THE ROLE OF SIZE AND CRYSTALLINITY ON MAGNETIC NANOPARTICLE RESPONSE

-BY HOAN HENRY LE

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MOTIVATION

• Hyperthermia
  • Alternative cancer treatment where alternating magnetic fields are used to locally heat nanoparticles and nearby tumor tissue

• MRI contrast
  • Nanoparticles alter the magnetic signal from the absorbing tissue, providing contrast

• Need to better understand magnetic response to applied fields to optimize applications

Our goal is to determine how size nanoparticle size and surfactant coating alter magnetic properties.
• The nanoparticles we worked on were Magnetite(Fe$_3$O$_4$) which were coated with an Oleic Acid Shell (C$_{18}$H$_{34}$O$_2$)
• We looked at 10 nm and 30 nm with and without extra surfactant
• Recipe: Ocean Nanotech nanoparticles (10 nm, 30 nm), chloroform, and PEG (Polyethylene Glycol: 6000, 20,000)
• Process: Sonicate 3:1 ratio of chloroform to PEG and then sonicate the solution with a 3:1 ratio of chloroform to nanoparticles
SMALL-ANGLE NEUTRON SCATTERING (SANS)

- SANS provides information on structural and magnetic morphology
- It is sensitive to length scales from nm to 100’s μm

Bragg’s law:

\[
\frac{4\pi \sin(\theta)}{\lambda} = \frac{2\pi}{d} = |Q|
\]

Small Q = Larger objects
Big Q = smaller objects

Q (θ) = \frac{2\pi}{distance}
POLARIZATION ANALYZED SANS (PASANS)

• Enables separation of nuclear from magnetic scattering
• See spins (\(M\)) \(\perp\) to \(Q\)
• Non spin-flip includes structural scattering (\(N\)) and \(M \parallel H\)
• Spin-flip scattering includes \(M \perp H\)

Measure four conditions:

\(\uparrow\) to \(\uparrow\)
\(\downarrow\) to \(\downarrow\)
\(\uparrow\) to \(\down\)
\(\down\) to \(\uparrow\)
SECTOR CUTS (DATA PROCESSING)

Original Data

$M^2_{\text{parallel}}$

$N^2$

$M^2_{\text{perp}}$
MAGNETIZATION (10NM) – COMPARE MAGNETIC TO NUCLEAR RATIO

Structural (N^2) Scattering

Magnetic (M || H) Scattering

<table>
<thead>
<tr>
<th>10nm Nanoparticles</th>
<th>M/N Ratio</th>
<th>% of bulk magnetization</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005 T</td>
<td>0.062553</td>
<td>29.9</td>
</tr>
<tr>
<td>0.045 T</td>
<td>0.09961</td>
<td>47.6</td>
</tr>
<tr>
<td>0.2 T</td>
<td>0.134113</td>
<td>64.0</td>
</tr>
<tr>
<td>0.51 GT</td>
<td>0.144078</td>
<td>68.8</td>
</tr>
<tr>
<td>1.2T</td>
<td>0.145248</td>
<td>69.3</td>
</tr>
<tr>
<td>Bulk</td>
<td>0.209469</td>
<td></td>
</tr>
</tbody>
</table>
MAGNETIZATION (30NM)

30nm Nanoparticles | M/N | % of bulk magnetization
---|---|---
0.005 T | 0.023556 | 11.2
0.0450 T | 0.042517 | 20.3
0.1 T | 0.053002 | 25.3
0.2 T | 0.073398 | 35.0
1.2T | 0.097099 | 46.4
Bulk | 0.209469 |

Mystery: Why are 10 nm nanoparticles more magnetic than 30 nm nanoparticles? The 10 nm particles are more susceptible to surface area so we’d expect them to be less magnetic....
X-RAY DIFFRACTION SHOWS MULTI-DOMAINS IN 30 NM PARTICLES

- Use specular reflection (angle in = angle out) to measure 311 Fe₃O₄ diffraction peak
- Width of peak (β) tells us about crystalline size (L)

\[ L = \frac{\lambda}{\beta \cos \theta} \]  
Scherrer Equation

\[ \beta = .0225 \quad \Rightarrow \quad L = 6.87 \text{ nm} \]

\[ \beta = .0204 \quad \Rightarrow \quad L = 7.55 \text{ nm} \]

Conclusion: 30 nm nanoparticles are comprised of more crystalline domains than the 10 nm nanoparticles. This could explain reduction in saturation magnetization!
Measure Canting Angle as Function of Field

30 nm Nanoparticles  |  Cant angle (degrees)  
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td>0.045 T</td>
<td>5.6</td>
</tr>
<tr>
<td>0.1 T</td>
<td>4.9</td>
</tr>
<tr>
<td>0.2 T</td>
<td>3.6</td>
</tr>
<tr>
<td>1.2T</td>
<td>2.5</td>
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</table>

10 nm Plain  |  Cant angle (degrees)  
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.045 T</td>
<td>30.9069022</td>
</tr>
<tr>
<td>0.2 T</td>
<td>5.27870668</td>
</tr>
<tr>
<td>0.5 T</td>
<td>3.604395158</td>
</tr>
<tr>
<td>1.2T</td>
<td>1.361867614</td>
</tr>
</tbody>
</table>
Zeeman Energy: Energy of individual magnetic moments oriented in field
\[ E_{\text{Zeeman}} = M \cdot H (1 - \cos(\epsilon)) \]

Anisotropy: Energy of magnetic moments to align towards a certain preferred axis (111)
\[ E_{\text{Anisotropy}} = \kappa (\cos(55 - \epsilon) - \cos(55)) \]

Iron Oxide has an average anisotropy on the scale of \(10^4 \frac{J}{m^3}\).

STRUCTURE (PEG)

\[
\frac{M}{N} = \frac{2MN}{N^2} \cdot \frac{1}{2}
\]

Error of SLD within \(10^{-3}\)

<table>
<thead>
<tr>
<th>30nm PEG</th>
<th>N2</th>
<th>2MN</th>
<th>M/N</th>
<th>% bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>450G</td>
<td>0.1849</td>
<td>0.0088</td>
<td>0.023797</td>
<td>11.36045</td>
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<tr>
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<tr>
<td>30nm Plain</td>
<td>1.46</td>
<td>6.97</td>
<td>0.209469</td>
<td>46.35457</td>
</tr>
</tbody>
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<th>% bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>0G</td>
<td>0.3069</td>
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<td>0.01971326</td>
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<tr>
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<td>31.42204</td>
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<tr>
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<td>0.0729</td>
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<tr>
<td>2000G</td>
<td>0.3069</td>
<td>0.09</td>
<td>0.14662757</td>
<td>69.9996</td>
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<tr>
<td>5100G</td>
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<td>0.0961</td>
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<tr>
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<td>0.3069</td>
<td>0.1007</td>
<td>0.16405995</td>
<td>78.32177</td>
</tr>
<tr>
<td>10nm Plain</td>
<td>1.46</td>
<td>6.97</td>
<td>0.20946915</td>
<td>69.34111</td>
</tr>
</tbody>
</table>

\(\frac{M}{N} = \frac{2MN}{N^2} \cdot \frac{1}{2}\)
CONCLUSIONS

• 30nm particles less magnetic than 10 nm
• 30nm has separate broken domains
• Mostly surface effects
• PEG allows for more freedom
• Also unknowingly created a Ferro fluid

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QUESTIONS?