Interactions of Magnetic Nanoparticles

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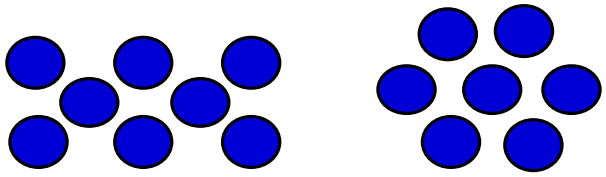
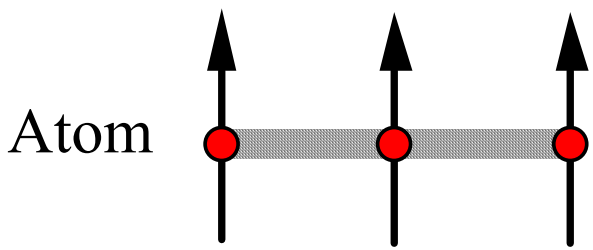
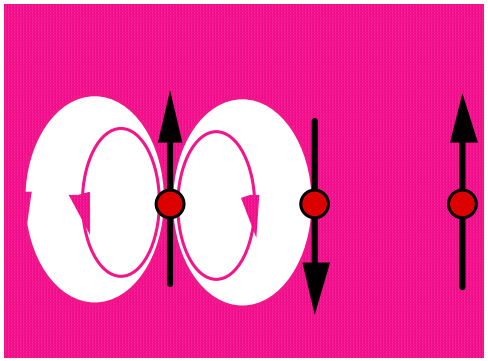


Magnetic Domains

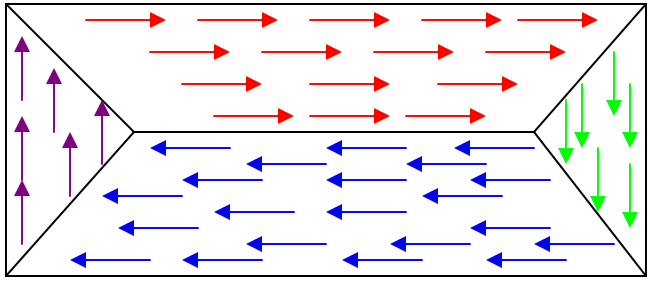
Exchange Interactions



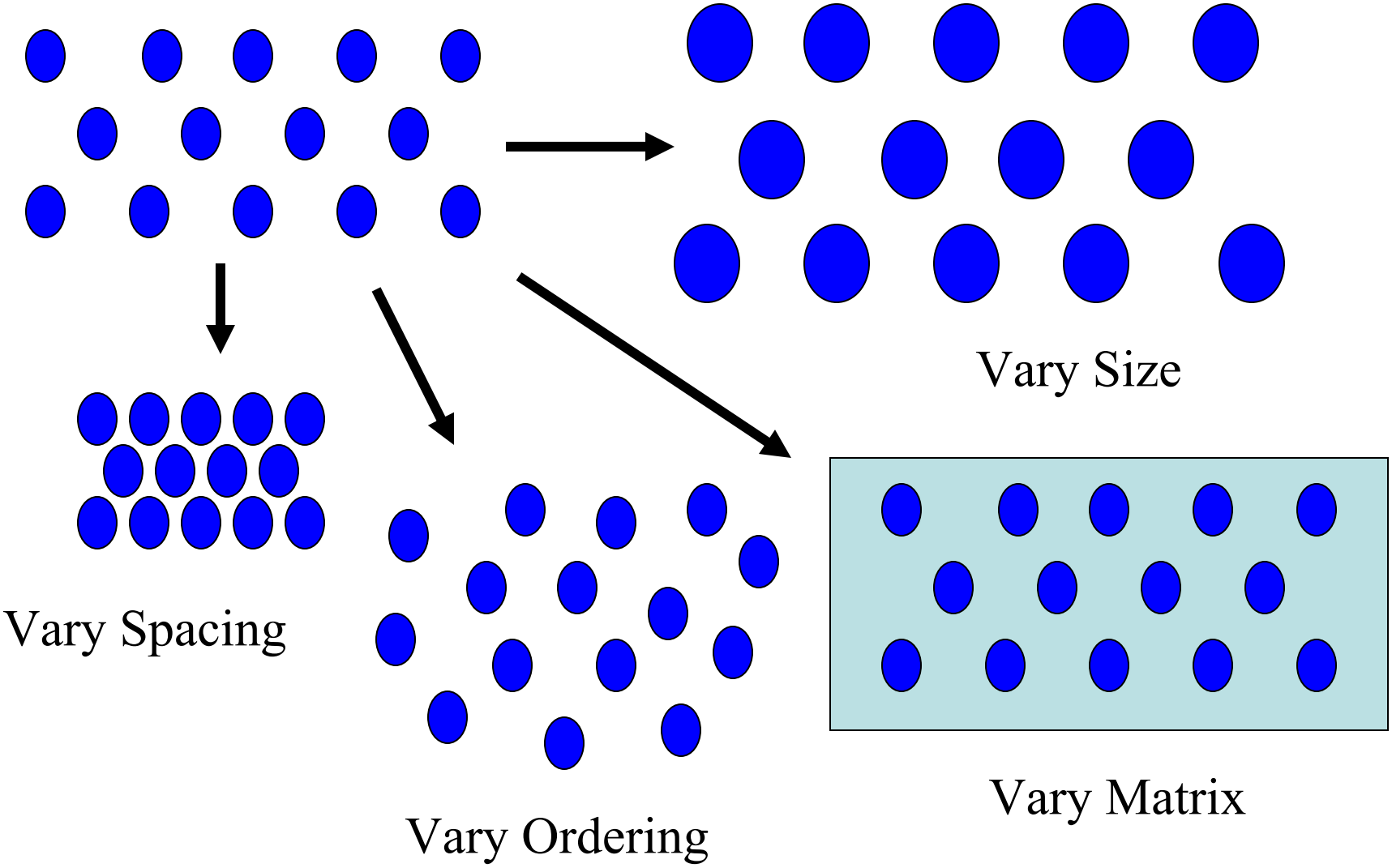
Dipolar Interactions



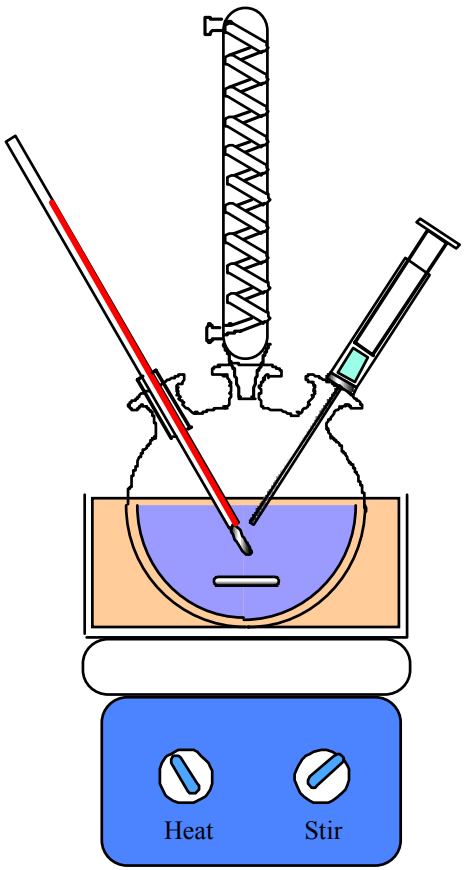
Competition between exchange and dipolar interactions leads to domain formation



Magnetic Nanoparticle Arrays



Nanoparticle Synthesis

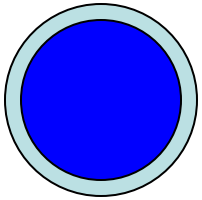


- Fe synthesized using air free solution chemistry methods
- Thermal decomposition of $Fe(CO)_5$ in octyl ether
- Particles coated with surfactant
- Washed with ethanol and dispersed in hexane

D. F. Farrell, S. A. Majetich, and J. P. Wilcoxon, *J. Phys. Chem. B* **107**, 11022 (2003)

Oxide Shell Thickness

- Relate σ_s (= M_s/ρ) of particles to mass weighted average of σ_s of Fe core and σ_s of Fe_3O_4 shell



$$\sigma_{s,part} m_{part} = \sigma_{s,core} m_{core} + \sigma_{s,shell} m_{shell}$$

Diameter	σ_s	Fe core	Oxide shell
7.0 ± 0.7 nm heterogeneous	175 emu/g	5.8 nm	0.6 nm
9.2 ± 0.7 nm heterogeneous	**200 emu/g**	8.4 nm	0.4 nm
11.2 ± 1.0 nm homogeneous	132 emu/g	7.0 nm	2.1 nm

Self-Assembled Nanoparticle Structures

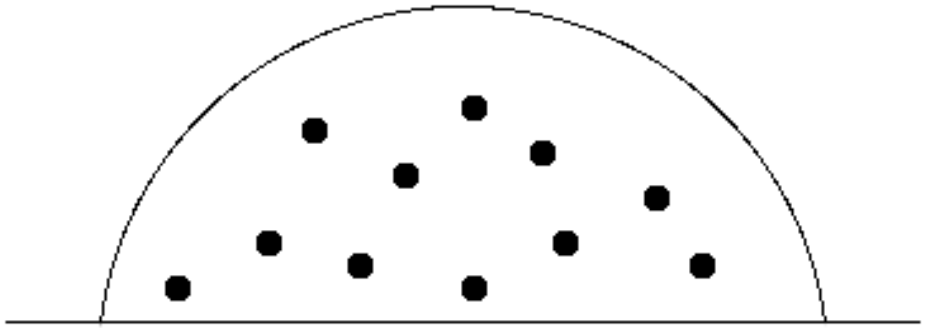
Key Questions:

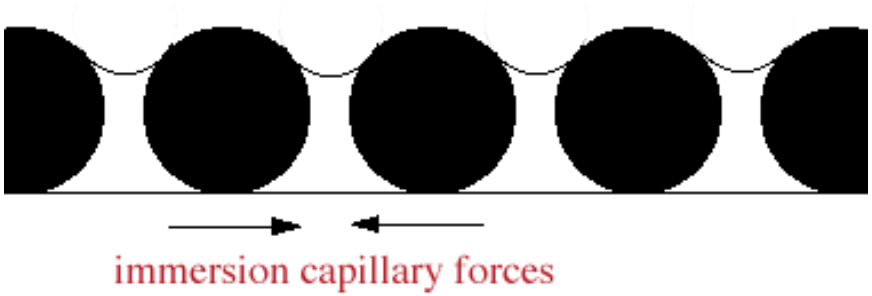
What kinds of (magnetically) interesting structures can be formed?

How do they form (nanoscale forces, nucleation and growth mechanisms)?

How can the degree of perfection be extended to macroscopic length scales?

Evaporative Array Formation





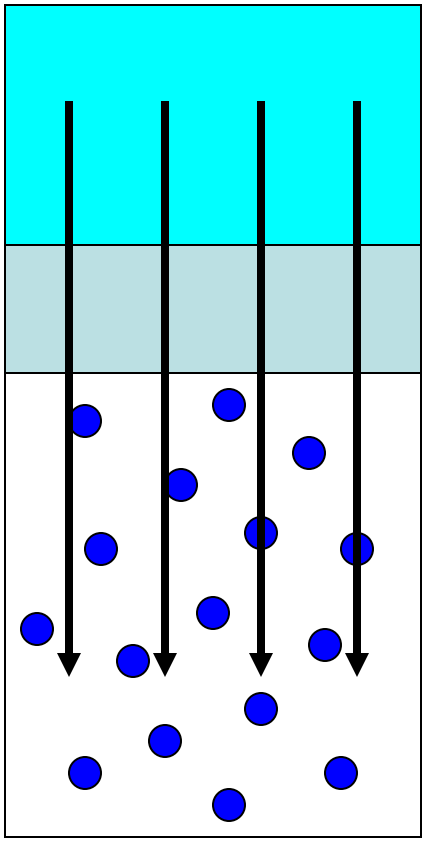
- Particles initially distributed throughout droplet
- As droplet evaporates, monolayer of particles forms
- Immersion capillary forces and disjoining pressures on the particles

→ arrays form in < 5 min

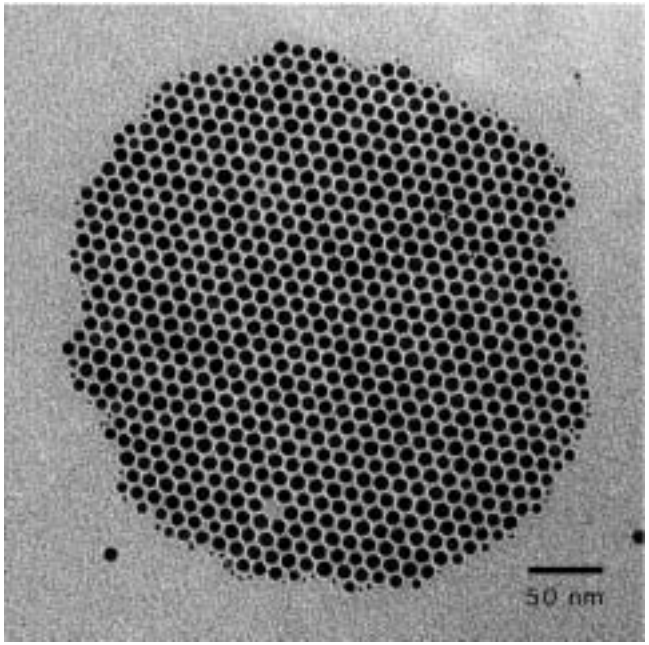
Colloidal Arrays or 3D Nanoparticle Crystals

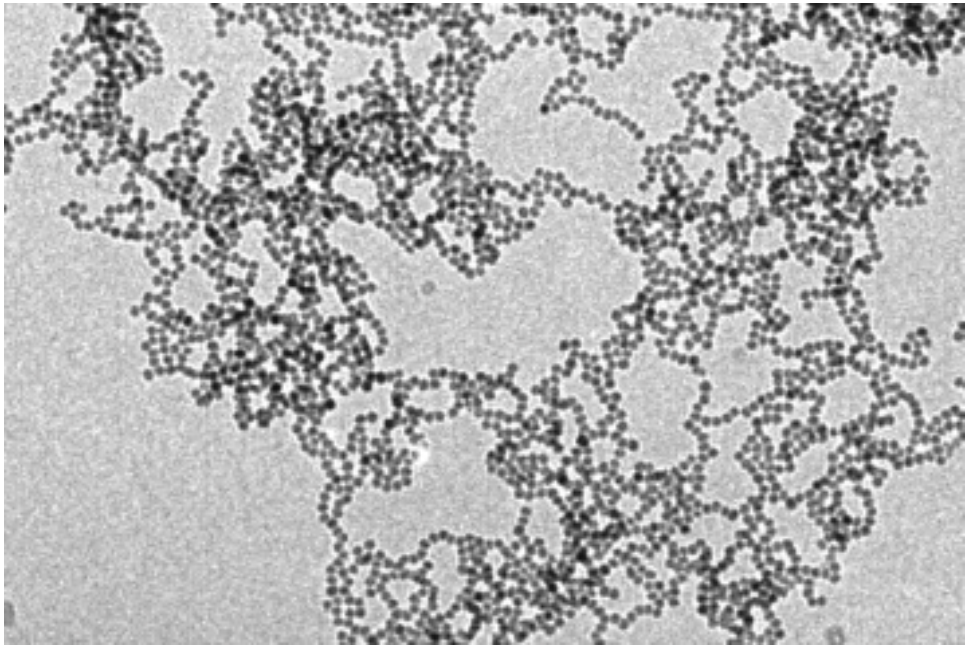
Use very slow precipitation (hours, weeks, months) by diffusion of poorly coordinating solvent

Can make 3D crystals up to 10 microns in size



Self-Assembly Parameters



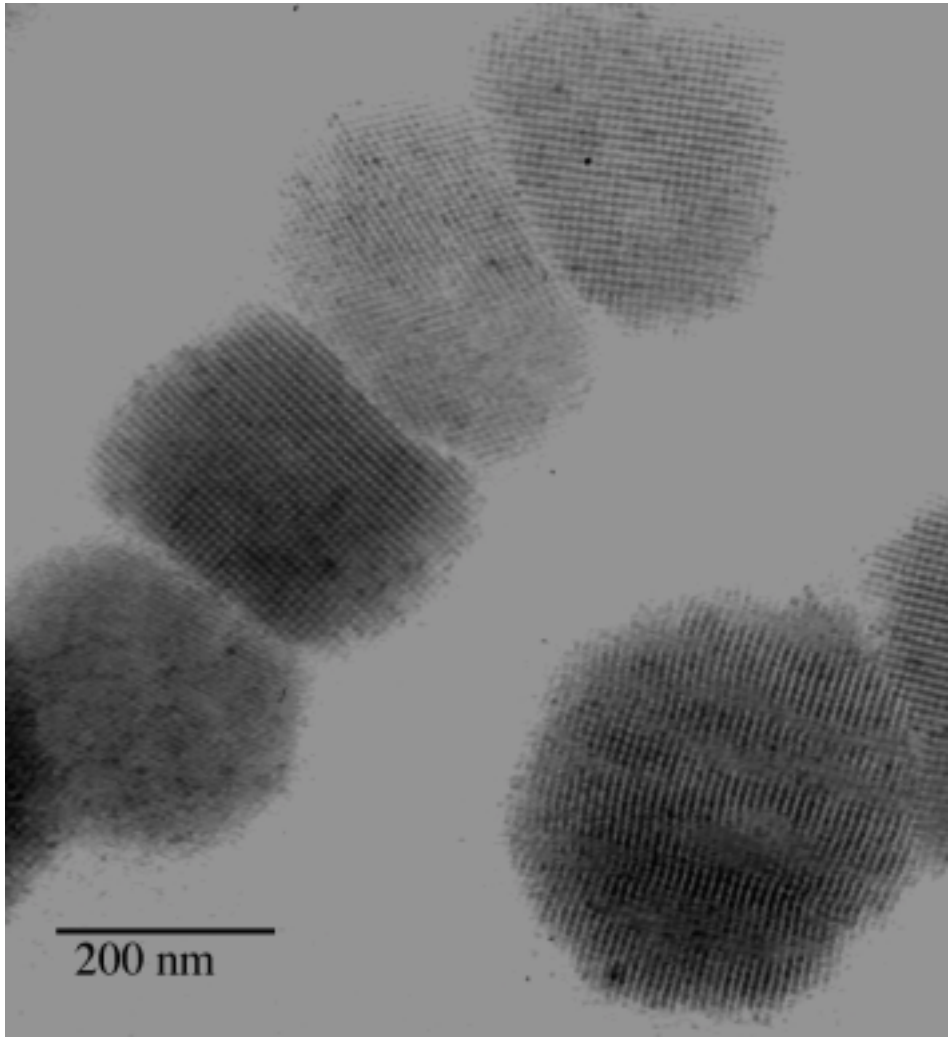


Evaporate organic solution of surfactant-coated particles to form arrays

aqueous

Magnetic forces <<< van der Waals forces for arrays
(particle moment and spacing important)

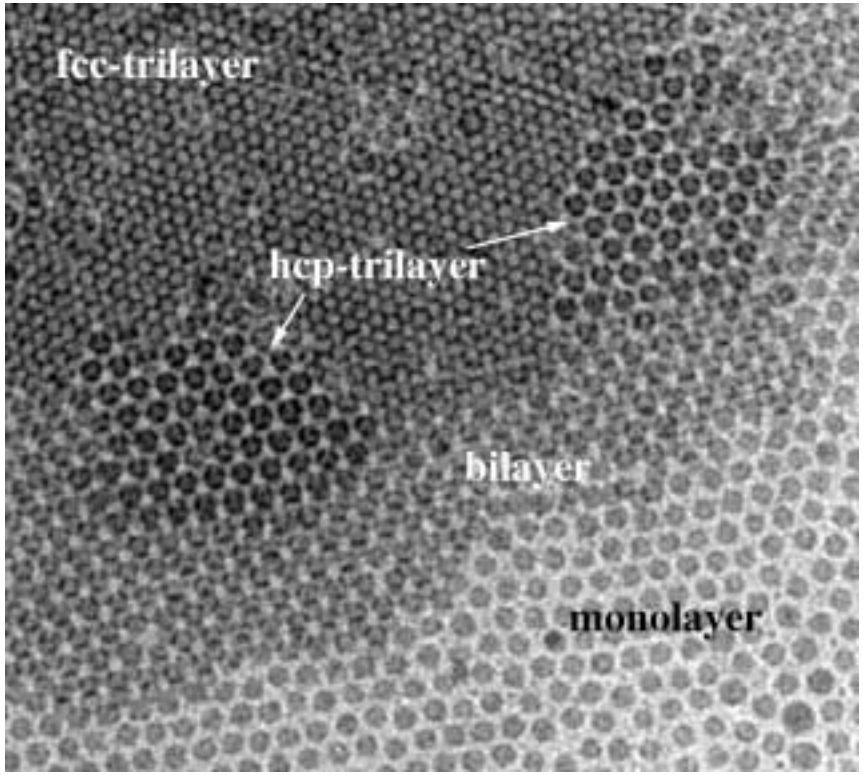
Array Nucleation and Growth

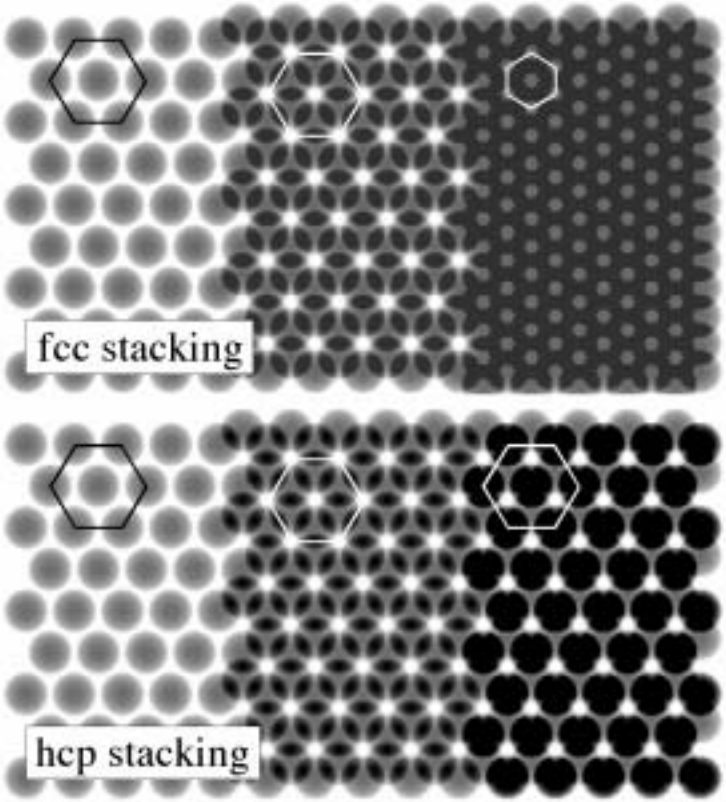


Once nucleated, array "grains" grow until they impinge on each other

TEM only shows final state

Layer Stacking

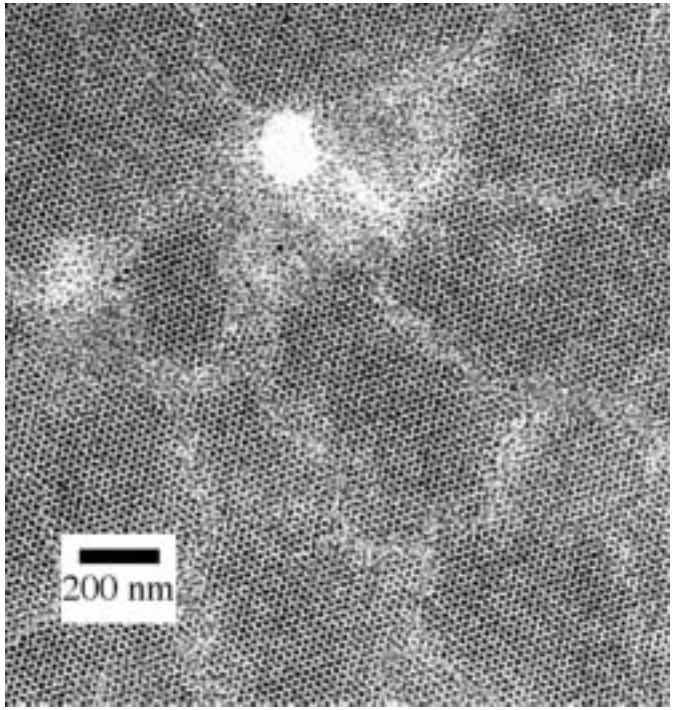


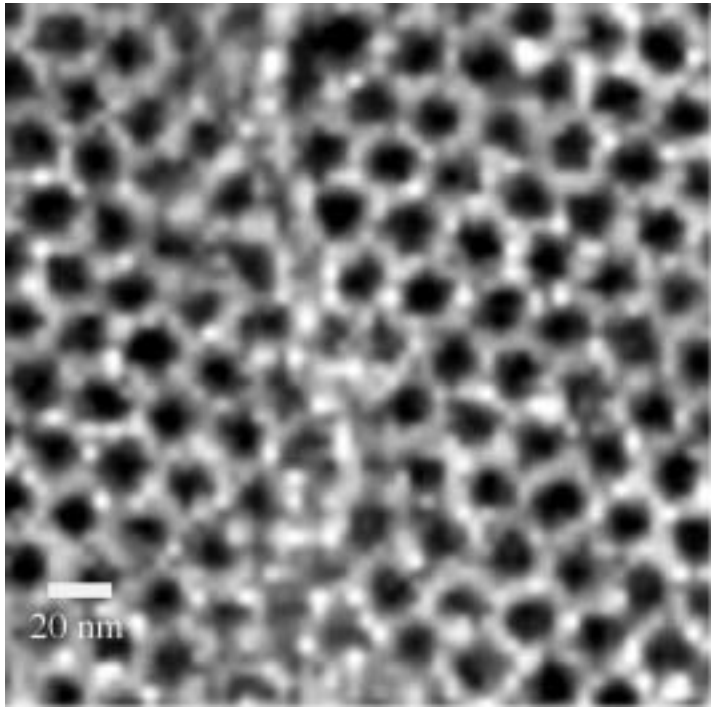


TEM image

Simulated phase contrast

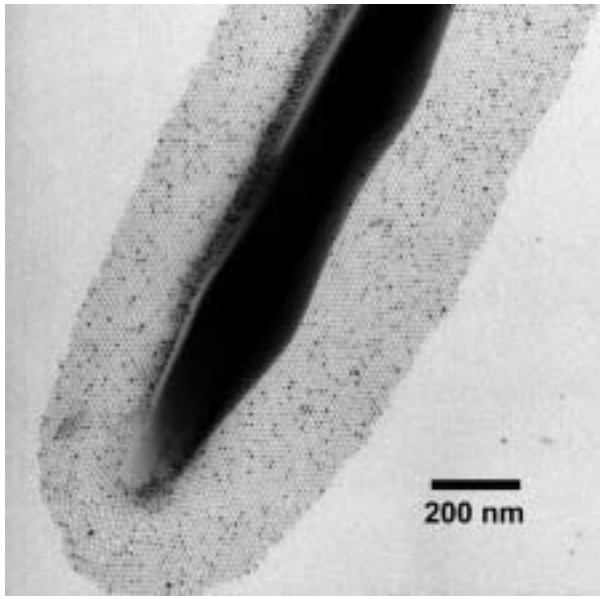
Length Scale of Structural Ordering

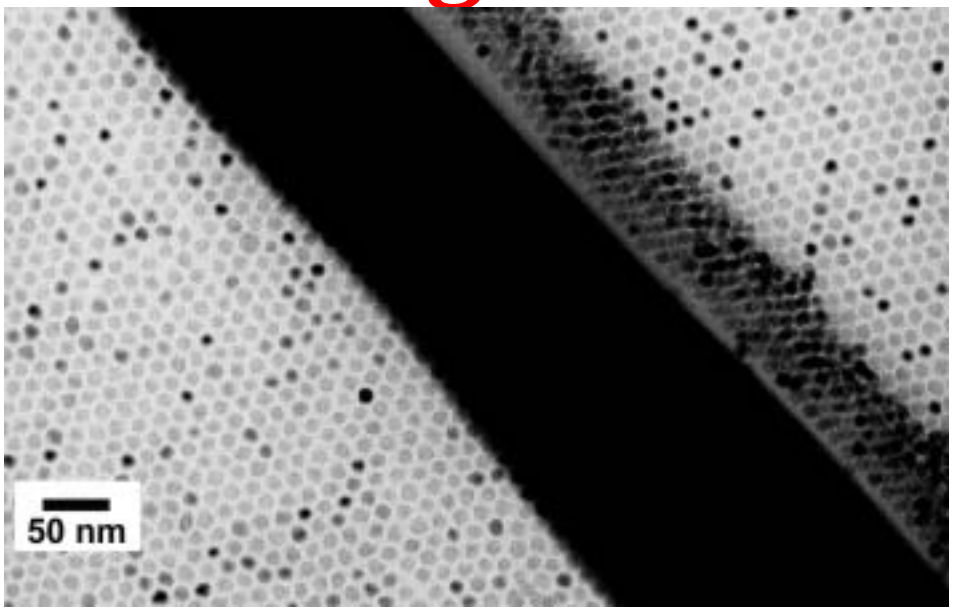




Cracking currently limits the length scale of ordering for multilayer nanoparticle arrays

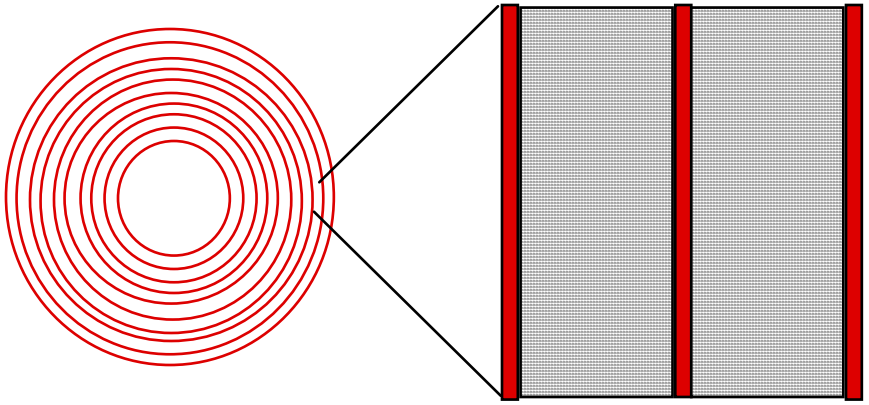
Templates and Long Range 2D Ordering



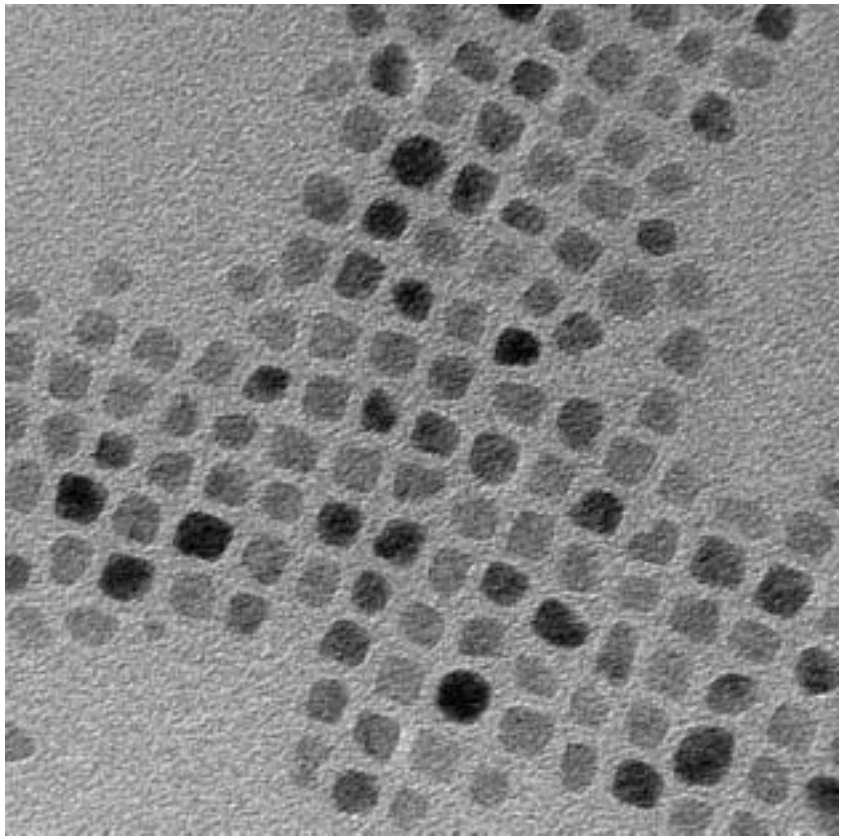


Templates facilitate long-range ordering in nanoparticle arrays

Could use templates to pattern tracks on disks



(Nearly) Cubic Nanoparticles



Saeki Yamamuro, Nagoya Institute of Technology

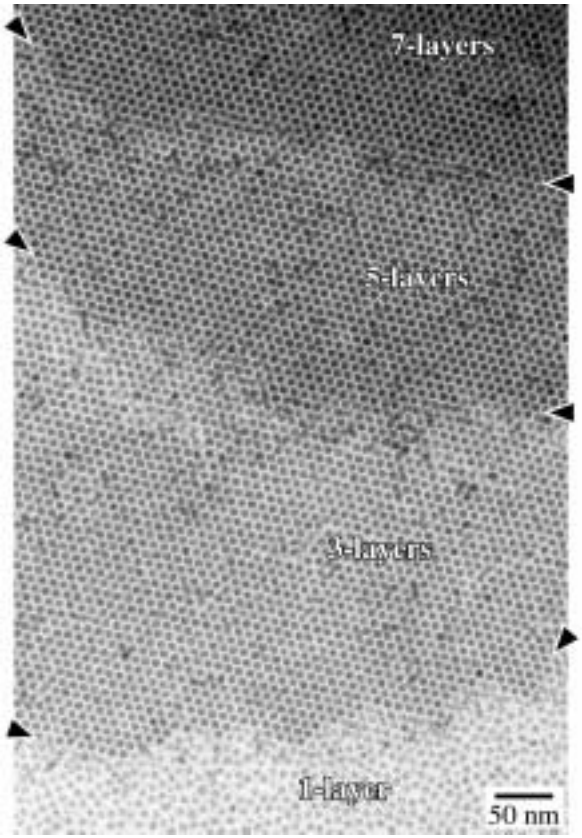
- Square lattice arrays

  Square, hexagonal arrays of point dipoles have different magnetic ground states

- Show some crystallo-graphic orientation

  Useful feature for data storage media

Preference for an Odd Number of Layers



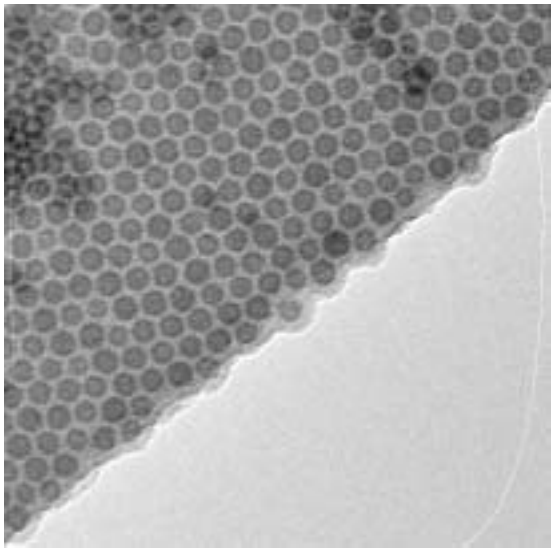
Found for hexagonal close packed arrays of large moment Fe nanoparticles

S. Yamamuro, D. Farrell, and S. A. Majetich, *Phys. Rev. B* **65**, 224431 (2002)

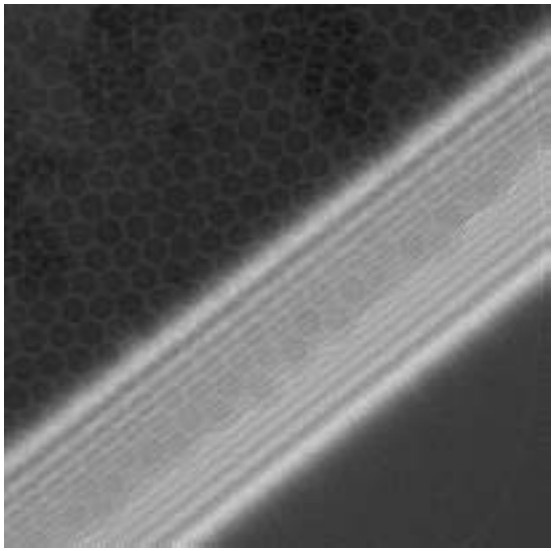
Magnetic imaging?

Electron Holography

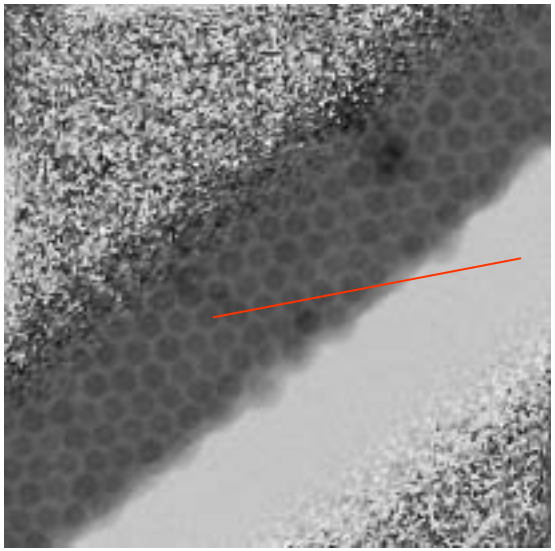
TEM image



Hologram

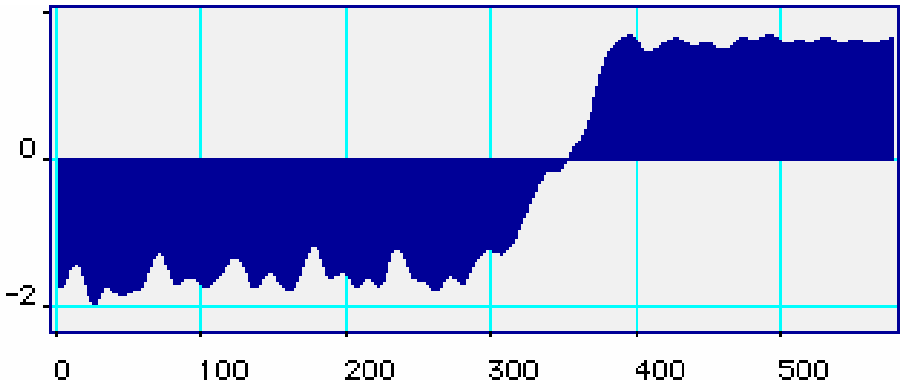


Phase Image



20 nm

With Kazuo Yamamoto, Tsukasa Hirayama, Japan Fine Ceramics Center, and Saeki Yamamuro, Nagoya Institute of Technology



Magnetic Properties of Nanoparticle Arrays

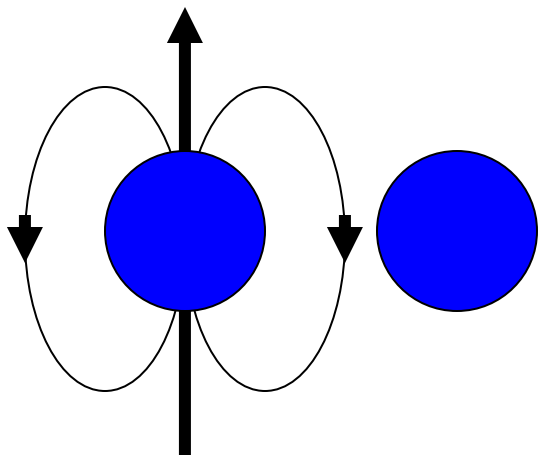
Key Questions:

How can the interaction strength be tuned by adjusting the particle moment or the separation between moments?

How does the degree of structural order (or specific structural defects) affect the magnetization of the assembly?

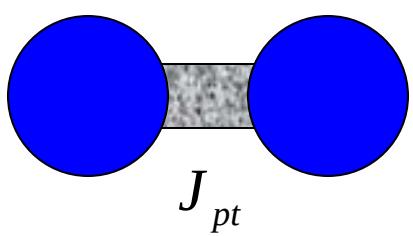
How is the magnetization pattern depend on the number of layers? On the nanoparticle lattice?

Magnetostatic and Exchange Interactions



$$\vec{H}_{dipole} = \frac{1}{4\pi}\left[\frac{3(\vec{\mu}\bullet\vec{r})\vec{r}}{r^5} - \frac{\vec{\mu}}{r^3}\right] \approx \text{ 100's of Oe}$$

With close particle spacing, include multipolar interactions as well



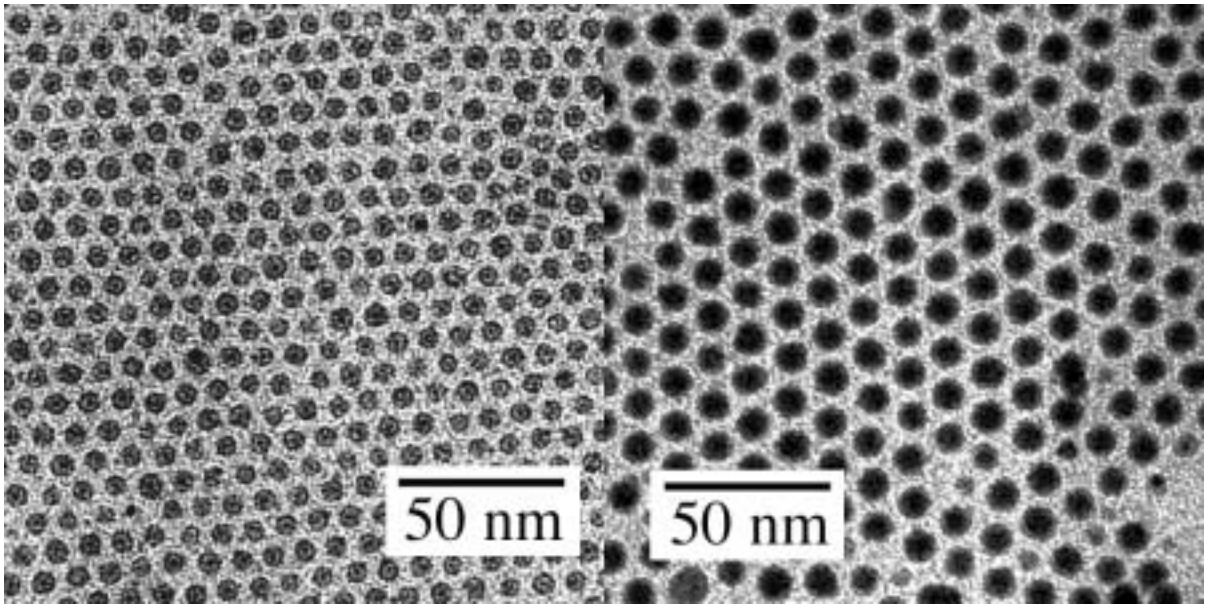
For atoms, know that $J = J_0 \exp(-r/r_0)$

$r_0 \leq 1$ nm for significant tunneling

Don't know J_{pt} but assume similar decay from edge of particle

Vary the Particle Size

Edge-to edge spacing ~ 2.5 nm, so minimal exchange

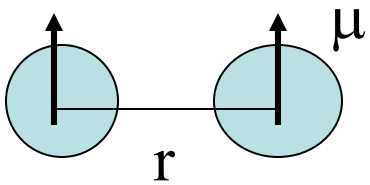


10 K: $\Phi_{mag} = 1.4kT$ $\Phi_{mag} = 2.4kT$

Dipolar energy

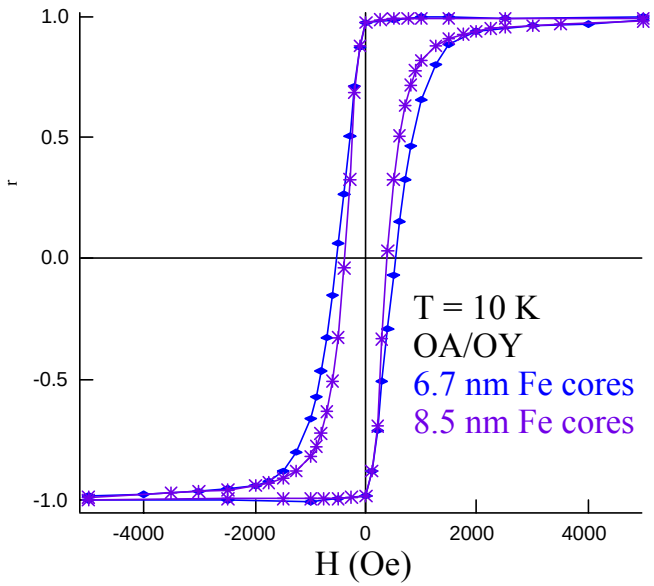
$$\Phi_{mag} = \frac{\mu_0 \mu^2}{4\pi r^3}$$

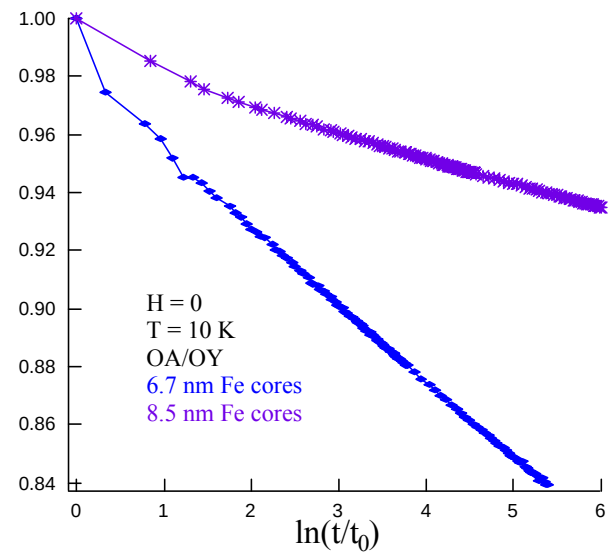
per pair of particles

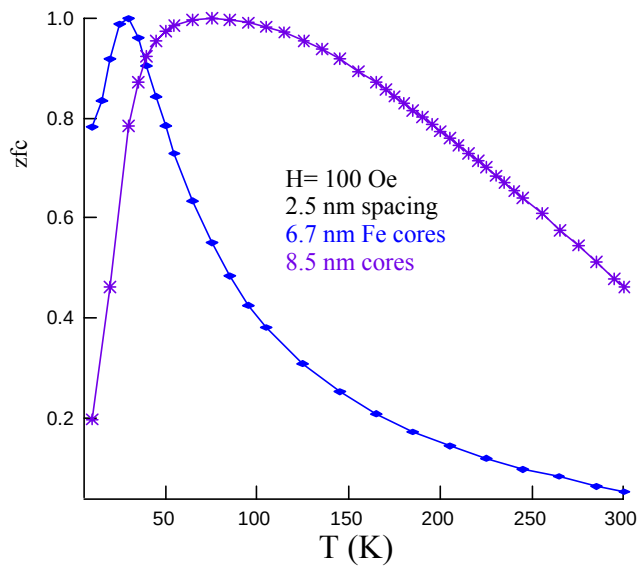


D. Farrell, Y. Ding, S. A. Majetich, C. Sanchez-Hanke, and C. C. Kao, *J. Appl. Phys.* **95**, 6636 (2004).

Particle Size Effects





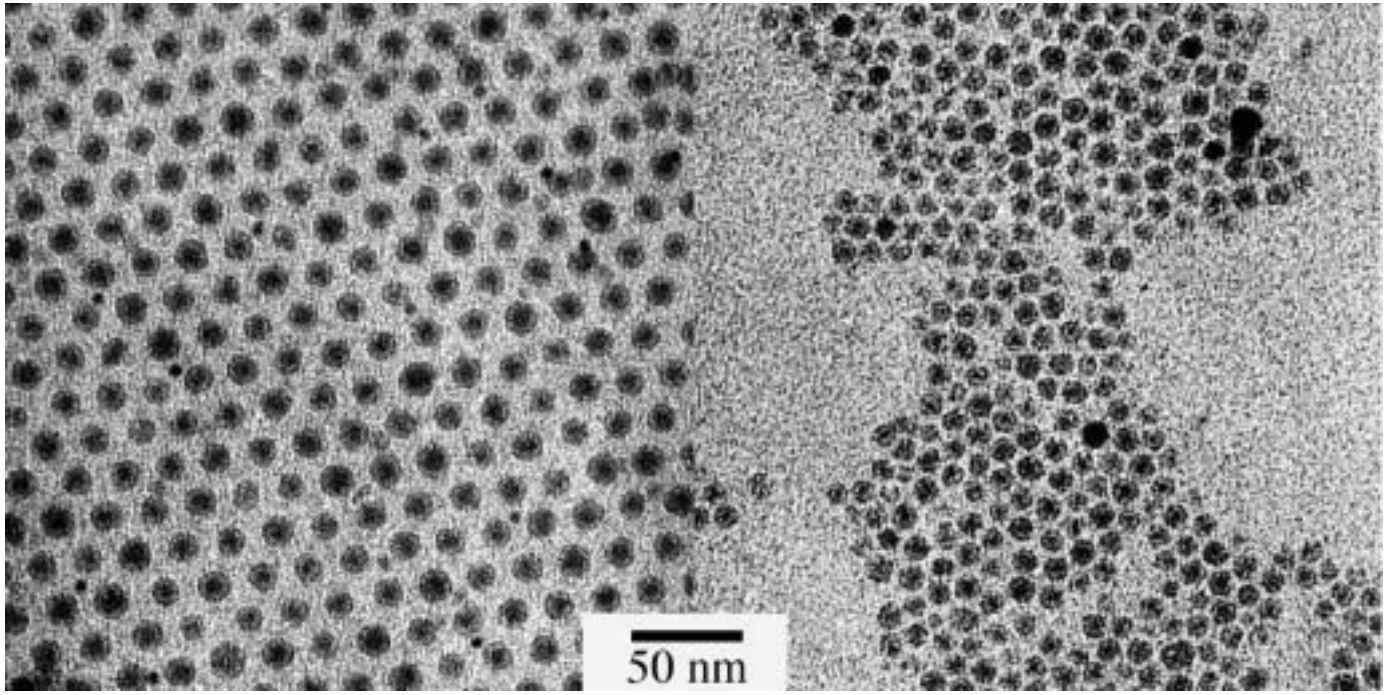


Larger particles have:

- slightly faster approach to saturation
- slower decay in M(t)
- higher T_B and broader $M_{ZFC}(T)$

Varying the Particle Spacing

Same batch of 6.7 nm Fe particles with different surfactants



Oleic Acid/Oleyl Amine

Avg. spacing 2.5±0.3 nm

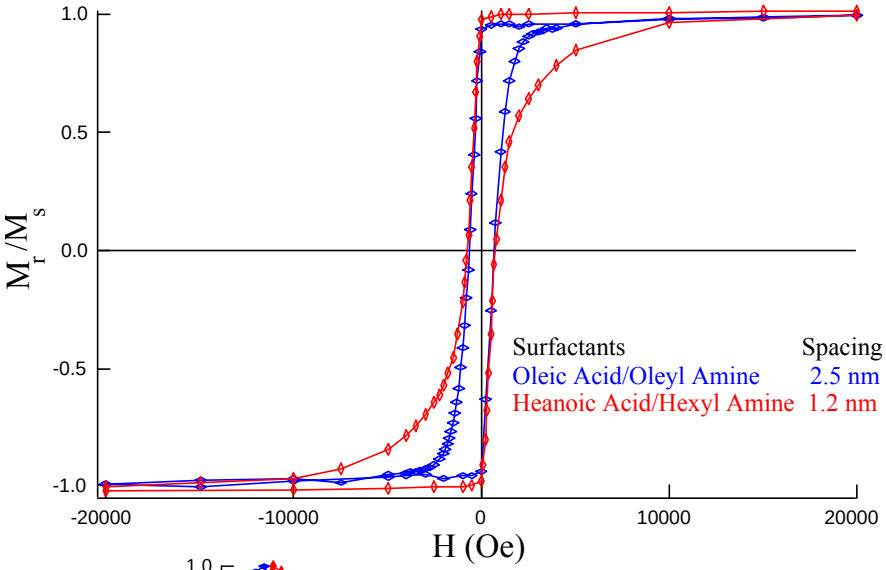
At T = 10 K $\Phi_{mag} = 1.4kT$

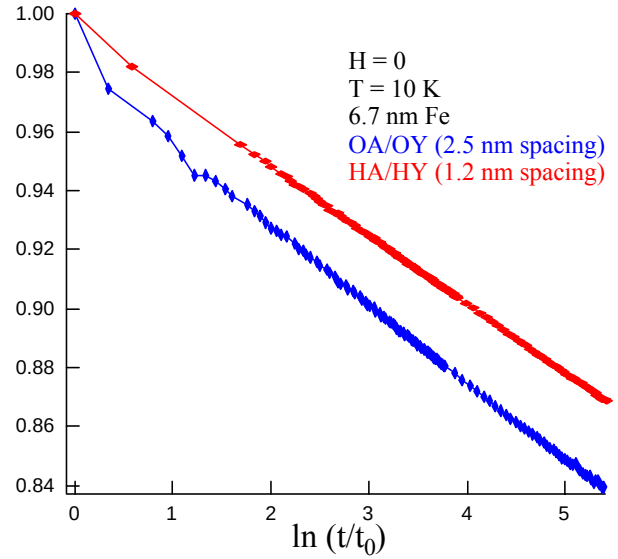
Hexanoic Acid/Hexyl Amine

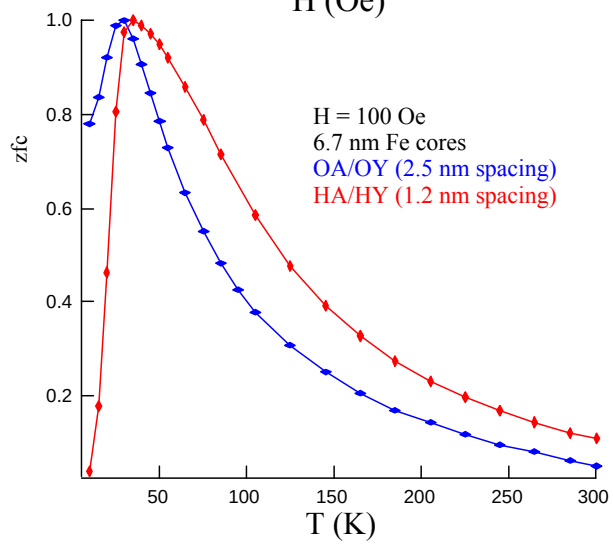
1.2±0.3 nm

$\Phi_{mag} = 2.8kT$

Interparticle Spacing Effects



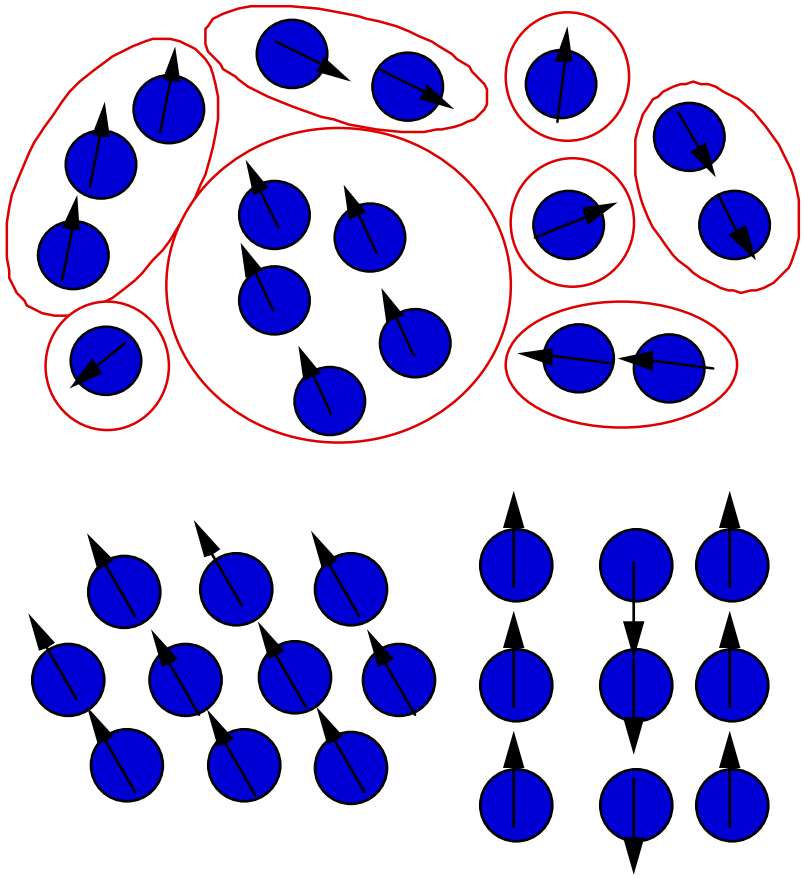




Smaller spacing leads to:

- more gradual saturation
- slower decay in M(t)
- a slightly higher Blocking T

Effect of Structural Disorder in Bulk Ferromagnets



Form a Spin Glass

- Ferromagnetically coupled clusters of many different sizes (< 300 nm)
- Very broad range of relaxation times → slow decay of M(t)
- Periodicity affects magnetic structure

Vary the Degree of Structural Ordering

Make arrays from similar particles, but vary the self-assembly time

Evaporated arrays, 8.5 nm Fe:

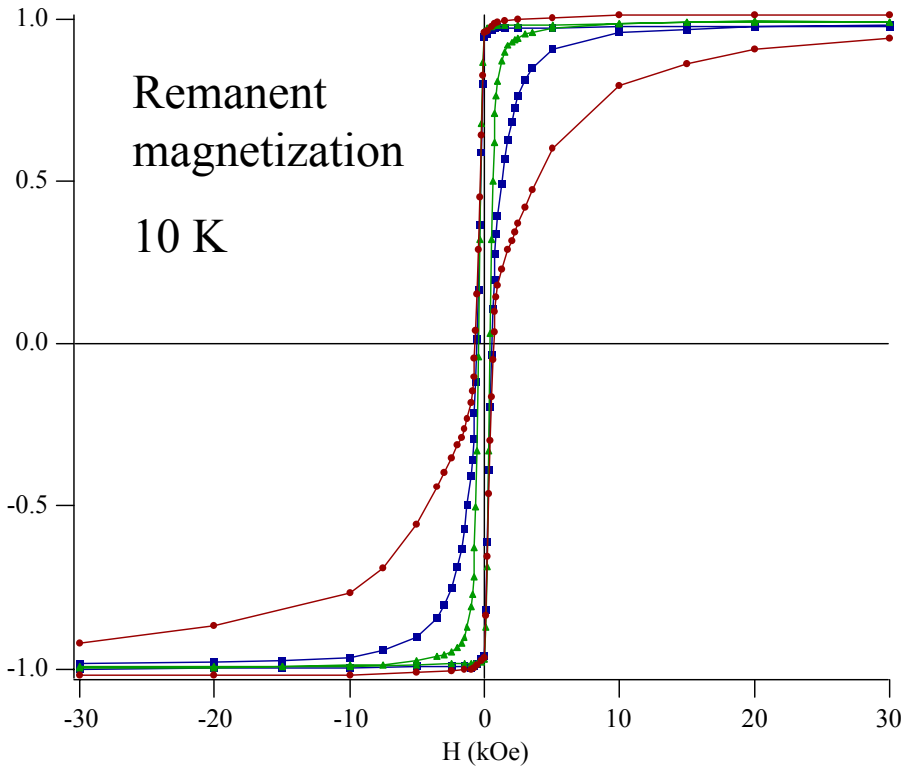
$t \approx 5$ minutes

Colloidally crystallized nanoparticle crystals, 8.6 nm Fe:

$t = 2$ weeks

$t = 4$ weeks

Approach to Saturation



D. Farrell, Y. Cheng, Y. Ding, Saeki Yamamuro, C. Sanchez-Hanke, C.-C. Kao, and S. A. Majetich, *J. Mag. Mag. Mater*. (in press, 2004).

$$\Delta M(H) \propto H^{x}$$

x = -2 Ferromagnet

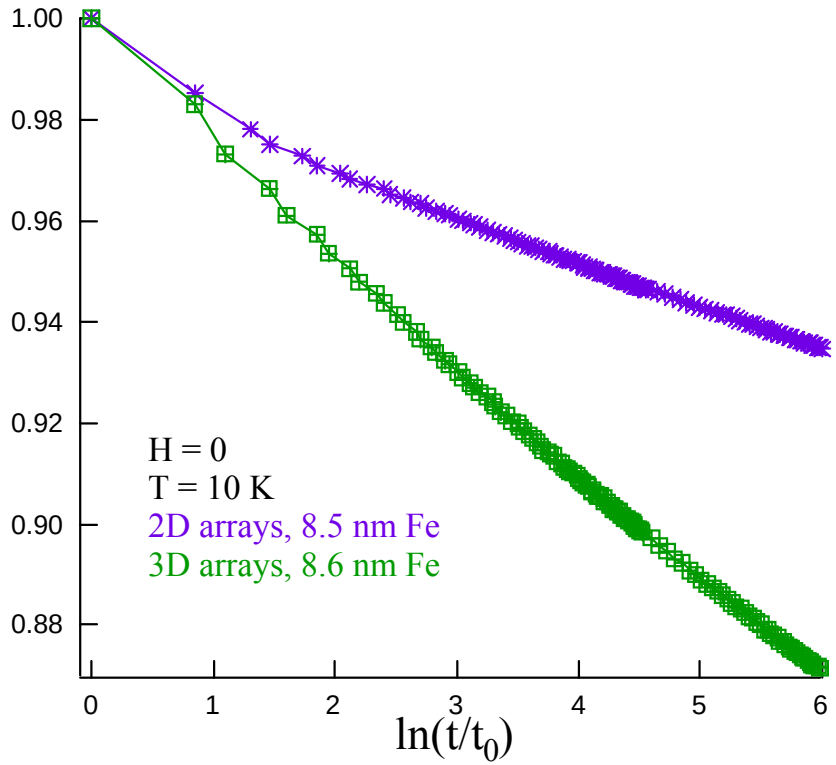
x = -1/2 amorphous magnet (spin glass-like)

5 minutes; x = -0.67
2 weeks: x = -1.17
4 weeks: x = -1.89

Small L_{coh} like spin glass

Large L_{coh} FM

Magnetic Relaxation



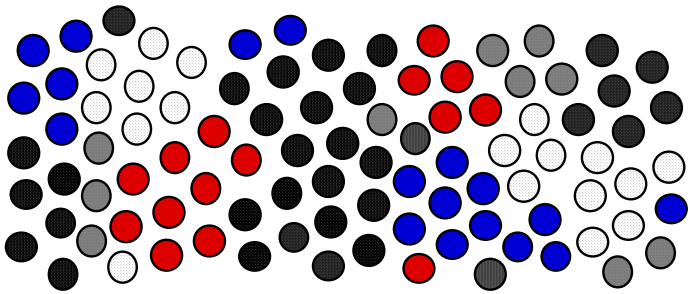
Arrays made in 5 minutes have much slower decay than those formed over 4 weeks

Structural ordering has *shifted the distribution of energy barriers* for relaxation to shorter times, and may have sharpened the distribution

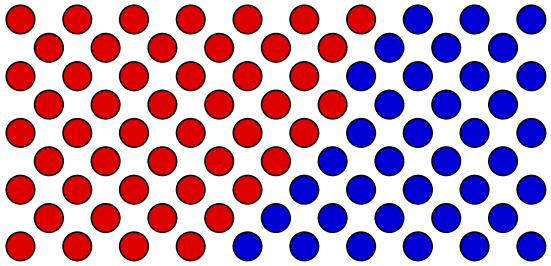
Magnetostatics Summary

• Both magnetostatic forces and the structural coherence length L_{coh} affect the magnetic properties of nanoparticle arrays

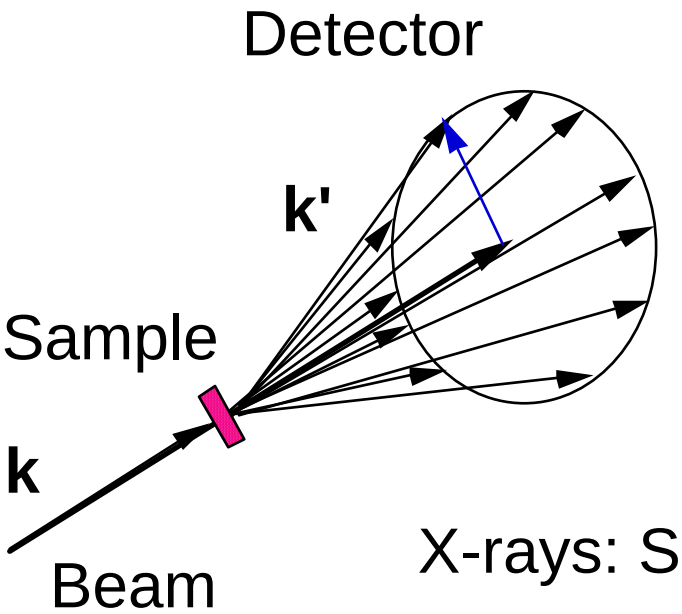
• Stronger dipolar interactions slow the magnetic relaxation when L_{coh} is short, and the arrays are spin glass-like

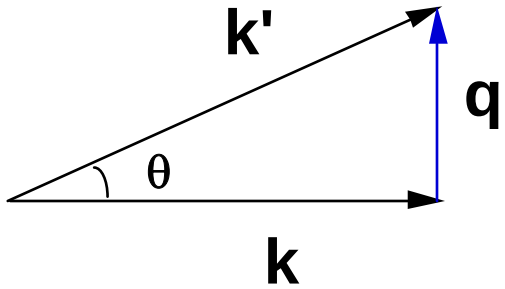


• When L_{coh} is long, there is less magnetic relaxation over very long time scales, and the arrays act more like a bulk ferromagnet



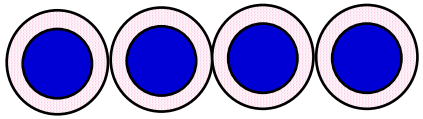
Scattering Experiments and Coherence Lengths



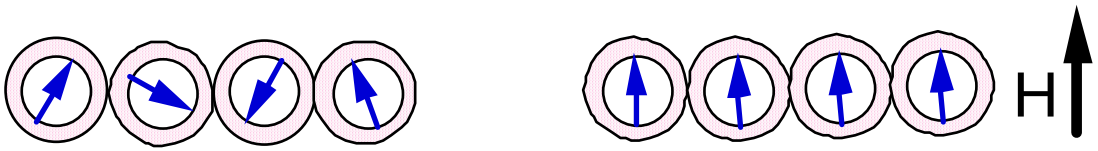


$$q = \frac{4\pi \sin\theta}{\lambda}$$

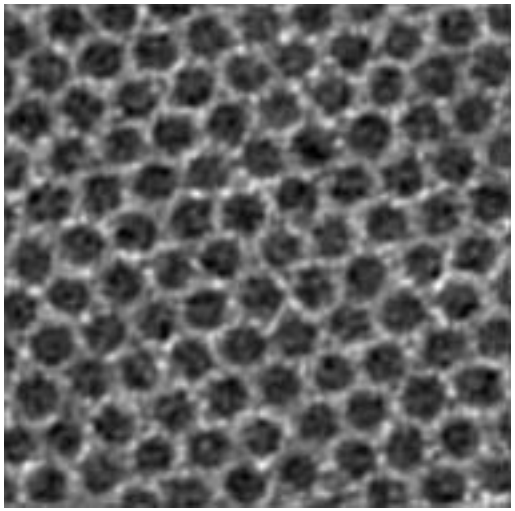
X-rays: Scattering ~ Z

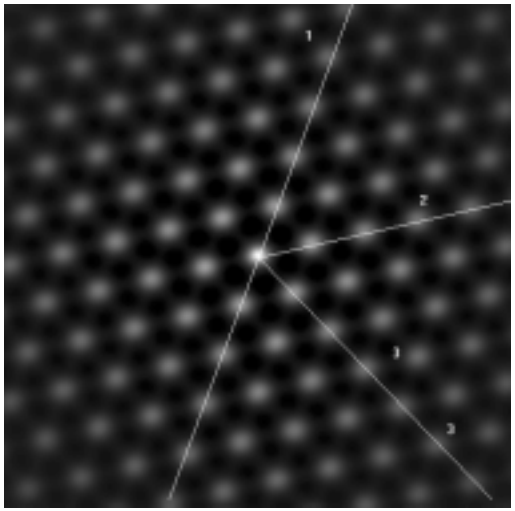


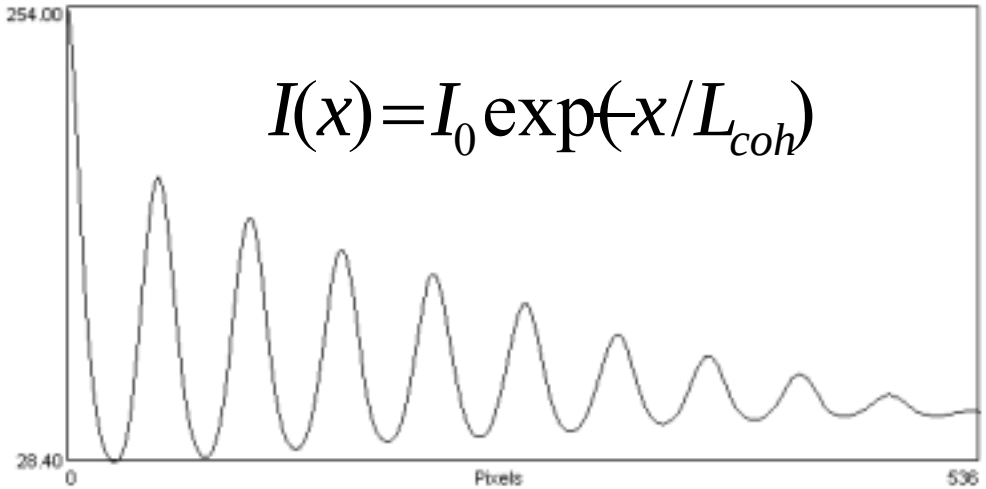
Neutrons: Scattering $\mu_{nuclear}$, $M_{perpendicular}$



Coherence Length







$$I(x) = I_0 \exp(-x/L_{coh})$$

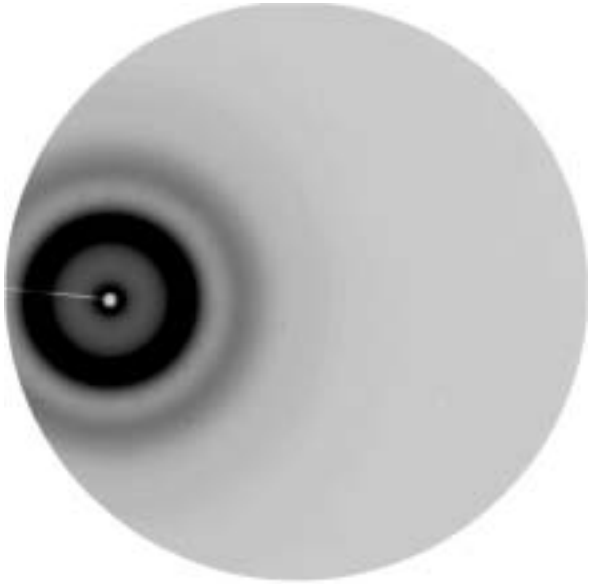
Structural coherence length found for small regions from TEM images

SAXS: Structural L_{coh} average

SANS: Structural and Magnetic L_{coh} averages

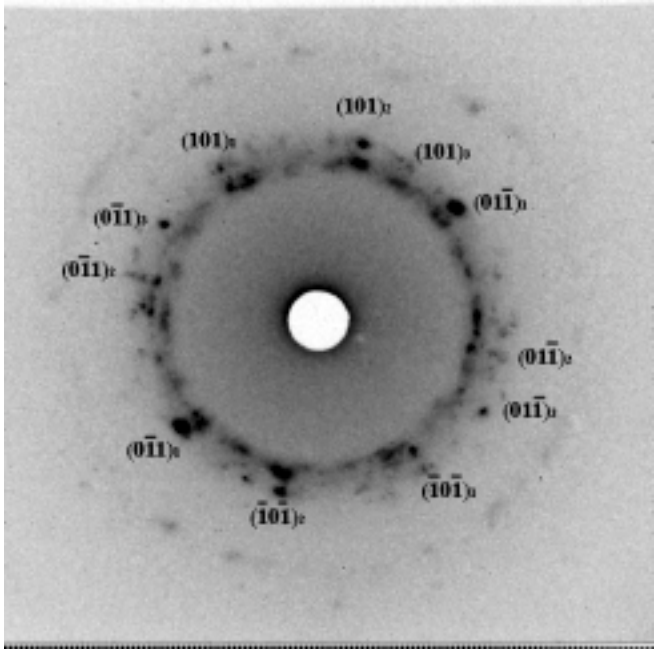
SAXS Results

3D array made over 2 weeks by slow diffusion of 2-propanol and ethanol



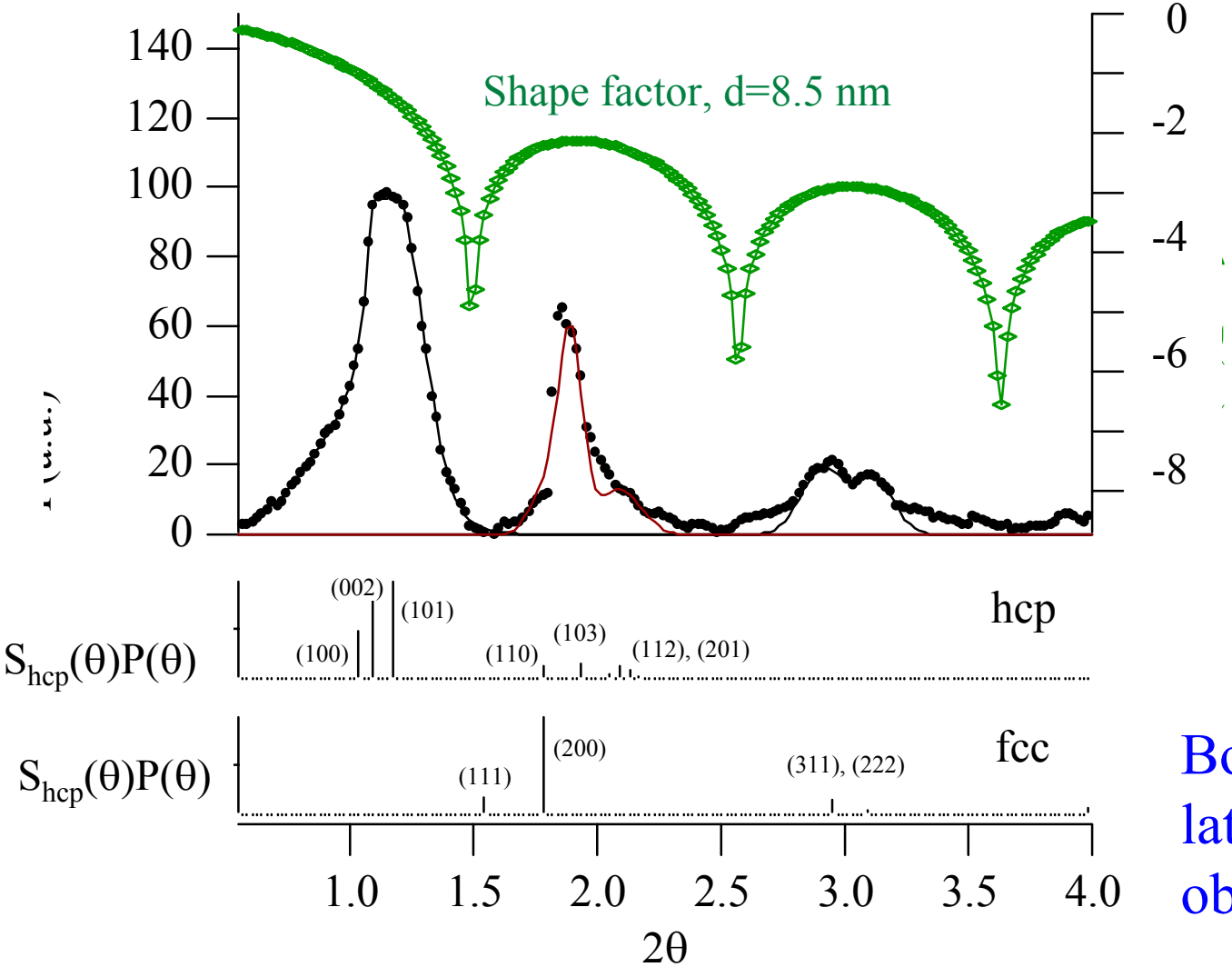
Many small arrays with different orientations

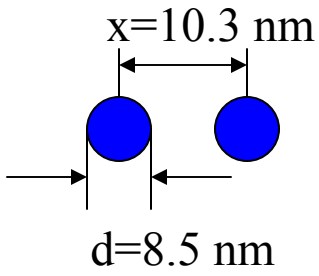
3D array made over 4 weeks by slow diffusion of 2-propanol

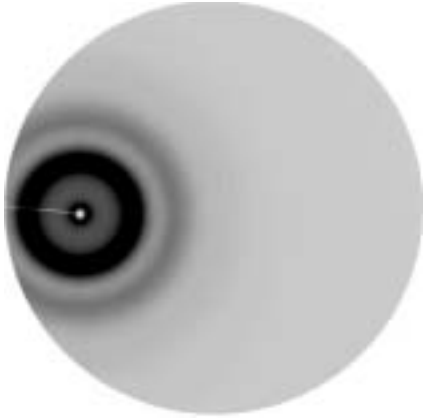


Larger L_{coh} and smaller spacing

Nanoparticle Crystals Made *Over 2 Weeks*

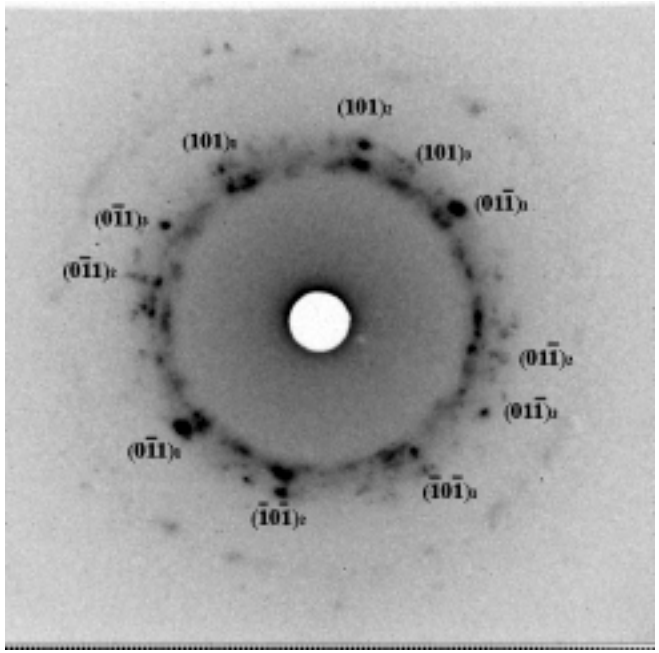


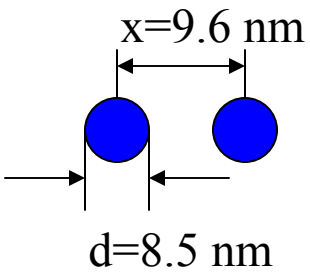




Both hcp and fcc lattice structures observed

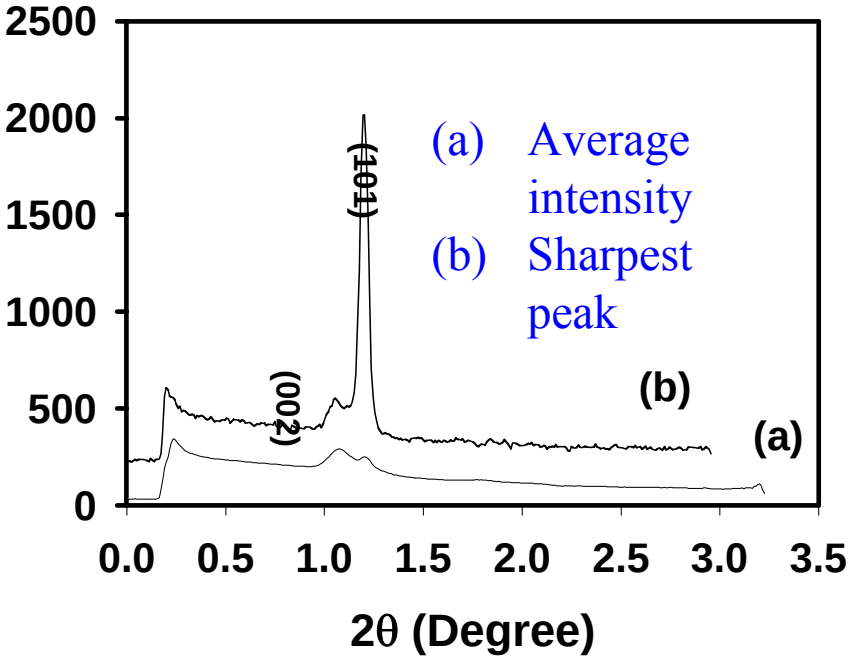
Nanoparticle Crystals Made *Over 4 Weeks*



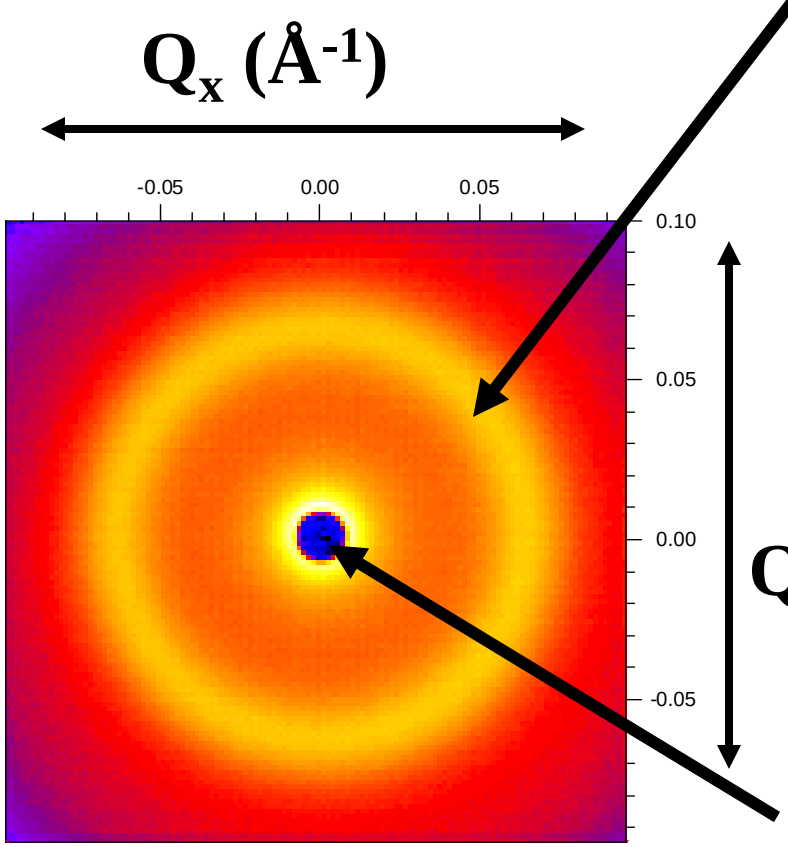


Interparticle spacing slightly reduced

Spots due to 3 hcp "supergrains"- Large L_{coh}



Small Angle Neutron Scattering



Diffraction-like peak

$Q = 0.10$ Å^{-1} for 5.7 nm Fe

$\rightarrow$ Spacing $2\pi/Q = 6.5 \pm 1.5$ nm

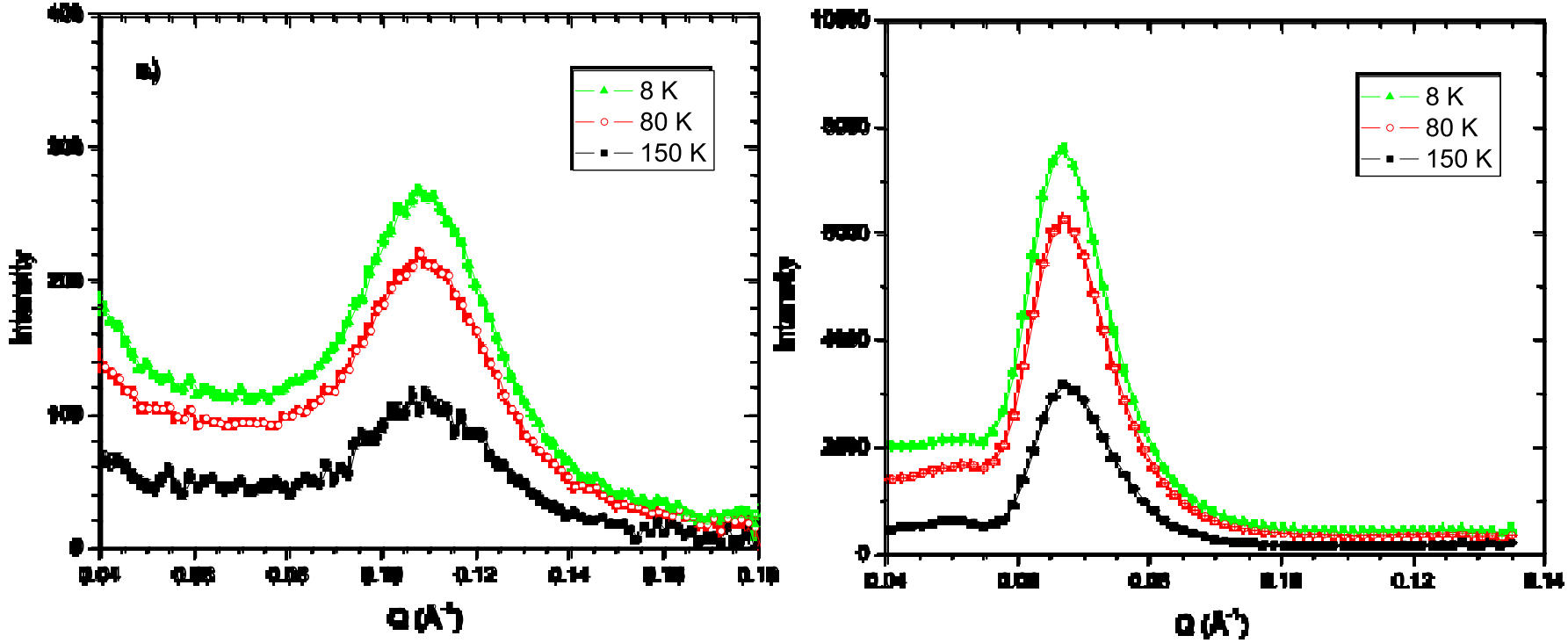
At $Q = 0.67$ Å^{-1} for 8.2 nm Fe

$\rightarrow$ Spacing 10 ± 2 nm

Upturn at Low Q

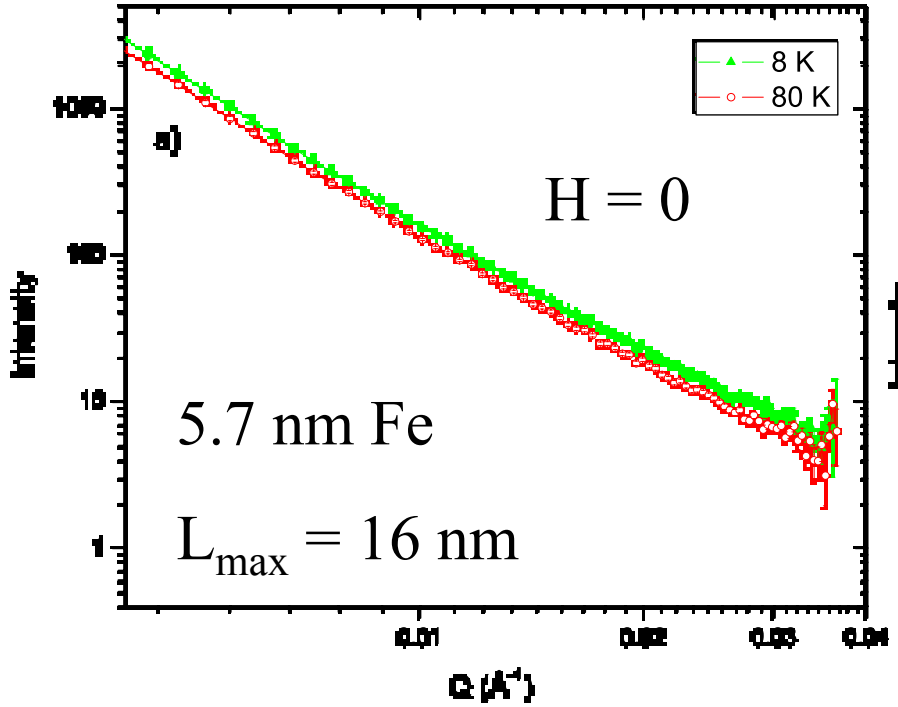
8.2 nm Fe , H = 0, T = 5 K

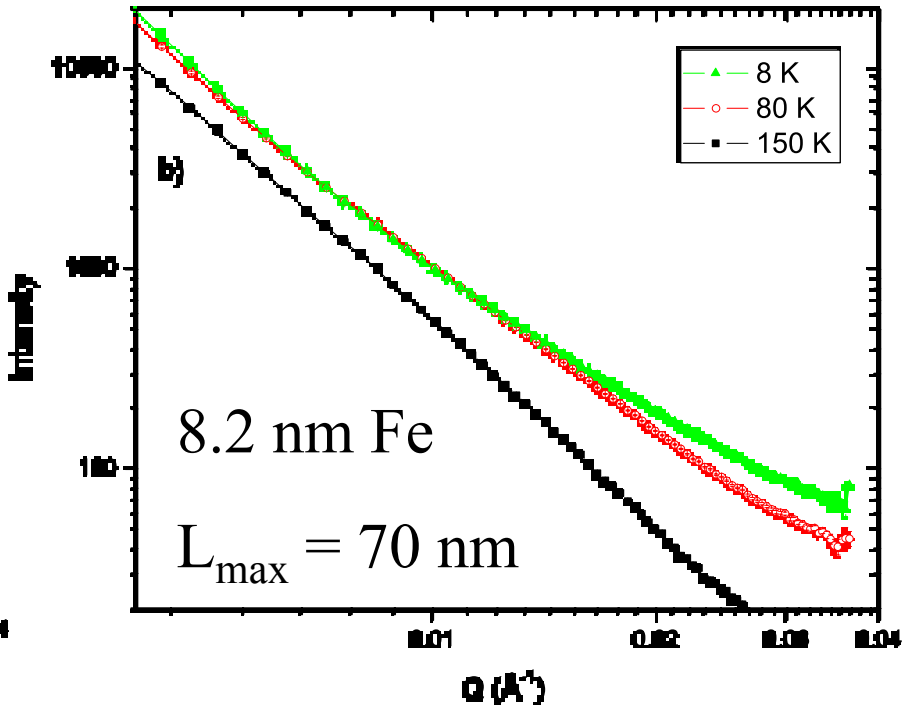
Temperature Dependence of SANS Diffraction Peak



- Circular average data in the high Q (to ~0.15-0.20 Å^{-1}) region
- Higher magnetic order → more scattering at low T

Low Q Intensity I(Q)





Deviations from (Lorentzian)^2 behavior due to long range magnetic correlations

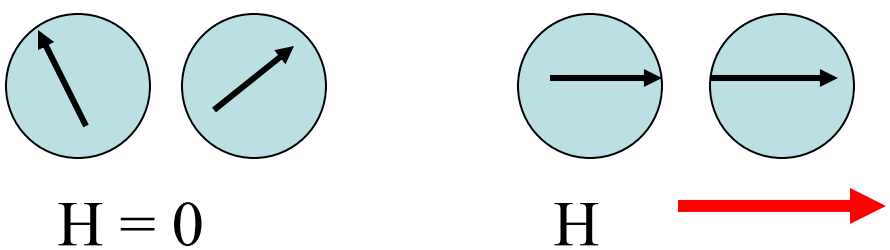
$L_{corr}=2\pi/Q_{corr}$ Could look at monolayer with X-rays

Angular Dependence of Magnetic Scattering

Define ΔI = I(5 T)-I(0) to distinguish magnetic and nuclear contributions

Only the perpendicular magnetization component contributes to the measured SANS intensity

Peaks at 90°, 270° indicate magnetization parallel to the applied field (as expected for ferromagnets and Fe particles)



$$\Delta I \propto -B \sin^2 \theta$$

SANS I(Q,H)

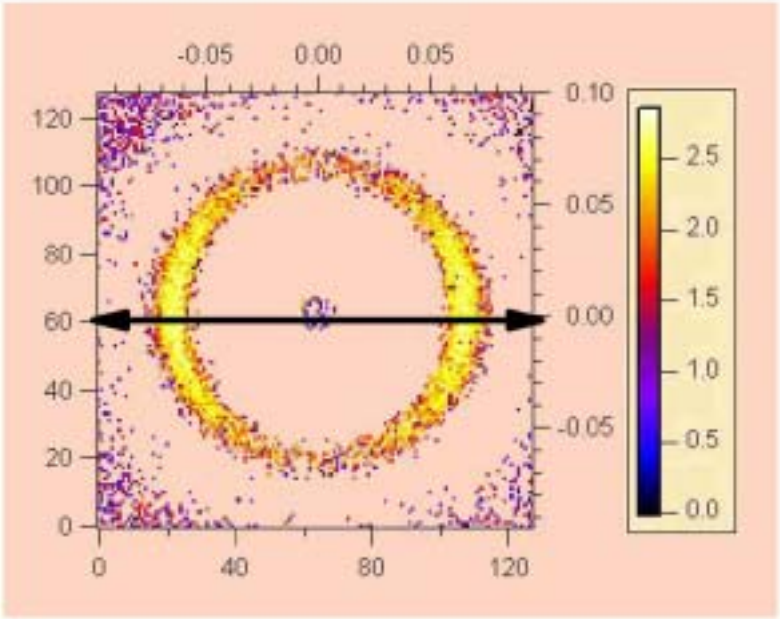
8.2 nm Fe, *partly oxidized*
$\Delta I = I(5\ T) - I(0)$

Enhanced scattering parallel to H (0°, 180°) due to perpendicular magnetization component

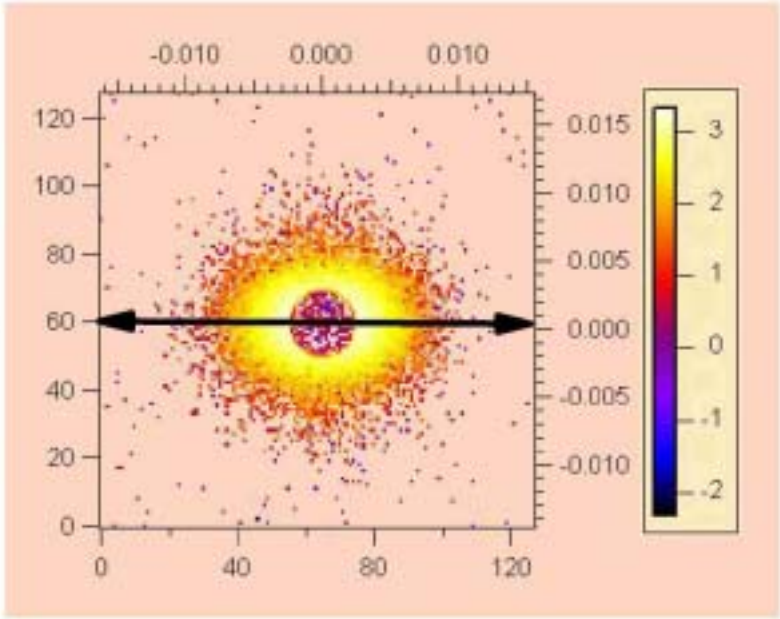
AF's, Ferrimagnets have a spin flop phase at moderate fields, where the spins align perpendicular to H

$Q_x \rightarrow$ $\uparrow Q_y$ H $\rightarrow$

High Q ΔI
At diffraction peak



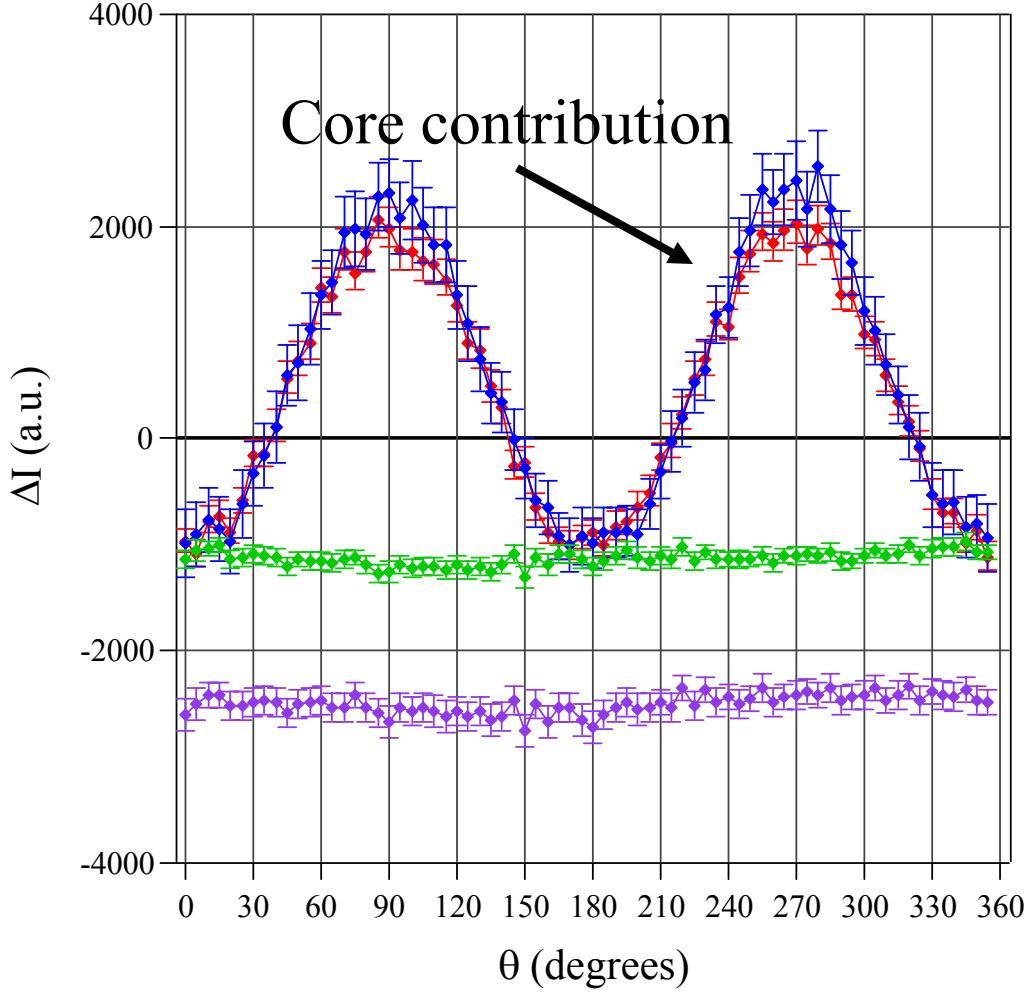
Low Q ΔI



applied field direction

5 K, λ = 8 Å

Angular Dependence of ΔI(Q)



Minimally oxidized
8.6 nm Fe cores

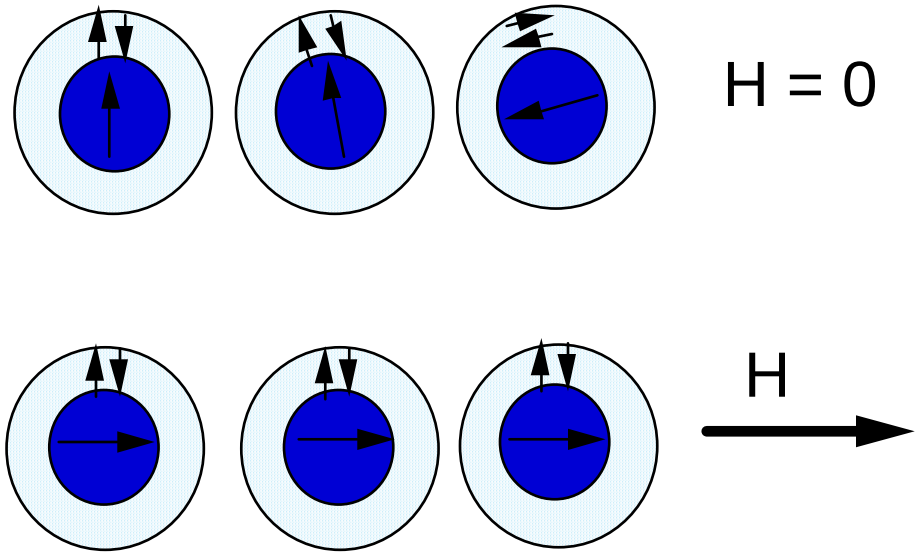
T = 5 K

See peaks in ΔI at 90°, 270 ° and

$$\Delta I \propto -B \sin^2 \theta$$

H_{appl} at 0°

SANS Core-Shell Summary



The Fe core is exchange coupled to the Fe oxide shell

When an external field is applied, the soft cores align, while the ferrimagnetic shells orient perpendicular in a spin-flop phase

The oxide dominates ΔI since the aligned cores don't contribute

Requirements for Exchange Interactions

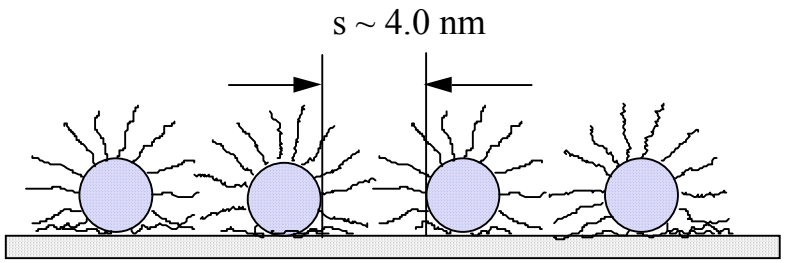
$$J_{pt} \sim (1/s^2)\exp\left[\sqrt{2m^*\phi}\,s/\hbar\right]$$

To enhance the amount of exchange coupling, relative to magnetostatic interactions, use a more conducting matrix, so the energy barrier ϕ is reduced, or else reduce the interparticle spacing s.

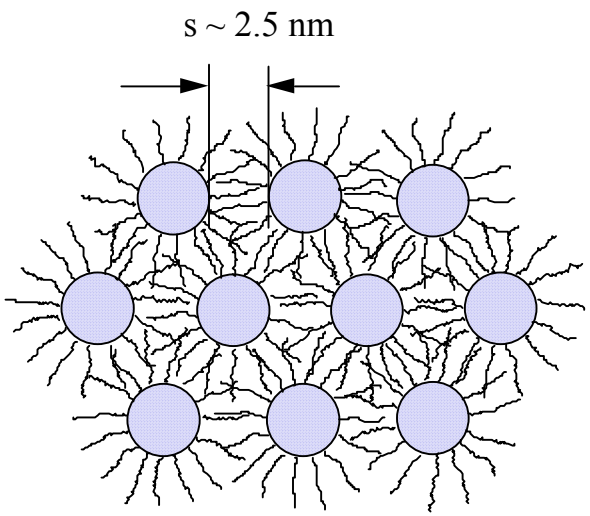
With a surfactant ($\phi \sim 3$ eV), exchange interactions become significant only for separations < 1 nm, and dominant for s < 0.5 nm

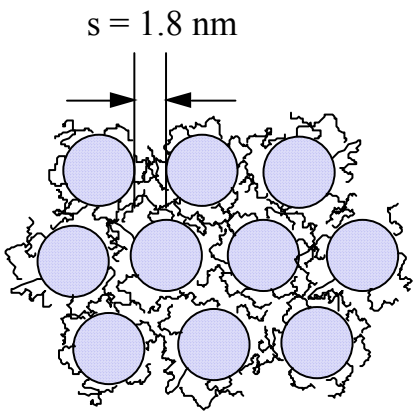
For more conducting matrices (lower ϕ), exchange can dominate at longer length scales

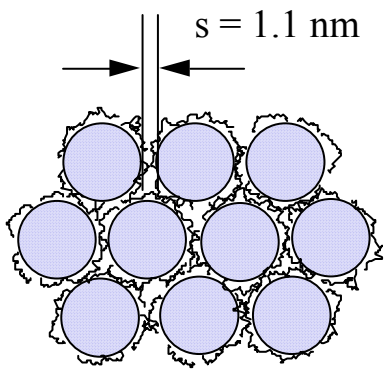
Reduction in Particle Spacing with Colloidal Crystallization



Evaporated monolayer



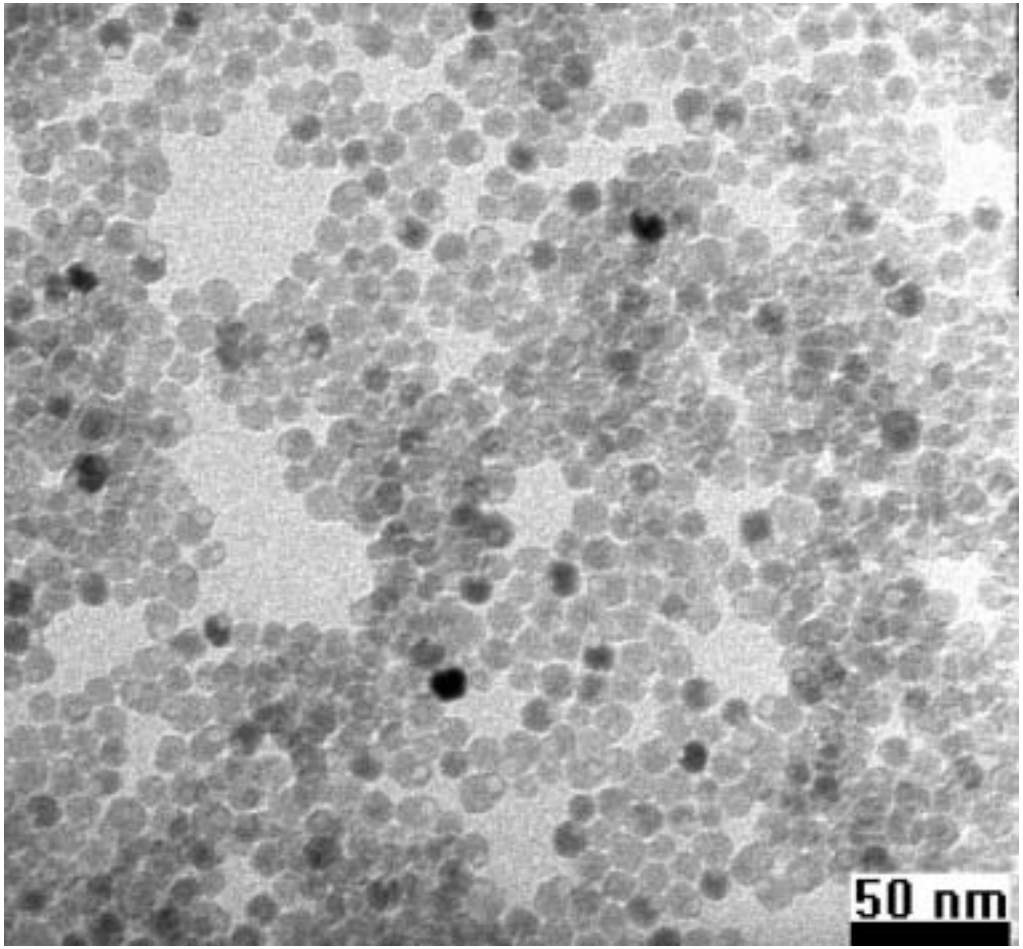




Evaporated multilayer

Nanoparticle crystals

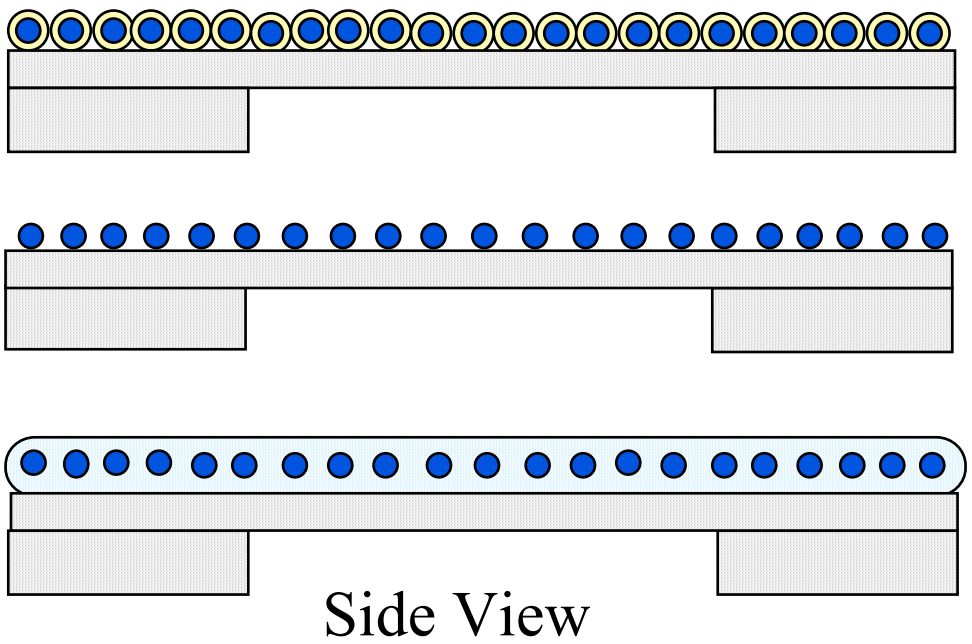
Limits to Particle Spacing Reduction



- First form highly ordered monolayer array, then *rapidly* washed with ethanol to remove excess surfactant
- Nearest neighbor separation ~ 0.6 nm
- With *slow* colloidal crystallization, it may be possible to retain the ordering

→ **exchange?**

Matrix Replacement to Change Energy Barrier



Self-assemble monolayer array on Si_3N_4 TEM grid

Anneal to decompose surfactant

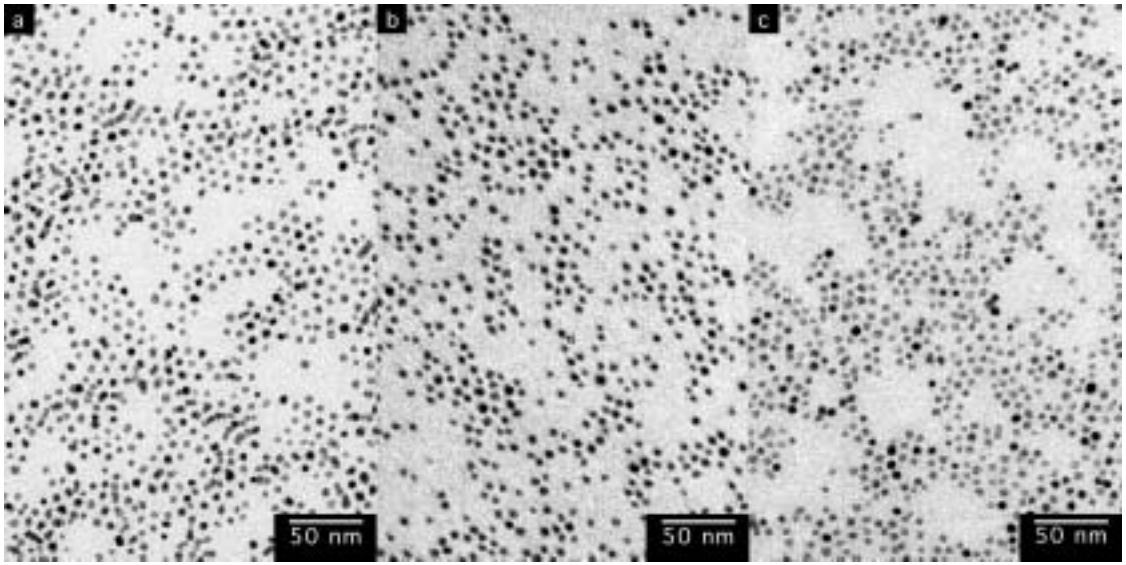
Sputter immiscible overcoat

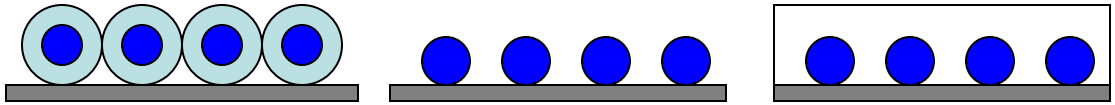
FePt nanoparticles and SiO_x overcoat:

Y. Ding, S. A. Majetich, J. Kim, K. Barmak, H. Rollins, P. Sides, *J. Magn. Magn. Mater.* (in press, 2004)

Can also make matrix conducting, ferromagnetic, …

Matrix Replacement FePt/SiO_2



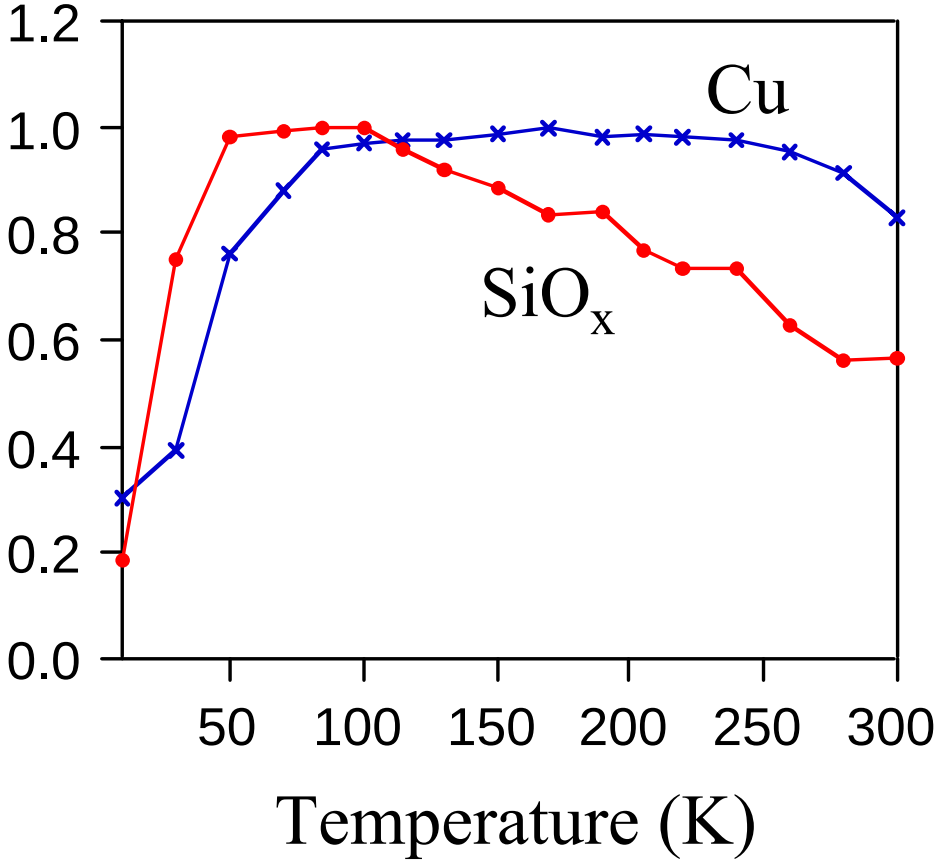


As made | Surfactant removed | With SiO_2 overcoat

Processing doesn't change particle morphology or spacing

Need chemical probes as feedback to optimize processing and minimize residual impurities

Matrix Replacement and Exchange Effects

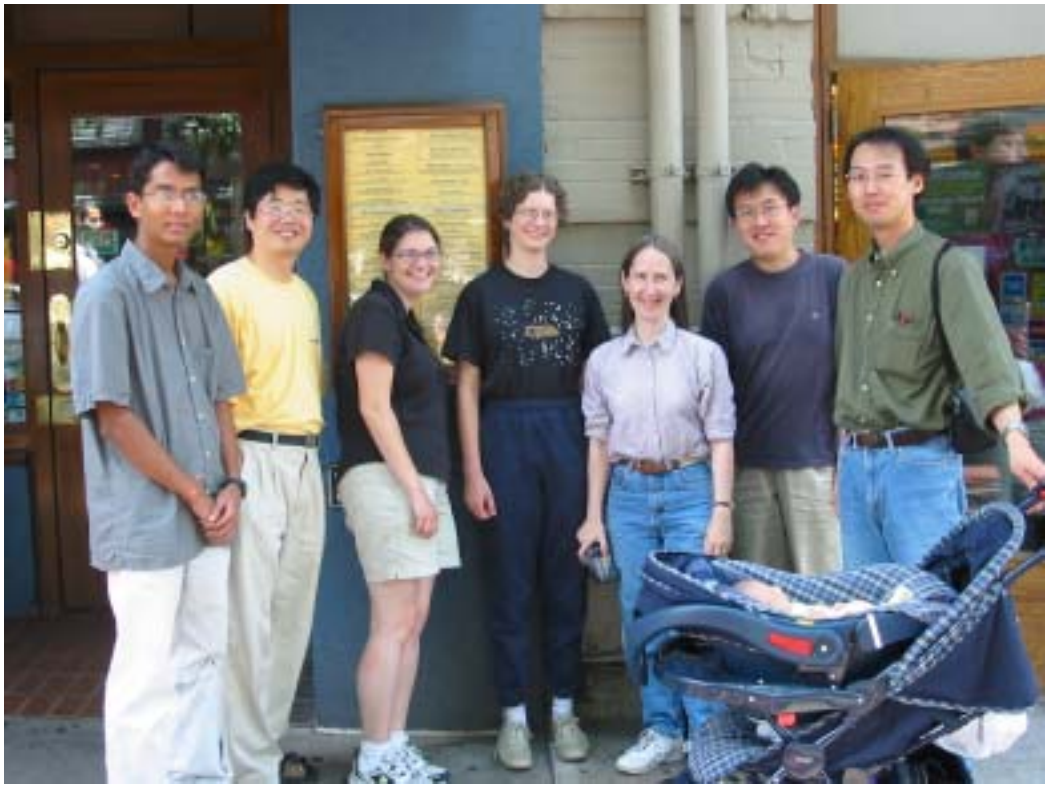


- 8.5 nm Fe nanoparticles with a SiO_x matrix have a lower blocking temperature than those with a Cu matrix

Synchotron Research Opportunities

- Magnetic domain imaging (magnetic speckle scattering)
- Monitoring the dynamics of self-assembly (SAXS)
- Layer-by-layer magnetic ordering (XMCD, vary angle)
- Inelastic scattering (magnons, phonons)
- Element-specific hysteresis loops in arrays with magnetic matrices

Acknowledgments



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