

Magnetic Structure of Cobalt Ferrite Nanoparticle Arrays



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PHYSICAL REVIEW B **90**, 180405(R) (2014)

Particle moment canting in CoFe_2O_4 nanoparticles

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(Received 10 September 2014; revised manuscript received 3 November 2014; published 19 November 2014)

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.

DOI: [10.1103/PhysRevB.90.180405](https://doi.org/10.1103/PhysRevB.90.180405)

PACS number(s): 75.25.-j, 75.75.-c



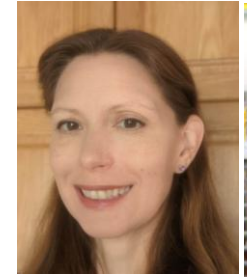
Ryan Booth



Sam Oberdick



Sara Majetich

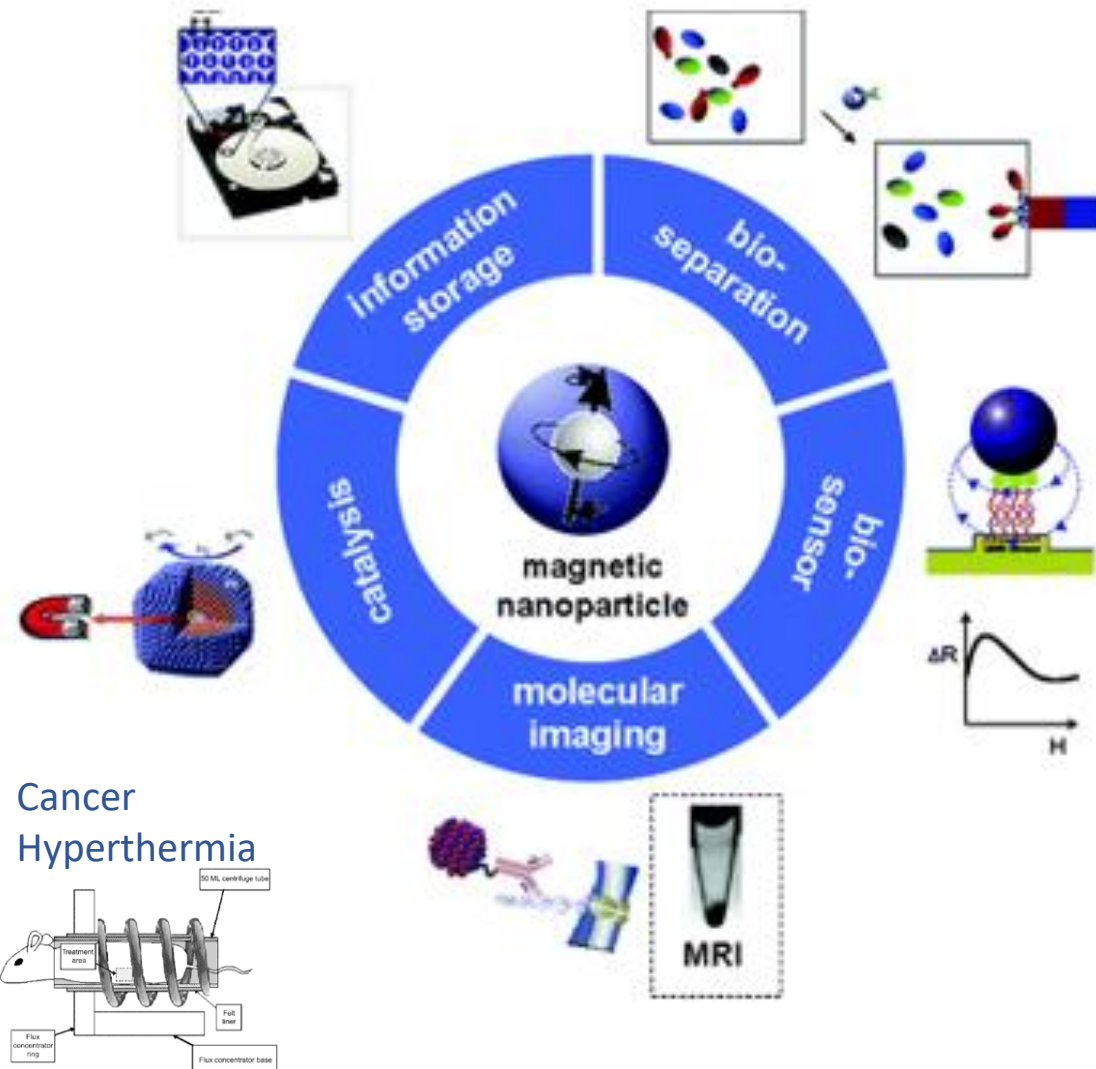


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Julie Borchers

Magnetic Nanoparticle Applications



Motivation:

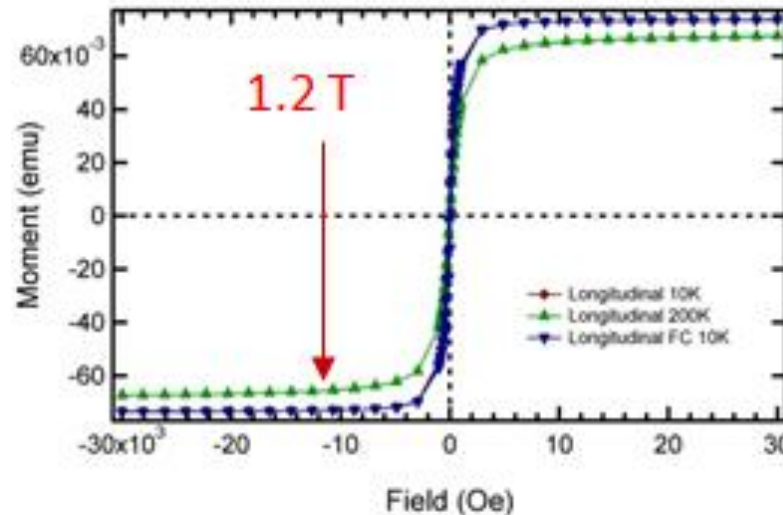
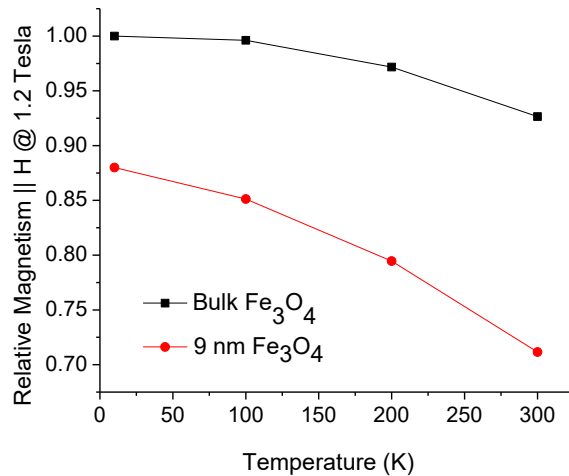
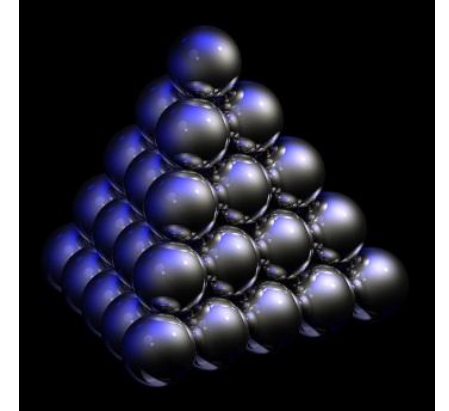
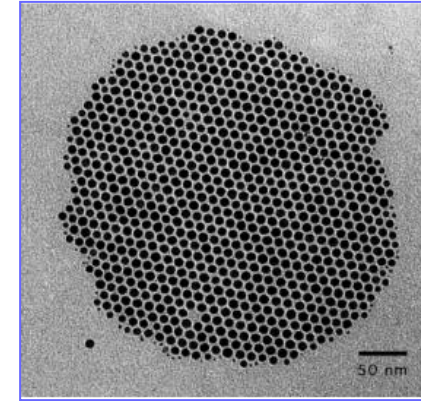
- Large quantities of uniform nanoparticles can be produced due to advancements in chemical synthesis procedures.
- Magnetic nanoparticles are under development for a wide range of applications.
- Performance is very sensitive to nanoparticle composition, size, surface defects, interparticle interactions,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

Spinel $M\text{Fe}_2\text{O}_4$ $M=(\text{Fe}, \text{Co}, \text{Mn})$ Nanoparticles



System:

- Biocompatible 7 – 10 nm diameter CoFe_2O_4 , Fe_3O_4 , MnFe_2O_4 , and $\text{MnFe}_2\text{O}_4/\text{Fe}_3\text{O}_4$ nanoparticles
- Single-crystal and uniform (10-20% polydispersity)
- Self assembled into closed-packed 3D nanocrystals
- Nanocrystal is ordered on micron scale¹.



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

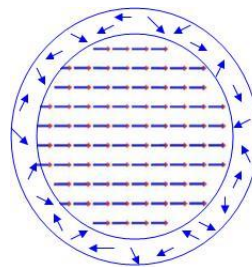
Why is the magnetization reduced? What is the spin arrangement?

Possible Origin of Reduced Magnetization

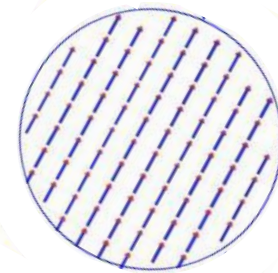


- Simplistic explanation is surface disorder¹

*Disordered -
“Dead Layer”*

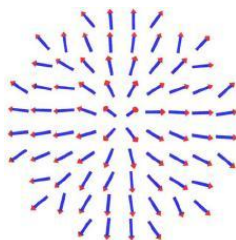


or uniform canting

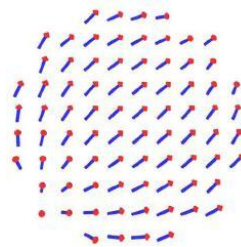


- However, high surface/crystalline anisotropy² could result in many model variations.

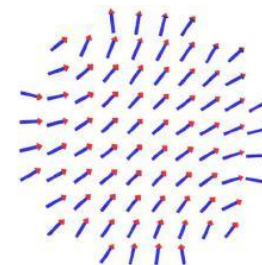
Hedgehog



Artichoke



Throttled

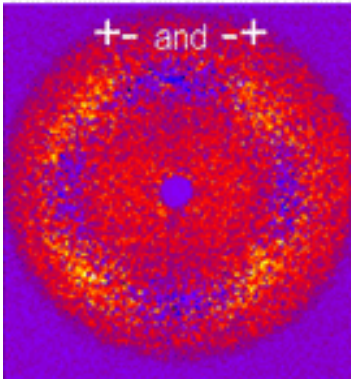
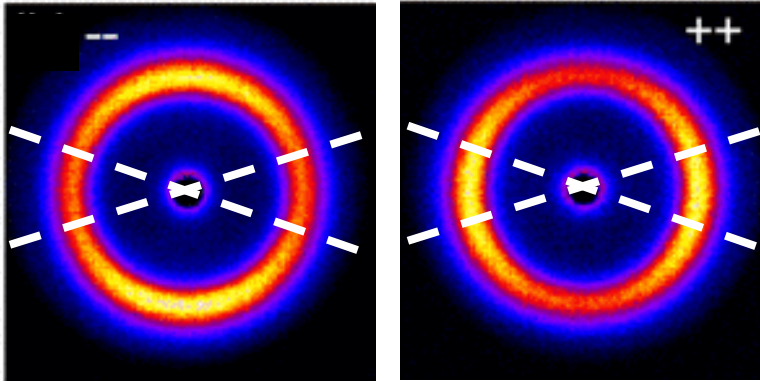


Polarization-analyzed SANS (PASANS) can distinguish between models.

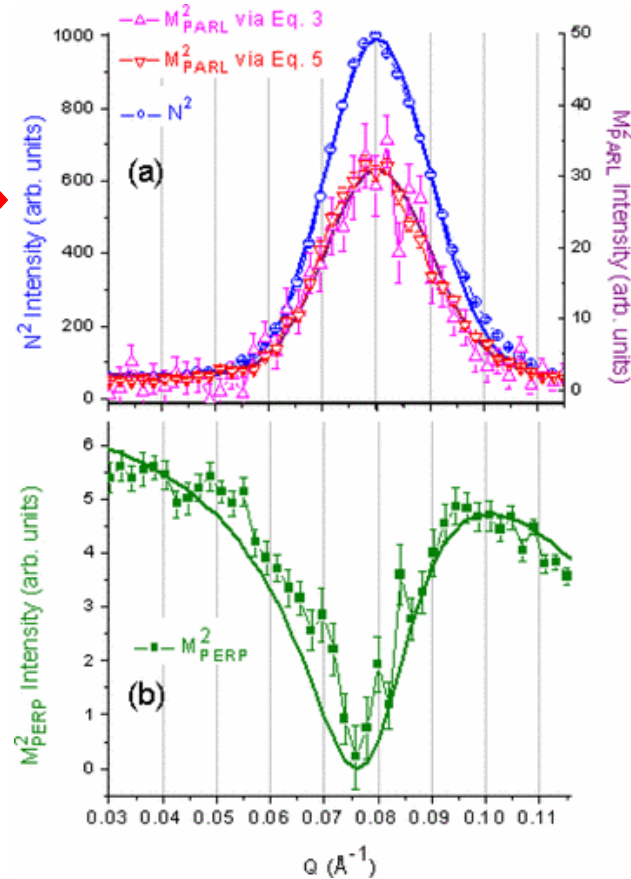
PASANS of 9 nm Fe_3O_4 Nanocrystals in 1.4T, 200K



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



Spin Flip (+ -) and (- +)

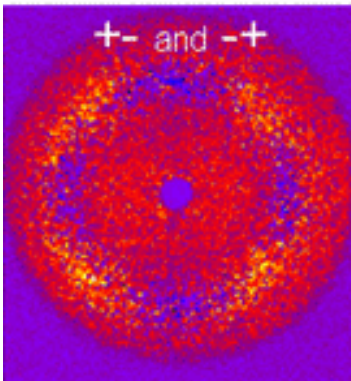
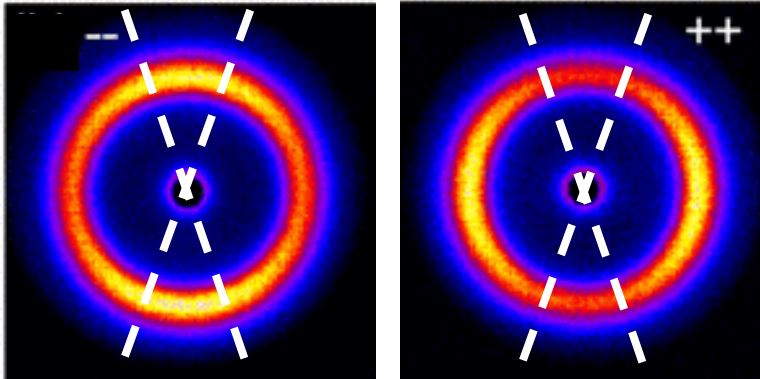


- Addition of (+ +) and (- -) horizontal for N^2
- Peak (ring) confirms long-range FCC order

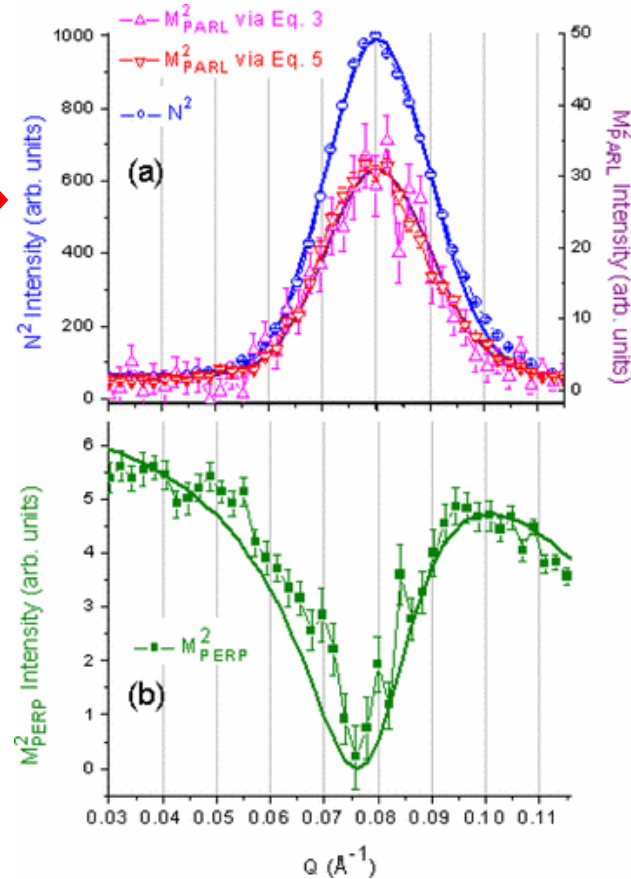
PASANS of 9 nm Fe_3O_4 Nanocrystals in 1.4T, 200K



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Spin Flip (+ -) and (- +)

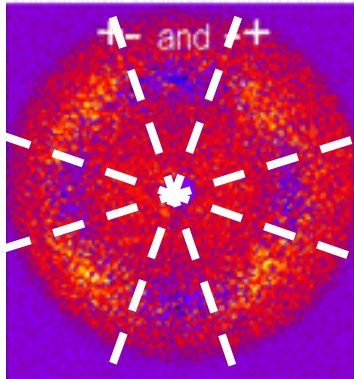
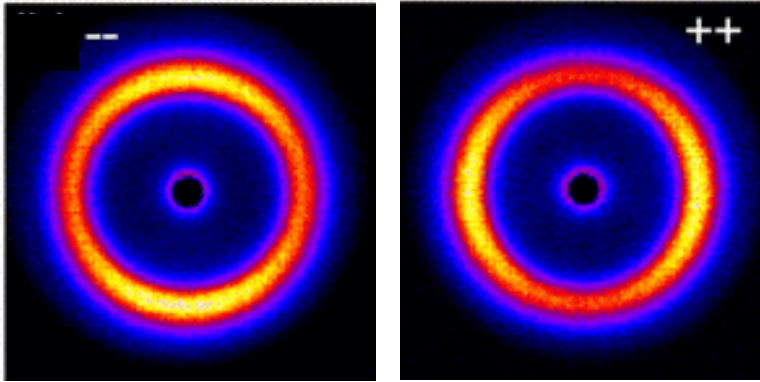


- Addition of (+ +) and (- -) horizontal for N^2
- Peak (ring) confirms long-range FCC order
- Subtraction of (+ +) from (- -) vertical for M^2_{parl}
- Peak confirms long range magnetic order

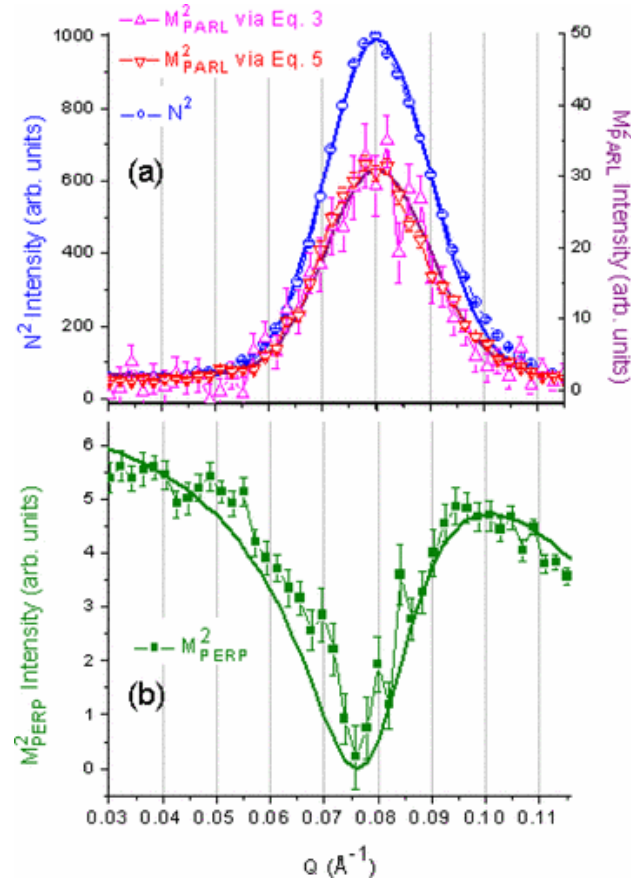
PASANS of 9 nm Fe_3O_4 Nanocrystals in 1.4T, 200K



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



Spin Flip (+ -) and (- +)

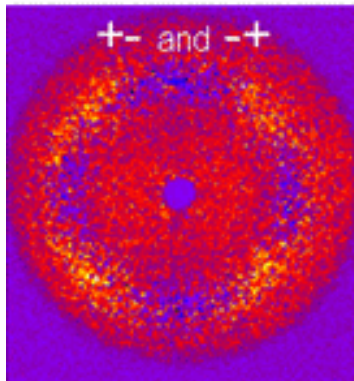
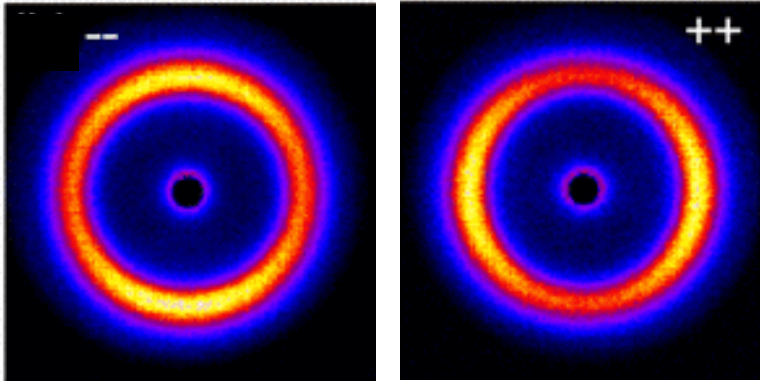


- Addition of (+ +) and (- -) horizontal for N^2
- Peak (ring) confirms long-range FCC order
- Subtraction of (+ +) from (- -) vertical for M^2_{parl}
- Peak confirms long range magnetic order
- Spin flip has dip at peak position
- M^2_{perp} is characteristic of shell scattering

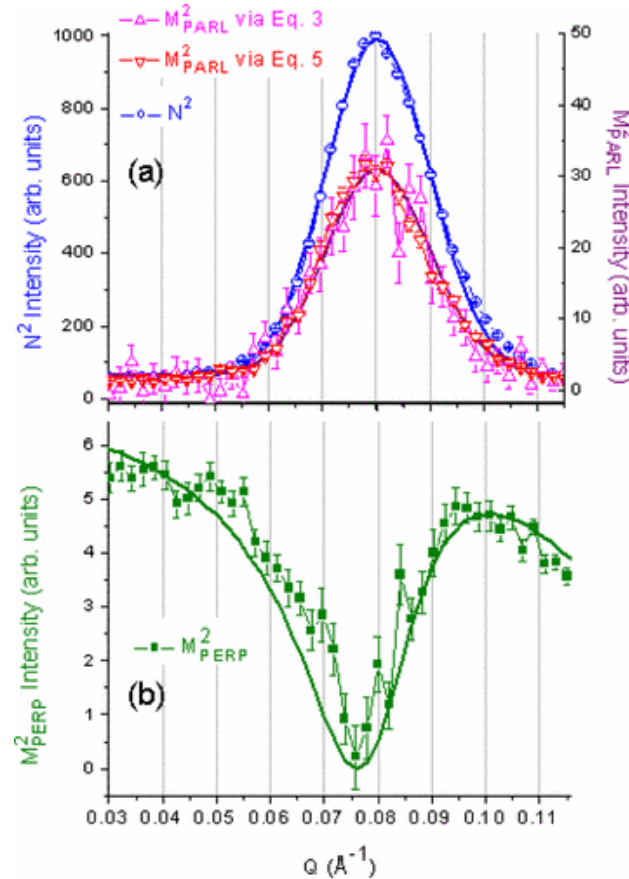
PASANS of 9 nm Fe_3O_4 Nanocrystals in 1.4T, 200K



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

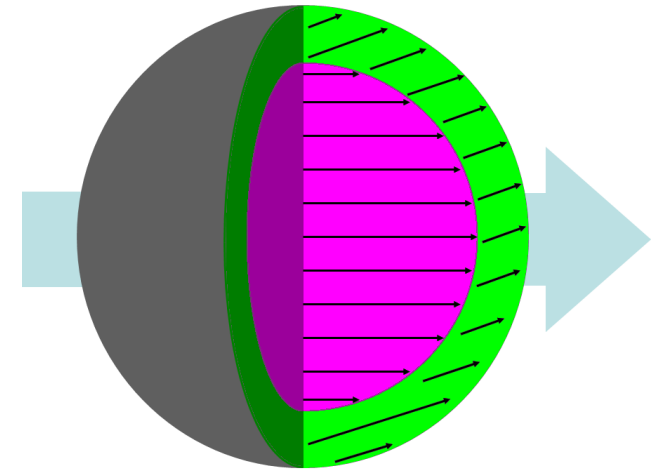


Spin Flip (+ -) and (- +)



Solution:

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



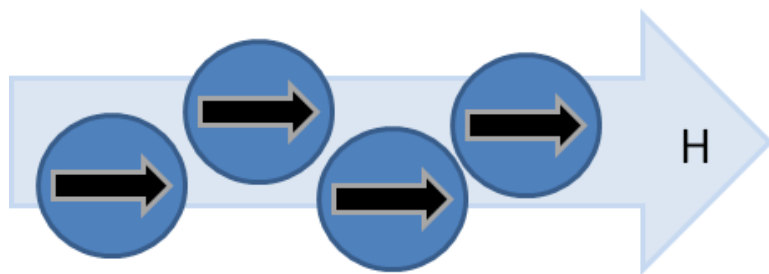
Unexpected! Why?

Competing Energetics in Fe₃O₄ from Bulk Behavior



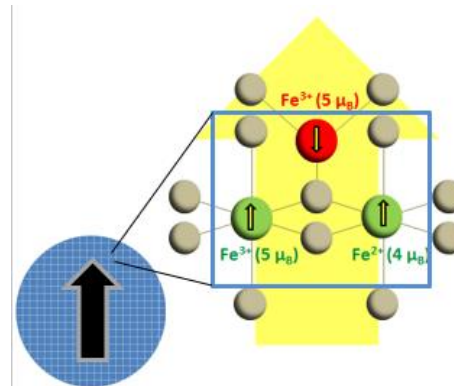
Zeeman (applied field, H) =

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



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

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

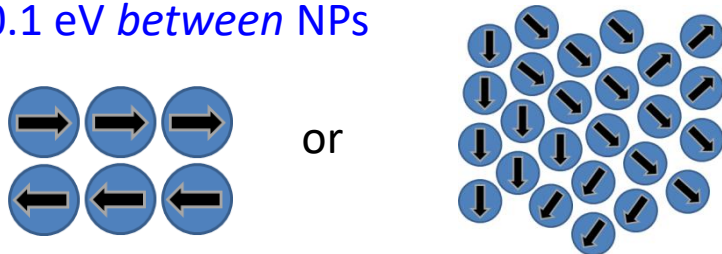


Tetrahedral sites (red) couple ferrimagnetically to the octahedral (green) sites with $\sim 2\text{-}3 \text{ meV}$

Dipolar coupling =

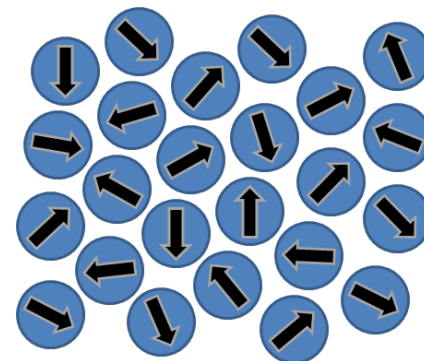
$$\sum_i \sum_{j \neq i} \frac{\mu_o (\vec{m}_i \cdot \vec{m}_j - 3(\vec{m}_i \cdot \vec{r}_{ij})(\vec{m}_j \cdot \vec{r}_{ij}))}{4\pi |\vec{r}_{ij}|^3}$$

= $\sim 0.1 \text{ eV}$ 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)



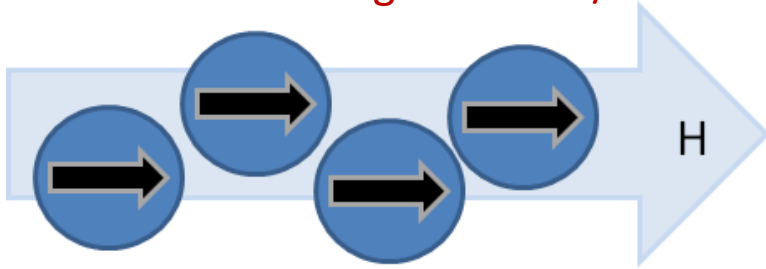
Changes in Fe₃O₄ Energetics with Canted Shell



Zeeman (applied field, H) =

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

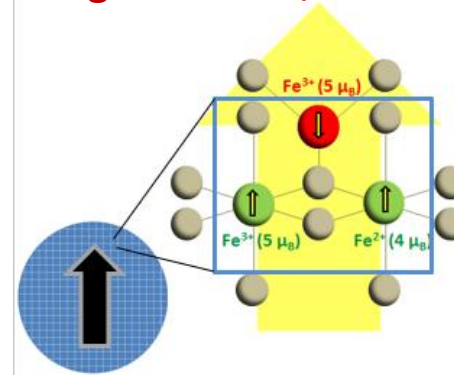
Canting: -0.11 eV / 1 nm shell



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)

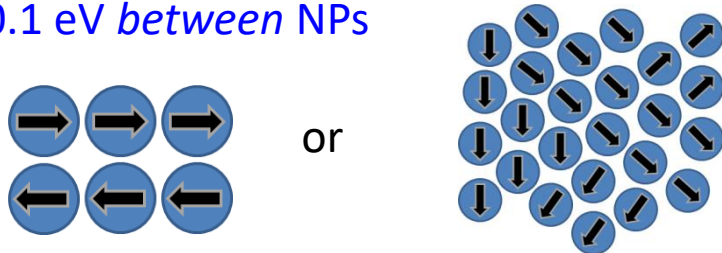


Tetrahedral sites (red) might cant w.r.t. to their ferrimagnetic alignment with octahedral (green) sites

Dipolar coupling =

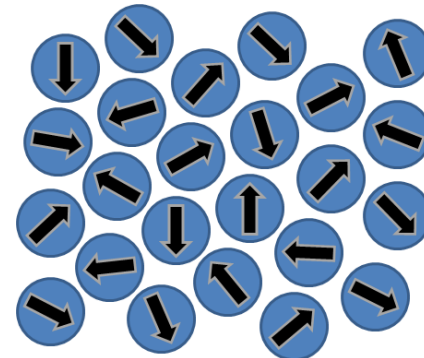
$$\sum_i \sum_{j \neq i} \frac{\mu_o (\vec{m}_i \cdot \vec{m}_j - 3(\vec{m}_i \cdot \vec{r}_{ij})(\vec{m}_j \cdot \vec{r}_{ij}))}{4\pi |\vec{r}_{ij}|^3}$$

= $\sim 0.1 \text{ eV}$ 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)



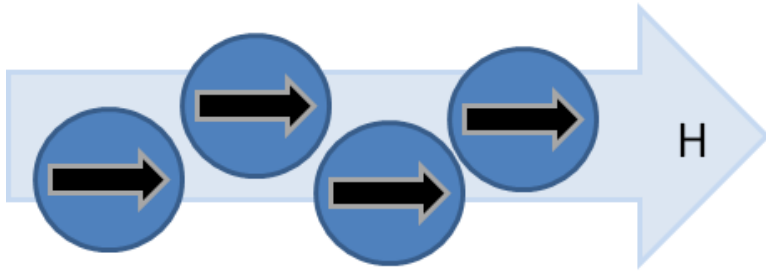
Canting: -0.15 eV / 1 nm shell

Higher Anisotropy in CoFe_2O_4 Nanoparticles

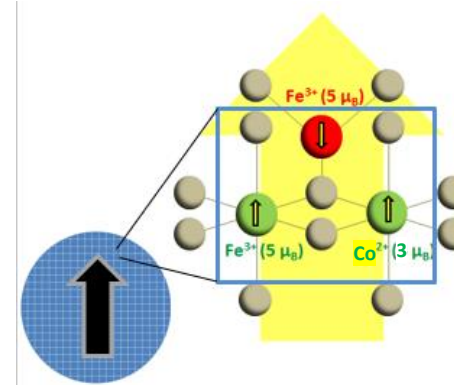


Zeeman (applied field, H) =

$$- \sum_{i \text{ within NP}} \vec{m}_i \cdot \vec{H} = \sim 1.4 \text{ eV / NP (at 1.2 T)}$$



Exchange coupling $\sim 1.8 \text{ meV+ / f.u.} \rightarrow$
 $\sim 9 \text{ eV / NP (holds ferrimagnetic alignment)}$

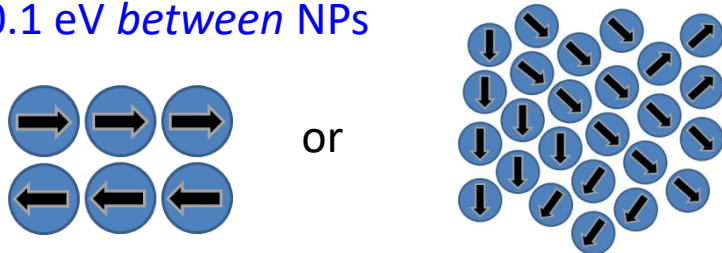


Tetrahedral sites
 (red) couple
 ferrimagnetically to
 the octahedral
 (green) sites with
 $\sim 1.5\text{-}2.5 \text{ meV}$

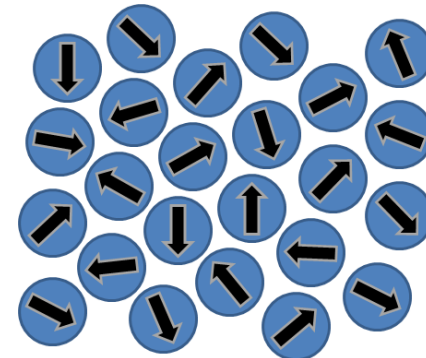
Dipolar coupling =

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

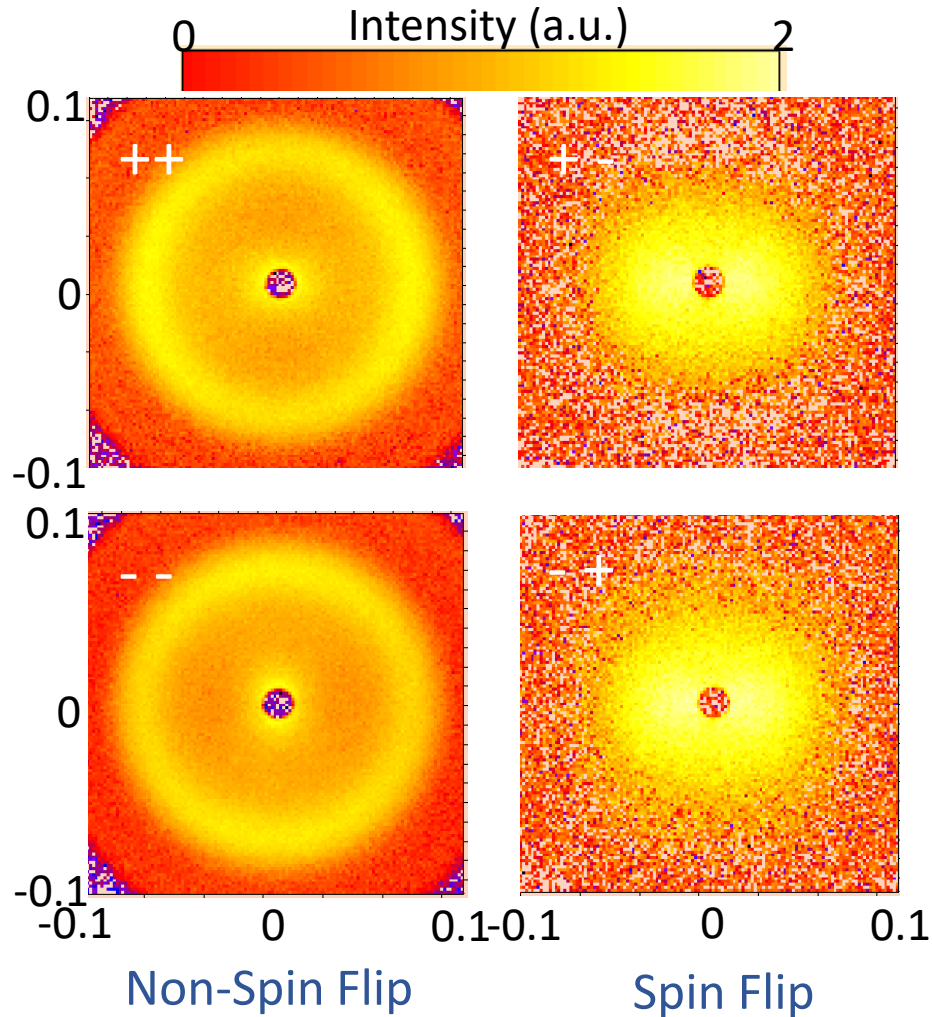
= $\sim 0.1 \text{ eV between NPs}$



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_4 Nanocrystals in 1.2T, (FC) 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?

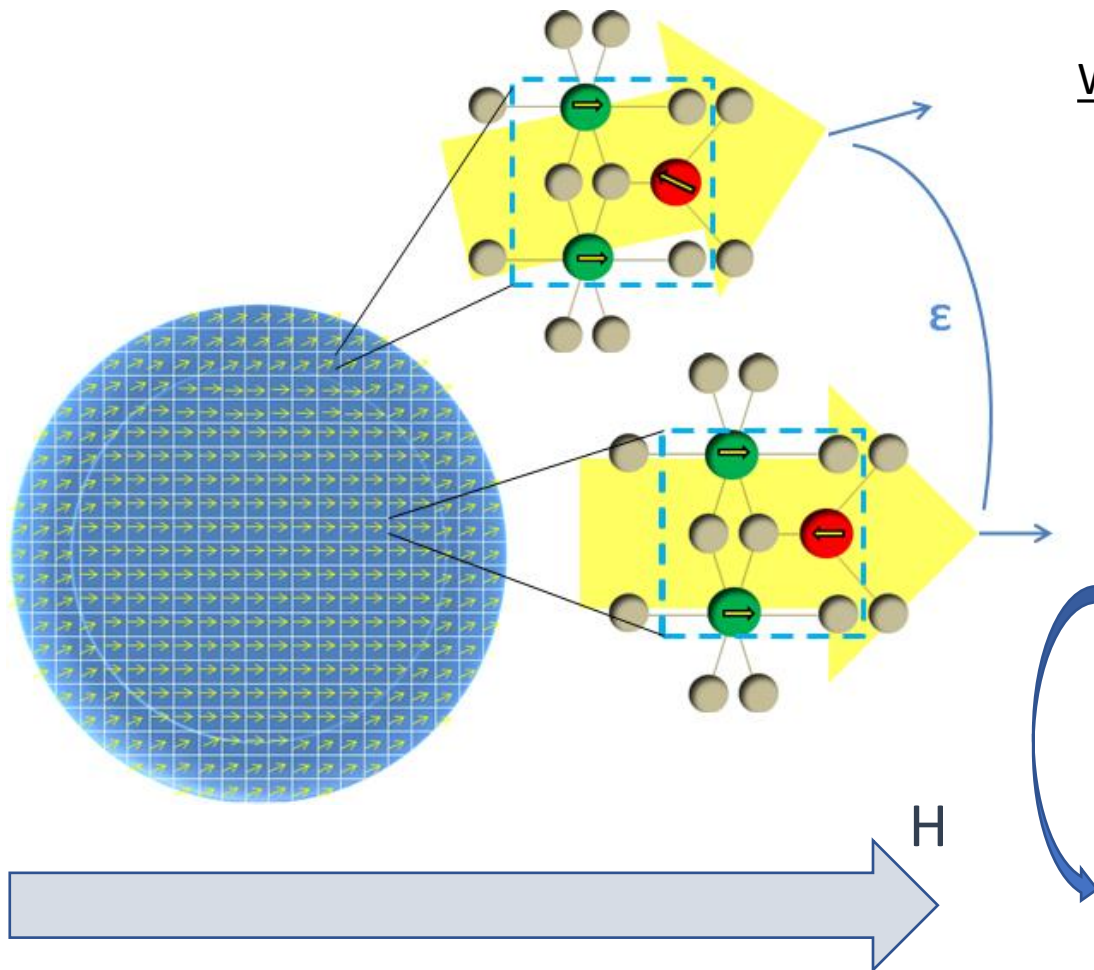
Goals:

- Model PASANS data at 1.2T, FC 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

(for the presentation):

- Model PASANS data of nanoparticles at other conditions (10 K @ 1.2 T (ZFC), 200 K @ 1.2 T, 300 K @ 1.2 T, 300 K @ 0.005 T)

Extra slides: more on PASANS of other ferrites



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 thick¹!

The surface magnetism is preserved²

Average $\epsilon = \sim 30^\circ$

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

New J. Phys. 20 (2018) 123020

<https://doi.org/10.1088/1367-2630/aaef17>

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PAPER

Spin waves across three-dimensional, close-packed nanoparticles

Kathryn L Krycka¹, James J Rhyne¹, Samuel D Oberdick², Ahmed M Abdelgawad³, Julie A Borchers¹, Yumi Ijiri⁴, Sara A Majetich³ and Jeffrey W Lynn¹

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

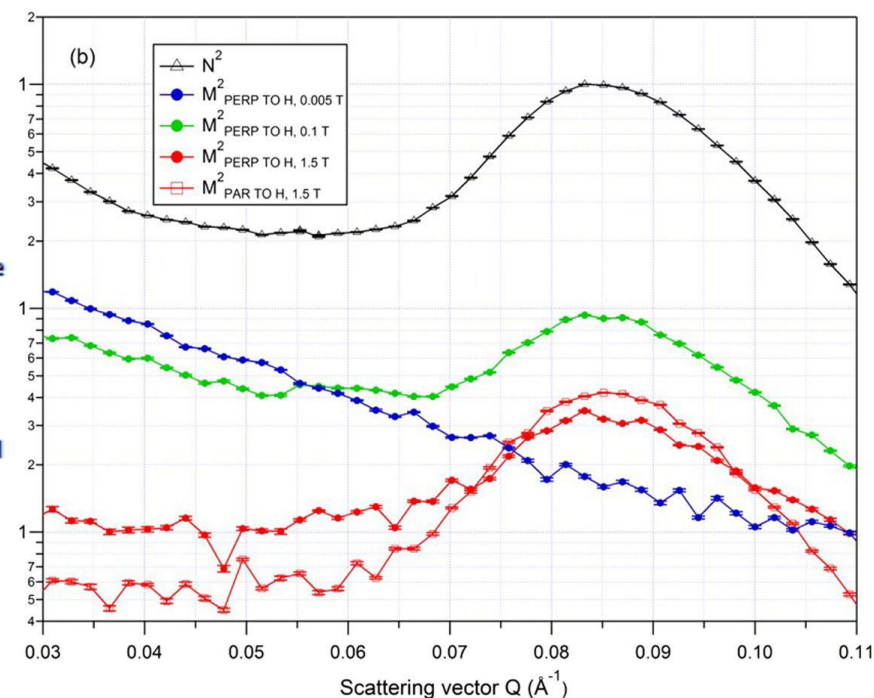
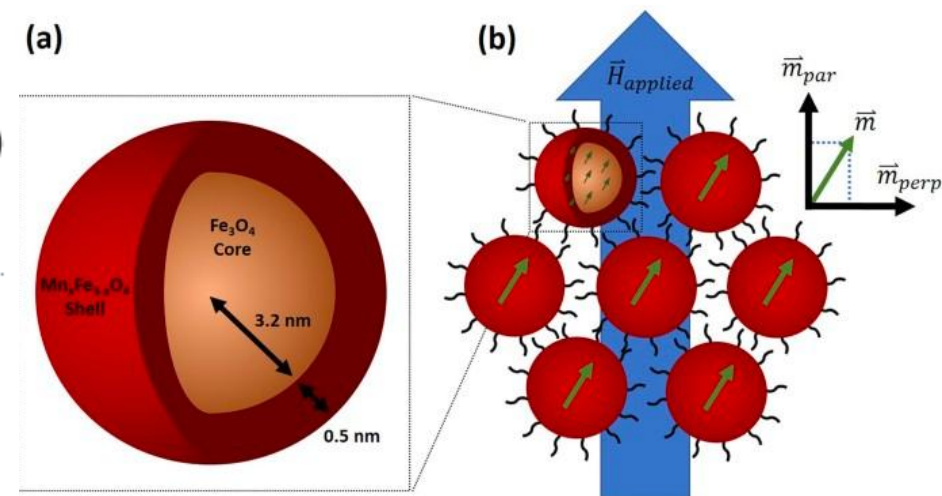
OPEN

Spin canting across core/shell $\text{Fe}_3\text{O}_4/\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ nanoparticles

Samuel D. Oberdick^{1,2}, Ahmed Abdelgawad^{1,3}, Carlos Moya¹, Samaneh Mesbahi-Vasey⁴, Demie Kepaptsoglou^{5,6,7}, Vlado K. Lazarov⁶, Richard F. L. Evans⁶, Daniel Meilak⁶, Elizabeth Skoropata⁸, Johan van Lierop⁸, Ian Hunt-Isaak⁹, Hillary Pan⁹, Yumi Ijiri⁹, Kathryn L. Krycka¹⁰, Julie A. Borchers¹⁰ & Sara A. Majetich¹

Magnetic nanoparticles (MNPs) have become increasingly important in biomedical applications like magnetic imaging and hyperthermia based cancer treatment. Understanding their magnetic spin configurations is important for optimizing these applications. The measured magnetization of MNPs can be significantly lower than bulk counterparts, often due to canted spins. This has previously been presumed to be a surface effect, where reduced exchange allows spins closest to the nanoparticle surface to deviate locally from collinear structures. We demonstrate that intraparticle effects can induce spin canting throughout a MNP via the Dzyaloshinskii-Moriya interaction (DMI). We study ~ 7.4 nm diameter, core/shell $\text{Fe}_3\text{O}_4/\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ MNPs with a 0.5 nm Mn-ferrite shell. Mössbauer spectroscopy, x-ray absorption spectroscopy and x-ray magnetic circular dichroism are used to determine chemical structure of core and shell. Polarized small angle neutron scattering shows parallel and perpendicular magnetic correlations, suggesting multiparticle coherent spin canting in an applied field. Atomistic simulations reveal the underlying mechanism of the observed spin canting. These show that strong DMI can lead to magnetic frustration within the shell and cause canting of the net particle moment. These results illuminate how core/shell nanoparticle systems can be engineered for spin canting across the whole of the particle, rather than solely at the surface.

SCIENTIFIC REPORTS | (2018) 8:3425 | DOI:10.1038/s41598-018-21626-0



Correlated spin canting in ordered core-shell $\text{Fe}_3\text{O}_4/\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ nanoparticle assemblies

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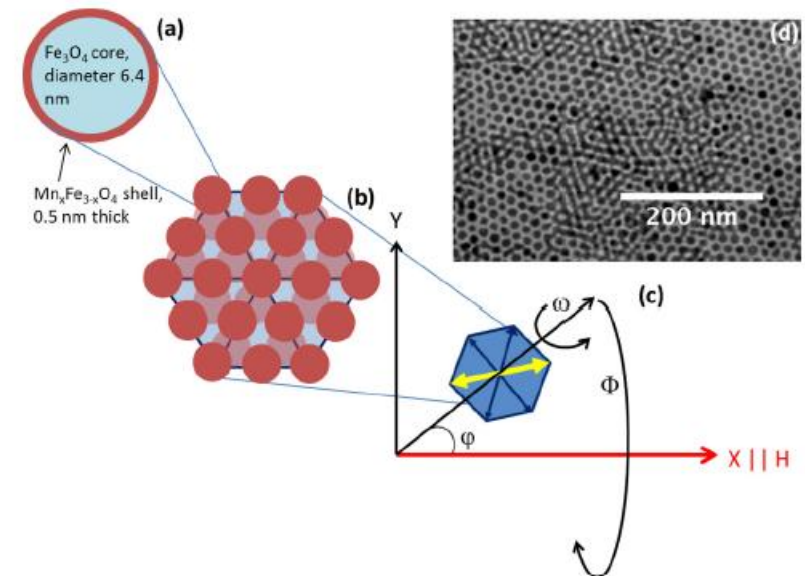
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(Received 30 September 2018; revised manuscript received 2 March 2019; published 18 March 2019)

Polarization-analyzed small-angle neutron-scattering methods are used to determine the spin arrangements and experimental length scales of magnetic correlations in ordered three-dimensional assemblies of ~ 7.4 -nm-diam core-shell $\text{Fe}_3\text{O}_4/\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ nanoparticles. In moderate to high magnetic fields, the assemblies display a canted magnetic structure where the canting direction is coherent from nanoparticle to nanoparticle, in contrast to the less extended, more single-particle-like behavior for similar ferrite assemblies. The observed magnetic scattering is modeled by assuming that the interparticle dipolar coupling combined with Zeeman effects in a field leads to nanoparticle domains with preferred net spin alignments relative to packing symmetry axes. Over a range of fields and temperatures, the model qualitatively explains the observed scattering anomalies in terms of clusters that vary in area and thickness, highlighting the complex structures adopted in real, dense nanoparticle systems. The clusters often have a strong two-dimensional magnetic character which is attributed to structural stacking faults and the resulting influence of interparticle dipolar interactions for these magnetically soft nanoparticles.

DOI: [10.1103/PhysRevB.99.094421](https://doi.org/10.1103/PhysRevB.99.094421)



Anisotropy-driven magnetic structures in manganese ferrite nanoparticle assemblies

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(Dated: April 20, 2026)

Polarization-analyzed small-angle neutron scattering methods are used to determine the spin arrangements and experimental length scales of magnetic correlations in ordered three-dimensional assemblies of ~ 7.6 nm diameter chemically homogeneous manganese ferrite nanoparticles. While the perpendicular magnetic scattering at remanence mostly follows single particle behavior at high temperature, the scattering deviates upon cooling the particles, growing maximally at intermediate temperatures (≈ 50 -100 K) with intermediate field values also displaying canted magnetic structures. The data are fit with a sphere-based mass fractal model and are interpreted further via a micromagnetic simulation approach. The unusual temperature and field dependencies are explained in terms of a delicate balance between magnetic anisotropy and demagnetization. These results highlight the ability of PASANS to extract key features in nanoscale systems and the importance of correlating micromagnetic simulations.

Submitted, Phys. Rev. B

