CHAPTER VIII
MAGNETIC PROPERTIES OF PURE AND RARE EARTH IONS DOPED IRON OXIDE NANOPARTICLES

8.1 INTRODUCTION

In 1961, Neel suggested that antiferromagnetic materials in finely dispersed form should exhibit some interesting magnetic properties, including superparamagnetism and a weak ferromagnetism at different particle sizes [441]. This idea was first tested experimentally in 1962 by Schuele and Deetscreek [441], who showed that the magnetic susceptibility of NiO particles increase with decreasing particle size. There were also experimental evidences for size effects in hematite ($\alpha$-Fe$_2$O$_3$) [442-445] and magnetite (Fe$_3$O$_4$) [446-449] particles. However in systems of broad size distribution and varying geometries, it is difficult to relate the data to a given average size parameter and to control the effects of particle shape, which could also influence the experimental results. At present, methods have been created for the controlled synthesis of magnetite nanoparticles of specific size and narrow size distribution [419-421, 423, 450]. In addition to controlled synthesis, the structure and properties of the parent nanoparticles can also be modified by doping of iron oxide nanoparticles with other metal ions [390, 422-425].

Magnetic properties of the nanoparticles can be modified by doping d-block elements like cobalt, manganese or zinc. Cobalt and manganese both have large magnetic moments, which can increase the saturation magnetization [451, 452]. However, the influence of f-block elements on iron oxide properties has not been investigated thoroughly. Rare earth ions are known to have exceptionally large magnetic moments as well as luminescent properties. Another important application of these elements is their usage as a magnetic resonance imaging (MRI) contrast reagents [453, 454]. Ho (III) has
one of the highest magnetic moments of all elements (10.6 μb) and also exhibits characteristic luminescence. However, doping of iron oxides with rare earth elements will become challenging when the Fe\(^{3+}\) and the rare earth trivalent ions are in different sizes.

In the present study, some interesting magnetic behavior of pure and rare earth ions doped α-Fe\(_2\)O\(_3\) nanoparticles have been obtained. Similarly, for the pure and doped Fe\(_3\)O\(_4\) nanoparticles, the same experiments were performed to compare the parameters obtained and the effect of dopants on the magnetic properties of the two polymorphs of iron oxide nanopowders.

### 8.2 Magnetic Properties of Pure and Doped α-Fe\(_2\)O\(_3\) Nanoparticles

Magnetic dynamics provided by magnetic interactions in materials is an area of interest to theoreticians and material scientists alike. Tuning these dynamics can provide novel magnetic materials. One way of altering the material’s properties is by reducing the size of individual particles or structures (e.g., thin-films, nanoparticles, nano-structures). The other way is to intentionally dope foreign ions into the native lattice that modify the cell constant and other related structural properties. Once in the nanoscale region, it is widely known that magnetic properties can differ greatly from the material’s “bulk” counterpart. One such material, nanoscale hematite has shown potential in a variety of fields, in particular its application in magnetic devices [290, 455, 456]. Among the iron oxides, α-Fe\(_2\)O\(_3\) crystallizes in the rhombohedral corundum structure (space group \(R-3c\)). So its structure itself has a great impact on their chemical and physical properties. Hexagonal unit cell of α-Fe\(_2\)O\(_3\) (left) together with the rhombohedral primitive cell (right) is shown in Fig. 8.1.
In Fig. 8.1, blue spheres represent ‘Fe’ atoms, red spheres display the ‘O’ atoms. The bilayer structure for the ‘Fe’ atoms is clearly visible. Along the [1 1 1] axis there are two sorts of pairs of ‘Fe’ atoms, one (denoted as type A) with a short and one (type B) with a larger Fe-Fe distance. The ‘O’ atoms form close-packed basal planes, each ‘Fe’ atom is coordinated octahedrally by six ‘O’ atoms. All iron atoms have an equivalent octahedral environment. Therefore, electronic and magnetic properties will be the same at each iron site. However, the octahedron built by oxygen atoms and centred by iron atoms are slightly rotated against each other. Hence its structure consists of slightly distorted, hexagonal close-packed (0 0 1) layers of ‘O’ atoms (O-O separations of 2.6 and 3.1 Å), with ‘Fe’ atoms finding two-thirds of the octahedral sites.

8.2.1 Magnetic Structure of Hematite

Hematite adopts the corundum structure (R-3c crystallographic space group) with puckered layers of Fe$^{3+}$ ions (S = 5/2). It has a Néel temperature at $\approx 955$ K, with two ferromagnetic sublattices $s_i$ and $s_j$ coupled antiferromagnetically to each other. The
moments align perpendicular to the rhombohedral axis (hexagonal ‘c’ axis, denoted x) and lying inside the hexagonal ‘ab’ basal plane, with a slight canting of the magnetic sublattices towards each other (caused by the Dzyaloshinsky-Moriya interaction, D) leading to weak ferromagnetism (WFM-phase).

Fig. 8.2 Canted magnetic sub-lattices of $\alpha$-Fe$_2$O$_3$

Hence below the Néel temperature, $T_N = 955$ K, $\alpha$-Fe$_2$O$_3$ is an antiferromagnetic insulator showing weak ferromagnetism above the Morin temperature, $T_M = 260$ K, due to a slight canting of the two sub-lattice magnetizations [457-462].

Upon cooling down through $\approx 263$ K, a first order magnetic transition occurs, reorienting the magnetic moments to lie almost parallel to the rhombohedral axis. This is known as the Morin transition ($T_M$). In the low temperature phase, the magnetic moments lie anti-parallel to each other giving a pure antiferromagnetic material (AFM-phase). This spin re-orientation is down to a change in sign of the overall anisotropy of the system made up of $\kappa_1$ and $\kappa_2$ (Eq. (8.1)), where, ‘$\kappa_1$’ is related to the anisotropy constant of the [1 1 1]
direction (the $[0 0 1]$ hexagonal direction) and $\kappa_2$ is related to the uniaxial anisotropy constant in the basal plane and is positive [382, 463, 464]:

$$H = \sum_{ij} (U_{ij} s_i) - D \cdot \sum_{ij} (s_i \cdot s_j) - (\sum_i k_{1i} [s_i^x]^2 + \sum_i k_{2i} [s_i^y]^2) \quad (8.1)$$

In the WFM-phase, $\kappa_1$ is negative, and thus the energy is minimized when the spins lie in the $yz$-plane. Cooling to the AFM-phase, $\kappa_1$ changes from negative to positive, and the spins flip to point along the $x$ axis. The change of sign of $\kappa_1$ is what causes the Morin transition. The values of $\kappa_1$ and $\kappa_2$ are related to nanoparticle anisotropy constants $K_1$ and $K_2$ by $K_i V = \kappa_i N s^2$ [465]. The magnitude of $\kappa_1$ is considered several times larger than the $\kappa_2$ term, ignoring the small time-interval where, $\kappa_1$ changes sign [466]. Hence below the Morin transition, two magnetic sub-lattices are oriented along the rhombohedral $(1 1 1)$ and are antiparallel [219, 220]. Also the Morin temperature was found to be strongly dependent on particle size, tending to disappear below particle size of 20-40 nm [231, 467].

As a summary, at room temperature, hematite is weakly ferromagnetic and undergoes a phase transition at 260 K (the Morin temperature, $T_M$) to an antiferromagnetic state [42, 221, 222, 468]. Also there are reports stating hematite exhibiting superparamagnetic and paramagnetic properties at temperatures above its Curie temperature of 956 K [232]. Hence it is well-known that the magnetic properties of hematite are sensitive to temperature along with its morphology, crystallinity, and inter-particle interactions [469, 470]. Thus the magnetic properties of the small particles are still not understood fully, even if many reports concerning hematite nanoparticles have appeared [471-474].

In the present study, both the room temperature isothermal magnetization measurements and low temperature measurements at a constant magnetic field have been
carried out to understand the magnetic behavior of the prepared α-Fe₂O₃ nanoparticles in its pure and doped form.

8.2.2 Isothermal Magnetization Measurements on Pure α-Fe₂O₃ Nanoparticles

In order to measure the magnetic properties of the particles, the main focus is given to determination of the magnetization of the particles as functions of their size. For that, the as-prepared iron oxide nanoparticles are calcined at two different temperatures 400 and 800°C. The DC measurements were made using a commercial Vibrating Sample Magnetometer. The hysteresis loops were obtained at room temperature for the field cycling range of ± 15000 G. The magnetization curves of the hematite nanoparticles (as-prepared, sample annealed at 400°C and the sample annealed at 800°C) are shown in Fig. 8.3.

All the samples exhibit different magnetic behavior, paramagnetism, superparamagnetism and weak ferromagnetism. Fig. 8.3 (a) reveals the ramp shaped loop and on magnification it has less values of remanent magnetization (M_r) and coercivity (H_c). Usually when the particle size is very low, room temperature (RT) hysteresis loops become narrower and evolve as ramp-shaped “loops” due to changes in magnetic domain state [475, 476]. It was already reported in Al doped hematite samples, the room temperature hysteresis parameters decrease gradually with decreasing particle size. In the present study, the particle size of the as-prepared sample is 35 nm and therefore the as-prepared sample exhibits a very small hysteresis loop with a remanent magnetization (M_r) of 0.5639 x 10⁻³ emu/g and coercivity (H_c) of only 10.627 G. This shows the presence of dominant paramagnetic character of the prepared pure α-Fe₂O₃ nanoparticles with minute ferromagnetic character.
Conversely, the hysteresis loop of the sample calcined at 400°C showed a weak ferromagnetic behavior with a remanent magnetization of 0.2063 emu/g, but the magnetic coercivity is somewhat improved to 30.787 G. On further increasing the calcination to 800°C, size of the prepared particles are about 60 nm and therefore the hysteresis loop is wide, indicating a stronger ferromagnetic behavior with remanent magnetization 0.0597 emu/g and coercivity values of 1778.4 G. Note, however that the hysteresis loops not reach to magnetization saturation, even at the maximum applied magnetic field. Nonetheless, these data clearly indicate a drastic change in magnetic properties with increasing calcination temperature. The measured values of saturation magnetization, remanent magnetization, coercivity and remanence ratio of are tabulated in Table 8.1.
Table 8.1 Dependence of magnetic parameters to calcination temperatures

<table>
<thead>
<tr>
<th>Sample Details</th>
<th>Particle size nm</th>
<th>Saturation magnetization ( (M_s) ) emu/g</th>
<th>Remanent magnetization ( (M_r) ) emu/g</th>
<th>Coercivity ( (H_c) ) G</th>
<th>Remanence ratio ( (M_r/M_s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>35</td>
<td>0.7355</td>
<td>0.5639 ( \times 10^{-3} )</td>
<td>10.627</td>
<td>0.0008</td>
</tr>
<tr>
<td>Calcined at 400°C</td>
<td>18</td>
<td>7.745</td>
<td>0.2063</td>
<td>30.787</td>
<td>0.2664</td>
</tr>
<tr>
<td>Calcined at 800°C</td>
<td>60</td>
<td>0.2911</td>
<td>0.0597</td>
<td>1778.4</td>
<td>0.2043</td>
</tr>
</tbody>
</table>

The coercivity and the remanence ratio increase with increase in crystallite size. Also, the saturation magnetization and remanent magnetization increases with increase in crystallite size [84]. This is due to the transition that take place from multi-domain to a single domain system on reduction of particle size [120]. The understanding of this calcination-dependent magnetic behavior requires comparison with the nanoscale structural characteristics of the \( \alpha \)-Fe\(_2\)O\(_3\). The variation of magnetic coercivity with crystallite size, and calcination temperature follows a logarithmic trend. This trend is in agreement with several studies [477-480]. Annealing decreases the amount of lattice strain and defects in powder, hence causing the aggregation of crystallites. Therefore, the ferromagnetic nature of nanosized hematite particles is enhanced. Although annealing normally decreases the amount of lattice strain and defects in a powder, it can also cause coalescence of crystallites, increasing the average crystallite size. This effect will certainly strengthen the ferromagnetic nature of nanosized hematite particles, which makes it difficult to separate the influence of the lattice strain and defects from the influence of the crystallite on the ferromagnetic nature.
8.2.3 Isothermal Magnetization Measurements on Doped $\alpha$-Fe$_2$O$_3$ Nanoparticles

A way to modify substantially the magnetic properties of hematite particles, beyond the effect of calcination is the structural incorporation of foreign cations, particularly facile for trivalent cations having similar ionic radius [235]. Guest cations may alter the particles shape [481], or induce change in optical properties, as observed for La-substituted micro-hematite [482]. Rare earth elements possess special optical and magnetic properties generated by their unique 4f electronic configurations and have been widely used in luminescence [483-486], catalysts [487, 488] and magnetic fields [489, 490]. It has been generally accepted that doping with rare earth elements can effectively modify the physicochemical properties of the host materials. For instance, Chen et al. [491] have demonstrated that efficient emission could be achieved by doping samarium. De Silva et al. [203] have reported that both Sm$^{3+}$ and Eu$^{3+}$ doping in Fe$_3$O$_4$ nanoparticles could transform the inherent superparamagnetism into ferromagnetism by causing an increase in magnetic anisotropy. Similar findings were also reported for Eu doped $\alpha$-Fe$_2$O$_3$ nanoparticles by Freyria et al. [134]. The changes in magnetic character were assigned to higher anisotropy and lower magnetic moment with respect to iron cations.

To this respect, rare earth elements are an attractive class of dopant elements, as they give easily trivalent cations with peculiar magnetic and optical properties related to their f-electronic configuration. Doping of hematite with rare earth elements is however challenging, due to the different size of Fe 3$p$ and rare earth trivalent ions. Both $\alpha$-Fe$_2$O$_3$ and rare earth ions doped samples share the same crystal structure, which is referred to as hexagonal, the oxygen anions (O$^{2-}$) make up hexagonal close-packed layers, while Fe$^{3+}$ or the dopant ions Ho$^{3+}$ and La$^{3+}$ occupies the intervening cation layers. The hexagonal unit cell edge lengths ‘a’ and ‘c’ for hematite are around 0.5034 and 1.375 nm, respectively. However, a slight distortion of the octahedral (six anions surround each cation) occurs
when Ho$^{3+}$ and La$^{3+}$ substitutes for Fe$^{3+}$, which is implied to induce a fair amount of surface anisotropy in very small particles. In practice, it is possible that the distorted cation positions are not completely compensated for. Such surface anisotropy of lattice-distortion origin would be particularly significant for small grains due to their high surface/volume ratio. Surface anisotropy may induce new magnetic behavior in the doped $\alpha$-Fe$_2$O$_3$ nanoparticles.

Room temperature magnetization curve of pure and rare earth ions doped hematite nanoparticles calcined at 800°C are shown in Fig. 8.4. All the three samples exhibit similar magnetic character.

![Room temperature magnetization curves of the pure and rare earth ions doped hematite nanoparticles](image)

**Fig. 8.4 Room temperature magnetization curves of the pure and rare earth ions doped hematite nanoparticles**
In Fig. 8.4, the magnetization curve of the pure hematite nanoparticles of size 60 nm is shown. It is clearly visible that these larger particles exhibit hysteresis. However, the shape of the hysteresis curve not suggests the presence of ferromagnetic behavior, but the hysteresis shows the presence of weak ferromagnetism imposed on the antiferromagnetism. Crystalline $\alpha$-Fe$_2$O$_3$, has a corundum structure and it orders antiferromagnetically at the Neel temperature, $T_N$ which varies between 948 and 963 K [468, 492]. Between $T_N$ and the Morin temperature $T_M = 263$ K, $\alpha$-Fe$_2$O$_3$ is a canted antiferromagnet ("weak ferromagnet") with the spins perpendicular to the ‘c’ axis except for slight canting out of the basal plane [221]. Moriya [493] has shown that small canting angle between $T_M$ and $T_N$ results from an anisotropic exchange interaction. There is no canting below $T_M$, where this substance is antiferromagnetic. Because of the particular moment arrangement and the existence of antiferromagnetic domains in $\alpha$-Fe$_2$O$_3$, there is a weak ferromagnetism imposed on the antiferromagnetism. Neel and Pauthenet [494] found that this weak ferromagnetism contains two components, one isotropic and another anisotropic. The anisotropic component results from the spin canting and can be explained by the Dzyaloshinsky mechanism [495]. The isotropic moment is complicated because a part of it is sensitive to the structural defects in the crystal.

The particle size dependent magnetic properties are listed in Table 8.2. Pure sample has significant values for coercivity, remanent magnetization and hence remanent ratio. Since $\alpha$-Fe$_2$O$_3$ has weak ferromagnetism that imposed on the antiferromagnetism, measured higher values of $H_c$ (1778.4 G) and $M_r/M_s$ (0.2043) suggest the dominance of ferromagnetic behavior. However, these values are comparative low than that the values observed for the doped $\alpha$-Fe$_2$O$_3$ samples. So the doped samples are having more ferromagnetic character.
Table 8.2 Magnetic parameters of pure and doped α-Fe₂O₃ nanoparticles

<table>
<thead>
<tr>
<th>Sample Details</th>
<th>Particle size nm</th>
<th>Aspect Ratio</th>
<th>Saturation magnetization (Mₛ) emu/g</th>
<th>Remanent magnetization (Mᵣ) emu/g</th>
<th>Coercivity (Hᵱ) G</th>
<th>Remanence ratio (Mᵣ/Mₛ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>93</td>
<td>1.59</td>
<td>0.2911</td>
<td>0.0597</td>
<td>1778.4</td>
<td>0.2043</td>
</tr>
<tr>
<td>Ho doped</td>
<td>40</td>
<td>1.31</td>
<td>0.3896</td>
<td>0.0886</td>
<td>2235.4</td>
<td>0.2274</td>
</tr>
<tr>
<td>La doped</td>
<td>51</td>
<td>1.43</td>
<td>0.4286</td>
<td>0.1062</td>
<td>2644.5</td>
<td>0.2478</td>
</tr>
</tbody>
</table>

On doping with rare earth Ho and La ions, the shape of the hysteresis loop prevails and therefore one can predict the presence of both ferromagnetic and antiferromagnetic character as that of the pure sample. Since the dopant ions are having similar oxidation state and ionic radii, the dopant ions perfectly replace the Fe ions without creation of any defect. These observations are already confirmed through the XRD results. Doped samples also retain the corundum structure even after doping with the present level. The defect parameters are remained very nearer to the pure sample. Hence the doped samples exhibit similar hysteresis curve as that of the pure sample.

However, on noting the magnetic parameters of the doped samples (Table 8.2), the coercivity, remanent magnetization and the Mᵣ/Mₛ ratios are increased. It was already reported that the shape and microstructure of the particles have dependence to coercivity is well known, coercivity increases with increasing aspect ratio [496-504]. There are also reports for five times rise of aspect ratio that increases the coercivity ten times [505]; and for change in the shape of nanoparticles [295]. In general, the coercivity increases with the increase of aspect ratio, i.e. with an increase of shape anisotropy. Spherically shaped crystals do not have any net shape anisotropy (aspect ratio = 1). In addition, Table 8.2
provides a comparative review of magnetic parameters for pure and doped α-Fe₂O₃ samples. The dependence of the magnetic properties on the morphology is noticeable and the shape anisotropy may play important role in the magnetic properties of samples. Even though the aspect ratio of the pure α-Fe₂O₃ sample is higher than that of the doped samples, observed coercivity is comparatively less. This is because of the size of the particles. However in the case of the rare earth ions doped α-Fe₂O₃ sample, the aspect ratio of the La ions doped sample is high and therefore the coercivity is more than the Ho doped samples with particle aspect ratio 1.43. It is well known that, in particles with aspect ratio higher than one, the magnetic spins are preferentially aligned along the long axes and their reversal to the opposite direction requires higher energies in comparison with spherical particles [506].

High coercivity materials have become one of the key materials in high-technology developments. There are two routes for enhancing coercivity: (i) enhancing the resistance of domain rotation whose prerequisite is a single-domain particle and increasing the material’s magnetic anisotropy and (ii) enhancing the resistance of the domain wall displacement via enhancing the undulatory distribution of internal stress and increasing the volume concentration of the impurity. As reported, the coercivity of the α-Fe₂O₃ particles was influenced by many factors such as the size [507], shape [295], aspect ratio [50] and synthesis conditions [225, 508]. Spherical nanoparticles were found to show a low coercive force at room temperature [508]. Compared to spherical nanoparticles, one-dimensional nanostructures have increased anisotropies in both the shape anisotropy and magnetocrystalline anisotropy, which exert an influence on their magnetic properties [509]. Shape anisotropy can increase the coercivity. Enhanced anisotropy induces large magnetic coercivity, where the magnetic spins are preferentially aligned along the long
axis and their reversal in the opposite direction requires higher energies than that for spheres [509].

Moreover, it is noted that spontaneous magnetization (calculated from the linear extrapolation $M (H > 10 \text{kG})$ data to the $M$ axis at $H = \text{zero value}$) of the doped samples are comparatively more than the pure $\alpha$-Fe$_2$O$_3$ sample. The main reason for this observed increase in magnetization may be due to the decrease of the crystallite size with doping. In turn this behavior shows a preferential incorporation of Ho and La ions in the rhombohedral planes of antiferromagnetic Fe$^{3+}$ spins. This result is in alternation of two different magnetic layers, one Fe rich (ferromagnetic) and other one Ho/La rich (antiferromagnetic), in rhombohedral structure. Different magnitude and direction of magnetic moment in Fe and doped ions rich layers produce uncompensated ferromagnetic moment in doped $\alpha$-Fe$_2$O$_3$ [510–512].

However, distorted ferromagnetic loop without saturation magnetization in doped samples suggests the coexistence of different type magnetic layers; one from Fe rich and other from doped ions rich layers in rhombohedral structure. These distorted loops indicate typical signature of lamellar ferromagnetism, exchange bias effect, and exchange spring magnet due to exchange coupling between two different magnetic layers in metal doped $\alpha$-Fe$_2$O$_3$ system [510-514].

8.2.4 Temperature Dependent Magnetization Measurements on Pure and Doped $\alpha$-Fe$_2$O$_3$

The temperature dependence magnetization was measured in the magnetic field 5 KG in zero field cooling and field cooling modes. Fig. 8.5 shows the ZFC and FC magnetization as a function of temperature for the pure $\alpha$-Fe$_2$O$_3$ nanoparticles calcined at 800°C.
It is clearly observed that pure α-Fe$_2$O$_3$ shows their temperature dependence and also the separation between the ZFC and FC curves. This variation between the magnetization in ZFC and FC process does not exist in bulk hematite and therefore this deviation is the characteristic of small particles [506, 515, 516]. When temperature is increased, magnetization increases from low susceptibility (M/H) value, indicating the magnetic phase change from antiferromagnetic phase to the weak ferromagnetic phase. The unique property of hematite is that the rhombohedral (1 1 1) planes form the layers of Fe$^{3+}$ ions in the temperature range of 950–260 K. The planes are separated by layers of oxygen O$^{2-}$ ions. The spins of Fe$^{3+}$ ions in any (1 1 1) plane remains parallel, i.e.,
ferromagnet below 300 K, but adjacent planes are antiparallel, i.e., antiferromagnet. The canting between (1 1 1) plane produces uncompensated magnetic moments of Fe$^{3+}$ spins between adjacent planes. This is the cause for exhibiting weak ferromagnetism or canted ferromagnetism in hematite.

The Morin transition can be obtained from the temperature at which the magnetization has its main inflection point, half-way between the AFM state and the WFM state value of the M(T) curve. The width of Morin transition, $\Delta T_M$, is defined as the difference of the temperatures at which the magnetization deviates from its smoothly varying values in the AFM and WFM states, respectively. From Fig. 8.5, the value obtained for $\Delta T_M = 45$ K.

The sharp increase of magnetization at $T_M \approx 250$ K is clearly observed in both curves (ZFC and FC), which may be assigned as the Morin temperature. Obtained Morin transition temperature for the pure $\alpha$-Fe$_2$O$_3$ sample is less than the value obtained for the bulk hematite. In general, bulk $\alpha$-Fe$_2$O$_3$ has a Morin transition from the low-temperature antiferromagnetic phase to a weakly ferromagnetic phase at 263 K [221]. This variation in Morin temperature is due to the small size of the nanoparticles [506, 515]. Usually, $T_M$ value strongly depends on the size and morphology of particles. Generally it is found that the $T_M$ value shifts toward lower values for smaller particles [517, 518].

Various polymorphs of iron oxide are sensitive to low temperatures, they transform from one phase to the other. Especially, magnetite and hematite show distinctive magnetic phase transitions below room temperature. Hence magnetization vs. temperature measurements were performed on doped samples by following the standard zero field cooled and field cooled procedures. Fig. 8.6 and 8.7 shows the temperature dependence of ZFC and FC magnetization of the rare earth Ho and La ions doped hematite nanoparticles.
Fig. 8.6 Temperature dependence of ZFC and FC magnetization of the Ho doped hematite nanoparticles

Fig. 8.7 Temperature dependence of ZFC and FC magnetization of the La doped hematite nanoparticles
In the low temperature region, the temperature dependent magnetic moment not remains constant as that of pure $\alpha$-Fe$_2$O$_3$. Pure hematite system has magnetically multi-layered spin structure, where in-plane Fe$^{3+}$ spins form ferromagnetic order and Fe$^{3+}$ spins in alternating magnetic sublattices (A and B) along off-plane direction form AFM order through Fe$^{3+}_A$ - O$^{2-}$ - Fe$^{3+}_B$ superexchange interactions [519, 520]. The WFM arises due to canting among antiferromagnetically aligned spins in magnetic sub-lattices. The replacement of the sites of Fe$^{3+}$ magnetic ions by non-magnetic Ho$^{3+}$ and La$^{3+}$ ions induce magnetic imbalance between A and B planes. A small atomic displacement along out of plane direction also observed from the analysis of XRD data. These are the favorable cause that forms the basis of enhanced spin–lattice coupling in doped hematite system. The modified magnetic properties in doped hematite system were already reported and the assigned cause is due the effect of non-equal distribution of dopant ions among A and B planes of the rhombohedral structure [521]. Below 150 K, this change is drastically visible with higher magnetic moment initially in the low temperature region and then gradually decreases and attains an inflection point near 200 K, after that there is sudden increase in the magnetic moment. These variations may be due to the anisotropy of the unequal moments of Fe and doped ions.

In the magnetic structure of $\alpha$-Fe$_2$O$_3$, the spins in a plane are ferromagnetically and antiferromagnetically coupled. The difference in the magnetic moment of the Fe ions due to the incorporation of nonmagnetic ions in a plane leads to magnetic frustrations and results magnetic anisotropy. The effective magnetic anisotropy constant $K_{eff}$ can be calculated using the formula [522]:

$$K_{eff} = \frac{25 k_BT_B}{V}$$  \hspace{1cm} (8.2)

where, ‘$K_{eff}$’ is the magnetic anisotropic constant; ‘$V$’ is the particle volume; ‘$k_B$’ is the Boltzmann’s constant ($1.38 \times 10^{-16}$ erg K$^{-1}$); ‘$T_B$’ is the blocking temperature.
Assuming that the particles are spherical in shape and the particle size (averaged) is considered as the particle diameter, the $K_{\text{eff}}$ for the pure and rare earth ion doped $\alpha$-Fe$_2$O$_3$ samples has been calculated using the above formula. Calculated values are respectively $5.13 \times 10^7$, $1.96 \times 10^9$ and $0.95 \times 10^9$ erg/m$^3$ for the pure and doped (Ho and La ions) hematite samples. On doping, the particle size becomes less and therefore magnetic anisotropy constant is comparatively high. Hence the magnetic moment variations are not systematic in the low temperature regions. Basic mechanism of this unusual magnetic properties in the low temperature region in metal doped $\alpha$-Fe$_2$O$_3$ lies on the modifications of rhombohedral (1 1 1) planes of crystal structure. The planes of Fe$^{3+}$ ions are separated by layers of oxygen (O$^{2-}$) ions and adjacent planes form alternating ferromagnetic and antiferromagnetic planes of Fe$^{3+}$ spins in $\alpha$-Fe$_2$O$_3$ crystal. Substitution of Fe$^{3+}$ ions in AFM planes by non-magnetic metal ions will result in uncompensated ferromagnetic moment [431].

Calculated Morin transition temperatures ($T_M$) are 245 and 242 K respectively for the Ho and La doped hematite nanoparticles. The width of Morin transitions are respectively 37 and 52 K. Obtained Morin transition temperature is lower than the pure hematite sample (250 K). This reduction may be due to two reasons, one is the particle size effect and other is due to the defect magnetic structure due to the dopant ions. Recently, experiments have shown the decrease in ‘$T_M$’ with particle size reduction [231, 445, 523-525]. From Table 8.2, the crystallite size of the rare earth ions doped hematite samples are lower than that of the pure sample and hence there is reduction in the Morin transition temperature. The decrease in ‘$T_M$’ is similar to the decrease in superparamagnetic blocking temperature ‘$T_B$’ with the decrease in particle size [526, 527]. The significant difference is that superparamagnetic blocking occurs due to the relaxation of magnetic particles along local anisotropic axes, whereas Morin transition occurs due to the compensation of two antiferromagnetic sub-lattices. The second reason for low values for Morin transition is
due to disordered spins in various planes of the lattice. On doping with nonmagnetic ions, there may be any induced anisotropy in spin orientations, which reduce the temperature for the phase transition from ferromagnetic to antiferromagnetic nature through compensation of spins.

These experimental results indicate that the magnetic behavior of hematite nanoparticles mainly depends on surface effects, viz., surface anisotropy, exchange anisotropy, core-shell spin structure, and coupling between disordered surface spins.

8.3 MAGNETIC PROPERTIES OF PURE AND DOPED Fe₃O₄ NANOPARTICLES

A study of the crystal structure is essential to the fundamental understanding of the mechanism of the magnetic properties of magnetite (Fe₃O₄). Magnetite is a transition metal oxide has interesting magnetic properties and it has been investigated extensively [528-534]. Fe₃O₄ has the inverse-spinel structure with space group Fd-3m at atmospheric pressure and room temperature. The oxygen ions form a close-packed cubic lattice with the iron ions located at interstices between the oxygen ions. There are two different interstices that the metal ions can take, tetrahedral (A) sites and octahedral (B) sites as shown in Fig. 8.8.
A unit cell consists of thirty two \( O^{2-} \) ions forming an fcc lattice, eight \( Fe^{3+} \) ions occupying tetrahedral sites, and eight \( Fe^{2+} \) and eight \( Fe^{3+} \) ions occupying octahedral sites. The positions of O atoms are defined by the parameter ‘u’ (oxygen positional parameter). The spinel structure was refined by Hamilton [535] using neutron diffraction data and by Fleet [536] using X-ray diffraction data. The value of ‘u’ was reported as 0.2548 (2) and 0.2549 (1), respectively. With these values, the atomic arrangement is stable at higher temperatures. As the temperature is lowered, there is a temperature called the Verwey temperature (119 K), where there is a sharp drop in electrical conductivity of the order of 90 times. This change is associated with a change in crystal structure from cubic spinel with lattice constant \( a = 8.3963 \) Å, to a lower symmetry ordering, possibly orthorhombic [537], with tetramolecular units \( a = 5.912 \) Å, \( b = 5.945 \) Å, \( c = 8.388 \) Å [538].

**8.3.1 Magnetic Structure of Magnetite**

Magnetite is an example of a ferrimagnet. Ferrimagnets are similar in properties to ferromagnets with a magnetic structure comparable to an antiferromagnet. In a simple ferromagnet, the electron spins (and thus the magnetic moments) are aligned in one direction giving a large net magnetic moment in the material. In an antiferromagnet, the spins are aligned so that the magnetic moments are of equal magnitude but point in opposite directions, giving a zero net magnetic moment. Ferrimagnetic ordering is an extension of antiferromagnetic ordering but with the anti-parallel spins being of unequal magnitude so that there is a net magnetic moment due to the presence of the \( Fe^{3+} \) and \( Fe^{2+} \) ions in the octahedral sites of the \( Fe_3O_4 \) lattice. The ferrimagnetic ordering of electron spins in a unit cell of magnetite is illustrated in Fig. 8.7.
As observed in Fig. 8.7, the ions on the ‘A’ sites in magnetite are coupled antiferromagnetically to those on the ‘B’ sites. In such a coupling, in fact, the contribution of the ferric ions (Fe$^{3+}$) is null since they are distributed in equal numbers on both A and B sites. On the other hand, the contribution of the ferrous ions (Fe$^{2+}$) is maximal, since all of them are on the B sites. So the magnetic moment of the unit cell only comes from the Fe$^{2+}$ ions, with a magnetic moment of 4 $\mu_B$ each, giving 24 $\mu_B$ per unit cell (4 $\mu_B$ per formula unit). This ferrimagnetic structure of magnetite was confirmed by Shull et al. [539] using neutron powder diffraction data in the analysis. Above the Neel temperature, 853 K ($T_N$), magnetite is magnetically disordered. In this state, the Fe ions are too far apart for them to interact directly; they interact through the oxygen atom located between them. The resultant interaction is called a superexchange interaction, and is responsible for the magnetic ordering temperature $T_N$. The superexchange interaction is therefore, a function of the interatomic distances and thus depends not only on the lattice parameter ‘a’ but also on the oxygen positional parameter ‘u’.

Fig. 8.9 Ferrimagnetic ordering of electron spins in a unit cell of magnetite
However, Frenkel and Doefman [540] were the first to predict that a particle of ferromagnetic material, below a critical particle size would consist of a single magnetic domain. More recently, Brown [541] and Frei, Shtrikman and Treves [542] have treated this subject more rigorously. They gave the meaning for "single domain particle", a particle that is in a state of uniform magnetization at any field. Hence magnetic particles below a critical diameter cannot support more than one domain, and are thus described as 'single domain'. This critical diameter is approximately, $2A^{1/2}/M_S$ (\(A = \) exchange constant, \(M_S = \) moment per unit volume) [542], and for typical materials this parameter is 10-100 nm. The theory of critical diameters and magnetization reversal modes of particles was reviewed by Zijlstra [543]. This critical particle size has been estimated by Kittel and others [544], and an approximate figure for a spherical sample of the common ferromagnetic materials is a size of 30 nm. Hence the behavior of single-domain particles can be described by assuming that all the atomic moments are rigidly aligned as a single 'giant' spin. This is the essence of the theory of superparamagnetism [545].

Similar tendency also be seen on magnetite nanoparticles, when the size of the particles are below the critical size. On size reduction, magnetite exhibit the phenomenon of “superparamagnetism”, i.e., on application of an external magnetic field, they become magnetized up to their saturation magnetization, and on removal of the magnetic field, they no longer exhibit any residual magnetic interaction. This property is size-dependent and generally arises when the size of nanoparticles is as low as 10–30 nm. At such a small size, these nanoparticles do not exhibit multiple domains as found in large magnets; on the other hand, they become a single magnetic domain and act as a “single super spin” that exhibits high magnetic susceptibility. Thus, on application of a magnetic field, these nanoparticles provide a stronger and more rapid magnetic response compared with bulk magnets with negligible remanence (residual magnetization) and coercivity (the field required to bring
the magnetism to zero). Hence magnetite and maghemite nanoparticles are the most widely used Superparamagnetic Iron Oxide Nanoparticles in various biomedical applications.

SPIONs have an organic or inorganic coating, on or within which a drug is loaded, and they are then guided by an external magnet to their target tissue [546, 547]. This superparamagnetism, unique to nanoparticles is very important for their use as drug delivery vehicles because these nanoparticles can literally drag drug molecules to their target site in the body under the influence of an applied magnet field. Moreover, once the applied magnetic field is removed, the magnetic particles retain no residual magnetism at room temperature and hence are unlikely to agglomerate (i.e., they are easily dispersed), thus evading uptake by phagocytes and increasing their half-life in the circulation. Moreover, due to a negligible tendency to agglomerate, SPIONs pose no danger of thrombosis or blockage of blood capillaries.

In the present study, both the room temperature isothermal magnetization measurements and low temperature measurements at a constant magnetic field have been carried out to understand the magnetic behavior of the prepared Fe$_3$O$_4$ nanoparticles in its pure and doped form.

8.3.2 Isothermal Magnetization Measurements on Pure Fe$_3$O$_4$ Nanoparticles

Magnetic properties of Fe$_3$O$_4$ nanoparticles were studied using a vibrating sample magnetometer (15 KG magnetic field) at room temperature. Room temperature magnetic hysteresis curves for as-prepared, Fe$_3$O$_4$ and α-Fe$_2$O$_3$ nanoparticles processed at different conditions are shown in Fig. 8.10. The as-prepared sample is amorphous, whereas the annealed sample at 400°C is in Fe$_3$O$_4$ phase and the third one annealed at 800°C is in α-Fe$_2$O$_3$ phase.
As-prepared sample is Fe\textsubscript{3}O\textsubscript{4} as evidenced from FTIR and EDX studies; however it is amorphous as per XRD analysis. In crystalline Fe\textsubscript{3}O\textsubscript{4} lattice, eight Fe\textsuperscript{3+} ions occupying tetrahedral (A) sites, and eight Fe\textsuperscript{2+} and eight Fe\textsuperscript{3+} ions occupying octahedral (B) sites. So the magnetic moment of the unit cell only comes from the Fe\textsuperscript{2+} ions. But in the case of amorphous materials, there is no regular pattern of atomic arrangements in various planes. Hence all atoms with incomplete atomic orbitals with unpaired electrons have a magnetic dipole moment and act as tiny magnets. An external magnetic field causes the electrons' spins to align parallel to the field, causing a net attraction. Paramagnets do not retain any magnetization in the absence of an externally applied magnetic field. Thus the total magnetization drops to zero when the applied field is removed. Even in the presence of the field there is only a small induced magnetization because only a small fraction of the spins
will be oriented by the field. The observed magnetic moment is therefore very small, only 1.6 emu/g even for a strong applied field of 15 KG. Also the produced magnetic moment is proportional to the field strength. Thus the as-prepared nanoparticles exhibit paramagnetic nature with linear dependency to the applied field.

M-H curve of crystalline Fe₃O₄ sample is shown in Fig. 8.10 (b). It shows the superparamagnetic behavior of the prepared magnetite particles. Almost zero remanence with negligible coercivity (7 G) in the absence of the external magnetic field indicates the superparamagnetic properties at room temperature [164, 181, 188]. This is because of their size, which is so small (6 nm) and therefore each particle acts as a single domain and the energy barrier for its spin reversal is easily overcome by thermal vibrations [188]. Usually, Fe₃O₄ nanoparticles have single magnetic domain when their size becomes 50 nm or less [162, 548]. At such a small size, these nanoparticles do not exhibit multiple domains as found in large magnets. On application of a magnetic field, these nanoparticles provide a stronger and more rapid magnetic response compared with bulk magnets with negligible remanence and coercivity. Observed saturation magnetization, remanent magnetization, and coercivity values of the prepared Fe₃O₄ sample are respectively, 8.4592 emu/g, 0.0551 emu/g and 7.2796 G. This may be due to their smaller particle size (6 nm) or larger surface effect [188, 549-553]. The saturation magnetization value of bulk Fe₃O₄ is 85 - 100 emu/g [172, 178, 554-556] and the coercivity for bulk Fe₃O₄ is 500 – 800 Oe [557]. These kinds of variations in magnetic parameters of Fe₃O₄ nanoparticles are very sensitive to particle sizes [558, 559]. This kind of strong effect of particle sizes of Fe₃O₄ nanoparticles on magnetization values is well documented now and there [560–562]. Since the prepared magnetite nanoparticles are superparamagnetic with very weak ferromagnetic hysteresis and moderate magnetic saturation, it could be utilized for bionanoelectronic applications, drug delivery and magnetic resonance imaging [144, 563].
When the as-prepared sample is annealed at 400°C, the resulted particles are Fe$_3$O$_4$ which possesses superparamagnetic structure. The same nanoparticles on annealing at 800°C are transformed from its magnetite phase to the hematite phase. So the shape of the M-H curve is completely different, as evidenced from Fig. 8.10 (c). The superparamagnetic structure completely disappears and the hysteresis loop emerges without saturation magnetization. This shows the weak ferromagnetic character of the sample. Weak ferromagnetism arises due to the presence of antiferromagnetic components. Observed remanent magnetization and coercivity values are respectively 0.1384 emu/g and 947.25 G. A hysteresis loop with much lower values of remanent magnetization is usually due to the presence of partial uncompensated spins in crystal planes [564]. However, higher value of coercivity confirmed the presence of ferromagnetic character. This ferromagnetism, which contains two components, one anisotropic and another isotropic, results from small spin canting out of the basal plane in the corundum structure and from moment bearing antiferromagnetic domain walls stabilized by lattice defects, respectively [441]. Hence the prepared hematite particles exhibits a weak ferromagnetism superimposed on antiferromagnetic character.

8.3.3 Isothermal Magnetization Measurements on Doped Fe$_3$O$_4$ Nanoparticles

Magnetite has an inverse cubic spinel structure (Space group: Fd-3m), in which 32 O$^{2-}$ ions form a face centered cubic unit cell containing eight formula units (Fe$_{24}$O$_{32}$) with stoichiometric cations (Fe(III)/Fe(II) = 2) [94]. Magnetite is frequently non-stoichiometric, in which case some other cations (such as Al, Mn, Ni, Cu, Co, etc.) are substituted for Fe due to the flexibility of the oxygen framework [94]. Rare earth ions can also be incorporated into magnetic oxides to modify crystalline structure, magnetic anisotropy, optical properties, and magnetic damping. Rare earth ions can have large spin and orbital
moments and, since the moments reside in the f-shell, the orbital moment is often not quenched when the ion is in a lattice. The strong spin-orbit coupling along with a large local moment then causes a large increase in anisotropy and magnetic damping. Impurity doping introduces preferred magnetic orientation and alters the magnetic properties [565, 566]. Meanwhile, impurity doping plays a crucial role in nucleation and growth of nanocrystals and is successfully used to modify the size of nanocrystals [567-569]. However, relatively little attention has been paid to the size control of magnetite nanoparticles by chemical doping [565, 566].

Several research groups have attempted doping to modulate magnetism in magnetite nanoparticles [203, 422, 426, 565, 566, 570]. It was already reported the doping of Ga$^{3+}$ into Fe$_3$O$_4$ lattice and the occupant sites Ga$^{3+}$ were measured using X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) [571]. In their observation, Ga$^{3+}$ dopant ions are substituting for Fe$^{3+}$ in the tetrahedral A-site of the spinel structure. Also they conclude that the impregnated Ga$^{3+}$ in the tetrahedral A site resulting in an overall increase in the total moment of Fe$_3$O$_4$. Also there are reports for Co doping in Fe$_3$O$_4$ and the ratio of Fe$^{2+}$/Fe$^{3+}$ was perceived using X-ray photoelectron spectroscopy [572]. According to their findings, the expected ratio of Fe$^{2+}$/Fe$^{3+}$ = 0.5 is found to be about 0.2 and 0 for the Fe$_3$O$_4$ films doped with 18% and 33% Co, respectively, indicating a reduction in Fe$^{2+}$ ions. These results suggest that the Co ions substitute the Fe$^{2+}$ ions at the B site of the Fe$_3$O$_4$. Substitution of Co$^{2+}$ in the B-site reduced the magnetization value and also notified the reduction due to the smaller magnetic moment (3 $\mu_B$) of Co$^{2+}$ than that of Fe$^{2+}$ (4 $\mu_B$), thus the total magnetic moment decreases with the substitution of Co$^{2+}$ for Fe$^{2+}$. Alternately, Co, Ni, Mn, Cr, and Cu substituted magnetites were prepared and all substitutions employed were found to prefer the B sub-lattice of
Superparamagnetism was observed at room temperature in the case of Cu- and Cr-substituted magnetites [573, 574].

Doping magnetite with lanthanide ions has been reported [203, 422, 426, 570], as lanthanides potentially offer unique optical and magnetic properties due to their partially occupied 4f electronic state [575]. Katherine P. Rice et al. [205] have reported Tb$^{3+}$ incorporation into the octahedral 3+ sites of Fe$_3$O$_4$. X-ray magnetic circular dichroism data indicate that the Tb spins are unpolarized and weakly coupled to the iron spin lattice at room temperature, and begin to polarize and couple to the iron oxide lattice at temperatures below 50 K. According to C.R. De Silva et al. [203], doping of Eu and Sm rare earth ions transformed the superparamagnetic magnetite nanoparticles to ferromagnetic at room temperature. This transition in magnetic behavior is ascribed to the introduction of lanthanide ions and possibly due to an increase in magnetic anisotropy of the doped particles. Also this type of transition from superparamagnetic structure to ferromagnetic structure on doping lanthanide ions has been reported [426, 570]. Out of the samples doped with Sm, Lu, Gd, Nd, and Y ions, Fe$_3$O$_4$ powders doped with Sm, Lu, and Gd are superparamagnetic with zero coercivity in contrast to the samples doped with Nd and Y, which exhibit a small hysteresis loop. Similar report regarding Gd doping with Fe$_3$O$_4$, revealed the superparamagnetic nature of the sample [422]. On doping Fe$_3$O$_4$ with Ho ions, the saturation magnetization value decreases with dopant concentrations and degrade the superparamagnetic properties [576]. The superparamagnetic behavior of Fe$_3$O$_4$ and Yb$^{3+}$ and Er$^{3+}$ co–doped Fe$_3$O$_4$ nanoparticles was also verified by the hysteresis loop [577].

Thus the Fe cations in the Fe$_3$O$_4$ structure can be isomorphically substituted with different types of rare earth metal cations which can significantly modify magnetic characters, making them suitable for many applications. Hence an effective step has been taken to analyze the magnetization of rare earth ions doped magnetite nanoparticles in the
Fig. 8.11 shows the room temperature magnetization curves of the pure and Ho, La rare earth cations doped samples.

As observed, all the three samples, both the pure and rare earth ions doped Fe$_3$O$_4$ samples exhibit similar variation in magnetization with respect to applied field. They show the superparamagnetic behavior with negligible remanence and coercivity. However on doping, the saturation magnetization and the coercivity are found changing appreciably. The magnetic parameters of the pure and Ho, La ions doped magnetite nanoparticles are listed in Table 8.3.
Table 8.3 Magnetic parameters of pure and doped Fe\textsubscript{3}O\textsubscript{4} nanoparticles

<table>
<thead>
<tr>
<th>Sample Details</th>
<th>Particle Size (nm)</th>
<th>Saturation magnetization (M\textsubscript{s}) emu/g</th>
<th>Remanent magnetization (M\textsubscript{r}) emu/g</th>
<th>Coercivity (H\textsubscript{c}) G</th>
<th>Remanence ratio (M\textsubscript{r}/M\textsubscript{s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Fe\textsubscript{3}O\textsubscript{4}</td>
<td>6</td>
<td>8.4592</td>
<td>0.0551</td>
<td>7.2796</td>
<td>0.0065</td>
</tr>
<tr>
<td>Ho doped</td>
<td>17</td>
<td>32.9170</td>
<td>0.2629</td>
<td>9.3226</td>
<td>0.0080</td>
</tr>
<tr>
<td>La doped</td>
<td>18</td>
<td>35.5467</td>
<td>0.5965</td>
<td>18.503</td>
<td>0.0168</td>
</tr>
</tbody>
</table>

Table 8.3 data clearly indicates the variation of magnetic parameters with doping. The changes in remanent magnetization and coercivity values are insignificant; however considerable change in saturation magnetization is noticed on doping. This variation is mainly due to the incorporation of the doped ions in to the Fe\textsubscript{3}O\textsubscript{4} lattice. Doped rare earth metal cations Ho and La are 3\textsuperscript{+} valence ions, so they are likely to be present as a 3\textsuperscript{+} valence ion in Fe\textsubscript{3}O\textsubscript{4}. Accommodation of these dopants in to spinel structure has two options, since two kinds of cation sites exist in the crystal: site A and site B [578]. Site A is tetrahedrally coordinated to oxygen and occupied only by Fe\textsuperscript{3\textsuperscript{+}}, and site B is octahedrally coordinated to oxygen and occupied by equal numbers of Fe\textsuperscript{2\textsuperscript{+}} and Fe\textsuperscript{3\textsuperscript{+}}. According to Katherine P. Rice et al. [205], rare earth Tb\textsuperscript{3\textsuperscript{+}} incorporation into Fe\textsubscript{3}O\textsubscript{4} prefers the second option, ie. Dopant Tb\textsuperscript{3\textsuperscript{+}} enters the octahedral 3\textsuperscript{+} sites of Fe\textsubscript{3}O\textsubscript{4}. Tb\textsuperscript{3\textsuperscript{+}} goes into the magnetite lattice despite the large ionic radii mismatch: 78.5 pm for high-spin Fe\textsuperscript{3\textsuperscript{+}} and 106.3 pm for Tb\textsuperscript{3\textsuperscript{+}} [579]. Similarly for the present dopant ions Ho\textsuperscript{3\textsuperscript{+}} and La\textsuperscript{3\textsuperscript{+}}, the atomic radii are respectively 90.1 and 103.2 pm. The octahedral site of Fe\textsubscript{3}O\textsubscript{4}, which is larger than the tetrahedral site, can nominally accommodate cations up to \( \approx 86 \) pm, which indicates both the Ho and La ions incorporation requires local lattice distortion. In many of the reported results, the room temperature magnetization is found decreasing with dopant lanthanide ions. This decrease in magnetization is due to magnetization description given
by the Brillouin function, which predicts magnetization suppression [94, 580-583]. However in the present study, the saturation magnetization $M_s$ measured for the pure Fe$_3$O$_4$ nanoparticles is found to be 8 emu/g. On doping, this magnetization value increases to 32 and 35 emu/g respectively for the Ho and La doped samples. These values are analogous to the value reported for Ln:Fe$_3$O$_4$ nanoparticles synthesized by the co-precipitation route [426]. Also the observed 8 emu/g magnetization for the pure Fe$_3$O$_4$ sample is very low compared to that of the bulk sample (92 emu/g) [584]. It is known that the energy of a magnetic particle in an external magnetic field is proportional to its size via the number of magnetic molecules in a single magnetic domain. When this energy becomes comparable to the thermal energy, thermal fluctuations near the surface of Fe$_3$O$_4$ nanoparticles cause magnetically disordered surface that will significantly reduce the total magnetic moments at a given field [585, 586]. This phenomenon is more significant for the nanoparticles due to their large surface to volume ratio. Therefore, the smaller saturation magnetization value for the Fe$_3$O$_4$ nanoparticles in comparison with the bulk Fe$_3$O$_4$ is reasonable. Hence the observed increase in magnetization with doping is mainly due to the increase in particle size. Particle size not only alters the magnetization of the produced products, but also the allied magnetic parameters.

Particle size of magnetite also affects the coercivity of Fe$_3$O$_4$ nanoparticles. The coercivity, $H_c$, of pure magnetite nanoparticles is zero when the size is below the superparamagnetic threshold size ($d < d_s$), and increases slowly from zero as a function of particle size $d$ ($H_c \propto (1-(d/d_s)^{1.5})$) in the single-domain region ($d_s < d < d_0$) [587]. This trend reflects in the present study also. From Table 8.2, it is noticed that the coercivity of the pure Fe$_3$O$_4$ nanoparticles of size of 6 nm is 7.2 G. On doping, the size of the Ho and La doped ions are respectively 17 and 18 nm. Hence the coercivity also found increasing from
7 to 18 G. Hence Ho\(^{3+}\) and La\(^{3+}\) doping and simultaneous increase in size contributed together to result in the increase of \(H_c\) and \(M_s\).

8.3.4 Temperature Dependent Magnetization Measurements on Pure and Doped Fe\(_3\)O\(_4\)

When a magnetic sample is cooled in a zero applied DC magnetic field through its critical temperature (Curie temperature in the case of ferromagnetic and ferrimagnetic systems, blocking temperature for superparamagnetic systems and freezing temperature for spin-glasses) and the magnetization is recorded while warming the sample in the presence of a magnetic field, zero field cooled magnetization, \(M_{ZFC}\), is obtained. This mode of measuring the magnetization is different from the field cooled magnetization measurements. In the field-cooled case, the sample is cooled through the critical temperature while a magnetic field is applied and the magnetization, \(M_{FC}\), is measured while cooling or while warming the sample after the cooling process. The nature of variation of ZFC and FC gives information related to spontaneous magnetic ordering, magnetocrystalline anisotropy, domain wall pinning effect etc.

Fig. 8.12 shows the zero field cooled and field cooled magnetization curves of pure Fe\(_3\)O\(_4\) nanoparticles. For ZFC measurements, the sample was cooled down to 4 K with zero magnetic fields and then the magnetization data were obtained by heating the sample till 300 K with an applied field of 5000 G. Then the sample is cooled to 4 K, with the above applied field and the FC curve is obtained. As seen in Fig. 8.12, the curves coincide at high temperatures but diverge at low temperatures, showing a maximum (in the case of the ZFC curve) at 60.5 K \((T_{\text{max}})\). Such behavior is the characteristic of superparamagnetism, where there is progressive deblocking of particles as the temperature increases [588].
The specific temperature at which maximum magnetization occurs in ZFC curve is the blocking temperature ($T_B$). It is generally assumed that blocking temperature depends on the average particle size. Again, while the temperature at which the FC and ZFC curves start to diverge corresponds to the blocking temperature of the largest particles. The blocking temperature of the pure Fe$_3$O$_4$ nanoparticle is 200 K. Recent studies have indicated that even magnetically ordered systems show thermomagnetic irreversibility below $T_M$ and a maximum in $M_{ZFC}$, when measured using small DC magnetic fields [589-593]. Hence the study informs the presence of superparamagnetic order in the prepared Fe$_3$O$_4$ sample. This result is analogous to the findings through the M-H hysteresis curve. Also it is well known that the broad cusp in ZFC curve generally implies the large distribution in particle size and the presence of anisotropy in nanoparticles [594, 595]. Above this blocking temperature, the anisotropy energy barrier is overcome by thermal...
energy and each magnetic moment fluctuates randomly, thus the total magnetization decreases with increasing temperature. Hence above the blocking temperature, both the magnetization curves are almost same and this indicates that the Fe$_3$O$_4$ nanoparticles have superparamagnetic behavior [596]. According to Stoner-Wohlfarth model, non-interacting single domain particles have uniaxial anisotropy and hence the prepared Fe$_3$O$_4$ nanoparticles have uniaxial anisotropy [150, 159, 174].

Fig. 8.13 and 8.14 are the zero field cooled and field cooled magnetization curves of rare earth ions Ho and La doped Fe$_3$O$_4$ nanoparticles. Magnetization vs. temperature measurements were performed on the prepared doped samples by applying a constant field. The ZFC and FC variations are similar to the one observed for the pure Fe$_3$O$_4$ sample. Upon increasing the temperature, all the ZFC magnetic moments increase and reach a maximum at blocking temperature ($T_B$). At this temperature $T_B$, the nanoparticles’
moments do not relax (known as blocked) during the time scale of the measurement. Even though the variations are similar, the $T_B$ values differ in the doped samples. Observed blocking temperature values are respectively 117.8 and 105 K for the holmium and lanthanum doped Fe$_3$O$_4$ samples.

Fig. 8.14 ZFC and FC magnetization as a function of temperature for the La ions doped Fe$_3$O$_4$ sample

On comparing the $T_B$ values, pure sample has a value 200 K, which is higher than that of the doped samples (117.8 and 105 K). In general, a reduction in $T_B$ is attributed to weak dipole–dipole interactions and local exchange coupling between nanoparticles. It should be noted that doping increases the particle size from 6 to 18 nm. A reduction in ‘$T_B$’ is expected due to increase in spin disorder with increase in particle size [597, 598]. As the size of the magnetic particle is below a critical size, a large fraction of atoms reside at the surface of the particles with broken translation symmetry. Here, the magnetic behavior of these nanoparticles becomes highly dependent on the magnetic anisotropy energy of the
individual particle and the magnetic dipole-dipole interaction between particles. Since flat rise in magnetization in ZFC is observed in both the samples, the particle size distribution is non-uniform.

8.4 CONCLUSION

Since iron atom has a strong magnetic moment due to four unpaired electrons in its 3d orbitals, iron oxides demonstrates complex magnetic structures depending on its crystal structure. Hence the effect of structural, temperature, particle size and morphology on magnetic properties of $\alpha$-Fe$_2$O$_3$ and Fe$_3$O$_4$ nanoparticles are realized. In the case of pure $\alpha$-Fe$_2$O$_3$ nanoparticles, the as-prepared sample exhibited dominant paramagnetic nature along with trace of weak ferromagnetic component. On calcination, ferromagnetic character is enhanced, but saturation magnetization was not achieved even after calcination to a temperature of 800°C. On doping $\alpha$-Fe$_2$O$_3$ with holmium and lanthanum ions, the remanent magnetization and coercivity values are enhanced, respectively 0.1062 emu/g, 2644 G for the La doped samples. Hence the weak ferromagnetic character is improved on doping and the magnetization values are also much enhanced. On varying the temperature, the unusual variations in magnetization in the low temperature region was explained on the basis of induced magnetic anisotropy. Calculated Morin transition temperatures, 245 and 242 K respectively for the Ho and La doped hematite nanoparticles were found less compared to that of pure hematite sample (250 K). Width of Morin transition is also more in doped samples, because transition from its antiferromagnetic to weak ferromagnetic state is not sharp with temperature. In the case of Fe$_3$O$_4$, the as-prepared amorphous sample has irregular atomic arrangements and was therefore paramagnet. Annealed sample at 400°C was crystalline Fe$_3$O$_4$ and therefore exhibited superparamagnetic behavior with almost zero remanence and coercivity. Annealed sample at 800°C is hematite, and so it
was in its weak ferromagnetic character. The pure and rare earth ions doped Fe$_3$O$_4$ samples revealed superparamagnetic behavior with negligible remanence and coercivity. However on doping, the saturation magnetization is found changing appreciably from 8.46 to 35.54 emu/g. On comparing the blocking temperature, pure sample has a value of 200 K, which is higher than that of the doped samples (117.8 and 105 K).