Chapter - 3

Results & Discussion

Diffraction patterns for sample C.

TEM image, SAED and size distribution for FHD8 fluid

XRD-pattern of CdFe$_2$O$_4$ nano-ferrite
3.1 Nanomagnetic particles of CdFe$_2$O$_4$

In the present study, CdFe$_2$O$_4$ ferrite particles were synthesized using modified chemical co-precipitation technique. These particles were characterized using x-ray diffraction, FTIR, ac-susceptibility, 293K and 5K magnetizations and dc magnetization at low field measurement techniques. In this section we discuss the results obtained for CdFe$_2$O$_4$.

3.1.1 Physical Characterizations

Figure 1a shows the XRD pattern of 'as prepared' sample (sample A). The pattern is very complex and it is composed of lines corresponding to cadmium ferrite, Cd(OH)$_2$, Fe$_2$O$_3$ and FeO(OH). The major contribution to the phase is Cd(OH)$_2$. Pure cadmium ferrite is formed partially and the peak is very broad. Which suggest that a particle size is very small. In order to get a single phase spinel ferrite the 'as prepared' sample was annealed at two different temperatures. Here, we have adopted two different procedures. In the first case (a) the 'as prepared' powder was pelletized and annealed at two different temperatures i.e. 473 K and 873 K while in the second case (b) the 'as prepared' powder was mixed with NaCl in 1:1 ratio and pelletized and annealed. The x-ray diffraction patterns of these samples are discussed below.

![Figure 1a: X-ray diffraction pattern for as prepared sample.](image-url)
On annealing at 473 K, sample A exhibits peaks corresponding to impurity phases (figure 1b inset). These phases are of Fe$_2$O$_3$, Cd(OH)$_2$ and FeO(OH). The upper curve in figure 1b shows the XRD pattern for the sample annealed with NaCl at 473 K. The major phase corresponds to spinel CdFe$_2$O$_4$ and a small contribution from hematite (H) is also found. These results suggest that incorporation of NaCl during annealing helps to form spinel structure. The complete transformation of spinel phase could not achieve at 473 K. Therefore, similar procedure was adopted and samples were annealed at 873 K for 4 hours.

![X-ray diffraction pattern](image)

*Figure 1b: X-ray diffraction pattern for as prepared sample (bottom curve), samples annealed at 473 K with NaCl (upper curve). Inset: sample annealed at 473 K without NaCl.*

XRD pattern for sampled annealed at 873 K with NaCl (sample C) show the complete formation of spinel CdFe$_2$O$_4$ phase while that without NaCl (sample B) shows an impurity phase at 2θ value 32° corresponds to Fe$_2$O$_3$ phase (Figure 1c). The particle diameter ($D_{XR}$) obtained from the Scherrer formalism for most intense peak (311) comes out to be 430 ± 5 Å and the lattice constant (a) for CdFe$_2$O$_4$ phase is 8.692 ± 0.001 Å, which agrees with the bulk sample (8.697 Å). This suggest that the because of direct heating of precursor the formation of Fe$_2$O$_3$ phase takes place but with the addition of NaCl, the probability of formation of this phase is negligible. Thus the presence of NaCl does not allow particles to oxidize. The Rietveld analysis for sample C was performed.
Figure 1c: X-ray diffraction pattern for sample C annealed at 873 K without NaCl (lower curve) and annealed at 873 K with NaCl (upper curve) as described in the text. The * indicates the presence of impurity phase.

Figure 2: Rietveld refinement pattern for sample C. The X-ray data are shown as dots; the solid line is best fit to the data. The lower curve represents the difference between the observed and calculated profile.
Fig. 2 exhibits the Rietveld refined pattern. The parameters derived from the fit are given in the Table 1. The particle diameter determined by Rietveld refinement ($D_{\text{Ref}}$) is in good agreement with those calculated using Scherrer formalism. The refined occupancy ($x$) at tetrahedral A-site and octahedral B-site indicate that the sample suggests a mixed structure. The cation distribution obtained agrees with those obtained by earlier workers for bulk cadmium ferrite [1]. However, the positional parameter of oxygen ($u$) is slightly higher than the expected value for ideal closed packed arrangements (equal to 0.25). The determined lattice constant from the XRD data agrees well with the ASTM tables (No. 22-1063). The above result indicates that the incorporation of NaCl not only inhibits the growth of the particles but also helps to get better crystalline structure.

Table 1: Structural parameters and Rietveld agreement for sample C.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$x$</th>
<th>$u$</th>
<th>$a_{(\text{Ref})}$ Å</th>
<th>$a_{(\text{ASTM})}$ Å</th>
<th>$D_{\text{Ref}}$ Å</th>
<th>$D_{\text{XR}}$ Å</th>
<th>$\chi^2$</th>
<th>$R_p$ (%)</th>
<th>$R_{wp}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample C</td>
<td>0.3(5)</td>
<td>2.56(2)</td>
<td>8.692(0.3)</td>
<td>8.6972</td>
<td>430</td>
<td>450</td>
<td>1.11</td>
<td>3.57</td>
<td>4.25</td>
</tr>
</tbody>
</table>

To further confirm our argument of the formation of different phases we have carried out the non-destructive method of characterization such as infra-red spectroscopy. The IR absorption spectra recorded at room temperature in the range 1000 cm$^{-1}$ -400 cm$^{-1}$ is shown in Figure 3. It exhibits two main absorption bands at wave number 600 cm$^{-1}$ ($\nu_1$) and 400 cm$^{-1}$ ($\nu_2$). These are attributed to tetrahedral A and octahedral B sites of the spinel structure, respectively [2]. Sample A exhibits a broad peak at 560 cm$^{-1}$ with a shoulder at 640 cm$^{-1}$, which can be attributed to O-H weak interaction band. The shoulder and the extra peak observed at 900 cm$^{-1}$ in sample A suggest the presence of other phases along with the ferrite phase. This agrees with the x-ray results. Samples B and C show band assigned to ferrite phases only. The only difference in spectra is the sharpness of the peaks. The intense peaks at 420 cm$^{-1}$ and 560 cm$^{-1}$ for sample C compare to B suggest the strong interaction at B and A sites, respectively for sample C. Thus the sample C has more precise configuration of atoms or ions in the structure. These results are in agreement with our x-ray results. Therefore, in the following section we only discuss the magnetic properties of sample C, i.e. well crystalline nano-magnetic particles of Cd-ferrite.
Figure 3: Infra-red spectra for samples A, B and C recorded at room temperature in KBr matrix.

Figure 4a: Magnetic hysteretic loops at room temperature 293K.
3.1.2 Magnetic Characterization

Figure 4a shows the magnetization curves for sample C recorded at 293 K. The magnetization curve do not saturate up to 10 kOe field. This non-saturating behavior indicates the presence of two components, i.e., ferromagnetic (super-paramagnetic) and a paramagnetic one. However, CdFe$_2$O$_4$, in the bulk form, is known to be a normal spinel exhibiting antiferromagnetic ordering below 10 K [3]. This suggests that bulk CdFe$_2$O$_4$ should not show any finite magnetic moment at room temperature. In contrast to this, Yokoyama et al [1] have reported that, in ultrafine CdFe$_2$O$_4$ particles magnetization at 6 K increases with decreasing particle size. They have reported that fine particles (size ~ 80 Å) of CdFe$_2$O$_4$ exhibit ferromagnetic behavior and have a saturation magnetization value as high as 89 emu/g at 6 K. They have suggested that there may be many ferromagnetic clusters consisting of Fe$^{+3}$ ions at the B-site around Fe$^{+3}$ ions at the A-site by the A-B interactions. They have explained the observed ferromagnetism by considering higher octahedral preference energy of Cd$^{+2}$ (-31.6 kCal/mol) compare to Zn$^{+2}$ (-29.1 kCal/mol). Because under ideal condition Fe$^{+3}$ ions in CdFe$_2$O$_4$ should have 0 % site occupancy of A-site, in contrast 54 % inversion was observed. This observed occupancy is much higher than that observed in ZnFe$_2$O$_4$ (14 %). Similar behavior was observed by Kamiyama et al [4] in ultrafine particles of ZnFe$_2$O$_4$. They have reported an increase in number of magnetic clusters with decreasing particle size.

Later, Yokoyama et al [5] have reported the magnetic properties of bulk CdFe$_2$O$_4$ and ultrafine CdFe$_2$O$_4$ particles from 6 K to 300 K. This study shows that magnetization of bulk Cadmium ferrite drastically increases with an increase in magnetic field up to ~ 1000 Oe. The sample did not saturate even at 55 kOe magnetic field. In the case of ultrafine (size ~ 80 Å) CdFe$_2$O$_4$ particles magnetization curve saturates at 20 kOe. The magnetization of ultrafine cadmium ferrites is one order higher than the bulk cadmium ferrites. The temperature dependent behavior shows that saturation magnetization decreases monotonically with an increase in temperature indicating ferromagnetic behavior. Two different types of spin structure were suggested to explain this behavior, i.e. (i) a core shell spin structure with a ferromagnetic core and inactive magnetic shell and (ii) non-collinear spin arrangement over the particle volume.
Chinnasamy et al [6] have synthesized the fine particles of cadmium ferrites using high energy ball milling technique. They have milled the bulk CdFe$_2$O$_4$ sample for the various time and found that average grain size decreases with milling time. The magnetic moment and coercive field of the 20 hour milled (40 Å) sample were larger than those of the 0 hour milled (600 Å) sample. In the former sample they observed a saturation magnetization of 21.7 emu/g at 5 K even in an applied field of 90 kOe. This indicates that the sample possesses larger anisotropy. Temperature dependent zero-field and in-field Mossbauer spectroscopy were carried out to study the magnetic ordering of the milled samples. Zero-field Mossbauer spectra show paramagnetic doublet at 300 K and 77 K, while it exhibits hyperfine structure at 4.2 K. Under an external magnetic field of 85 kOe, significant change in hyperfine structure was observed at 4.2 K. Tetrahedral and octahedral sites were clearly separated, indicating the ferrimagnetic ordering in CdFe$_2$O$_4$ as a result of the Fe$^{+3}$(A)-O$^{2-}$-Fe$^{+3}$(B) superexchange interaction.

Recently, O. Silva et. al [7] have investigated canting in CdFe$_2$O$_4$ magnetic fluid using magnetic resonance technique. Using angular dependence of resonance field they have shown that in fine particles of cadmium ferrite, a different spin structure exists, namely a core-shell structure. In this core-shell model, core is antiferromagnetic while the shell structure is characterized by a canting like spin structure which is responsible for the spontaneous magnetization. The anti-ferromagnetic core volume fraction will increases with the increase in the size, which results into decrease in magnetization.

In the present study, sample C (particle size ~ 420 Å) does not saturate at 293 K (figure 4a). Saturation magnetization deduced after correcting the paramagnetic contribution from the magnetization data (figure 4(b). Value thus obtained is 1.4 emu/g. The Finite coercivity values of ~ 70 Oe were also observed at 293K. This shows that system exhibits ferromagnetic or ferrimagnetic ordering. In order to find out the type of magnetic ordering low temperature (5 K) magnetization measurement was carried out.
Figure 4b: Magnetic hysteretic loops at room temperature magnetization curve after subtracting the paramagnetic contribution. Inset: low field magnetization curve.

Figure 4c: Magnetic hysteretic loops at 5 K for sample C. System does not saturate even at this temperature and field.
Figure 4c shows the magnetization curve recorded at 5 K. Magnetization curve does not saturate even in an applied field of 10 kOe and shows finite coercive field of 470 Oe. At 5 K magnetization increases and loop just closes at 10 kOe field. The observed non-saturating behavior and increase in coercivity with decrease in temperature can not be accounted by considering ferro-or-ferrimagnetic type magnetic ordering in the system. Earlier [1,5,6] the increased in magnetization were also explained on the basis of deviation in cation distribution. Rietveld refined data of sample C shows that the percentage of magnetic ions at the tetrahedral A-site (0.03) (Table-1) is well below the percolation threshold for A-site (0.33) [8]. Therefore a long range ferro-ferrimagnetic ordering cannot exist. Thus the observed non-saturating behavior at 293K and 5K indicates probability of formation of magnetic clusters having surface dominated anisotropy (the particle size is < 600 Å).

Figure 5a: Temperature dependent magnetization measured in $H = 10 kOe$

for sample C

The temperature dependent magnetization at 10 kOe field (Fig. 5a) shows a maximum at 10K and change in curvature at around 100K. The observed maximum at 10K is attributed to anti-ferromagnetic ordering arising from the core, which agrees with that reported for the bulk cadmium ferrite. The observed change in curvature at 100K indicates the blocking temperature of magnetic clusters having the canted surface spins. This effect is much evident in the zero field cooled (ZFC) and field cooled (FC) magnetization curves (Fig.5b). Under ZFC and FC conditions, the magnetization showed a down trend at ~20K irrespective of the magnitude of magnetic field (5 to 1000 Oe).
Figure 5b: Temperature dependence of magnetization for the sample C measured in \( H = 5 \text{ Oe} \), and \( 1 \text{ kOe} \) under both Zero field (ZFC, open symbol) and field cooled (FC, filled symbol) conditions. Inset shows ZFC and FC at 100 Oe.

Thus confirming that core is antiferromagnetic having ordering temperature \( < 15 \text{ K} \). Due to two competing interaction between antiferromagnetic core and canted surface spins, the peak at 10K in \( M \) versus \( T \) curve is broaden in ZFC for low field cooled values. But at 1kOe the ZFC peaks around 15K. In addition, the ZFC and FC curves show a hump at around 100K (in low field cooled condition it is more prominent fig. 5b) and irreversibility start for 5Oe field right from 300K. On the other hand for sample cooled in 1 kOe field this irreversibility start from 100 K. The broad hump at 100 K and irreversibility are found to be independent of the cooling field magnitude. This contradicts the Ferro and/or ferrimagnetic type of ordering in the system in which the blocking temperature shifts with field cooling conditions. These observed results can be explained as follows.
(i) For low field cooled condition, the applied field is much less than the coercive field at room temperature (70 Oe). Therefore irreversibility starts from 293K.

(ii) At 100 Oe and 1kOe, the applied magnetic field is greater than coercive field at room temperature therefore one observes the merging of FC and ZFC curve upto 100K.

(iii) The observed fields independent behavior of the irreversibility of FC and ZFC indicates that the surface anisotropy due to canted surface spins dominate below 100K.

(iv) This surface anisotropy also contributes to the hysteresis observed at 293K and 5K as suggested by O Silva et al [7].

Under this case one can consider the particle having a large anti-ferromagnetic core with a canted surface spins. The anisotropy of the surface spin can give rise to coercivity observed at 293K and 5K. The increase in coercivity at 5K indicates that the surface spins dominate at low temperature.

Figure 6a: Temperature and frequency dependence AC-susceptibility real part ($\chi'_{ac}$) measured with an AC field 1 Oe for the sample C.
Figure 6b: Temperature and frequency dependence AC-susceptibility imaginary part ($\chi''_{ac}$) measured with an AC field 1 Oe for the sample C.

Figure 6a-6b shows the frequency dependent real and imaginary part of the susceptibilities for the sample C under the 1 Oe ac-fields. The real part of the AC susceptibility (Fig. 6a) shows a broad maximum at around 125K and secondary hump at around 293K. This is also reflected in the imaginary part of the AC susceptibility (Fig. 6b). These observed peaks are independent of frequency suggesting that the observed magnetic ordering is not a volume effect i.e. the spin disorder is not in entire volume of the particles, but it is only at the surface. These observations are consistent with the magnetic resonance study on cadmium ferrite magnetic fluid by O. Silva et. al [7].

The present investigations suggest that it is possible to synthesize the cadmium ferrite using this modified co-precipitation synthesis route using NaCl as a controlling catalyst at low annealing temperature and significantly reduced the time interval. The bulk magnetic properties are still retained even though the particle size is below 600 Å. The observed magnetic properties can be explained on the basis of an anti-ferromagnetic core with a shell containing ‘ferromagnetic-like’, but canted spin structure.
3.2 Magnetic particles coated with bio-compatible molecules

3.2.1 Physical Characterizations

Figure 7a-b shows the x-ray diffraction pattern for the samples FDX and FECALT respectively. X-ray diffraction pattern for all the three samples exhibited distinct spinel structure with no other impurities phases. The observed lines are broad, indicating the formation of ultrafine single phase spinel structure. Using Scherer’s formula particle size was obtained from most intense (311) reflection and are respectively 113 ± 5 Å, 70 ± 5 Å and 80 ± 5 Å for FDX, FECALT and MZCA samples. The sample prepared at low temperature (~ 288 K) preparative condition (FECALT) exhibits smaller particle size compare to the one prepared at room temperature (FDX).

Figure 7a: X-ray diffraction pattern of FDX sample.
Figure 7b: X-ray diffraction pattern for FECALT sample.

Figure 8: Fourier Transform Infrared Spectra recorded for (a) neat dextran, uncoated Fe$_3$O$_4$ particles and FDX powder, (b) neat citric acid, Fe$_3$O$_4$ particles and FECALT sample and (c) neat citric acid, uncoated MZ5 powder and MZCA particles.
FTIR spectroscopy serves two purposes in characterizing the biocompatible nanomagnetic particles. In ferrites, the metal ions are situated in two different sub lattices designated as tetrahedral A-site and octahedral B-site according to the geometrical configuration of the oxygen nearest neighbors. Waldron [2] and Hafner [9] have attributed the band ~ 600 cm\(^{-1}\) to stretching vibration of the tetrahedral groups (\(v_1\)), while band at 400 cm\(^{-1}\) to the octahedral groups (\(v_2\)). The spectra of neat Dextran, magnetite particle coated with dextran (FDX) and uncoated particle of magnetite are shown in figure-8a. The vibration bands for the dextran are found to be rather broad, as expected due to strong intra- and intermolecular hydrogen bonding. The 1655 cm\(^{-1}\) peak assignable to the C=O vibration in neat dextran is present in the sample as a sharp stretching band. Other stretching bands are at 1012 cm\(^{-1}\), 1159 cm\(^{-1}\), 1459 cm\(^{-1}\) and 2360 cm\(^{-1}\) with shoulders at nearer frequencies. These can be attributed to the C-O-H, C-N/-C-O-C-, C=O/R-CO-NH\(_2\)/RCONHR, C-H bonding. It is evident from the figure-8a that in the uncoated Fe\(_3\)O\(_4\) these bands are absent while coating the same particles with dextran shows the shifts in peak positions. Intensities of all the peaks are comparable to the neat dextran. It suggests the formation of ferrite phase as well as binding of dextran on the Fe\(_3\)O\(_4\) surface through chemi-adsorption’s process.

Figure 8b shows the FTIR spectra of neat Citric acid (CA), Fe\(_3\)O\(_4\) coated with CA and uncoated Fe\(_3\)O\(_4\) particles. Findings are almost similar to that observed by Goodarzi et al [10]. In the present case also the broad band around 1751 cm\(^{-1}\) in neat CA is assigned to the C=O vibration band. Small difference in values can accounted to difference in preparation method, pH and purity of CA. Ferrite phase is clearly visible through the site distribution at ~ 455 cm\(^{-1}\) for A-site and ~ 480 cm\(^{-1}\) and 528 cm\(^{-1}\) for B-site.

Figure 8c shows spectra for the Mn-Zn samples. The first principle band related to ferrite is found near 605 cm\(^{-1}\) (A-site) and the others are at ~ 435 cm\(^{-1}\) and ~ 480 cm\(^{-1}\) (B-site). Clear splitting in MZCA may be attributed to the presence of Mn\(^{2+}\), Zn\(^{2+}\) and Fe\(^{3+}\) ions. A neat CA spectrum shows several peaks between 800 cm\(^{-1}\) to 1400 cm\(^{-1}\). The intensities of all the peaks observed in MZCA are comparable to the neat CA, this suggests that the peaks correspond to physi-absorbed CA and/or unbound CA. No significant shift in the peak values was observed. Further carboxylate C=O peak at ~ 1751 cm\(^{-1}\) observed in neat CA is shifted to ~ 1249 cm\(^{-1}\) in MZCA. This suggests the chemisorption of citrate molecules on MZ5 nanoparticles. TGA data also support these findings.
Figure 9a shows percentage weight loss for FECALT sample. Goodarzi et al [10] have observed that neat CA completely decomposes at temperature ~ 270 °C. They have reported the 40% weight loss up to 300 °C. In FECALT the weight loss is ~ 15% up to 300 °C. This may be due to stronger bonding of CA on Fe₃O₄ particles. Moreover there is about 60°C difference (195 °C and 260 °C) in the weight loss onset temperature rather than 30 °C as observed in ref [10]. Thus in the present case the enthalpy of adsorption of CA molecules on the magnetite surface is larger. The expected net weight loss in the neat CA is 100%, while in FECALT observed total weight loss is 35%. This is attributed to the weight loss to desorption of citric acid molecules from the surface of the magnetite particles. The mass of the surfactant coated on the surface of ferrite particle is calculated using the following equations [10]. If single layer of coating is assumed and there is close-packing of the coating molecules, than the net weight of the particle and that of the molecules all together will be,

\[
\frac{\pi D^3 \rho}{6} + \frac{\pi D^2 M}{a N_0} = A
\]  

Where D is the diameter of the magnetic particle, \( \rho \) is the density, a is the head area of the surfactant molecules. M and \( N_0 \) are molecular weight of the surfactant and Avogadro’s number respectively. With the assumption that only the surface bound surfactant molecules will be lost during the TGA heating then the percentage weight loss from a particle of diameter D is,

\[
\%\text{wt.loss} = 100 \times \left[ \frac{\pi D^2 M}{a N_0} \right] / A
\]

With D = 70 Å (x-ray size), \( \rho = 5.14 \text{ gm/cc} \), a = 21 Å and M = 192.93 the calculated weight loss for FECALT is ~ 20 %. This is lower then the experimental data i.e. 35%. Difference in the experimental value and that of calculated one may be due to the excess and/or unbound surfactant. Because of the strong hydrogen bonding in CA, the molecules might still remain bound and leave a mass on desorption, giving rise to a single step weight loss feature.
Figure 9: TGA graph of (a) FECALT, (b) MZCA and (c) FDX samples.
Figure 9b gives the percentage weight loss for the MZCA sample. It is observed that the total weight loss for this sample is larger than that of FECALT. The curve can be divided into two steps. On increasing the temperature from room temperature up to ~ 250 °C yields first step weight loss and thereafter up to 400 °C these gives the second step weight loss. This two step weight loss can be explained as follows. In the first case weight loss is ~ 35 % and in the second case it is ~ 33 %. The first step may be attributed to the physi-adsorbed molecules of CA. The chemi-adsorbed molecules required larger energy to dissociate from the particle surface and the second step may be attributed to this. The double layer coating of the CA molecules were also inferred from IR spectra. Shen et al [11] have also attributed occurrence of two steps process of weight loss to the existence of chemiadsorbed as well as physi-adsorbed layers.

Figure 9c shows TGA curve for FDX sample. The initial weight loss of ~ 4% in the range 0-200 °C may be attributed to desorption of physically adsorbed water molecules. The remaining 11 % weight loss may be accounted due to removal of dextran. A very small hump around 625 °C indicates that the dextran is loosely bound with the nanoparticles.

3.2.2 Magnetic Characterizations

Figure 10a shows M verses H curve for the samples FDX and FECALT. As expected both samples exhibits superparamagnetic behavior. Magnetization curve of MZCA sample is shown in figure 10b. Table 2 indicates the saturation magnetization (M_s) of the uncoated and coated particles. The lower value of magnetization after coating is due to the coating of the non-magnetic surfactant layer. The percentage of coating derived from these values agrees with that obtained from TGA and IR.
Figure 10: Room temperature magnetization curve of (a) FDX and FECALT samples and (b) MZCA sample.
Table 2 Magnetization values for coated and uncoated samples at 300K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle Size</th>
<th>$M_s$ (uncoated particle)</th>
<th>$M_s$ (coated particle)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{XRD}$ (Å)</td>
<td>(emu/g)</td>
<td>(emu/g)</td>
</tr>
<tr>
<td>FECALT</td>
<td>70</td>
<td>26</td>
<td>16.00</td>
</tr>
<tr>
<td>MZCA</td>
<td>80</td>
<td>15</td>
<td>04.00</td>
</tr>
<tr>
<td>FDX</td>
<td>113</td>
<td>60</td>
<td>51.00</td>
</tr>
</tbody>
</table>

Figure 11: Temperature dependence ac-susceptibility data of FDX (solid line) and $\text{Fe}_3\text{O}_4$ (dashed line) sample.

Temperature dependence of ac-susceptibility for FDX and $\text{Fe}_3\text{O}_4$ samples are shown in figure 11. The coated FDX particle shows the shift in the blocking temperature which is an indicative of coating of the surfactant on the particle surface. Because of coating, physical size of the particle increases which in turn increases the blocking temperature for the spin reversal. Similar behavior was also observed in FECALT (figure 12) and MZCA, but the effective increase in blocking temperature is less compared to FDX. In FECALT the blocking temperature increases with increase in frequency which is a characteristic feature of superparamagnetic particles.
Figure 12: Temperature and frequency dependence AC-susceptibility real part ($\chi_{ac}$) measured with an AC field 1 Oe for the sample FECALT.

The present investigation shows that it is possible to coat the nano-magnetic particles of Fe$_3$O$_4$ and Mn-Zn by biocompatible molecules like dextran and citrate ions. The study reveals that dextran is loosely bounded to the surface of Fe$_3$O$_4$ while a strong bonding was found in the case of citrate ions. The percentage of binding deduced from TGA and magnetization agree well. These coated particles can be used for further bio-medical studies.

3.5 Rare earth Ho-substituted magnetite magnetic fluids

In the present paper our aim is to synthesize and characterize the physical and magnetic properties of rare earth Ho ion doped Fe$_3$O$_4$ magnetic fluid. The motivation for this is the results of our recent studies on syntheses and magnetic properties of Gd doped Mn-Zn magnetic fluid as a potential candidate for the magnetic fluid hyperthermia [12, 13]. In MFH the mechanism of loss is dominated by Neel relaxation and it increases with the increase in Neel relaxation time $\tau_N$ [14, 15]. The substitution of rare earth metal plays an important role in determining the magneto-crystalline anisotropy in 4f-3d inter-metallic compounds. In
view of the above, we have synthesized the stable Ho-substituted Fe$_3$O$_4$ magnetic fluid. The characterization shows that it is possible to substitute Ho rare earth ion in Fe$_3$O$_4$ without disturbing the single phase behavior of the lattice and this substitution enhances the magnetocrystalline anisotropy of the system.

### 3.3.1 Structural characterization of FH particles

Figure 1 shows the x-ray diffraction pattern for the Fe$_{2.9}$Ho$_{0.1}$O$_4$ (FH) particles. XRD pattern shows the single phase spinel structure. Any impurity phase does not exist. The pattern was analyzed using Rietveld refinement program. The analysis confirms the formation of single phase cubic spinel structure. The particle size was determined by Scherrer’s formula for (311) reflection. The volume weighted average crystallite size (diameter D$_{vol}$) and the lattice parameter thus obtained were 117 ± 5 Å and 8.372 ± 0.001 Å, respectively. The Ho ion occupies the octahedral B site of the lattice.

*Figure 13: XRD pattern of FH powder sample.*
3.3.2 Magnetic characterization of FH particles

Room temperature magnetization curve for the Fe$_3$O$_4$ and FH powder sample is shown in figure 14. In the case of magnetite nanomagnetic particles, the value of saturation magnetization is $\sim$ 53 emu/g and for the FH particles it is $\sim$ 42 emu/g. Although the curve suggests that, after substituting Ho-ions in the magnetite particles, it still exhibits a superparamagnetic nature. The magnetite particles, which are synthesized using coprecipitation techniques are usually spherical in nature, therefore to investigate the morphology and the size of the FH particles transmission electron microscopy of the fluid sample were taken.
3.3.3 Structural characterization of FH fluid

The bright field image (Fig-15a) shows that the particles are spherical in shape. In fact, high resolution image of the particles show faceted structures with cube or hexagonal shapes which are tending to grow towards more spherical shape. The selected area electron diffraction (SAED) from a finely dispersed region show the rings made up of discrete spots indicating the highly crystalline nature of the nano-particulates (figure 15b). The SAED pattern is consistent with the spinel ferrite structure with intense ring patterns from (hkl) planes as indexed in the electron diffraction pattern. No other secondary phases could be identified from SAED pattern. Further uniform size and shape indicate the single phase composition of the particles. The size distribution histograms constructed by measuring the size of over 500 particles show >50% of the particles with narrow size of 100 (±10) Å and the rest are distributing over ± 40 Å from the average size of 100 Å.

The size distribution derived from the TEM image is shown in Fig. 2c. The distribution obeys log-normal distribution function given by

\[
P(D) d(D) = \frac{1}{D \sigma \sqrt{2\pi}} \exp \left[ - \frac{\left( \ln \left( \frac{D}{D_m} \right) \right)^2}{2\sigma^2} \right] d(D) \quad \text{.............. (3)}
\]

Where \( \sigma \) is the standard deviation of \( \ln(D) \), \( D \) is the diameter of the particle and \( \ln(Dm) \) is the mean diameter of \( \ln(D) \). The best fit values give the median diameter 97Å and \( \sigma = 0.28 \).
Figure 15: (a) TEM image of FH fluid (b) selected area electron diffraction pattern and (c) particle size distribution histogram.
### Magnetic characterization of FH fluids

Room temperature magnetization curves for the different dilutions (0 to 80% designated as FHD0-D8) are shown in figure 16. Maximum magnetization is observed for the most concentrated sample (FHD0) while on dilution magnetization decreases linearly. The plot of magnetization versus volume fraction (not-shown) shows the linear decrease in magnetization with volume fraction, indicating that fluid is stable on dilution and the probability of cluster formation is negligible. This is also confirms in the case of most diluted fluid (FHD8) sample.

**Figure 16:** Room temperature magnetization measurement for the FH fluid sample with different dilutions. In decreasing order from the upper most curves, the data of FHD0, FHD2, FHD4 and FHD6 fluids respectively.
Figure 17: Room temperature M-H curve for the FHD8 sample. Circle indicates the data point and line is fit to the equation (4).

Figure 18: M-H curve of FHD8 sample at 5K. Finite coercivity observed at this temperature.
The room temperature magnetization curve for the FHD8 sample is shown in Figure 17. The system exhibits zero remanence and coercivity at room temperature. The magnetic behavior of magnetic fluid results from the stable suspension of single domain magnetic particles. For a dilute sample (magnetic volume fraction < 2%) the magnetization curve reflects the orientational effect of an external magnetic field, $H$, on an ensemble of non-interacting magnetic particles which are free to rotate in the solvent. This rotational degree of freedom is responsible for super-paramagnetic behavior in magnetic fluid i.e. zero remanence and coercivity. But at 5K this rotational degree of freedom is hindered by freezing of carrier and one observes the coercivity and remanence (figure 18). The value of which depends on the intrinsic properties of the material. Thus the magnetization of an ideal magnetic fluid, i.e. non-interacting mono-dispersed magnetic particles, is well described by Langevin’s equation,

$$M(H) = M_s L(\alpha)$$

$$L(\alpha) = \coth(\alpha) - 1/\alpha$$

$$\alpha = \mu H / k_B T; \quad M_s = \phi_m M_d$$

Where $L(\alpha)$ is Langevin’s function and $\mu$ is the magnetic moment of the particle, $k_B$ and $T$ are the Boltzmann constant and temperature, respectively. Nevertheless, since the magnetic fluids are always poly-dispersed one has to take into account the size and size distribution (i.e. moment distribution). Considering the equation (3), equation (4) can be rewritten as,

$$M = n \int_0^\infty \mu(D) L(\alpha) P(D) d(D)$$

Where $n$ is the number density of the magnetic particles. The solid line in Fig. 17 is the best fit to equation 5 obtained with $D_m = 80 \pm 5$ Å, $\sigma = 0.30 \pm 0.01$ and $M_d = 320 \pm 10$ emu/cc. The median diameter obtained from magnetization is related to volume weighted average diameter obtained by x-ray by the relation $D_v = D_m \exp(3.5\sigma^2)$. The value thus obtained is 114 Å. This value agrees with that obtained from x-ray.
Figure 19: Temperature dependent magnetization curve for FHD0 sample at 10 kOe. Line is fit to $T^{3/2}$ dependence.

Figure 19 shows the temperature dependent magnetization for FHD0 sample in the field of 10 kOe. There are two regions (i) $T > 50K$ and (ii) $T \leq 50K$. In the $T > 50K$ the magnetization decreases with increase in temperature. This behavior can be explained by considering $T^{3/2}$ dependence (Line through the data point). However this is not true for $T \leq 50K$, an increase in magnetization was observed as temperature decreases. This transition at $T \sim 50K$ indicates Ho spin alignment due to applied external magnetic field. Similar behaviors were also reported by others Ho doped samples [17, 18].

Temperature dependence magnetizations were carried out for FHD8 and FHD0 samples for the FC and ZFC conditions. For the zero fields cooled (ZFC) measurements the sample was cooled down to 5K in absence of magnetic field and a constant magnetic field was applied during the warming up scan. In the field cooled measurements (FC) the samples was cooled down to 170K (below the solidification of the carrier) in absence of field and then cooled in the presence of magnetic field down to 5K. The FC data were recorded in warm up cycle in the same magnetic field.
Figure 20: Temperature dependence magnetization for the FHD0 sample measured at 100 Oe field under both the conditions zero field (ZFC, open symbol) and field cooled (FC, filled symbol) conditions.

Figure 21: Temperature dependence magnetization for the FHD8 sample measured at 50 Oe field under both the conditions zero field (ZFC, open symbol) and field cooled (FC, filled symbol) conditions.
Figure 20 & 21 shows FC-ZFC data of FHD0 and FHD8 samples respectively. For the concentrated sample the irreversibility between the field cooled and zero field cooled curves starts at 90 K while for diluted sample it starts from 75K. There is also striking difference between the two FC curves. For concentrated sample the FC curves levels off at low temperatures in contrast to the diluted sample that show a continuous increase in magnetization with decreasing temperature. This is due to the influence of dipole-dipole interaction in the concentrated sample.

The temperature dependence of zero field cooled samples for FHD8 and FHD0 are shown in Figure 22 and 23 respectively. As expected the ZFC magnetization increases with increasing temperature to reach a maximum and then decreases. If one assumes that particles are mono-dispersed non-interacting than the maximum of the ZFC curve (blocking temperature $T_B$) can be used to calculate anisotropy constant following the relationship $KV = k_B T_B \ln(\tau_m / \tau_0)$ with the measuring time $\tau_m = 100s$ and $\tau_0 = 10^{-10}s$. The initial susceptibility for a single domain particle of volume $V$ is given by,

$$\chi_{SPM} = \frac{M_s^2 V}{3k_B T}; \quad \text{For superparamagnetic particles (T > } T_B)$$

$$\chi_{bl} = \frac{M_s^2}{3K}; \quad \text{For blocked particles (T < } T_B)$$

In a real fine particle system, there is a distribution of particles sizes which gives rise to a distribution of blocking temperatures. Therefore, a system of particles having a well defined, narrow size distribution exhibits a sharp peak in ZFC curve and the broadening of this curve indicates presence of particles with larger size distribution. To take into account of the size distribution in the determination of anisotropy constant, a simple model is used

$$\frac{M_{ZFC}(T)}{H} = \frac{M_s^2(T)}{3k_B T} \int_0^{V_b} f(V) V^2 dV \quad \text{......... (6)}$$
Figure 22: Temperature dependence of the ZFC for concentrated FHD8 magnetic fluid. The measured values of the susceptibility have been normalized by the factor $3.7\%/\phi_m$.

Figure 21: Temperature dependence of the ZFC for concentrated (FHD0) and diluted (FHD8) magnetic fluid. The measured values of the susceptibility have been normalized by the factor $3.7\%/\phi_m$. 
Where $M_{ZFC}$, $V$, $f(V)$ and $V_B$ are the magnetization in the ZFC process, the particle volume, volume distribution, and the blocking volume, respectively. The model assumes that saturation magnetization is volume independent. The effective anisotropy energy barrier for our magnetic fluid sample was estimated from experimental results on the most diluted sample, which models a system of non-interacting particles. Using the fact that the particle volumes are approximately log-normally distributed (equation 3), the temperature dependence of the ZFC for FHD8 was calculated. A good fit was obtained using the values of $D_m = 80 \pm 5$ Å, $\sigma = 0.30 \pm 0.01$ and $K = 3.5 \times 10^5$ erg/cc. These values of particle size and size distribution agree well with that obtained from magnetization and TEM data. The increase in anisotropy value for the Ho doped sample compare to pure magnetite ($10^4$ erg/cc) may be due to the large anisotropy of Ho moments.

With increasing volume concentration of magnetic particles, dipole-dipole interaction increases. Under this condition the energy barrier for particle rotation increases and the blocking temperature shifts towards higher temperature. Similar behavior is observed in the case of concentrated sample. The blocking temperature shifts from 55K for FHD8 to 66K for FHD0 magnetic fluid. Therefore considering the energy barrier distribution we have tried to fit the concentrated magnetic fluid ZFC behavior. The best fit was obtained for $D_m = 80\pm5$ Å, $\sigma = 0.40\pm0.01$ and $K = 4 \times 10^5$ erg/cc. This shows that dipole-dipole interaction increase the value of $\sigma$ and anisotropy energy.

In the present study, we show that it is possible to incorporate Ho rare earth ion in the matrix of magnetite without altering the single phase behavior. The substitution has drastically modified the energy barrier height and the blocking temperature shifts towards the low temperature. The value of saturation magnetization of Ho-doped magnetite is not decreased compare to un-doped sample. This helps in to achieve the super paramagnetic range till 150 K.
3.4 CTABr – magnetic fluid emulsion

3.4.1 Magnetic & rheological properties of water based magnetic fluids

Room temperature magnetization measurements were carried out for the water based magnetic fluid (figure 24). Langevin’s theory and log normal size distribution were used to fit the magnetization data. The fit parameters obtained are: \( M_d = 320 \text{ emu/cc} \), \( D_m = 105 \text{ Å} \), \( \sigma = 0.26 \) and \( M_s = 50 \text{ Gauss} \). Here, \( M_d \), \( D_m \), \( \sigma \) and \( M_s \) are domain magnetization of particle, median diameter of particle, standard deviation in lnD and saturation magnetization of fluid, respectively.

![Figure 24: Room temperature magnetization curve of water based magnetic fluid. Solid line is fit to theory and circles are experimental data points.](image)
The zero magnetic field viscosity \( \eta(H=0) \) of water based magnetic fluid exhibits Newtonian behavior with viscosity of 1.7 cP @ 303K. Figure 25 shows reduced rotational viscosity (\( \eta_R \)) versus applied magnetic field (H) for different temperatures. Here, viscosity increases with the field. This increase in viscosity may be explained using ferrohydrodynamical model given by Shliomis [18]. According to this model the reduced rotational viscosity is given by,

\[
\eta_R = \frac{\eta_r(\alpha)}{\eta_r(\infty)} = \frac{\alpha L^2(\alpha)}{\alpha - L(\alpha)} \quad \text{………….. (7)}
\]

Where \( L(\alpha) \) is Langevin’s function with \( \alpha = \mu H/k_B T \), \( \mu \) is magnetic moment of particle, \( H \) is applied field, \( k_B \) is Boltzmann constant and \( T \) is absolute temperature. Rajesh et al [19] have verified this model by incorporating polydispersity in size. Thus it is also possible to derive the size and size distribution from the field dependent viscosity measurement.

\[\text{Figure 25: Reduced rotational viscosity of water based magnetic fluids versus applied magnetic field at different temperature 313 K (△), 323 K(■) and 333 K(●).}\]
In figure 25 the solid line is fit to the equation (7). The best-fit parameters obtained are $M_d = 320$ emu/cc, $D_m = 110$ Å and $\sigma = 0.4$. These values are close to that obtained from magnetization measurements. Using Rosensweig’s equation [20] and fit parameters, surfactant thickness of 36 Å was obtained. This value agrees with that obtained from the Small Angle Neutron Scattering experiment (SANS) (34 Å). Activation energy for flow was calculated using Andrade’s law for the temperature 313K, 323K and 333K (figure-26)[21]. With increasing magnetic field activation energy increases up to 250 Oe thereafter exhibits saturation behavior. This indicates that field induced structural changes are completed for $H > 250$ Oe.

![Figure 26: Activation energy (kCal/mol) verses applied field (Oe).](image-url)
3.4.2 *Rheological properties of CTABr-magnetic fluid emulsion*

Earlier, as discussed in chapter 1(section 1.3.2), magnetic fluid (MF) is successfully used to orient the CTABr micelles in moderate magnetic field. Their molarity of CTABr micelles was fixed i.e. 0.1M with various concentration of magnetic fluids i.e. 5 to 30%. To investigate the same system in-detail, we have prepared the CTABr-magnetic fluid emulsion with various molarity of CTABr and different concentrations of magnetic fluid.

Stability of any magnetic fluid can be checked by diluting the fluid. On dilution, if the characteristics e.g. magnetization, viscosity etc. of the fluid varies linearly, than the fluid is said to be stable over dilutions. Figure 27 shows the zero field viscosity of pure magnetic fluid with varying hydrodynamic volume fraction. On increasing magnetic fluid concentration viscosity increases linearly. This linearity shows the Newtonian behavior of the fluid and also suggests that fluid is stable over the dilutions. The increase in viscosity can be explained using Einstein’s relation, which is valid only for the non-interacting fluid system. It shows that in the magnetic fluid, the probability of cluster formation is negligible.

Figure 28 shows the zero field viscosity data of CTABr micelles with different molarity. Viscosity increases linearly with increasing molar concentrations. This suggests that, in this range, the probability of aggregation is very less.

A rheological property of both the parent solutions, i.e. CTABr solution and magnetic fluid varies linearly on dilutions and are Newtonian in nature. However, CTABr – MF emulsion with varying molarity of CTABr micelles shows some different result. Zero field viscosity of 5% magnetic fluid-CTABr emulsion with varying CTABr concentrations is shown in figure 29. Where, a peak was observed at 0.01M CTABr concentrations. A gradual increase in viscosity was observed above 0.03M CTABr concentrations. It was also observed that this peak shifts towards high concentration with increasing fluid concentration.
Figure 27: Zero field viscosity data of water based magnetic fluids for different concentrations.

Figure 28: Viscosity of CTABr micellar solutions with various molarity of CTABr.
Figure 29: Zero field viscosity of 5% MF-CTABr emulsion versus varying CTABr concentrations.

Figure 30: Reduced rotational viscosity of 5% MF (●), C51 (■), C53 (▲) and C55 (○) samples with varying applied magnetic field.
In order to study the effect of magnetic field on CTABr micelles, in-field viscosity measurements were carried out for three different samples containing different concentration of CTABr micelles i.e. C51, C53 and C55. Figure 30 shows the reduced rotational viscosity as a function of magnetic field. It appears that as the concentration of micelles increases magnitude of the field dependent changes decreases.

The observed nonlinear behavior in figures 29 & 30 for emulsion could be due to (i) two body interactions as predicted by Batchelor for spheres [22], (ii) non-spherical particle shape or (iii) non-steric interactions between particles (which could be dominant for a system containing charged surfactant!). Any of the above may cause nonlinearity in the viscosity. At present it is difficult to explain these behaviors.

The present work indicates that the soft CTABr micelles can have significant effect on flow behavior of the mixture under an applied magnetic field. The non-linearity in the viscosity may be due to the existence of an interaction between micelles and magnetic particles whose nature is yet to be established.
3.5 Dispersion of Magnetic fluid & μ-sized particles

A stable colloidal suspension of micron sized spheres in magnetic fluid is known as magnetic fluid composite. Recently, our group has observed an unusual diffraction effect in a dispersion of magnetic particles in a ferrofluid [23]. The sample consists of 3- micron sized magnetite particles stabilized by the surfactant and dispersed in a magnetic fluid. Result shows that, the diffraction pattern completely disappears at a particular magnetic field [23]. On further increase in the field the pattern reappears. The observed disappearance of diffraction pattern may be due to the competing torques viz. that due to the effective magnetic moment associated with the hole and the approximate permanent moment of the magnetic large particle. As the field increases, the moment of the large particle will tend to align more and more along the direction of the field. At the same time the effective moment of the hole which is antiparallel to the field also increases [24]. At a critical field, $H_c$, both moments will be equal and opposite and on further increase in the field the net moment will be reversed with respect to the direction of the applied field. This can explain modulation of diffraction pattern with field but not disappearance of the pattern. Suppose at the field $H_c$ large cluster forms and this obstruct the light but then further increase of the field should not let the cluster dissociate and the pattern again reappears. Thus we can not explain the phenomenon on the basis of the above model. So as to get better understanding of this phenomenon some more experiments were needed. Thus, we have decided to study in detail optical characterization of magnetic fluid composite for various concentrations of micron size particles and tried to understand the phenomenon of disappearance.

Magnetic fluid composites were prepared for different micron size magnetic particles i.e. 0.5 μm, 1.0 μm, 2.0 μm and 3.0 μm. The detail characterization of magnetic fluid and micron sized magnetic particles are discussed below.
3.5.1 Magnetic characterization of magnetic fluid

Figure 31 shows the room temperature magnetization curve for Fe$_3$O$_4$ kerosene based magnetic fluids. Using the equation (5) the magnetization curve was fitted; the solid line in the figure 31 is the best fit. The fit parameters obtained are: $M_d = 310$ emu/cc, $D_m = 98$ Å, $\sigma = 0.3$ and $M_s = 312$ Gauss. Here, $M_d$, $D_m$, $\sigma$ and $M_s$ are domain magnetization of particle, median diameter of particle, standard deviation in lnD and saturation magnetization of fluid, respectively. Density of magnetic fluid is 1.0936 g/cc and number density of nanomagnetic particles is $5.45 \times 10^{17}$ per cc.

Figure 31: Room temperature magnetization of Fe$_3$O$_4$ magnetic fluid. Circles correspond to data points and line is fit to the Langevin’s theory.
Figure 32: Microscopic images of surfactant coated (a) 0.5 µm (1 cm = 3.6 µm), (b) 1.0 µm (1 cm = 0.9 µm) and (c) 2.0 µm (1 cm = 0.9 µm) sized magnetite particles.
3.5.2 Characterization of micron sized magnetite particles

The preparation of micron sized particles is discussed in Chapter 2 (page 42). To get the specific sized of micron sized particles, bulk magnetite particles (> 30 micrometer) were milled for different time duration. The milled particles were cleaned and coated with oleic acid. The dispersion of these coated particles in kerosene gives a stable magnetic fluid in gradient magnetic field. Microscopic images were taken to confirm the size of the particles. Figure 32a-c show typical picture of particles obtained after 390mts, 260mts and 130 mts of grinding, respectively. The average particle sizes were found to be ~0.5µm, 1µm and 2µm, respectively. The density of these suspended particles is 0.8472 g/cc, 0.8122 g/cc and 0.8915 g/cc for the 0.5µm, 1µm and 2µm particles respectively. The diffraction patterns were recorded for the four different micron sized particles having different volume concentrations (Table 2). In the present study, the original suspension (i.e. with the addition of micron sized particles and magnetic fluids) was diluted by 80%, to eliminate multiple scattering effects.

Table 2: Magnetic micron sized particle suspension.

<table>
<thead>
<tr>
<th>Particle size (µm)</th>
<th>Suspension of µ-sized particles Y (ml)</th>
<th>Magnetic fluid X (ml)</th>
<th>Sample Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.2</td>
<td>1.0</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.8</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.6</td>
<td>C</td>
</tr>
<tr>
<td>1.0</td>
<td>0.2</td>
<td>1.0</td>
<td>D</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.8</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.6</td>
<td>F</td>
</tr>
<tr>
<td>2.0</td>
<td>0.2</td>
<td>1.0</td>
<td>G</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.8</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.6</td>
<td>I</td>
</tr>
<tr>
<td>3.0</td>
<td>0.2</td>
<td>1.0</td>
<td>J</td>
</tr>
</tbody>
</table>
A linearly polarized He-Ne laser beam of 10 mW power was used as the light source. This beam was passed through the sample contained in a 0.2 cm optical path length glass cell. The cell was placed between the pole pieces of small electromagnet (maximum field ~850 Gauss) energies by a constant power supply. The polarization vector of the incident light was oriented parallel or perpendicular to the transverse electromagnetic field by the magneto-optical technique [25]. Forward scattering patterns as a function of the applied magnetic field were recorded by CCD camera connected to a personal computer.

Recently it was shown that when micron size magnetite particles are dispersed in kerosene based ferrofluid the field induced Fraunhoffer diffraction pattern disappears at a certain critical field [23]. This effect could not be accounted on the basis of available theoretical models of magneto-optical effects [24]. Our further investigations on the above effects revealed that the disappearance of the Fraunhoffer diffraction occurs only when the magnetite spheres are dispersed in a ferrofluid and we attribute it to the zero forward scattering by the magnetic spheres. The detail description of the investigation is discussed as follows.

Figure 33 and 34 show the diffraction patterns for the sample J, in the case of electric vector $\mathbf{E}$ of the incident light parallel and perpendicular to the applied magnetic field $\mathbf{H}$ respectively. At zero field the diffraction pattern exhibits isotropic scattering due to the micron sized magnetic particles. On increasing the magnetic field, the ferrofluid becomes electrically as well as magnetically anisotropic. The field modulates the diffraction patterns for both the polarization states $\mathbf{E} \parallel \mathbf{H}$ and $\mathbf{E} \perp \mathbf{H}$. In the case of $\mathbf{E} \perp \mathbf{H}$ (Fig.34), critical field of disappearance was observed at 100 Gauss (Figure 34 (fourth pattern)). While in the case of $\mathbf{E} \parallel \mathbf{H}$ no such disappearance of diffraction pattern was observed. This results have lead us to believe that the observed disappearance of diffraction pattern, in the composite of magnetic fluids and micron sized spheres, at critical field may be attributed to the zero forward scattering by the magnetic micron sized spheres, first predicted by Kerker et al [26].
In order to verify that the zero forward scattering occurs only when the magnetic scatterers are dispersed in the ferrofluid, we have recorded diffraction patterns for the following samples.

(i) Medium is ferrofluid but dispersed phase is non-magnetic micron sized silica particles.

(ii) Dispersed particles are micron sized magnetite particles and the medium is magnetically passive liquid i.e. kerosene.

The zero forward scattering was not observed in either of the samples for $E \perp H$ as well as $E \parallel H$. Typical diffraction patterns are shown for $E \perp H$ (figures 35 & 36). This confirms that the zero forward scattering occurs only when the dispersed phase is magnetic and the medium is ferrofluid.

Single scattering of electromagnetic waves by magnetic spheres was studied earlier by Kerker et.al. [26]. Theoretically, several unusual scattering effects were predicted. In small particle limit, the forward scattering will become zero when the scatterers satisfy the condition between the relative electric permittivity ($\varepsilon$) and the relative magnetic permeability ($\mu$). Such effects are rather difficult to observe at optical frequencies under normal conditions since in this range $\mu \approx 1$ [26]. Experimental verification of the above unusual effect has not been so far reported. Hence the present finding of ZFC is the first experimental observation of this effect. We shall first briefly describe salient features of Kerker theory and thus interpret the present finding on the above theory.
Figure 33: Diffraction pattern for $E \parallel H$ to the applied magnetic field for sample J.

Figure 34: Diffraction pattern for $E \perp H$ to the applied magnetic field for sample J. Diffraction pattern completely disappears at $H_c = 100$ Gauss (fourth pattern).

Figure 35: Diffraction pattern for $E \perp H$ to the applied magnetic field in the case of 2-3 µm silica spheres dispersed in a magnetic fluid.

Figure 36: Diffraction pattern for $E \perp H$ to the applied magnetic field in the case of 3 µm magnetic spheres dispersed in kerosene.
When a beam of electromagnetic radiation passes through a medium, part of the energy of radiation is removed and remaining is transmitted through the medium. The fraction of the removed part may be absorbed in the medium and the remaining fraction is scattered in the same as well as all other directions. The amount of absorbed and scattered energy depends upon the nature of the scatterers as well as upon the wavelength of the incident radiation in the medium ($\lambda$). When the scatterers are magnetic spheres dispersed in a homogeneous medium, the intensity and state of polarization of the scattered beam depend on size, the relative electric permittivity ($\varepsilon = \varepsilon_s / \varepsilon_m$) and the relative magnetic permeability ($\mu = \mu_s / \mu_m$) [26]. Where subscript $s$ ‘s’ and ‘m’ stands for scatterers and medium with $\mu_m = \mu_0$, which leads to real refractive index $m_m = \sqrt{\varepsilon_m \mu_0}$. The relative refractive index of the scatterers will be $\frac{m}{m} = \frac{\mu_s}{\mu_m} = \sqrt{\mu \varepsilon}$ where $\mu = \mu' + i \mu''$ and $\varepsilon = \varepsilon' + i \varepsilon''$ are the complex relative magnetic permeability and electric permittivity respectively. Then using Mie formalism, the scattered intensities of two polarized components are given by [27,28],

\[ I_1 = \left(\frac{\lambda^2}{4\pi r^2}\right) S_1 \left| \frac{\partial}{\partial \phi} \sin^2 \phi \right| \]  
\[ I_2 = \left(\frac{\lambda^2}{4\pi r^2}\right) S_2 \left| \frac{\partial}{\partial \phi} \cos^2 \phi \right| \] ......... (8)  

Where $r$ is the distance between the scatterers and the observer, $\phi$ is the angle between the electric vector of the incident wave and the scattering plane and $I_1$ and $I_2$ are the intensities for the two orthogonal states of polarization viz. for the electric vector perpendicular and parallel to the scattering plane.

The scattering amplitudes are given by,

\[ S_1 = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \left[ a_n \pi_n (\cos \theta) + b_n \tau_n (\cos \theta) \right] \]  
\[ S_2 = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \left[ a_n \pi_n (\cos \theta) + b_n \tau_n (\cos \theta) \right] \] ......... (10)

The $\pi_n (\cos \theta)$ and $\tau_n (\cos \theta)$ are the partial derivatives of the Legendre Polynomials and $\theta$ is the angle between the forward and scattering directions. $a_n$ and $b_n$ are the electric and magnetic moments of multipole sources located at the origin. Expressions for $a_n$ and $b_n$ are
given by Kerker et al. [26]. For small particles only the first term of \( a_n \) and \( b_n \) will be significant and are given by [26]

\[
a_1 = \frac{2i}{3} \left( \frac{2\pi a}{\lambda} \right)^3 \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) \quad \text{................. (12)}
\]

\[
b_1 = \frac{2i}{3} \left( \frac{2\pi a}{\lambda} \right)^3 \left( \frac{\mu - 1}{\mu + 2} \right) \quad \text{................. (13)}
\]

Substituting these values in Eq. (10) and (11) \( I_1 \) and \( I_2 \) transforms to,

\[
I_1 = \frac{\lambda^2}{4\pi^2 r^2} \left( \frac{2\pi a}{\lambda} \right)^6 \left[ \frac{\varepsilon - 1}{\varepsilon + 2} \cos \theta + \left( \frac{\mu - 1}{\mu + 2} \right)^2 \cos^2 \phi \right] \sin^2 \phi \quad \text{................. (14)}
\]

\[
I_2 = \frac{\lambda^2}{4\pi^2 r^2} \left( \frac{2\pi a}{\lambda} \right)^6 \left[ \frac{\varepsilon - 1}{\varepsilon + 2} \cos \theta + \left( \frac{\mu - 1}{\mu + 2} \right)^2 \cos^2 \phi \right] \quad \text{................. (15)}
\]

Therefore the condition to observe zero forward scattering i.e. \( I_1(0^0) \) and/or \( I_2(0^0) = 0 \) for \( \theta = 0 \) is given by,

\[
\varepsilon = \frac{4 - \mu}{2\mu + 1} \quad \text{............... (16)}
\]

Obliviously the condition will not be satisfied for both the states of polarization simultaneous when both \( \varepsilon \) and \( \mu \) are field as well as polarization dependent.

Under the influence of magnetic field ferrofluid exhibits induced anisotropy and the medium becomes birefringent [29]. Consequently the condition for zero forward scattering (equation 16) will be different for parallel and perpendicular states of polarization.

As discussed earlier, disappearance of diffraction pattern was observed only in the case of \( \mathbf{E} \perp \mathbf{H} \), while no such phenomena was observed for \( \mathbf{E} \parallel \mathbf{H} \) configuration. According to Mehta [29], a ferrofluid becomes birefringent under the influence of applied magnetic field. Hence \( \varepsilon_{\parallel} \) and \( \varepsilon_{\perp} \) will be different for the two orthogonal polarization states. The condition for zero forward scattering is found to be satisfied only for \( \mathbf{E} \perp \mathbf{H} \) i.e \( I_1 \) and not for \( \mathbf{E} \parallel \mathbf{H} \) i.e \( I_2 \). This also confirms the deduction by Kerker et.al. [26]. Thus all the observed effects described above can be accounted if we consider field variation of relative
permittivity and relative permeability of the magnetic scatterers with respect to the magnetic fluid and assumes that at a particular field expression (16) is satisfied. For further confirmation of this model we carried out the following experiments.

In low concentration regime (dipole-dipole interactions is negligible) permittivity and permeability will vary linearly with the concentration. Hence it is expected that the critical field, $H_c$, at which the zero forward scattering is observed, will also vary linearly with concentration. We have carried out the study for three different concentration of the original fluid.

The diffraction patterns were recorded for samples A to C. The change in diffraction pattern was observed for all the three samples with increasing field. In the case of sample C, disappearance of diffraction pattern was observed at a critical field, $H_c = 560$ Oe magnetic field (Figure 37). No disappearance of diffraction pattern was observed for sample A and B up to 800 Oe field. There are two possibilities, (i) either the field required to observe the disappearance of diffraction pattern is greater than the applied limit or (ii) the number density of particle is large (because the domain magnetization of magnetite particle remains constant for this size range).

Figures 38a -c show the diffraction patterns for samples D-F. It is evident from the figures that the critical field of disappearance is different for different volume fraction of the large particles ($Y$) and it decreases linearly with the increasing $Y$ (Figure 39). The change in the critical field with $Y$ is $1200$ Oe/ml. Similar behavior was also observed in the case of samples G to I. (Figures 40a-c). In this case also the linear decrease in $H_c$ with $Y$ was observed, but the rate is $120$ Oe/ml (fig. 39). The last two results indicate that the change in critical field with $Y$ drastically increase with decrease in the size of the micron size magnetic particles. This supports the argument that the field required to observe disappearance in diffraction pattern is higher than 1000 Oe for samples A and B.
Figure 37:  Diffraction patterns for sample C.

Figure 38a:  Diffraction patterns for sample D.

Figure 38b:  Diffraction patterns for sample E.

Figure 38c:  Diffraction patterns for sample F.
Figure 39  Variation in critical magnetic field with different volume concentration of 1 micron (●) and 2 micron (◆) magnetite particles.

Figure 40:   Diffraction patterns for sample G (top) for sample H (middle) and for sample I (bottom)
Table 3: Critical magnetic field for the different samples.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample Code</th>
<th>Critical magnetic field ($H_c$) (Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>560</td>
</tr>
<tr>
<td>2</td>
<td>D</td>
<td>800</td>
</tr>
<tr>
<td>3</td>
<td>E</td>
<td>450</td>
</tr>
<tr>
<td>4</td>
<td>F</td>
<td>320</td>
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<tr>
<td>5</td>
<td>G</td>
<td>308</td>
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<tr>
<td>6</td>
<td>H</td>
<td>290</td>
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<tr>
<td>7</td>
<td>I</td>
<td>260</td>
</tr>
<tr>
<td>8</td>
<td>J</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 41: Dependency of critical magnetic field ($H_c$) for zero forward scattering on concentration and on the size of the scatterers dispersed in a magnetic fluid.
Figure 41 shows the plot of $H_c$ vs. concentration of magnetic fluids. The linearity confirms the above deduction. Similarly, $H_c$, also depends on the volume of the micron sized magnetic scatterers (figure 41). The dependency of $H_c$ on (i) concentration and (ii) on the size of the scatterers being analyzed on the basis of effective medium theory given by Maxwell_Gernett [30]

The present investigations demonstrate that it is possible to magnetically induce the zero forward scattering at optical frequency with proper combination of ferrofluid and magnetic scatterers. Recently, Mach et al [31] have reported electrically switchable Bragg diffraction, utilizing liquid crystal in colloid-base structures. A similar study with comparatively simpler materials and experimental condition is possible with the present method. Like liquid crystals magnetic fluid can also be ordered by magnetic fields. Dielectric polymers here are replaced by micron sized magnetic particles.

Similarly photonic crystals of self assembled colloids have recently generated a good deal of interest [32,33]. Like those crystals in the present system too suitable periodicities, symmetries and magnetic contrast (there it was dielectric constant) can be generated and exhibit stop bands or full band gaps at optical or near-ir wavelength. Thus we can have optical switches and waveguides.
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