# Magnetic SANS Summer School 2020
(Held February 2021)

Instructors: Kathryn Krycka, Julie Borchers, Jonathan Gaudet, and Peter Beaucage

- Biocompatible Fe-oxide based magnetic particles promising for applications such as MRI contrast, hyperthermia treatment of cancer, and data storage


- Focus on 9-10 nm Fe_3O_4 and $CoFe_2O_4$ nanoparticles arranged in close-packed three-dimensional crystallites, ordered on micron scale[1].
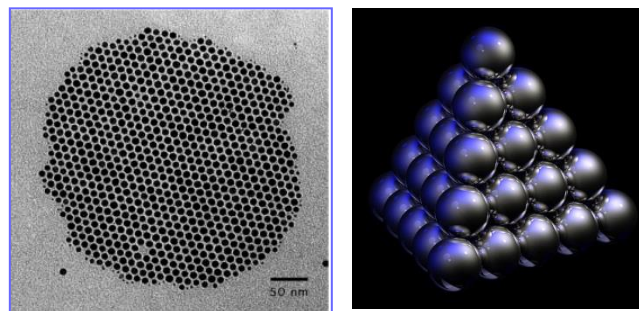
- Size / surface effects can have profound impact on performance, including magnetic stability[2] and inter-particle coupling[3].
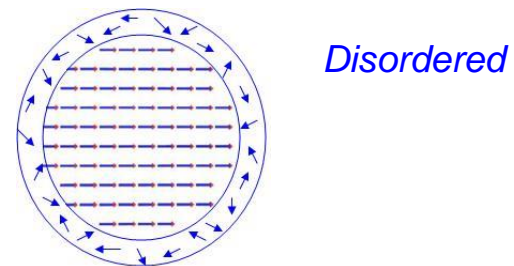
- For example, nanoparticle magnetism is greatly reduced compared with bulk material at "saturation"

1. Prepared by S. Majetich group; synthesis in S. Sun *et al*. J. Am. Chem. Soc. 126. 273 (2004)
2. J. Nogues et al., PRL 97, 157203 (2006)
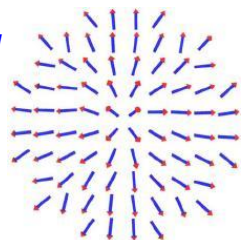3. D. Kechrakos et al., JMMM 316, E291 (2007)
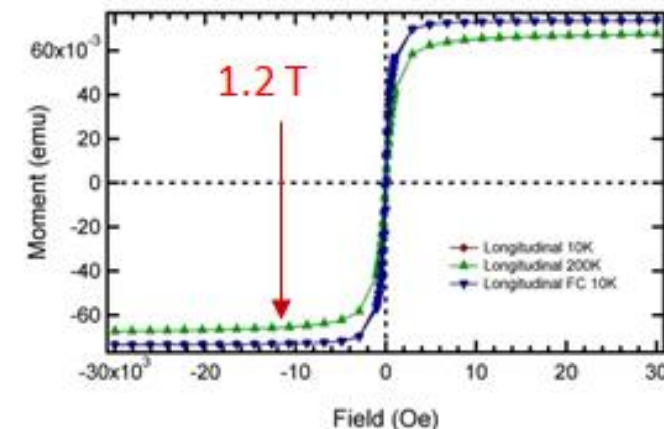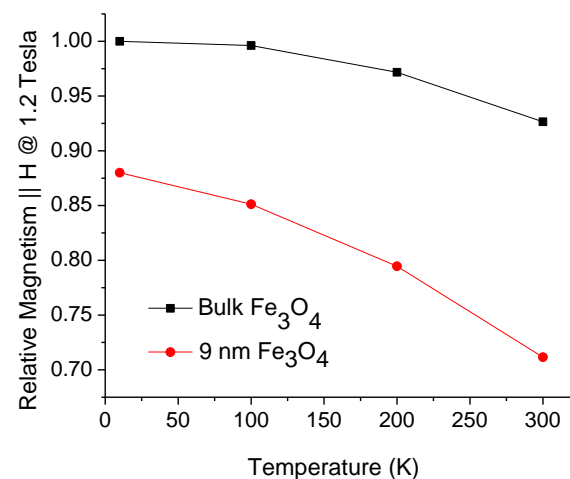
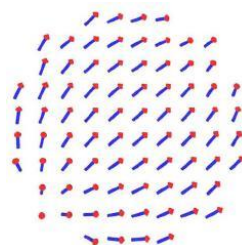➢ Common explanation is surface disordering[1].

Disordered

➢ However, sufficient surface/crystalline anisotropy[2] could result in many model variations.
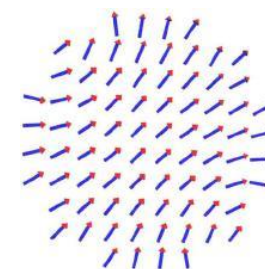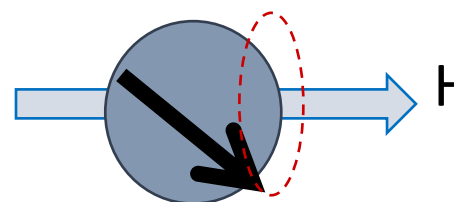
Hedgehog

Artichoke

Throttled

➢ Thermal, size-dependent superparamagnetic effects are also possible[3]

H

➢ Polarization-analyzed SANS (PASANS) can distinguish between models.

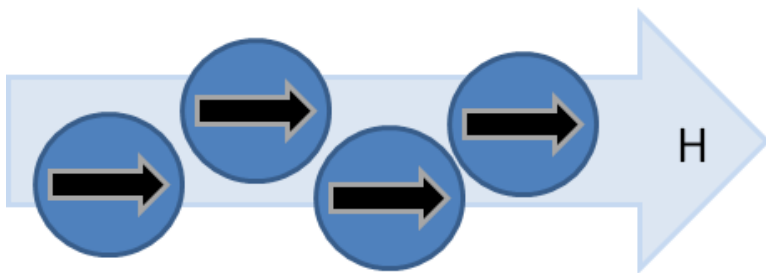1. P. Dutta et al., JAP 105, 07B510 (2009); J. Curiale et al., Appl. Phys. Lett. 95, 043106 (2009)

2. L. Berger et al., Phys. Rev. B 77, 104431 (2008); J. Mazo-Zuluaga et al., JAP 105, 123907 (2009)

3. S. Mørup and B. R. Hansen, Phys. Rev. B 72, 024418 (2005)
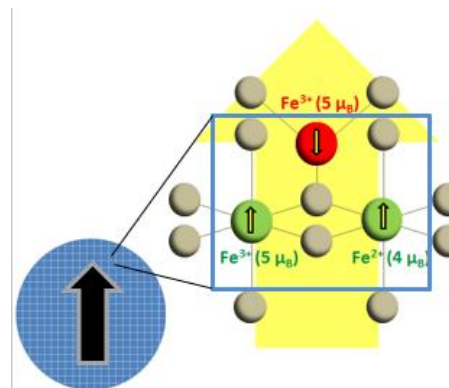
Zeeman (applied field, H) =

$$-\sum_{i\ within\ NP} \vec{m}_i \cdot \vec{H}$$ = ~1.5 eV / NP (at 1.2+ T)

Exchange coupling ~ 2 meV+ / f.u. ->
~10 eV / NP (holds ferrimagnetic alignment)

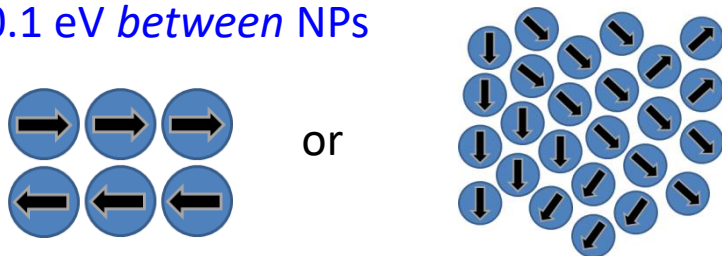Tetrahedral sites (red) couple ferrimagentically to the octahedral (green) sites with ~2-3 meV
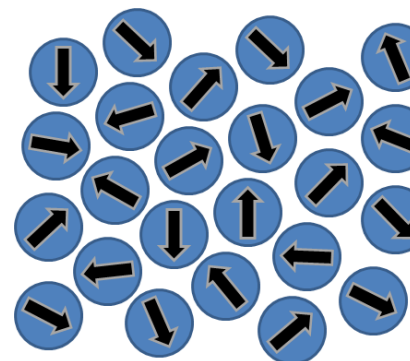
Dipolar coupling =

$$\sum_i \sum_{j \neq i} \frac{\mu_o (\vec{m}_i \cdot \vec{m}_j - 3(\vec{m}_i \cdot \vec{r}_{ij})(\vec{m}_j \cdot \vec{r}_{ij}))}{4\pi \|\vec{r}_{ij}^3\|}$$

= ~0.1 eV *between* NPs

 or

Crystalline anisotropy (K_V) at ~4.4 x 10^4 J / m^3 =
~0.1 eV / NP (orientation along 100 axis)

What actually happens at high-field (1.2 Tesla)?
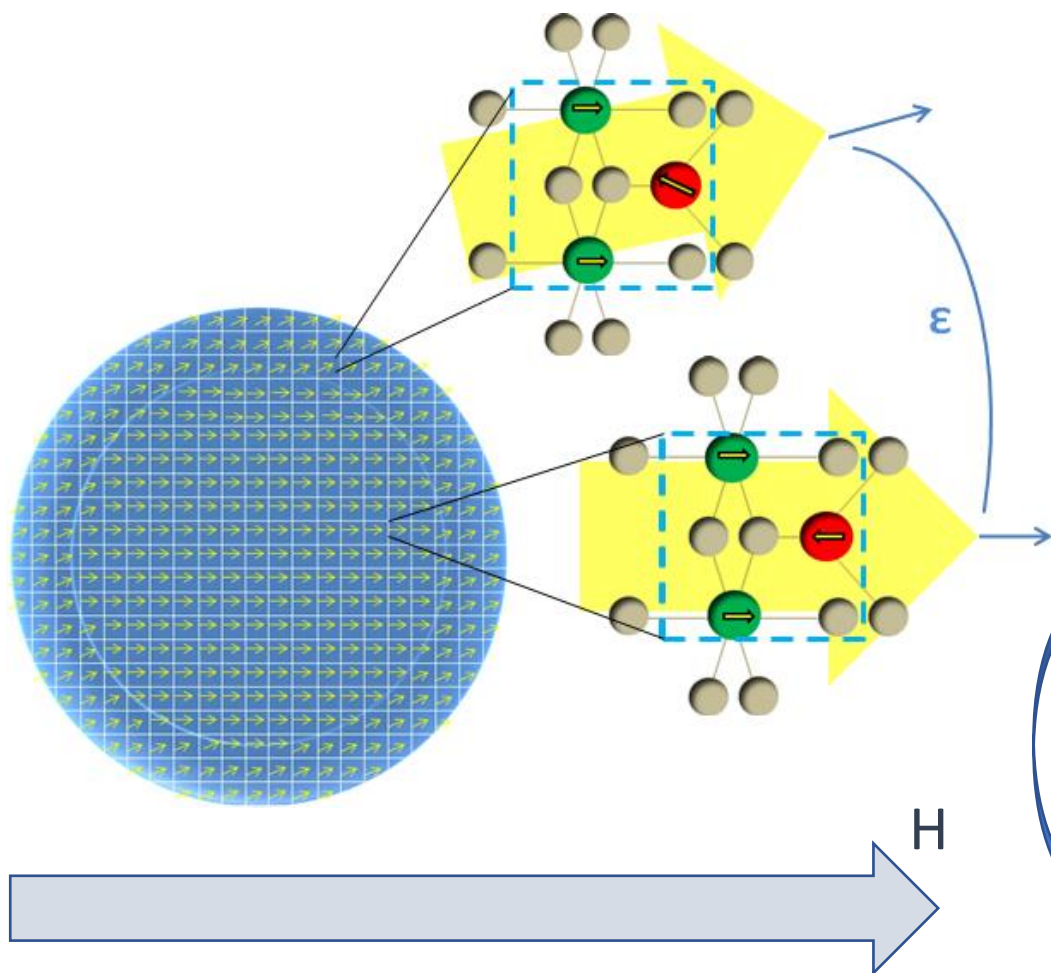
SANS reveals that we have *magnetically* canted shells at 200 K to 300 K between 1.0 nm and 1.5 nm thick[1]!

The surface magnetism is preserved[2]

Average ε = ~30°

Thermal reduction of magnetism appears to be a function of uniform nanoparticle excitations

1. K.L. Krycka *et al*. Phys. Rev. Lett. 104, 207203 (2010)
2. J. Salafranca *et al*. Nano Lett. 12, 2499 (2012)

Zeeman (applied field, H) =

$$-\sum_{i \text{ within } NP} \vec{m}_i \cdot \vec{H} \quad = \text{~}1.5 \text{ eV / NP (at 1.2 T)}$$

Canting: -0.11 eV / 1 nm shell

H

Exchange coupling ~ 2 meV+ / f.u. ->
~10 eV / NP (holds ferrimagnetic alignment)

Canting: +0.21 eV/1 nm shell (at surface, cost higher at center)
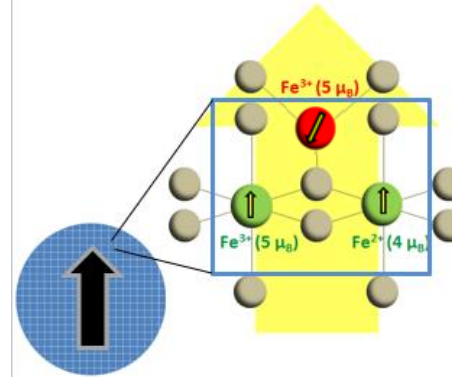
Tetrahedral sites (red) might cant w.r.t. to their ferrimagnetic alignment with octahedral (green) sites

Dipolar coupling =

$$\sum_{i}\sum_{j\neq i} \frac{\mu_o \left(\vec{m}_i \cdot \vec{m}_j - 3(\vec{m}_i \cdot \vec{r}_{ij})(\vec{m}_j \cdot \vec{r}_{ij})\right)}{4\pi \|\vec{r}_{ij}^3\|}$$
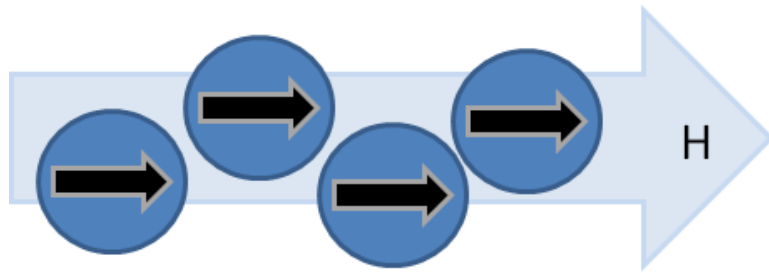
= ~0.1 eV *between* NPs

or
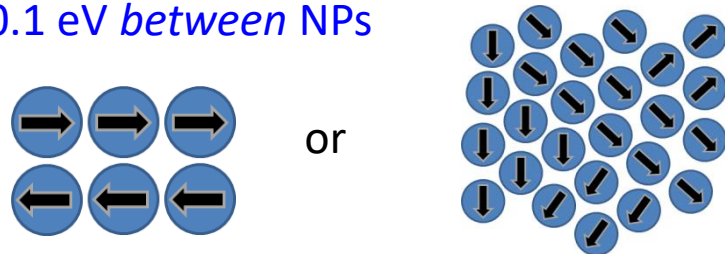
Crystalline anisotropy (K_V) at [1 to 3] x 4.4 x 10^4 J / m^3
= ~0.3 eV / NP (orientation along 100 axis)

Canting:-0.15 eV / 1 nm shell

More details in *Phys. Rev. Lett.* 113, 147203 (2014)

Zeeman (applied field, H) =

$$- \sum_{i \; within \; NP} \vec{m}_i \cdot \vec{H} \quad = \sim 1.5 \text{ eV / NP (at 1.2+ T)}$$

H

Exchange coupling ~ 2 meV+ / f.u. ->
~10 eV / NP (holds ferrimagnetic alignment)

Tetrahedral sites (red) couple ferrimagentically to the octahedral (green) sites with ~2-3 meV
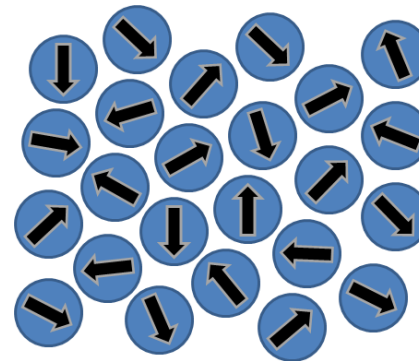
Dipolar coupling =

$$\sum_i \sum_{j \neq i} \frac{\mu_o \left(\vec{m}_i \cdot \vec{m}_j - 3(\vec{m}_i \cdot \vec{r}_{ij})(\vec{m}_j \cdot \vec{r}_{ij}) \right)}{4\pi \|\vec{r}_{ij}^3\|}$$

= ~0.1 eV *between* NPs

 or
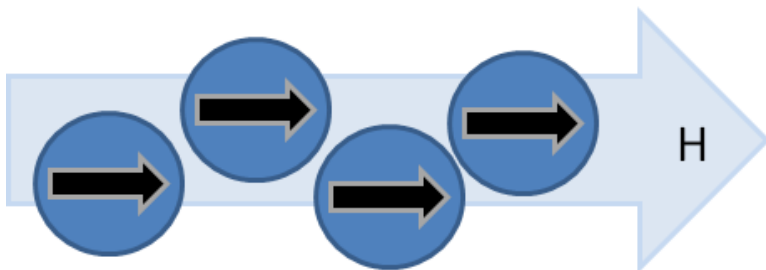
Crystalline anisotropy (K$_V$) increases 18 x's compared to Fe$_3$O$_4$ = ~5.4 eV / NP (orientation along 100 axis)

Behavior dominated by interaction between Zeeman and Crystalline Anisotropy

Particle Moment Canting in $CoFe_2O_4$ Nanoparticles

Physical Review B 90, 180405(R) (2014)

FIG. 1. (Color online.)Hysteresis loops for $CoFe_2O_4$ nanoparticle assemblies at 10, 100, 200, and 300 K. The 10 K hysteresis loop for bulk $CoFe_2O_4$ is shown for comparison. Inset shows TEM image of as-grown particles.
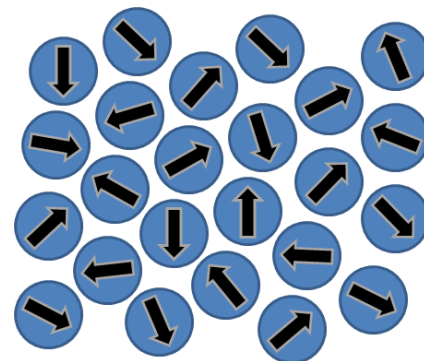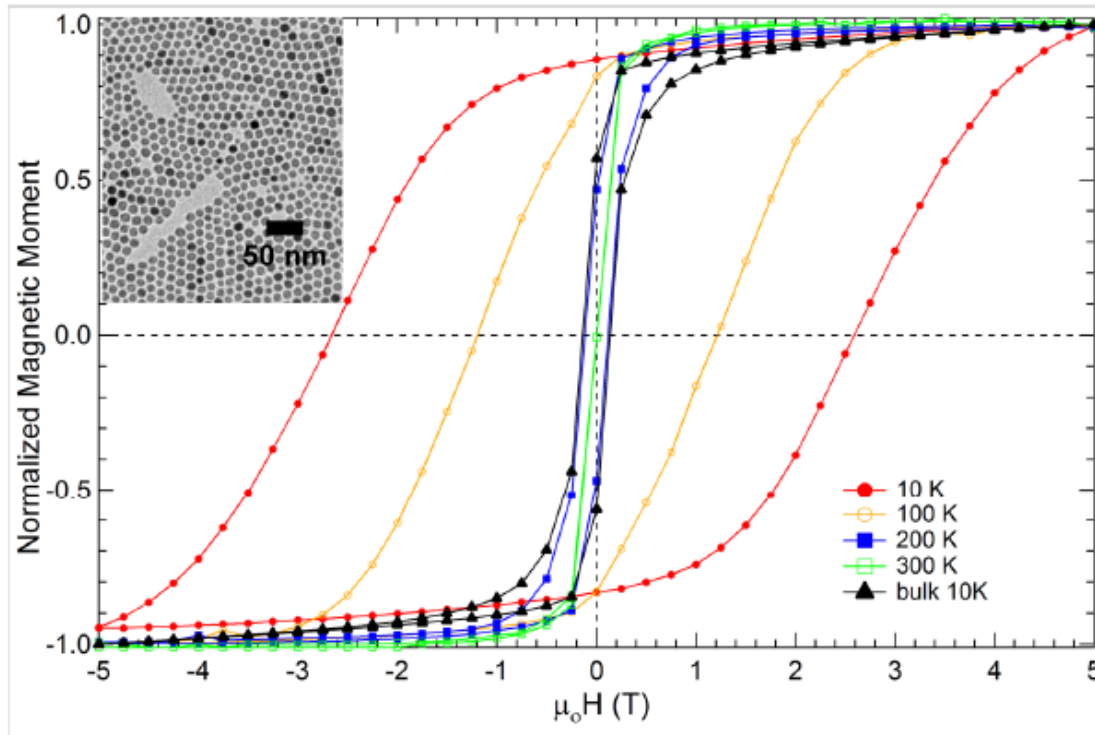
- Made by Dr. Sara Majetich's group, Carnegie Mellon University

- 10 nm $CoFe_2O_4$ Nanoparticles, 10% polydispersity

- Washed to retain about a monolayer of oleic acid

- Slowly co-precipitated into close-packed, face-center cubic like structures with order up to a micron in extent

- Particle to particle spacing ~ 15 nm

- Multiple grains powder packed together form structurally isotropic sample with a prominent 111 diffraction ring

- Oleic acid network is thought to physically prevent the nanoparticles from rotating with the applied magnetic field

- Goal is to analyze magnetic morphology of 10 nm, close-packed $CoFe_2O_4$ nanoparticles using NG7 SANS and VSANS polarized measurements

- Next time, we will go through a "hands-on" IGOR reduction (on older NG7 SANS data), followed by a more automated python-script reduction (on newer VSANS data). We discuss the differences between fully polarized, half-polarized, and unpolarized data and what sample depolarization means in terms of domain formation.

- We will together analyze the reduced $CoFe_2O_4$ nanoparticle data at 10 K, 1.4 Tesla. Then you will be able to examine the magnetic response of the nanoparticles at other conditions (10 K @ 0 T, 100 K @ 0 T and 1.4 T, 200 K at 0 T, and 300 K at 1.4 T). You will also have a brand new set of data on $CoFe_2O_4$ nanoparticles in a more highly packed lattice at 300 K, 0 T and 1.5 T for comparison.

- With PASANS you will be able to:

    1*) Model shape of N, M || H, and M $\perp$ H scattering to determine if core-shell magnetic morphology exists

    2*) Determine the magnitudes of M || H and M $\perp$ H as a function of field / temperature

    3*) Determine the total magnetization per volume (and any canting) of the nanoparticles

    4) Observe additional inter-particle domain formation at low-Q with decreasing field

    5) Compare the magnetic behavior of higher-anisotropy $CoFe_2O_4$ and lower-anisotropy Fe_3O_4 nanoparticles.