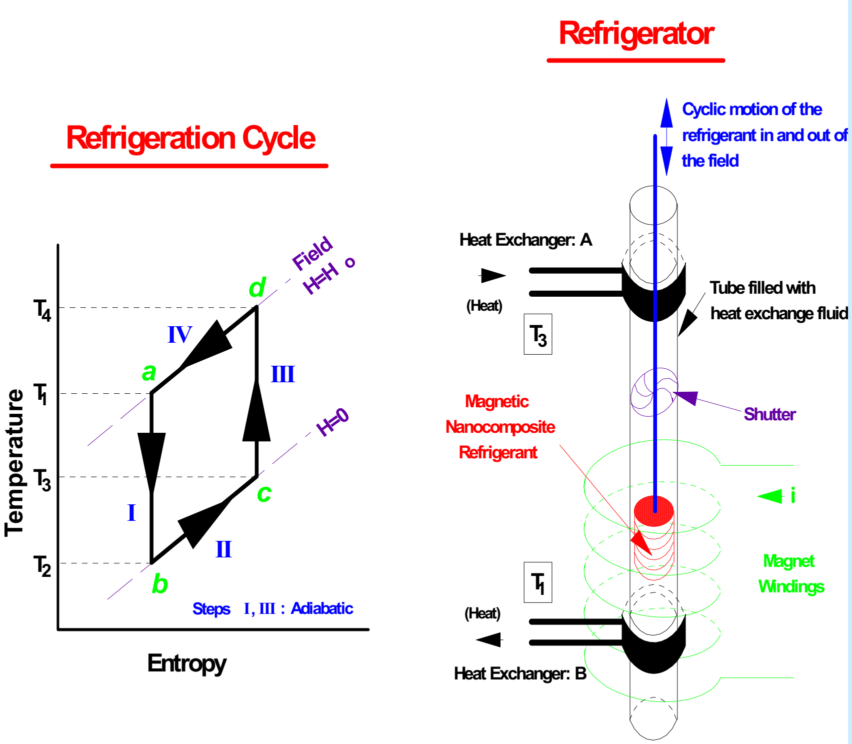
National Institute of Standards and Technology

MAGNETIC REFRIGERATION



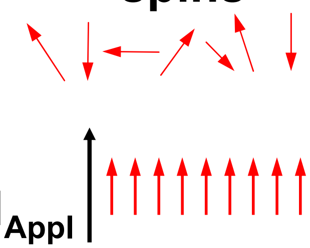
MAGNETOCALORIC EFFECT

SYSTEM = SPIN + LATTICE

spins lattice

at H = 0 $T = T_0$

at $H = H_{Appl}$ $T = T_1$



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 = $dT = (T_1 - T_0)$.

Basic dS and dT Equations:

(1) $dU = \delta Q - \delta W$ [System = Spin + Lattice]

(2) $= TdS - pdV + \sum_i \mu_i dN_i + \mu_0 V_M H \cdot dM$

(3) $= TdS + \mu_0 V_M H \cdot dM$

if Volume and Material are Not changed

Creating the Maxwell relation from the Exact differential of (3):

(4) $$\left(\frac{\partial S}{\partial H}\right)_T = \mu_0 V_M \left(\frac{\partial M}{\partial T}\right)_H$$

To obtain dT, express dS(H,T):

(5) $$dS = \left(\frac{\partial S}{\partial T}\right)_H dT + \left(\frac{\partial S}{\partial H}\right)_T dH$$

For a Reversible change in T:

(6) $$\left(\frac{\partial S}{\partial T}\right)_H = \frac{C_H}{T}$$

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WHY MAGNETIC REFRIGERATORS ?????

- **Large Entropy Change in 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)
- **No Compressor & Few Moving Parts**
  (Low vibration, High durability)

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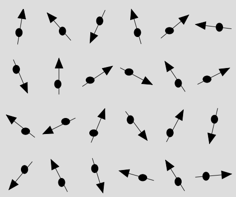
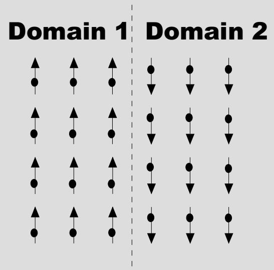


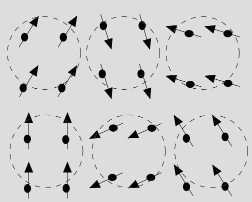
Paramagnetic Material:

Assembly of elemental moments, each of magnitude μ acting independently



Ferromagnetic Material:

Assembly of magnetic domains (each comprised of many elemental moments of magnitude μ aligned in the field direction in concert with the other domains



Superparamagnetic Material:

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

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Substituting (4) and (6) into equation (5):

(7) $$dS = \left(\frac{C_H}{T}\right) dT + \mu_0 V_m \left(\frac{\partial M}{\partial T}\right)_H dH$$

$$= 0$$ for an adiabatic process

(8) $$\therefore \boxed{dT = -\left(\frac{T}{C_H}\right) \mu_0 V_m \left(\frac{\partial M}{\partial T}\right)_H dH}$$

for a given ΔH:

$$\text{Total } \Delta T = \int dT = \int_0^H -\left(\frac{T}{C_H}\right) \mu_0 V_m \left(\frac{\partial M}{\partial T}\right)_H dH$$

and

$$\boxed{\text{Total } \Delta S = \int_0^H \mu_0 V_m \left(\frac{\partial M}{\partial T}\right)_H dH}$$

in general: $\left(\frac{\partial M}{\partial T}\right)_H = f(H,T)$

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For an Ideal Paramagnet:

(An assembly of N non-interacting spins of magnetic moment μ)

$$M = \sum_i \mu_i$$

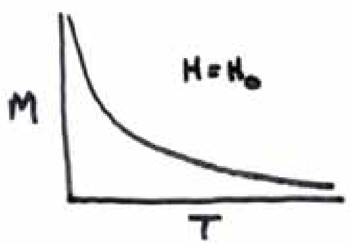
$$\frac{M}{M_0} = \coth(a) - \frac{1}{a}$$

where $a = \frac{\mu H}{kT}$

$M_0 = N\mu$

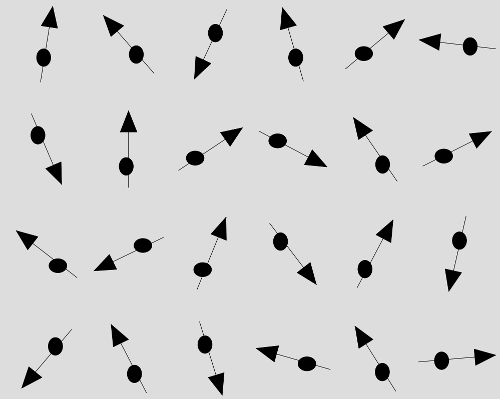
Low Field Limit:

$$M = \frac{N\mu^2 H}{3kT}$$ Curie Law



$$\left[\Delta S = Nk_B\left[1 - a\coth(a) + \ln\left(\frac{\sinh(a)}{a}\right)\right] = \frac{N\mu^2 H^2}{6k_B T^2}\right]$$

VERY SMALL PARTICLE LIMIT



Assembly of elemental moments, each of magnitude μ, acting independently

Paramagnetic Material:

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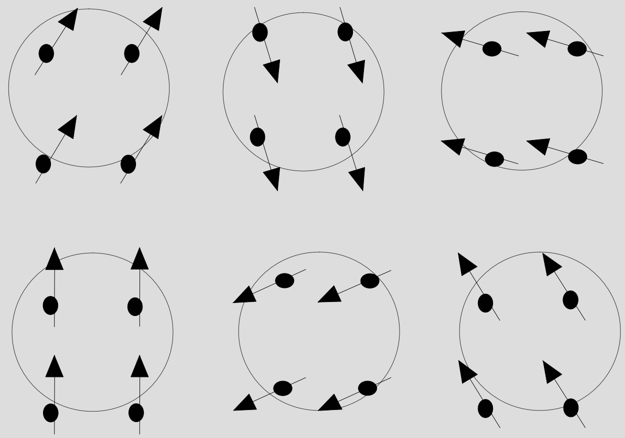
SMALL PARTICLE BEHAVIOR



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

Superparamagnetic Material:

["The Magnetocaloric Effect in Nanocomposites", R. Shull, L. Swartzendruber, L. Bennett, Proc. of the 6th Int'l. Cryocoolers Conf., eds. G. Green, M. Knox, David Taylor Res. Cntr. Publ. #DTRC-91/002, Annapolis, MD (1991) 231.]

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$$M = N\mu^2 H/3k_BT$$

$$\partial M/\partial T = -N\mu^2 H/3k_BT^2$$

$$\Delta T = -(T/C_H)\mu_o V_M(\partial M/\partial T)_H \Delta H$$

$$\Delta T = (1/C_H)\mu_o V_M(N\mu^2 H/3k_BT)\Delta H$$

The temperature change for a paramagnet Is inversely proportional to the temperature And proportional to the field change.

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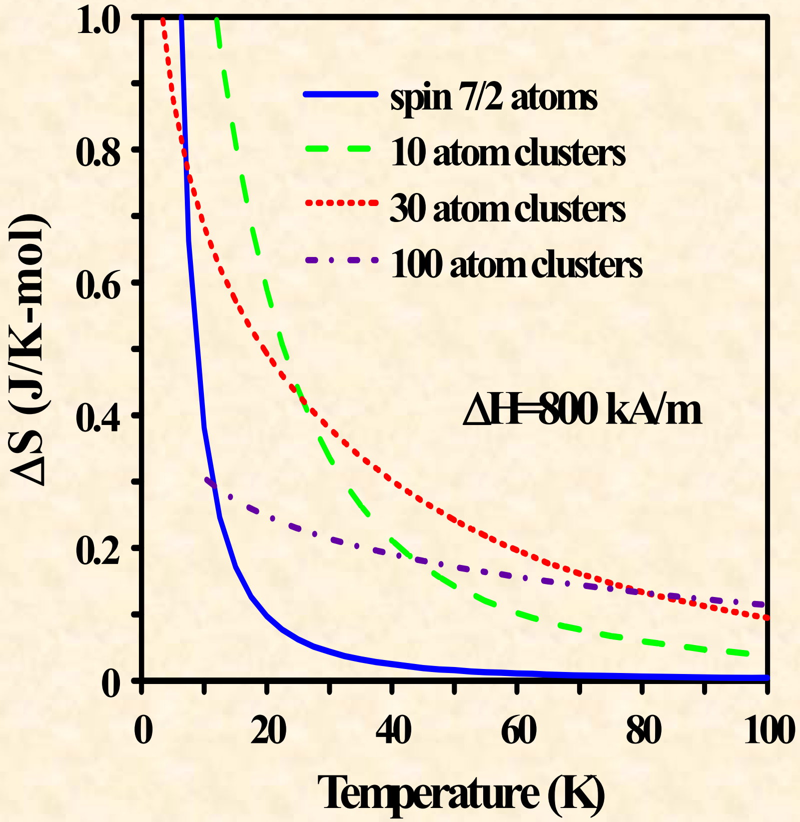
Entropy Enhancement in Nanocomposites



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

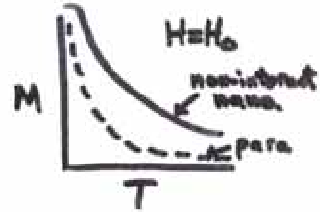
For a Nanocomposite

– possessing superparamagnetic behavior (without interaction):

"N" spins in "n" ferromagnetic regions

$$\mu_{region} = \left(\frac{N}{n}\right)\mu_{spin}$$

$$\frac{M}{N\mu} = \coth\left(\frac{\mu H}{kT}\right) - \frac{kT}{\mu H}$$



Low field limit:

$$M = \frac{N\mu^2 H}{3kT} \rightarrow \frac{n\left(\frac{N}{n}\right)^2 H}{3kT}$$

Magnetocaloric Effect: $dT = -\left(\frac{T}{C_H}\right)\mu_0 V_m \left(\frac{\partial M}{\partial T}\right)_H dH$

$$dT_{\substack{nano.\\(n.i.)}} = \left(\frac{\mu_0 V_M}{C_H}\right) n\left(\frac{N}{n}\right)^2 \frac{\mu_{spin}^2 H}{3k}\frac{1}{T}\,dH$$

compared to paramagnetism:

$$dT_{para} = \left(\frac{\mu_0 V_M}{C_H}\right) N \frac{\mu_{spin}^2 H}{3k}\frac{1}{T}\,dH$$

$$n\left(\frac{N}{n}\right)^2 = \frac{N^2}{n} >> N$$

$$\therefore\ dT_{\substack{nano\\(n.i.)}} >> dT_{para}$$

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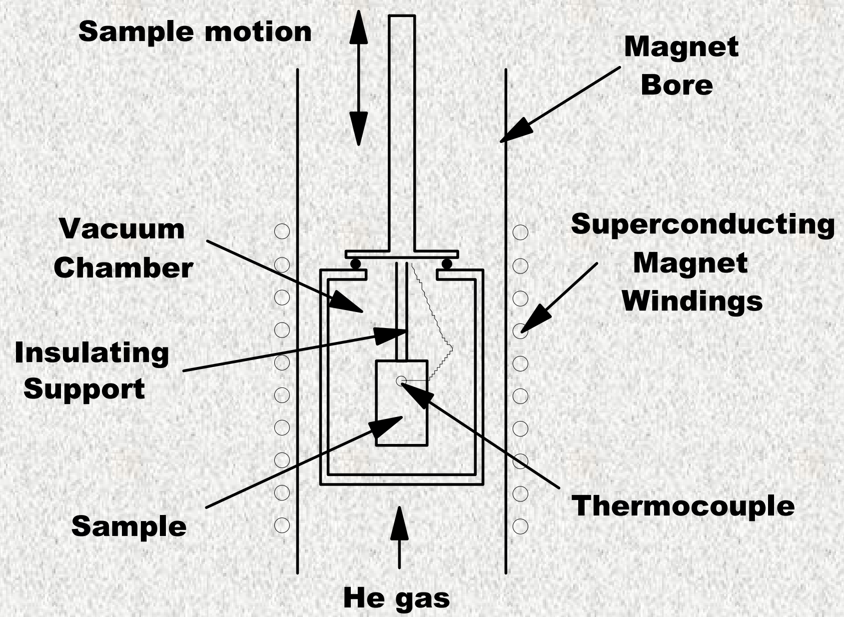
Measurement of the Magnetocaloric Effect (MCE)

CALORIMETER



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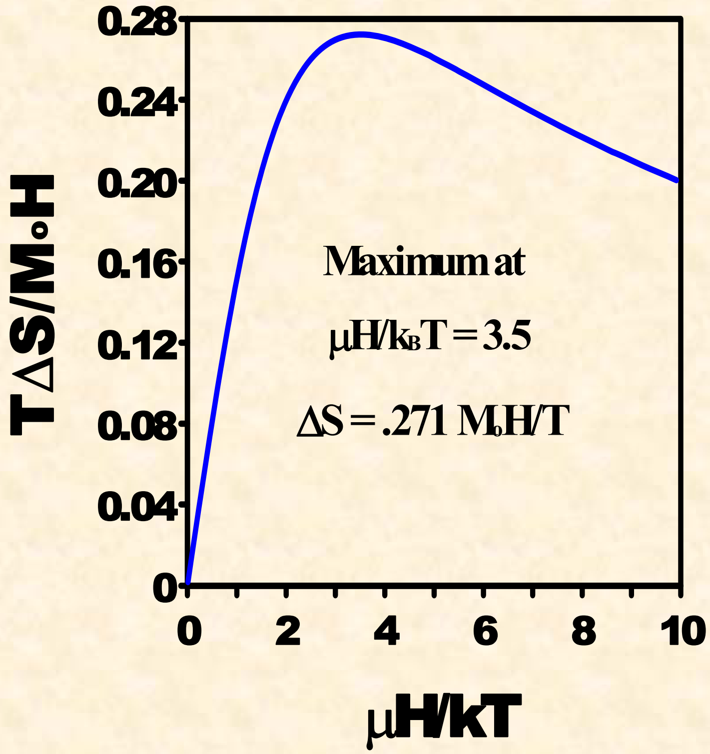
"Universal" Entropy Change Curve



[R. McMichael, R. Shull, L. Swartzendruber, L. Bennett, R.E. Watson, J. Mag. & Magn. Mat. 111, 29 (1992)]

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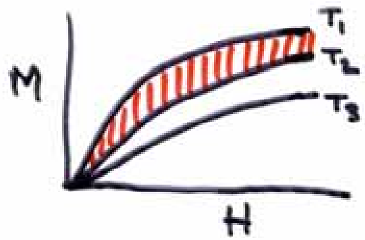
Calculation of the MCE from Magnetization Data

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$$

$$\Delta S = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$$



$$\Delta S_i = \frac{1}{\Delta T_i} \int_0^H \left[M(T_{i+1}, H) - M(T_i, H) \right] dH$$

where $\Delta T_i = T_{i+1} - T_i$

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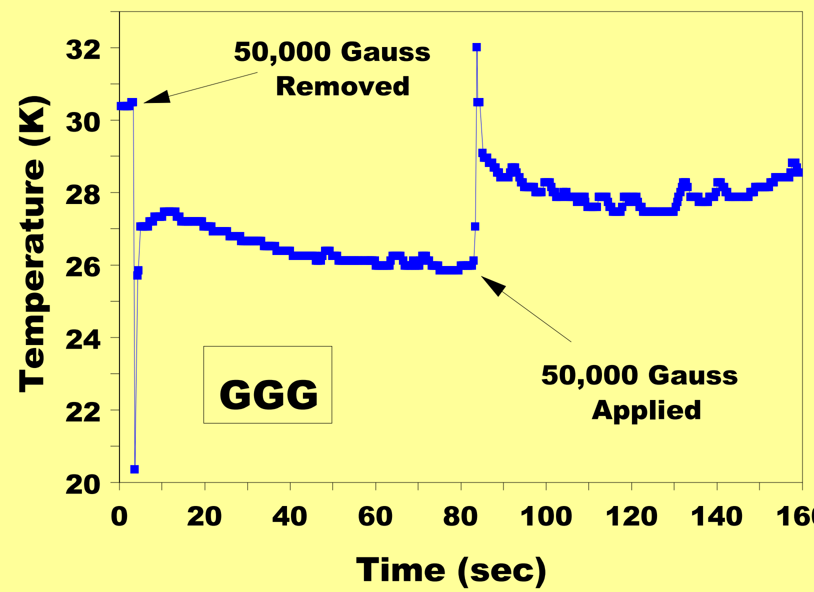
Magnetocaloric Effect in Gadolinium Gallium Garnet



(This is the material with the largest magnetocaloric effect at low temperatures and is useful as a magnetic refrigerant up to 15 K)

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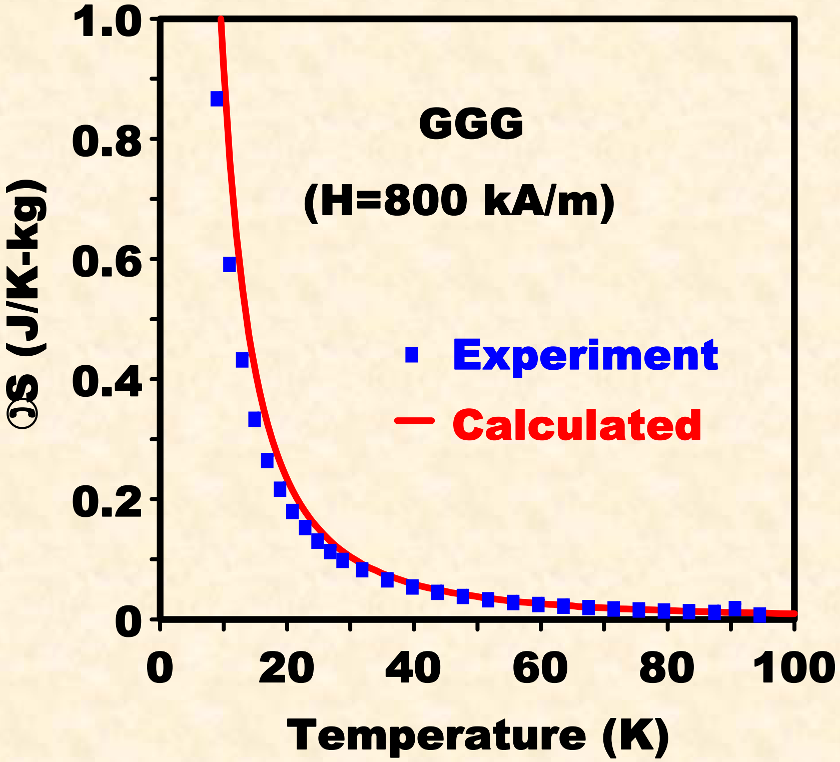
$Gd_3Ga_5O_{12}$

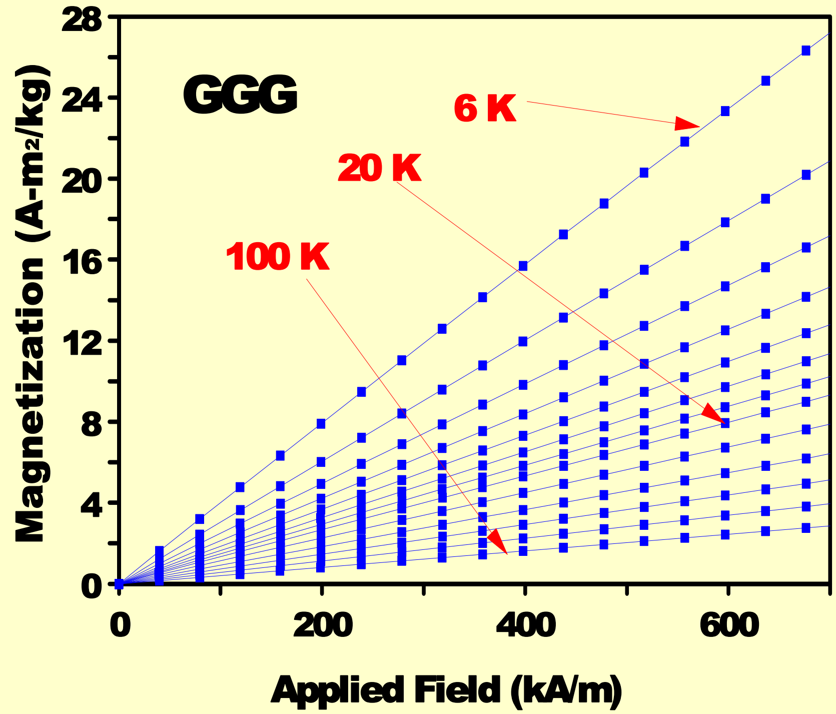
Magnetocaloric Effect



Calculation of the MCE values from magnetization data is a good way to determine MCE (& it is much faster).

$Gd_3Ga_5O_{12}$

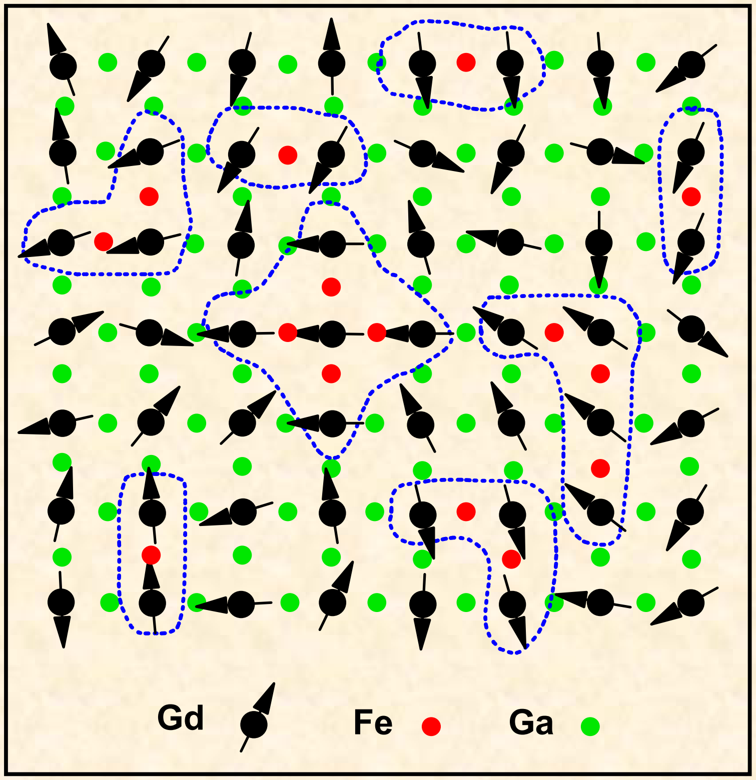
Magnetization Isotherms
(for Entropy Calculations)



Schematic Picture of

$Gd_{3-y}Ga_{5-x}Fe_{x}O_{12}$ Garnet

Magnetic Nanocomposites



Fe spins create magnetic clusters (dashed areas)

Bulk

$Gd_3Ga_{5-x}Fe_xO_{12}$

Nanocomposites

- Prepared nanocomposites by adding aqueous solutions of the mixed metal nitrates to excess tartaric acid (for complexing)
- Air dried (200-325 C)
- Formed Garnet Structure
  (1) Air (950 C)
- Samples characterized
  X-ray diffraction
  Mossbauer Effect
  Ferromagnetic Resonance
  Magnetic susceptibility

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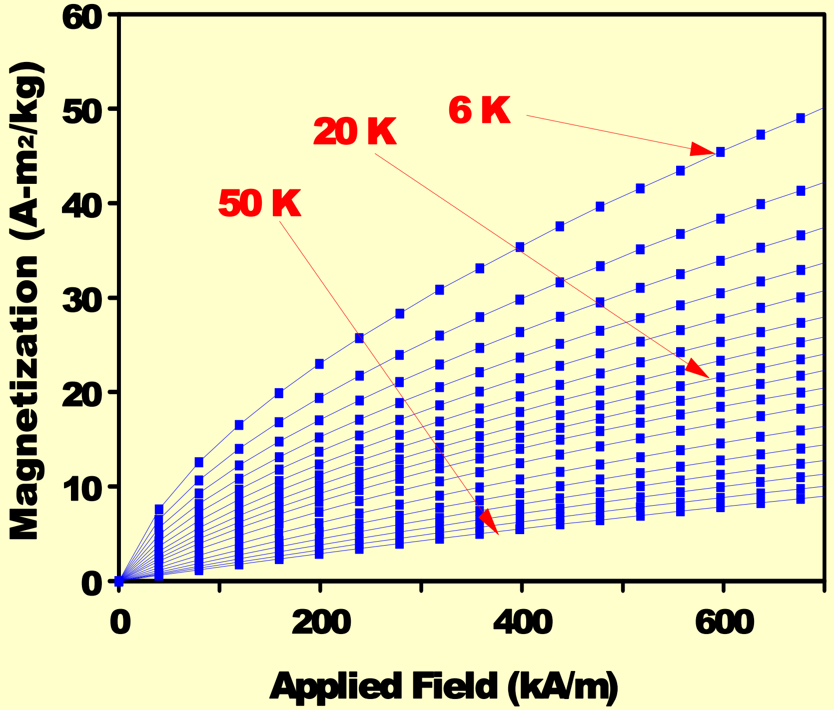
$Gd_3Ga_{3.25}Fe_{1.75}O_{12}$

Magnetization Isotherms
(for Entropy Calculations)



Curved isotherms show superparamagnetic behavior & therefore the presence of magnetic clusters

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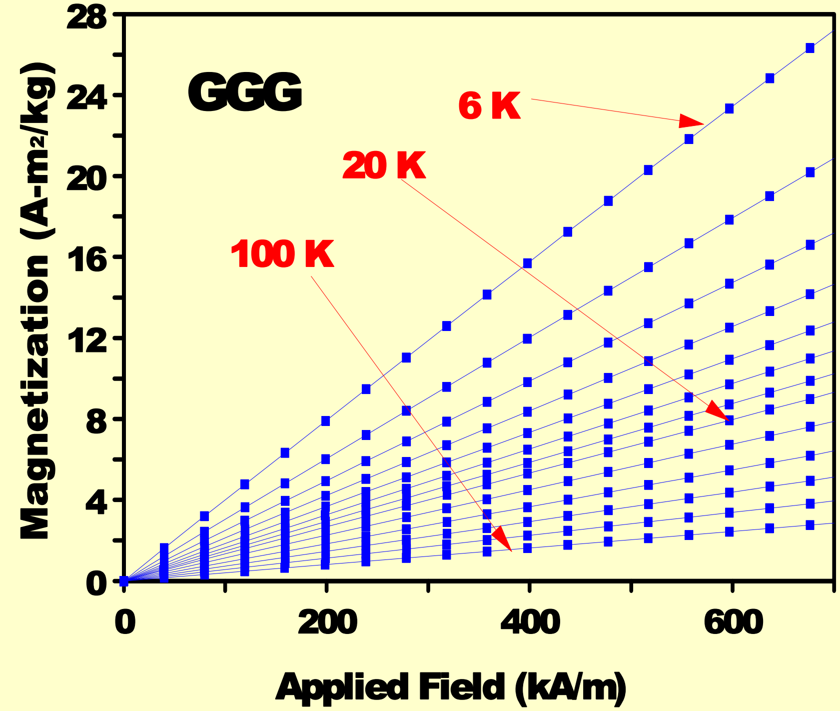
$Gd_3Ga_5O_{12}$

Magnetization Isotherms
(for Entropy Calculations)



Straight line isotherms show paramagnetic behavior & therefore no interaction between magnetic spins

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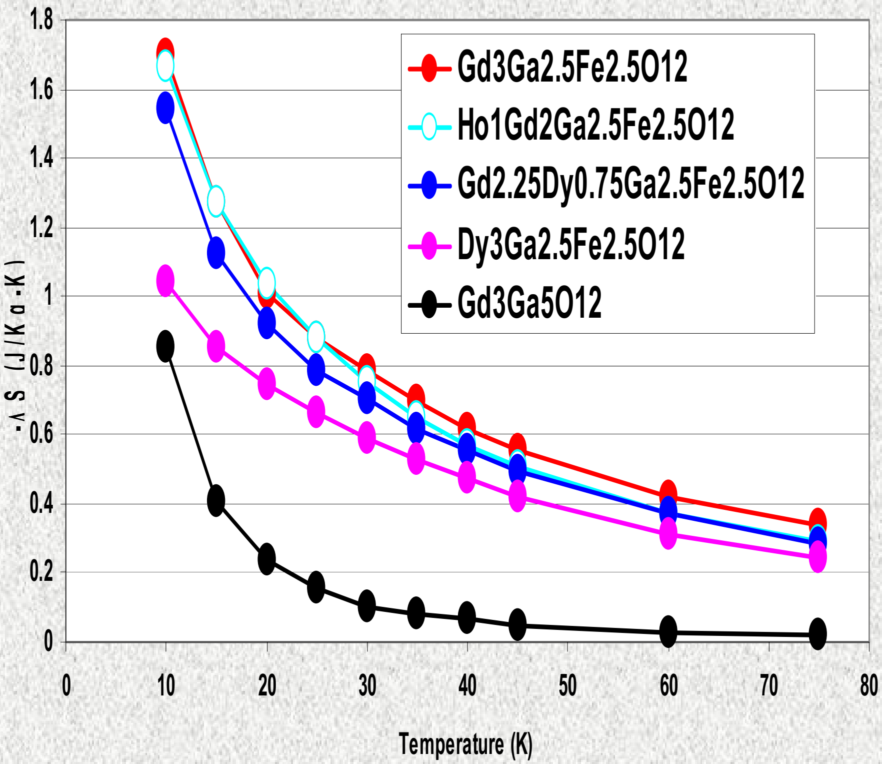
-ΔS vs T for GGI, HGGI, GDGI, DGI Garnet Nanocomposites and GGG Heat Treated for 15 h at 1200°C (ΔH=1T)



[V. Provenzano, J. Li, T. King, E. Canavan, P. Shirron, M. DiPirro, and R.D. Shull, JMMM 266, 185 (2003)]

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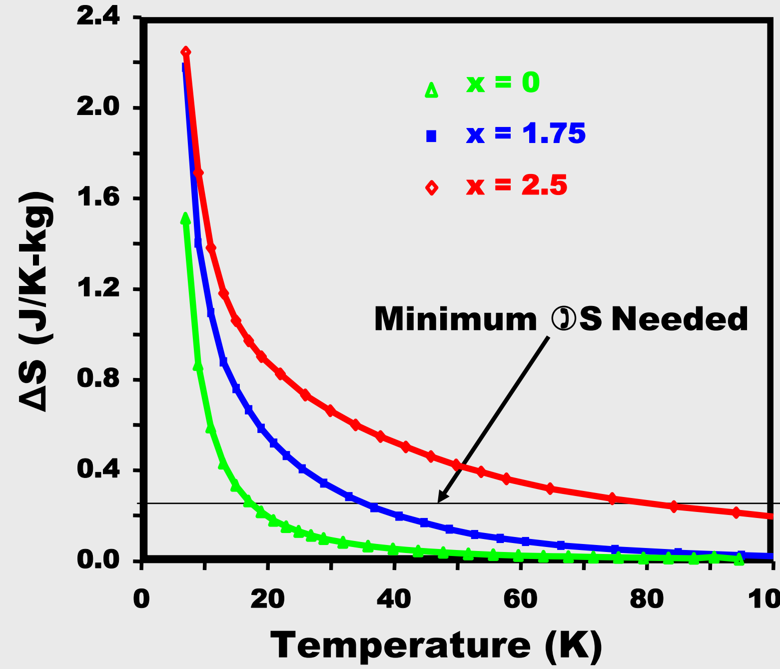
Magnetocaloric Effect Entropy Changes for $Gd_3Ga_{5-x}Fe_xO_{12}$ Nanocomposites

(ΔH=800 kA/m)



[R.D. McMichael, J.J. Ritter, and R.D. Shull, J. Appl. Phys. 73(10), 6946 (1993)]

Nanocomposites show one way to move the technology up in temperature at reduced fields

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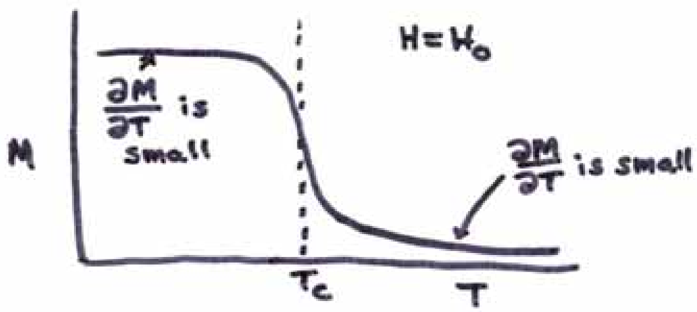
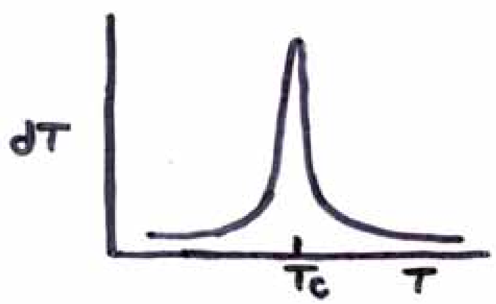
For a Ferromagnet:



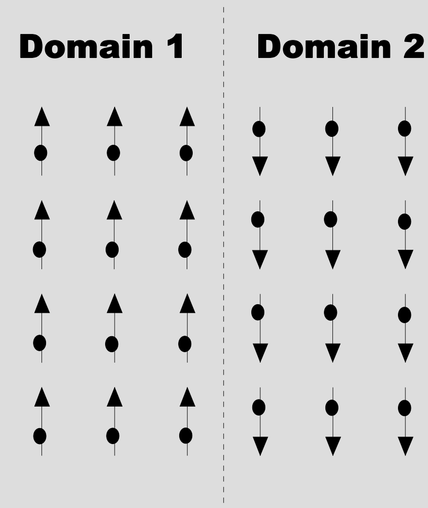
$$dT = -\left(\frac{T}{C_H}\right)\mu_0 V_M \left(\frac{\partial M}{\partial T}\right)_H dH$$



for $T < T_c$:

H (1) orders spins within domains
(2) eliminates domain walls

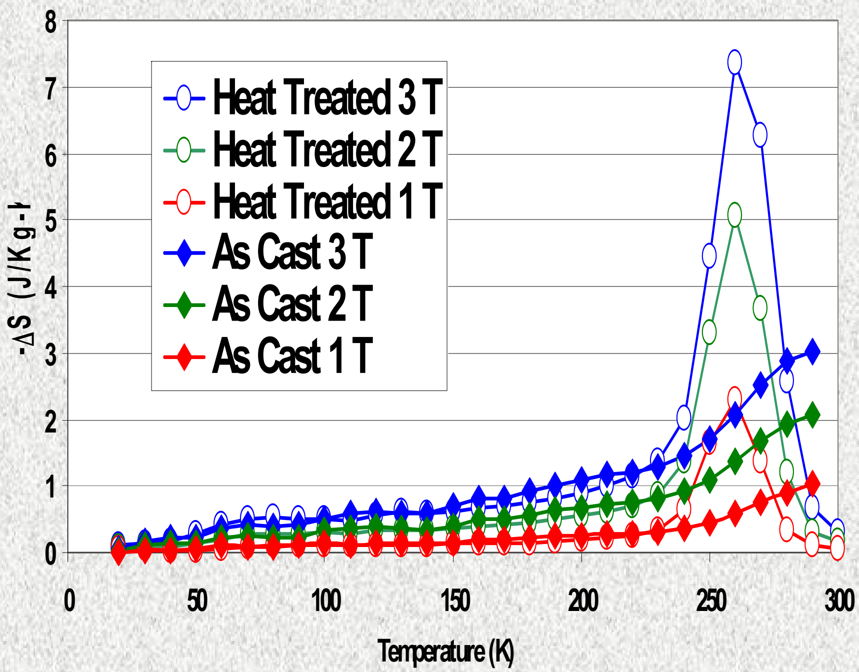
LARGE PARTICLE LIMIT



Assembly of magnetic domains (each comprised of many elemental moments of magnitude μ) aligned in the field direction in concert with the other domains

Ferromagnetic Material:

ΔS vs T for $Gd_5Ge_2Si_2$: As-Cast and Heat Treated (1100°C, 1 h + 1400°C, .2 h)



[V. Provenzano, A.J. Shapiro, and R.D. Shull, Nature 429, 853 (2004)]

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for $T > T_c$:

(N weakly interacting spins)

$$M = \frac{N\mu^2 H}{3k(T-T_c)}$$

$$\therefore \left(\frac{\partial M}{\partial T}\right)_H = -\frac{N\mu^2 H}{3k(T-T_c)^2}$$

$$\therefore \boxed{dT_{ferromagnet} = \left(\frac{\mu_0 V_M}{C_H}\right) \frac{N g^2 J(J+1)\mu_B^2}{3k} \frac{T}{(T-T_c)^2} H\,dH}$$

$$\frac{T}{(T-T_c)^2} >> \frac{1}{T}$$

$$\therefore dT_{ferro}\left(\text{above } T_c\right) >> dT_{para}$$

$$\left(dT_{para} = \left(\frac{\mu_0 V_M}{C_H}\right) \frac{N g^2 J(J+1)\mu_B^2}{3k} \frac{1}{T} H\,dH\right)$$

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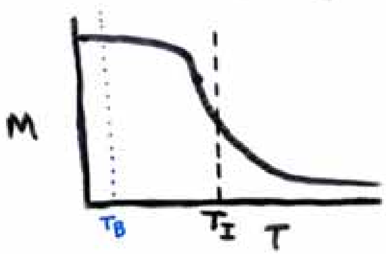
For a Nanocomposite:

- possessing superparamagnetic behavior with interaction:

n ferromagnetic regions weakly interacting with each other

$$\mu_{region} = \left(\frac{N}{n}\right)\mu$$

$$M = \frac{n\left(\frac{N}{n}\mu\right)^2 H}{3k(T-T_I)}$$



$$\therefore \quad \left(\frac{\partial M}{\partial T}\right)_H = -\frac{n\left(\frac{N}{n}\mu\right)^2 H}{k(T-T_I)^2}$$

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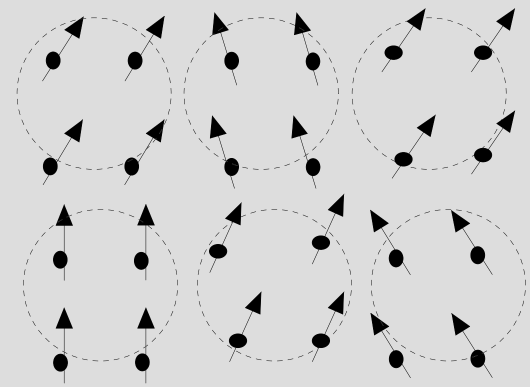
INTERACTING SMALL-PARTICLE BEHAVIOR



Assembly of magnetic clusters (each comprised of many ferromagnetically-aligned elemental moments of magnitude μ) acting in concert with other clusters.

Superferromagnetic Material:

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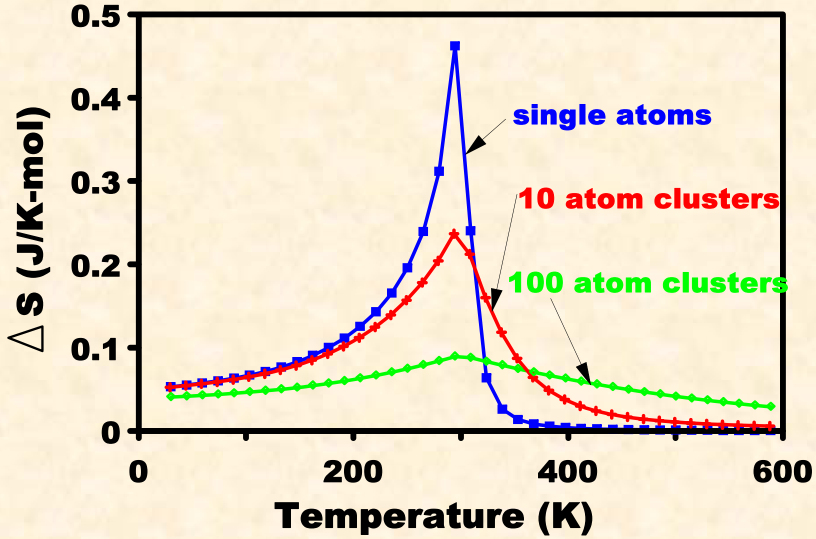
Entropy Change for Interacting Clusters of Spin 7/2 Atoms (ℑH=1T)



[R.D. Shull, IEEE Trans. on Magnetics 29, 2614 (1993)]

Interacting clusters of atoms possess smaller MCE values at the critical temperature, but larger MCE values at all higher temperatures.

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$$\therefore\; dT_{nano} = \left(\frac{\mu_o V_M}{C_H}\right) n\left(\frac{N}{n}\right)^2 \frac{\mu^2 H}{3k} \frac{T}{(T-T_I)^2}\, dH$$

$$n\left(\frac{N}{n}\right)^2 >> N$$

$\therefore$ for $T_I \approx T_c$

$$dT_{nano} >> dT_{ferro} >> dT_{para}$$

$$dT_{para} = \left(\frac{\mu_o V_M}{C_H}\right) N \frac{\mu^2 H}{3k} \frac{1}{T}\, dH$$

$$dT_{ferro} = \left(\frac{\mu_o V_M}{C_H}\right) N \frac{\mu^2 H}{3k} \frac{T}{(T-T_c)^2}\, dH$$

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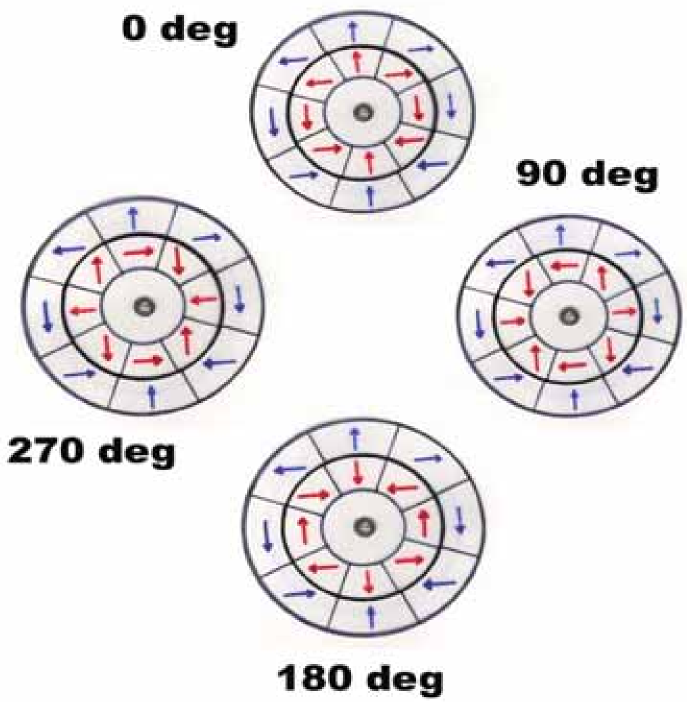
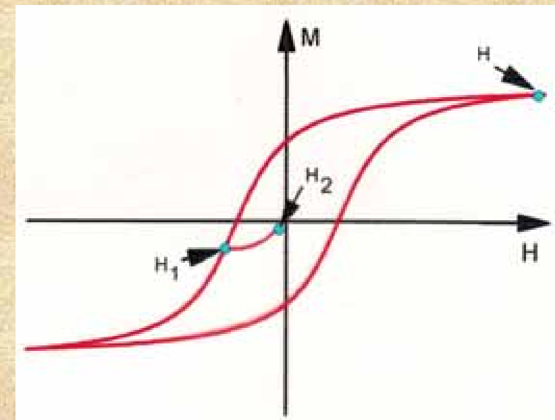
MAGIC RING

(VARIABLE PERMANENT MAGNET)



This is a good way to vary the magnetic field from a permanent magnet in a compact volume. Perhaps for a magnetic refrigerator???

WHAT ABOUT MCE CALCULATION FOR A FERROMAGNET???



M is NOT a Single Valued Function!

M is No Longer a Good Order Parameter !!!

Hysteresis Loss NEEDS to be subtracted from the MCE!!!

[V. Provenzano, A.J. Shapiro, and R.D. Shull, Nature 429, 853 (2004); V. Provenzano, B. Baumgold, R.D. Shull, A.J. Shapiro, K. Koyama, K. Watanabe, N.K. Singh, K.G. Suresh, A.K. Nigam, and S.K. Malik, J. Appl. Phys. 99, 08K906 (2006)]

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Conclusions

- Magnetocaloric effects are **dependent** on particle size and distribution
- **Enhanced** Magnetocaloric Effects can be obtained in **small particle** materials (e.g., in magnetic nanocomposites)
- Their maximum enhancements are at **LOW** fields and/or **HIGH** temperatures
- $Gd_3Ga_{5-x}Fe_xO_{12}$ nanocomposites may be usable now as a magnetic refrigerant at low temperatures
- RSP: $Nd_{13.75}(Fe_{1-X}Al_X)_{80.25}B_6$ nanocomposites:
  - show predicted systematics
  - are potentially usable near 300 K
- For ferromagnets, hysteresis loops should Always be shown if magnetic data is used to calculate the MCE

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