Particle size effects on the magnetic behaviour of 5 to 11 nm Fe₃O₄ nanoparticles coated with oleic acid

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Abstract. The magnetic behaviour of 5 to 11 nm magnetite (Fe₃O₄) nanoparticles (NPs) was measured at various temperatures (Tₛ) from 20 to 400 K. The particles were fabricated via thermal decomposition of an iron precursor, and involved a coating of the particles with oleic acid. The particle size distribution was analysed by XRD measurements and TEM imaging. Magnetization loops, measured at various Tₛ, indicate a superparamagnetic behaviour at high T and the occurrence of hysteresis at low T, with a stronger coercivity for the larger particles. Zero-Field-Cooling (ZFC) and Field Cooling (FC) curves indicate a superparamagnetic behaviour, with a blocking temperature varying significantly with the particle size. Namely, the peak temperature, Tₘₙₐₓ, increases from 30 K to 170 K when the particle size increases from 5 nm to 11 nm. Magnetic couplings between particles appear stronger for larger particles.

Magnetic NPs are key materials for a variety of applications in nanotechnologies and biomedicine.¹ Magnetite (Fe₃O₄) NPs are excellent candidates for medical applications because of their non-toxicity and ability to be highly functionalized.² The magnetic properties of bulk magnetite Fe₃O₄, which orders ferrimagnetically below Tᵉ ~850K, have been widely studied. These bulk properties are however altered when magnetite is nanometric in size. Fe₃O₄ NP assemblies exhibit superparamagnetic behaviors, where the NPs behave as single macrospins and collectively reach a frozen state at low T. One important question is how this magnetic behaviour is modified by NP size. In this paper, we report magnetic measurements of Fe₃O₄ NPs, ranging from 5 to 11 nm in size. Results are discussed and compared to other measurements of Fe₃O₄ NPs reported elsewhere.

We synthesized our Fe₃O₄ NPs by thermal decomposition of an iron precursor and coated the NPs with oleic acid. Different procedures and reaction temperatures were used to achieve different particle sizes. The 5 nm NPs (sample A), were fabricated by heating iron(III) oleate in oleic acid and octadecene to 300 °C for 30 min, and cooled to room T.³ The 8 nm NPs (sample B), were fabricated from Fe(III) acetylacetonate, mixed with hexadecane, octadecene, oleic acid and oleyamine, and heated to 200 °C for 30 minutes, then heated under nitrogen at 290 °C for another 30 minutes, and cooled to room T.⁴ The 11 nm NPs (sample C), were prepared following a similar procedure to sample A, but heated at 320 °C for 30 min. All the NPs were precipitated with ethanol and decanted.

Figure 1: TEM images and XRD patterns of the Fe₃O₄ nanoparticles (A) 5 nm (B) 8 nm (C) 11 nm.
Transmission electron microscopy (TEM) images of the three NP samples are shown in Figure 1. A statistical analysis of the NP sizes yields an average particle diameter of $5.3 \pm 0.7$ nm, $8.1 \pm 1.7$ nm, and $11.3 \pm 2.5$ nm for samples A, B and C, respectively. The X-ray diffraction (XRD) patterns all exhibit a cubic $Fd\bar{3}m$ structure, consistent with $\text{Fe}_3\text{O}_4$ magnetite, with no sign of hematite ($\gamma\text{-Fe}_2\text{O}_3$). Average crystallite sizes were estimated from the peak widths: $5.8 \pm 1.7$nm, $8.5 \pm 2.9$ nm and $11.0 \pm 4.6$ nm for samples A, B and C, respectively, which are in agreement with the TEM results, suggesting monocrystalline NPs. Larger size distributions for sample B and C may have been due to temperature fluctuations during synthesis.

Figure 2a shows VSM magnetization curves for the 8 nm NPs, measured at 400, 300, 80 and 20 K. The curves indicate a superparamagnetic behaviour at 400K, well fitted by the Langevin model. The curves at lower $T$ gradually deviate from that behaviour. When $T$ decreases, the susceptibility at $H = 0$ increases and the NPs magnetically align more easily. Also, significant hysteresis occurs at 20 K, indicating a blocked state where the NPs show a ferromagnetic behaviour.

Figure 3 shows Zero Field Cooling (ZFC) and Field Cooling (FC) curves for sample B. FC and ZFC curves were measured at different $H$ values from 50 to 500 Oe. All the ZFC curves exhibit a peak, indicating a transition from a magnetically blocked state (at low temperature) to a superparamagnetic state (at high temperature). The peak position $T_{\text{max}}$ varies with the magnitude $H$ of the external field, as plotted in Figure 3b. When $H \leq 75$ Oe, $T_{\text{max}}$ reaches an optimal value of 130 K, which we ascribe to the blocking temperature $T_B$. The FC and ZFC curves do not join at $T_{\text{max}}$ but at a higher temperature, $T_{\text{join}}$. The gap $\Delta T = T_{\text{join}} - T_{\text{max}}$ is on the order of 100K for sample B, indicating strong magnetic couplings between the NPs. Figure 4(a-c) shows ZFC / FC curves measured at 100 Oe, for the three NP samples. As expected, $T_{\text{max}}$ increases significantly when the NP size increases. Sample A exhibits the lowest $T_{\text{max}} = 28$ K, and sample C the highest $T_{\text{max}} = 170$ K, as reported in Table 1. Figure 4(d-e) shows magnetization loops measured at 400 K and 20 K for the three NP sizes. The larger 11 nm NPs align more easily than the smaller 5 nm NPs. At 20K, the 5 nm NPs exhibit very little hysteresis, indicating a pure superparamagnetic behaviour, while the larger NPs exhibit a significant hysteresis, with an increased coercivity $H_c \sim 235$ Oe (from $\sim 0$ at 400K), indicating ferromagnetic-like couplings.

The magnetic behavior of our 5 to 11 nm $\text{Fe}_3\text{O}_4$ NPs agrees with data measured on other $\text{Fe}_3\text{O}_4$ NPs by other groups.[6-8] Some models predict that, due to surface effects, $H_c$ should increase when the NP size decreases.[9,10] We found that $H_c$ actually decreases when the NP size decreases from 11 to 5 nm (see Table 1). Such trend is also observed by Guardia et al. [8] on 6 to 20 nm NPs, and by Goya et al. [6], on 5 to 150 nm $\text{Fe}_3\text{O}_4$ NPs. The consistency of the results, obtained on different NP samples, suggests that surface spin-disorder and resulting magnetic anisotropy are strongly reduced by the presence of oleic acid ligands covalently bonded to the surface.[11] With a ligand shell, the NPs exhibit bulk-like magnetic anisotropy. Our ZFC/FC results, showing that $T_{\text{max}}$ drastically increase with NP size, also agree with other reported findings on 5 to 20 nm NPs.[11,12] The discrepancies between the observed $T_{\text{max}}$ from the various reports may be due to different particle chemical environments. Also, our observed increase of magnetic couplings (where $T_{\text{join}} > T_{\text{max}}$) for 8 and 11 nm NPs compared to the 5nm NPs agrees with other measurements and is attributed to increased magnetic moment.[6]
Figure 4. (a-c) ZFC / FC measurements of sample A (5 nm), B (8 nm) and C (11 nm) measured at 100 Oe. (d) Magnetization curves for the three samples, measured at 400K and (e) at 20 K. Insets: close-up on hysteresis.

Table 1. Structural and magnetic parameters for samples A, B and C.

<table>
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<th>TEM (nm)</th>
<th>XRD (nm)</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$\Delta T$ (K)</th>
<th>$H_s$ at 400K (Oe)</th>
<th>$H_s$ at 20K (Oe)</th>
<th>$H_{0.95}$ (Oe) at 400K*</th>
<th>$H_{0.95}$ (Oe) at 20K*</th>
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</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>5.3 ± 0.7</td>
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<td>28</td>
<td>~ 10</td>
<td>~ 0</td>
<td>~ 25</td>
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<tr>
<td>Sample B</td>
<td>8.1 ± 1.7</td>
<td>8.5 ± 2.9</td>
<td>130</td>
<td>~ 100</td>
<td>~ 20</td>
<td>105</td>
<td>13,100</td>
<td>3900</td>
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<tr>
<td>Sample C</td>
<td>11.3 ± 2.5</td>
<td>11.0 ± 4.6</td>
<td>170</td>
<td>~ 50</td>
<td>50</td>
<td>235</td>
<td>9145</td>
<td>10,272</td>
</tr>
</tbody>
</table>

$\Delta T$ is the difference between $T_{\text{max}}$ and the joining point for the ZFC and FC curves (above $T_{\text{max}}$)

* $H_s$ is measured at the shoulder of the magnetization curve, preceding saturation

In conclusion, we have measured the magnetic behavior of 5 to 11 nm Fe$_3$O$_4$ NPs that were prepared by thermal decomposition of an iron precursor and coated with oleic acid. We found that the magnetic properties of the NPs are greatly impacted by the particle size. Magnetization curves indicate a superparamagnetic behavior at high $T$ with very little hysteresis. Moderate hysteresis that increases with the NP size appears at low $T$ once the NPs are in a blocked state. ZFC/FC measurements confirm the superparamagnetic behavior and show a transition to a magnetically blocked state at low temperature for all the NP sizes. The peak temperature $T_{\text{max}}$ drastically increases with the NP size.

We would like to thank Jeffrey Farrer for help with TEM imaging, and Branton Campbell for helpful discussions about the Fe$_3$O$_4$ crystallographic structures. This work has been supported by ORCA and MEG grants from Brigham Young University.

References