

Magnetic Structure of Cobalt Ferrite Nanoparticle Arrays



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Particle moment canting in CoFe_2O_4 nanoparticles

K. Hasz and Y. Ijiri*

Oberlin College, Department of Physics and Astronomy, Oberlin, Ohio 44074, USA

K. L. Krycka and J. A. Borchers

National Institute of Standards and Technology, NIST Center for Neutron Research, Gaithersburg, Maryland 20899, USA

R. A. Booth, S. Oberdick, and S. A. Majetich

Carnegie Mellon University, Department of Physics, Pittsburgh, Pennsylvania 15213, USA

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Polarization-analyzed small-angle neutron scattering methods are used to determine the spin morphology in high crystalline anisotropy, 11 nm diameter CoFe_2O_4 nanoparticle assemblies with randomly oriented easy axes. In moderate to high magnetic fields, the nanoparticles adopt a uniformly canted structure, rather than forming domains, shells, or other arrangements. The observed canting angles agree quantitatively with those predicted from an energy model dominated by Zeeman and anisotropy competition, with implications for the technological use of such nanoparticles.

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Kathryn Krycka



Yumi Ijiri

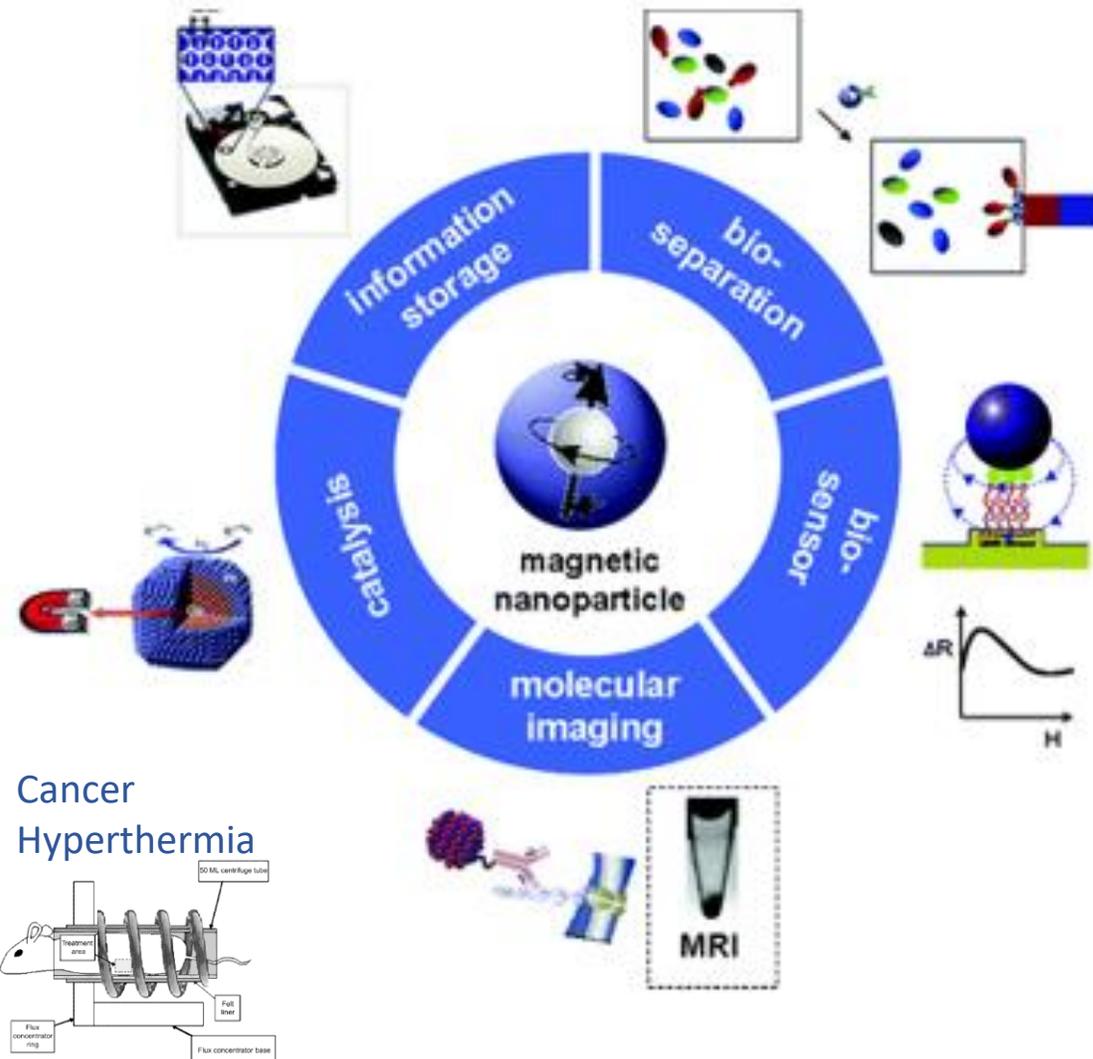


Sara Majetich



Sam Oberdick

Magnetic Nanoparticle Applications



Motivation:

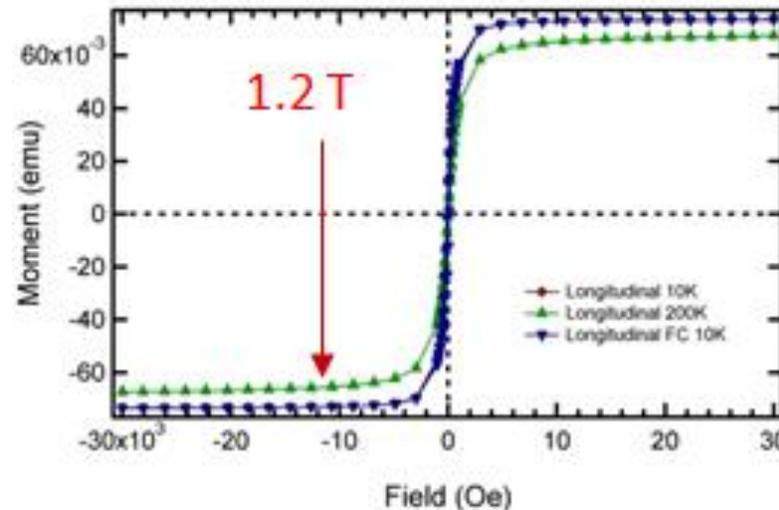
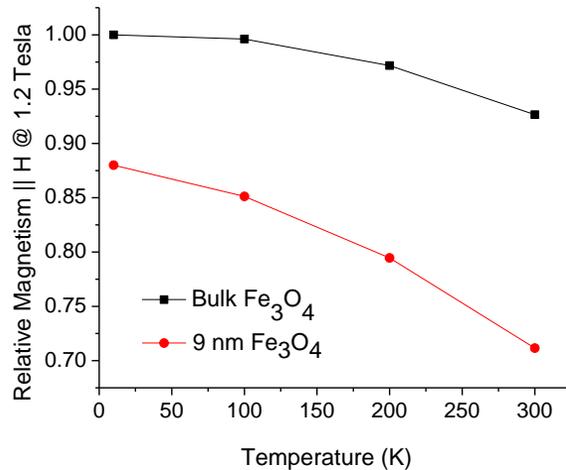
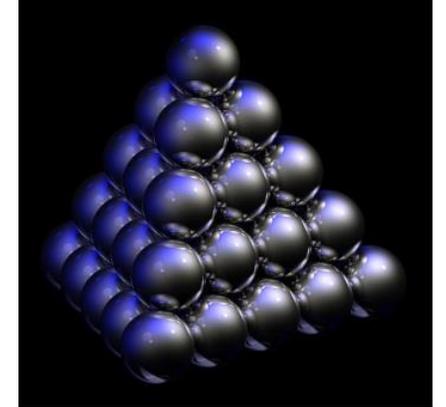
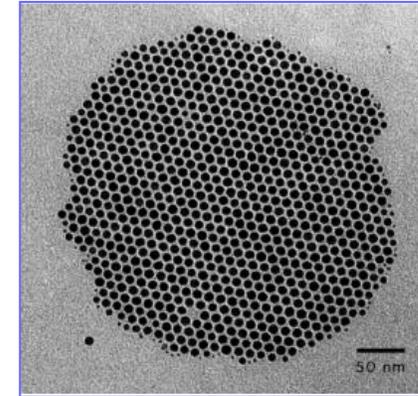
- Large quantities of uniform nanoparticles can be produced due to advancements in chemical synthesis procedures.
- Magnetic nanoparticles are under development for a wide range of applications.
- Performance is very sensitive to nanoparticle composition, size, surface defects, interparticle interactions, etc.
- A variety of experimental techniques are used to characterize behavior of nanoparticles for specific applications.

Fe₃O₄ and CoFe₂O₄ Nanoparticles



System:

- Biocompatible 9 – 10 nm diameter Fe₃O₄ and CoFe₂O₄ nanoparticles
- Single-crystal and uniform (10% polydispersity)
- Self assembled into closed-packed 3D nanocrystals
- Nanocrystal is ordered on micron scale¹.



Bulk magnetization measurements show that nanoparticle magnetism is greatly reduced compared with bulk material at in high fields.

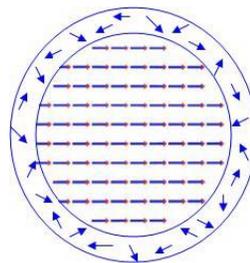
Why is the magnetization reduced?

Possible Origin of Reduced Magnetization

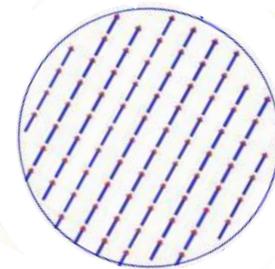


- Simplistic explanation is surface disorder¹

*Disordered -
"Dead Layer"*

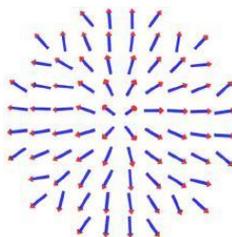


or uniform canting

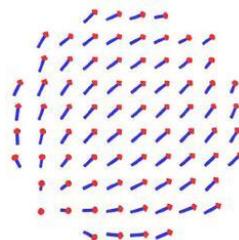


- However, high surface/crystalline anisotropy² could result in many model variations.

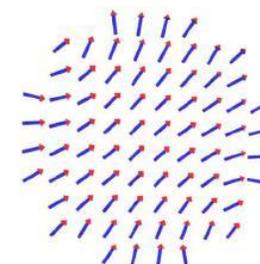
Hedgehog



Artichoke



Throttled

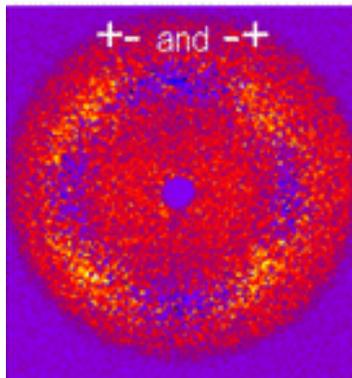
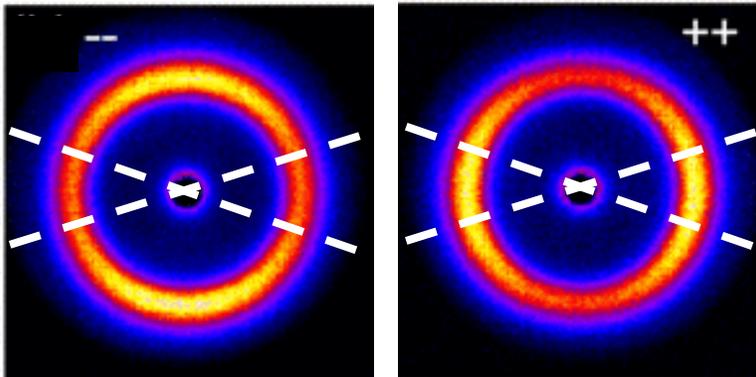


Polarization-analyzed SANS (PASANS) can distinguish between models.

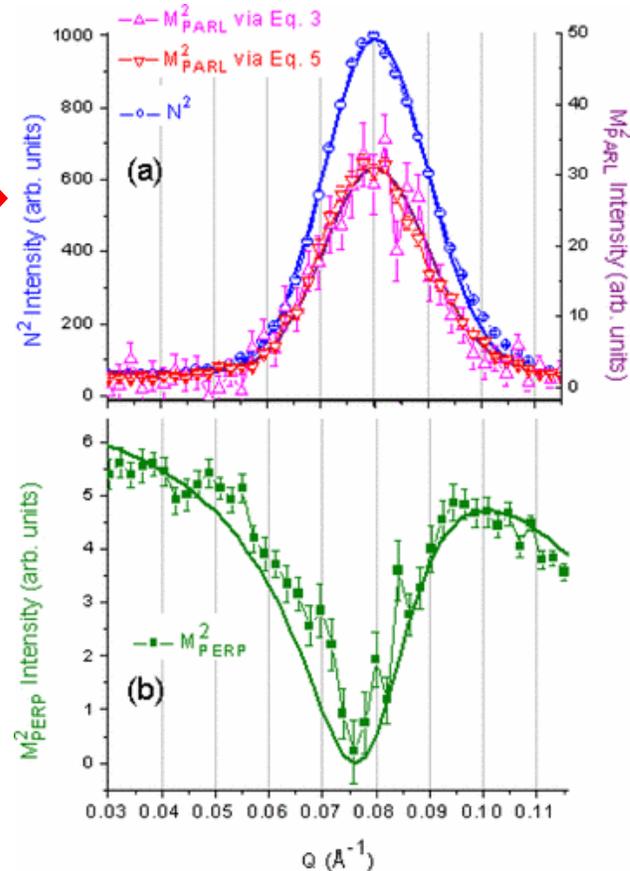
PASANS of 9 nm Fe_3O_4 Nanocrystals in 1.4T, 200K



Non-Spin Flip (- -) Non-Spin Flip (++)



Spin Flip (+ -) and (- +)

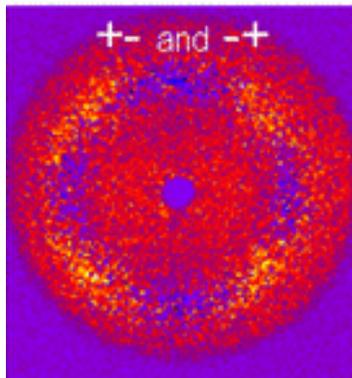
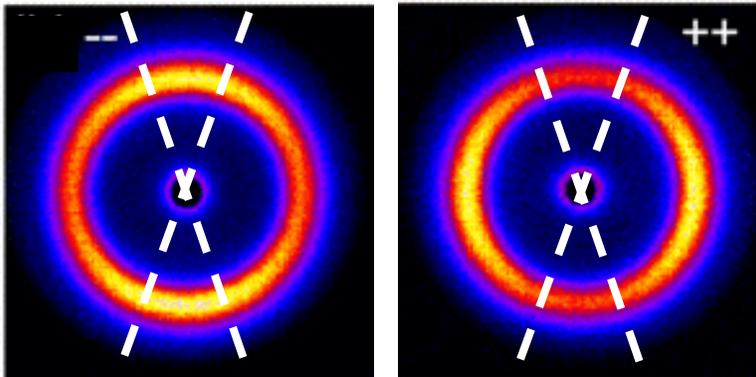


- Addition of (+ +) and (- -) horizontal for N^2
- Peak (ring) confirms long-range FCC order

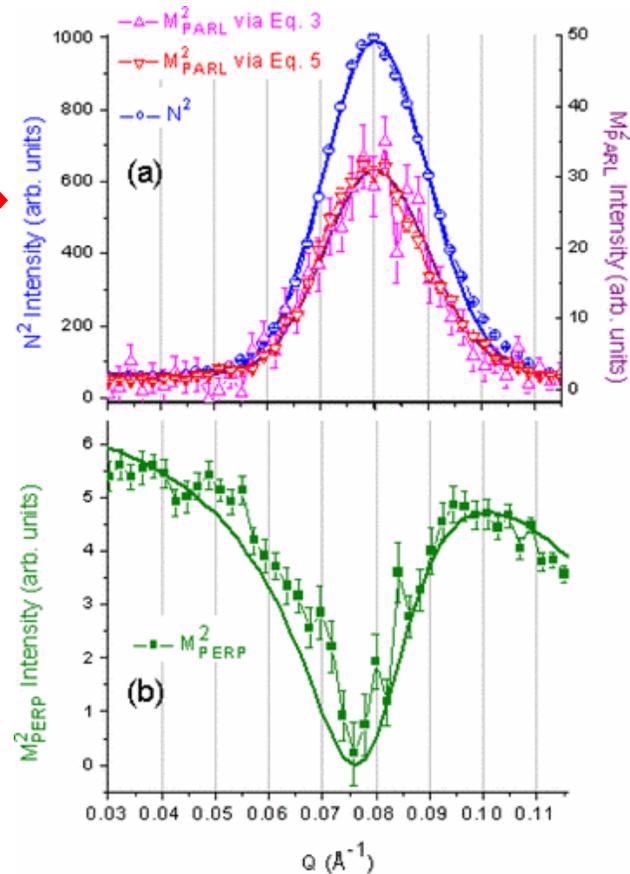
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Spin Flip (+ -) and (- +)

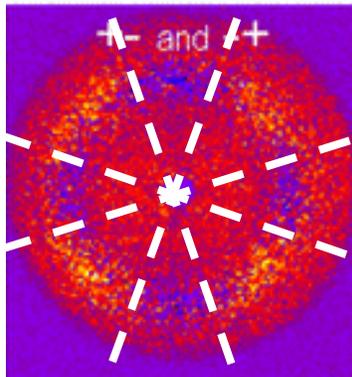
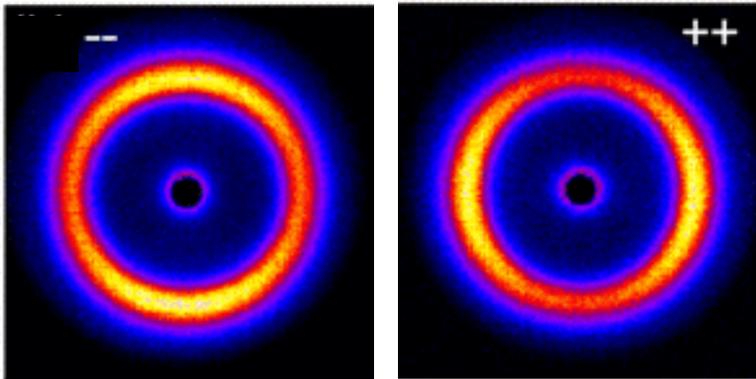


- Addition of (+ +) and (- -) horizontal for N^2
- Peak (ring) confirms long-range FCC order
- Subtraction of (+ +) from (- -) vertical for M^2_{parl}
- Peak confirms long range magnetic order

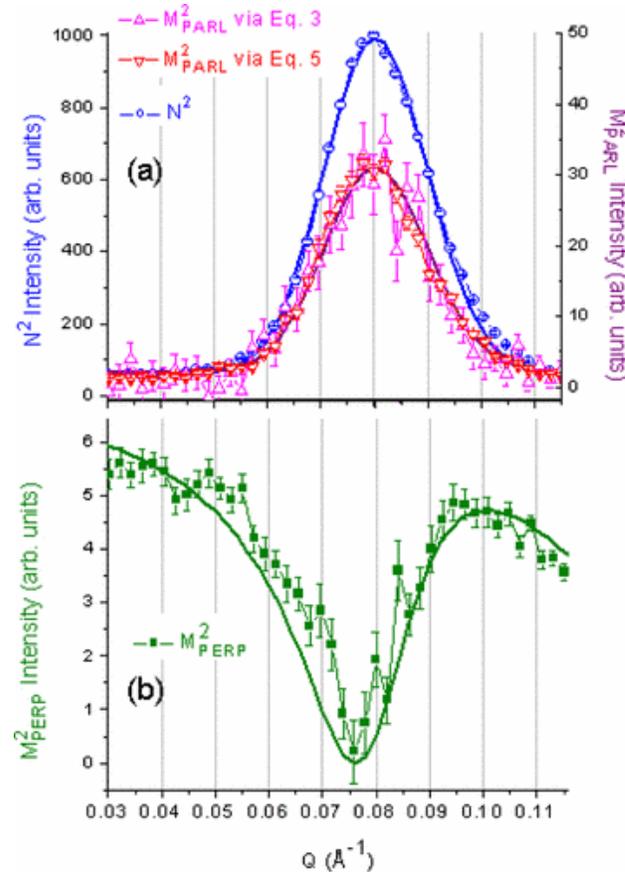
PASANS of 9 nm Fe_3O_4 Nanocrystals in 1.4T, 200K



Non-Spin Flip (- -) Non-Spin Flip (++)



Spin Flip (+ -) and (- +)

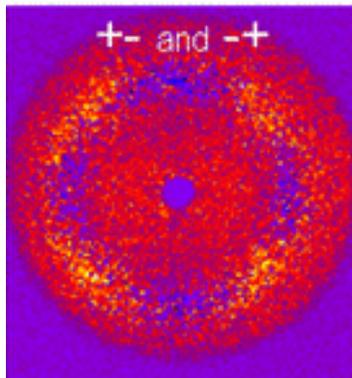
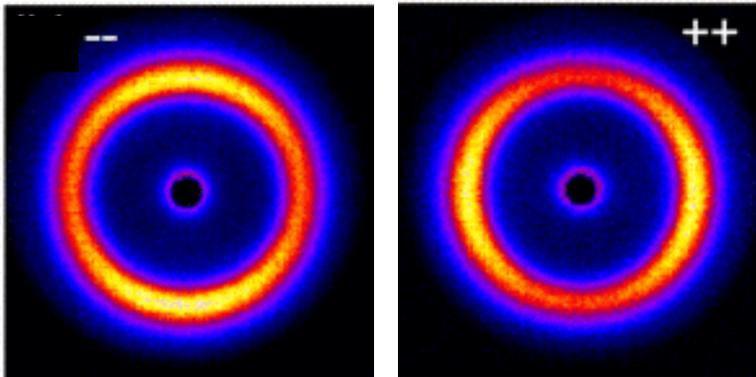


- Addition of (+ +) and (- -) horizontal for N^2
- Peak (ring) confirms long-range FCC order
- Subtraction of (+ +) from (- -) vertical for M^2_{parl}
- Peak confirms long range magnetic order
- Spin flip has dip at peak position
- M^2_{perp} is characteristic of shell scattering

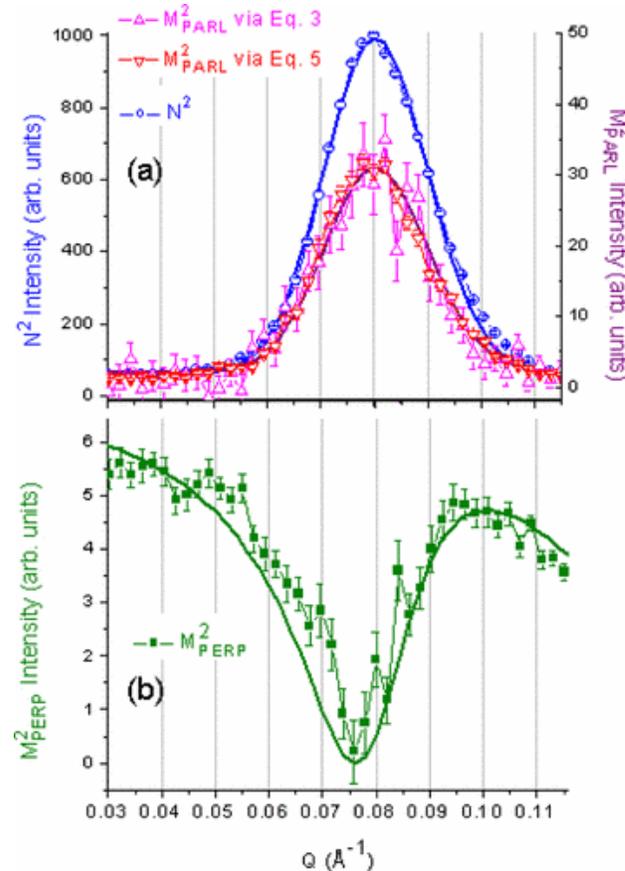
PASANS of 9 nm Fe_3O_4 Nanocrystals in 1.4T, 200K



Non-Spin Flip (- -) Non-Spin Flip (++)

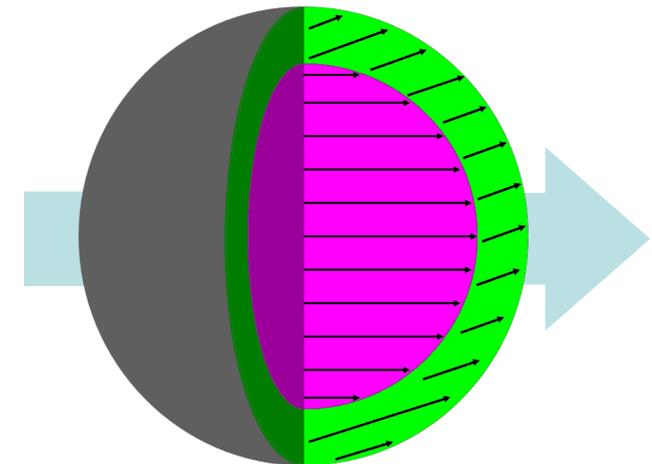


Spin Flip (+ -) and (- +)



Solution:

1 – 2 nm magnetic shell with canted magnetization in high fields despite structural uniformity!
Random canting angle from one nanoparticle to the next.



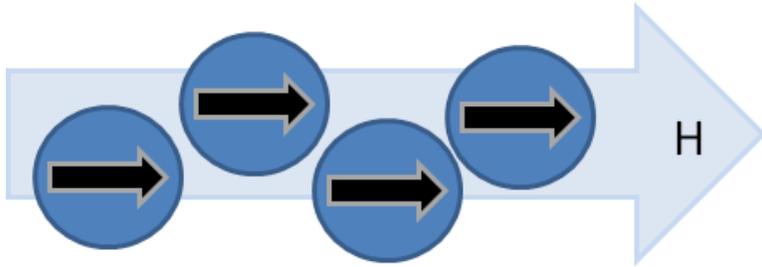
Unexpected! Why?

Competing Energetics in Bulk Fe₃O₄

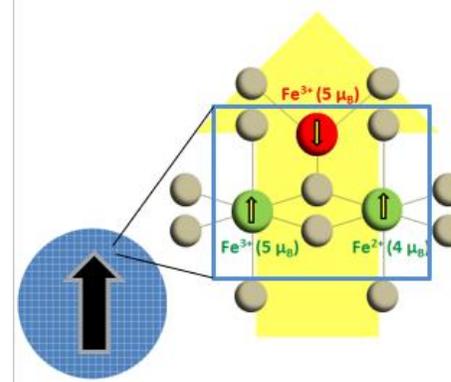


Zeeman (applied field, H) =

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



Exchange coupling $\sim 2 \text{ meV+ / f.u.} \rightarrow$
 $\sim 10 \text{ eV / NP (holds ferrimagnetic alignment)}$

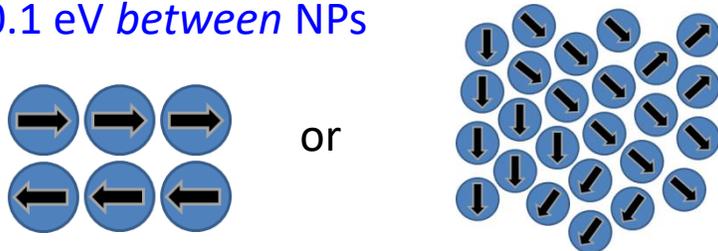


Tetrahedral sites (red) couple ferrimagnetically to the octahedral (green) sites with $\sim 2\text{-}3 \text{ meV}$

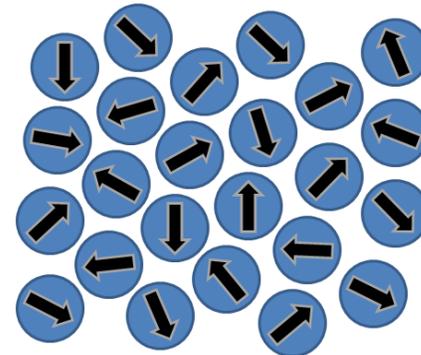
Dipolar coupling =

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

= $\sim 0.1 \text{ eV between NPs}$



Crystalline anisotropy (K_V) at $\sim 4.4 \times 10^4 \text{ J / m}^3 =$
 $\sim 0.1 \text{ eV / NP (orientation along 100 axis)}$



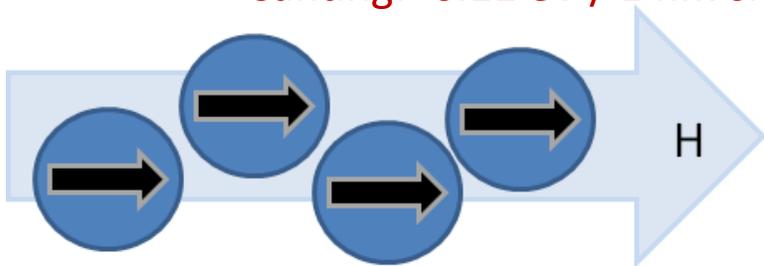
Changes in Energetics with Canted Shell



Zeeman (applied field, H) =

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

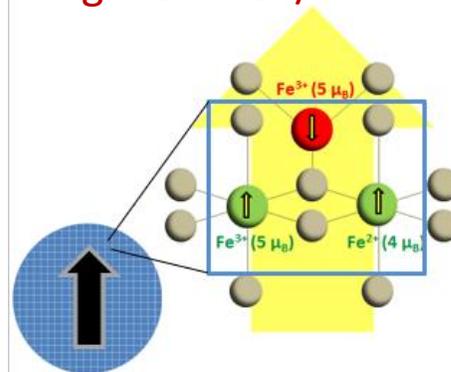
Canting: -0.11 eV / 1 nm shell



Exchange coupling $\sim 2 \text{ meV+ / f.u.} \rightarrow$

$\sim 10 \text{ eV / NP}$ (holds ferrimagnetic alignment)

Canting: +0.21 eV/1 nm shell (at surface, cost higher at center)

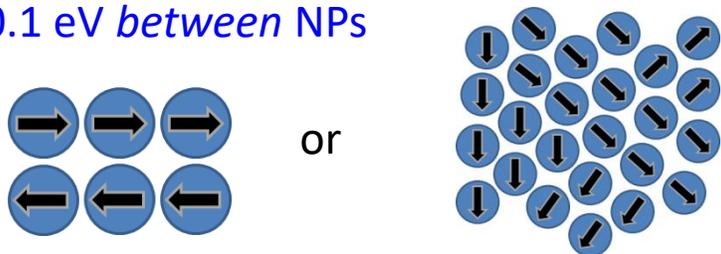


Tetrahedral sites (red) might cant w.r.t. to their ferrimagnetic alignment with octahedral (green) sites

Dipolar coupling =

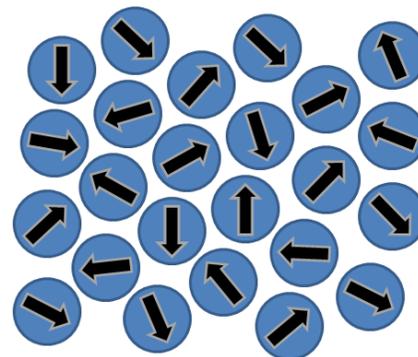
$$\sum_i \sum_{j \neq i} \frac{\mu_o (\vec{m}_i \cdot \vec{m}_j - 3(\vec{m}_i \cdot \vec{r}_{ij})(\vec{m}_j \cdot \vec{r}_{ij}))}{4\pi |\vec{r}_{ij}|^3}$$

= $\sim 0.1 \text{ eV}$ between NPs



Crystalline anisotropy (K_V) at [1 to 3] $\times 4.4 \times 10^4 \text{ J / m}^3$

= $\sim 0.3 \text{ eV / NP}$ (orientation along 100 axis)



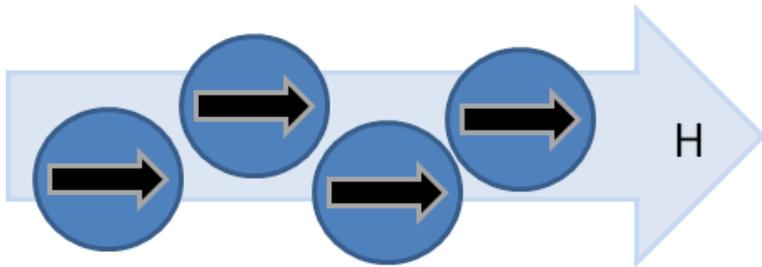
Canting: -0.15 eV / 1 nm shell

Higher Anisotropy in CoFe_2O_4 Nanoparticles

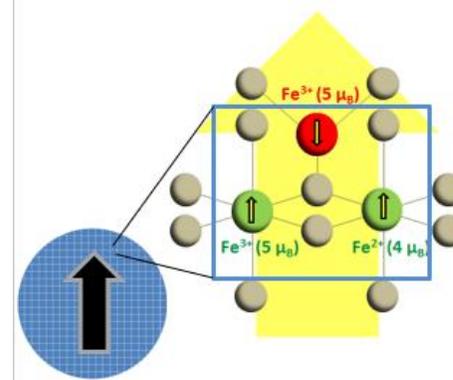


Zeeman (applied field, H) =

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



Exchange coupling $\sim 2 \text{ meV+ / f.u.} \rightarrow$
 $\sim 10 \text{ eV / NP (holds ferrimagnetic alignment)}$

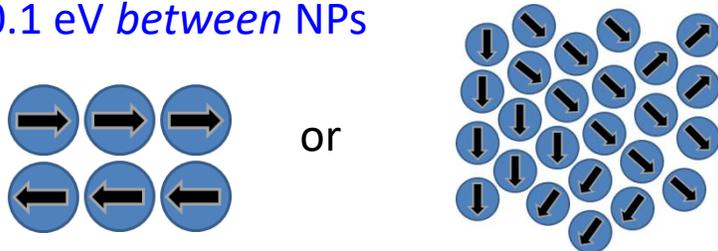


Tetrahedral sites (red) couple ferrimagnetically to the octahedral (green) sites with $\sim 2\text{-}3 \text{ meV}$

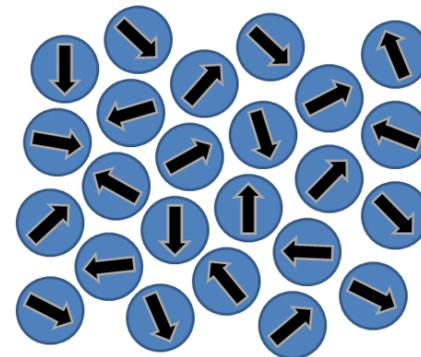
Dipolar coupling =

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

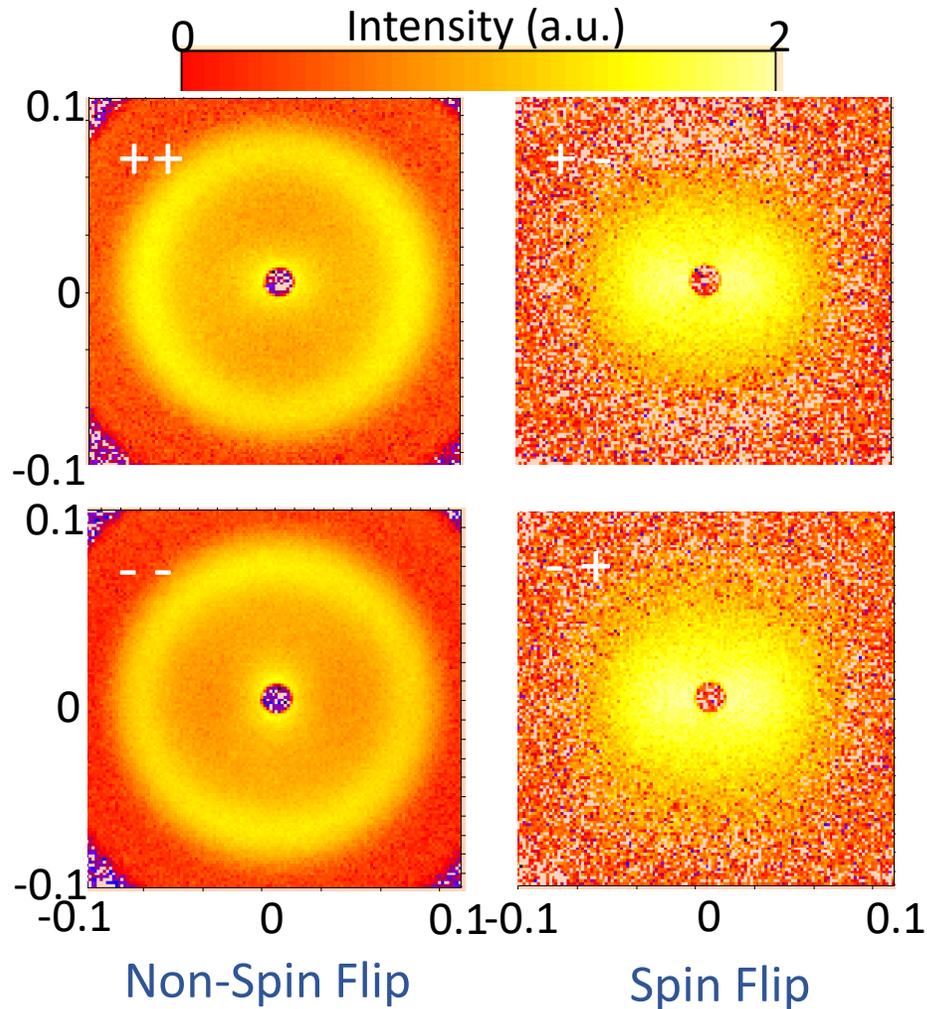
= $\sim 0.1 \text{ eV between NPs}$



Crystalline anisotropy (K_V) increases 18 x's compared to $\text{Fe}_3\text{O}_4 = \sim 5.4 \text{ eV / NP}$ (orientation along 100 axis)



PASANS of 10 nm CoFe_2O_3 Nanocrystals in 1.2T, 10K



Questions:

- Is the magnetic structure long range or does it break into domains?
- Is the magnetization uniform within each nanoparticle?
- Is there a shell? Other unusual magnetic structure?
- What is the magnitude of the magnetization?
- What is the orientation of the magnetization relative to the field?
- How does higher anisotropy change the magnetic structure?

Goals:

- Model PASANS data at 1.2T, 10K to characterize structure, magnetization parallel to the field and magnetization perpendicular to the field
- Combine results to form a physical “picture” of the nanocrystal system

Extra Credit:

- Model PASANS data of nanoparticles at other conditions (10 K @ 0 T, 100 K @ 0 T and 1.4 T, 200 K @ 0 T, and 300 K @ 1.4 T)