CHAPTER 9

MAGNETIC PROPERTIES OF NANOPARTICLES

9.1 Introduction

Magnetic properties of nanoscale particles are of great interest since they are expected to differ substantially from their bulk counterparts. The quest for smaller particles which can be used for recording purposes continues since smaller particles implies higher data storage densities. New magnetic materials are also being used for reading and recording magnetically encoded information. Recently nanocomposites composed of ferromagnetic particles exhibited giant magneto-resistance (GMR) and are important for magnetic sensors to read magnetically stored data. Magnetic nanostructures are also important objects of investigations for basic materials research. Many interesting magnetic properties are related to the dynamics of the spin system. At low temperatures, the magnetic moment (total electronic spin) of the system may spontaneously change direction in a quantum tunnelling process. At higher temperatures, the spin direction will fluctuate due to thermal agitation and at the same time the magnitude of the magnetic moment will reduce, and eventually vanish at high enough temperatures (Curie temperature).

The magnetic properties at the surface of small particles are significantly altered from those of the bulk. Since the number of nearest neighbours is reduced in a nanoparticle, the valence electron tends to spend more time at each ionic site. Weaker bonding to neighbouring sites causes the ions to have more isolated atom character, i.e., the electrons and hence the moments are more localized than in the bulk. Thus the surface of nanoparticles contains a large number of magnetic ions with lower coordination and broken exchange bonds.
particle size increases, the spin imbalance decreases. In the bulk material, magnetic field energy is considerably reduced through the formation of domains. Within a domain, the magnetisation is uniform in one direction and the direction varies from one domain to the next. The net effect is a great reduction in the magnetic field strength and hence the magnetic field energy. Domain walls (Bloch walls) are energetically costly, since in traversing a wall, the spin orientation changes at the expense of the exchange coupling, which prefers aligned spins. Consequently domains tend to be relatively large of the order of 1 μm. Small magnetic particles therefore, are typically monodomain since the energy cost to form a domain wall outweighs the reduction in magnetic energy. Typically critical sizes for monodomain particles are in the range of 20-200 nm and depend on the material under consideration.

The direction of the magnetic moment in a small particle is determined by both the shape of the particle and its crystal structure through the anisotropy effects. Shape anisotropy accounts for preferential orientation of the magnetic polarization along the long axis for elongated particles. This is due to the fact that total magnetic field energy is minimised for this polarisation. The magnetisation also prefers alignment along specific crystallographic axes. This is the crystalline anisotropy effect, which dominates over the shape anisotropy in very small particles. Physically the spin system couples to the crystal lattice via the spin orbit interaction. Axes of preferential magnetization are called the easy axes of magnetization.

There are two important characteristics exhibited by magnetic nanoparticles, viz. superparamagnetism and spin canting. Superparamagnetism is the paramagnetism of small particles with a large magnetic moment. In simple paramagnetism, each atom is considered as having a resultant spin depending on the number of unpaired electrons. In the case of nanoparticles, all the moments (resultant spin) of the atoms of that particle will be in one direction giving rise to a large net moment for that particle. This nanomagnetic particle
with a huge particle moment is a superparamagnet if it can behave like a
paramagnet above certain temperature called blocking temperature. The
thermally activated switching behaviour of the particle leads to
superparamagnetism and one can find 1/T-temperature dependence above the
blocking temperature. Spin canting is a phenomenon especially seen in
magnetic nanoparticles when the spins at the surface deviate from the normal
orientation and cant to form a wave like (magnon like) arrangement to reduce
the net energy. When a magnetic field is applied, there is lack of full alignment
of the spins in the direction of the field in the case of small particles.

There are a number of reports dealing with the magnetic property
investigation of nanoparticles by studying the variation of magnetization as a
function of temperature.\textsuperscript{2-9,16-19} Unusual magnetic properties have been observed
in nanocrystals of ZnFe\textsubscript{2}O\textsubscript{4}\textsuperscript{16,20} due to surface effect and ferrimagnetic ordering.
The magnetic study of CuO\textsuperscript{7} nanoparticles of size below 10nm exhibited
nanoparticle magnetism with uncompensated surface spins resulting in a weak
ferromagnetic component. Also Neel temperature was found to be lower than
that of bulk CuO. Magnetic anisotropic contributions have been studied in
single Co\textsuperscript{21} nanocluster using a micro-SQUID set up on the basis of surface
property of nanoparticles. The magnetic study of nanocrystals of
Ba\textsubscript{2}CO\textsubscript{2}Fe\textsubscript{28}O\textsubscript{46} has revealed that the specific saturation magnetisation is lower
than that of its bulk and inversely proportional to grain size.\textsuperscript{22} Antiferromagnetic
ordering of Mn\textsubscript{3}O\textsubscript{8} nanoparticles was studied using temperature variation-
magnetic susceptibility measurements.\textsuperscript{23}

It has been found that electron paramagnetic resonance (EPR) or
electron spin resonance (ESR) spectroscopy is a useful tool for studying
magnetic structures and their change under the influence of external parameters
like magnetic field, temperature etc. X-band ESR investigations were carried
out on a number of nanoparticles to study the spin dynamics and magnetic
nature of particles.\textsuperscript{9,23-26} In the case of ferrihydrite nanoparticles, the observed
ESR spectrum was attributed to the uncompensated surface $\text{Fe}^{3+}$ spins resulted from broken exchange bonds.\textsuperscript{26} X-band EPR spectrum of $\text{Mn}_{12}$ acetate nanoparticle has been used to give valuable information about the spin dynamics at low temperatures.\textsuperscript{25} The temperature variation of ESR spectrum of $\text{Fe}_2\text{O}_3$ nanoparticles has been used to give information about the anisotropy energy and interparticles interaction.\textsuperscript{24} Based on the study of these results it was felt that magnetic study of nanoparticles would yield interesting results.

In this chapter, magnetic studies of $\text{FePO}_4$ and $\text{ZnFe}_2\text{O}_4$ nanoparticles are described. In the case of $\text{FePO}_4$, measurements were carried out using VSM, SQUID magnetometer and X-band ESR spectra. For $\text{ZnFe}_2\text{O}_4$ nanoparticles of size range 4 nm to 28 nm, the magnetic moment variation with field was measured using VSM at room temperature. Temperature variation of magnetic moment was also studied using SQUID magnetometer. For $\text{FePO}_4$ nanoparticles, the temperature variation of magnetic susceptibility and ESR spectra were studied. The purpose of this work is to study how the magnetic properties of $\text{FePO}_4$ and $\text{ZnFe}_2\text{O}_4$ are influenced by the small size of the particles. Before discussing the nanomagnetic properties, it is relevant to know the structure and magnetic behaviour of bulk $\text{FePO}_4$ and $\text{ZnFe}_2\text{O}_4$ studied so far.

$\text{FePO}_4$-Structure and Magnetic Behaviour

At room temperatures, $\text{FePO}_4$ has the berlinite $[\text{AlPO}_4]$ structure which is closely related to that of $\alpha$-quartz having iron and phosphorus tetrahedrally co-ordinated with oxygen. Bulk $\text{FePO}_4$ has been studied as an antiferromagnetic material ordered below $25K$.\textsuperscript{27,28} But magnetic studies of nanocrystalline $\text{FePO}_4$ has not been reported.
**ZnFe$_2$O$_4$ - Structure and Magnetic Studies Carried out so far**

The structure of spinel oxides AB$_2$O$_4$ consists of a close packed fcc arrangement of oxygen atoms with two non-equivalent crystallographic sites A and B with tetrahedral and octahedral coordination. For the ferrite spinel ZnFe$_2$O$_4$, Zn$^{2+}$ and Fe$^{3+}$ distribution at A and B sites within the structure can be represented by the formula [Zn$_{8}$ Fe$_{1-\delta}$]$^A$ [Zn$_{1-\delta}$ Fe$_{1+\delta}$]$^B$ O$_4$, where $\delta$ is the inversion parameter. In the case of normal spinel $\delta = 1$ and for inverse spinel $\delta = 0$. For partly inverted spinel $\delta$ is in between 0 and 1.\textsuperscript{29,30} The crystalline bulk form of ZnFe$_2$O$_4$ is a normal spinel ferrite with Zn$^{2+}$ ions only on the A site and Fe$^{3+}$ ions only on B site and is characterised as an antiferromagnet below 10K.\textsuperscript{20} Recent investigations of nanocrystalline ZnFe$_2$O$_4$ have suggested that the cation distribution in this material is partly inverted and exhibits anomaly in its magnetization.\textsuperscript{20,29,31} Magnetic studies on nanophase ZnFe$_2$O$_4$ by many scientists reported that they are ferrimagnetically ordered with high ordering temperature and high magnetic moment.\textsuperscript{20,29,31-34} From investigations of stoichiometric zinc ferrite nanoparticles,\textsuperscript{29,35,36} it has been found that ferrite particles of similar composition differ in their magnetic properties depending on the preparation techniques.

In nanoparticle zinc ferrites, some of the magnetic ions (Fe$^{3+}$) occupy the tetrahedral A sites which give rise to a strong coupling between Fe$^{3+}$ ions at A and B sites due to A-B super exchange interaction.\textsuperscript{29} This leads to ferrimagnetism. Changes in Fe$^{3+}$ distribution in octahedral and tetrahedral sites induce drastic changes in the magnetic properties.\textsuperscript{16} The octahedral and tetrahedral sublattices are therefore antiparallel and since the number of octahedral sites is twice the number of tetrahedral sites, an uncompensated magnetic moment occurs. This structure is called ferrimagnetic.\textsuperscript{16,37} In nanophase ZnFe$_2$O$_4$, disorder is introduced in the structure through occupancy of Zn$^{2+}$ ions on the octahedral sites and these sites are the main surface constituent in nanoparticles.\textsuperscript{29,37} The amount of Zn and Fe occupation is
dependent on the particle size. The finer the particles, the more the zinc on the B site and iron on A site.\textsuperscript{29,38} Thus it is reasonable to think that Fe\textsuperscript{3+} ions situated on A sites according to the cation distribution Zn\textsubscript{1-x}Fe\textsubscript{x} [Zn\textsubscript{x}Fe\textsubscript{2-x}]O\textsubscript{4} forms a cluster with its 12 nearest Fe\textsuperscript{3+} neighbours at B sites through coupling. Probably the number of clusters may increase with decreasing particle size.\textsuperscript{29}

High magnetization observed in nano ZnFe\textsubscript{2}O\textsubscript{4} may be due to short range ordering of the samples. It is reported that the saturation magnetization of ZnFe\textsubscript{2}O\textsubscript{4} is quite high (\textapprox 70 emu/gm) but lower than that expected for a ferrimagnetic structure.\textsuperscript{37} The difference between measured value and calculated value is attributed to spin canting in octahedral sites.\textsuperscript{37} It must be mentioned that the surface spins may also contribute to the observed magnetization as they are expected to be large in number due to size effect of particles.\textsuperscript{29} In the case of nonstoichiometric zinc ferrite nanocrystal, it was reported that the magnetic ions located at the surface have fewer neighbours than in the core or in the bulk material disturbing the magnetic phase at the particle surface and spin canting properties are observed.\textsuperscript{16} Thus surface effects, vacancies or poor crystallinity and disorder are expected to cause spin-glass behaviour or local spin canting in nano zinc ferrite.\textsuperscript{16,31,37}

The effect of reactant concentration on particle size and hence on magnetic properties is discussed here. Moreover ZnFe\textsubscript{2}O\textsubscript{4} is found to be the most interesting ferrite to study the effect of grain size on magnetic properties. It was reported that the reduction of the magnetic material leads to novel properties as compared to bulk material, due to the small volume (superparamagnetism) or the high surface to volume ratio (spin canting).\textsuperscript{6} So the studies have been carried out to learn more about the magnetic behaviour of nanoparticle ZnFe\textsubscript{2}O\textsubscript{4}. 

9.2 Experimental

9.2.1 FePO₄ Nanoparticles

Nanoparticles of FePO₄ were prepared by chemical method as described in section 3.2.2 of chapter 3. Three samples of FePO₄ of reactant concentrations (1M, 0.1M and 0.02M) were used for the magnetic moment and susceptibility measurements with VSM. Room temperature measurements were carried out by EG & G model 155 vibrating sample magnetometer. The ESR spectra of 0.02M sample were recorded with a standard reflection type X-band (9.25 GHz) spectrometer equipped with a Varian microwave cavity and a variable temperature cryostat system (4-350K). Measurements of magnetisation versus temperature (4-300K) for 0.02M FePO₄ sample were done with a SQUID magnetometer (Quantum Design Model).

9.2.2 ZnFe₂O₄ Nanoparticles

Nanoparticles of ZnFe₂O₄ were prepared by co-precipitation technique as described in section 3.2.3 of chapter 3. Three samples of reactant concentrations 0.1M, 0.01M and 0.002M having particle sizes 6, 5.5 and 5.4 nm were used for the magnetic moment and magnetic susceptibility measurements at room temperature using VSM. Different samples of 0.1M ZnFe₂O₄ were annealed at temperatures 300, 500, 700 and 850°C so as to vary the particle size. The particle size determined from XRD line broadening as described in section 3.6.3 of chapter 3 is 6, 12, 21 and 28nm respectively. Magnetic moment was measured for these samples using VSM by varying the magnetic field from 2 to 10 kGauss. Then the gram susceptibility ψₖ and molar susceptibility ψₘ were calculated. The effective magnetic moment μₘₐₓ = 2.828 (ψₘT)₁/₂ was calculated for each sample. Here T is the room temperature in Kelvin. Measurements of magnetization against temperature in field-cooled (FC) and zero-field-cooled (ZFC) modes were performed in a SQUID magnetometer between 5 and 300K for three samples. In these measurements, the samples were zero-field cooled.
to 5K and a magnetic field $H=1000$ Oe was then applied and magnetic moments were measured with increasing temperature. In FC measurements, the sample was cooled to 5K with the field $H=1000$ Oe and then magnetic moments were measured with increasing temperature.

9.3 Results and Discussion

9.3.1 FePO$_4$ Nanoparticles

Fig. 9.1 and 9.2 show the variation of magnetic moment and molar susceptibility with reactant concentration measured at room temperature. It is found that magnetic moment and molar susceptibility vary with reactant concentration and are minimum for 0.02M sample having smallest particle size. This change in magnetic moment can be attributed to size effect of small particles. As the particle size decreases, the disorder of the magnetic moment orientation on the surface of the particles increases resulting in decrease of magnetic moment.\textsuperscript{16,22}

![Graph showing variation of magnetic moment with magnetic field for different molarities of FePO$_4$.](image)

**Fig. 9.1:** Variation of magnetic moment with magnetic field for different molarities of FePO$_4$
Fig. 9.2: Variation of molar susceptibility with reactant concentration for FePO₄

Fig. 9.3 shows the temperature variation of FC and ZFC magnetic susceptibilities of 0.02M sample. Here the ZFC and FC curves coincide at high temperature, while at lower temperature they start to separate reaching a maximum value in $\psi$ corresponding to 26°C. This temperature may correspond to the blocking temperature of FePO₄ nanoparticles and also corresponds to the blocking of the largest particle, since blocking temperature ($T_B$) is particle size dependent. Below this temperature, $\psi$ decreases with decrease in $T$. Such behaviour is characteristic of superparamagnetism exhibited by nanoparticles. Thus $\psi$-$T$ graph clearly shows that the FePO₄ particles studied are in the nanometer size range. Superparamagnetism is the temperature dependent blocking of the magnetisation of particles whose size determines a magnetic anisotropy comparable to thermal energy. Since the anisotropy is proportional to volume of the particles, the blocking deblocking process is different for particles of different size. As seen from the plot, the increase in magnetisation with the decrease in temperature is due to the decrease in thermal energy. It is known that the energy of a magnetic particle in an external field is proportional to its
size via the number of magnetic molecules in a single magnetic domain. When this energy becomes comparable to thermal energy, thermal fluctuations will considerably reduce the total magnetic moment at a given field. \(^{30}\)

![Graph showing variation of FC and ZFC magnetic susceptibilities with temperature](image)

**Fig. 9.3:** Variation of FC and ZFC magnetic susceptibilities with temperature

It can be observed that in Fig. 9.3, FC curve shows a peak. Most of the data described in literature shows either an increase or a plateau in the magnetization with decreasing temperature in FC curve.\(^7\),\(^17\),\(^24\) Usually, large interactions between particles induce a plateau or increase in magnetization not far below the separation between FC and ZFC curves without any peak.\(^16\),\(^17\) However, a peak was observed at low temperature for haematite\(^40\) (\(\alpha\)-Fe\(_2\)O\(_3\)) and maghemite\(^41\) (\(\gamma\)-Fe\(_2\)O\(_3\)) nanocrystals. In the case of cobalt ferrite nanocrystals of size 3.2nm also a peak was observed in the FC curve.\(^17\) In most cases it was observed that the process which could explain such change in FC curve shape could be interactions between particles.\(^16\),\(^17\),\(^41\) Based on the above results the FC peak observed in Fig. 9.3 may be attributed to an indication of assembly of non-interacting FePO\(_4\) nanoparticles. Moreover the magnetic moment is found to be small. If there was interaction between particles the
magnetic moment value would have been high.\textsuperscript{17} Thus FC and ZFC curves of FePO\textsubscript{4} show that the particles are non interacting and superparamagnetic with varying size distribution.

In antiferromagnetic material, the peak in $\psi$ occurs at a temperature called Neel temperature ($T_N$). It is reported that the actual value of Neel temperature is few percent lower than the peak value.\textsuperscript{23,42,43} In the case of FePO\textsubscript{4} the peak value is 26\textdegree C and the actual value of Neel temperature will be less than this value.

Fig.9.4 and fig.9.5 show the temperature variation of ESR line width ($\delta H$) and resonance field ($H_r$). The line width reported here is the peak to peak separation in the absorption derivative. Large increase in the line width ($\delta H$) and shifts of the resonance field ($H_r$) to lower fields can be observed as the temperature decreases. The increase in the width of the signal due to low temperature may be due to the progress in freezing of the surface spins expected below the blocking temperature.\textsuperscript{9} It is known that the ESR line broadens out on approach to $T_N$ from high temperature side and it is characteristic of anisotropic antiferromagnet.\textsuperscript{16,22} It is also reported that the mechanism which could diminish the ESR observability of ferric ions in glasses include antiferromagnetic ordering and/or crystal-field line broadening.\textsuperscript{44} Based on the above discussions, the Neel temperature, which is characteristic of antiferromagnetic ordering is 21K for 0.1M sample and 20.8K for 0.02M sample. From this we can infer that $T_N$ decreases with decrease in molarity (decrease in particle size). We can also confirm that the peak in $\psi$-$T$ graph (26K) is the blocking temperature and few degrees higher than the actual $T_N$ value (21K) obtained from ESR studies.
Fig. 9.4: Temperature variation of ESR line width for 0.1M and 0.02M FePO₄.

Fig. 9.5: Temperature variation of ESR resonance field for 0.1M and 0.02M FePO₄.
Fig. 9.6 shows the temperature dependence of derivative of ESR spectrum of 0.02M sample. At low temperature, the line shape is asymmetric and at high temperature, symmetric line shape is obtained. At low temperature the anisotropy energy barrier is larger than the thermal fluctuations and the absorption will be distributed along the random direction of the anisotropy axes, providing an asymmetric line shape. The effect of temperature will be that of providing a progressively sharper and less asymmetrical line. At higher temperatures, when the relaxation of the magnetization through the anisotropy energy barrier is much faster, the thermal fluctuations will smear out the influence of anisotropy. Then the resonance spectrum is just like a normal paramagnetic resonance spectrum.

![Temperature dependence of derivative of ESR spectrum for 0.02M FePO₄](image)

Fig. 9.6: Temperature dependence of derivative of ESR spectrum for 0.02M FePO₄

### 9.3.2 ZnFe₂O₄ Nanoparticles

The magnetic moment of nanoparticle ZnFe₂O₄ was determined for different external fields using a VSM at room temperature. The molar susceptibility (\(\psi_m\)) and effective magnetic \(\mu_{\text{effect}} = 2.828 (\psi_m T)^{1/2}\) were calculated.
where T is the room temperature in Kelvin. Table 9.1 and table 9.2 show the effective magnetic moment and molar susceptibility values for different ZnFe₂O₄ samples. Fig. 9.7 shows the variation of magnetic moment (emu/gm) with external magnetic field (kGauss). Fig. 9.8 shows the molar susceptibility variation with particle size. The results show that magnetisation increases as the grain size decreases and this can be explained by the redistribution of cations in nanoparticle ZnFe₂O₄. Some percentage of Fe³⁺ ions is pushed to tetrahedral A site and some percentage of Zn²⁺ to octahedral B site which starts A-B superexchange interaction between Fe³⁺ ions on both sites giving rise to ferrimagnetic ordering. This ferrimagnetic ordering produces a large magnetic moment. Annealing leads to a decrease in the cation inversion parameter, which results in a reduced magnetisation value. From fig. 9.8 we can observe that as the reactant concentration (particle size) decreases, the magnetisation decreases against the expectation of increase in magnetic moment. This anomaly is observed for particles less than 6nm size. This may be due to the increase in the disorder of the magnetic moment orientation in A and B sites producing spin canting, when the ratio of surface to volume increases.

Table 9.1 Variation of particle size and magnetic parameters with annealing temperature

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Particle size from XRD (nm)</th>
<th>Effective magnetic moment (Bohrmagneton Kelvin)</th>
<th>Molar susceptibility (Ψm) (Bohrmagneton)</th>
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</thead>
<tbody>
<tr>
<td>150°C</td>
<td>4</td>
<td>7.241</td>
<td>0.022</td>
</tr>
<tr>
<td>300°C</td>
<td>6</td>
<td>7.794</td>
<td>0.0256</td>
</tr>
<tr>
<td>500°C</td>
<td>12</td>
<td>3.232</td>
<td>0.0044</td>
</tr>
<tr>
<td>700°C</td>
<td>21</td>
<td>3.022</td>
<td>0.00385</td>
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<tr>
<td>850°C</td>
<td>28</td>
<td>2.901</td>
<td>0.00352</td>
</tr>
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</table>
Table 9.2 Variation of particle size and magnetic parameters with reactant concentration

<table>
<thead>
<tr>
<th>Reactant concentration (M)</th>
<th>Particle size from XRD (nm)</th>
<th>Effective magnetic moment (Bohrmagneton Kelvin)</th>
<th>Molar susceptibility (γm) (Bohrmagneton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
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<td>7.4201</td>
<td>0.0232</td>
</tr>
<tr>
<td>0.01</td>
<td>5.5</td>
<td>7.499</td>
<td>0.0236</td>
</tr>
<tr>
<td>0.1</td>
<td>6</td>
<td>7.794</td>
<td>0.0256</td>
</tr>
</tbody>
</table>

Fig. 9.7: Variation of magnetic moment with magnetic field for different particles of ZnFe$_2$O$_4$
Fig. 9.8: Variation of molar susceptibility with particle size

Fig. 9.9, 9.10 and 9.11 show the temperature variation of magnetization for different particle sizes of ZnFe$_2$O$_4$. ZFC magnetization increases with decrease in temperature, reaches a broad maximum and then decreases. But the nature of FC curve is found to vary with particle size. In the case of 6nm particle (fig. 9.9) after reaching maximum value of magnetisation, the FC curve remains horizontal being unaffected by decrease in temperature. But in the case of 12nm particle (fig. 9.10) there is a small broad peak in FC curve. For 21nm particle (fig. 9.11) the FC peak becomes narrow and identical with ZFC curve with slight separation between them below the peak temperature. All the three curves show magnetisation peak in ZFC curve corresponding to the blocking temperature of superparamagnetic particles. The magnetization value is maximum for 6nm particle and is found to decrease with increase in particle size. The magnetic interactions must be stronger in 6nm (24 emu/gm) and 12nm (22 emu/gm) particles compared with 21nm (2.6 emu/gm) particles.
Fig. 9.9: Temperature variation of magnetic moment for 6nm particle

Fig. 9.10: Temperature variation of magnetic moment for 12nm particle
In the case of non-stoichiometric zinc ferrite, the FC peak was attributed to a decrease in magnetic interactions due to the inclusion of zinc ions in ferrite matrix. In the case of cobalt-zinc ferrite crystals, the FC peak was assigned to the material itself and not to interactions nor to experimental procedure. It has been found that in the case of cobalt ferrite, for 4.7 nm particles, the FC branch is rather flat and this has been assigned to the result of sizable interaction or aggregation effects. In real systems, ultrafine particles are seldom monodisperse and noninteracting. More often, interparticle dipolar and/or exchange interactions play an important role in determining a magnetic collective behaviour. Thus it has been revealed that large interactions induce a plateau not far below the separation between FC and ZFC curves without any peak. This is true in the case of 6 nm particles. As particle size decreases the occupancy of tetrahedral A site by Fe³⁺ ions increases, thereby increasing the interactions between the sublattices. With increase in annealing temperature, the particle size increases, decreasing the occupancy of Fe³⁺ ions on A site and thus reducing interactions. This is clearly seen in fig. 9.10 and 9.11 respectively.

**Fig. 9.11**: Temperature variation of magnetic moment for 21 nm particle
particle size increases, the interactions decrease producing sharp peak in FC curve.

For a particular system, the superparamagnetic transition temperature (blocking temperature) $T_B$, depends on the particle size, anisotropy energies and the time scale of the measuring technique.\(^{30}\) In the case of nano ZnFe$_2$O$_4$ particles studied in this chapter the blocking temperature $T_B$ is found to be approximately $35^\circ C$ for 6nm, $50^\circ C$ for 12nm and $30^\circ C$ for 21 nm particles (fig. 9.9-9.11). Blocking temperature increases from $35^\circ C$ to $50^\circ C$ when the particle size increases from 6nm to 12nm. But in the case of 21nm particles obtained by annealing the sample at $700^\circ C$, there is an anomaly showing a decrease in $T_B$ against the expectation of increase in blocking temperature. Blocking temperature is considered to be dependent on particle size.\(^{24}\) But in the case of zinc ferrite thin films, when the film was annealed at $650^\circ C$, a decrease in blocking temperature was observed.\(^{48}\) It was explained as due to oxygen deficiencies which cause rearrangement of zinc and oxygen atoms leading to the magnetic change. This recrystallisation process is beautifully observed in the DTA curve (fig. 5.3 of chapter 5) and is explained in section 5.3.3. In the DTA curve an exothermic peak was observed at $685^\circ C$ showing the recrystallisation and grain growth process of ZnFe$_2$O$_4$ nanoparticles. Therefore it is made clear that due to recrystallisation, a magnetic change is produced in the sample which causes a decrease in $T_B$.

9.4 Conclusion

Magnetic studies of nanoparticle FePO$_4$ and ZnFe$_2$O$_4$ have been carried out. Superparamagnetism is exhibited by both the samples showing that the size range of the particle is $\approx $ nanometer. FC-ZFC analysis of FePO$_4$ shows that the particles are non-interacting whereas small particles of ZnFe$_2$O$_4$ are highly interacting due to super exchange interaction between Fe$^{3+}$ ions on two sublattices A and B. The most interesting thing observed is that as particle size
increases the particle interaction decreases showing the appearance of a peak in FC curve. The Neel temperature in the case of FePO₄ changed from 21 K to 20.8 K when the reactant concentration changed to 0.02 M from 0.1 M indicating a decrease with decrease in particle size. The small decrease in magnetic moment with decrease in reactant concentration (decrease in particle size) measured at room temperature is attributed to surface spin disorder and spin canting effect of nanoparticles. ZnFe₂O₄ possess ferrimagnetic ordering with high value of magnetic moment due to the change in the cation distribution.

9.5 References


42. M.E. Fisher, Philos. Mag. 7 (1962) 1856