Nanomagnetism

Part 1: Physics of Nanomagnets

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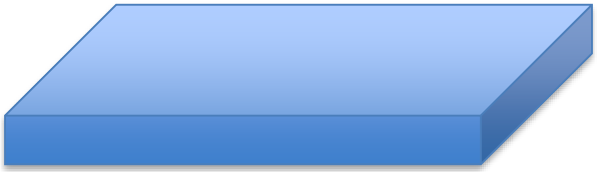
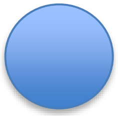
What Defines Nano?

At least one dimension is < 1000 nm



2 D: Thin film

1 D: nanowire

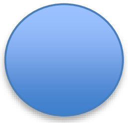


0 D: nanodot

Magnetic Length Scales

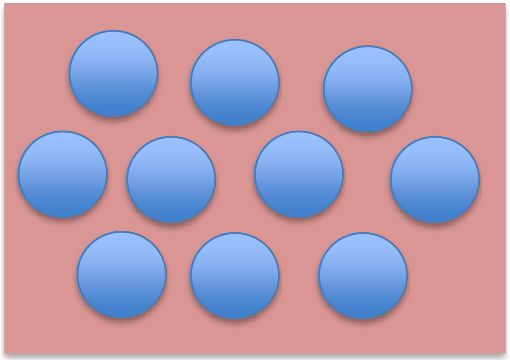
Length	**Symbol**	**Typical Magnitude (nm)**
Exchange length	l_{ex}	1 - 100
Domain wall width	δ	1 – 100
Spin diffusion length	λ_{sd}	1 - 100
Critical single domain diameter	d_{cr}	10 – 1000
Critical superparamagnetic diameter	d_{sp}	1 – 100

What’s Included Here in Nanomagnetism?



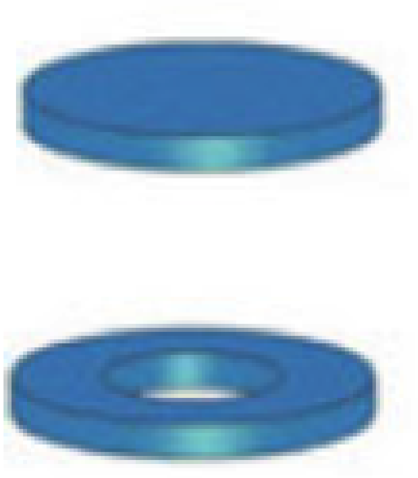
Nanoparticles

Nanowires



[Nanocomposites]

M. Yue, et al., Nanoscale **9** 3674 (2017).



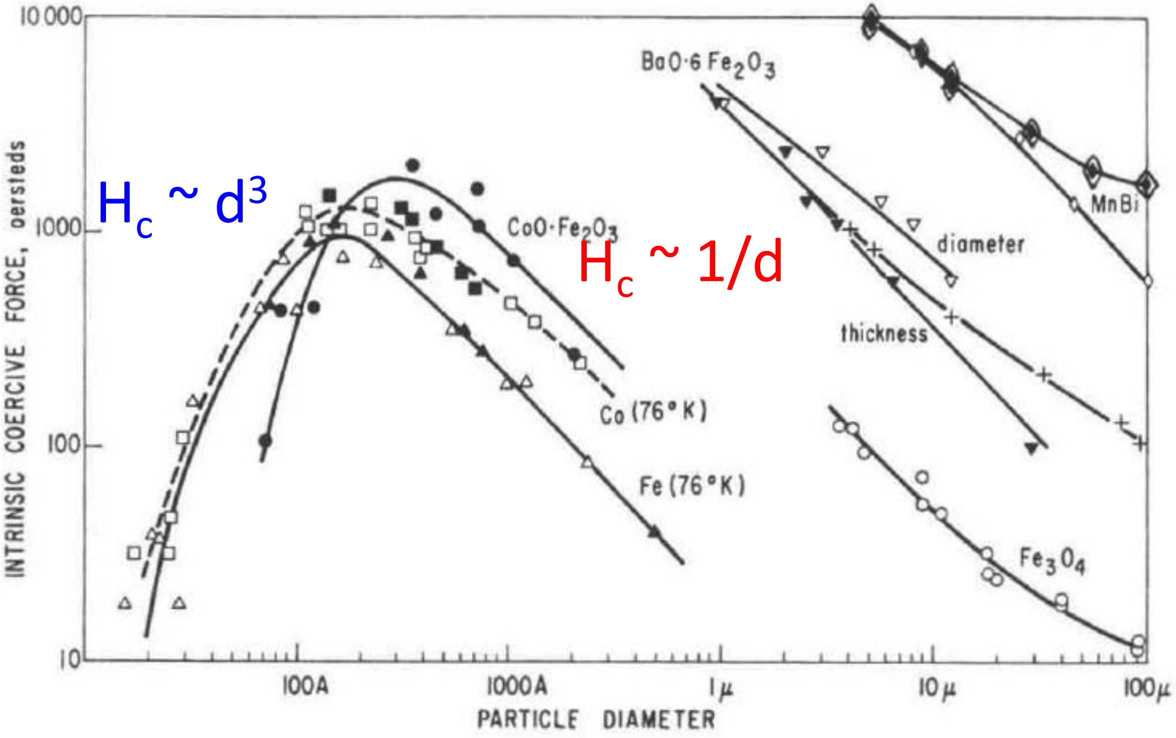
Nanopatterns

Skyrmions

Nanomagnetism Outline

1. Ideal Monodomain magnetic nanoparticles
2. Real magnetic nanoparticles
    a. surface effects
    b. exchange bias
3. Interactions of magnetic nanoparticles
    a. magnetostatic
    b. exchange coupling (nanocrystalline alloys)
4. Magnetic Nanowires
5. Magnetic Nanopatterns
    a. single domain
    b. magnetic vortices
    c. skyrmions

Size Dependence of Coercivity in Fine Particles



$H_c \sim d^3$

$H_c \sim 1/d$

Monodomain

Multidomain

Superparamagnetic, $H_c = 0$

F. E. Luborsky, J. Appl. Phys. **32**, S171 (1961)

3 Key Parameters

M_s --- Saturation magnetization

A --- Exchange stiffness

- $E_{ex} = |-2J\, S \bullet S\,| = 2\, aA$, a = lattice spacing
- $k_B T_C = E_{ex}$

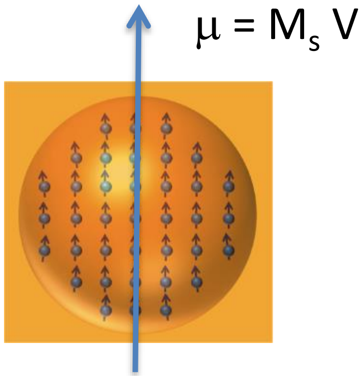
K --- Anisotropy

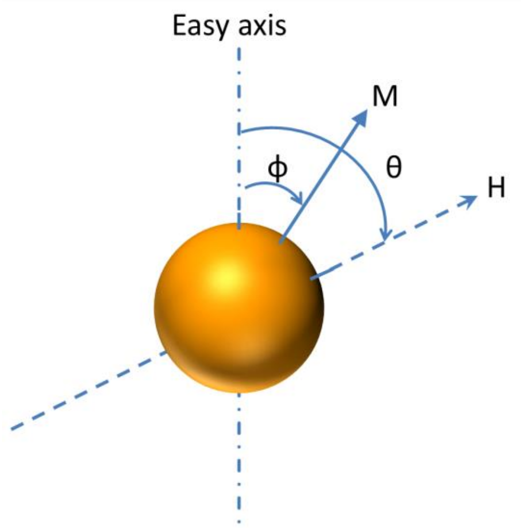
- Magnetocrystalline
- Shape (*0 for a spherical particle*)
- Magnetostriction (*ignore here*)
- Surface (*ignore for now*)

Monodomain Particles

Monodomain at a size below d_{cr}:

$$d_{cr} = \frac{72(AK)^{1/2}}{\mu_0 M_s^2}$$



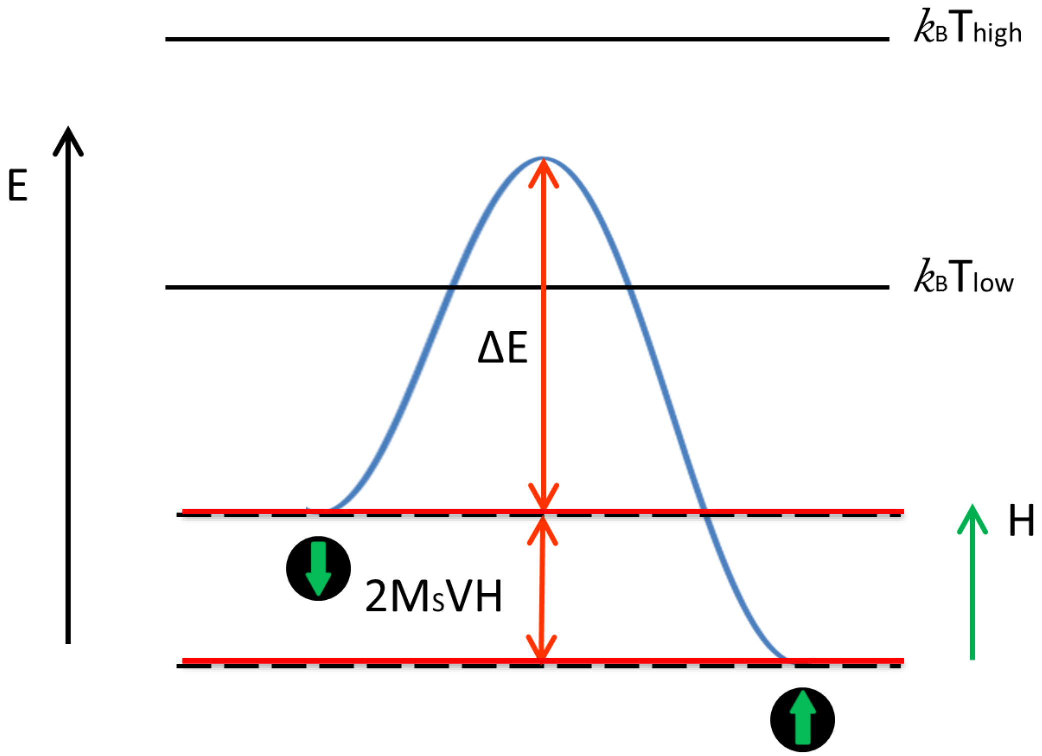


Assume uniform magnetization, treat as uniaxial

$$E = KV \sin^2\phi - M_s VH \cos(\theta - \phi)$$

If *H* parallel to the Easy Axis, 2 energy minima: $\phi = 0°, 180°$

Energy Barrier to Reversal

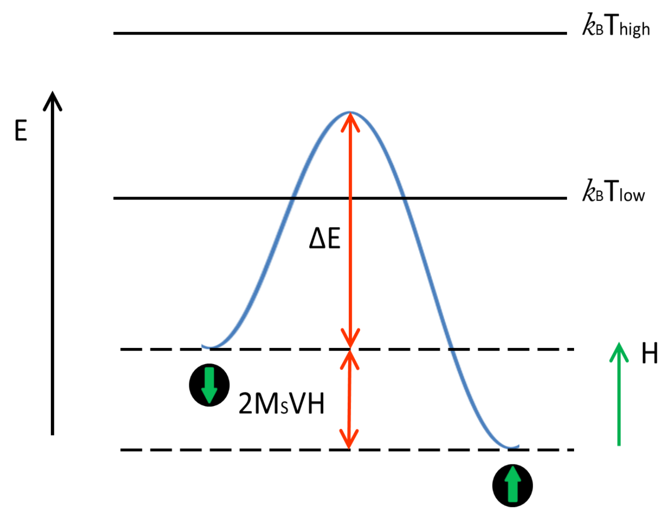


Minima at $\phi = 0°, 180°$

$$\Delta E = KV\,[1 - M_s H/2K]^2$$

Since no domain walls, reversal occurs by **Coherent Rotation** of particle spins

Energy Barrier Picture



Estimate rate of relaxation through Arrhenius law

$$\tau^{-1} = \tau_0^{-1} \exp(-\Delta E/k_B T)$$

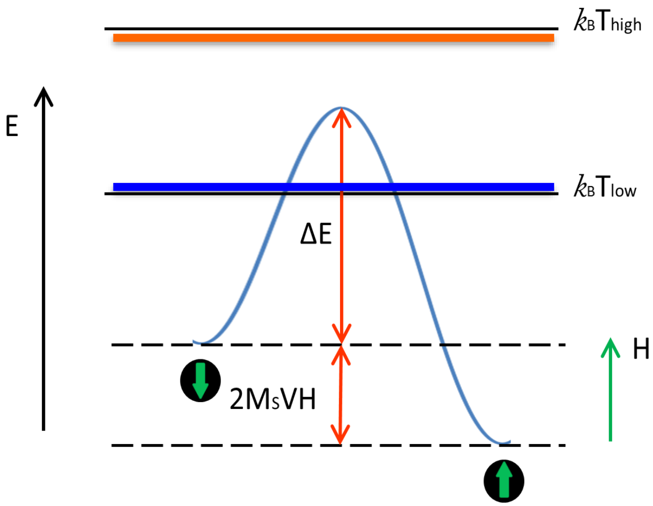
$$\tau^{-1} = \tau_0^{-1} \exp(-KV/k_B T)$$

where τ_0^{-1} is the Larmor precession frequency, ~ 1 GHz

Over time, the system will equilibrate

--- if this happens within the measurement time, the particles are said to be **Superparamagnetic**

Superparamagnetism



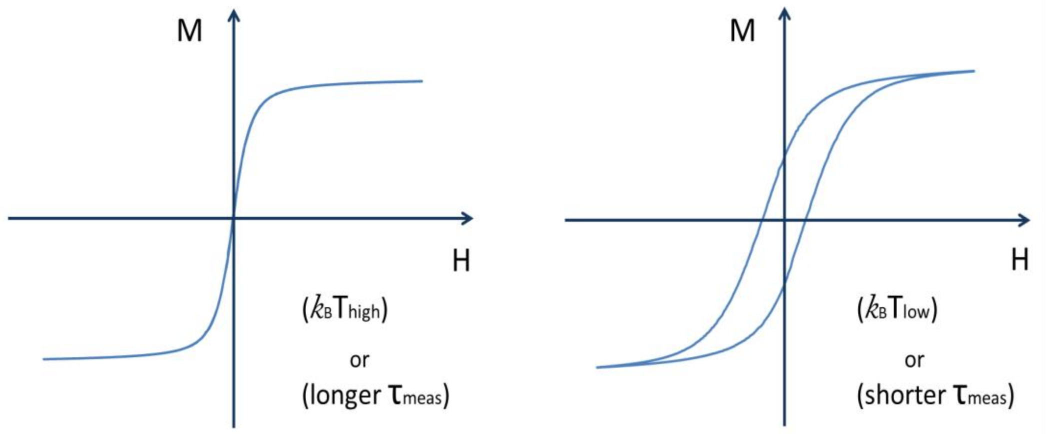
$$\tau^{-1} = \tau_0^{-1}\exp(-\Delta E/k_BT) = \tau_0^{-1}\exp(-KV/k_BT)$$

For **High temperature** relaxation is faster than at **Low temperature**

See no hysteresis if relaxes within measurement time

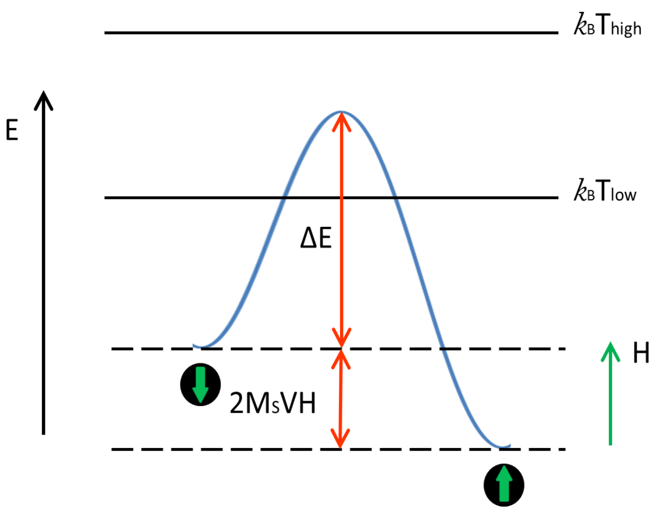
$$\tau < \tau_{meas}$$

$$d_{SP} = \left[\frac{6kT_B}{\pi K \ln(t_{meas}/t_0)}\right]^{1/3}$$



Superparamagnetic

Checking for Superparamagnetism



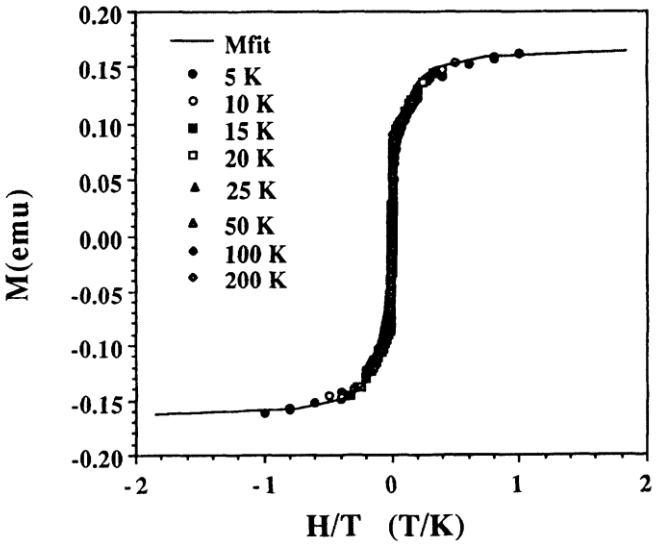
Estimate quasi-equilibrium populations based on Boltzmann factors

Langevin function,

$$L(x) = M/M_0 = \coth(x) - 1/x$$

where $x = M_sVH/k_BT$

$M = M(H/T)$, fit for dilute sample to determine particle moment $\mu = M_sV$

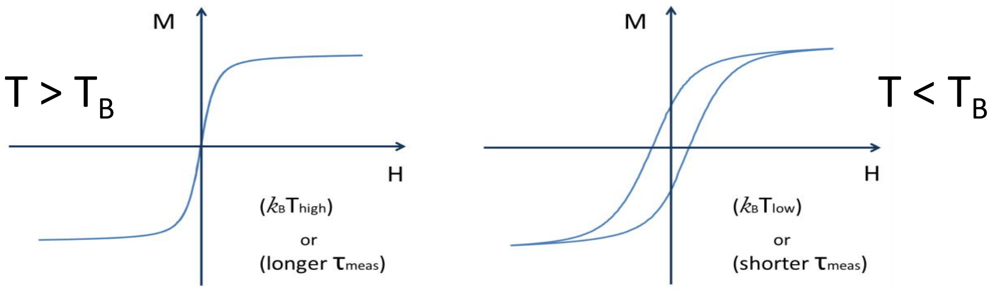


M. E. McHenry, et al., Phys. Rev. B **49**, 11358 (1994)

Blocking Temperature

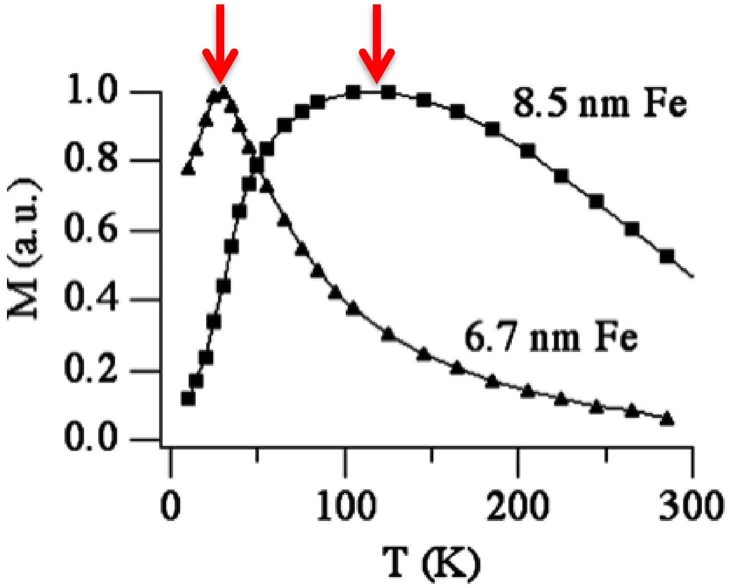
The coercivity H_c goes to zero at the Blocking temperature, T_B

$$T_B = KV\ln(t_{meas}/t_0)/k$$



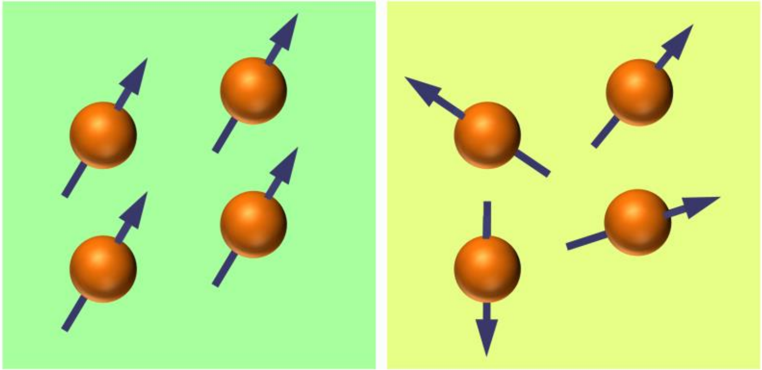
Find T_B from the peak in the Zero Field Cooled Magnetization, $M_{zfc}(T)$

- cool with $H = 0$
- turn on small H, measure M as increase T



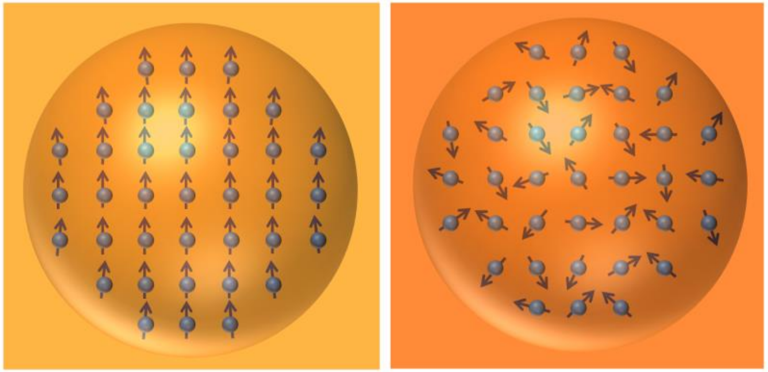
S.A. Majetich and M. Sachan, J. Phys. D **39**, R407 (2006)

Blocking vs. Curie Temperature



$T<T_B$ $T>T_B$

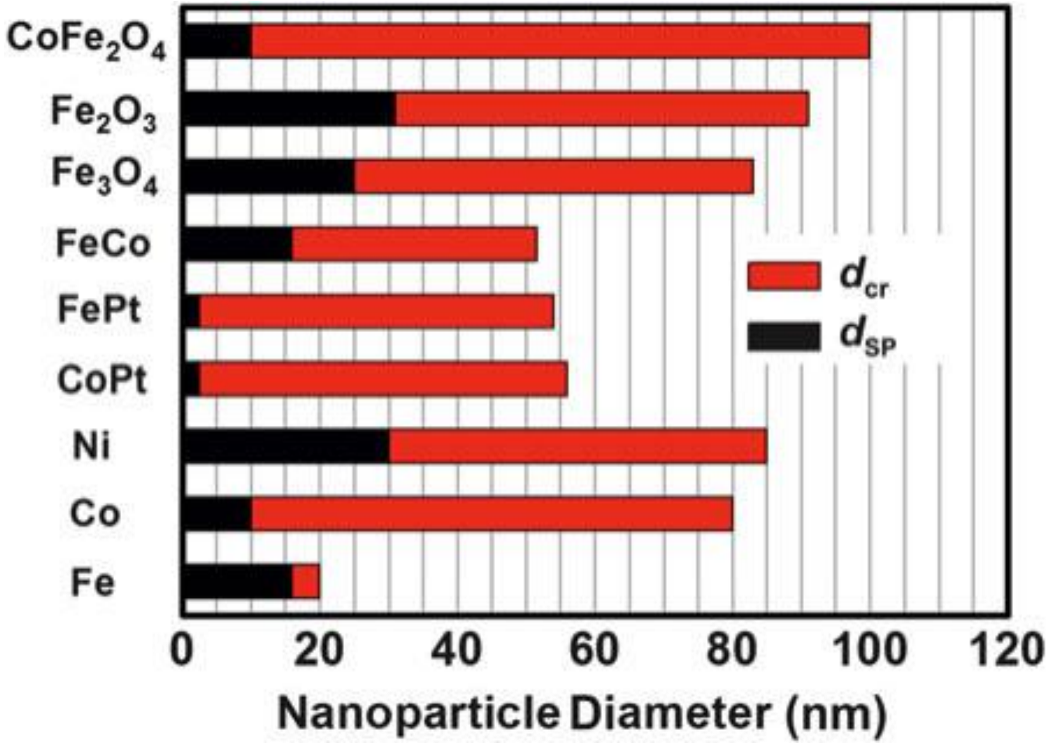
Hysteresis is seen below the **Blocking temperature** because the *particle spins* haven’t yet randomized



$T<T_C$ $T>T_C$

Hysteresis is seen below the **Curie temperature** because the *atomic spins* are not randomly oriented

Monodomain and Superparamagnetic Thresholds for Different Materials



For soft magnetic materials (low K),

$d_{sd} \sim l_{ex} <<$ domain wall width δ

For hard magnetic materials (big K),

$d_{sd} >> l_{ex} \geq$ domain wall width δ

S. A. Majetich, et al., *Materials Research Society Bulletin* **38**, 899 (2013)

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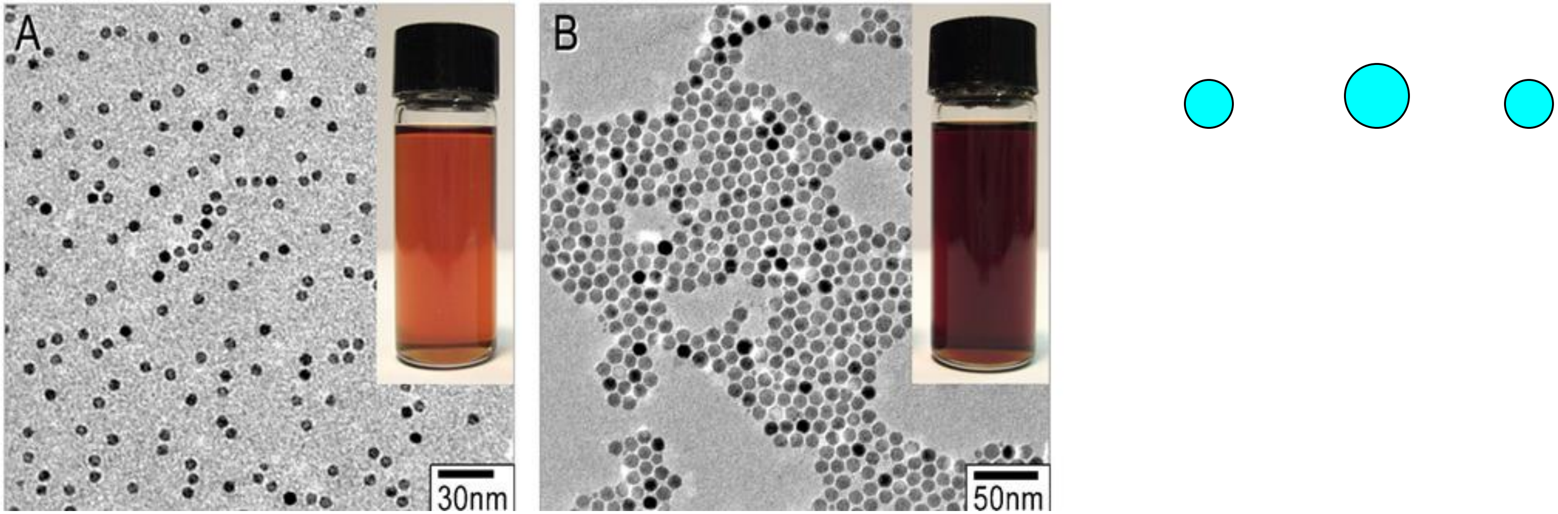
What Could Be Different for Real Nanoparticles?

M_s --- Saturation magnetization --- Could be reduced if there is surface oxide (e.g., Co/CoO), if there are antiphase boundaries (e.g., in Fe_3O_4), or if there is surface disorder

A --- Exchange stiffness --- Fewer near neighbors reduces E_{ex}, symmetry breaking at a surface or interface could enable noncollinear exchange (Dzyaloshinskii-Moriya interaction, DMI)

K --- Anisotropy --- Symmetry breaking and/or spin disorder at the surface modify the anisotropy

Thermal Decomposition in High Boiling Point Organic Solvents



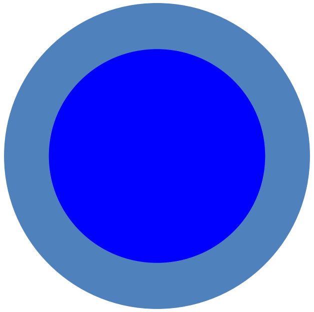
More monodisperse, high crystallinity

S. H. Sun, et al., J. Am. Chem. Soc. **126** 273 (2004). --- **~ 84 emu/g**

J. Park, et al. Nat. Mater. **3**, 891-895 (2004). --- **~ 42 emu/g but make gram quantities**

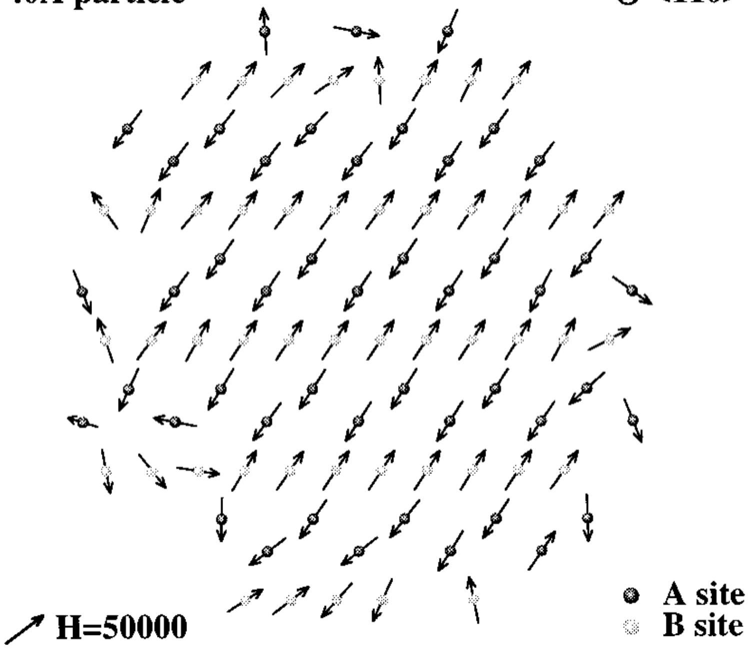
Reduced M_s in Nanoparticles

Magnetization less than expected based on the #spins



"Magnetic Dead Layer" = ?

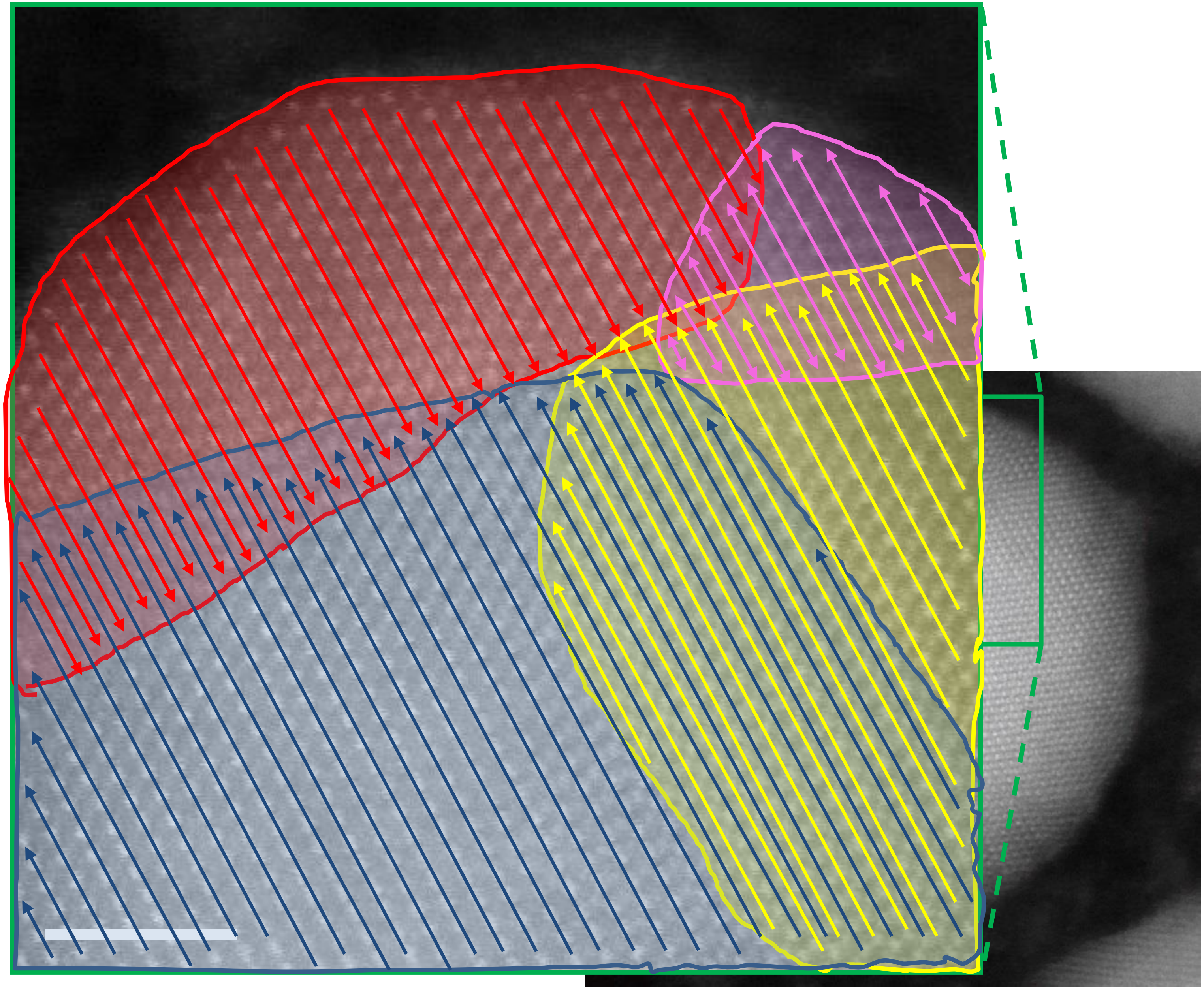
Surface Spin Glass



Model of $NiFe_2O_4$ made by ball milling

R. H. Kodama and A. E. Berkowitz, *Phys. Rev. B* **59**, 6321 (1999).

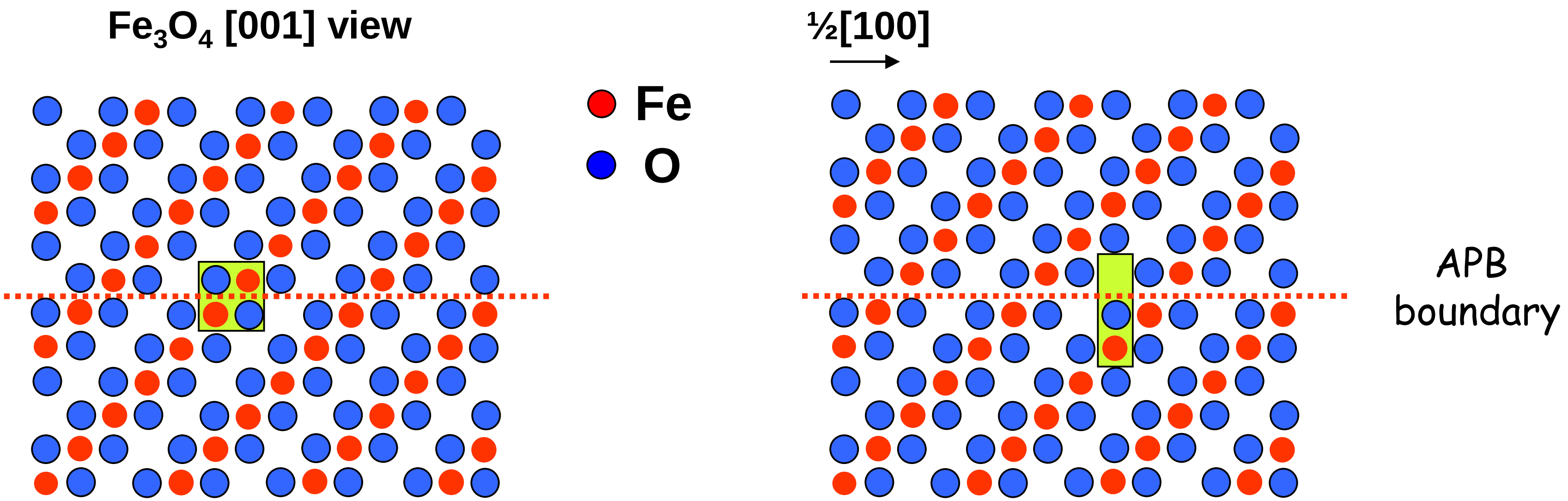
STEM-HAADF of Iron Oxide with APBs



Chemically ordered with extensive structural defects

Structural domains separated by anti-phase boundaries

Exchange Interactions Across Antiphase Boundaries in Fe_3O_4



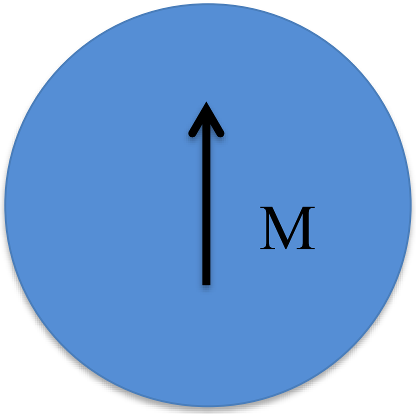
Super exchange interactions in bulk
(Fe_A-O-Fe_B)=AF
(Fe_B-O-Fe_B)=FM

Super exchange interactions across APB
(Fe_A-O-Fe_B): increased number of interactions
(Fe_B-O-Fe_B): interactions with 180° =AF

[Z. Nedelkoski, et al., *Sci. Rep.* **7**, 45997 (2017)]

Effect of Antiphase Boundaries on Spin Configuration

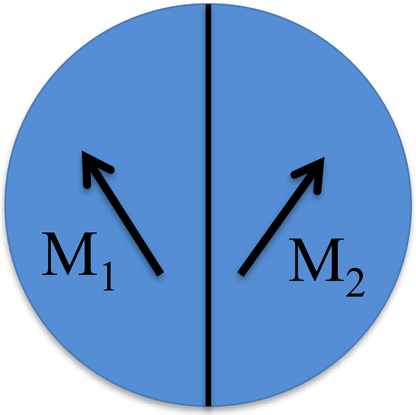
No Antiphase Boundary



Monodomain

[Z. Nedelkoski, et al., *Sci. Rep.* **7**, 45997 (2017)]

With Antiphase Boundary

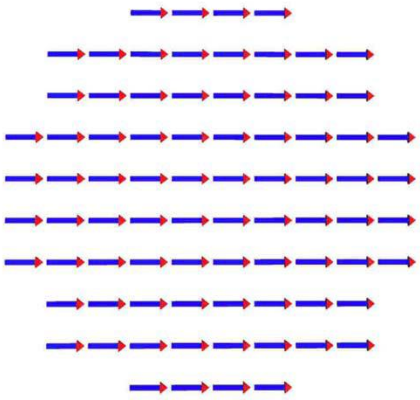


Not monodomain even though below d_{cr}

Lower M_s and acts like higher K

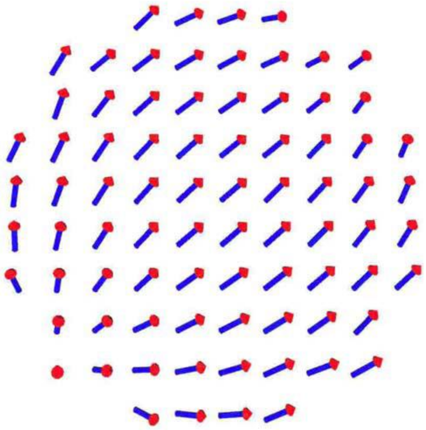
Effect of Surface Anisotropy K_s

Monodomain



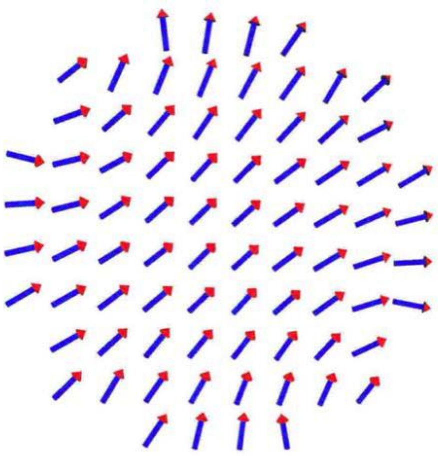
$K_s = 0$

Artichoke



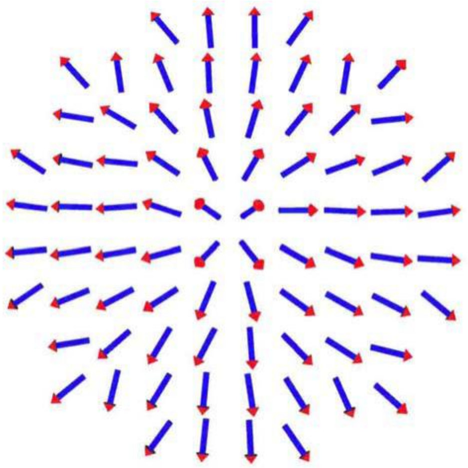
$K_s < 0$

Throttled



$K_s > 0$, small

Hedgehog



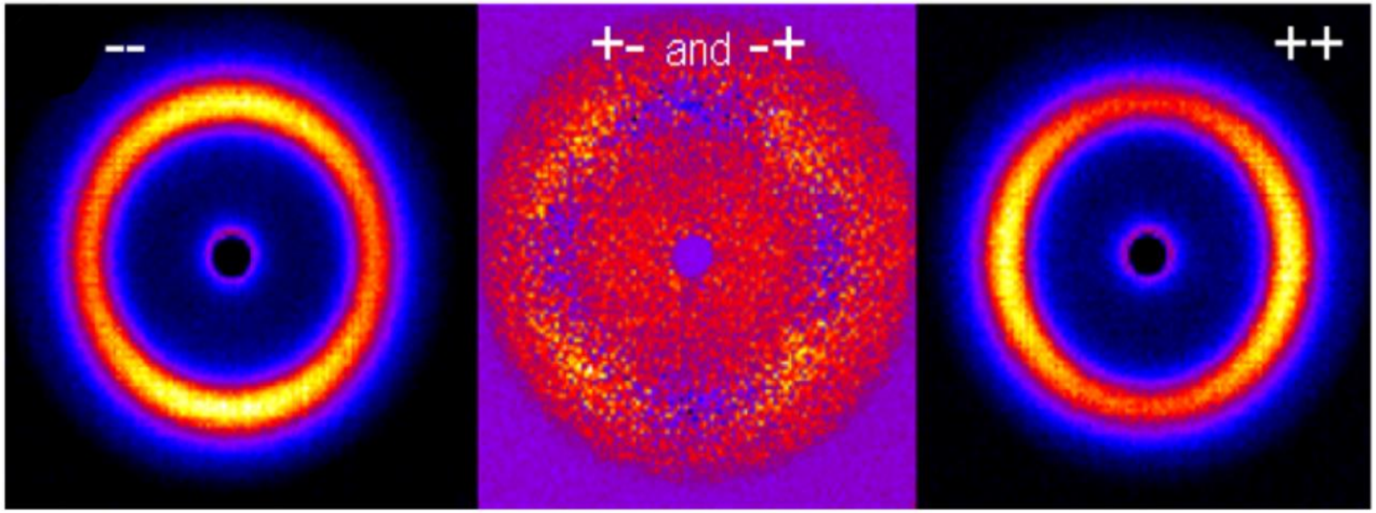
$K_s > 0$, large

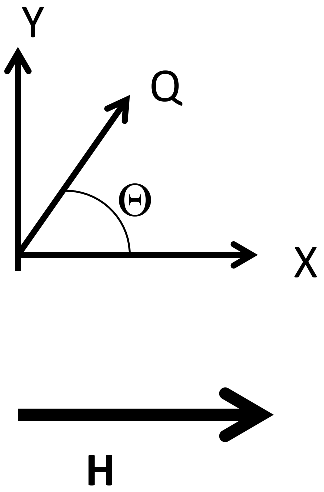
L. Berger, et al., *Phys. Rev. B* **77**, 104431 (2008).

Very difficult to determine K_s experimentally

Polarized Small Angle Neutron Scattering (SANS)

9.0 nm Fe_3O_4 nanoparticle crystals, 1.2 T



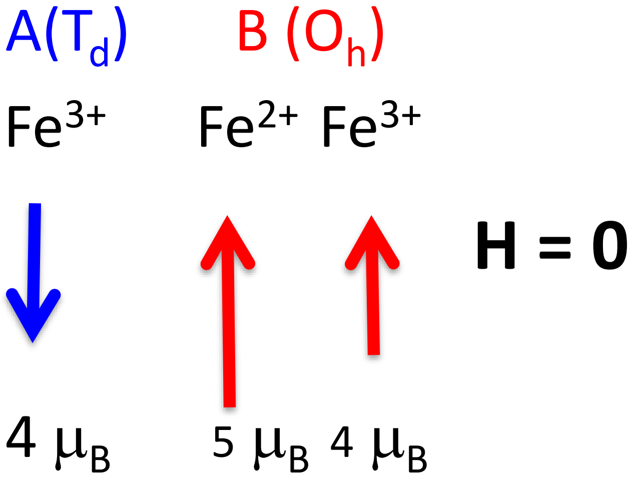


Unequivocally differentiate magnetic and nuclear scattering
- unlike with previously where relied on a “saturating” field

$M_x \neq M_y \neq M_z$, and see unexpected evidence of perpendicular M

K. L. Krycka, et al., Phys. Rev. Lett. **104** 207203 (2010).

Spin Canting in Fe_3O_4 NPs



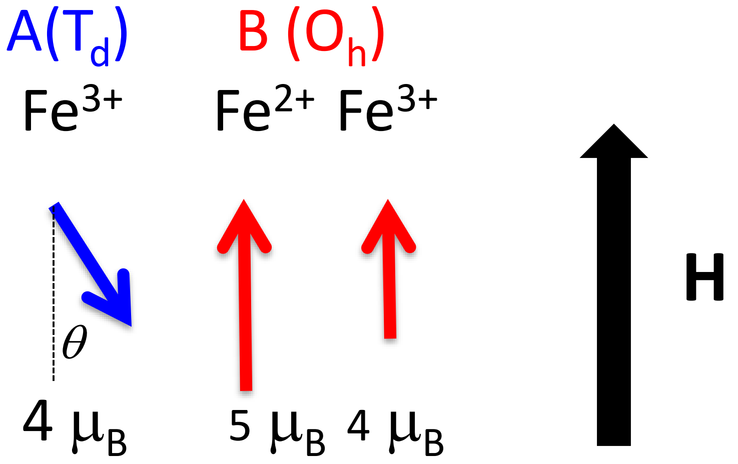
$A(T_d)$ $B(O_h)$

Fe^{3+} Fe^{2+} Fe^{3+}

H = 0

4 μ_B 5 μ_B 4 μ_B

Ferrimagnetic



$A(T_d)$ $B(O_h)$

Fe^{3+} Fe^{2+} Fe^{3+}

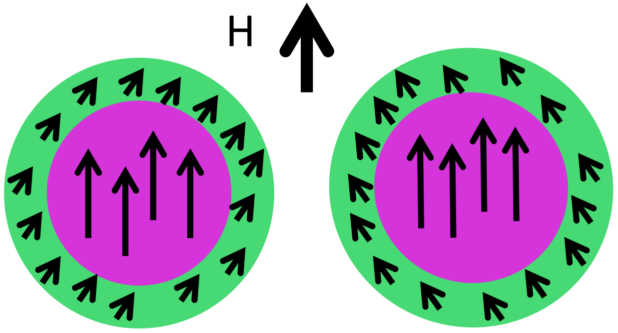
θ

H

4 μ_B 5 μ_B 4 μ_B

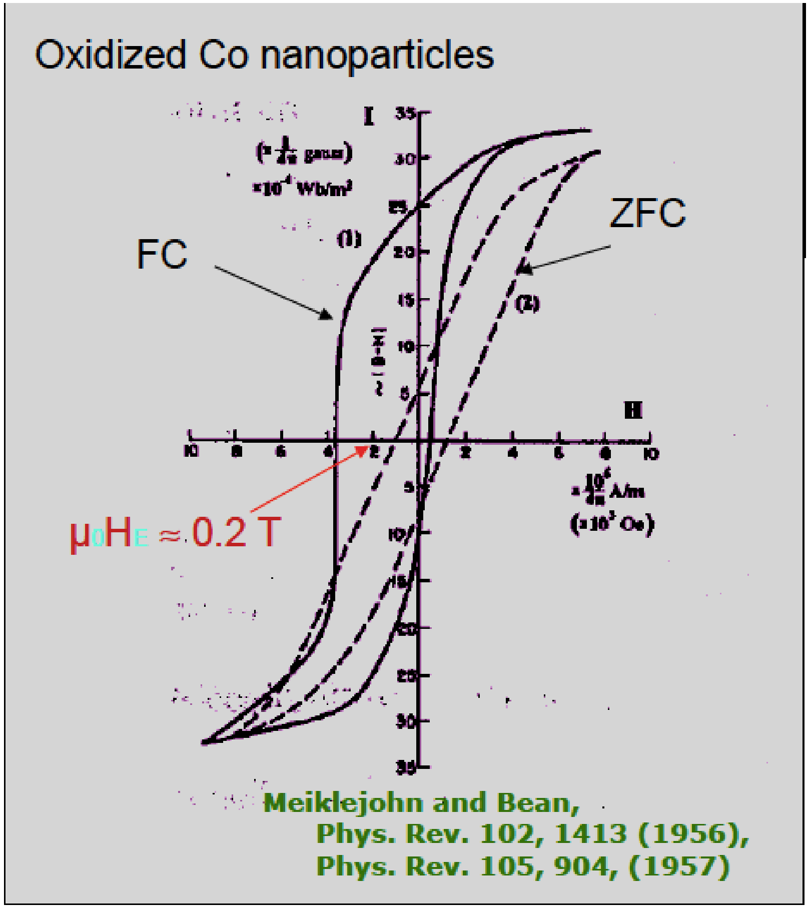
Zeeman interactions compete with exchange

Enhanced for spins near surface due to weaker exchange



K. L. Krycka, et al., Phys. Rev. Lett. **113,** 147203 (2014).

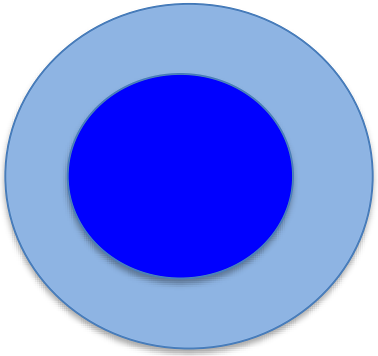
Exchange Bias in Core-Shell Particles



Oxidized Co nanoparticles

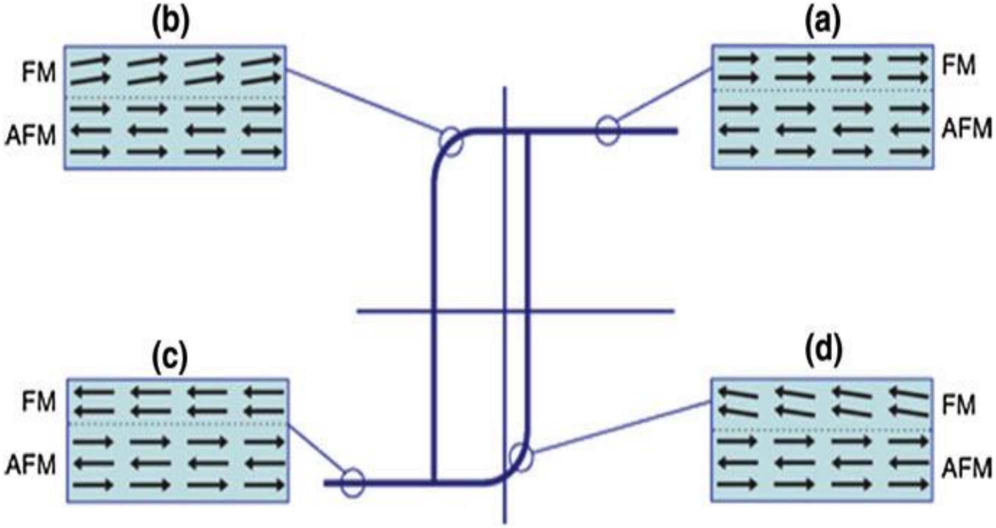
Meiklejohn and Bean,
Phys. Rev. 102, 1413 (1956),
Phys. Rev. 105, 904, (1957)

See difference in H_c and a loop shift if NPs are cooled in a magnetic field below the Neel temperature of CoO



Co (FM) core and CoO (AF) shell

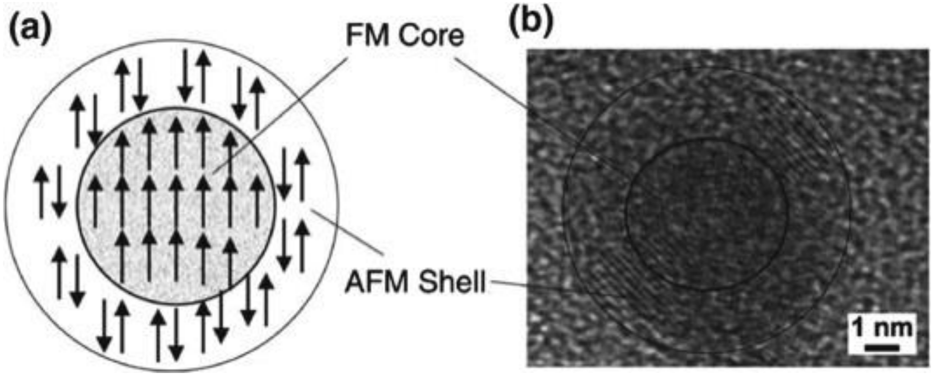
Exchange Bias in Core-Shell Particles



Field cooled loop

Training effects: the FM/AF interface spin configuration depends on H, time, and temperature

(A. Guimaraes, Nanomagnetism)



TEM image

Exchange bias more complex in particles than thin films because shell is polycrystalline

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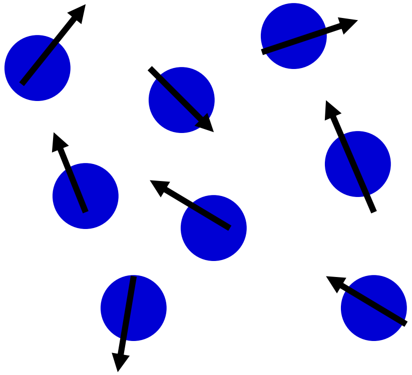
Magnetostatic Interactions

Superparamagnet



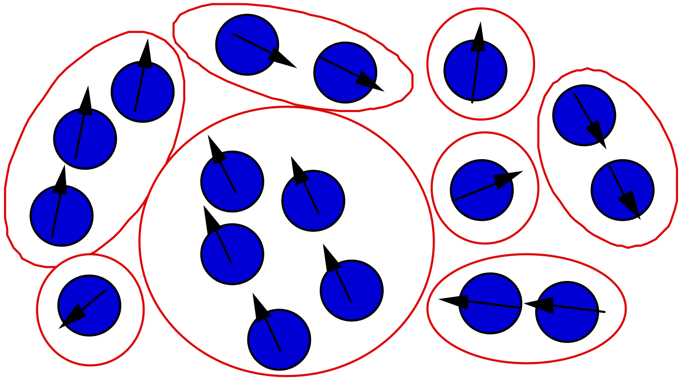
No interactions between particles

M~ Langevin function

M(t) decays exponentially

Dilute

Superferromagnet



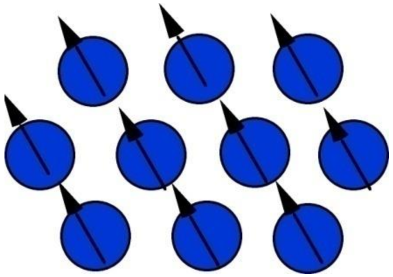
Some interactions

Short-range magnetic order

Glassy M(t) behavior

> 1 vol.%, but structurally disordered

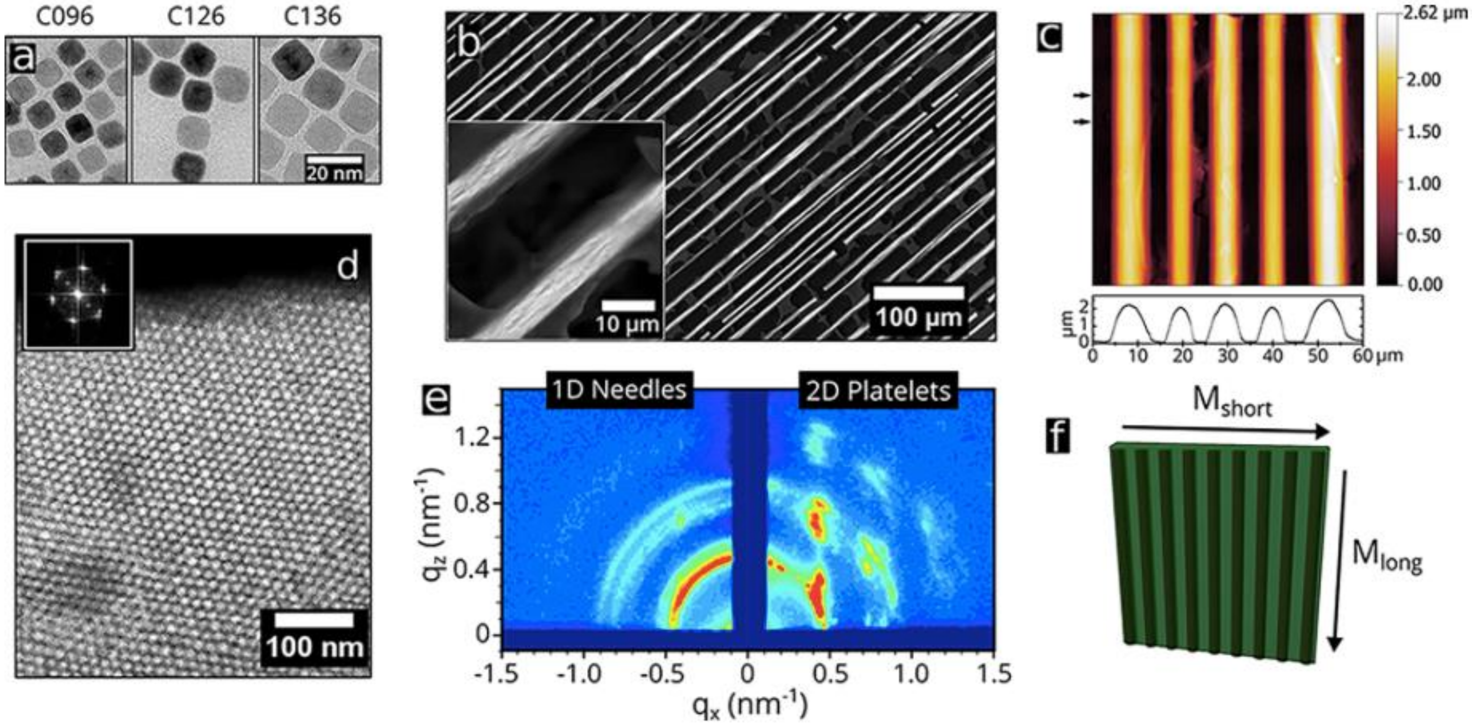
Dipolar Ferromagnet



Long-range magnetic order that is stable over time

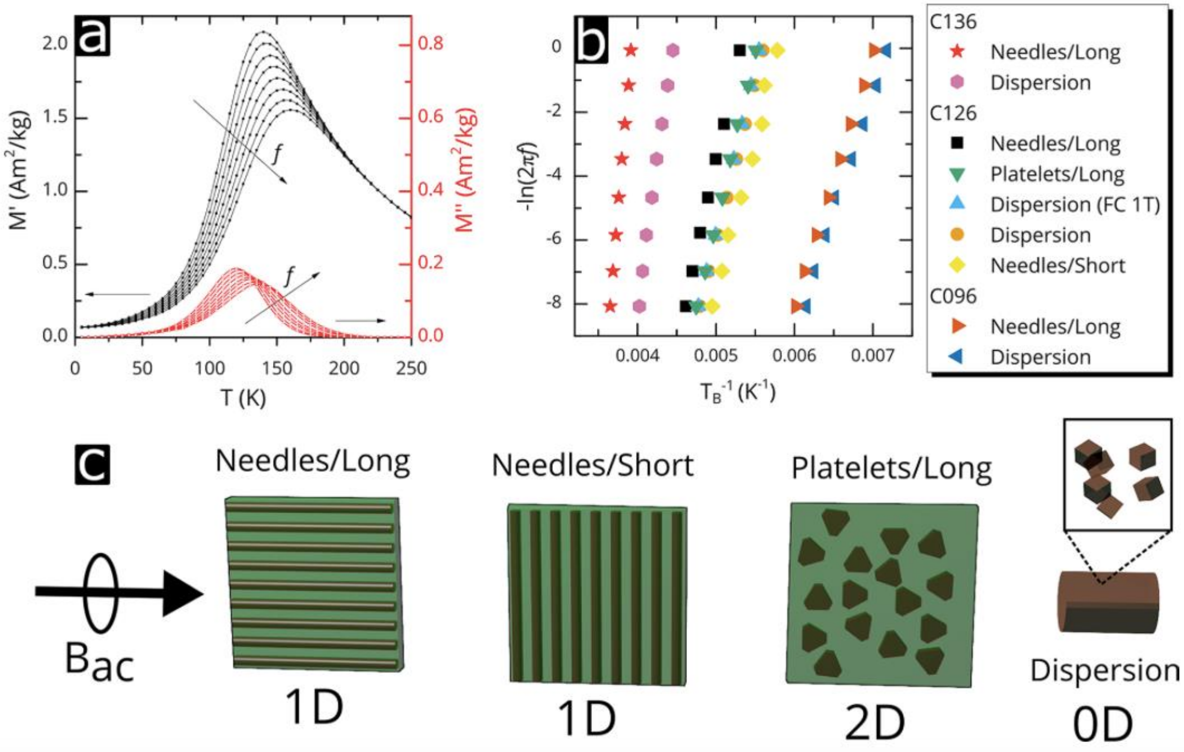
Highly ordered

Collective Behavior in Nanoparticle Assemblies with Dipolar Interactions



E. Wetterskog, et al., ACS Nano **12**, 1403 (2018)

AC Magnetic Response in Nanoparticle Assemblies and Superferromagnetism

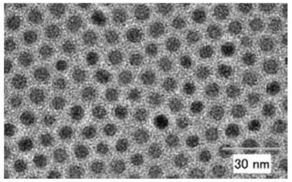


Magnetostatic interactions can increase the Blocking temperature, stabilizing multi-particle spin correlations

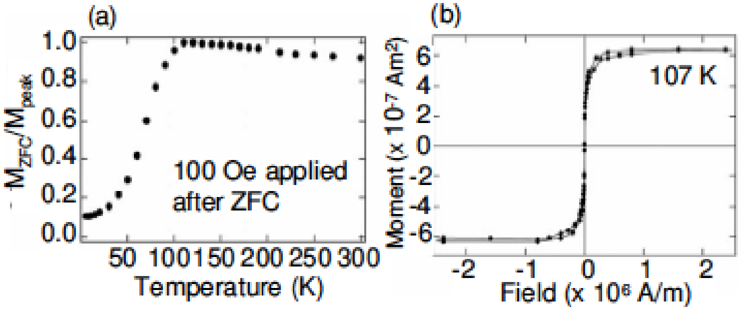
Superferromagnetism: Ordering of spins over neighboring particles, and collective switching due to thermal fluctuations

E. Wetterskog, et al., ACS Nano **12**, 1403 (2018)

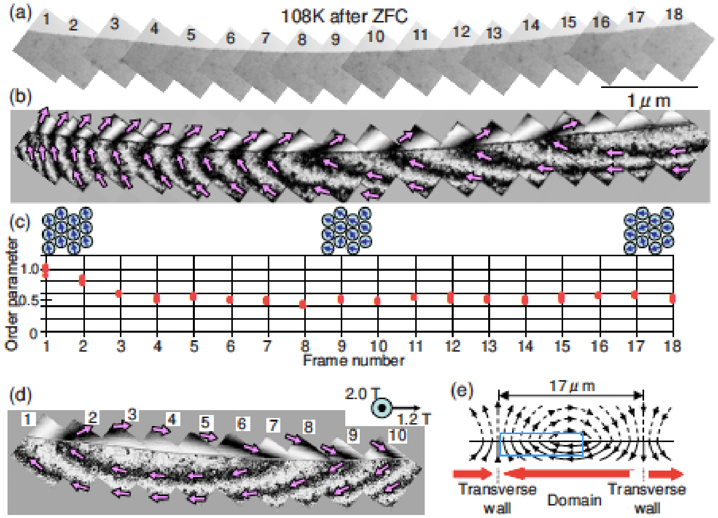
Magnetic Domains Observed by Electron Holography



8 nm Co nanoparticle monolayer



Seems like it should be superparamagnetic, but it's not

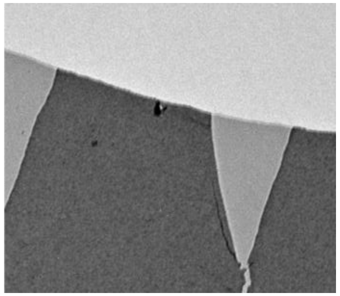


Spontaneous magnetization is stable over time, so ferromagnetic, but only dipolar interactions between particles

Assembly acts like a soft ferromagnet in DC measurements, with lower K_{eff} due to anisotropy averaging

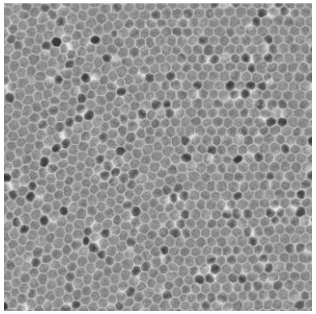
K. Yamamoto, et al., Appl. Phys. Lett. **93**, 082502 (2008)

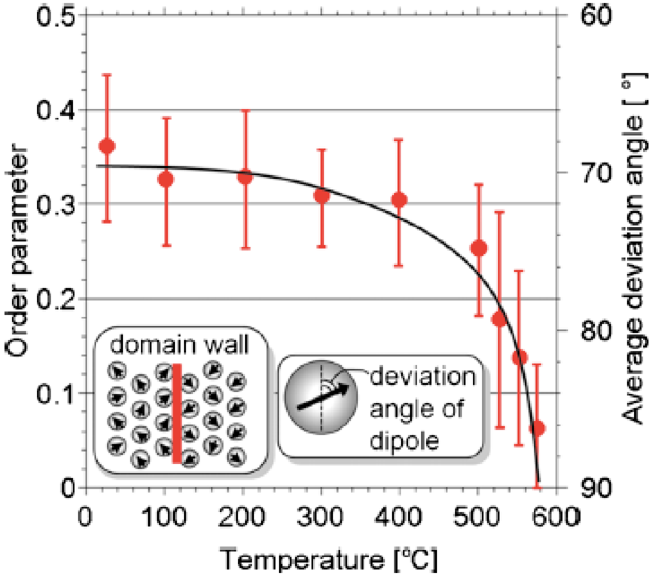
Dipolar Ferromagnetism in 13 nm Fe_3O_4 Nanoparticle Assemblies

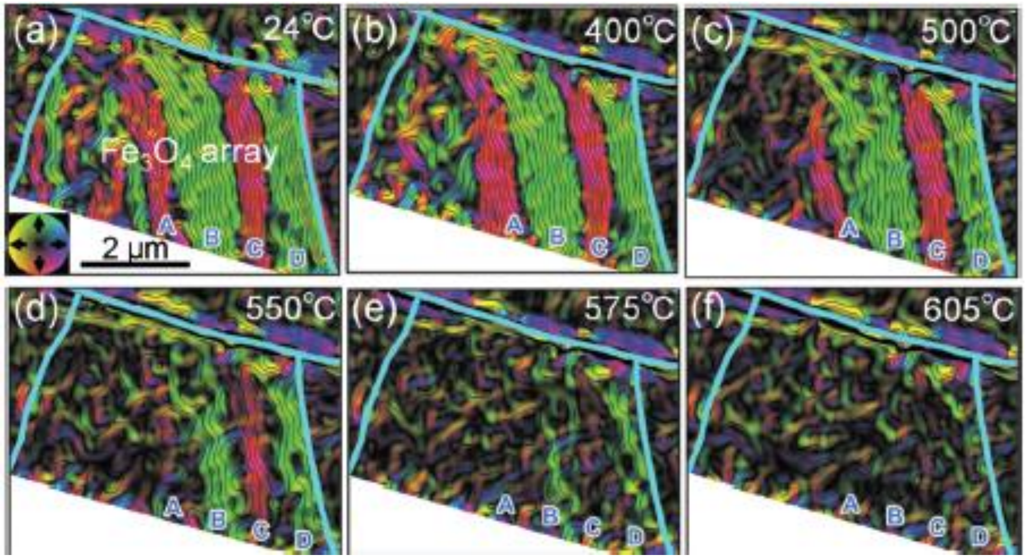


Lower magnification

Higher magnification







Electron Holography phase shift reveals in-plane B

Looks like M(T) for a ferromagnet

K. Yamamoto, et al., Appl. Phys. Lett. **98**, 072509 (2011).

What About Exchange Coupling?

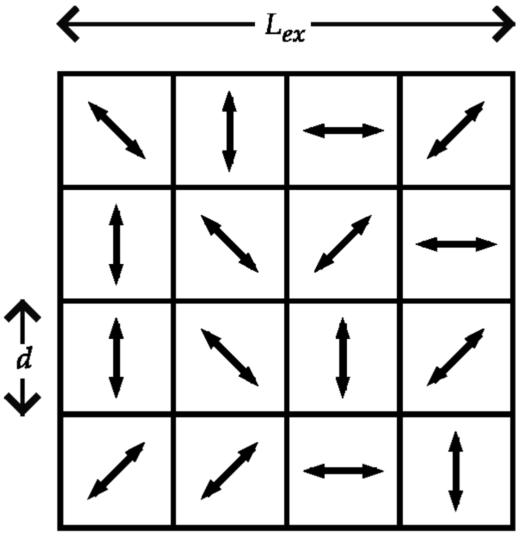
Length	Symbol	Typical Magnitude (nm)
Exchange length	l_{ex}	1 - 100
Critical single domain diameter	d_{cr}	10 – 1000
Critical superparamagnetic diameter	d_{sp}	1 – 100
Spin diffusion length	λ_{sd}	1 – 100
Domain wall width	δ	1 – 100

Exchange Interactions in Soft Nanocrystalline Materials

No surfactant between grains, make by melt spinning

N touching grains of size *d* with different orientations

$$N = \left(\frac{L_{ex}}{d}\right)^3 \qquad L_{ex} = \sqrt{\frac{2A}{\mu_0 M_s^2}}$$



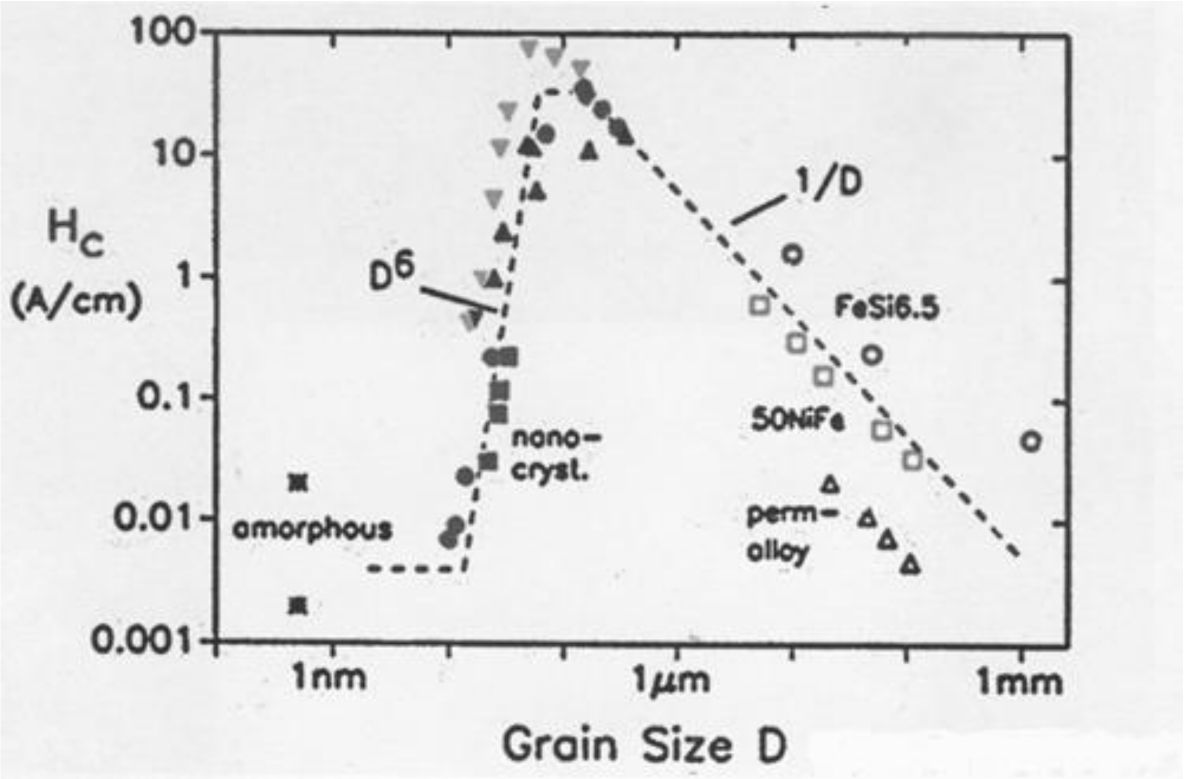
$$\langle K \rangle \approx \frac{K}{\sqrt{N}}$$

Reduced anisotropy

When exchange length > grain size, and grains have different easy axes, get anisotropy averaging

G. Herzer, IEEE Trans. Magn. **26** 1397 (1990)

Coercivity in Soft Nanocrystalline Materials



G. Herzer, IEEE Trans. Magn. **26** 1397 (1990)

Stronger size dependence than monomdomain nanoparticles

$H_c \sim D^6$ vs D^3

Reduced H_c since reduced K

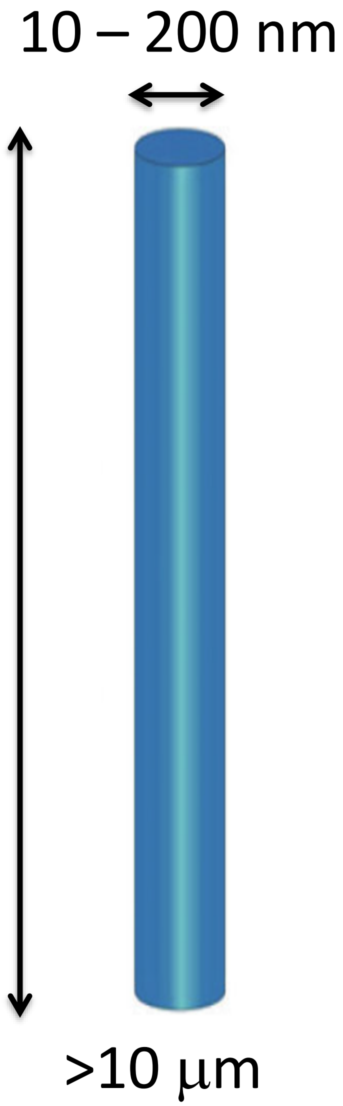
Finemet: $Fe_{73}Si_{13.5}B_9Nb_3Cu_1$

Nanoperm: $Fe_{89}Zr_7B_3Cu_1$

Nanomagnetism Outline

1. Ideal monodomain magnetic nanoparticles
2. Real magnetic nanoparticles
    a. surface effects
    b. exchange bias
3. Interactions of magnetic nanoparticles
    a. magnetostatic
    b. exchange coupling (nanocrystalline alloys)
4. Magnetic Nanowires
5. Magnetic Nanopatterns
    a. single domain
    b. magnetic vortices
    c. skyrmions

Magnetic Nanowires



Because of the large shape anisotropy, they can ideally be single domain

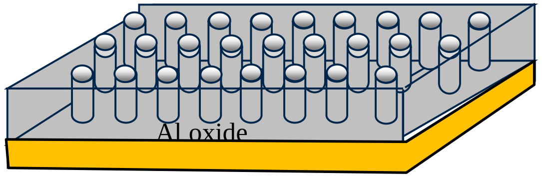
Real nanowires often have surface effects and magnetostatic interactions, just like nanoparticles

Because there is more magnetic volume, they are unlikely to be superparamagnetic

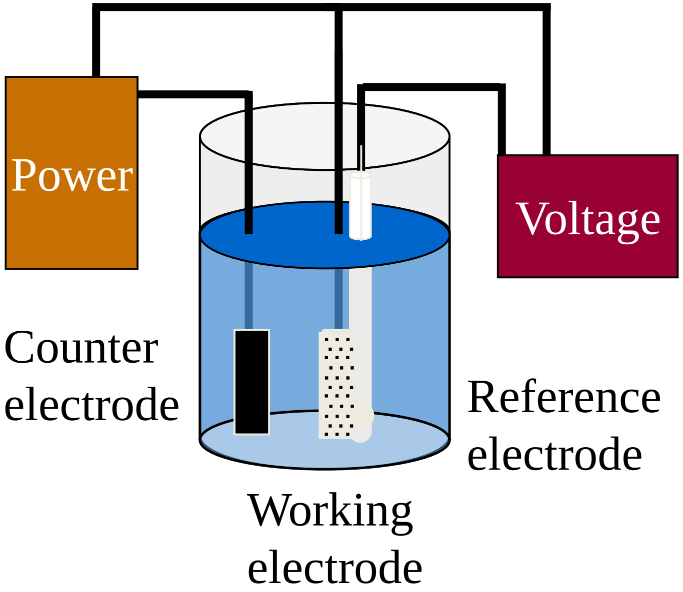
They do not switch their magnetization direction by Coherent Rotation; domain walls nucleate and travel down the length of the wire

Making Nanowires

- **Make nanoporous template by anodizing aluminum:**



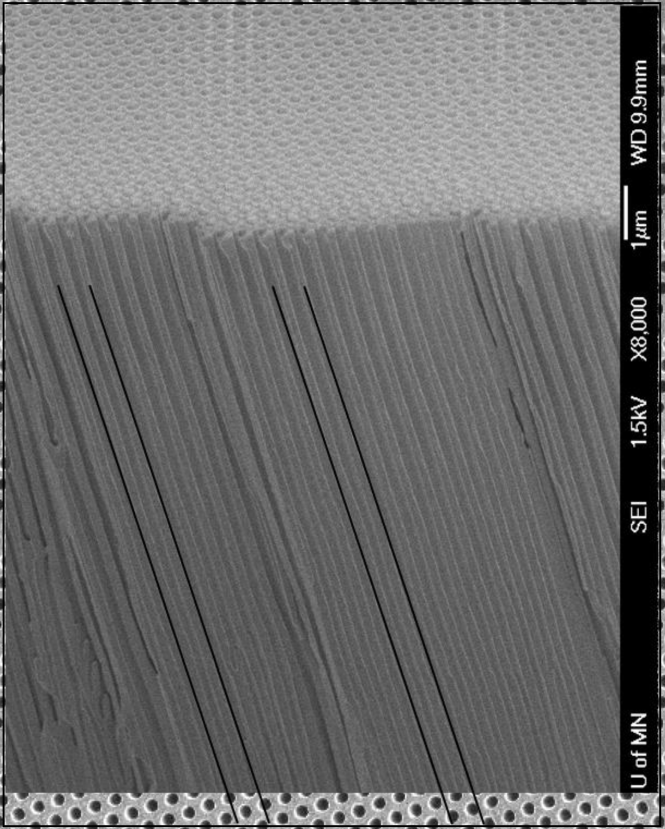
Schematic:
10-200nm pores can be achieved

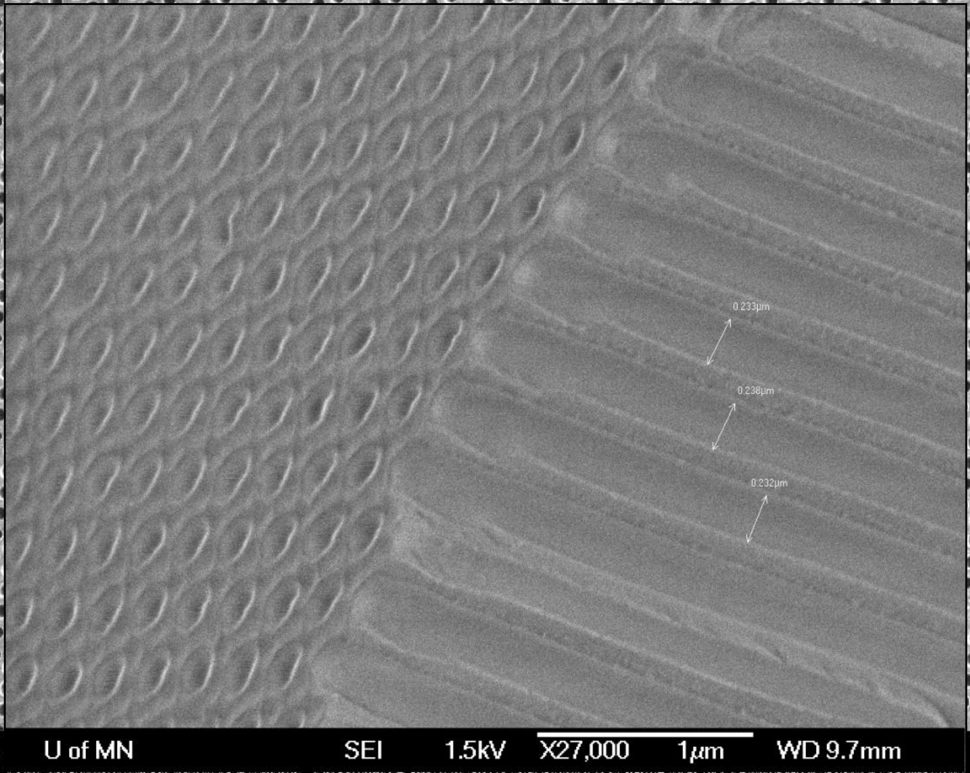


- **Contact film on bottom template**
  - Can pattern contact for anisotropic arrays
- **Electroplate nanowires into pores**
  - Any conductive material can be made
- **Etch template to release wires if application requires**

(Bethanie Stadler, U. Minnesota)

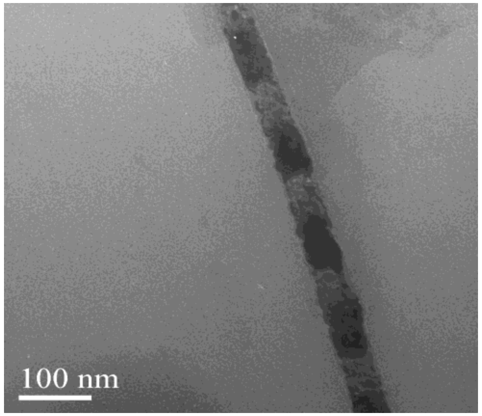
SEM of Nanowire Templates

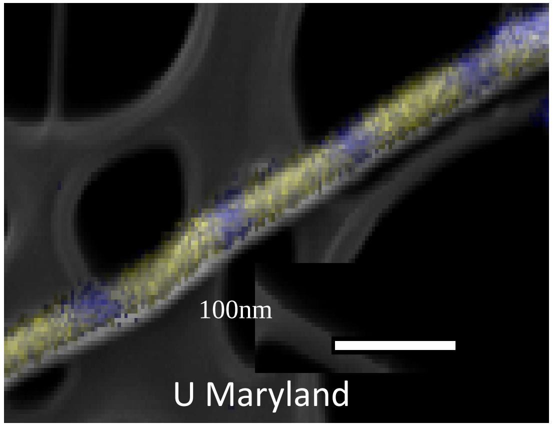




Maqablah et al. *IEEE Trans. Mag.* **48** (2012).
Sung et al. *IEEE Trans. Mag.* **50** (2014).

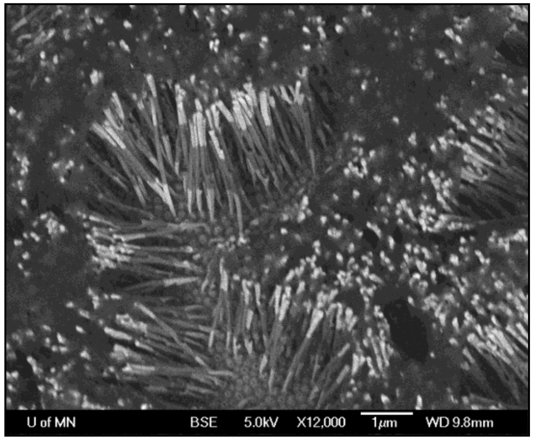
Can Fill Pores with:
Co, Cu, Ni, FeGa, Au… any metal?



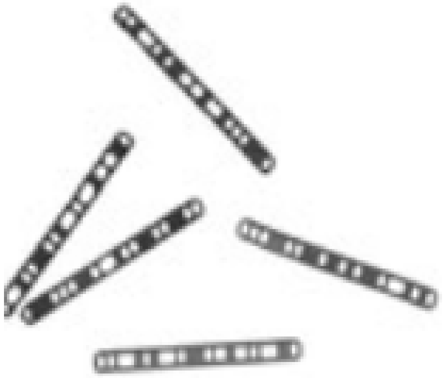


TEM/EELS of $[Cu/FeGa (Galfenol)]_n$ wire -- - apply force through magnetostriction

TEM of $[Co/Cu]_n$ wire with Giant Magnetoresistance (GMR)



SEM of $[Au/Ni/Au]_n$ wires where Au is used to enable selective attachment of biomolecules



(Bethanie Stadler, U. Minnesota)

Nanomagnetism Outline

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    c. skyrmions

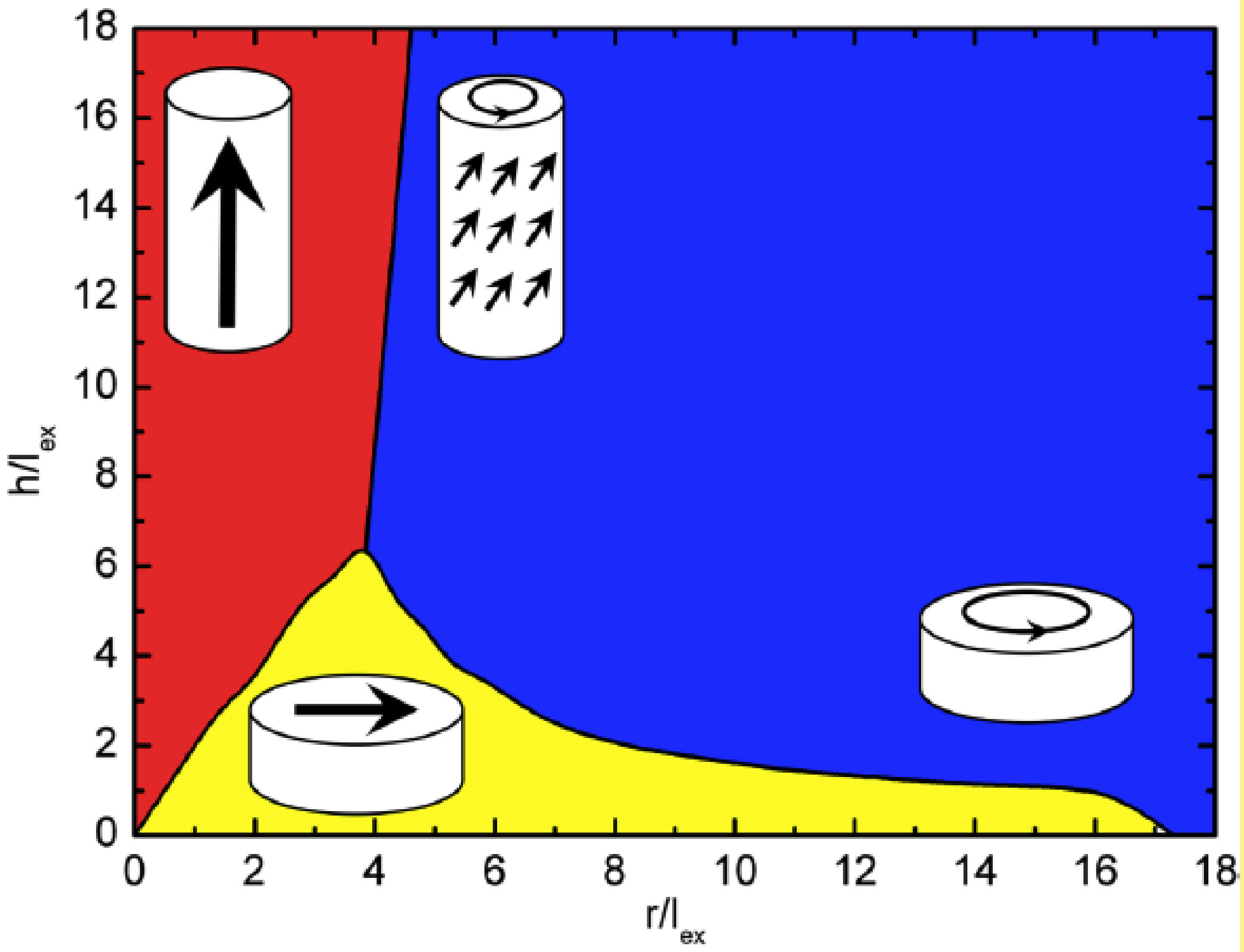
2D Nanopatterns

Most nanopatterns are formed lithographically from thin films

Can have crystallographic orientation, multilayer structures, and epitaxy with substrate (good for spintronics)

More recently, 2D spin configurations called skyrmions have been found that are stable without a confining pattern

Disks can be monodomain or vortices, depending on the dimensions and L_{ex}



$$L_{ex} = \sqrt{\frac{2A}{\mu_0 M_s^2}}$$

Different spin configurations

Graph:
Height vs. thickness

Novais JAP 110, 053917 (2011)

Thin Circular Discs

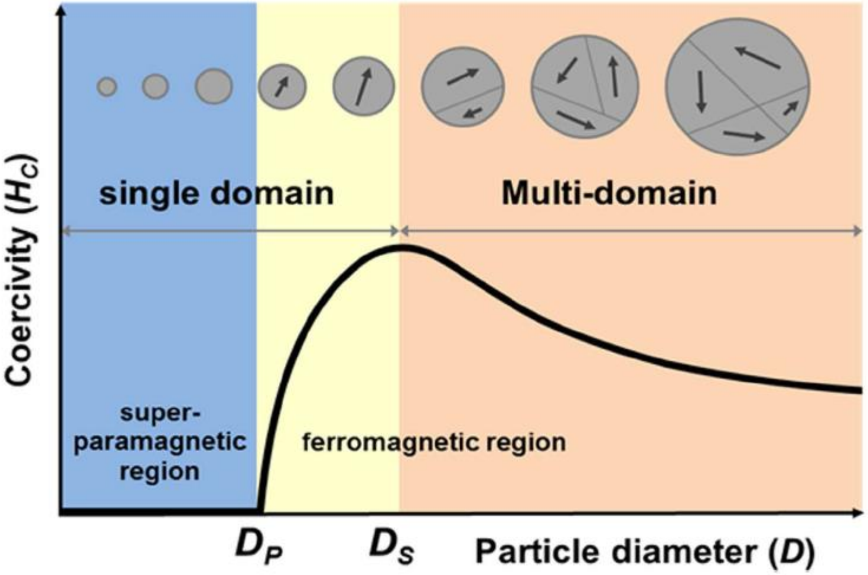
There is shape anisotropy

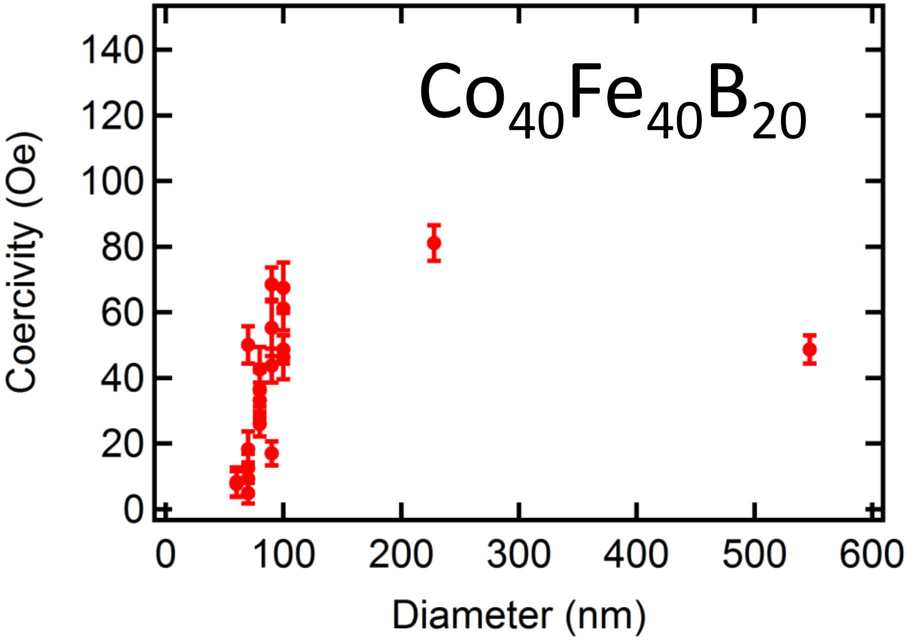
They can be stable in a monodomain state, but don’t reverse their magnetization by Coherent Rotation except < 10 nm and < 10 K

They can be superparamagnetic for small diameters and thicknesses

For larger diameters a vortex structure can be stable instead of a single domain

Size Dependence of H_c for a 1.5 nm Thick Disc





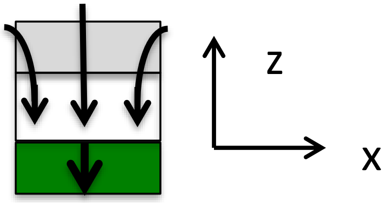
Single domain ground state below 100 nm, but doesn't reverse by simple coherent rotation due to shape K

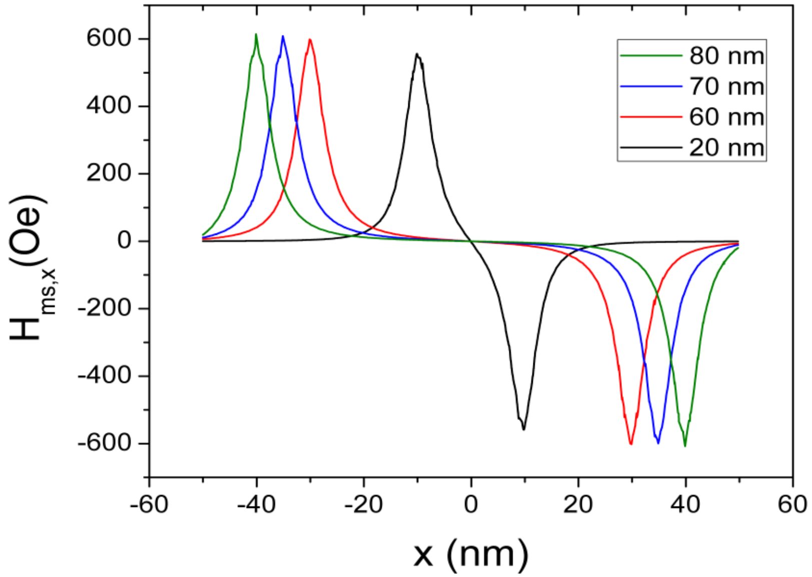
Domain wall width δ ~100 nm

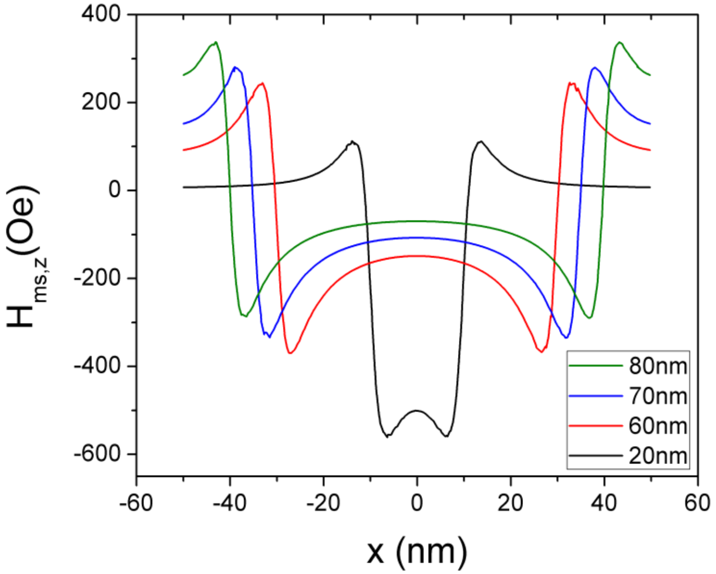
S. K. Piotrowski, et al., *Phys. Rev. B* **94**, 014404 (2016)

Stray Field from a Magnetic Disc in a Perpendicular Tunnel Junction

H_{ms} at Soft Layer



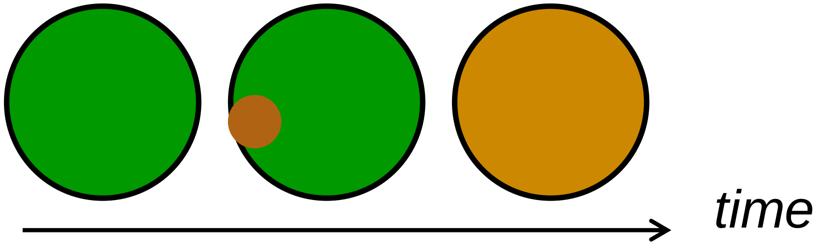




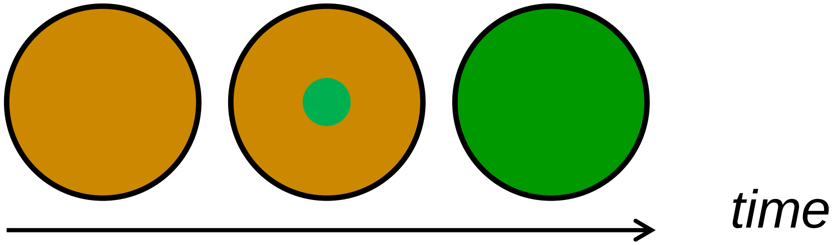
$H_{ms,x}$ large near edges but weakly size-dependent
$H_{ms,z}$ size-dependent at both edges and interior

Reversal in Magnetic Tunnel Junctions

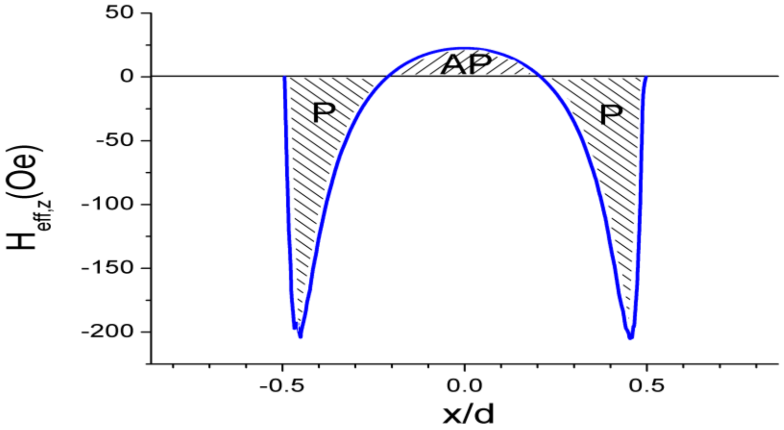
Top View of Soft Layer



AP→P switching nucleates at edge



P→AP switching nucleates in interior



🟩 M up

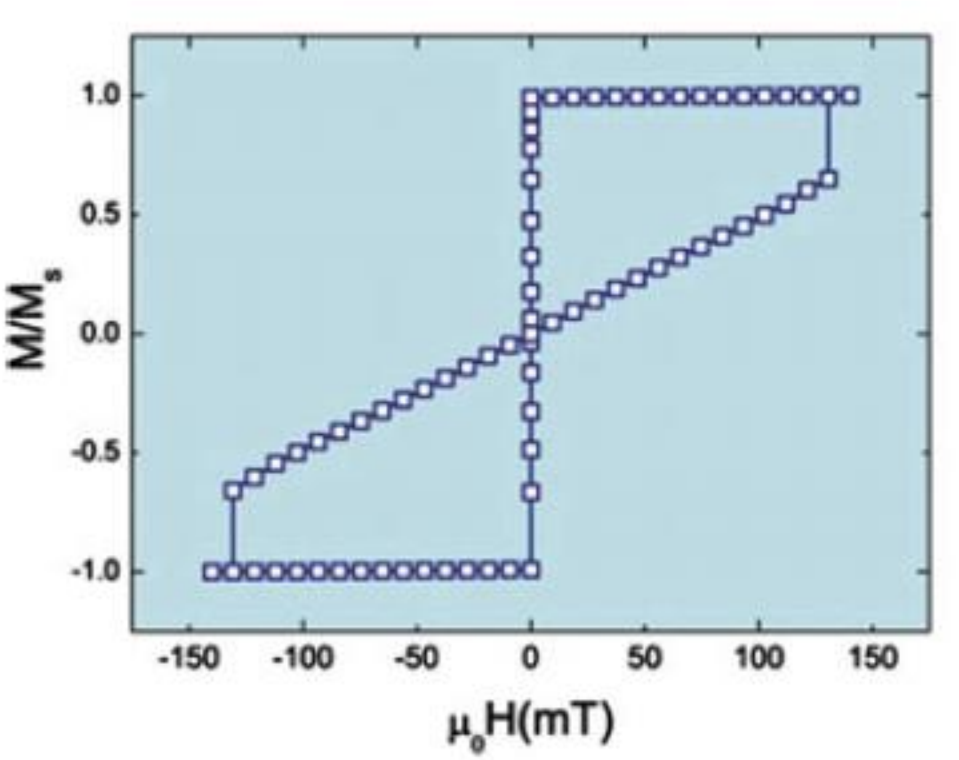
🟧 M down

Different energy barriers for switching “1” to “0” and “0” to “1” in perpendicular MR devices

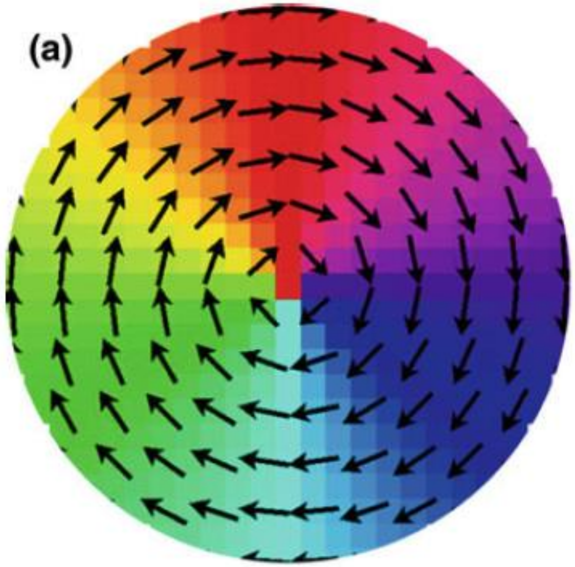
M. Bapna, et al., *Appl. Phys. Lett.* **108**, 022406 (2016)

How Can You Tell If There's a Vortex State?

Hysteresis Loop with In-Plane Field



Top View of Vortex



A. Guimaraes, Nanomagnetism

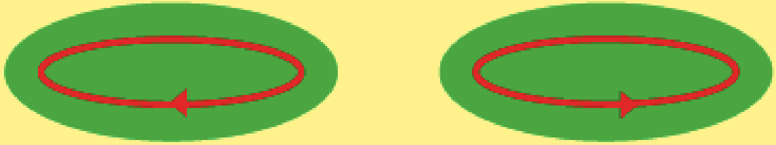
H = 0: centered vortex

H > 0: shift vortex core to edge and eliminate, leaving monodomain pattern

Properties of magnetic vortices

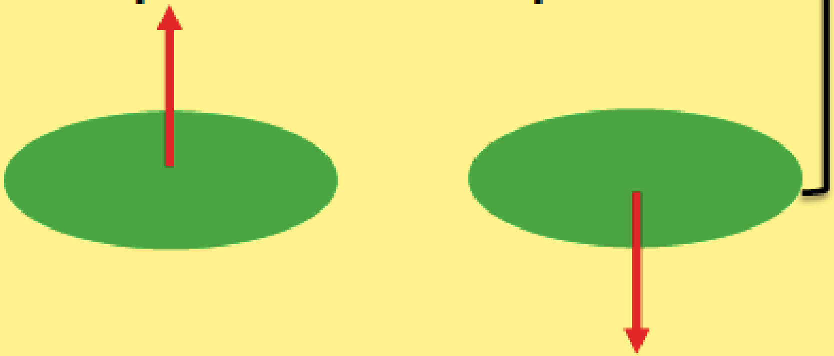
- Circulation:

c=+1 (CCW) c=-1 (CW)



- Polarity:

p=+1 p=-1



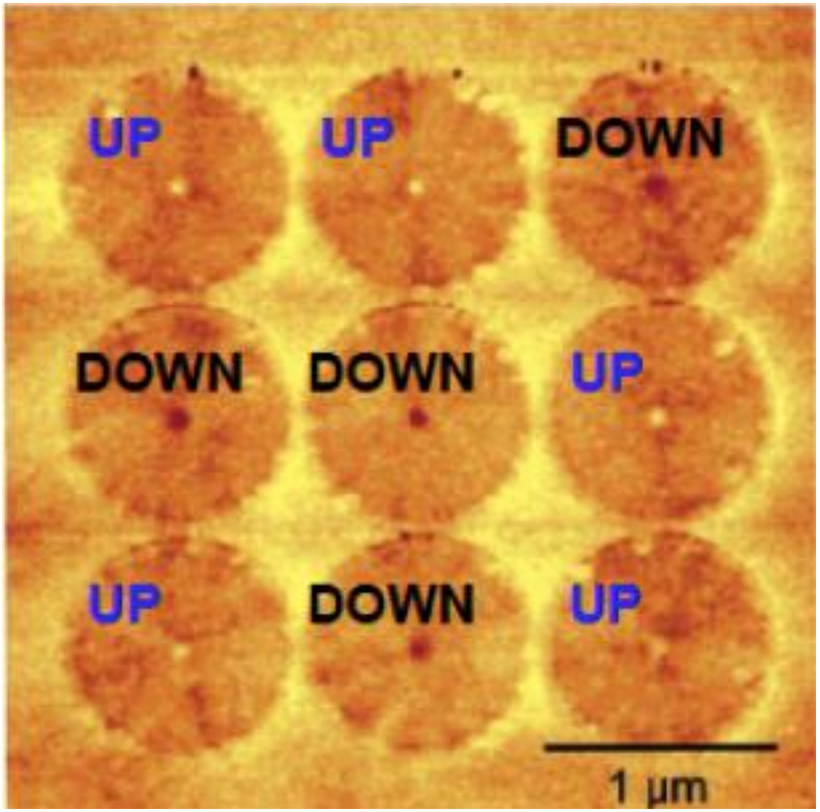
Combining c and p:

chirality or handedness:
cp=±1

A. Guimaraes, Nanomagnetism

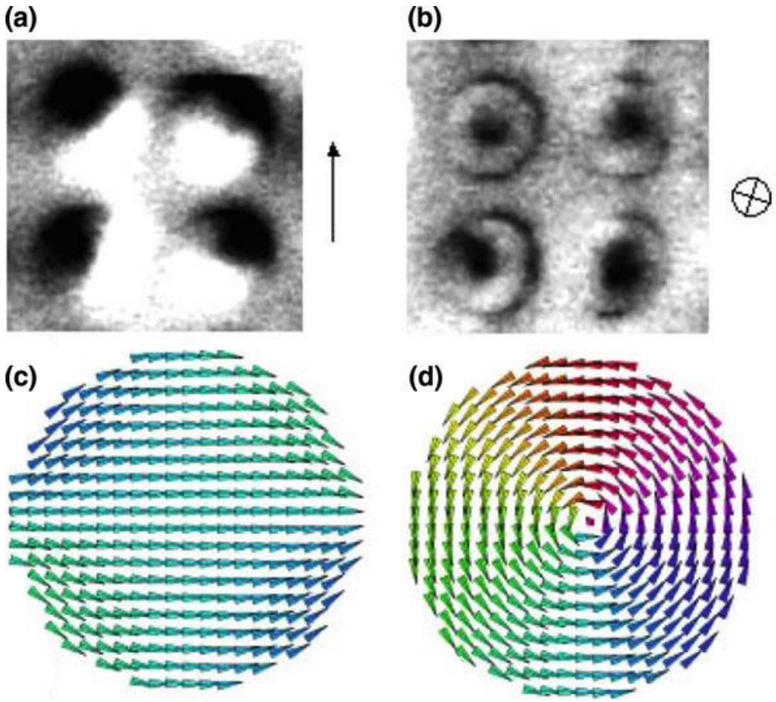
Magnetic Force Microscopy of Vortices

Vortex cores at remanence



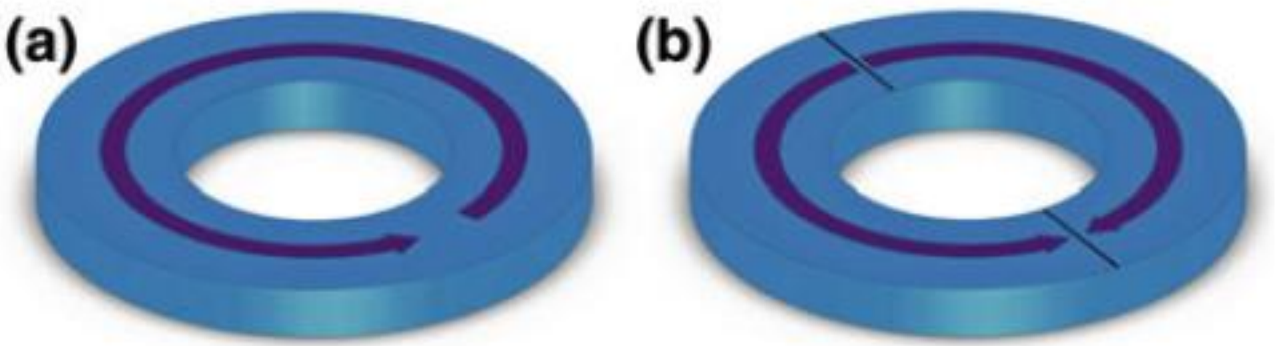
T. Shinjo, et al., Science **289**, 930 (2000)

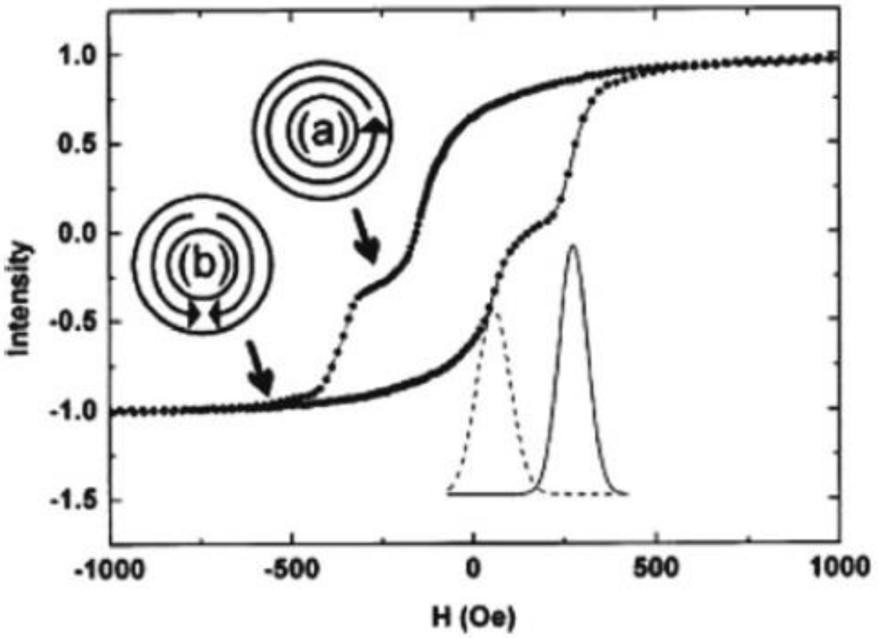
MFM Images



Single Domain Vortex

Magnetic Rings: Vortex versus Onion State



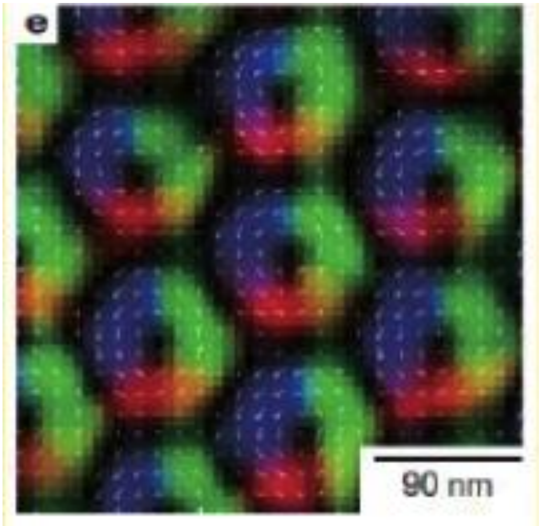


Onion state has tail-to-tail and head-to-head domain walls

Last But Not Least: Skyrmions

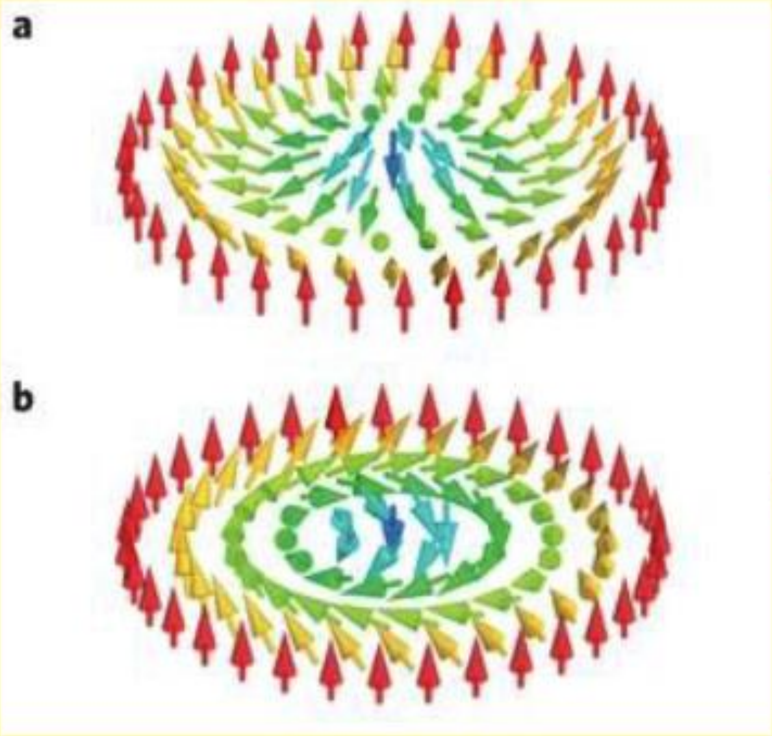
Skyrmions exist only because of Dzyaloshinskii-Moriya exchange, which requires there in no inversion symmetry

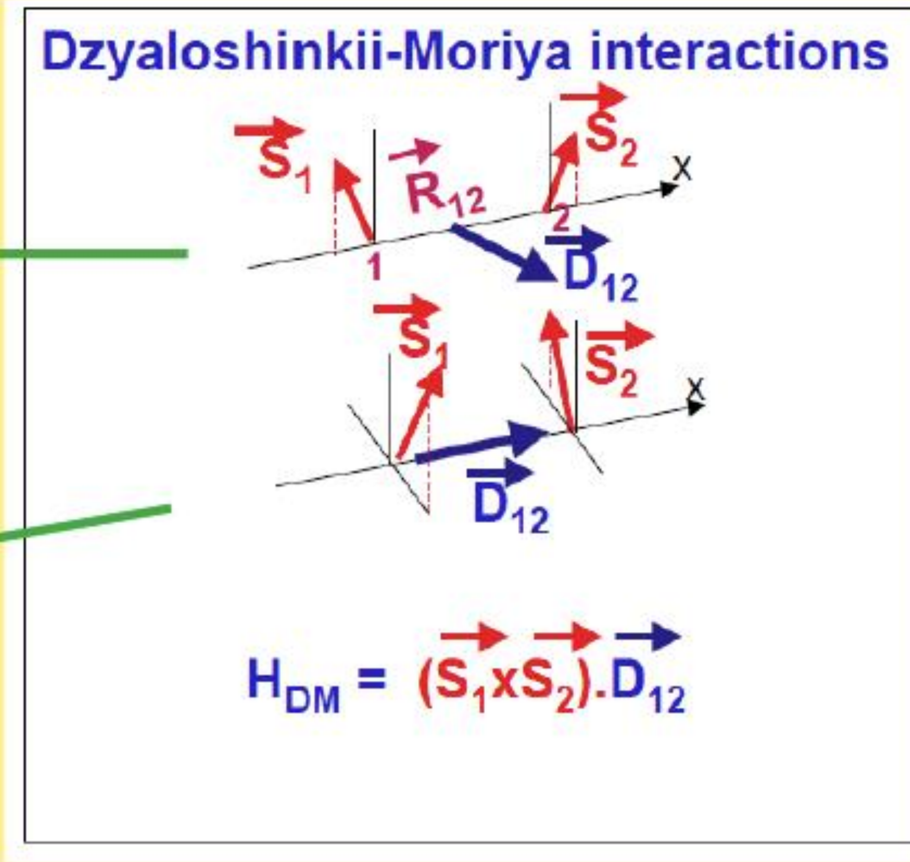
First observed at low temperature in special B20 crystals without inversion symmetry, now seen in multilayer thin films at 300 K



Yu (2010); Fresnel Lorentz microscopy of skyrmion lattice in $Fe_{0.5}Co_{0.5}Si$

Dzyaloshinskii–Moriya interactions





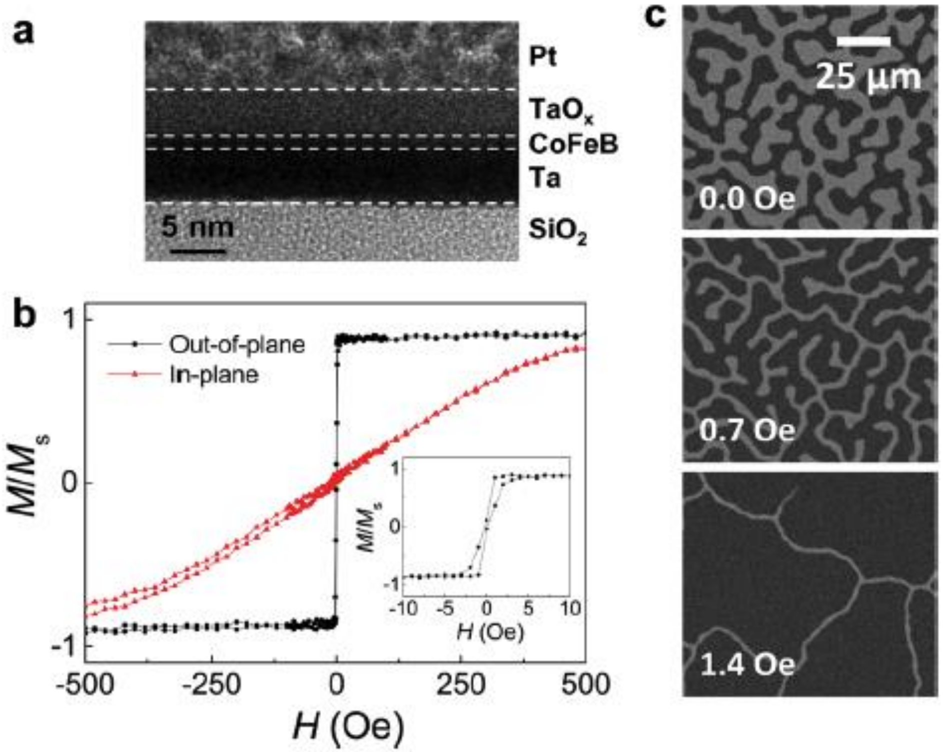
Dzyaloshinkii-Moriya interactions

$H_{DM} = (\vec{S}_1 x \vec{S}_2).\vec{D}_{12}$

Fert 2012

Skyrmionic Thin Films

Start with a multilayer film with perpendicular K and asymmetric interfaces with strong DMI

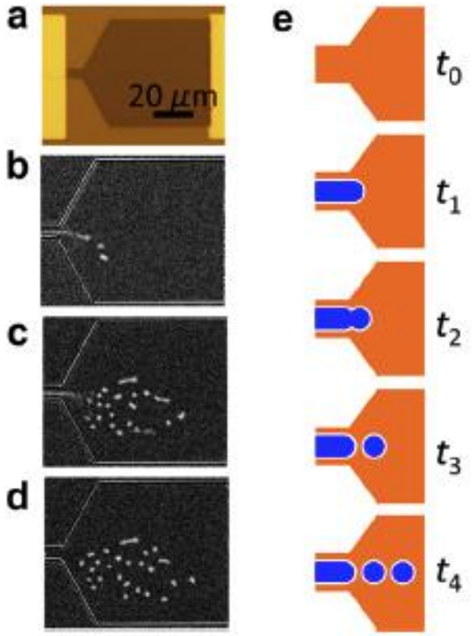


In a continuous film, reversal occurs by the formation and growth of labrinth domains

G. Yu, et al. Nano Lett. **17**, 261 (2017)

How do you make Skyrmions?

Pattern the skyrmionic film stack with a narrow region leading to a wider channel



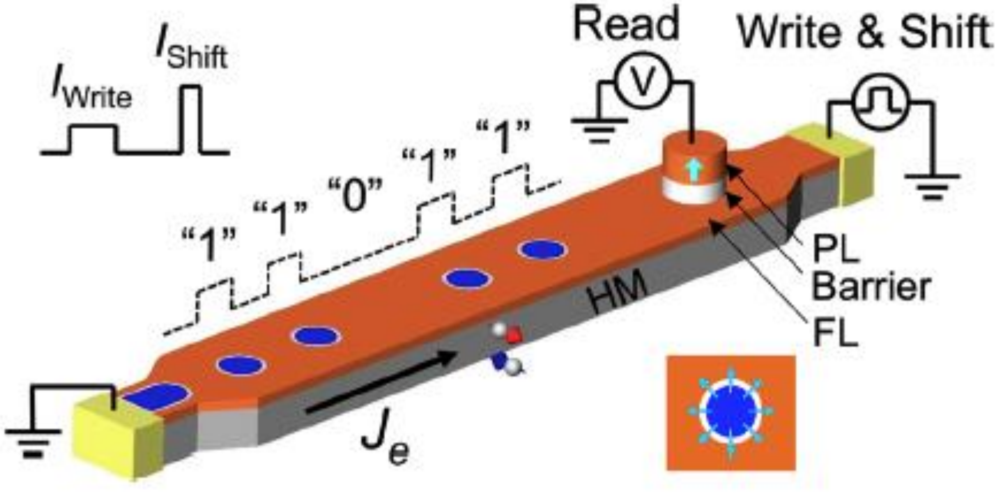
Apply a small perpendicular field sufficient to form a labrynth domain in the narrow region but not elsewhere

Apply a DC current along the channel to apply spin transfer torque (STT) to the domain wall

In analogy to blowing bubbles due to surface tension, the current generates a stream of skyrmions

G. Yu, et al. Nano Lett. **17**, 261 (2017)

What could you do with Skyrmions?



G. Yu, et al.,
Nano Lett. **17**, 261 (2017)

Ideally, they are topologically protected and can be moved by a smaller current density than a domain wall, making them interesting for race track memory

Ideally they could be only a few nm in diameter (now 100s of nm)

…stay tuned!

Physics of Nanomagnetism Summary

The concept of a single domain is relevant to the understanding of many different kinds of nanostructures, though each has unique complexities and capabilities

Vortices and skyrmions are also important nanomagnets. There is a lot of physics yet to be understood, especially with skyrmions.

Acknowledgments

Alberto P. Guimaraes --- For much more, see *Principles of Nanomagnetism*, 2nd edition, Springer, 2017

Bethanie Stadler – University of Minnesota

Many past and present Majetich group students and collaborators