

# Magnetic Structure of Cobalt Ferrite Nanoparticle Arrays



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## Particle moment canting in $\text{CoFe}_2\text{O}_4$ nanoparticles

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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  $\text{CoFe}_2\text{O}_4$  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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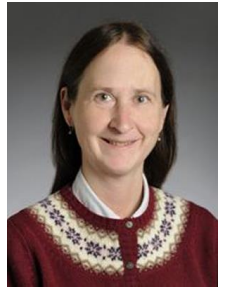
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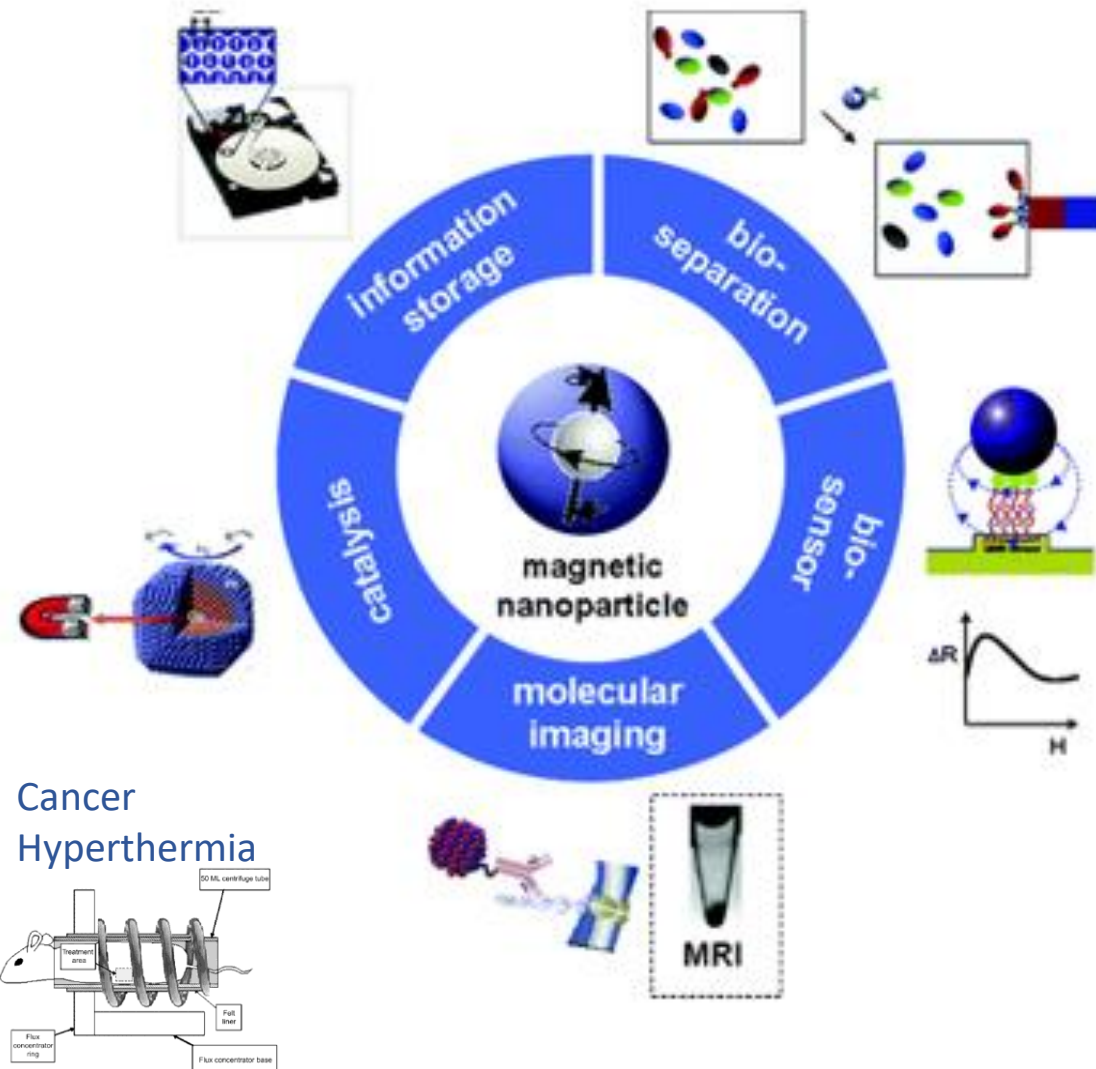


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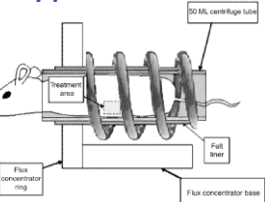
# Magnetic Nanoparticle Applications



## 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.

Cancer  
Hyperthermia

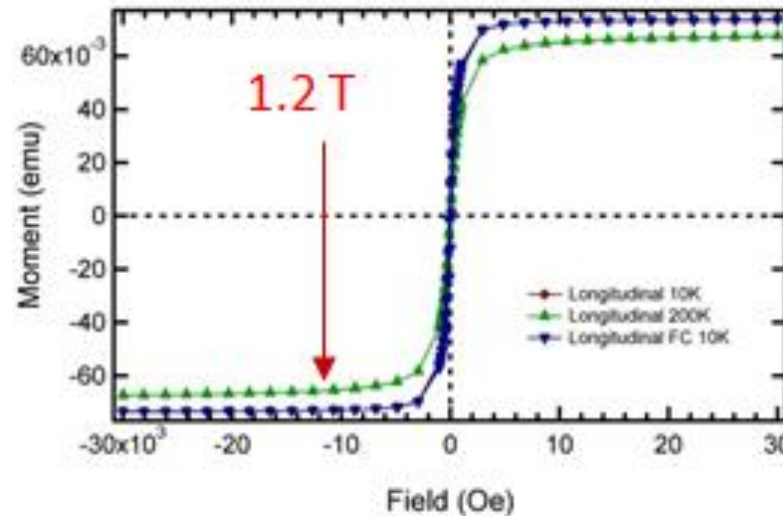
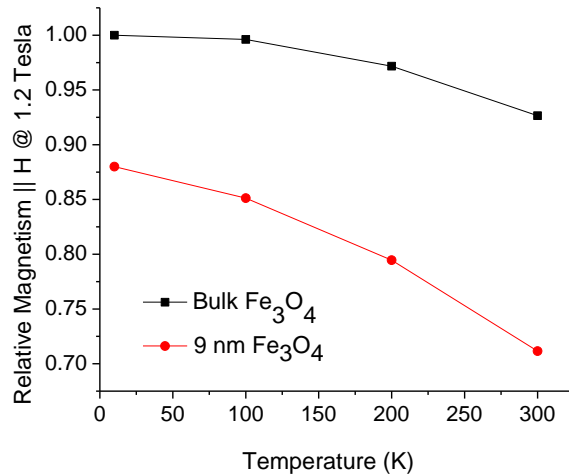
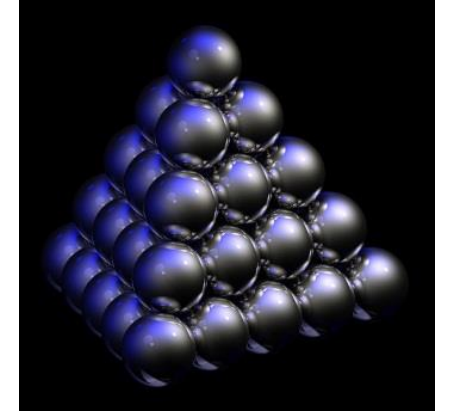
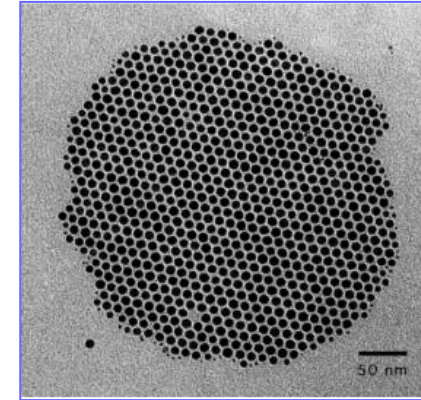


# Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> Nanoparticles



## System:

- Biocompatible 9 – 10 nm diameter Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> nanoparticles
- Single-crystal and uniform (10% polydispersity)
- Self assembled into closed-packed 3D nanocrystals
- Nanocrystal is ordered on micron scale<sup>1</sup>.



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

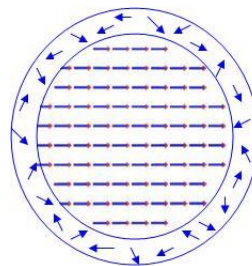
Why is the magnetization reduced?

# Possible Origin of Reduced Magnetization

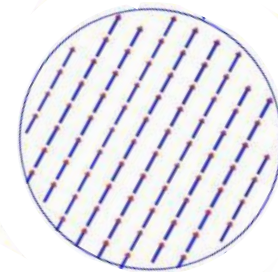


- Simplistic explanation is surface disorder<sup>1</sup>

*Disordered -  
“Dead Layer”*

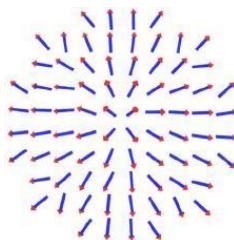


or uniform canting

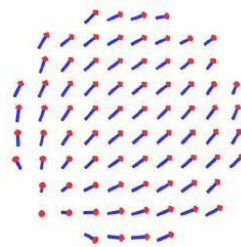


- However, high surface/crystalline anisotropy<sup>2</sup> could result in many model variations.

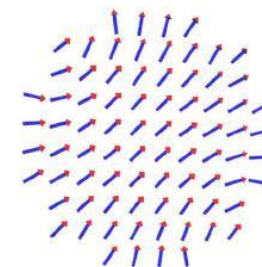
*Hedgehog*



*Artichoke*



*Throttled*



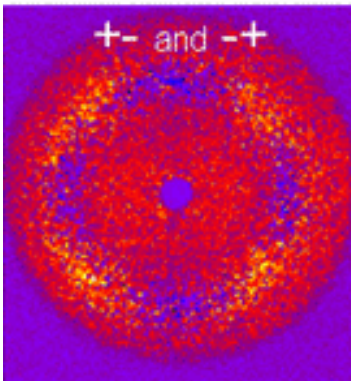
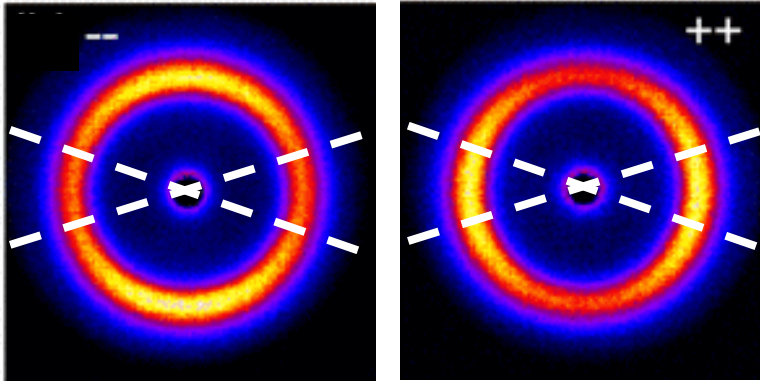
Polarization-analyzed SANS (PASANS) can distinguish between models.



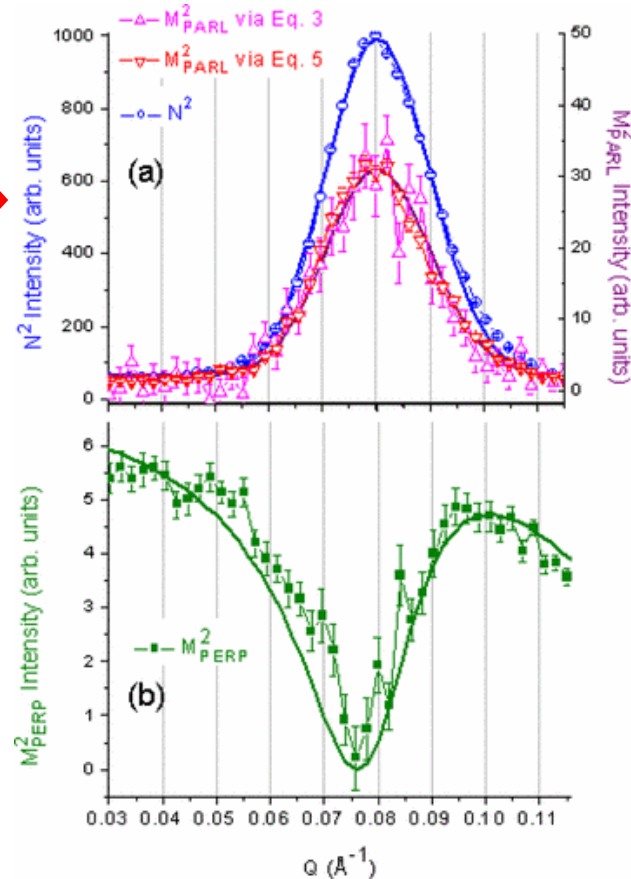
# PASANS of 9 nm $\text{Fe}_3\text{O}_4$ Nanocrystals in 1.4T, 200K



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



Spin Flip (+ -) and (- +)

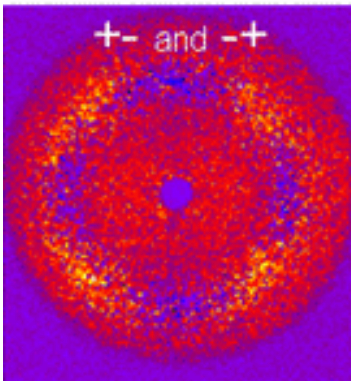
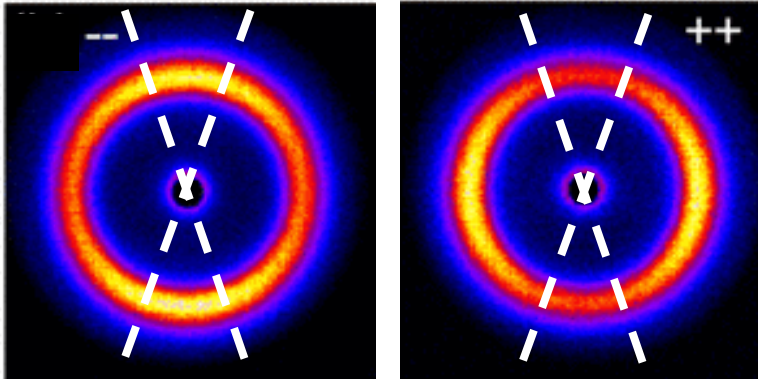


- Addition of (+ +) and (- -) horizontal for  $N^2$
- Peak (ring) confirms long-range FCC order

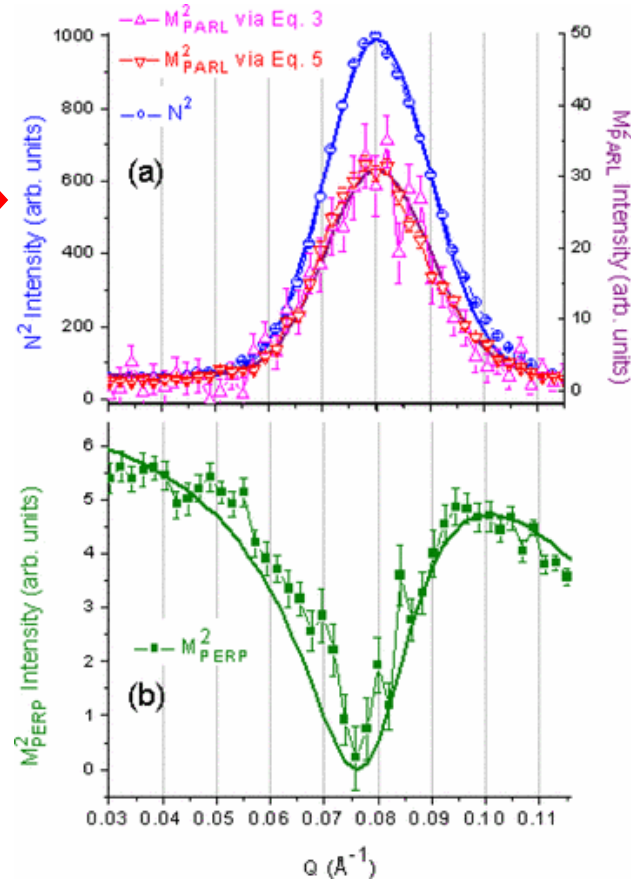
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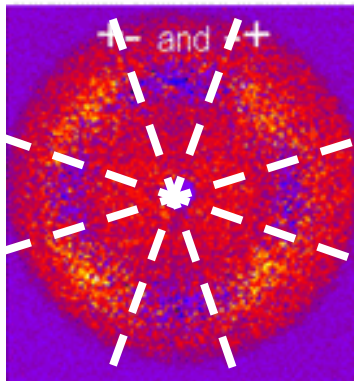
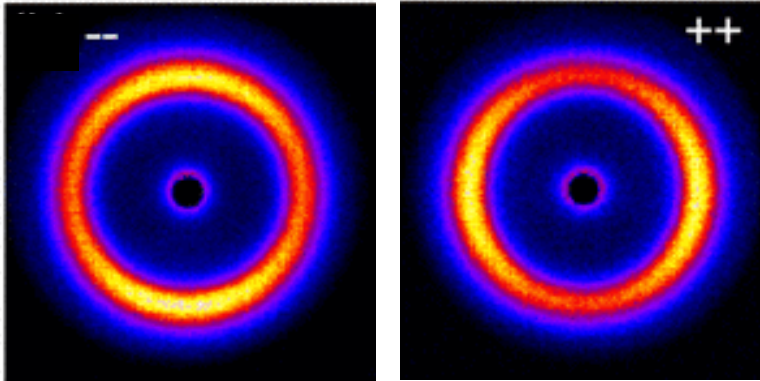


- Addition of (+ +) and (- -) horizontal for  $N^2$
- Peak (ring) confirms long-range FCC order
- Subtraction of (+ +) from (- -) vertical for  $M^2_{\text{parl}}$
- Peak confirms long range magnetic order

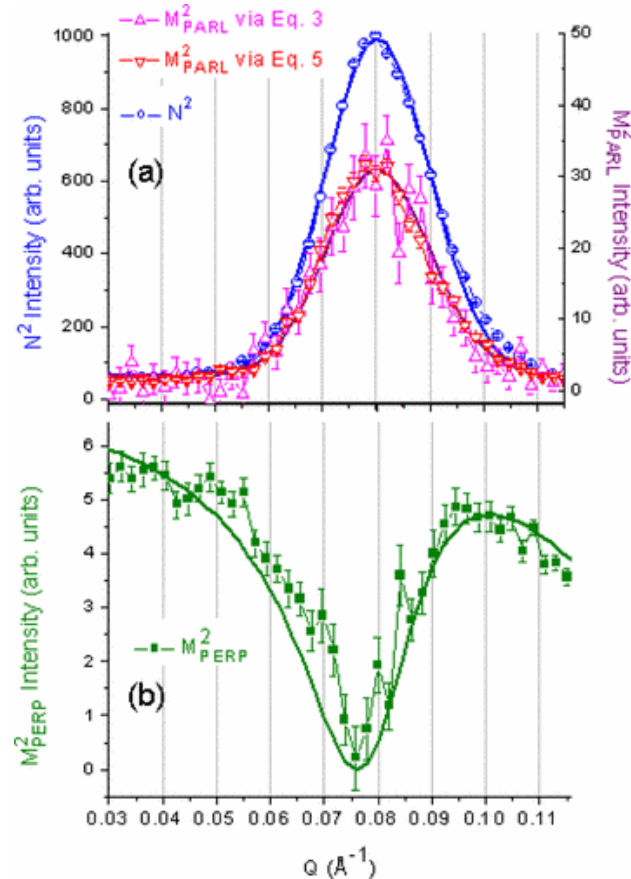
# PASANS of 9 nm $\text{Fe}_3\text{O}_4$ Nanocrystals in 1.4T, 200K



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



Spin Flip (+ -) and (- +)



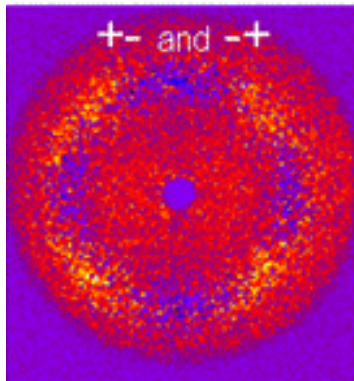
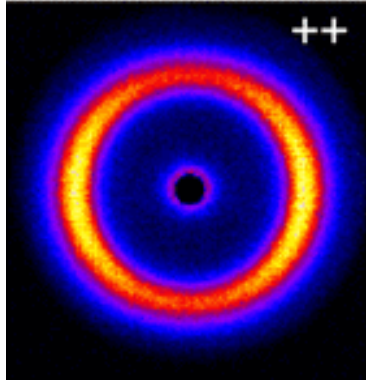
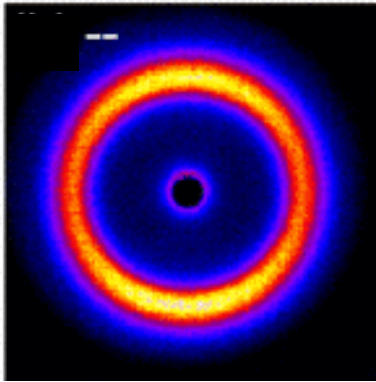
- Addition of (+ +) and (- -) horizontal for  $N^2$
- Peak (ring) confirms long-range FCC order
- Subtraction of (+ +) from (- -) vertical for  $M^2_{\text{parl}}$
- Peak confirms long range magnetic order
- Spin flip has dip at peak position
- $M^2_{\text{perp}}$  is characteristic of shell scattering



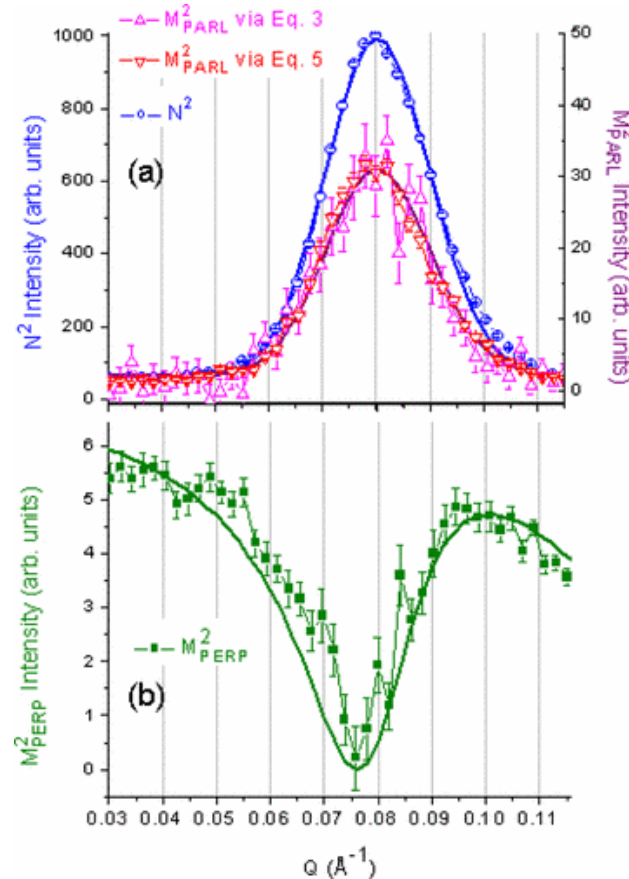
# PASANS of 9 nm $\text{Fe}_3\text{O}_4$ Nanocrystals in 1.4T, 200K



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

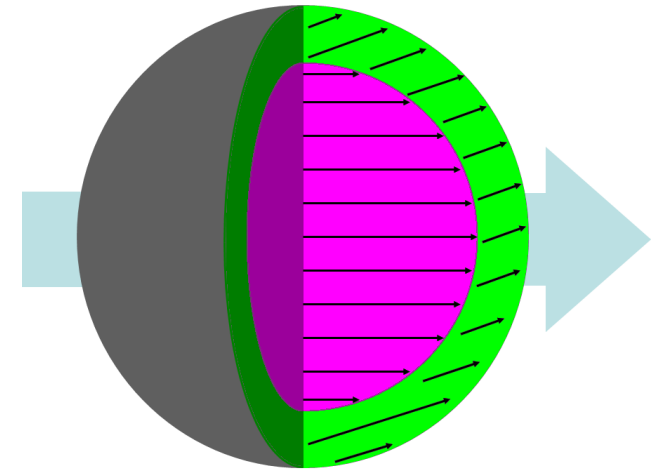


Spin Flip (+ -) and (- +)



## 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?

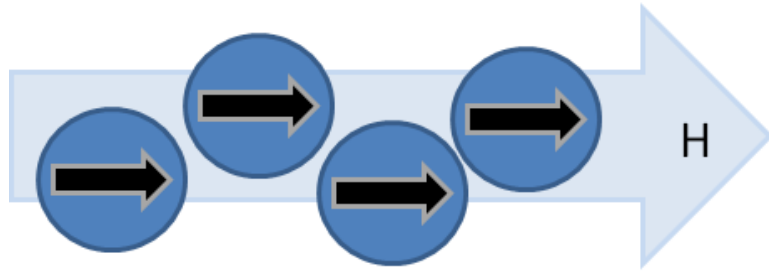


# Competing Energetics in Bulk Fe<sub>3</sub>O<sub>4</sub>

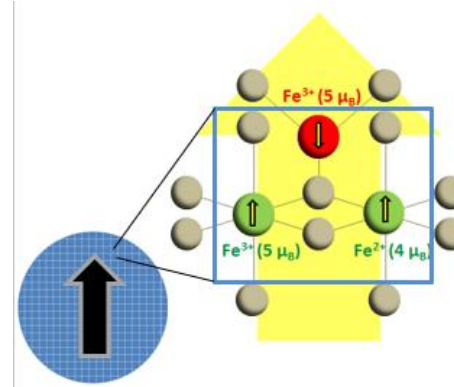


Zeeman (applied field, H) =

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



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

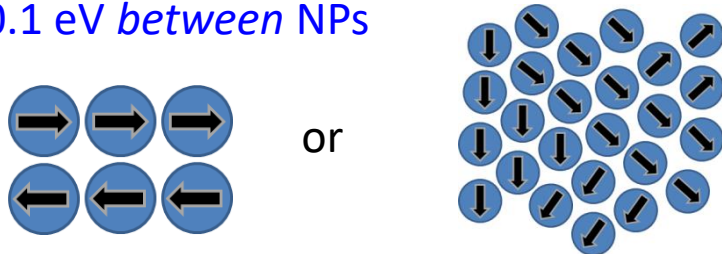


Tetrahedral sites (red) couple ferrimagnetically to the octahedral (green) sites with  $\sim 2\text{-}3 \text{ meV}$

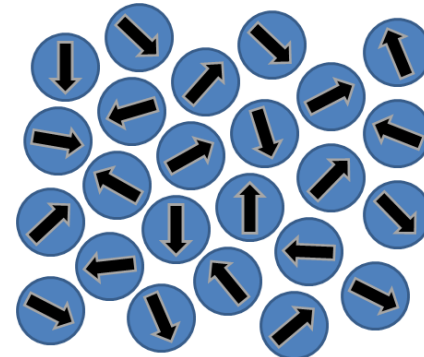
Dipolar coupling =

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

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



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



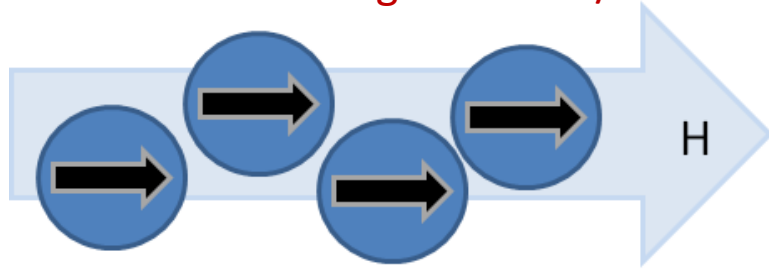
# Changes in Energetics with Canted Shell



Zeeman (applied field, H) =

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

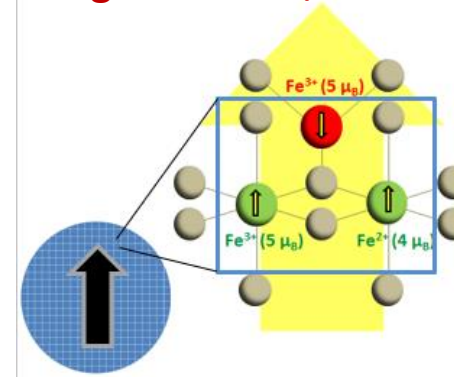
Canting: -0.11 eV / 1 nm shell



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)

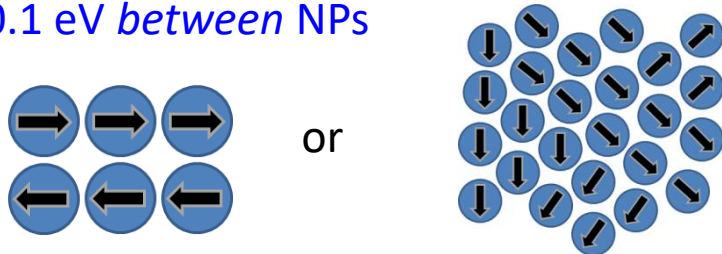


Tetrahedral sites (red) might cant w.r.t. to their ferrimagnetic alignment with octahedral (green) sites

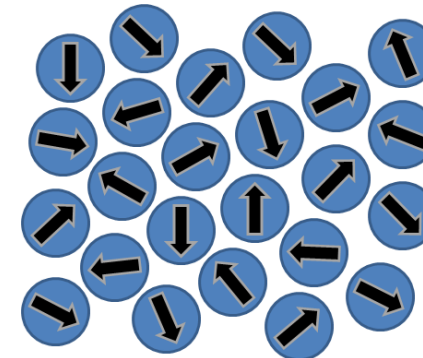
Dipolar coupling =

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

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



Crystalline anisotropy ( $K_V$ ) at  $[1 \text{ to } 3] \times 4.4 \times 10^4 \text{ J / m}^3$   
=  $\sim 0.3 \text{ eV / NP}$  (orientation along 100 axis)



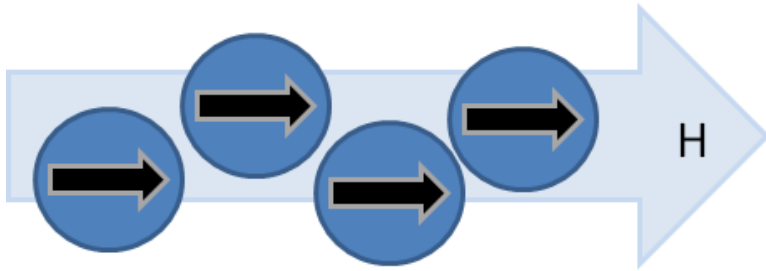
Canting: -0.15 eV / 1 nm shell

# Higher Anisotropy in $\text{CoFe}_2\text{O}_4$ Nanoparticles

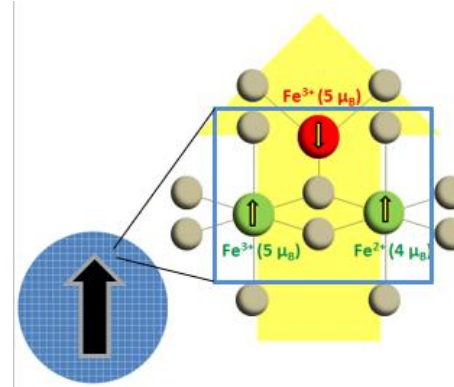


Zeeman (applied field, H) =

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



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

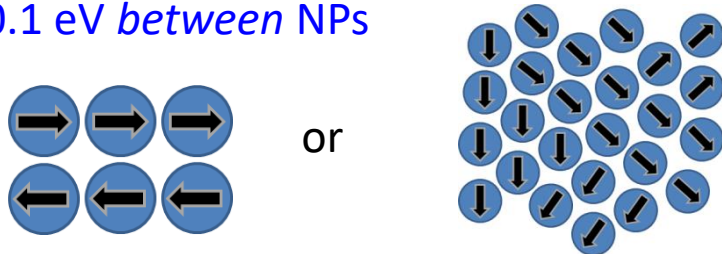


Tetrahedral sites (red) couple ferrimagnetically to the octahedral (green) sites with  $\sim 2\text{-}3 \text{ meV}$

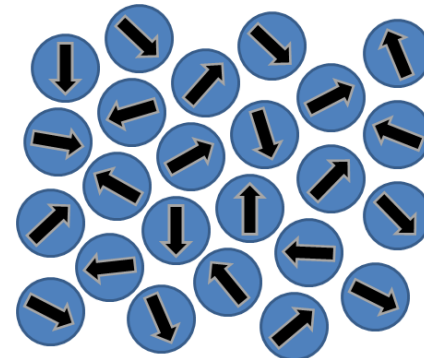
Dipolar coupling =

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

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

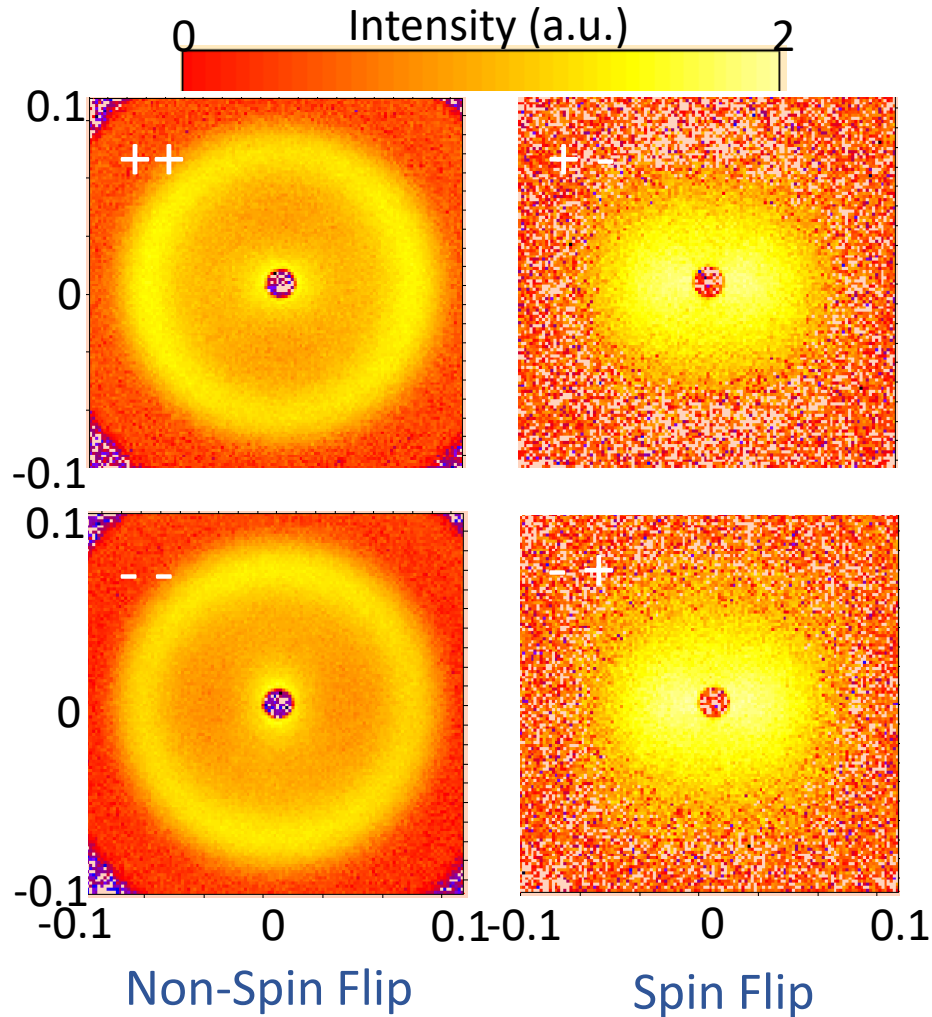


Crystalline anisotropy ( $K_V$ ) increases 18 x's compared to  $\text{Fe}_3\text{O}_4$  =  $\sim 5.4 \text{ eV / NP}$  (orientation along 100 axis)





# PASANS of 10 nm $\text{CoFe}_2\text{O}_3$ 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)