Chapter 4: Temperature dependent magnetic and structural ordering of self assembled magnetic array of FePt nanoparticles

A 2D assembly of 3 nm monodispersed FePt nanoparticles synthesised by co-reduction method is reported in this chapter. A structural transformation from a chemically disordered face centred cubic (FCC) phase to a chemically ordered face centred tetragonal (FCT) phase with heat treatment was observed. The percentage chemical ordering was estimated by XRD profile fitting. The structural transformation was further confirmed by the presence of two superlattice rings using the selected area electron diffraction (SAED). Transmission electron microscopy (TEM) shows the grain growth with annealing temperature. TEM also shows the presence of a coating of carbonaceous layer confirmed through Raman studies. An attempt to understand the array using FFT of TEM is presented. The soft/hard compositions have also been investigated using the hysteresis measurements.
4.1 Introduction

The number of bits per unit area (i.e. areal density) of the media recording devices is increasing now days. The increase in the areal density can be achieved by (i) reduction of size of the recording bits of the recording media (ii) reduction of the size of reading and writing head and (iii) reduction of the spacing between the magnetic recording media and reading / writing head. The reduction in size of recording bit is limited by the thermal fluctuation of the magnetic moments/spins resulting in a spontaneous magnetization reversal process known as superparamagnetism below a certain critical diameter. To overcome this undesirable limitation, a material with high magnetocrystalline anisotropy is required. The alloy of iron-platinum (FePt) (tetragonal, $L1_0$ type structure and space group P4/mmm) with nearly equiatomic composition have high magneto crystalline anisotropy ($7 \times 10^7$ J/m$^3$) and chemical stability (Sun et al. 2000; Kim et al. 2007; Nguyen et al. 2006; Yao et al. 2008; Zeng et al. 2003; Sasaki et al. 2004; Andrew et al. 2004). This high value of $K$ is due to the spin orbit interaction between Fe and Pt and hybridization between the 3d state of Fe and 5d state of Pt elements (Gutfleish et al. 2005; Medwal et al. 2012; Laughlin et al. 2005; Skomski et al. 2003).

The FePt films prepared by physical techniques are found to be highly crystalline but with an inhomogeneous size distribution. However, chemically synthesized FePt nanoparticles capped with a surfactant, results not only in a very homogeneous distribution of size and shape but also provide chemical stability to the system. Chemical processes e.g. reduction, co-reduction and seed-mediated growth etc have been used to synthesize FePt nanoparticles (Sun et al. 2000; Elkins et al. 2003; Sasaki et al. 2005; Sun et al. 2003). Depending on the preparation methods, different shapes and structures can be obtained. (Chen et al. 2006; Chen et al. 2004; Hou et al. 2006). The most common precursor used in the synthesis of FePt alloy are iron pentacarbonyl (Fe(CO)$_5$) and Pt(acac)$_2$. The disadvantages associated with Fe(CO)$_5$ are its highly toxic nature and highly flammable nature even at room temperature. The boiling point of Fe(CO)$_5$ is low (103$^\circ$C) as compared to the melting point of Pt(acac)$_2$ (249$^\circ$C) thereby making it difficult to maintain the composition of the alloy $Fe_xPt_{1-x}$ (Nguyen et al. 2006). The Fe(acac)$_2$ is also used in
the synthesis of FePt alloy as an alternative precursor to form monodispersed 2D array and in this chapter, Fe(acac)$_2$ have been used as iron precursor for the synthesis of FePt array nanoparticles.

Annealing at higher temperatures results in the process of coalescence to form bigger particles followed by the conversion of the superparamagnetic FCC phase to ferromagnetic FCT phase. Achieving the ordering temperature at which the FCC phase transform completely to FCT (L1$_0$) phase before coalescence process starts is of current research interest. Hence, lowering down the ordering temperature while retaining the smaller particle size is an important aspect of L1$_0$ system. Rong et al. demonstrated an alternative method of controlling the sintering growth of nanoparticles by annealing the FePt nanoparticles in the nonmagnetic matrix which can sustain high degree of heat (Rong et al. 2008).

In this chapter, an attempt has been made to synthesize monodispersed array of FePt nanoparticles using the co-reduction chemical method in the presence of different concentration of surfactant. The systematic studies of the structural and magnetic transformation using the Rietveld and deconvolution of hysteresis respectively have been investigated as a function of annealing temperature. The effect of the surfactant on the 2D array has also been investigated.

### 4.2 Experimental Procedure: Synthesis of FePt array

FePt nanoparticles were synthesized by the chemical co-reduction method (Sun et al. 2000; Medwal et al. 2012). The metal precursors iron(III) acetylacetonate (Fe(acac)$_3$, 97% pure) and platinum(II) acetylacetonate (Pt(acac)$_2$, 97% pure) were co-reduced using 1,2 hexadecanediol which serves as a reducing reagent. Phenyl ether was used as a solvent in presence of oleic acid and oleylamine which act as surfactants. All the above mentioned chemicals were procured from Sigma Aldrich and were used as obtained for the preparation of the FePt nanoparticles.

Fe (acac)$_3$ is a ferric salt which gets easily oxidized in oxygen atmosphere. Hence an oxygen free environment is created throughout the experiment. A stoichiometric amount of Pt (acac)$_2$ (0.5 mmol) and Fe(acac)$_3$ (0.5 mmol) were mixed in 40 ml
phenyl ether in the presence of 0.5 mmol of oleic acid and oleylamine with 4 mmol of 1,2 hexadecanediol. This mixture was stirred for one hour at room temperature under argon atmosphere. The chemical co-reduction of metallic precursors into metal nanoparticles occurs by refluxing the solution at 250 °C for one hour with continuous stirring in the presence of high purity argon gas. During refluxing the colour of the solution changes from yellowish pink to black indicating the formation of FePt nanoparticles. The solution was allowed to settle down at room temperature under inert atmosphere. On the addition of 40 ml ethanol a precipitate was obtained which was separated by centrifugation at 12000 rpm for 15 minute and washed with ethanol twice. Finally, the powder obtained was dispersed in hexane and used for further characterization. The flow chart describing the synthesis is given in Figure 4.1. Different concentration of oleic acid and oleylamine were used to control the array and self-assemblage.

![Flow chart describing the synthesis of FePt nanoparticles](image)

**Figure 4.1: Flow chart describing the synthesis of FePt nanoparticles**
The solution obtained was dispersed on polished silicon substrate <001> for characterization and annealing. The samples were annealed at 600 °C, 700 °C and 750 °C to investigate the structural and magnetic transformation. In order to confirm monodispersity and self assemblage, TEM were first performed and the results are presented in the following section.

4.3 Results and Discussion

4.3.1 Transmission Electron Microscopy

![TEM image of monodispersed FePt array with oleic acid: oleylamine in mM](a) 0.5:0.5 showing hexagonal closed packing (b) 0.5:1 showing honey comb packing (c) 1:0.5 showing increased interparticle distance (d) 1:1 showing disturbed array (e) Typical SAED obtained for the above arrays.)
Figure 4.2 (a,b,c and d) shows TEM images of the as prepared FePt nanoparticles dispersed on carbon coated copper grid synthesized by using the different ratios of oleic acid to oleylamine viz. 0.5:0.5, 0.5:1, 1:0.5 and 1:1 respectively. All the TEM images reveal a very well organized monodispersed FePt array with the particle size ~3 nm. The interparticle distance can be controlled with oleic acid and oleylamine used as a surfactant during the synthesis. The hexagonal closed packed FePt array shown in Figure 4.2(a) is observed for the 0.5 mmol; 0.5 mmol concentration of oleic acid and oleylamine respectively. The hexagonal closed packed structure can be tuned to honey comb packed array by increasing the surfactant ratio as shown in Figure 4.2(b). On further increasing the concentration of surfactant, the interparticle distance can be increased as visualised in Figure 4.2(c) and Figure 4.2(d) followed by disturbance of array. The surfactant not only acts as stabilizing ligands for the FePt nanoparticles but also help in the formation of array of larger area which is essential for recording media. Typical SAED is shown in Figure 4.2(e) obtained for the above array and confirms the formation of FCC phase. The interparticle distances were estimated using the digital micrograph software shown in Figure 4.3. The estimates obtained for the different concentrations of oleic acid and oleylamine is tabulated in Table 4.1. It is important to mention that the largest area of the array was observed for the hexagonal closed pack system with 0.5mmol: 0.5mmol oleic acid and oleylamine for which further investigations were performed on the system.
Table 4.1: Interparticle distances as a function of spacer

<table>
<thead>
<tr>
<th>Oleic acid : Oleylamine</th>
<th>Interparticle distances</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5:0.5</td>
<td>3.3 nm</td>
</tr>
<tr>
<td>0.5:1</td>
<td>3.2 nm</td>
</tr>
<tr>
<td>1:0.5</td>
<td>5.0 nm</td>
</tr>
<tr>
<td>1:1</td>
<td>5.5 nm</td>
</tr>
</tbody>
</table>

4.3.2 Understanding FFT tool in TEM analysis

The self assembly obtained using the chemical synthesis of FePt has been understood using the Fast Fourier Transformation (FFT). Fourier transform is a very good tool for the image processing. Fourier transform can be defined as given below:

\[
X(\omega) = \int_{-\infty}^{\infty} X(t) e^{-j\omega t} dt
\]

(4.1)

This integral defines an operation over \(X(t)\) in time domain to \(X(\omega)\) in frequency domain where \(\omega\) is in frequency.

\[
X(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} X(\omega) e^{-j\omega t} d\omega
\]

(4.2)

Analogy to this, inverse Fourier transforms can be defined as a decomposition of function \(X(t)\) into the basis functions i.e. sum of sines and cosines which carry information of amplitude and frequency of the function. The coefficients of these basis functions in the expansion carry phase information. Alteration in the amplitude of components with certain frequencies of the function \(X(t)\) one can be easily understood in terms of different frequencies present in the function \(X(t)\). Digital data contains the discrete data points that are mapped as the quantization of continuous signals in the image. Hence Discrete Fourier transforms work on the sampled image signal. It is used to analyze various frequencies contained in image with certain periodic cycle. In order to understand, a set of data is assumed which can be formulated as:

\[
X_k = \sum_{n=0}^{N-1} X_n e^{-j\frac{2\pi}{N} kn}; k = 0, \ldots, N - 1
\]

(4.3)

Its discrete inverse transform is defined as

\[
X_n = \frac{1}{N} \sum_{k=0}^{N-1} X_k e^{j\frac{2\pi}{N} kn}; n = 0, \ldots, N - 1
\]

(4.4)
Let us assume the two dimensional function \( h(x,y) \), the Fourier transform for this function is defined as

\[
\begin{align*}
    h(u,v) &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} h(x,y) e^{-j2\pi xy} \, dx \, dy \\
    &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} h(x,y) e^{-j2\pi ux} dx \, dy \\
    &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} h(x,y) e^{-j2\pi uy} dy \, dx \\
\end{align*}
\]

(4.5)

Similar to the one dimension case, two dimensional transformations can be executed as two successive one dimensional Fourier transforms. Hence, function \( h(x,y) \) can also be decomposed in the form of \( \cos[2\pi(ux + vy)] \) and \( \sin[2\pi(ux + vy)] \)

The inverse of this two dimensional Fourier transform can be defined as

\[
\begin{align*}
    h(x,y) &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} h(u,v) e^{j2\pi(ux+vy)} du \, dv \\
\end{align*}
\]

(4.6)

The discrete quanta of the data in the spatial domain can be easily mapped with reciprocal space using discrete Fourier transform tool as shown in Equation 4.2. Hence, similar to the one dimensional discrete Fourier transform, two dimensional parent of any continuous pattern can be defined in two dimensional discrete Fourier transformations.

\[
\begin{align*}
    h(u,v) &= \frac{1}{MN} \sum_{x=0}^{M} \sum_{y=0}^{N} h(x,y) e^{-j2\pi \left(\frac{ux}{M} + \frac{vy}{N}\right)} \\
\end{align*}
\]

(4.7)

The inverse of the above Fourier transformation is given as:

\[
\begin{align*}
    h(x,y) &= \frac{1}{MN} \sum_{x=0}^{M} \sum_{y=0}^{N} h(u,v) e^{j2\pi \left(\frac{ux}{M} + \frac{vy}{N}\right)} \\
\end{align*}
\]

(4.8)

where \( N \) and \( M \) are pixels of processed image.

### 4.3.3 Filtering and reconstruction

The obtained image is filtered by performing the FFT of the image in the spatial domain. The bright spots corresponding to different frequencies are observed in the FFT processed image. This image is used to apply masking and removal of some unwanted frequencies in an image. Thereafter, the image is reconstructed using the inverse discrete transformation in two dimensional real spaces. An illustration and flow diagram of the image filtering and reconstruction is pictorially represented in Figure 4.4 and Figure 4.5 respectively.
The method of filtering and reconstruction is employed to understand the building block of FePt array formation in the hexagonal close packed structure and represented in Figure 4.6. FFT performed on the image reveals the hexagonal...
positional ordering of nanoparticles in 2D assembles and shown as Figure 4.7. The indexing of the FFT pattern has been done using the JEMS software and shown in Figure 4.8 by considering the zone axis along [001].

**Filtering in the Frequency Domain: Convolution**

![Flow diagram of the process of the image sampling](image)

**Figure 4.6: Flow diagram of the process of the image sampling**

![Hexagonal closed packed FePt array with hexagonal FFT pattern as an inset.](image)

**Figure 4.7: As obtained hexagonal closed packed FePt array with hexagonal FFT pattern as an inset.**
The filtering and reconstruction on the TEM image of FePt array has been performed using the Digital Micrograph. Using Fourier filtering technique, a special spatial frequency filter is used by applying the masking on the FFT image. By applying the masking, to allow and block a specific frequency of periodic arrangement, the separation of signal and noise can be obtained. A similar procedure has been applied for the array shown in Figure 4.7 and the constructed image with their FFT is shown as an inset in Figure 4.9 and Figure 4.10. Figure 4.9 shows the processed image with four different frequencies. Figure 4.9(a) shows the background signal which may be due to the carbon coated grid surface or the capping agents while Figure 4.9(b,c,d) shows the filtered image for other allowed frequencies. Among all three frequencies Figure 4.9(c) shows the best filtered image. It can be understood that rest of frequencies may be attributed to the different form of noise signals. In the practical case, these noise signals arise from (i) over or underlayers (ii) non-uniform capping at certain distance (iii) physically disturbed array.

Figure 4.8: Indexing of obtained hexagonal pattern using the JEMS software with [001] as a zone axis.
In order to reconstruct the image, an exercise has been performed by superimposing the images one over the other. This can be done by the use of math tool in the Gatan digital micrograph. **Table 4.2** list the reconstruction of image as given in Figure 4.9 using the superposition of the figures given in Figure 4.10. Figure 4.10(c) exactly resembles with the as obtained FePt array showing the presence of three different periodic arrangements with different frequencies.

**Figure 4.9** FFT Filtered hexagonal closed pack array with their respective FFT as an inset.

**Table 4.2**: Reconstruction of FePt array using the FFT

<table>
<thead>
<tr>
<th>Figure 4.9</th>
<th>Figure 4.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>a+b</td>
</tr>
<tr>
<td>b</td>
<td>a+b+c</td>
</tr>
<tr>
<td>c</td>
<td>a+b+c+b</td>
</tr>
<tr>
<td>d</td>
<td>Original image obtained from TEM (Figure 4.7)</td>
</tr>
</tbody>
</table>
4.3.4 Effect of annealing on array of FePt nanoparticles

The dispersed arrays were subjected to different annealing temperature and HRTEM and SAED were recorded. At high temperature the surfactant starts degrading and the particles coalesce. The sintering growth effect dominates leading to the formation of particles with bigger size. Figure 4.11 shows the TEM of sample annealed at 600°C along with HRTEM showing the lattice fringes with an interplaner distance of 2.22\(\text{Å}\) corresponding to (111) plane of FePt. The presence of the superlattice rings (001) and (110) in the SAED given in inset (Figure 4.10) reveals the formation of chemically ordered FCT phase. The evolution of superlattice rings is due to the chemically arranged Fe and Pt stacking in the FePt unit cell on annealing. The size of nanoparticles has been estimated with log normal distribution function with average particle size of 5nm as shown in Figure 4.11(c).

On further annealing at 750°C the particles are found to attain irregular shape of bigger size as shown in Figure 4.12(a). The indexed SAED pattern is shown in Figure 4.12(b). The presence of superlattice ring corresponding to (001) and (110)
confirms the formation of ordered L1\textsubscript{0} phase. The sharpness of the ring indicates the enhanced crystallinity.

**Figure 4.11:** (a) TEM images of FePt array annealed at 600\textdegree C with SAED as an inset (b) HRTEM image showing lattice fringes (c) particle size distribution

HRTEM shown in **Figure 4.12(c)** shows the interplaner distance of 2.20 Å which is indentified as the (111) plane. A capping over the FePt nanoparticles has also been observed in HRTEM. It is well known that with annealing, the organic surfactant capped nanoparticles converts into the carbonaceous coating on the surface of FePt nanoparticles. This carbonaceous capping was investigated using Raman spectra. The Raman spectra showed the presence of D band and G band peak as shown in **Figure 4.12(d)** due to the presence of graphitic carbon layer over the FePt nanoparticles (Medwal et al. 2012). **Figure 4.13** shows the TEM image for the particles annealed at 750\textdegree C, demonstrating coalesce and sintered growth of the nanoparticles. The area under the marked circle shows the inter particle diffusion bridge between two coalesced nanoparticles. The random interparticle diffusion and fast growth rate leads to the formation of the irregular and elongated shapes of the annealed nanoparticles. Further XRD measurements were performed on the samples annealed at different temperatures to confirm the phase transformation and the details are given below.
Figure 4.12: (a) TEM images of FePt array annealed at 750°C (b) corresponding SAED (c) HRTEM image showing the lattice fringes corresponding to (111) (d) Raman spectra corresponding to carbonaceous layer over the FePt nanoparticles.

Figure 4.13: TEM images of hexagonal closed packed FePt array annealed at 750°C showing the coalescence and sintered growth of the FePt nanoparticles.
4.3.5 Structural studies

XRD measurements have been performed on as prepared samples and samples annealed at different temperatures. The annealed samples exhibit both FCC and FCT phase. The percentage of FCC and FCT in the annealed samples depends upon the annealing time and temperature. To investigate the phase composition of FCC and FCT in the system the Rietveld analysis has been performed on the as prepared and annealed samples. The fitting of experimental XRD patterns has been performed using double phase model for Fm3m and P4/mmm space group. The details of the Wyckoff position of both Fe and Pt in the unit cell used for the analysis are given in Chapter 3 and reported elsewhere (Medwal et al. 2012; Hahn 2005). Figure 4.14 shows the XRD pattern of as prepared nanoparticles with plane corresponding to (111) indicating the presence of disordered face centered cubic phase (A1). The samples were subjected to heat treatments at 600°C, 700°C and 750°C for investigating the structural transformation. The samples annealed at 600°C shows the evolution of FCT with superlattice peaks corresponding to (001) and (110) of L1_0 phase confirming the onset of FCT phase (L1_0 Type) shown in Figure 4.15(a) and Figure 4.15(b). Further annealing at higher temperature (700°C and 750°C) also enhance the intensity of superlattice peaks at 2θ 24.01° and 32.89° corresponding to (001) and (110) respectively. The splitting observed for (200) reveals the transformation from cubic (A1, Fm3m) to tetragonal (L1_0, P4/mmm) as shown in Figure 4.16 and Figure 4.17.

The estimated percentage for FCC and FCT phase with an error of ±1% using the profile fitting at different annealing temperatures are tabulated in Table 4.3. The percentage of FCT phase is enhanced on annealing reaching a maximum of 95% for sample annealed at 750°C. Hence some amount of retention of FCC phase was observed.

This evolution of superlattice peaks is due to the rearrangement of the Fe and Pt position in the unit cell of FePt alloy giving rise to chemical ordering. The rearrangement of Fe and Pt position depends upon the degree of annealing temperature and time for which sample is exposed. This rearrangement results in a distortion in the unit cell and a contraction of lattice in c direction. This is due to the difference in the atomic radii of Fe and Pt. This is also accompanied with shift in 2θ value for (111) and splitting of (200) peaks.

Lattice parameter has been estimated for both FCC and FCT phase. The estimated c/a ratio for FCC and FCT phase were used for the analysis of degree of ordering while
intensity of superlattice peaks are taken into account to investigate the ordering parameter. The estimation of degree of ordering (S) and ordering parameter S* is given in detail in Chapter 3. These are tabulated in Table 4.4. The ordering estimated from (c/a) ratio was about 97.95% while ordering parameter gives an estimate of 93%. The S* determined from intensity of superlattice peaks are more reliable compared to S, to estimate the chemical ordering. The estimate is close to that obtained using Rietveld refinement.

Table 4.3: Percentage of FCC and FCT phase of FePt alloy using Rietveld analysis

<table>
<thead>
<tr>
<th>FePt Annealing Temperature (°C)</th>
<th>FCC (%)</th>
<th>FCT (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Prepared</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
<td>38</td>
<td>62</td>
</tr>
<tr>
<td>700</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>750</td>
<td>5</td>
<td>95</td>
</tr>
</tbody>
</table>

Table 4.4: Degree of ordering and ordering parameter as a function of annealing temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>c/a</th>
<th>Degree of ordering S</th>
<th>I_{001}/I_{111} (%)</th>
<th>Ordering parameter (S_{001}) (%)</th>
<th>S*</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Prepared</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
<td>0.9848</td>
<td>0.6881</td>
<td>8</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>0.9801</td>
<td>0.7873</td>
<td>19</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>0.9692</td>
<td>0.9795</td>
<td>26</td>
<td>93</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.14: Phase investigation from Rietveld refined X-ray diffraction pattern of as prepared FePt array.
Figure 4.15: Phase investigation from Rietveld refined X-ray diffraction pattern (in red) of FePt array annealed at 600°C (a) contribution to FCC (b) contribution to FCT.

Figure 4.16: Phase investigation from Rietveld refined X-ray diffraction pattern of FePt array annealed at 700°C (a) contribution to FCC (b) contribution to FCT.
4.3.6 Magnetic studies

In order to study the effect of annealing on magnetic properties of FePt nanoparticles, hysteresis loop of the array dispersed on silicon substrate was recorded for all the samples. The as prepared nanoparticles exhibit superparamagnetic behaviour with zero coercivity and no tendency to saturate as shown in Figure 4.18. An estimate of the $H_c$ contributed by the individual soft and hard magnetic phase for the annealed samples was made, using the percentage obtained from XRD Rietveld analysis. The enhancement in the coercivity with annealing temperature is visible from the loop. A maximum coercivity of about 1T is observed for 750°C annealed sample. The observation of a shoulder at low fields indicates the coexistence of the hard and soft magnetic phase. The normalized M-H loops corresponding to annealed samples were deconvoluted using the equation 4.9 (Kang et al. 2005).

$$M(H) = \sum_n \frac{2M_s}{\Pi} \text{arctan} \left( \frac{H + H_c}{H_c} \right) \tan \left( \frac{S_q}{2} \right)$$  \hspace{1cm} (4.9)
where $M_s$ is the saturation magnetization, $H_c$ is the coercivity, $S_q$ is the squareness (ratio of $M_r$ to $M_s$) and $n$ is the ferromagnetic components in the system.

The deconvoluted loop along with the curve fitting for sample annealed at $600^\circ$C, $700^\circ$C and $750^\circ$C are shown in Figure 4.19, Figure 4.20 and Figure 4.21 respectively. The fitting has been performed with two ferromagnetic components, the hard magnetic FCT ($L1_0$) and soft magnetic FCC (A1) phases. The contribution of hard magnetic and soft magnetic part from the total has been determined from the deconvolution of experimental data and tabulated in Table 4.5.

From the Table 4.5, for the sample annealed at $600^\circ$C the net coercivity of the FePt nanoparticles is low due to the presence of high percentage of soft magnetic phase confirming the partial ordering of phase. The increase in coercivity is observed with increase in the annealing temperature with low degree of soft phase which is in conformity with the XRD analysis. The onset of the hard phase is observed at $600^\circ$C with low value of $H_c$ $0.27$ T. This transforms to a hard magnetic phase with large value of $H_c$ $\sim 1$ Tesla at $750^\circ$C, along with small amount of soft phase, which is in agreement with the XRD measurement.
Figure 4.19: M-H loop of FePt array annealed at 600°C

Figure 4.20: M-H loop of FePt array annealed at 700°C
Table 4.5: Estimated hard and soft magnetic composition of annealed FePt array at different temperature using the deconvolution of MH loop.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Experimental (Hc in Oe)</th>
<th>Hc (in Oe) Soft</th>
<th>Hc (in Oe) Hard</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Prepared</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
<td>2700</td>
<td>890</td>
<td>11930</td>
</tr>
<tr>
<td>700</td>
<td>9420</td>
<td>3250</td>
<td>12310</td>
</tr>
<tr>
<td>750</td>
<td>10030</td>
<td>6970</td>
<td>13940</td>
</tr>
</tbody>
</table>

4.4 Conclusion

Formation of monodispersed FePt nanoparticles in the form of 2D array using oleic acid and oleylamine as a spacer has been demonstrated. It was observed that the interparticle distance in the FePt array can be manipulated by varying the ratio of oleic acid and oleylamine. The 0.5 mM oleic acid and 0.5 mM oleylamine gives the completely closed packed hexagonal array which can be tuned to honey comb closed packing with 1 mM oleylamine. The use of FFT as a tool to reconstruct the TEM image of the hexagonal closed packed array was demonstrated (Figure 4.22).
The long range positional ordering up to 100 nm has been observed with as prepared nanoparticles due to the presence of spacer. The structural transformation in the case of the hexagonal closed packed assembly is found to be $95 \pm 1\%$ using XRD profile fitting at $750^0$C. At higher temperatures, disorder in the 2D FePt array along with increase in the particle size is observed which is attributed to coalesce and sintered growth of the nanoparticles. The deconvolution of room temperature hysteresis loop recorded for different annealing temperature was used to estimate the fraction of composition of hard and soft magnetic phase. The theoretical investigation for the various fraction of soft and hard phase is essential to understand the above behaviour and this work is in progress.
4.5 References


