Effect of surfactant mediated inter-particle interactions on the magnetic properties of Manganese Zinc Ferrite ferrofluid

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Abstract. Ferrofluids of spinel ferrites presents a multitude of applications in engineering and biomedical fields. The nature of the divalent ions and their occupancy decides the magnetic properties of the spinel ferrites. The nanoparticles of these ferrites and their suspensions in various liquids are of great fundamental interest as well. This paper reports the synthesis and magnetic relaxation studies on fluid particles of Zinc substituted manganese ferrite. Nanoparticles of manganese zinc ferrite with a particle size around 5 -6 nm, are synthesized by chemical method and suspended in kerosene and water, with proper surfactants. The structural characterization is carried out by x-ray diffraction and electron microscopy. The magnetic properties are studied by employing a SQUID magnetometer. The temperature dependent static magnetic measurements and analysis reveal the inter particle interaction effects on the overall magnetic behavior of the constituent magnetic nanoparticles. The modification of the magnetic relaxation based on the surfactant is analysed.

Keywords: inter-particle interaction, surfactant, zero field cooled, brownian relaxation, superparamagnetism

1. Introduction
Manganese Zinc ferrite is a spinel soft ferrite with high saturation magnetisation and fast magnetic response. Nanoparticles and fluids of these ferrites have been studied for engineering applications such as heat transfer fluids, and bio applications like magnetic hyperthermia \cite{1,2}. The saturation magnetisation and coercivity depends on the cation distribution in the lattice sites. The saturation magnetisation is found to increase upto 40\% Zn substitution by chemical method and further the increase of Zn decreases the saturation magnetisation. As the size of the particles goes to nano regime, around 10 nm, they become superparamagnetic in nature. Nevertheless the surface effects and the inter-particle interactions decide the net magnetic response. Ferrofluids are magnetic nanoparticles suspended in suitable carrier liquid with proper surfactants. The surfactants separate the particles from one another and cause the particles to get suspended well to form stable ferrofluid. These fluids could also present different mechanisms including brownian relaxation, and the temperature dependent magnetization...
reversal depends on the type of surfactants and carrier liquid that result in modified magnetic properties. The magnetic moment of the divalent anion (M) in the formula \((M_{1-x}Fe_x)[M_xFe_{2-x}]O_4\) and their preferred occupancy in tetrahedral or octahedral site \((x\) being the degree of inversion) decides the overall magnetization\([3,4]\) of the ferrite. They also exhibit surface anisotropy effects originating from the finite size effects and crystallinity\([5]\) together with the inter-particle interactions and cation distribution. The synthesis routes decide the cationic occupancy in lattice sites and oxidation states of anions in Manganese Zinc ferrites\([6,7,8]\).

Here we report the inter-particle interaction based on the magnetic studies of hydrocarbon based and water based manganese zinc ferrite fluid particles. The composition of \(\text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4\), is which has been reported with maximum magnetization following the chosen synthesis route \([4]\). Nanoparticles of this particular composition are prepared and dispersed in both hydrocarbon base and aqueous base. Since in either case the surfactants are different and hence the inter particle separation and hence varied magnetic properties. Tailoring the interparticle interaction and understanding the magnetic relaxation is important in biomedical applications \([2,3,9,10]\).

2. Experimental Details
The nanofluids under study are synthesized by controlled chemical co precipitation technique. Anhydrous ferric chloride \((\text{FeCl}_3)\), Manganese chloride tetrahydrate \((\text{MnCl}_2.4\text{H}_2\text{O})\) and zinc chloride \((\text{ZnCl}_2)\) in a stoichiometry of 2: 0.6: 0.4, is dissolved in water. This solution is made to react with 1 M boiling NaOH solution in water. This reaction mixture is stirred for five minutes. The precipitate is filtered from the supernatant solution to remove unreacted radicals and water soluble byproducts. 50 ml distilled water and 2 ml oleic acid are added to the mixture and stirred for another 90 minutes at 40\(^\circ\)C. Then the resultant precipitate is allowed to cool while stirring and then a few drops of con. HCl are added so as to reduce the pH of the mixture below 7. The precipitate is coated with surfactant oleic acid and is washed several times with water and dried well with acetone and dispersed in kerosene by ultrasound agitation. The fluid obtained is named as MZFK.

The water based fluid is prepared from the precipitate obtained after supersaturating with NaOH and stirring for two minutes. The precipitate is magnetically decanted and to this 50ml distilled water, and 2g citric acid dissolved in 5ml water is added. The temperature is raised to 90\(^\circ\)C and stirred for 60 minutes. The mixture is cooled and kept under a strong electromagnet to remove the supernatant solution. The mixture is washed with water to remove the excess of citric acid and at a pH of 7 the precipitate gets suspended in water.

The structural characterisation was carried out by X Ray diffraction(XRD) technique \((\text{Rgaku D Max at Cu Ka like})\), and Transmission Electron microscopy \((\text{JEM 2100F TEM})\) measurements. The magnetic measurements were carried out in in superconducting Quantum Interference Device \((\text{SQUID Quantum Design})\).

3. Results and Discussions
Figure 1 depicts the XRD pattern of the sample by drying off the carrier liquid. It's seen that the particles are crystallized in the fcc spinel structure. All the major diffraction peaks are identified \((\text{ICDD: 74-2401})\). The peak broadening evidences the nanocrystalline nature of the ferrite. The crystallite size calculated by employing the Debye Scherer’s formula is 6 nm. The selected area electron diffraction (SAED) pattern of the MZFK is shown in figure 1b. The diffused rings indicate the nanocrystalline nature of the particles in the sample. The major crystallographic planes \((311)\ (331)\ (220)\ (400)\ (422)\ and \(440)\ of fcc spinel structure of \(\text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4\) are identified. Transmission electron microscopy (TEM) conducted on the samples give the particle size and distribution of size. The samples for TEM are prepared by drying off the base liquids for both the samples.
Figures 2a depict the TEM images of MZFK and figure 2b is the particle size distribution histogram obtained from the images. The mean size is obtained as 5 nm with standard deviation of 0.7 nm. Figure 3a shows the TEM image of MZFW and figure 3b the size distribution with a mean size of 7 nm and standard deviation of 0.6 nm. It could be seen that the particles are uniformly distributed in size in both cases. A slight increase in size for water dispersed fluid particles is attributed to the digestion conditions. The MZFW is heated at 90°C and allowed to crystallize after the citric acid is added. While in MZFK, the sample is heated at lower temperature and the growth is more inhibited.

A close examination of figure 2a reveals the formation of tiny clusters consisting of 6 to 8 particles and the clusters are well separated from one another. This is reported for nanoparticles passivated with steric surfactants[11]. Nevertheless each nanoparticle within the cluster is separately visible in TEM, since the particles are coated oleic acid which separates them.
The TEM image of MZFW(fig 2c) shows well distributed particles and no pattern formation is seen due to clustering as in OA coated MZFK sample.

3.1 **Magnetic hysteresis measurements**

Figure 3 depicts the magnetisation loops measured at different temperatures. The moment increases with decrease in temperature as expected. The moment is not saturated even at high applied magnetic fields, owing to the surface effects exhibited by the nanoferrites[12]. The magnetic order at the surface gets deformed from the bulk moment and when the surface becomes prominent these effects are reflected in the net magnetic behaviour.
Table 1 consolidates the saturation magnetisation of MZFK and MZFW at different temperatures. The surface spins in ferrites are reported to form a dead layer that decreases the net magnetisation of the material from the bulk. The saturation magnetisation for both the samples decreases with increase of temperature, as expected by Curie-Weiss law, while at all temperatures MZFK presents a lower specific magnetisation than MZFW. This is because the oleic acid (with a molecular wt 282 g) is a larger surfactant than citric acid (molecular wt 192 g) hence the weight fraction of nanoparticles is smaller in MZFK hence smaller value of technical saturation magnetisation for comparable particle sizes in both the samples. The magnetisation loop at room temperature presents negligible remanence and hysteresis showing the superparamagnetic nature of both samples as expected for a single domain particle with size of 5 - 6 nm.

Table 1: Comparison of magnetisation at various temperatures

| Sample | 300K  | 100K  | 4.2K  |
|--------|-------|-------|-------|
| MZFK   | 20 emu/g | 36 emu/g | 46 emu/g |
| MZF W  | 30 emu/g | 66 emu/g | 78.4 emu/g |

Figure 3(c): M-H loop (VSM) at room temperature and at 100K

Figure 3(d): M(H) graphs (SQUID measurements) at 4.2K; on MZFW
Figure 4: moment variation with temperature showing Tc(a): MZFK, (b): MZFW

Figure 4 is the temperature dependent moment variation at an applied field of 300 Oe. The measurement has been recorded from liquid nitrogen temperature to 200°C, showing the curie temperature as the temperature at which the moment reduces to zero. The Tc values obtained is 120°C which is lowered from the bulk value [12,13]. A detailed study regarding the curie temperature with respect to the zinc substitution shows that Tc increases for 30% zinc ions and then it decreases[13]. The variation in Tc could be originated from the cationic distribution in the sample. This requires further studies. The variation of graph 4(a) is typically paramagnetic in nature with a linear function of temperature as curie's law. This indicates the perfect langevin type behaviour of non interacting superparamagnetic particles. The particles in MZFK are well separated from one another by the surfactant oleic acid which is covalently bound to the particle surface. Whereas the CA coated particles (figure 4b) shows slight deviation from the linear variation. This indicates the presence of interparticle interaction. since CA provides ionic/ electrostatic stabilization in water besides the nominal steric repulsion. So when the water is dried off, the electrostatic repulsion decreases and this causes the interaction among particles in MZFW.

3.2 FC/ZFC measurements

The field cooled (FC) and zero field cooled (ZFC) magnetic moment variation as a function of temperature are measured in a SQUID at two different applied fields. The results are presented in figures 5 and 6. In ZFC measurement, the sample is cooled down to 5K from room temperature with zero applied field. The particles get cooled with their moments in random directions. An external magnetic field corresponding to the initial magnetisation is applied and the moment of the sample is measured by increasing the temperature. In FC measurement, the sample is cooled in an applied field equal to the measurement field and the moment at different temperatures is recorded. Both ZFC –FC measurements are carried out for two applied fields for both the samples.

Figure 5(a) and 5(b) show the FC-ZFC measurements at two different applied fields on MZFK. Both TB and T.ir get shifted to low temperature as the applied field increases. The blocking is affected by zeeman energy, reflected in the energy for the magnetisation reorientation. TB is a function of the measuring field (inset of figure 5(b)). The ZFC moment increases, becomes a maximum at the blocking temperature and then monotonically decreases in all the cases. This shows the particles undergo magnetisation reversal more or less independently. The two temperatures, TB and T.ir are closer with a separation of 23K in both fields. The interaction among the particles are less. This is evident from the TEM measurements that the particles are uniformly distributed and are well separated. The clustering effects could be a reason for the increased effective size of the particles, which is reflected in this
difference. The FC curve is measured from room temperature to 5K. The moment increases with decrease of temperature since the thermal fluctuation gets lowered, the moment variation deviates from ZFC at $T_{irr}$ and continues to increase at and below $T_B$. Moment continues to increase with a change of slope. This may be due to the cluster formation; in each cluster, the particles interacting through surfaces increase the anisotropy and hence are not free to rotate independently. This impedes otherwise free moments to align in the field and result in steady increase of magnetic moment with decrease of temperature. The narrow distribution of blocking temperatures (the $T_B$ and $T_{irr}$ are quite closer) indicate the uniform particle size and absence of strong interaction among the particles[14-17].

![Figure 5: ZFC FC moment variation at applied fields (a) 25Oe, (b): 75Oe on MZFK](image)

![Figure 6: ZFC FC moment variation at applied fields (a) 25Oe, (b): 75Oe on MZFW](image)

Figure 6 depicts the ZFC FC measurements on MZFW at two measuring fields. For low field, the blocking and irreversibility occurs at the same temperature which is spread around 100K at a measuring field of 25 Oe. The ZFC curve exhibits a broad maximum typically for superparamagnetic nanoparticles with uniform size distribution. The progressive deblocking of nanoparticles results in this phenomena. At $T > T_B$ both curves follow decrease of moment obeying a Curie -Weiss law. The FC moment for $T < T_B$ remains constant, which could be explained as a result of interparticle interaction which increases...
the anisotropy making the moments pinned to one another and the thermal energy is too small to overcome the energy barriers and cause a magnetisation reversal.

The curves obtained at 75 Oe measuring field shows lowering of blocking temperature which is quite expected as in the case of MZFK. However the bifurcation takes place at a far higher temperature from $T_B$. This shows the presence of larger particles in the sample. The strength of interaction depends on the moment of the particles and the increased measuring field causes stronger interaction resulting in an increase in larger effective volume and hence the higher $T_{irr}$. The ZFC curve shows a broader maximum and the magnetic relaxation for $T > T_B$ slightly deviates from exact Curie weiss law indicating the existence of dipole-dipole interaction among the particles.

4. Conclusions

Ferrofluids, both aqueous and hydrocarbon base fluids, of spinel manganese zinc ferrite particles of size around 5 nm, in the composition $\text{Mn}_{0.6} \text{Zn}_{0.4} \text{Fe}_2\text{O}_4$ is synthesized by supersaturating with sodium hydroxide at boiling temperature. It has been observed that the temperature, rate of addition and temperature during the whole reaction process are highly crucial in the formation of the magnetic phase. The fluids prepared are highly stable against sedimentation and possess good shelf life. Water based fluids are surfacted with citric acid which provides electrostatic stabilization which reduces when the carrier is dried off. The dipolar interaction is strong among the particles. The oleic acid coating of nanoparticles provides separation between particles and hence the dipolar exchange is found to be lowered. These fluids are expected to be good heat transfer nanofluids and can be good candidates for magnetic hyperthermia. The inter particle interaction among superparamagnetic particles are explained based on temperature dependent static magnetic measurements.

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