



The Synthesis and Characterization of Magnetic α -Fe₂O₃ and ϵ -Fe₂O₃ Nanoparticles

by

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Abstract

Magnetic iron oxide (Fe_2O_3) nanoparticles were synthesized by sol-gel method to produce; $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ and $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles. The samples were thermally treated, using different annealing temperatures for 3 hours in air. The characterization techniques involved the X-ray diffraction, transmission electron microscope, Mössbauer spectroscopy and a Vibrating Sample Magnetometer (VSM). X-ray diffraction patterns revealed the formation of a single phase hematite $\alpha\text{-Fe}_2\text{O}_3$, a single phase hematite in silica matrix $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ and the presence of two phases, $\epsilon\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ in silica matrix $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles. The morphology of the iron oxide nanoparticles was examined using the transmission electron microscope and were found to range from, an ellipse-like shape to roughly spherical nanoparticles.

The room temperature Mössbauer spectroscopy presented magnetically ordering in all the samples. The spectra for both $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ were fitted with a model consisting of a single Lorentzian-shaped sextet representing the only one lattice site for Fe^{3+} in hematite. The resulted Mössbauer parameters from the fitting of $\alpha\text{-Fe}_2\text{O}_3$ phase were; the isomer shift (CS) of 0.37 mm/s, quadrupole shift (ϵ) of -0.10 mm/s, and the hyperfine magnetic field (H) of 51.3 T. The $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ sample was well fitted with the following Mössbauer parameters; (CS) of 0.37 mm/s, (ϵ) of -0.10 mm/s, and (H) of 51.5 T. Noteworthy mentioning is the negative quadrupole shift which indicates that the two samples were in a weakly ferromagnetic states at room temperature. Four sextuplets were required to sufficiently fit the $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ sample, where one sextuplet represented the $\alpha\text{-Fe}_2\text{O}_3$ phase and the three sextuplets represented the three different lattice sites of Fe^{3+} in $\epsilon\text{-Fe}_2\text{O}_3$.

M vs H magnetization curves (hysteresis loops) were recorded in the temperature range between -263 °C (10 K) and 27 °C (300 K) for the three samples. There was a variation of magnetization properties with respect to temperature. Room temperature magnetization measurements i.e. coercivity field and remanent magnetization for the pure $\alpha\text{-Fe}_2\text{O}_3$ sample were $H_c = 0.35$ kOe and $M_r = 0.24$ emu/g, respectively. A surprisingly high coercivity field of $H_c = 10$ kOe for the $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ sample was recorded at room temperature, and this was explained in terms of the aggregation of nanoparticles. The room temperature remanent magnetization of $M_r = 0.25$ emu/g for this sample was almost similar to the pure $\alpha\text{-Fe}_2\text{O}_3$ sample. The $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles displayed a very large coercivity of $H_c = 15.5$ kOe and remanent magnetization of $M_r = 0.27$ emu/g at room temperature, as expected

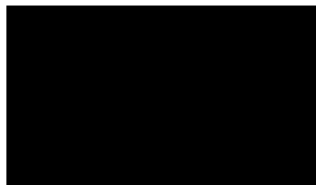
for the ϵ -Fe₂O₃ phase. Generally, all three samples showed a collapse in the coercivity field when the samples were cooled to low temperatures. This was due to the change in the magnetic structure of the samples at these specific temperatures. The ϵ/α -Fe₂O₃/ SiO₂ showed a sudden decrease in the coercive field at a temperature of about ≈ 100 K, while for the pure and silica α -Fe₂O₃ samples this behaviour was observed at temperatures about 200 K.

Declaration

I, Aphile Eustice Chithwayo, declare that

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Chapter 1

Introduction

1.1 Nanoparticles

Nanotechnologies have greatly grown in many areas of research such as; biomedical, (neuro) biological, electronics, space science, chemistry, physics and many others[1]. The growth serves to improve or replace already existing methods and invent new applications. Particular attention has been drawn to nanotechnologies due to the properties of nanostructured materials. It is known that novel properties arise at a nanoscale as the surface-to-volume ratio increases[1]. Some of the novel properties are mechanical, optical, magnetic, electrical, chemical reactivity and superparamagnetism in magnetic materials [1]. Superparamagnetism is one of the most interesting properties that arises below a critical size of a nanomaterial. This is due to that they have a high magnetic susceptibility, hence opens doors for new magnetic applications [1]. The research interest is in the synthesis of magnetic nanoparticles with definite shape and size, high coercive field that can be suitable for magnetic applications; for example: as a contrasting agent in MRI scans, as a transporter for drug delivery, in diagnostics and therapy of cancer disease[2, 3].

1.2 Iron Oxide Nanoparticles

Iron (Fe) is an interesting element that is magnetic due to the fact that it has four unpaired electrons and can be found in the +2 (ferrous) or the +3 (ferric) oxidation states[1, 2]. Magnetic iron oxide at nanoscale have shown to be the best preference for the fore mention applications since they show controllable chemical and physical properties. Some of the magnetic iron oxide compounds can be grouped according to the oxidation state of iron into Fe^{3+} , these are ferric oxide compounds (i.e magnetite(Fe_3O_4)) and Fe^{2+} , which are ferrous oxide compounds (i.e wustite(FeO), maghemite $\gamma\text{-Fe}_2\text{O}_3$, hematite $\alpha\text{-Fe}_2\text{O}_3$, and epsilon $\epsilon\text{-Fe}_2\text{O}_3$). The requirement for these nanoparticles is a particle size less than 100 nm, a narrow size distribution and high coercive field.

In this thesis three samples will be synthesized and characterized in order to compare differences in the magnetic properties, size and morphology. In this work

one method which will be employed is the sol-gel method in order to synthesize; hematite α -Fe₂O₃/ SiO₂, ϵ -Fe₂O₃/ SiO₂ coated with silica matrix and hematite α -Fe₂O₃) uncoated. The silica shell makes the magnetic iron oxide nanoparticle inert to atmospheric oxidation and controls particle size. Hematite α -Fe₂O₃ nanoparticles are the most thermodynamically stable magnetic iron oxide with tunable magnetic properties, while ϵ -Fe₂O₃ nanoparticles are least thermally stable under air atmosphere, hard to synthesize as a single phase, but possesses high coercive field (2T). The main purpose for employing the sol-gel method is; the ability to control the overall size and the morphology, where a spherical shape is the most preferable. The aim of this thesis is to: (a) establish a reproducible synthesis route for magnetic iron oxide nanoparticles, (b) employ characterization techniques in particular, using Transmission Electron Microscopy(TEM) to look at the morphology, the Mössbauer Spectroscopy to confirm study the magnetic state of the nanoparticles, the Vibrating Sample Magnetometer(VSM) to confirm magnetic measurements of the magnetic field dependence on of isothermal magnetization.

This thesis is divided into five main chapters; **Chapter1:** Introduction, **Chapter 2:** Literature Review, **Chapter 3:** Methodology, **Chapter 4:** Results and Discussion, **Chapter 5:** Conclusions and Future works.

The first chapter introduces the topic and gives the reader an overview of the work that is going to be done.

The second chapter gives an introduction to magnetism, a review of previously known studies and results obtained about hematite α -Fe₂O₃ and ϵ -Fe₂O₃ magnetic iron oxide nanoparticles.

The third chapter gives the characterization techniques used and their working principles on obtaining useful information about the synthesised magnetic iron oxide nanoparticles. The chapter also gives the methodology employed, a condensed experimental procedure for the synthesis of the nanoparticles and the characterization techniques to be undertaken.

The fourth chapter displays and discusses the results obtained during laboratory work.

The fifth chapter gives general conclusions on the key-findings based on this current work.

Chapter 2

Literature Review

2.1 Magnetism

The concept of magnetism in materials and the different types of magnetic ordering usually observed for iron oxides nanoparticles is discussed. The iron atom has a strong magnetic moment [1]. The reason for this, is due to four unpaired electrons in its 3d orbitals. Different magnetic cases are occurred when the crystals are formed from the iron atoms [1, 3].

2.1.1 Magnetic Dipole Moment

In order to understand magnetic materials, we first need to understand the concept of magnetism and how magnetic materials respond to an external magnetic field [4]. A magnetic solid is one in which at least some atoms have a permanent magnetic dipole moment due to unpaired electrons [4, 5]. The magnetic dipole moment associated with an unpaired electron originates from the orbital motion around the nucleus and its intrinsic spin is shown in figure 2.1. The magnetic dipole moment, $\vec{\mu}$ for an

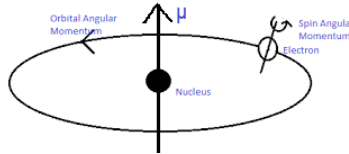


Figure 2.1: A schematic representation of the precession of an unpaired electron around the nucleus[6].

unpaired electron orbiting a nucleus can be written as;

$$\vec{\mu} = \frac{-\mu_B}{\hbar}(\vec{l} + g\vec{s}) \quad (2.1)$$

where $\mu_B = \frac{e\hbar}{2m_e}$ is the Bohr magneton, $\vec{l}$ is the orbital angular momentum of a single electron, $\vec{s}$ is the spin angular momentum and g is the electron g-factor $\cong 2$. When an applied magnetic field, $\vec{B}$ is applied in the $\hat{z}$ direction, the magnetic dipole

moment will experience a torque that will orient it along the $\hat{z}$ direction [7]. The energy of orientation is given by;

$$E = -\vec{\mu} \cdot \vec{B} \quad (2.2)$$

The total orbital angular momentum is the sum of the orbital angular momenta $\vec{l}$ from each of the electrons ; it has magnitude of $\sqrt{L(L+1)}(\hbar)$, in which $\vec{L}$ is an integer[6, 7]. The possible values of $\vec{L}$ depend on the individual $\vec{l}$ values and the orientations of their orbits for all the electrons composing the atom. The total spin momentum has magnitude of $\sqrt{S(S+1)}(\hbar)$, in which $\vec{S}$ is an integer or half an odd integer, depending on whether the number of electrons is even or odd[6, 7]. In most magnetic atoms, two or more electrons contribute to the total magnetic dipole moment of the atom(d or f electrons), assuming all other electrons (s and p) are paired up[7]. The total angular momentum, $\vec{J}$ for the entire atom is then given by;

$$\vec{J} = \vec{L} + \vec{S} \quad (2.3)$$

where $\vec{L}$ is the total orbital angular momentum and $\vec{S}$ is the total spin angular momentum of the electron that contribute to the magnetic dipole moment.

2.1.2 Magnetization

The magnetization, $\vec{M}$ of a sample of material is defined as the total magnetic dipole moment per unit volume;

$$\vec{M} = \frac{1}{V} \sum_{i=1}^n \vec{\mu}_i \quad (2.4)$$

The magnetization is sensitive to temperature and the coupling between magnetic moments[7]. This quantity, $\vec{M}$ is the same everywhere in a homogeneous medium, but at the edges where homogeneity is lost, the magnetization differs from the bulk value [8]. The volume of a sample of material is affected by the change in temperature, therefore the magnetization can be redefined as the total magnetic dipole moment per unit mass of sample;

$$\vec{M} = \frac{1}{m} \sum_{i=1}^n \vec{\mu} \quad (2.5)$$

In vacuum , the applied magnetic field is related to another magnetic field known as the magnetic flux, $\vec{B}$.

$$\vec{B} = \mu_0 \vec{H} \quad (2.6)$$

where μ_0 is the permetivity of free space. The field, $\vec{H}$ is an applied magnetic field resulting from a current or magnet and the field $\vec{B}$ is a response to the applied

magnetic field, either in free space or material medium [7]. In material medium, the relationship becomes;

$$\vec{B} = \mu_0(\vec{H} + \vec{M}) \quad (2.7)$$

where $\vec{H}$ is the applied magnetic field and $\vec{M}$ is the magnetization resulting from the material. In a homogeneous material, the magnetization, $\vec{M}$ is proportional to the applied magnetic field, $\vec{H}$;

$$\vec{M} = \chi \vec{H} \quad (2.8)$$

The proportionality constant, χ is called the magnetic susceptibility. A diamagnetic material is known to have a negative value of the magnetic susceptibility [7]. Paramagnetic, Ferromagnetic, Ferrimagnetic and Antiferromagnetic materials have a positive magnetic susceptibility [7]. There are two types of magnetism that are generally known; diamagnetism and paramagnetism [8]. Different magnetic cases are occurred when the crystals are formed from iron (Fe) atoms. These are magnetically ordered states which are classified as ferromagnetic, antiferromagnetic, ferrimagnetic[7].

2.1.3 Coercivity and Remenence

The magnetization $\vec{M}$, represents the net magnetic dipole moment per unit volume that is aligned parallel to the applied magnetic field. The magnitude of $\vec{M}$ is generally less than the value when all the magnetic moments are perfectly aligned, because different magnetic domains exist in a crystal. The magnetic dipole moments of all the magnetic domains are usually not aligned, so the magnetization decreases [8]. Figure 2.2 shows the hysteresis loop, that relates the coercivity field, H_c , the remanent magnetization M_r , the saturation magnetization M_s , and the applied magnetic field $\vec{H}$. When an applied magnetic field, $\vec{H}$, is applied to a crystal which has magnetization, $\vec{M}$, the magnetization $\vec{M}$ increases with the increase of $\vec{H}$ until it reaches its maximum value called saturation magnetization, M_s [8]. When the field is removed, there is still a non-zero magnetization called remanent magnetization, M_r . To bring the magnetization back to zero, a coercivity field, H_c , must be applied in an antiparallel fashion.

When the size of the crystal decreases, the number of domains decreases as well. The crystal becomes a single domain when the size is blow some critical value. A single domain magnetic crystal has no hysteresis loop; it is superparamagnetic, which means it demagnetizes completely ($M=0$) when the field is removed. Iron oxide nanoparticles smaller than about 20 nm often display superparamagnetic behavior at room temperature [7, 8]. The degree of alignment of magnetic dipole moments is a function of temperature. The alignment is more disordered when the temperature increases, and beyond a critical temperature, the magnetization of the crystal becomes zero [7, 8]. Superparamagnetic particles are different from this normal behavior; it occurs when the temperature is below a blocking temperature T_B [7, 8]. Due to the very small size of the particles, the surface has a very large percentage of the atoms. Therefore, the surface effects are very important for nanoparticles. For

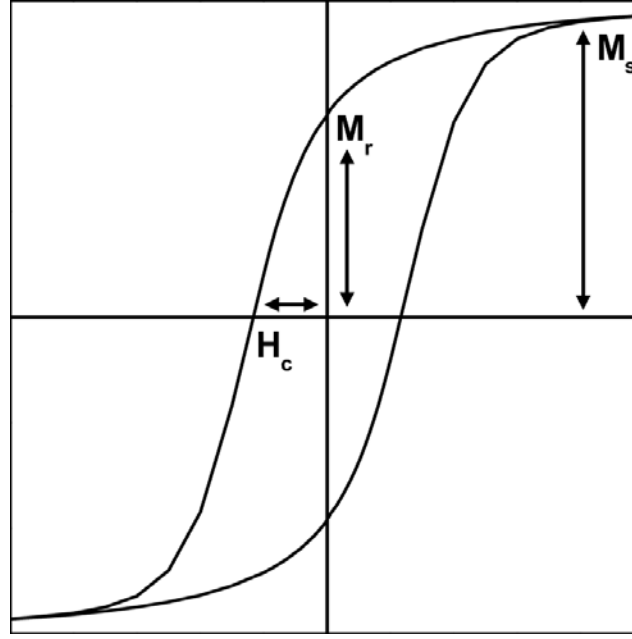


Figure 2.2: A typical hysteresis loop of a ferromagnetic material[7].

the same material, the magnetization of small particles can be smaller than that of bulk materials. This reduction has been associated with different mechanisms, such as the existence of a magnetically dead layer on the surface of the particles, the existence of canted spins, or the existence of a spin-glass-like behavior of the surface spins. Surface modifications are also very influential to the magnetic properties of the particles [7].

2.1.4 Diamagnetism

Diamagnetism is a very weak quantum mechanical magnetic effect that occurs in all materials in the presence of an applied magnetic field. A material is called a diamagnetic material if it has no magnetic dipole moment in the absence of an external magnetic field, (see fig. 2.3). In diamagnetic materials, the atoms that constitute them have no permanent magnetic moment since the magnetic dipole moments produced by electrons are in opposite directions[7]. Classically, when an external magnetic field is applied, the motion of the electrons is altered by an effect that is essentially the same as Lenz's law in electromagnetism. Thus the change in electron motion in a diamagnetic material in a magnetic field always causes an additional field in the opposite direction to that of the applied field[7]. This effect is always small and acts to decrease the total field in the material and such materials are temperature independent. All materials have some diamagnetic contribution to the total magnetization[7, 8]. However, the effect is very small and is overwhelmed in a paramagnetic, ferromagnetic, ferrimagnetic and antiferromagnetic material.

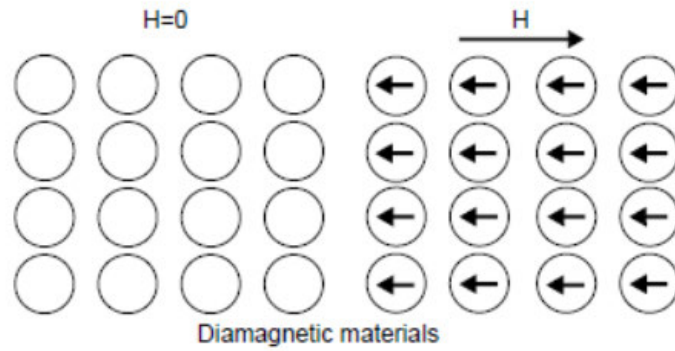


Figure 2.3: A schematic representation of the behaviour of magnetic dipole moments in a diamagnetic material in the presence and in the absence of an applied magnetic field [7].

2.1.5 Paramagnetism

Paramagnetic materials have magnetic dipole moments that are randomly oriented in the absence of an applied magnetic field [7, 8]. If a magnetic field is applied (fig. 2.4), the magnetic dipole moment will experience a torque which will align them in the same direction as the applied magnetic field [7, 8]. The magnetic dipole moment of the materials will add to the applied magnetic field. Paramagnets do not retain any magnetization in the absence of an externally applied magnetic field because thermal motion randomizes the spin orientations [7, 8]. Paramagnetic materials retain spin disorder even at absolute zero, meaning they are paramagnetic in the ground state, (i.e. in the absence of thermal motion). Thus the total magnetization drops to zero when the applied field is removed.

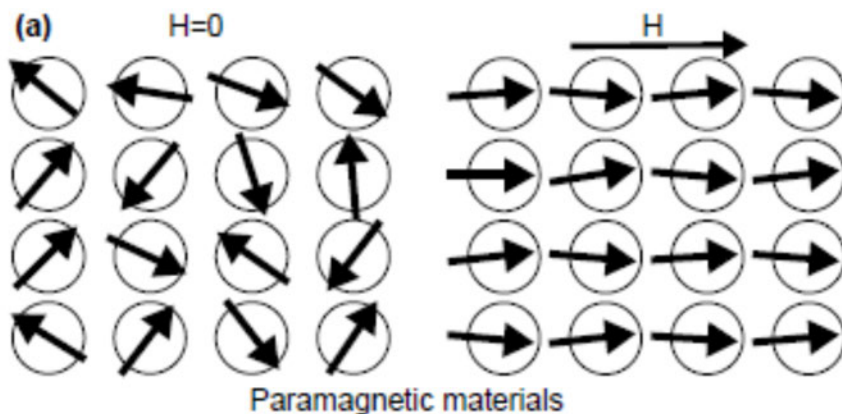


Figure 2.4: A schematic representation of the behaviour of magnetic dipole moments in a paramagnetic material in the presence and in the absence of an applied magnetic field [7].

2.1.6 Ferromagnetism

Ferromagnetic materials have ordered magnetic dipole moments. In such materials the molecular field (Molecular Field Theory) is responsible for the strong interactions between magnetic dipole moments, which causes them to line up parallel to each other in regions called domains. Molecular Field Theory: In 1907, Pierre-Ernest Weiss postulated mutual interaction between the magnetic moments keep them parallel and aligned together (see fig. 2.5) in one direction [8]. At low enough temperature, the aligning influence of the molecular field overcomes the disordering influence of thermal energy and the material becomes spontaneously ordered [8]. There is parallel alignment of the magnetic dipole moments in the absence of the applied magnetic field over magnetic domains. This constitutes ferromagnetism.

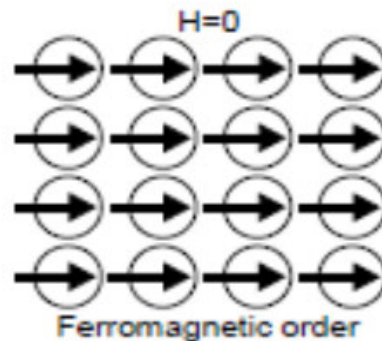


Figure 2.5: A schematic representation of magnetic dipole moments in a ferromagnetic material [7].

The Molecular Field: Origin of the ordering field

The dominant magnetic interactions would be magnetic dipole-dipole interactions. The strength of the nearest neighbour dipole-dipole interactions is of order 1 K which is much smaller than the transition temperature (T_C) for a ferromagnet [7, 8]. The dipole interactions cannot account for magnetic ordering. The origin of the ordering field is a quantum mechanical exchange effect. The Coulomb interaction between two spins depends on whether the spins form a singlet or a triplet [7]. A triplet state is antisymmetric in real space while the singlet state has a symmetric wavefunction in real space. The electrons stay out of each other's way more when they are in the triplet state. As a result, the Coulomb interaction between two electrons is less when they are in a triplet state than when they are in a singlet state [7]. So, the interaction energy depends on the relative orientations of the spins. This can be generalized so the spins don't have to belong to electrons and the spins need not be spin $-1/2$. This interaction between spins is called the exchange interaction.

2.1.7 Antiferromagnetism

Antiferromagnetic materials consist of two magnetic sub-lattices. In each sub-lattice, the magnetic dipole moments are coupled ferromagnetically (see fig. 2.6), but the magnetic moments belonging to these two sub-lattices are oriented antiparallel [7, 8]. The net magnetization is zero when no magnetic field is applied.

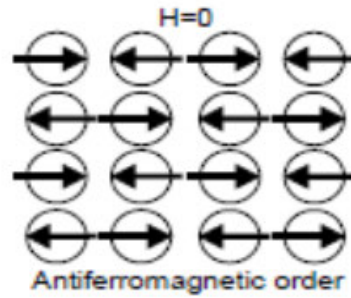


Figure 2.6: A schematic representation of the magnetic dipole moments in a Antiferromagnetic material [7].

In the presence of an applied magnetic field, ferromagnetic behaviour may be displayed in the antiferromagnetic phase, resulting in a non-zero magnetization [8].

2.1.8 Ferrimagnetism

Ferrimagnetic materials have neighbouring magnetic dipole moments that are unequal and point in opposite directions [7, 8]. In the absence of an applied magnetic field, weaker magnetic dipoles align antiparallel to their stronger magnetic dipole to reduce the magnetization, (see fig. 2.7). The ferrimagnetic material does not lose its magnetism even in the absence of the applied magnetic field.

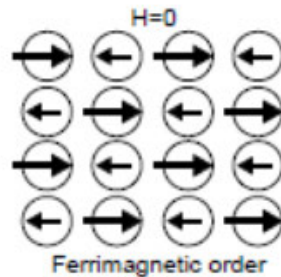


Figure 2.7: A schematic representation of magnetic dipole moments in a Ferrimagnetic material [7].

2.1.9 Superparamagnetism

This is a form of magnetism exhibited by small ferromagnetic, ferrimagnetic and antiferromagnetic materials. At very small sizes less than 10 nm, they are single domain, (see fig. 2.8). When a magnetic field is applied, the nanoparticles are magnetized like paramagnets, but with much greater susceptibility [7, 8]. In these

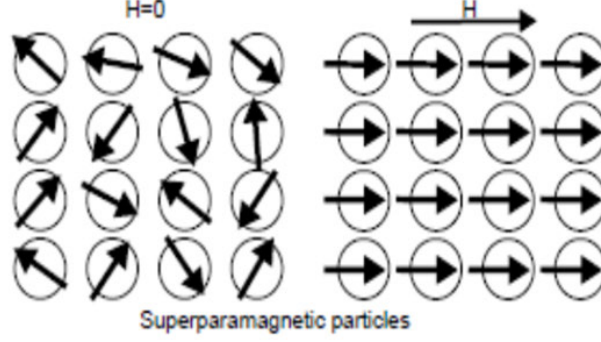


Figure 2.8: A schematic representation of the magnetic dipole moments in a Superparamagnetic material in the presence and in the absence of an external magnetic field [7].

single-domain particles the balance between the thermal fluctuation, E ;

$$E = k_B T$$

where k_B is the Boltzmann constant and T is the temperature and magnetic anisotropy energy;

$$E_k = KV \sin^2 \phi \quad (2.9)$$

determines the dynamics, where V is the volume, K is the anisotropy constant, and ϕ is the angle between the easy axis and the particles magnetisation.

2.1.10 Neel Relaxation time

As temperature increases, the quantity $k_B T$ becomes bigger and eventually at some point it overcomes the energy barrier E_k . In this situation, their magnetization can flip direction randomly over short periods of time (see fig. 2.9) and the time between two flips in direction is called the Neel relaxation time [7]. The nanoparticle's magnetic anisotropy, the magnetic dipole moment has usually only two stable orientations antiparallel to each other, separated by an energy barrier E_k . The stable orientations define the magnetic easy axis of the nanoparticle. Thermal energy causes the nanoparticles to randomly flip the direction of their magnetization and the average time between two flips or the Neel relaxation time;

$$\tau_N = \tau_m e^{\frac{KV}{k_B T}} \quad (2.10)$$

where τ_N is the Neel relaxation time and τ_m is the measurement time for a magnetic dipole moment to flip direction. If $\tau_m \gg \tau_N$, this time is much greater than the relaxation time τ_N , the nanoparticle magnetization will flip several times during the measurement. In zero field, the measured magnetization will average to zero [7]. The nanoparticle will appear to be in the superparamagnetic state.

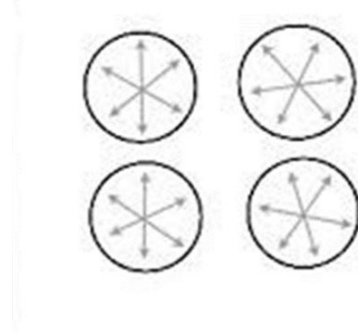


Figure 2.9: A schematic representation of magnetic dipole moments in a Superparamagnetic state [7].

If $\tau_m \ll \tau_N$, the magnetization will not flip during the measurement, so the measured magnetization will be equal to the initial magnetization. The nanoparticle will be in a blocked state (see fig 2.10).

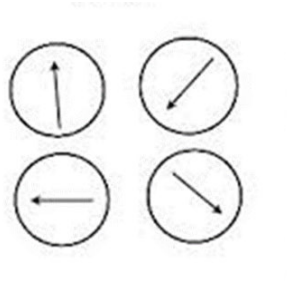


Figure 2.10: A schematic representation of magnetic dipole moments in a Blocked state [7].

2.1.11 Blocking temperature

A transition between superparamagnetism and the blocked state occurs when $\tau_m = \tau_N$. The temperature for which $\tau_m = \tau_N$ is called the blocking temperature (see eqn 2.11). In several experiments, the measurement time is kept constant but the temperature is varied, so the transition between superparamagnetism and blocked state is a function of the temperature [7, 8]. Rearranging eqn 2.10 and solving for the blocking temperature, T_B gives:

$$T_B = \frac{KV}{k_B \ln(\frac{\tau_m}{\tau_o})} \quad (2.11)$$

where τ_o is the length of time characteristic of material attempt time.

2.1.12 Zero field and field cooling

Figure 2.11 below shows the Zero field and field cooling curves. In zero field cooling (ZFC), the sample is cooled from high temperature to low temperature in the absence of an applied field [8, 9]. At that lowest temperature a field is applied as the sample is heated up, we approach the blocking temperature, which is the temperature for which there is sufficient thermal energy to overcome the energy barrier between parallel and antiparallel alignment of the magnetic moments [8, 9]. So, as temperature increases, more and more particles go from 'blocked' to 'superparamagnetic' and are able to align with the small external field applied. As temperature is further increased, the random fluctuations from thermal energy begin to dominate and the magnetic moments become randomly oriented once again, producing the $1/T$ exponential decrease of the magnetization that we see at higher temperatures. Field cooling (FC) is achieved by cooling in the presence of an applied field [8, 9]. The measurement in both cases is done during heating up of the sample in small applied field is presented in figure 2.11 below.

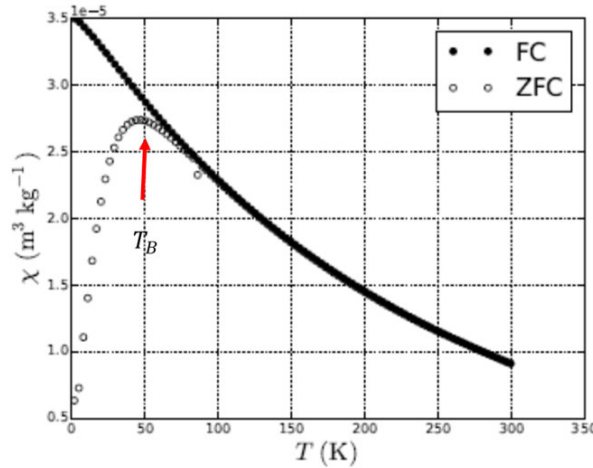


Figure 2.11: Zero Field Cooling and Field Cooling curves for sample of maghemite magnetic nanoparticles [7].

2.2 Magnetic Iron Oxide Nanoparticles

Iron is one of the first row transition metals. The two common oxidation states that iron is normally found in is the Fe^{3+} and Fe^{2+} with electron configuration; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ and $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ respectively [9, 10]. It is the 3d electrons that determine the electronic, magnetic, and some spectroscopic properties. In a solid, the electrons of Fe ions interact with those of other ions and this leads to a change in the energy states of iron [10]. In iron oxides and oxide-hydroxides, the cations are octahedrally and / or tetrahedrally coordinated to negatively charged O^{2-} / OH^- ions [10]. Iron oxides (Fe_2O_3) can be found in nature or can artificially

prepared and they are classified by the oxidation state of iron into; ferrous oxide (i.e β

$-\text{Fe}_2\text{O}_3$, $\epsilon\text{-Fe}_2\text{O}_3$), and ferric oxides (i.e Fe_3O_4) [9, 10]. Iron oxides primarily relevant to the thesis are hematite $\alpha\text{-Fe}_2\text{O}_3$ and epsilon $\epsilon\text{-Fe}_2\text{O}_3$.

2.2.1 Hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanoparticles

Hematite, $\alpha\text{-Fe}_2\text{O}_3$ is an iron oxide that is blood-red in colour and the mostly thermodynamically stable under specific conditions compared to other oxides [11–13]. The crystal structure of hematite is a corundum type crystal structure that is rhombohedrally centered hexagonal comprising of hexagonally closed packed arrays of oxygen anions stacked along the [001] direction [11–13]. Sixty-six percent (two-thirds) of the octahedral sites are filled with Fe^{3+} ions which are arranged regularly with two filled sites being followed by one empty site in the [001] plane and forming sixfold rings, (see fig. 2.12).

It crystallizes in the $R\bar{3}c$ space group, with lattice parameters $a = 5.036 \text{ \AA}$ and $c = 13.749 \text{ \AA}$, and six formula units per unit cell [11–13]. The way the cations are arranged produces sets of FeO_6 octahedra. Every octahedron shares edges with three neighboring octahedra in a similar plane and one face with an octahedron in an adjacent plane [11–13]. Face sharing octahedra is responsible for distortion of the cation sublattice from perfect packing, (see fig. 2.12 (b)) [12, 13]. The Fe atom in the octahedra which share faces are repelled along the direction perpendicular to the [001], making the cations move nearer to the unshared faces [11–13]. The O-O distances along the shared faces of an octahedron are shorter than the distance along the unshared edge, thus the octahedron is trigonally distorted, (see fig. 2.12 (a)). This Fe-O₃-Fe triplet structure, (see fig. 2.12 (c)), influences the magnetic properties of the oxide [11–13].

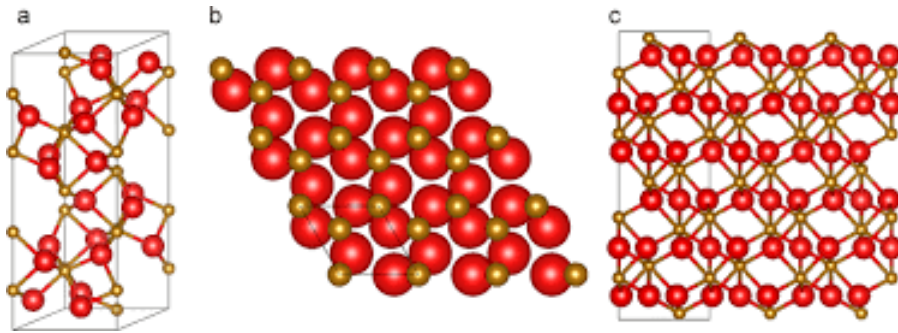


Figure 2.12: (a) The ball and stick model of the unit cell (red = O(Oxygen), brown = Fe(Iron)). (b) Hexagonal close packing of the oxygen anions and the cations in the interstices. c) The Fe-O₃-Fe triplet structure. [11].

A new strategy employing a supporting matrix (silica) with pores of definite sizes has been introduced to obtain $\alpha\text{-Fe}_2\text{O}_3$ at a much higher yield, or either as a single phase[11, 13]. There is an uncommon way for synthesizing hematite of very uniform size and shape, in the micro scale, so called "monodispersed" hematites, that guarantees a highly uniform crystal size and shape, and a high product yield

[11, 13, 14]. If we vary the types and concentrations of the additives different shaped crystals can be formed. When synthesized as nanoparticles, a variety of morphologies and thicknesses are observed such as plates and disks, rods, spheres, ellipsoids, rhombohedra, stars, and cubes[11, 12]. If no additives are added hematite nanoparticles are often found to grow to rounded hexagonal plates and rhombohedra, (see fig. 2.13) [11, 13, 14]. Morphologies of synthetic hematite incorporate plates and discs, rods, spindles, spheres, ellipsoids, double ellipsoids, rhombohedra, stars, cubes and peanuts [11, 13].

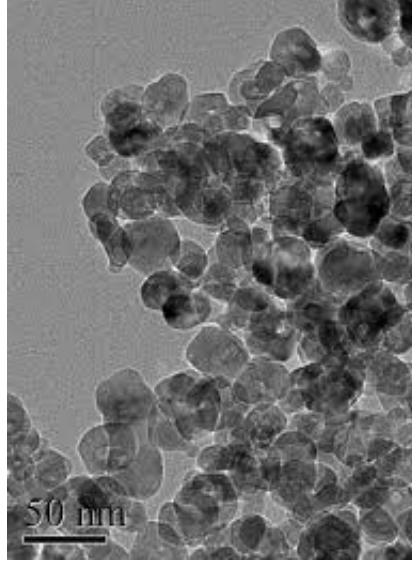


Figure 2.13: HRTEM image of hematite nanoparticles showing rhombohedral, platy and rounded morphology [11].

For phase composition, an X-ray diffractometer is used to investigate X-ray diffraction patterns of hematite nanoparticles. The X-ray diffraction patterns for the nanoparticles confirm the formation of monophasic hematite, (see fig. 2.14) [12]. All peaks have been indexed according to hexagonal $\alpha\text{-Fe}_2\text{O}_3$ as published by [12].

At room temperature and without the applied magnetic field, the Mossbauer spectrum of the $\alpha\text{-Fe}_2\text{O}_3$ sample shows one magnetically split component, (see fig. 2.15) with the values of the hyperfine parameters typical for $\alpha\text{-Fe}_2\text{O}_3$ [13, 15]. The value of quadrupole shift parameter ($\Delta\text{EQ} = -0.21$ mm/s) indicates a weakly ferromagnetic state of the studied $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles [13, 15]. If $\alpha\text{-Fe}_2\text{O}_3$ sample is placed under external magnetic field, its in-field Mossbauer spectrum consists of two resolved sextet components, moreover, the intensities of the 2nd and 5th sextet line are enhanced [13, 15]. Hematite is antiferromagnetic in its bulk form below the Morin transition temperature $T_M = 260$ K, and it presents canted antiferromagnetic or weak ferromagnetic behavior above T_M and below the Neel temperature $T_N = 956$ K, and ends up paramagnetic above T_N [12, 13]. Particles below 8 nm in size showcase superparamagnetic relaxation at room temperature[12, 13]. Above T_M , the Fe^{3+} particles are antiferromagnetically coupled along the shared octahedral faces[11–14]. There are two interpenetrating antiferromagnetic sublattices. As the electron spins of these sublattices are not actually antiparallel, with a canted angle

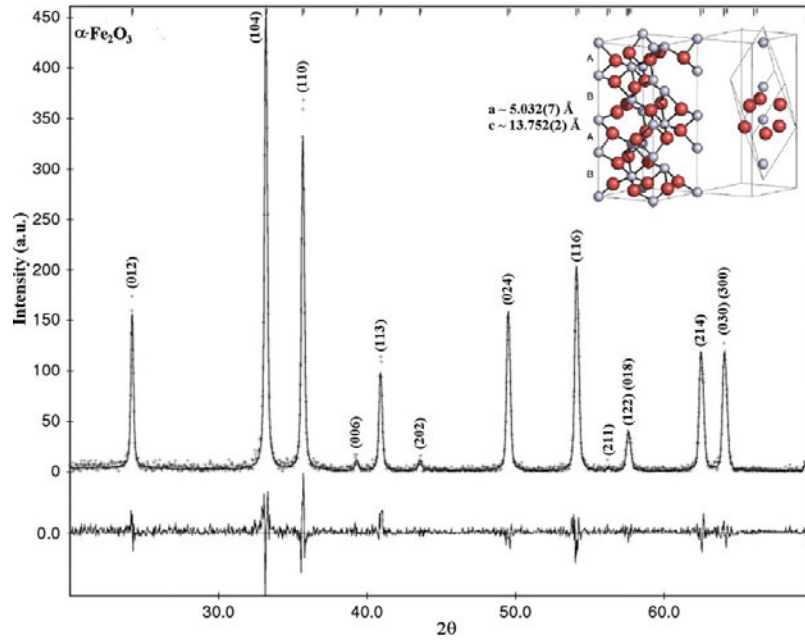


Figure 2.14: X-ray diffraction pattern of hematite nanoparticles and the hexagonal and rhombohedral unit cell structure [12].

of less than 0.1 degrees. At temperatures greater than the Morin transition temperature $T_M = 260 \text{ K}$ (at room temperature), this effect overwhelms the magnetic behavior. There is a competition at T_M between the weak magnetic anisotropy of the Fe^{3+} ion and the dipolar anisotropy, the electron spins reorient from the basal plane temperatures more greater than T_M . In this state the spins are actually antiparallel and hematite is antiferromagnetic[11, 12, 14].

At the point when pairs of Fe_3O_6 octahedra share faces, the Fe^{3+} ion in each octahedron of the pair can be viewed as being sandwiched between two triplets of O^{2-} ions. The Fe^{3+} ions in the $\text{Fe-O}_3\text{-Fe}$ units have opposite spins. Weak super-exchange occurs between the Fe^{3+} ions, which are antiferromagnetically coupled in light of opposite spins [11, 12, 14]. Stronger interactions exist where there is ferromagnetic coupling, in the corner sharing octahedra where Fe-O-Fe bond angle is large [11, 12, 14]. The magnetic behavior of hematite relies upon crystallinity or particles size and on the degree of cation substitution. Both poor crystalline and substitution of cation excluding (Rh) decrease the hyperfine field (B_{hf}) and T_M , substitution like-wise brings down the Curie temperature T_c [11, 12, 14]. Hematite magnetic properties depend strongly on the particle size and display most interesting effects when the size of the particles approaches the nanometer range [13]. As the particle size decreases the Morin temperature is reduced, and tends to vanish for particles smaller than about 8–20 nm [13]. Also, there is a reduction of the Neel temperature with decreasing particle size has been observed [13, 15]. If the particles become small enough, the direction of the magnetic moment in a single domain fluctuates due to thermal agitation, leading to superparamagnetic behaviour above the blocking temperature T_B , and to spatial freezing of these moments below T_B . It has been shown that surface effects induce a magnetic behavior of hematite which

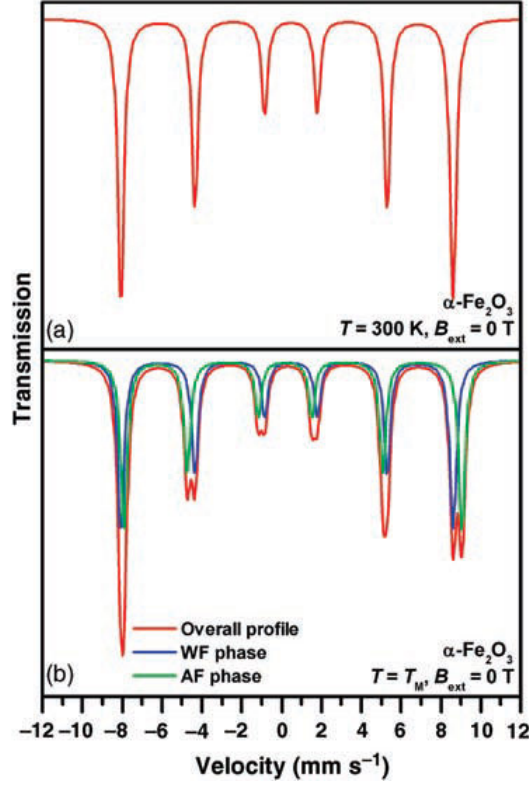


Figure 2.15: (a) Modeled typical zero-field room-temperature Mossbauer spectrum of bulk $\alpha\text{-Fe}_2\text{O}_3$ and (b) zero-field Mossbauer spectrum of $\alpha\text{-Fe}_2\text{O}_3$ nanosystem with a particle size distribution at the Morin transition temperature, showing the coexistence of weakly ferromagnetic and antiferromagnetic phase [13].

differs remarkably from the bulk hematite material [15]. The Zero-field cooled magnetization sharply increases at 54 K, reaching a maximum at 83 K with a subsequent decrease up to 300 K, (see fig. 2.16). This sharp jump and behavior of the magnetization is the property of $\alpha\text{-Fe}_2\text{O}_3$ phase and is called the Morin transition (T_M). Moreover, a blocking temperature at about 50 K that originates from the $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles is also visible in the Zero-Field Cooled curve, thus indicating the presence of the nanoparticles with smaller sizes.

The magnetization curve represented in figure. 2.17 shows the field dependence of the isothermal magnetization $M(H)$ curve at $T = 10$ K. Absence of the magnetization saturation as well as the existence of the hysteresis loop below the blocking temperature should be noticed [16]. The values of the coercivity, remanent, and mass saturation magnetization are $H_c(10\text{K}) = 646$ A/cm (810 Oe), $M_r(10\text{K}) = 1.34$ emu/g and $M_s(10\text{K}) = 6.1$ emu/g, respectively [13]. The $M(H)$ measurements were also recorded at $T = 300$ K for the sample, (see fig. 2.17). The absence of both coercivity ($H_c(300\text{K}) = 0$) and remanent magnetization ($M_r(300\text{K}) = 0$) suggests superparamagnetic behavior at this temperature.

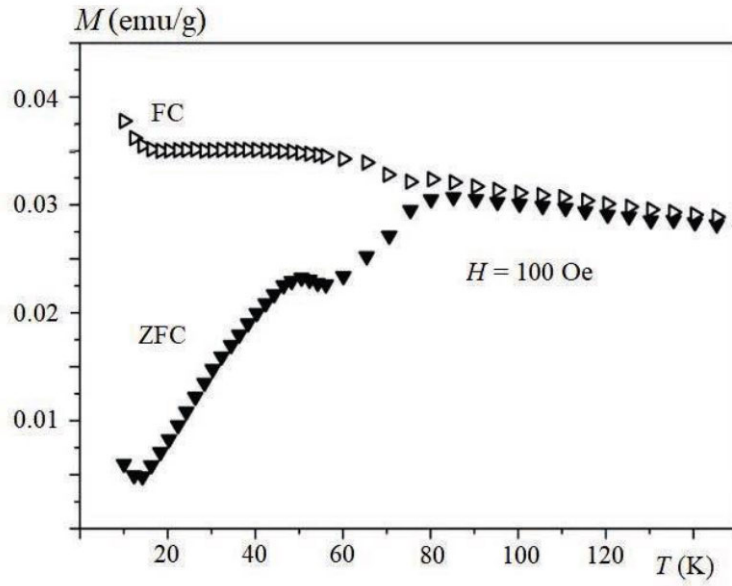


Figure 2.16: Temperature dependence of the Zero-field-cooled (ZFC) and Field-cooled (FC) magnetization measured in a field of 80 A/cm [12].

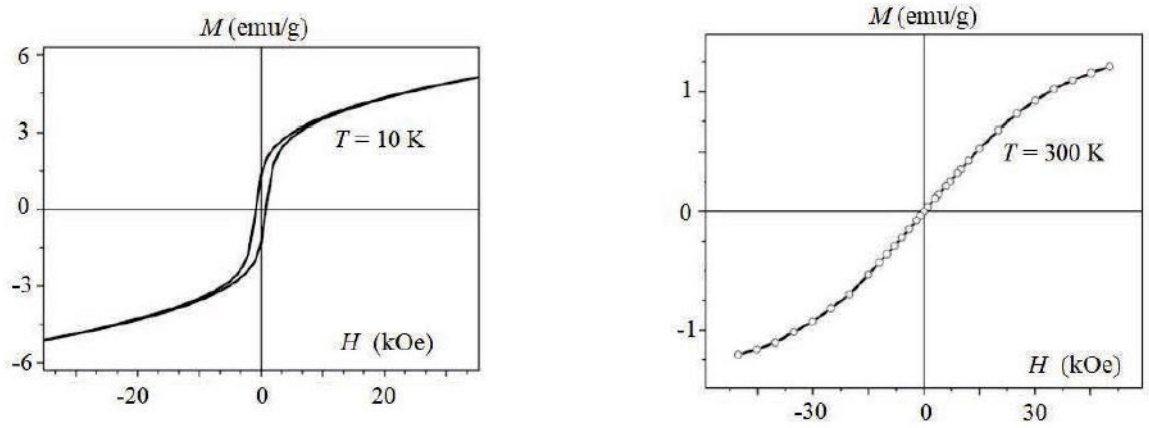


Figure 2.17: Magnetization versus applied magnetic field recorded at: (a) 10 K and (b) 300 K, (1 kOe = 800 A/cm) [12].

2.2.2 Epsilon (ϵ - Fe_2O_3) nanoparticles

Epsilon, dark brown in colour, ϵ - Fe_2O_3 is regarded as a rare phase that is scarce and just exists as nanoparticles. The epsilon phase is dark brown colored. It is extremely hard to synthesize as a single phase and is thermally unstable [15–17]. The growth of precursor nanoparticles toward the ϵ - Fe_2O_3 phase is a new strategy of employ-

ing a supporting matrix with pores of definite sizes to obtain much higher yields of ϵ - Fe_2O_3 , either as a single phase or with an experimentally detectable but, in some cases, negligible portion of other Fe_2O_3 polymorphs [16–18]. The mesoporous amorphous silica has been recently suggested to be a suitable medium for the controlled preparation of nanosized crystals of ϵ - Fe_2O_3 and as a protective medium from the oxidising power of the air atmosphere when annealing[16–18]. Two different morphologies of ϵ - Fe_2O_3 nanoparticles have been proposed thus far, which are sphere-like shapes, (see fig. 2.18) and nanorod (nanowire) shapes [16–18]. . The

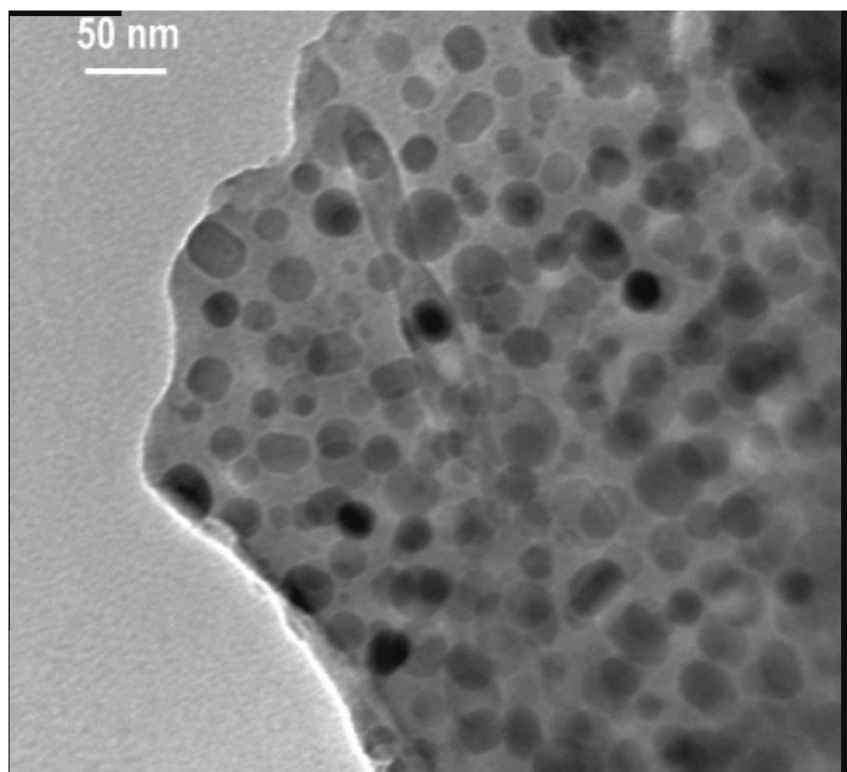


Figure 2.18: Representative examples of morphologies of the ϵ - Fe_2O_3 phase [19]

epsilon phase ϵ - Fe_2O_3 crystallizes within Pna21 space group with an orthorhombic unit cell having lattice parameters $a = 5.072 \text{ \AA}$, $b = 8.736 \text{ \AA}$, and $c = 9.418 \text{ \AA}$ [16–18].

The triple chains of octahedra share edges and single chains of octahedra which share corners. The triple chains are linked by corners and the arrangement forms cavities through which pass the chains of octahedra. The cations are circulated over both octahedra and tetrahedral site [18–20]. The crystal structure of ϵ - Fe_2O_3 contains four independent crystallographically non-equivalent iron sites, i.e. three different octahedral sites and one tetrahedral sites, (see fig. 2.19) [16–19]. It has been found that all four cation coordination polyhedra, i.e.,three octahedra and one tetrahedron, exhibit a different degrees of distortion [16–19]. A typical X-ray diffraction pattern of the epsilon phase ϵ - Fe_2O_3 at room temperature is shown, (see fig. 2.20) [17–19]. At room temperature and without external magnetic field, the Mössbauer spectrum of the ϵ - Fe_2O_3 sample shows three magnetically split spectral

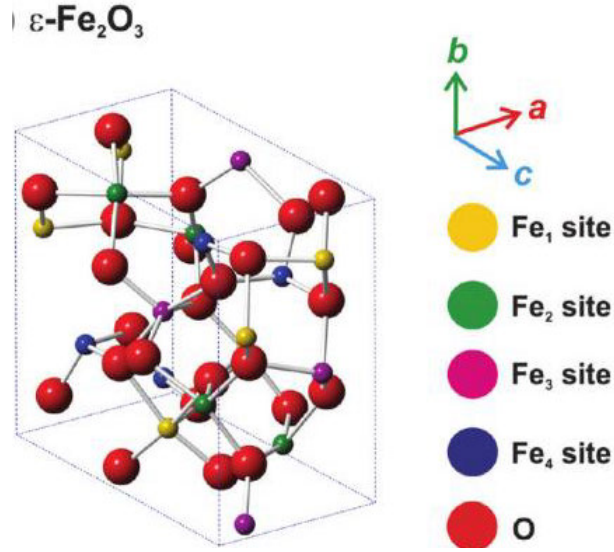


Figure 2.19: Schematic representation of the unit cell of $\epsilon\text{-Fe}_2\text{O}_3$ employing ball-stick model [17].

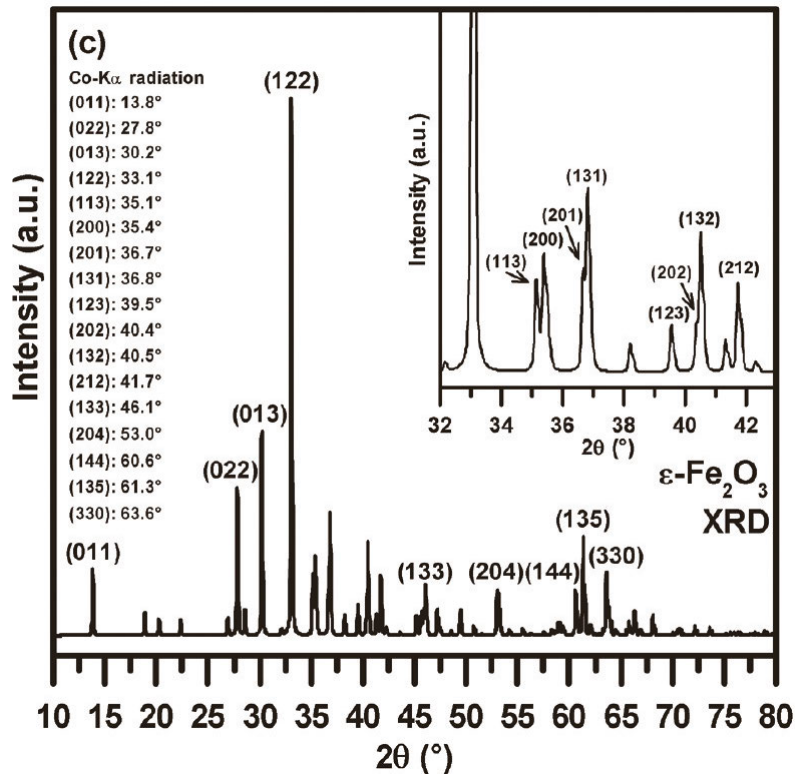


Figure 2.20: Typical XRD pattern of the epsilon phase $\epsilon\text{-Fe}_2\text{O}_3$ at room temperature, with the major atomic planes assigned to the corresponding Miller indices [17].

components. It is known that in the $\epsilon\text{-Fe}_2\text{O}_3$ crystal structure, four crystallograph-

ically non-equivalent sites are recognized, i.e, three different octahedral sites and tetrahedral sites. The octahedral sites, denoted as O_A - and O_B -sites, are significantly distorted and are often referred to as distorted octahedral sites [17, 18]. The third type of ϵ - Fe_2O_3 octahedral site show less distortion and are thus referred to as regular octahedral sites [18]. The different degree of distortion of cation polyhedra is reflected in the value of the quadrupole splitting parameter [17, 18]. For O_A - and O_B -sites, the quadrupole splitting value exceeds (-0.20 mm/s) whereas for O_C -sites, it is very close to zero[18]. The tetrahedral sites also exhibit a pronounced distortion of cation polyhedra and significantly lower hyperfine magnetic field, allowing distinguishing them very easily from octahedral sites. Due to similar values of the hyperfine parameters of the sextets corresponding to the O_A -sites and O_B -sites, it is not possible to resolve them at room temperature and without external magnetic field. Thus, at room temperature, the ϵ - Fe_2O_3 zero-field Mössbauer spectrum is frequently fitted with three sextets having a spectral area ratio of 2:1:1 [17, 19]. If ϵ - Fe_2O_3 is placed into external magnetic field, all four spectral components are clearly resolved, (see fig. 2.21) [16–18]. It shows a magnetic transition from para-

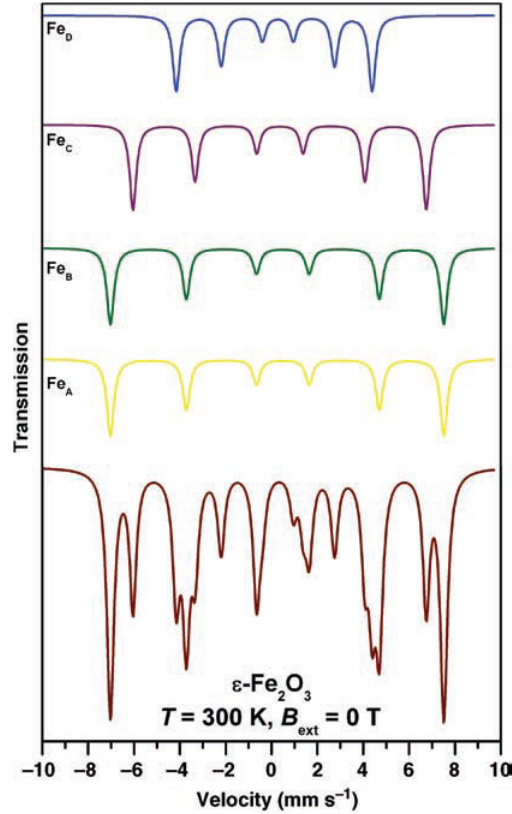


Figure 2.21: Modeled typical zero-field roomtemperature Mössbauer spectrum of ϵ - Fe_2O_3 [16]

magnetic state to an ordered magnetic state at T_c (490K). Its room temperature ground magnetic state is as yet not explained. It is guaranteed that at room temperature it acts as a collinear ferrimagnets or as inclined antiferromagnets [16–19]. At 110K, this phase experiences another magnetic transition joined by a series of

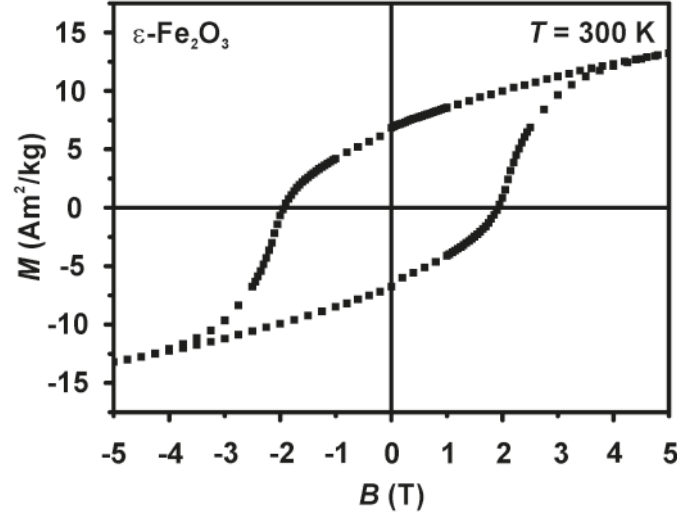


Figure 2.22: Typical room-temperature hysteresis loop of the epsilon phase $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles[19].

structural transformation and spin reorientation. The first synthesized pure $\epsilon\text{-Fe}_2\text{O}_3$ was found to have a high coercivity at room temperature ($\approx 2\text{T}$) (see fig. 2.22) [19]. Many research works have focused on the synthesis of $\epsilon\text{-Fe}_2\text{O}_3$ as a single phase, to clarify such room temperature magnetic hardness and its extraordinary collapse at 110K, and to improve the estimation of the coercive field in room temperature [18, 19]. Nonetheless, it is challenging to produce $\epsilon\text{-Fe}_2\text{O}_3$ as a bare nanoparticle, as a result of being thermally unstable and there is a sure level of agglomeration in the precursor powders or a requirement for a supporting (silica or network) [18, 19]. The $\epsilon\text{-Fe}_2\text{O}_3$ changes to hematite at 1040 K. It has a Curie temperature of 480 K. At room temperature the disordered forms (antiferromagnetic) with $T_N = 753\text{ K}$ [18, 19]. The magnetic properties relate to what might be anticipated from extremely small crystallites with an enormous number of random vacancies. Ordered $\epsilon\text{-Fe}_2\text{O}_3$ has a complex Mossbaure spectrum. At 9 K it behaves as a non-collinear ferrimagnet, the hyperfine fields are canted[18, 19].

Chapter 3

Methodology

3.1 Experimental techniques

3.1.1 Transmission Electron Microscopy (TEM)

A french physicist by the name, Louis de Broglie (1925) was the first to make note that electrons are dual in nature(have particle and wave-like characteristics), with a shorter wavelength than that of visible light [20, 21]. This was the idea behind the proposal of the transmission electron microscope , and surpassed the resolution of the light microscope. The Transmission electron microscopy (TEM) can provide a wide range of characterization techniques with such high spatial and analytical resolution, combined with a totally quantitative comprehension of the different techniques [20, 21]. The electron microscope is a combinations of counter parts that have specialized functions in oder for the microscope to function effectively. These counter parts are to be explored, in particular the physics behind the working principles for each counter part, and how it functions as a whole.This type of electron microscope is divide into three important parts; the electron gun- which produces the radiation ; the image producing system- consisting of lenses, specimen stage; and the image recording system- consisting of a camera, flourescent screen. A schematics diagram showing all the counter parts is presented in figure 3.1 [18].

The mechanism of image formation

X-rays have a short wavelength(in the order of armstrong), and good material penetration but they are hard to focus and are very damaging. A good source of electrons is an important part of a TEM when it comes to illuminating the specimen. There are two kinds of electron sources in TEMs: the first kind is called a thermionic source, which, as the name suggests, produces electrons when heated, and the second type is a field-emission source, which produces electrons when a large electric potential is applied between it and an anode [18–20]. A TEM consists of three stages of lensing with intermediate lenses – condenser lenses, objective lenses, and projector lenses, (see fig. 3.2) [21, 22]. Electron microscope (EM) lenses are electromagnetic converging lenses [21, 22]. The electromagnetic lenses typically consist of coils, and an electric current through the coils creates a magnetic field

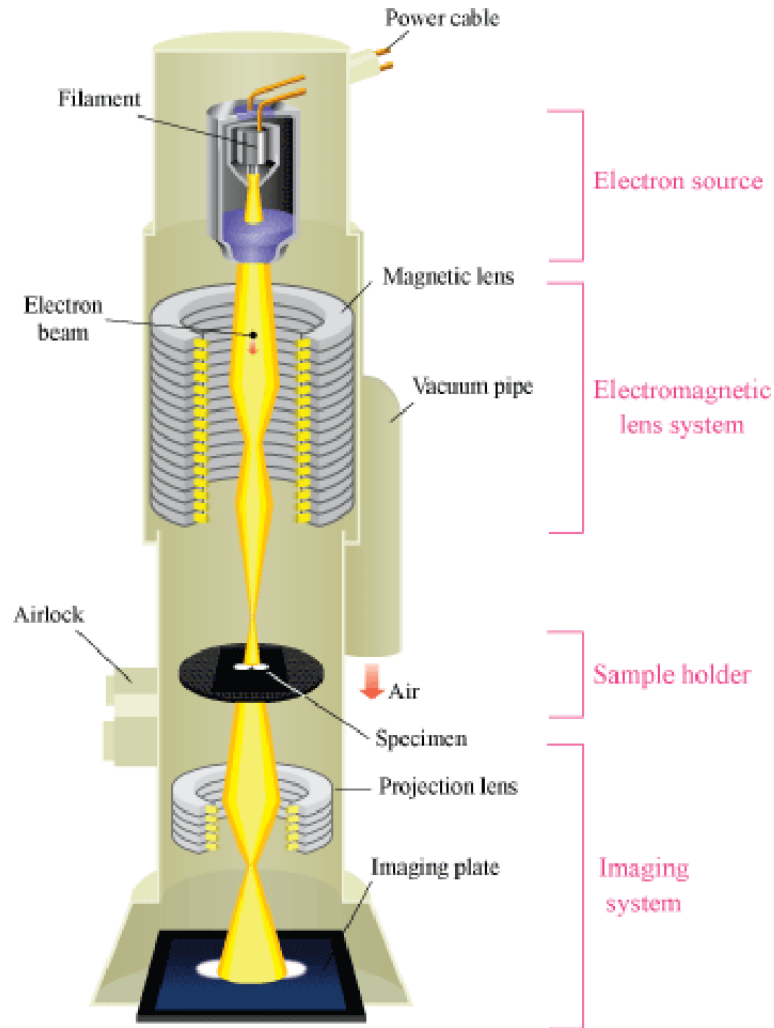


Figure 3.1: The schematic outline of a Transmission Electron Microscope [18].

that is rotationally symmetric but radially inhomogeneous: it is weak in the center of the lens but becomes stronger close to the bore in the iron cylinder.

The condenser lenses are responsible for primary beam formation. They gather the electrons of the first crossover image and focus them onto the specimen to illuminate only the area being examined. There is an aperture which comes with the condenser lens called the condenser aperture and is used to reduce spherical aberration [21, 22].

The objective lenses focus the beam that comes through the sample itself. Objective lens is used primarily to focus and initially magnify the image [21, 22]. The specimen stage is inserted into the objective lens for imaging purposes. A cold finger or anticontaminator also sits near the objective lens, so that contaminants are attracted to it.

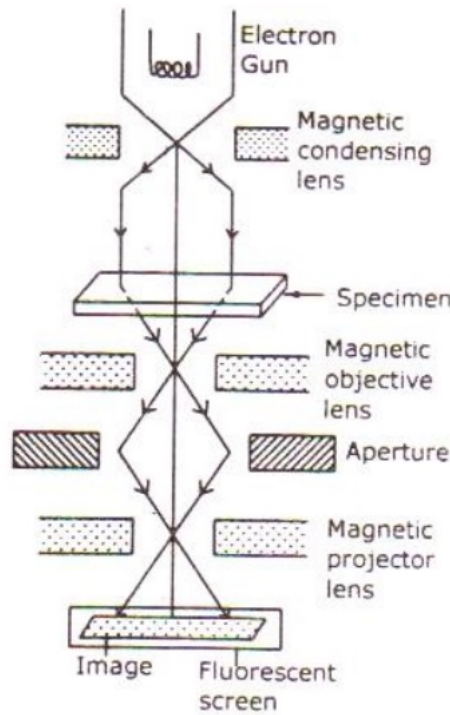


Figure 3.2: Schematic diagram of the lensing system[22].

Magnetic lenses also suffer from several imperfections. Figure 3.3(a), shows the perfect converging of the electron beam onto the optic axis focal point.

(i) **Astigmatism:** Iron-based polepieces are not perfectly circular. This causes

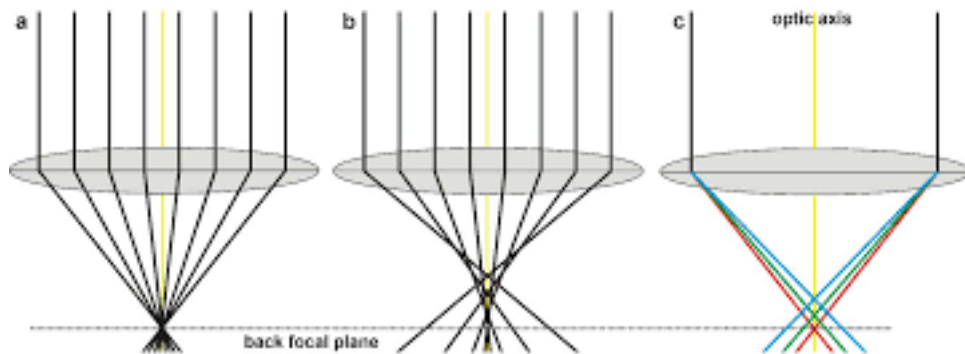


Figure 3.3: A ray diagram showing defects that occurs in lenses where (a) shows the perfect converging of the electron beam onto the optic axis focal point, (b) spherical aberration of the magnetic lens and (c) chromatic aberration of the magnetic lens [22].

a distortion of the magnetic field leading to deviations from rotational symmetry. The resulting astigmatism of the objective lens can distort the image seriously and

thus has to be corrected. Fortunately, astigmatism can easily be corrected by using quadrupole elements (so-called stigmators) which generate an additional electric field compensating the inhomogeneity of the magnetic field [21–23].

(ii) **Spherical aberration Cs**: off-axis electrons are deflected stronger than those close to the optic axis, (see fig. 3.3(b)). The result is a spread focal point of the beam. In light microscopy, an appropriate concave lens compensates the spherical aberration of a convex lens [21–23]. Although such dispersive lenses are not available in electron optics, a carefully designed corrector system, the so-called aberration corrector, can instead be applied to achieve a compensating dispersion effect analogous to a concave glass lens. A condenser aperture is used to reduce spherical aberration.

(iii) **Chromatic aberration Cc**: electrons of different wavelengths are deflected differently, leading to a focus spread as well, (see fig. 3.3(c)). Ideally, electrons accelerated to a certain energy have the same wavelength. However, the energy spread and as a result the wavelength as well varies depending on the type of electron gun. The energy spread is high in a thermoionic electron gun ($\delta E > 1\text{eV}$) but smaller if a conventional field emitter is used as the electron [21, 21, 23]. source ($\delta E = 0.6\text{ eV}$). An even smaller energy spread is achieved with cold field emitters ($\delta = 0.35\text{ eV}$) and monochromators ($\delta E = 0.1\text{ eV}$). Finally, projector lenses further magnify the image coming from the intermediate lens and projects it on to the phosphorescent screen. The projector lenses are used to expand the beam onto the phosphor screen or other imaging device such as film. Originally, TEMs used a fluorescent screen that emitted light when impacted by the transmitted electrons, for real-time imaging and adjustments; and a film camera to record permanent, high-resolution images. Modern instruments rely primarily on solid-state imaging devices, such as a CCD (charge-coupled device) camera, for image capture. They may still include a fluorescent screen, but it may be observed by a video camera [19–21]. The final image is viewed by projection onto a phosphorescent screen which gives off photons when irradiated by the electron beam. An alternative to photographic film is digital capture with a computer digitizing and archiving (CCD) camera.

Contrast in TEM

Amplitude-contrast Imaging

Amplitude-contrast images are formed by inserting an "objective" aperture into the back focal plane of the objective lens that blocks most of the diffraction pattern that lies outside of the aperture. Bright-field images are formed, if we use a small objective aperture to select only the directly transmitted beam of electrons. Dark-field images are formed, if we use the objective aperture to select electrons that have been scattered by the sample [22, 23]. In crystalline materials, diffraction contrast arises from coherent elastic scattering of electrons at special, Bragg angles. For good diffraction contrast, the sample is normally tilted such that only one diffracted beam is excited. This is referred to as a two-beam condition [22, 23]. In dark-field images, areas that appear bright correspond to areas where the atomic planes corresponding to the selected diffracted beam are locally in the Bragg condition [23].

Diffraction Contrast Imaging

Diffraction contrast imaging is particularly useful in studying the nature of defects in crystals. In quite a few materials (such as AlGaAs), the structure factor of some diffracted beams is sensitive to the difference in atomic scattering factors of the constituents. Dark-field imaging with such diffracted beams can reveal compositional changes in samples. Mass-thickness contrast arises because areas of higher atomic number (Z) or greater thickness scatter electrons more strongly thereby appearing dark in bright-field images and bright in dark-field images. It is particularly useful for imaging non-crystalline materials (such as polymers) and biological samples [20, 22, 23].

Phase-contrast Imaging

Phase contrast occurs whenever more than one beam contributes to the image, and we see fringes. It arises from the difference in phase of the electron waves that occurs when they are scattered while passing through a thin sample. Examples of phase contrast include moiré patterns; Fresnel contrast at defects; and high-resolution TEM (HRTEM) imaging [20–23]. Phase-contrast images can be difficult to interpret since the contrast is sensitive to many factors including sample thickness, orientation, and scattering factor and changes in the astigmatism and focus of the objective lens [20–23]. In HRTEM imaging, a large diameter objective aperture is used to select multiple beams to form an image containing lattice fringes that can reveal information about the atomic structure of the sample. The lattice fringes are not direct images of the atomic structure but can give information on the lattice spacing and atomic structure of the crystal [18–20]. Full interpretation of the images, e.g., of the atomic structure of defects and interfaces, requires extensive computer simulation, because when an experimental image is recorded one loses phase information, and this means one cannot directly infer the atomic structure from the image [18–21].

Electron Diffraction

In the Electron diffraction pattern, the spots indicate the presence of single microcrystals. The apertures (red circles) are localized around the direct beam for recording the bright field (BF) image and around a few diffracted beams for the dark field (DF) image, (see fig. 3.4) [21–23]. The intense direct beam is blocked by a metal rod (black shadow on the left center) to avoid overexposure.

Selected area electron diffraction (SAED)

The Diffraction pattern(DP) contains electrons from the whole area of the specimen that we illuminate with the beam. Such a pattern is not very useful because the specimen will often be buckled [21, 22]. Furthermore, the direct beam is often so intense that it will damage the viewing screen or saturate the CCD camera. So we perform a basic TEM operation which both selects a specific area of the specimen to contribute to the DP and reduces the intensity of the direct beam in the DP on the screen.

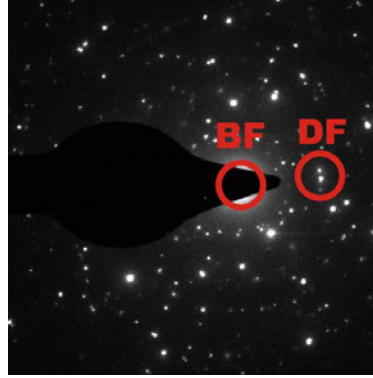


Figure 3.4: The Dark Field and Bright Field imaging[20, 21].

Bright field imaging

In the bright field (BF) mode of the TEM, (see fig. 3.5), an aperture is placed in the back focal plane of the objective lens which allows only the direct beam to pass. In this case, the image results from a weakening of the direct beam by its interaction with the sample. Therefore, mass-thickness and diffraction contrast contribute to image formation: thick areas, areas in which heavy atoms are enriched, and crystalline areas appear with dark contrast [20–22]. It should be mentioned that the interpretation of images is often impeded by the simultaneous occurrence of the contrast-forming phenomena [21, 22].

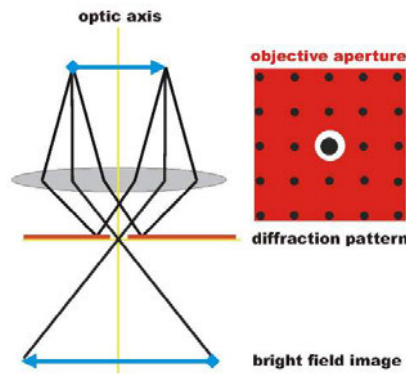


Figure 3.5: A ray diagram showing Bright Field imaging[21].

Dark field imaging

In dark field (DF) images, (see fig. 3.6), the direct beam is blocked by the aperture while one or more diffracted beams are allowed to pass the objective aperture. Since diffracted beams have strongly interacted with the specimen, very useful information is present in DF images, e.g., about planar defects, stacking faults or particle size [20–22].

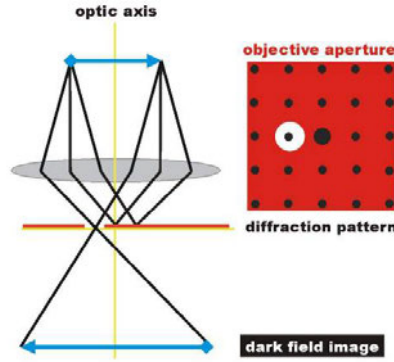


Figure 3.6: A ray diagram showing Dark Field imaging [21].

Imaging Magnetic Materials in a TEM

The modern transmission electron microscope (TEM) is a powerful tool for the study of a wide range of magnetic materials. Studies can be made of specimens, in remanent states and in the presence of applied fields[22, 24]. These can be derived basic micromagnetic information, the nature of domain walls, where nucleation occurs, the importance or otherwise of domain wall pinning and many other related phenomena. The principal difficulty encountered when using a TEM to study magnetic materials is that the specimen is usually immersed in the high magnetic field (typically 0.4-0.8T) of the objective lens[24]. This is sufficient to completely destroy or severely distort most domain structures of interest. A number of strategies have been devised to overcome the problem of the high field in the specimen region. These include (i) simply switching off the standard objective lens, (ii) changing the position of the specimen so that it is no longer immersed in the objective lens field, (iii) retaining the specimen in its standard position but changing the pole-pieces of the objective lens to provide a non-immersion environment, or (iv) adding super mini-lenses in addition to the standard objective lens which is once again switched off[22, 24]. Magnetic structures are most commonly revealed in the TEM using one of the modes of Lorentz microscopy[24]. This generic name is used to describe all imaging modes in which contrast is generated as a result of the deflection experienced by electrons as they pass through a region of magnetic induction.

3.1.2 Vibrating Sample Magnetometer

The Vibrating Sample Magnetometer (VSM) is a sensitive and versatile instrument for study of magnetic dipole moments in magnetic materials [23]. It is used to measure magnetization on a sample based on the Faraday's laws of electromagnetic induction as a function of magnetic field and temperature. The Vibrating sample Magnetometer was first designed by Simon Foner, in 1959 at the Lincoln laboratories. All the VSM work, involves the measurement of voltage induced in a stationary coil, otherwise called as detection coils, due to the harmonic vibration of the sample in a uniform magnetic field [23]. The Vibrating Sample Magnetometer is generally used for routine magnetic measurements as a function of temperature and field of a magnetic materials [23].

The working principle

The VSM operates based on Faraday's law of Electromagnetic Induction, which states that a changing magnetic field on a copper wire will produce an electric current which will result an electric field [23]. This produced electric field can be measured, thus can provide information about the magnetic field [23]. The sample is introduced to a constant applied magnetic field and individual magnetic spins will align with applied magnetic field if the sample is magnetic [23]. The stronger the constant applied magnetic field, the larger the magnetization will be. The magnetic dipole moment of the sample will create a magnetic field around the sample, sometimes called the magnetic stray field. The sample is moved up and down, and a set of pick-up coils can sense this changing magnetic stray field as a function of time, (see fig. 3.7). An electric current will be induced inside the pick-up coils, according to Faraday's law of electromagnetic induction, as a result of the changing magnetic field [23]. The current induced is directly proportional to the magnetization of the sample. The induction current is amplified by a transimpedance amplifier and a lock-in amplifier. The various components are hooked up to a computer interface. Using controlling and monitoring software, the system can tell us how much the sample is magnetized and how its magnetization depends on the strength of the constant magnetic field. The vibrating sample magnetometer operates on the principle that when a sample material is placed in a uniform magnetic field, a dipole moment proportional to the product of the sample susceptibility times the applied field is induced in the sample. A sample also undergoing sinusoidal motion induces an electrical signal in a set of stationary pick-up coils [23]. This signal is proportional to the magnetic moment, vibration amplitude, and vibration frequency. The material under study is contained in a sample holder, which is centered in the region between the pole pieces of an electromagnet, (see fig. 3.7). A vertical sample rod connects the sample holder with a transducer assembly located above the magnet, which supports the transducer assembly with sturdy, adjustable support rods [23]. The transducer then converts a sinusoidal AC drive signal, provided by a circuit located in the console, into a sinusoidal vertical vibration of the sample rod, and the sample thus undergoes a sinusoidal motion in a uniform magnetic field. Coils mounted on the pole pieces of the magnet pick up the signal resulting from the sample motion, (see fig. 3.7). This AC signal at the vibration frequency is proportional

to the magnitude of the moment induced in the sample, vibration amplitude and frequency [23]. A servo system maintains constancy in the drive amplitude and frequency so that the output accurately tracks the moment level without degradation due to variations in the amplitude and frequency of vibration. The samples can be characterized by weight or volume.

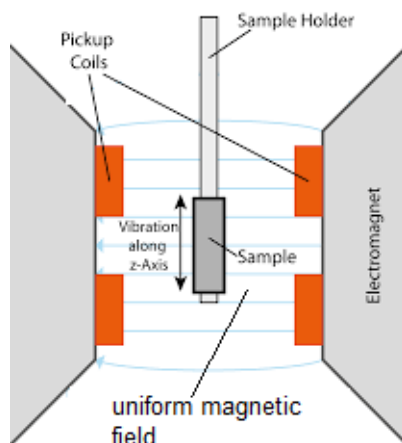


Figure 3.7: A schematic representation of the Vibrating Sample Magnetometer [22].

The set up of the Vibrating Sample Magnetometer consist of electromagnets that are constantly cooled by a water supply [23]. The constant applied magnetic field used to magnetize the sample is generated by an external power supply. The sample hangs in between the pole pieces, and is placed in a sample holder rod that is attached to a vibration exciter wich moves the sample up and down at a frequency of about 85Hz , (see fig. 3.7).The Control chassis controls the 85Hz oscillation of the exciter. The sample rod positions can be adjusted along the three dimensional coordinate system, to achieve the desired orientation of the sample to the constant magnetic field [23]. The current produced in the pick up coils is at the same frequency as the vibration of the sample and thus the signal generated gives information about the magnetization of the sample. The signal generated is passed on an amplifier. Lock in amplifier picks up signals at the vibrating frequency and eliminates noise from the background (environment). The Computer Interface uses software that makes data collection easier by automating the control of the various components during data collection and the data can be graphed and plotted on the printer.

3.1.3 Mössbauer Spectroscopy

Mössbauer spectroscopy is a spectroscopic technique that measures the energy at which specific atomic nuclei absorb gamma radiation, based on the quantum mechanical effect " Mössbauer effect" [25]. The technique is used as a ‘fingerprint’ technique in the identification of (Fe)-iron oxide phases based on their magnetic properties. An unstable ^{57}Co decays to ^{57}Fe by capturing an atomic electron by

a process called k- capture (electron capture) [25]. The ^{57}Fe is in an excited state which decays to ground state by giving off a gamma ray, (see fig. 3.8).

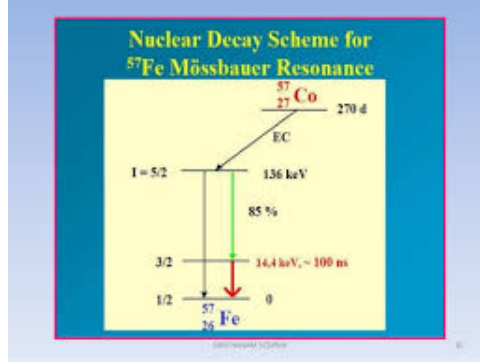


Figure 3.8: The decay of an unstable ^{57}Co atom and the emission of a gamma ray [25]

When the emitting nucleus gives off radiation in the form of a gamma-ray, the nucleus must recoil [25, 26]. The energy of the emitted gamma ray E_γ is ;

$$E_\gamma = E_0 - E_R$$

where E_0 is the energy of the nucleus and E_R is energy of recoil.

The conservation of energy must not be violated, therefore the absorbing nucleus (E_{absorbed}) must absorb a gamma ray with energy E_γ is;

$$E_{\text{absorbed}} = E_\gamma = E_0 + E_R$$

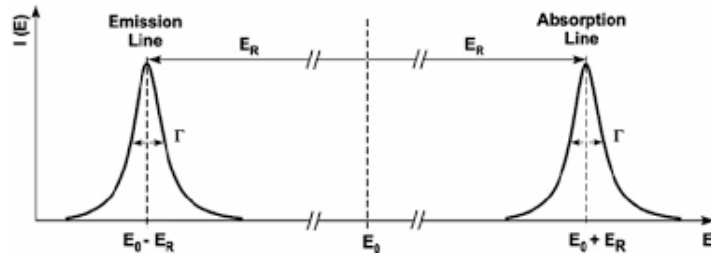


Figure 3.9: The emitting and absorbing atomic nucleus [25].

Thus the centres of the absorption and emission lines are displaced relative to one another by an energy separation $2E_R$ and if this is much greater than the line width, resonant absorption will not be observed [25]. In 1958, Rudolf Mössbauer demonstrated that if the emitting and absorbing nuclei are strongly bound in crystalline solids, strong resonant emission and absorption of gamma rays may occur and this is the so-called Mössbauer effect. Using conservation of momentum one can show that the recoil energy is given by;

$$E_R = \frac{E_\gamma^2}{2mc^2}$$

where M is the mass of the recoiling body, the nucleus. If the nuclei are bound to the lattice the recoil energy becomes;

$$E_R = \frac{E_\gamma^2}{2Mc^2}$$

The recoil energy is negligible because M in the equation is the mass of the whole lattice and recoilless emission and resonance absorption of the gamma ray becomes possible.

Mössbauer Spectroscopy Instrumentation

The basic elements of a Mössbauer spectrometer are a source, sample, detector, and a drive to move the source or absorber. Most commonly, this is done by moving the source toward and away from the sample, while varying velocity linearly with time[25, 26]. For example, for ^{57}Fe , moving the source at a velocity of 1 mm/sec toward the sample increases the energy of the emitted photons by about ten natural linewidths[25–27]. For simplicity, "mm/sec" is the conventional "energy" unit in Mössbauer spectroscopy. It is also possible to leave the source stationary and oscillate the sample, as is done with synchrotron Mössbauer[25, 27]. The location of the detector relative to the source and the sample defines the geometry of the experiment(see fig. 3.10); most commonly, either transmission or backscatter modes are used[26]. The radiation consists of gamma rays coming from nuclei that decay from a

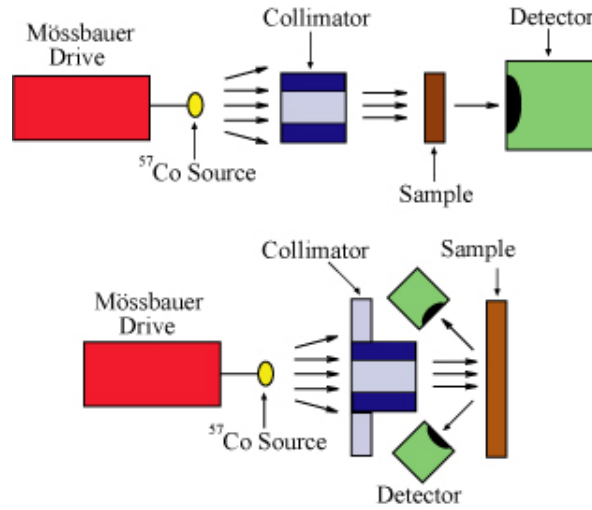


Figure 3.10: Schematic representation of the Mössbauer spectroscopy Instrument [27].

low-lying excited state to the ground state. This radiation is highly monochromatic, but incoherent[26]. Gamma rays that are emitted without recoil-energy loss from a particular type of nucleus have approximately the right energy to be resonantly reabsorbed by nuclei of the same type[26]. The spectroscopy is normally performed by varying the energy of the gamma rays incident on the absorber and observing the energy and the intensity of the resonant absorption[26]. The resonant absorption

can be observed either directly, by noting the increased attenuation (due to the nuclear absorption) of the gamma rays passing through the absorber, or by observing events following the resonant absorption of the gamma ray, such as the emission of a gamma ray or conversion electron in the subsequent decay of the excited level in the absorber[26]. The first technique, called “transmission geometry,” is used in virtually all cases[26]. It would at first appear to be highly advantageous to use the latter technique, “scattering geometry,” since this allows, in principle, detection of the resonant absorption events free of background, whereas the transmission technique normally allows one to observe only the small increase in absorption caused by the nuclear resonance process[26]. In practice, however, the fact that the counting rate is attenuated by an additional solid angle (the one from the absorber to the detector), the difficulty in providing suitable windows and absorber and detector geometries for the resonantly scattered radiation, and the existence of a strong background from Compton and Raleigh scattered radiation almost invariably make transmission geometry the more effective one[26]. The major research use of scattering geometry at the present time appears to be in the selective excitation of nuclear levels. Scattering geometry has also been used for the study of thick samples, as in metallurgical analysis, where transmission geometry is not realizable.

Mössbauer Parameters

There are three Mössbauer spectroscopy parameters that gives information about the material under investigation [27]. These parameters are Isomer shift, hyperfine splitting and quadrupole splitting. The study of solids using Mössbauer spectroscopy involves two nucleus that are in different chemical environments. This difference in the chemical environments in the absorber nucleus as relative to the emitting nucleus is caused by the interaction of the absorber nucleus with its local environment, these interactions are known as hyperfine interactions.

Isomer shift

The interaction between the nucleus and the inner shell , s-electron density results in an isomer shift [27]. The source and absorber nucleus are in different chemical environment, their s-electron densities are different. The excited nucleus of the absorber and the ground state of the emitter nucleus are not equal, their electrostatic interactions are different and that is measured as isomer shift in Mössbauer spectroscopy.

Quadrupole splitting

A nucleus with spin $I > 1/2$ have an electric quadrupole moment (eQ) that originates with its asymmetrical shape[27]. The interaction of the nuclear quadrupole moment with the electric field gradient leads to splitting of the nuclear energy levels , see fig. 3.11. For ^{57}Fe , this causes individual peaks in the transmission spectrum to split into doublets. For axially symmetric electric field gradient ($\eta = 0$) the splitting is given by

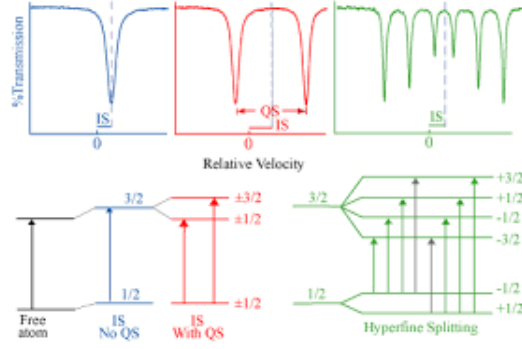


Figure 3.11: Mössbauer spectroscopy hyperfine interactions: Isomer Shift (blue), Quadrupole Splitting (red), and magnetic splitting (green) [25].

$$\Delta E_Q = \frac{eQV_{zz}}{2}$$

where V_{zz} is the principal electric field gradient tensor.

Magnetic Hyperfine Splitting

For magnetic materials a magnetic field is present at the nucleus. The interaction of the nuclear dipole moment and the field results in ‘Zeeman’ splitting, yielding a sextet pattern (see fig. 3.11, (green)). The energies of nuclear transitions are modified when the nucleus is in a magnetic field, the energy levels split into $2I + 1$ sublevels [27]. The ground state ($I = 1/2$) of ^{57}Fe in a magnetic field B_z is split into two energy sublevels ($MI = \pm 1/2$). And the excited state ($I = 3/2$) split into four sublevels ($M_I = \pm 3/2, \pm 1/2$). The selection rule $\Delta M_I = 0, \pm 1$ restricts the two transitions lines shown in grey in the green spectra [27].

3.1.4 X- ray Diffraction

X-ray diffraction (XRD) is an important tool use to provide information about a crystalline material, some of the common uses can include analyzing the crystal structure, performing quantitative analysis of phase composition, finding the crystalline size and micro strain, looking at residual strain (macro strain), identify defects, characterize polymorphs, texture orientation, unit cell parameters and bravais lattice symmetry can be found [28]. In 1912, Max von Laue, discovered that crystalline substances act as three dimensional diffraction gratings for X-rays with wavelengths similar to the spacing of planes in a crystal lattice [?]. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample, (see fig. 3.12) [28].

When conditions satisfy Bragg’s Law, the interaction of the incident rays with the sample produces constructive interference (and a diffracted ray).

$$n\lambda = 2d \sin \theta \quad (3.1)$$

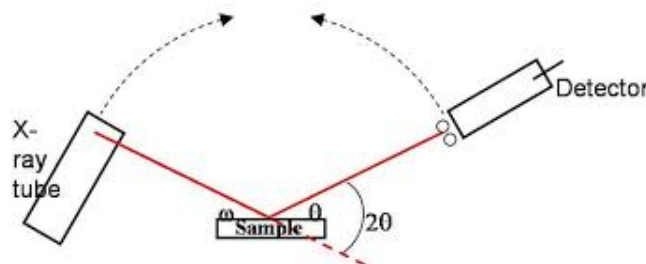


Figure 3.12: The Bragg-Brentano setup consist of an X-ray source, a detector and a sample mount [28].

where n is an integer, λ is the wavelength of the X-rays, d is the interplanar spacing generating the diffraction and θ is the diffraction angle, (see fig. 3.13).

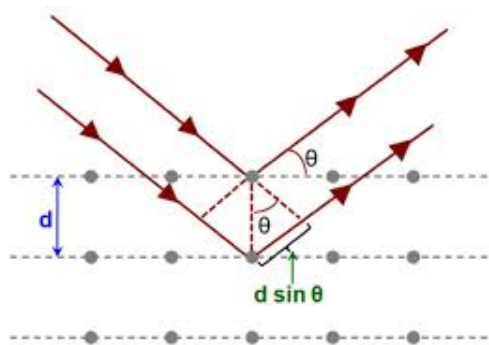


Figure 3.13: Geometric derivation of Bragg's law: Constructive interference occurs when waves scattered from adjacent lattice planes are in phase, while Destructive interference occurs when they are out of phase [28].

Rotation of the sample should take place so that the diffracted X-rays can be detected at various angles. Conversion of the diffraction peaks to d -spacings allows identification of the compound by comparing to a standard reference patterns because each compound has a set of unique d -spacings [28]. X-ray diffractometers consist basic parts; an X-ray tube, a sample holder, and an X-ray detector [28]. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target through a potential difference, and bombarding the target material with electrons. When electrons have sufficient kinetic energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced [28]. These spectra consist of several components, the most common being K_α and K_β , (see fig. 3.14). The K_α component consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$, where $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromators, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with Cu $K_{\alpha 1}$ radiation = $1.5418 \text{ \AA}$.

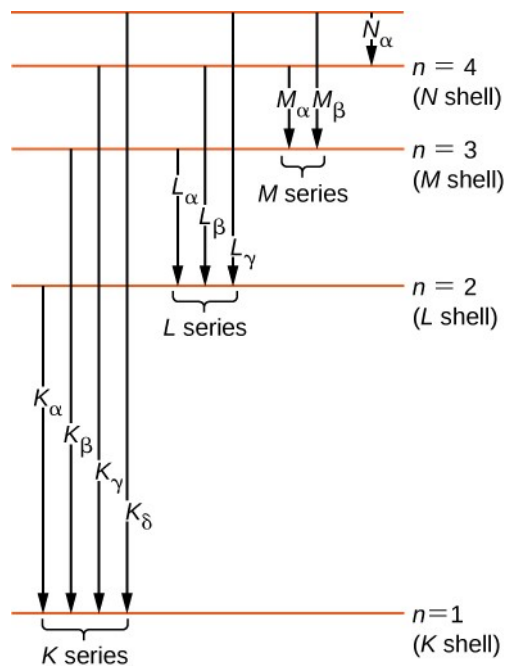


Figure 3.14: Lines occur because bombarding electrons knock out electrons from K shell ($n = 1$), which are filled by electrons in higher shells. Electrons falling from L shell ($n = 2$) give rise to K_α lines, whereas electrons from M shell ($n = 3$) give the K_β lines [28].

In many papers, also in the last decade, the most commonly applied configuration for XRD uses a copper radiation source (e.g., Amstaetter et al. 2012; Bharde et al. 2005, 2006; Wu et al. 2013)[29]. By using copper radiation when analyzing iron minerals however, it is often overlooked that the choice of radiation should be compatible to the sample composition in order to obtain a diffractogram of good quality[29]. A mismatch therein can lead to a high background signal that, especially in combination with a low peak intensity, makes interpretation more difficult and can even lead to incorrect phase identification[29]. The most striking example thereof is when dealing with magnetite and/or maghemite. Diffractograms of these two minerals are only distinguishable by a few low intensity peaks[29]. Both can form in similar environments and be converted into one another, in the case of magnetite to maghemite simply by exposure to ambient air[29]. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg law, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor [28]. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ . The instrument used to maintain the angle and rotate the sample is termed a goniometer [28]. For typical powder patterns, data are collected at 2θ

from 5° to 70° , angles that are preset in the X-ray scan. X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology. Other applications include characterization of crystalline materials; identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically; determination of unit cell dimensions; measurement of sample purity[28]. With specialized techniques, XRD can be used to: determine crystal structures by using Rietveld refinement; determine of modal amounts of minerals (quantitative analysis); characterize thin films samples; make textural measurements, such as the orientation of grains, in a polycrystalline sample [28]. There are some strengths and some limitations of X-ray Powder Diffraction (XRD), strengths include; Powerful and rapid (less than 20 min) technique for identification of an unknown mineral [28]. In most cases, it provides an unambiguous mineral determination; Minimal sample preparation is required; XRD units are widely available; Data interpretation is relatively straight forward. Limitations include; Homogeneous and single phase material is best for identification of an unknown; Must have access to a standard reference file of inorganic compounds; requires tenths of a gram of material which must be ground into a powder; for mixed materials, detection limit is approximately two percent of sample; for unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated; peak overlay may occur and worsens for high angle "reflections" [28]. X-ray Diffraction is a high-tech, non-destructive technique for analyzing a wide range of materials including fluids, metals, minerals, polymers, catalysts, plastics, pharmaceuticals, thin film coatings, ceramics, solar cells and semi conductors [28]. The technique finds innumerable practical applications in various industries, including microelectronics, power generation, aerospace, and many more. The XRD analysis can easily detect the existence of defects in a particular crystal, its resistance level to stress, its texture, its size and degree of crystallinity and virtually any other variable relating to the sample's basic structure [28].

The Scherrer equation is used to calculate the average crystallite sizes. It is important to note that Scherrer's equation can only be applied for average sizes up to about 100–200 nm (depending on the instrument, sample and signal-to-noise ratio), because diffraction-peak broadening decreases with increasing crystallite size and it becomes difficult to separate the peak broadening due to crystallite size from the broadening due to other factors.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3.2)$$

where K is the shape factor (the typical value for sphere is 0.89), λ is the wavelength of the incident beam, β is the broadening of the most intense peak at full width half maximum height (FWHM), θ is the Bragg's angle and D is the diameter of the crystallite.

3.2 Sample Preparation

3.2.1 Sol-gel Method

Sol-gel method is a way of preparing nanostructured metal oxides and mixed metal oxide nanocomposites [30]. The name "sol-gel" comes from the process of forming nanomaterials from a "sol", which is a dispersion of colloidal particles in a solution and a "gel", which is a semi solid or a continuous solid network which encloses liquid phase [30, 31]. The aim of this method is to dissolve a solid in order to form a solid in a controlled manner [30, 31]. This method allows fabrication of nanostructures with novel chemical and physical properties. There are few steps in the process of synthesizing a metal oxide nanostructure which are; hydrolysis, condensation and drying as shown in, see fig. 3.15. The hydrolysis step involves the hydrolysis of the metal precursor to form the metal hydroxide solution, after which follows the condensation to form a gel [30, 31]. Lastly, the gel is then dried to form either a xerogel or an aerogel depending on the method of drying [30, 31]. The sol-gel method can be achieved in two path ways called the aqueous sol-gel and the non-aqueous sol-gel method according to the solvent used. In an aqueous sol-gel method water is used the reaction medium, while in nonaqueous sol-gel method an organic solvent is a reaction medium [30, 31]. The metal precursor and the solvents used have a significant impact on the synthesis of metal oxide nanostructures. In aqueous sol-gel method the metal oxide is formed from the presence of oxygen atom from the water molecule. Metal precursors are usually metal alkoxides or acetates, nitrates, sulfates and chlorides [31].

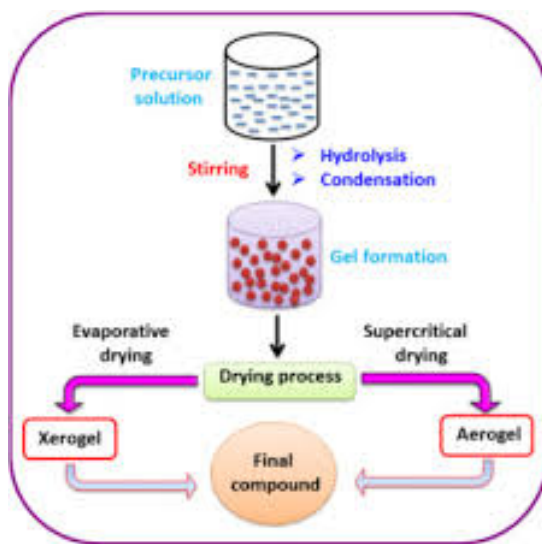


Figure 3.15: The Reaction Pathway for the Production of Metal Oxide Nanostructures in the Sol-Gel Method [31].

Nevertheless, there are some disadvantages associated with aqueous sol-gel method. The steps involved in the synthesis (hydrolysis, condensation and drying) can all take place at the same instance making it difficult to synthesize the nanostructured metal

oxide in a controlled manner. The aqueous sol-gel method is highly approved for synthesis of bulk metal oxides. In nonaqueous sol-gel method the organic solvent such as alcohol, ketones, aldehydes or metal precursors donates an oxygen atom required to form a metal oxide. The organic solvents not only donates the oxygen atom but plays a role in forming the desired chemical and physical properties like composition of the metal oxide, morphology and particle size [30–32]. The non-aqueous sol-gel method is highly approved for synthesis of nanostructured metal oxides. The nonaqueous sol-gel method can be split into two paths known as the surfactant-controlled and solvent-controlled approaches for the synthesis of metal oxide nanomaterials. Surfactant-controlled is the direct conversion of a metal precursor into a metal oxide at higher temperature range and this allows control over the shape, growth of the nanomaterials, and avoids the agglomeration of particles. Solvent-controlled approaches are based on the solvent effects that can change the chemical reactivity, such as solubility, reaction rates and thermodynamic and kinetic control over a chemical reaction.

It is advantageous to coat magnetic nanomaterial with a material that is non toxic and that can support the required amount of the magnetic nanomaterial [30–32]. A silica host protects and stabilises the magnetic nanomaterial, and also prevents any contamination with any foreign material. The sol-gel preparation of silica (Silicon dioxide) is done using tetraethyl orthosilicate (TEOS), ethanol and water. This one-phase solution undergoes sol-gel transition to a rigid, two-phase system of solid silica and solvent-filled pores. These reactions are acid-catalysed or base-catalysed. The removal of solvent from the gel by conventional drying, such as evaporation, will result in the formation of xerogel but if supercritical drying is used, aerogel will form [31, 32]. The acid-catalyzed xerogels exhibit extremely fine microstructural features, and the pores are extremely small and evenly spread. The individual silica particles cannot be resolved. Hence, light incident on these gels is mostly transmitted through the solid, and the gels are observed to be transparent. The base-catalysed xerogels are particulate, and the individual silica particles may be resolved (10 nm). They are less tightly packed than in the acid-catalysed sample. Hence, light incident on these gels is reflected from the solid, and the gels appear more opaque [30–32].

3.2.2 Factors affecting the sol-gel chemistry

pH

Any colloidal chemistry that involves water is sensitive to pH. In the case of silica gel formation, this has to do with the hydrolysis step of the silica precursor that results in silanol groups, which are what connect together to produce silica nanoparticles and eventually the gel network [31, 32].

Solvent

As molecules assemble together (polymerize) into nanoparticles, the solvent needs to be able to keep the nanoparticles dissolved so that they don't precipitate out of the liquid. Also, the solvent can play a role in helping nanoparticles connect together.

As a result, the solvent makes a big difference in ensuring a gel network can form.

Temperature

The chemical kinetics of the different reactions involved in the formation of nanoparticles and the assembly of nanoparticles into a gel network are accelerated by temperature, meaning the gel time is affected by temperature. If the temperature is too low, gelation may take weeks or months [30–32]. If the temperature is too high, the reactions that join nanoparticles together into the gel network occurs so quickly that clumps form instead and solid precipitates out of the liquid. Reaction-generated heat released from chemical reactions involved in the formation of nanoparticles and gel networks can feed back into the solution and cause things to react faster, releasing even more heat, causing things to react even faster, etc.

Time

Depending on the type of gel being made, different steps in the gel formation process work differently over different time scales. In general, slower is better for sol-gel. If a gel is allowed to form slowly, it usually has a much more uniform structure. This often means a stronger gel and, in the case of potentially transparent gels like silica, results in a clearer gel that has less Rayleigh scattering (appears less blue). Speeding reactions up too much causes precipitates to form instead of gel network, and can make a gel cloudy and weak or simply not form [32].

3.2.3 The synthesis of magnetic iron oxide nanoparticles

Synthesis of α -Fe₂O₃ nanoparticles

The Sol-gel method used was proposed by Zhang et al. to prepare an iron oxide gel from the precursor salt Fe(NO₃)₃ and citric acid [33]. A precursor solution was prepared by dissolving a known amount of Fe(NO₃)₃ in water, then citric acid was added. This was done according to the weight ratio between Fe(NO₃)₃ and citric acid of 0.5: 0.55. The mixture was refluxed at 343 K for 30 minutes under continuous stirring to ensure a perfect homogeneity. The gel was obtained from the mixture by rotary evaporation and was heat treated at 800K for 3 hours.

Synthesis of ϵ -Fe₂O₃/ SiO₂ nanoparticles

The ϵ -Fe₂O₃ nanoparticles were prepared using a method proposed by Sans et al. in a threestep approach[34]. this method was originally proposed by Jose et al.[17] and a few changes were made in terms of the quantities of the starting material used. In the first step silica gels containing iron were obtained from an hydroethanolic sol of tetraethyl orthosilicate (TEOS) of molar composition TEOS:Ethanol:water = 1:6:6 with dissolved iron nitrate Fe(NO₃)₃.9H₂O precursor. In a second step the gels were dried and thermally treated at high temperature to obtain a SiO₂/ ϵ -Fe₂O₃ composite. To prepare 2.3 g of ϵ -Fe₂O₃, 5.0 ml of distilled water and 31.4 ml

of absolute ethanol were stirred in a 100 ml beaker, to which 11.7 g of iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved before adding dropwise 20 ml of TEOS. The resulting sol were placed in chemical hood at room temperature, where gelation took place for about 2-3 weeks. The gel was dried in an oven at 353K and treated in air atmosphere at 1373 K for 3 h.

Synthesis of $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles

Sol-gel preparations followed a procedure similar to that described by Jose et al. [17]. A hydroethanolic solution of tetraethyl orthosilicate (TEOS) of molar composition, TEOS:Ethanol:water=1:5:6 containing dissolved iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was prepared. First, 5.4 ml of distilled water and 26 ml of absolute ethanol were added to a 100 ml beaker and stirred for 5 min. Then, the 10.60 g of iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved and the solution which attained a $\text{pH} \approx 0.35$. Finally 20 ml of TEOS were added dropwise to the solution under stirring. The stirring, with the beaker covered, was maintained for 20 minutes after adding the TEOS. The sol was then distributed in 6 cm diameter petri dishes, attaining a level of 2-4 mm, which were placed in a plastic box, closed with its cover but not hermetically sealed, and placed in chemical hood at room temperature. The gelation process took place in about 2-3 weeks. But instead of following the step-wise heating procedure by Jose et al. [17]. In this work the sample was only annealed at 1373 K for 3h in air atmosphere.

3.2.4 Characterization

X-ray Diffraction:

The samples were analysed using X-ray diffractometer and measurements were done over 2θ range $(20-80)^\circ$, with a typical step size of 0.034° in 2θ at wavelength $\lambda = 1.5306 \text{ \AA}$. The measurements are performed using a multi purpose X-ray diffractometer D8- Advance from Bruker operated in a continuous $\theta - \theta$ scan in locked coupled mode with $\text{Cu-K}_{\alpha 1}$ radiation. A position sensitive detector, Lynx-Eye, is used to record diffraction data at a typical speed of 0.5 sec/step which is equivalent to an effective time of 92 sec/step for a scintillation counter.

Transmission Electron Microscopy Micrographs:

The samples synthesized in this work were analyzed by Transmission electron microscopy (TEM). The observations were carried out using a JEOL JEM-1400 microscope, using Gatan Digital Microscope software, operating at 200 kV. The samples were crushed, ultrasonically dispersed in ethanol and placed on a TEM grid. The Image J program was used to measure the particle size of the nanoparticles presented on the TEM image.

Mossbauer Spectrometer:

The magnetic state of the samples were investigated using the Mossbauer spectroscopy. The Mossbauer spectra were acquired at room temperature using a conventional Mossbauer spectrometer with a $^{57}\text{Co}/\text{Rh}$ source for which calibration was done with a foil of metallic iron, the Mössbauer parameters are given relative to this standard at room temperature. The fitting of the data was carried out using

Recoil Mössbauer analysis software and were fitted using the Lorentzian site analysis.

Vibrating Sample Magnetometer:

The Hysteresis loops of isothermal magnetizations were measured at 300, 200, 100 and 10 K in the applied magnetic field range ± 3.6 T by using the PPMS-12T magnetometer. The remanent magnetization (M_r) and coercivity H_c were studied with respect to temperature.

Chapter 4

Results and Discussion

4.1 α -Fe₂O₃ nanoparticles

X-ray Diffraction

X-ray diffraction (XRD) technique was used to study phase composition of the samples. XRD pattern of α -Fe₂O₃ nanoparticles are reported in figure 4.1. The reflections that appear are from a pure iron oxide α -Fe₂O₃ phase matching with JCPDS file Card, no. 33-0664 and representing that the α -Fe₂O₃ particles are crystalline structure. A high background signal in combination with a low peak intensity is observed due to that the choice of radiation should match the sample composition. A good quality x-ray diffraction pattern is obtained when the radiation source is of iron for a sample containing iron[29]. The X-ray diffraction pattern shown

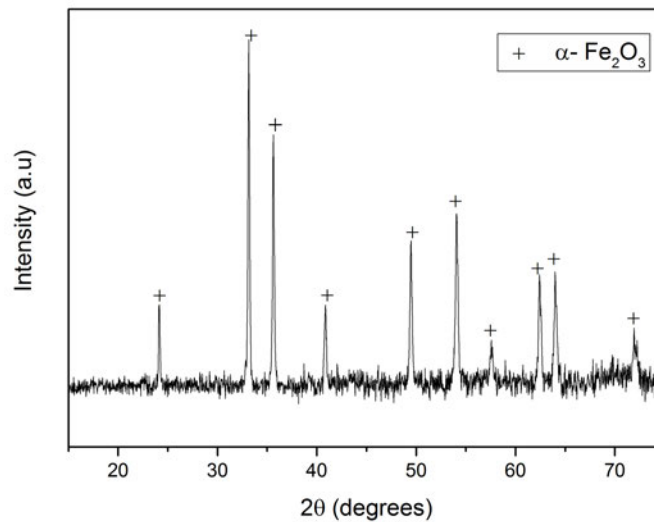


Figure 4.1: X-ray diffraction patterns of iron oxide α -Fe₂O₃ nanoparticles.

was in good agreement with the diffraction pattern reported by Xu et al. [11] and Tadic et al.[13] of pure α -Fe₂O₃ phase. The most intense peak was observed at

$2\theta = 33.45$ at full width at half maximum (FWHM) of 0.0115656424π rads. The average crystallite size was calculated using Scherrer's equation, and was found to be approximately ≈ 13 nm.

Transmission Electron Microscopy (TEM)

The TEM image of α -Fe₂O₃ in bright field mode is shown in figure 4.2. The image shows the presence of roughly spherical nanoparticles, with some agglomeration, which is in agreement with TEM image reported by Xu et al. [14] and Tadic et al. [11]. The average particle size was found to be ≈ 26 nm, measured using Image J

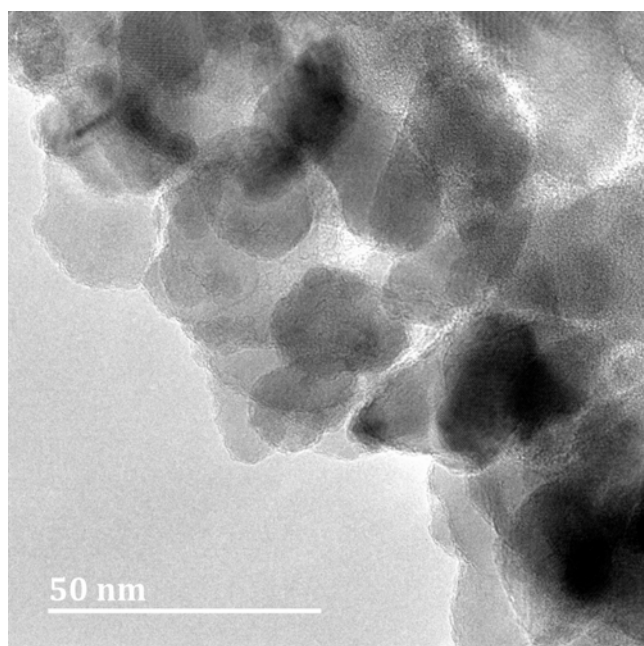


Figure 4.2: The TEM image of the α -Fe₂O₃ nanoparticles corresponding to α -Fe₂O₃.

program(version 1.52 V). The observed particle size from TEM is much higher than the crystallite size from XRD analysis. This was somehow expected since the two techniques measure two different things. The XRD technique enables us to estimate the crystallite size using Scherrer's equation while the TEM technique allows us to directly determine the particle size of the nanoparticles. It is known that a single particle can be formed by aggregation of few individual crystallites. This is the reason why particle size from TEM is usually higher than crystallite size estimated using XRD.

The Mössbauer Spectroscopy

The Mössbauer spectrum recorded at room temperature for α -Fe₂O₃ is shown in figure 4.3. The room temperature Mössbauer spectrum shows a magnetically ordered state represented by one sextet which belongs to the lattice site of Fe³⁺ in hematite, as discussed in chapter 2 [13, 15]. The Mössbauer parameters resulting from the fitting of α -Fe₂O₃ phase are; the isomer shift (CS) = 0.37 mm/s; the quadrupole shift

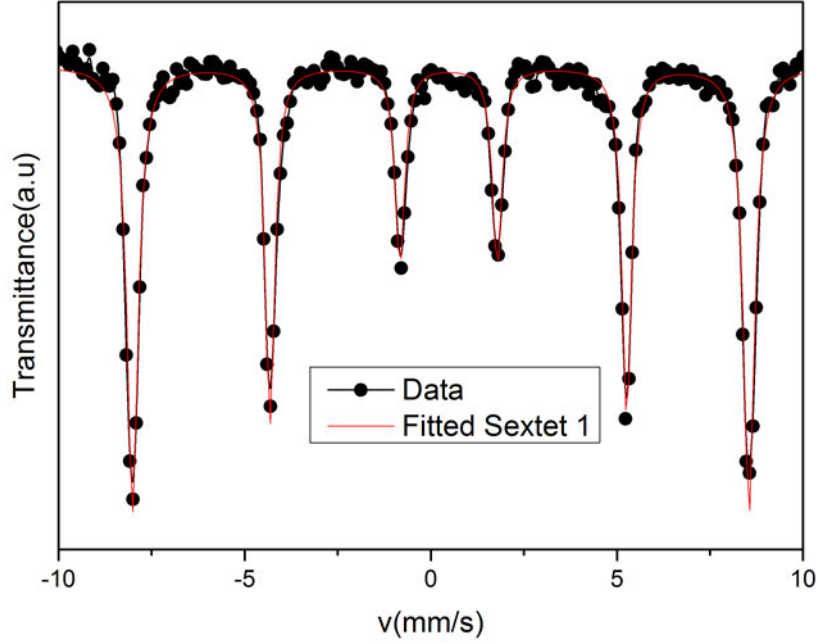


Figure 4.3: Zero-field Room temperature Mössbauer spectra of α - Fe_2O_3 phase

(ϵ) = -0.10 mm/s and the hyperfine magnetic field (H) = 51.3 T. These parameters and the Mössbauer spectrum are in accordance to the results reported by Lopez-Sanchez et al. [32]. The Mössbauer results are in full agreement with XRD results that the sample consists of a single pure α - Fe_2O_3 phase without any impurity phases.

Magnetization measurement

Figure 4.4 shows the hysteresis loop of α - Fe_2O_3 nanoparticles at different temperatures. The figure demonstrates the evolution of magnetization (where remanent magnetization is M_r and coercivity is H_c) with respect to an applied magnetic field (H) at different temperatures. At very low temperature of 10 K, a hysteresis loop is observed with remanent magnetization and coercive field. Upon heating from 10 K to 100 K, the value of the coercive field, remanent magnetization decreases and hysteresis loop collapses. There was no significant change in the shape of the hysteresis loop upon heating from 100 K to 200 K. The hysteresis loop is observed at 300 K showing remanent magnetization where (M_r is non-zero) and coercivity (H_c is non-zero). We observed no magnetic saturation but a hysteresis loop at 10 K and at 300 K. In figure 4.5, the coercive field and remanent magnetization, obtained at low field, (Inset: lower right corner) were approximately $H_c = 0.35$ kOe and $M_r = 0.24$ emu/g respectively. According to Bercoff et al. [35], depending on the microstructure of hematite particles, the coercive field ranges between 0.3 kOe and 4 kOe and sometimes even 6 kOe. The observed trends in the hysteresis loops can be explained by the temperature dependence of the magnetic parameters and mag-

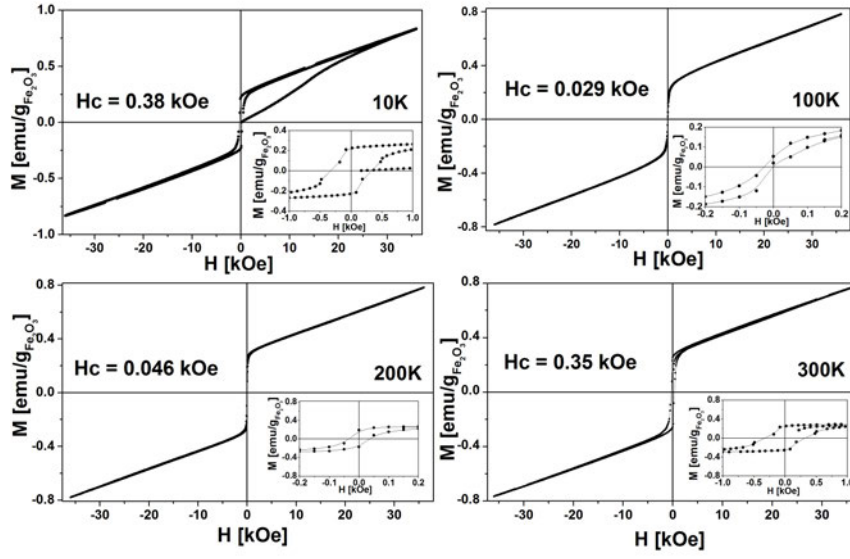


Figure 4.4: The Hysteresis loop showing the change in magnetization of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles recorded at different temperatures.

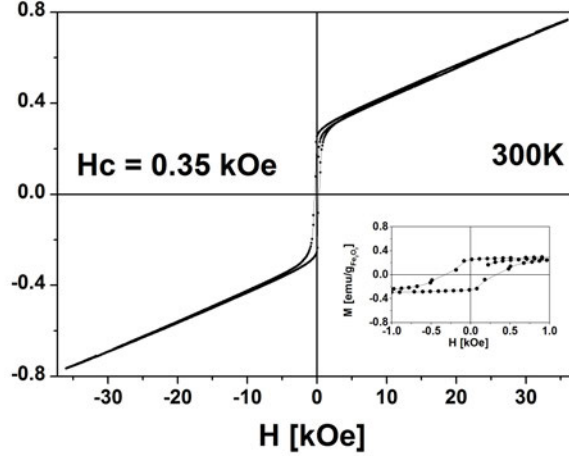


Figure 4.5: The Hysteresis loop showing the isothermal magnetization of $\alpha\text{-Fe}_2\text{O}_3$ recorded at 300 K. Inset: lower right corner: magnetization behaviour at low field recorded at 300 K.

netic transitions. According to Literature review (chapter 2), Bulk hematite is a weak ferromagnet below the Neel temperature T_N (where $T_N \approx 960$ K) that undergoes a magnetic phase transition at the Morin temperature (260 K) to a purely antiferromagnetic phase at lower temperatures [36]. Hematite magnetic properties

depend on the particle size and display the most interesting effects when the size of the particles decreases below 20 nm [36]. The Morin temperature reduces with decreasing of the particle size and tends to vanish for particles smaller than about 10 nm [36]. Tadic et al. [36] showed that hematite particles with sizes around 10 nm produced blocking temperature (at around 50 K) whereas the particles with higher sizes around 20 nm produced the Morin transition (at around 83 K). A reduction of the Neel temperature with decreasing particle size has been also observed [36]. In this study, the absence of the hysteresis loop is observed at 100 K and 200 K, which suggests a magnetic transition at the Morin transition temperature. The room temperature Mössbauer spectra and the room temperature hysteresis loop presented both show a magnetically ordered state. The values of the Mössbauer parameters, particularly, the quadrupole shift parameter is negative ($\epsilon = -0.10$ mm/s) indicating a weakly ferromagnetic state of the $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles which is in good agreement with the room temperature hysteresis [16, 37].

4.2 $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles

X-ray Diffraction

The phase composition of $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles was examined by X-ray diffraction measurements illustrated in figure 4.6. The emerging reflections are in accordance to the maxima characteristic of a pure $\alpha\text{-Fe}_2\text{O}_3$ phase (JCPDS file Card, no. 33-0664). The results are in agreement with Tadic et al. [36] and Bercoff et al. [35]. The most intense peak at $2\theta = 33.15$ with the full width at half maximum

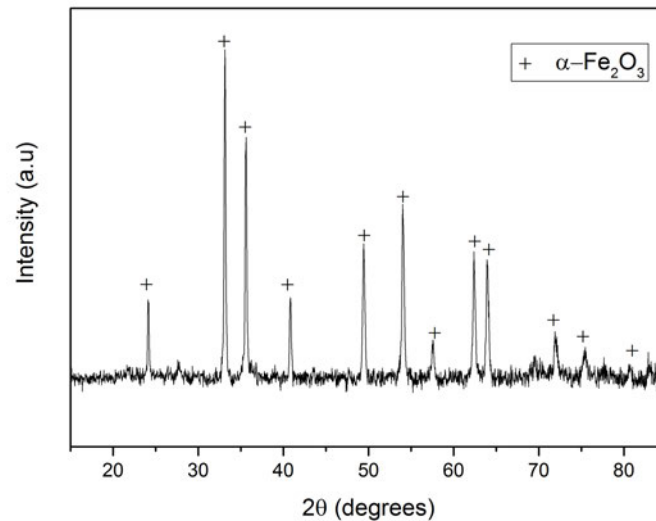


Figure 4.6: X-ray diffraction patterns of iron oxide Fe_2O_3 nanoparticles

(FWHM) of 0.00380795936 π rad was used to calculate the average crystallite size using the Scherrer's equation which was found to be ≈ 42 nm. The X-ray diffraction

pattern has high background signal in combination with a low peak intensity due to using a copper radiation source instead of iron radiation. Although a copper radiation was used the X-ray diffraction pattern was identical to that of $\alpha\text{-Fe}_2\text{O}_3$.

Transmission Electron Microscopy(TEM)

Figure 4.7 shows the bright field mode TEM image of spherical $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles inside a silica matrix. TEM analysis showed significantly large par-

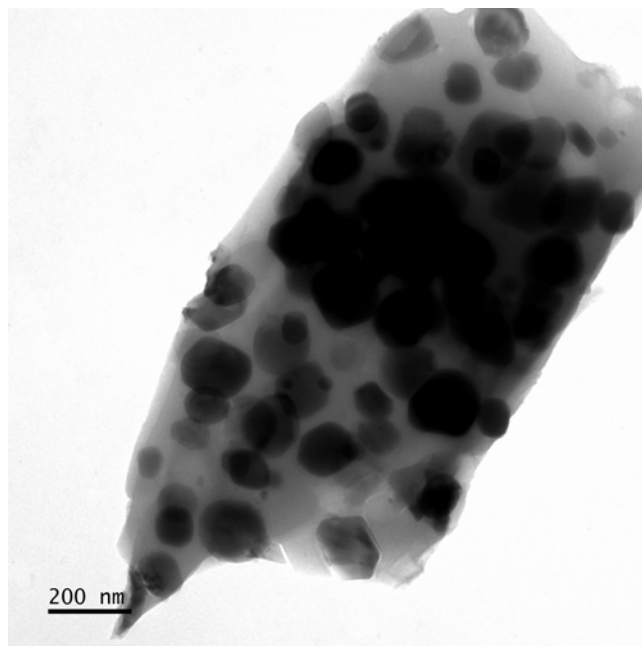


Figure 4.7: TEM image of the $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanocomposite corresponding to $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$

ticles as compared to crystallite size obtained from XRD. An average particle size of ≈ 124 nm determined using Image J program (version 1.52 v). This large average particle size was probably due to high annealing temperature of 1373 K. It is believed that this high temperature annealing resulted in the formation of a subparticle [35] (polycrystalline formed by large number of small crystallites) structure in the sample, hence the large particle size compared to XRD crystallite size. At higher temperatures, the growth of crystallites aggregates and the formation of a subparticle structure is favored. Kumar et al. [38] studied the effect of annealing temperature on the structure of hematite and concluded that there is a large change in the crystallite size with the annealing temperature.

The Mössbauer Spectroscopy

The room temperature Mössbauer spectrum in figure. 4.8 represents the magnetic state of $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles. The room temperature spectrum shows a magnetically ordered state represented by one sextet of Fe^{3+} site which is in agreement with Lopez-Sanchez et al.[32] and Bercoff [35]. The Mössbauer parameters

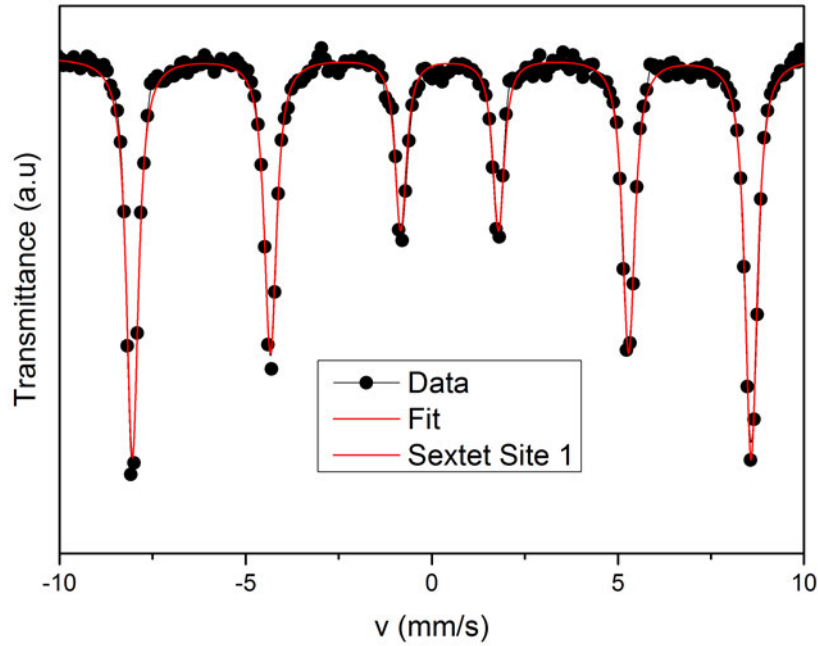


Figure 4.8: Zero-field Room temperature Mössbauer spectra of α -Fe₂O₃/ SiO₂ nanoparticles

resulting from the fitting of α -Fe₂O₃/ SiO₂ are; the isomer shift (CS) = 0.37 mm/s; the quadrupole shift (ϵ) = -0.10 mm/s; the hyperfine magnetic field (H) = 51.5 T. These parameters are consistent with what has been reported for α -Fe₂O₃ before and with a negative quadrupole shift indicating a weakly ferromagnetic state [35].

Magnetization measurements

$M(H)$ magnetization curves for α -Fe₂O₃/SiO₂ nanoparticles are shown in figure 4.9. Variation in the magnetic behaviour is observed when cooling from 300 K to 10 K. This is due to the change in the magnetic state of hematite at these different temperatures. Hematite in its bulk form is known to be weakly ferromagnetic below the Neel temperature (960 K) and undergoes a magnetic transition at the Morin transition temperature (260 K), to an antiferromagnetic state. The Morin transition temperature is known to decrease with particle size [39]. The room temperature Mössbauer spectra and the parameters confirmed a magnetically ordered state, a weakly ferromagnetic state in agreement with the room temperature magnetization measurements. And a collapse in the coercivity field was observed from 200 to 10 K due to a change in the magnetic structure in the sample.

The magnetization curve at 10 K (see fig. 4.9), exhibits remanent magnetization, some coercivity field and an open hysteresis loop. Upon heating to 100 K, there is a collapse in the hysteresis loop accompanied by a decrease in the remanent mag-

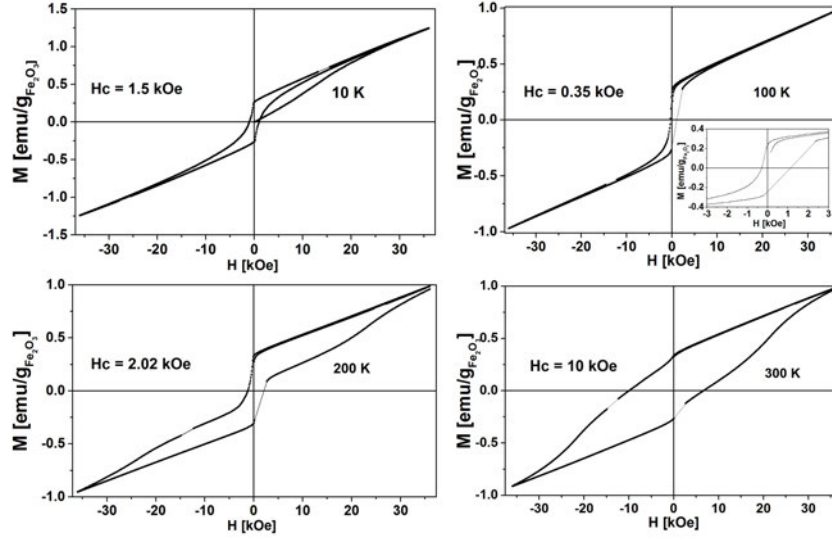


Figure 4.9: The Hysteresis loop showing the change in magnetization of α - $\text{Fe}_2\text{O}_3/\text{SiO}_2$ recorded at different temperatures.

netization and the coercive field. The coercivity field and remanent magnetization was observed to increase as the temperature increased from 200 K to 300 K. At

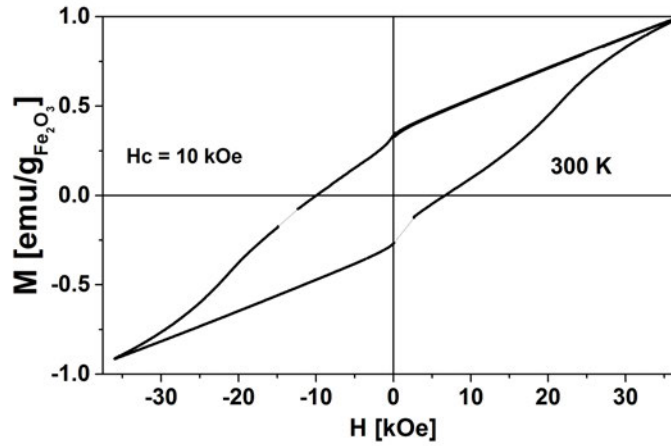


Figure 4.10: The Hysteresis loop showing the isothermal magnetization of ϵ/α - $\text{Fe}_2\text{O}_3/\text{SiO}_2$ recorded at 300 K. Inset: lower right corner: magnetization behaviour at low field recorded at 300 K.

300K, the magnetization curve in figure 4.10 presents a surprisingly high coercive field of about 10 kOe and remanent magnetization of about 0.25 emu/g. Several

studies of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles with coercivity field ranging from 0.3 kOe up to 5.2 kOe has been reported [40–43]. Hematite nanoparticles with large coercivity have also been reported by Bercoff et al.[35], with coercivity field that ranges from 4 kOe to 6 kOe when raising the temperature up to room temperature. The variation in the coercivity field from these studies has been attributed to the internal nanostructure of the particles. In this study, the TEM image showed large particles which suggest the synthesized particles are polycrystalline probably due to the high annealing temperature (1373 K). The observed high coercivity field of 10 kOe observed in this study is also attributed to the sub-particle structure [35] of the sample.

The sub-particle structure consist of crystalline part and the surface part. The crystalline part, also called the core of the nanoparticles, is ferromagnetically coupled by exchange energy interactions[37]. Up to a particular magnetic field, the core magnetic moments align with the applied magnetic field[37]. At some stage, the core magnetization of the system gets saturated[37]. Beyond this stage, any increase in the magnetic field has an effect only on the surface layers of the particles and thus the increase in the magnetization of the particle slows down[37].

This specific state of the surface entails a virtual absence of magnetic saturation that keeps the hysteresis loop unclosed even in very strong fields[37]. The surface layers of nanoparticles show enhanced spin disorder relative to large particles when measured under the same values of applied field and same temperature[37]. The surface layer magnetic moment anomalies may be due to broken exchange bond, high anisotropy layer on the surface, or a loss of the long-range order in the surface layer[37]. These effects are more intense in the case of iron oxides because of superexchange interactions through the oxygen ions[37].

4.3 $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles

X-ray Diffraction

The X-ray diffraction of $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles is shown in figure 4.11. Two phases emerge from the reflection of the X-ray diffraction pattern, consisting of $\epsilon\text{-Fe}_2\text{O}_3$ phase matching with JCPDS file Card, no. 16-0653) and $\alpha\text{-Fe}_2\text{O}_3$ phase matching with JCPDS file Card, no. 33-0664. A high background signal with a low peak intensity is observed due to the fact that copper radiation was instead of iron radiation. The presence of $\epsilon\text{-Fe}_2\text{O}_3$ phase is highly distinguishable from the $\alpha\text{-Fe}_2\text{O}_3$ phase by the fact that the reflections emerging from $\epsilon\text{-Fe}_2\text{O}_3$ phase are at different 2θ positions. The most intense peak was observed at $2\theta = 33.02$ and at full width half maximum of 0.00380795936 π rad. From Scherrer's equation, the average crystallite size was found to be ≈ 18 nm.

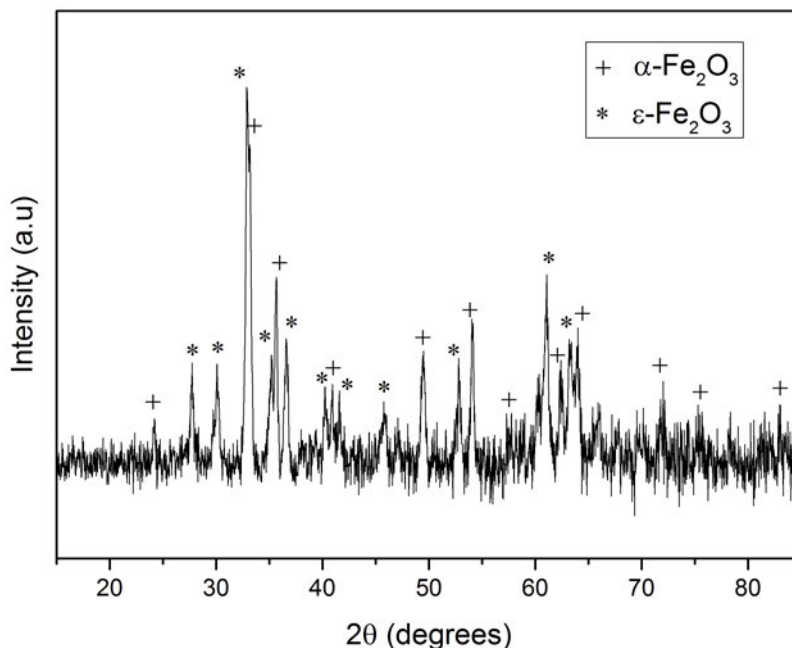


Figure 4.11: X-ray diffraction patterns of iron oxide $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles.

Transmission Electron Microscopy (TEM)

The Bright Field TEM image of $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles is shown in figure 4.12. A variety of sizes and shapes can be observed, ranging from an ellipse-like shape to roughly spherical nanoparticles inside a silica matrix. The average particle size were found to be ≈ 27 nm, measured using Image J program (version 1.52 v).

There are small particles and a few significantly large particles with some agglomeration in the image. This agglomeration may probably come from annealing the sample at a high temperature of 1373 K where the growth of crystalline aggregates and a subparticle structure is favored. The different particle and crystallite size growth rates that increase with annealing temperature forms subparticle structure at the nanoscale.

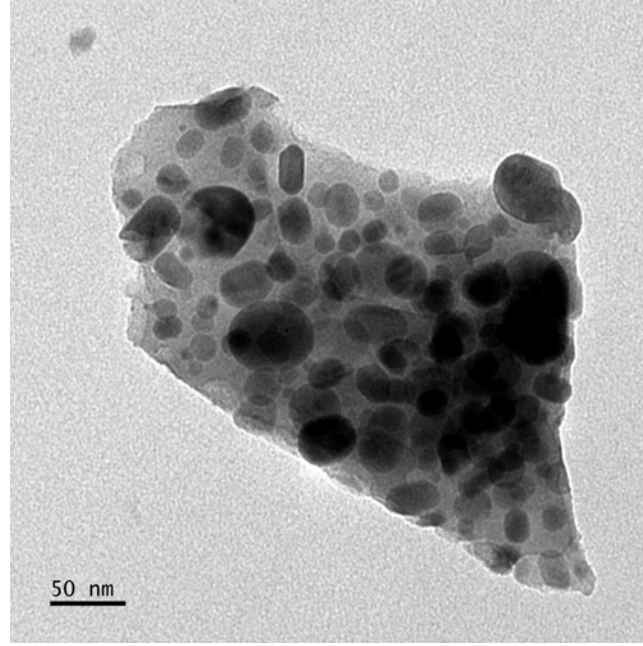


Figure 4.12: TEM image of $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles.

The Mössbauer Spectroscopy

Figure 4.13 shows room temperature Mössbauer spectrum of $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles. The room temperature spectrum shows a magnetically ordered state and has

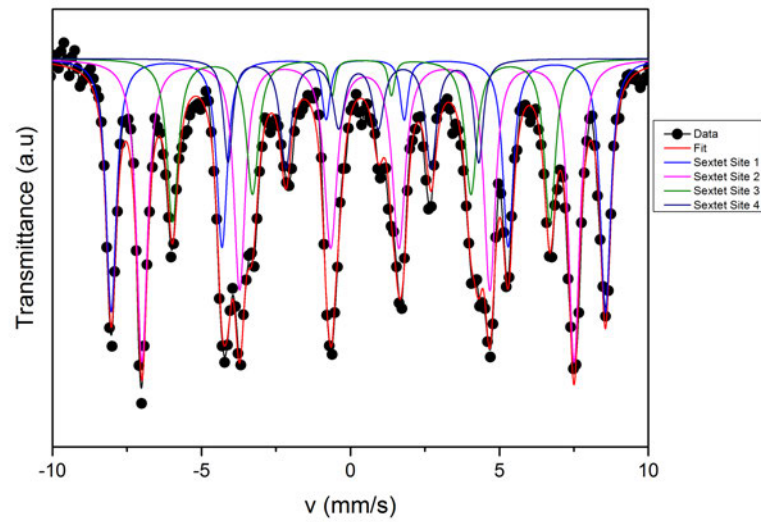


Figure 4.13: Zero-field Room temperature Mössbauer spectra of $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles

been fitted with four sextets belonging to different Fe^{3+} sites, considering the coex-

Table 4.1: Mössbauer parameters obtained from the fit of the $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ spectrum at room temperature. (CS) is the isomer shift; (ϵ) is the quadrupole shift and stands for sextets; (H) is the hyperfine magnetic field

Sextet	CS (mm/s)	ϵ (mm/s)	H (T)
1	0.37	-0.11	51.4
2	0.36	-0.11	44.9
3	0.37	-0.008	39.2
4	0.18	-0.08	26.0

instance of $\alpha\text{-Fe}_2\text{O}_3$ and $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles. Although $\epsilon\text{-Fe}_2\text{O}_3$ has four crystallographically non-equivalent sites, two of them have very similar hyperfine parameters and are difficult to resolve without an applied magnetic field. The zero-field room temperature Mössbauer spectra is frequently fitted with three sextets with relative spectral areas in the ratio 1 : 1 : 2, according to literature review [15]. In this The fourth sextet comes from the $\alpha\text{-Fe}_2\text{O}_3$ phase. The Mössbauer parameters of the fit are displayed in Table 4.1, are in good agreement parameters reported by Bercoff et al. [35] and Jacob et al. [37]. The fitting on sextet 1 was done with Mössbauer parameters corresponding to $\alpha\text{-Fe}_2\text{O}_3$ phase and sextet 2 corresponds to the two distorted, unresolved octahedral sites [33, 34, 44]. The regular octahedral site, which is less distorted shows the quadrupole splitting value that is very close to zero, this corresponds to sextet 3 [33, 34, 44]. The tetrahedral sites can be easily be distinguishable from the octahedral site by the fact that it significantly lowers the hyperfine magnetic field, this corresponds to sextet 4 [33, 34, 44].

Magnetization measurements

The magnetization curve in figure 4.14 shows the magnetic field dependence of isothermal magnetization for $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles. There was no major difference between the coercivity of $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ when the temperature decreases from 300 K to 200 K, but we observe a hysteresis loop. At 100 K, the hysteresis loop collapses and the coercive

field is reduced. At 10 K, a hysteresis loop is observed with increased remanent magnetization and coercive field. We observe no saturation magnetization but a hysteresis loop below and above 100 K. Hematite is known to be antiferromagnetic below its Morin transition temperature [32]. However, lower symmetry and uncompensated surface spins might give rise to deviations from the antiferromagnetic alignment in nanoparticles providing a weakly ferromagnetic behaviour below the Neel temperature of these nanoparticles [32]. Hematite nanoparticles also show a Morin transition (at around 83 K) for particles sizes around 20 nm [36]. However, it is known that at ≈ 110 K, the $\epsilon\text{-Fe}_2\text{O}_3$ phase undergoes a magnetic transition, accompanied by a series of structural transformations and spin reorientation phenomenon and manifested by a dramatic decrease in the $\epsilon\text{-Fe}_2\text{O}_3$ coercive field [18]. A large decrease in the coercivity from 22.5 to 0.8 kOe has been observed between 200 and 100 K [45]. There is a magnetic transition around 100 K which has been a characteristic of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles and $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles at 110 K in fig-

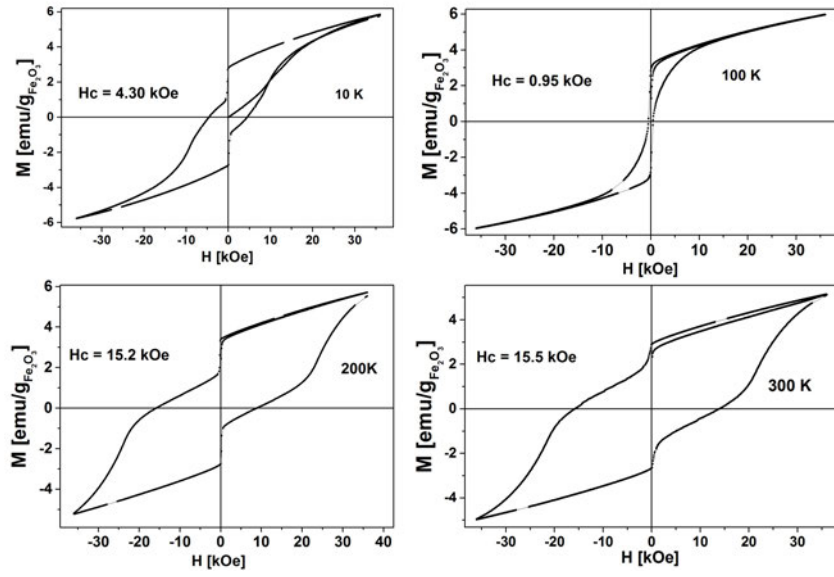


Figure 4.14: The Hysteresis loop showing the change in magnetization of $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles recorded at different temperatures.

ure 4.14. In this study, we have observed a major decrease in the coercivity field from

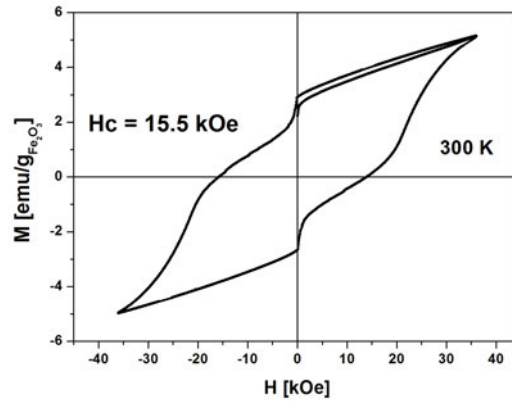


Figure 4.15: The Hysteresis loop showing the isothermal magnetization of $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ recorded at $T = 300$ K. Inset: lower right corner: magnetization behaviour at low field recorded at 300 K

to 15.2 kOe to 0.95 kOe when the sample was cooled from 200 K to 100 K. This change in the coercive field reflects a change in the magnetocrystalline anisotropy of $\epsilon\text{-Fe}_2\text{O}_3$, which may result from either a change in the geometry of the Fe sites in the crystal structure or a reorientation phenomenon of the Fe^{3+} magnetic moments. The magnetization curve at 300 K shown in figure 4.15, shows steady increase in the magnetization as the applied magnetic field increases and an open hysteresis loop. This relationship is observed even in the reversal of the applied field. The

values for the coercive field, remanance magnetization are 15.5 kOe and 2.7 emu/g, respectively.

This high coercivity field is in close agreement with the value reported by Jin et al. [18] who first synthesized a pure ϵ -Fe₂O₃ phase and observed a giant coercive field of 20 kOe exhibited by this rare iron oxide polymorph at room temperature. The epsilon ϵ -Fe₂O₃ nanoparticles (as discussed in chapter 2) are known to be collinear ferrimagnets or canted antiferromagnets at room temperature[18]. A report from Gichi et al.[18] have recently supported the idea of a ferrimagnetic structure of ϵ -Fe₂O₃ and consequently clarified what happens to magnetic moments of Fe³⁺ ions when ϵ -Fe₂O₃ is cooled [18]. The ϵ -Fe₂O₃ magnetic structure at low temperature of about 9 K has been studied by means of in-field mössbauer spectroscopy and a nearly collinear ferrimagnetic order at the octahedral sites and a misalignment with possible disorder at the tetrahedral sites was proposed[45]. It has been reported that at room temperature, ϵ -Fe₂O₃ behaves as a collinear ferrimagnet [18]. The results presented by room temperature mössbauer spectra of this sample presents an ordered magnetic state which agrees with results from the room temperature hysteresis loop. It should be noted from the mössbauer quadrupole shift value, that sextet 1 coming from hematite is weakly ferromagnetic at room temperature. Therefore, the major coercive field is mostly coming from the contribution of the ϵ -Fe₂O₃ phase which is ferrimagnetic at room temperature.

Chapter 5

Conclusion

In this work we present pure α -Fe₂O₃ nanoparticles, pure α -Fe₂O₃/ SiO₂ nanoparticles, and ϵ / α -Fe₂O₃/ SiO₂ mixture were successfully synthesized using the sol-gel method and characterized using XRD, TEM, Mössbauer spectroscopy, and VSM. XRD and Mössbauer spectroscopy analysis revealed the formation of pure α -Fe₂O₃ and α -Fe₂O₃/ SiO₂ phases. While the diffraction pattern and room temperature Mössbauer spectrum of the ϵ -Fe₂O₃/ SiO₂ sample showed the existence of two distinct iron oxide phases corresponding to α -Fe₂O₃ and ϵ -Fe₂O₃ phase.

The average particle size from TEM analysis for the pure hematite sample (α -Fe₂O₃) was found to be ≈ 26 nm with roughly spherical shape. The room temperature Mössbauer measurement presented a magnetically ordered state which belongs to the only one lattice site of Fe³⁺. And the negative quadrupole shift from Mössbauer fit indicated that the sample was in a weakly ferromagnetic state at room temperature. Magnetization curves at 300 K showed a magnetic behaviour very consistent with hematite with a measured coercivity field and remanent magnetization obtained were $H_c = 0.35$ kOe and $M_r = 0.24$ emu/g.

Transmission electron microscopy analysis for the α -Fe₂O₃/ SiO₂ sample showed an average particle size of ≈ 124 nm of roughly spherical shaped nanoparticles embedded in silica matrix. The room temperature Mössbauer spectra confirmed a magnetically ordered state for this sample with Mössbauer parameters consistent with hematite. M vs H curves at 300 K showed an unusually high coercivity of $H_c = 10$ kOe and remanent magnetization of about 0.25 emu/g. According to our knowledge, no such high coercivity value for hematite was reported before. This was explained using sub-particle structure formation of nanoparticles in the sample. It is important to note that this sample was synthesized using a method slightly modified to synthesize pure ϵ -Fe₂O₃ phase. Briefly, the formation of the sol-gels between the modified and original methods were exactly the same i.e. the same quantities of chemicals were mixed and gels were formed in the same way but the annealing procedure was modified. Instead of annealing the sample in a step-wise manner (i.e. gradual heating of the gel to 723 K at a heating rate of 983540 K/h to 983790 K at a heating rate of 353 K/h and held at 1373 K for 3 h). The results were significantly large α -Fe₂O₃/ SiO₂ nanoparticles. It is believed that this single high

temperature heating resulted in a sub-particle structure formation which resulted in the high coercivity field.

The synthesis of pure epsilon phase $\epsilon\text{-Fe}_2\text{O}_3/\text{SiO}_2$ resulted in two iron oxide phases where both the $\alpha\text{-Fe}_2\text{O}_3$ and epsilon phase $\epsilon\text{-Fe}_2\text{O}_3$ were observed on the X-ray diffraction pattern. The average crystallite size for $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ were approximately ≈ 18 nm. The TEM image of $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ showed ellipse-like shaped to roughly spherical nanoparticles, inside the silica matrix. The Mössbauer measurements performed at room temperature showed a magnetically ordered state. The sample $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ had a rather unusual complex spectra which came from the contribution of the two phases, the ϵ and α phase. The recorded coercivity field value for this sample from magnetization curve at 300K was $H_c = 15.5$ kOe which is consistent with previous known H_c field values for the $\epsilon\text{-Fe}_2\text{O}_3$ phase.

The sol-gel method used to synthesize $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles was different for $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ and $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles. This resulted in a magnetization obtained for $\alpha\text{-Fe}_2\text{O}_3$ were $H_c = 0.35$ kOe and showed an unusually high coercivity of $H_c = 10$ kOe for $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles. The $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles measured magnetization of $H_c = 15.5$ kOe. The $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ and $\epsilon/\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles are suitable for applications in inductor cores, recording heads, microwave devices, and magnetic shielding due to their magnetization parameters.

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