Particle size effects on the magnetic behaviour of 5 to 11 nm Fe_3O_4 nanoparticles coated with oleic acid

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Abstract. The magnetic behaviour of 5 to 11 nm magnetite (Fe_3O_4) nanoparticles (NPs) was measured at various temperatures (*T*s) 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 *T*s, 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, T_{max}, increases from 30 K to 170 K when the particle size increases from 5 nm to 11nm. 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 (Fe_3O_4) 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 Fe_3O_4, which orders ferrimagnetically below T_c ~850K, have been widely studied. These bulk properties are however altered when magnetite is nanometric in size. Fe_3O_4 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 Fe_3O_4 NPs, ranging from 5 to 11 nm in size. Results are discussed and compared to other measurements of Fe_3O_4 NPs reported elsewhere.

We synthesized our Fe_3O_4 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.[3,4] 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.[5] 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.

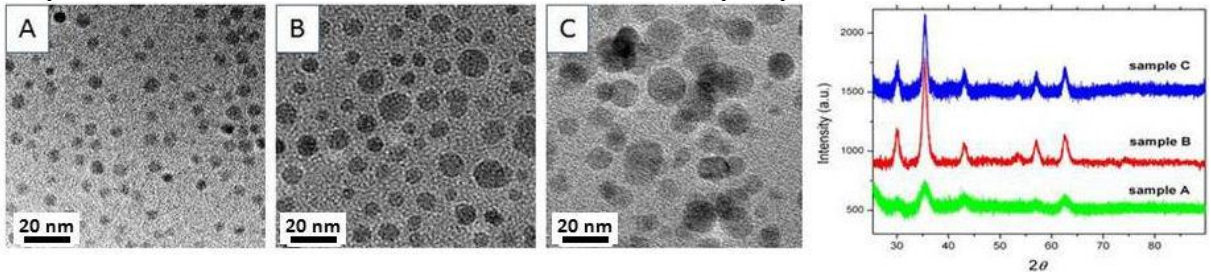

Figure 1: TEM images and XRD patterns of the Fe_3O_4 nanoparticles (A) 5 nm (B) 8 nm (C) 11 nm.

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 ± 0.7 nm, 8.1 ± 1.7 nm, and 11.3 ± 2.5 nm for samples A, B and C, respectively. The X-ray diffraction (XRD) patterns all exhibit a cubic *Fd3m* structure, consistent with Fe_3O_4 magnetite, with no sign of hematite (γ-Fe_2O_3). Average crystallite sizes were estimated from the peak widths: 5.8 ±1.7nm, 8.5 ±2.9 nm and 11.0 ± 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.

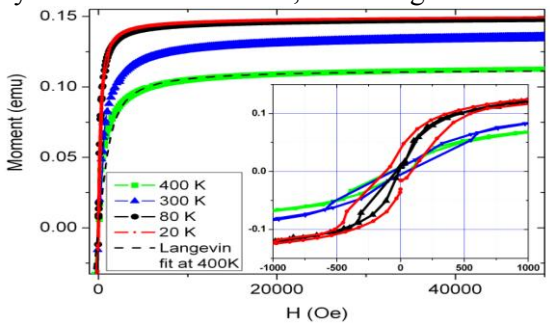

Figure 2. Magnetization curves of sample B (8 nm) at 400, 300, 80 and 20 K, with Langevin fit at 400K. Inset: close-up on the hysteresis at $H = 0$.

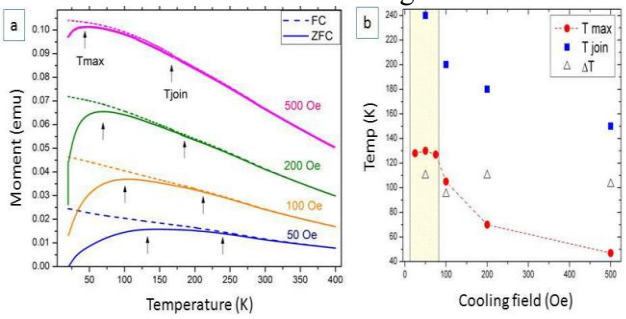

Figure 3 (a) ZFC / FC measurements of sample B (8 nm) at 50, 100, 200 and 500 Oe. (b) Graphs of T_{max} and T_{join} as functions of cooling field value.

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_{max} varies with the magnitude H of the external field, as plotted in Figure 3b. When $H \leq 75$ Oe, T_{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_{max} but at a higher temperature, T_{join}. The gap $\Delta T = T_{join} - T_{max}$ 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_{max} increases significantly when the NP size increases. Sample A exhibits the lowest T_{max} = 28 K, and sample C the highest T_{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 ~0 at 400K), indicating ferromagnetic-like couplings.

The magnetic behavior of our 5 to11 nm Fe_3O_4 NPs agrees with data measured on other Fe_3O_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 Fe_3O_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_{max} drastically increase with NP size, also agree with other reported findings on 5 to 20nm NPs.[11,12] The discrepancies between the observed T_{max} from the various reports may be due to different particle chemical environments. Also, our observed increase of magnetic couplings (where $T_{join} > T_{max}$) for 8 and 11nm NPs compared to the 5nm NPs agrees with other measurements and is attributed to increased magnetic moment.[6]

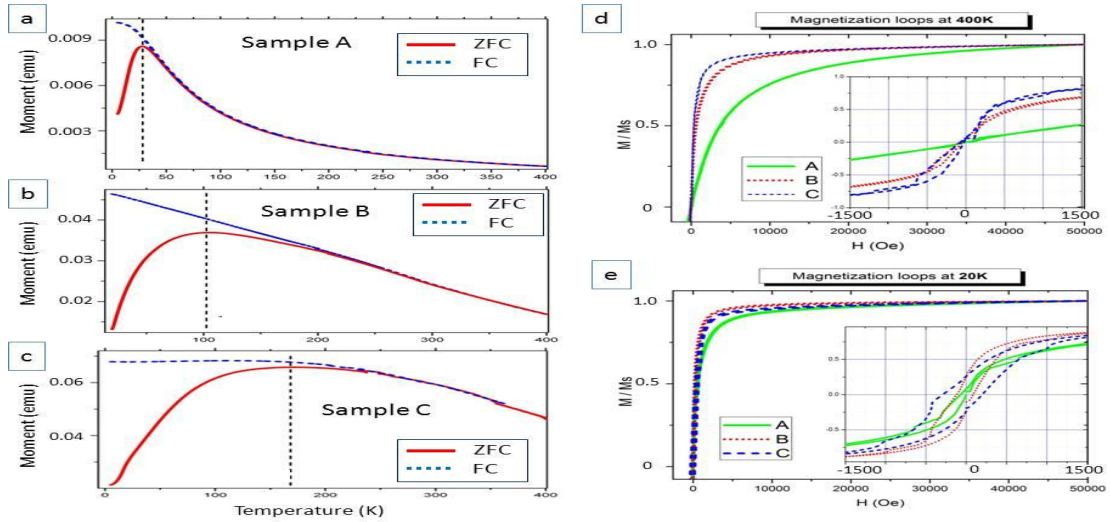

Figure 4. (a-c) ZFC / FC measurements of sample A (5 nm), B (8 nm) and C (11 nm) measured at 100 Oe. (d) Magnetization curves for the three samples, measured at 400K and (e) at 20 K. Insets: close-up on hysteresis.

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

	Particle size		ZFC/FC curves		Magnetization loops			
	TEM (nm)	XRD (nm)	T_{max} (K)	ΔT † (K)	H_c at 400K (Oe)	H_c at 20K (Oe)	$H_{0.95}$ (Oe) at 400K*	$H_{0.95}$ (Oe) at 20K*
Sample A	5.3 ± 0.7	5.8 ±1.7	28	~ 10	~ 0	~ 25	29,575	14,200
Sample B	8.1 ± 1.7	8.5 ±2.9	130	~ 100	~ 20	105	13,100	3900
Sample C	11.3 ± 2.5	11.0 ± 4.6	170	~ 50	50	235	9145	10,272

† *ΔT is the difference between T_{max} and the joining point for the ZFC and FC curves (above T_{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_3O_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_{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_3O_4 crystallographic structures. This work has been supported by ORCA and MEG grants from Brigham Young University.

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