Synthesis and Characterization of Nickel Hydroxide Nanoparticles

A Dissertation submitted

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In

PHYSICS

BY

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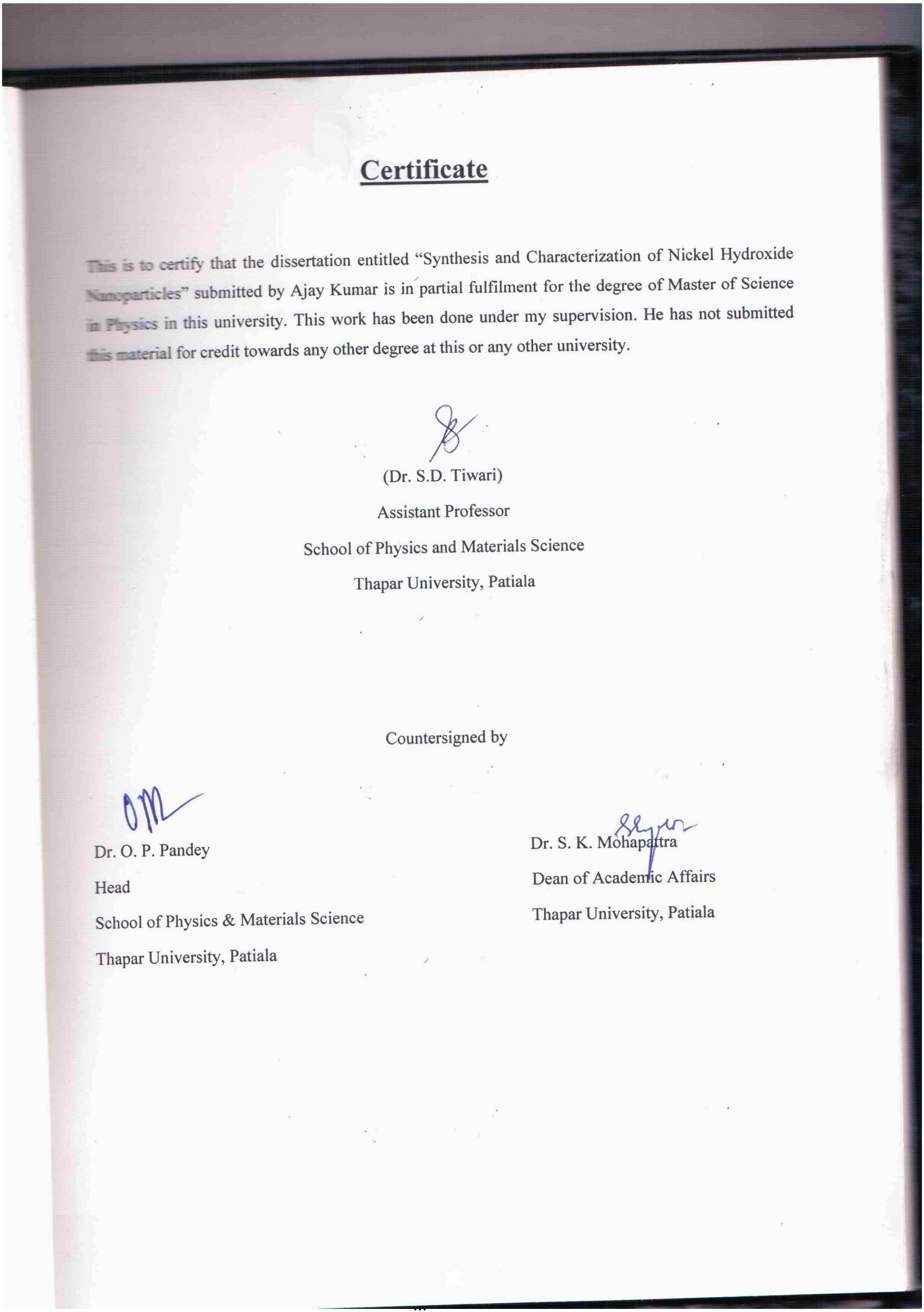
INDIA

July 2011

Dedicated to my family

and

God



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This is to certify that the dissertation entitled "Synthesis and Characterization of Nickel Hydroxide Nanoparticles" submitted by Ajay Kumar is in partial fulfilment for the degree of Master of Science in Physics in this university. This work has been done under my supervision. He has not submitted this material for credit towards any other degree at this or any other university.

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I hereby declare that the dissertation entitled "Synthesis and Characterization of Nickel Hydroxide Nanoparticles" is the work carried out by me under the supervision of Dr. S. D. Tiwari. I have not submitted this work anywhere else for the award of any degree.

Ajay kumar

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Ajay Kumar

Abstract

Nanoparticles of $Ni(OH)_2$ are prepared by sol gel method. This sample is characterized by x-ray diffractometer, Thermo gravimetric Analyzer, Differential Thermal Analyzer and vibrating sample magnetometer. The average crystallite size is found to be about 7 nm. The prepared nanoparticles of $Ni(OH)_2$ are found to be paramagnetic at room temperature.

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CHAPTER 1

Introduction

All matters around us are made up with atoms. Atoms have a centre known as nucleus having positive charge. A nucleus is consisting of positively charged protons and neutral neutrons. Nucleus is orbited by one or more negatively charged particles known as electrons. An electron describes its motion in two ways. It moves around nucleus and also spins along its own axis. The spin and orbital motion of an electron produce a magnetic field. According to Ampere, whenever any charge is in motion then it possesses magnetic field. The spin and orbital motion of an electron in an atom behave in a similar way like electrical current flowing through a wire and produce magnetic field. The direction of magnetic field is determined by the directions of spin and orbital motion of the electron and strength of this field is called magnetic moment. Hence the atom possesses magnetic moment in two ways. One is due to orbital motion of electron and the other is due to its spin around its own axis. The total magnetic moment is the vector sum of orbital magnetic moment and spin magnetic moment [1].

1.1 Classification of magnetic materials

Magnetization is defined as the magnetic moment per unit volume of the material and it is denoted by M. The susceptibility is the measure of how easily a unit volume of a material can be magnetized by a magnetizing field H. It is denoted by χ and it is given by

$$\chi = \frac{M}{H}.$$

When any material is placed in magnetic field, then some magnetization is produced within the material. The field at any point inside the material is resultant of magnetic field in free space and field due to magnetization of material itself. Magnetic permeability μ is the ratio of magnetic flux density B in material to the external field strength H i.e.

$$\mu = \frac{B}{H}$$

Depending on the behaviour of materials in an external magnetic field we can classify all the known materials in following categories [1].

1.1.1 Diamagnetism

The materials which induce weak magnetic field in opposite direction with respect to applied magnetic field are known as diamagnetic materials. These materials do not contain any unpaired electron i.e. all the electrons are paired and net magnetic moment is zero. It is a type of magnetism having negative susceptibility and relative permeability is less than one. Examples of diamagnetic materials are copper, bismuth, sodium chloride etc.

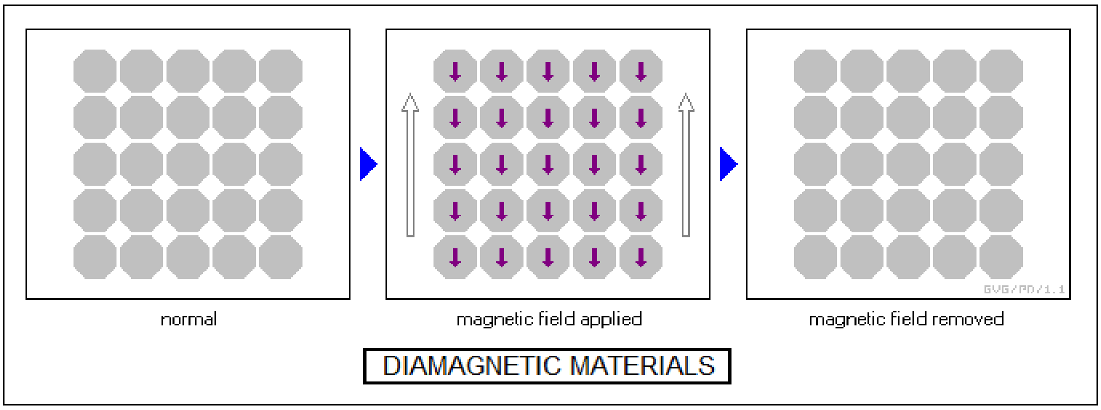


Figure 1.1: Arrangement of spins in diamagnetic materials. [2]

In an atom electrons revolve about nucleus. The orbiting electron around nucleus is equivalent to current carrying coil. Whenever any magnetic field is applied then according to Lenz’s law a magnetic field is induced in a direction opposite to the applied field.

Figure 1.2: M vs. H curve for a diamagnetic material.

1.1.2 Paramagnetism

This type of magnetism arises in solids having unpaired electrons in atoms. Due to its unpaired electrons the atom possesses net non-zero magnetic moment. When magnetic field is applied to these types of materials the dipole moments try to align along the direction of applied field.

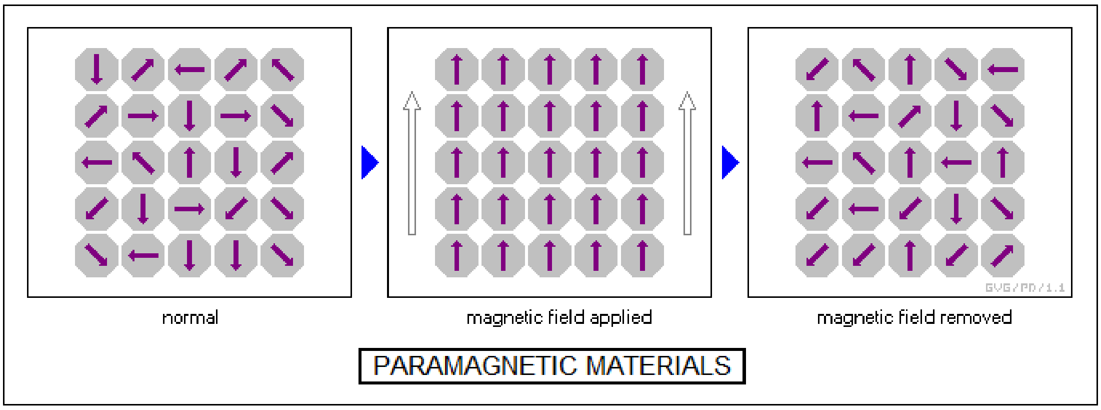


Figure 1.3: Arrangement of spins in paramagnetic materials. [2]

The magnetization of these materials decreases with increasing temperature according to relation

$$M = C\left(\frac{B}{T}\right)$$

Here, M is the Magnetization, C is the Curie constant which is different for different materials and T is the temperature. This relation is known as the Curie law. Paramagnetic materials remains magnetized as long as strong magnetic field acts on it and loses its magnetization when the magnetic field is removed.

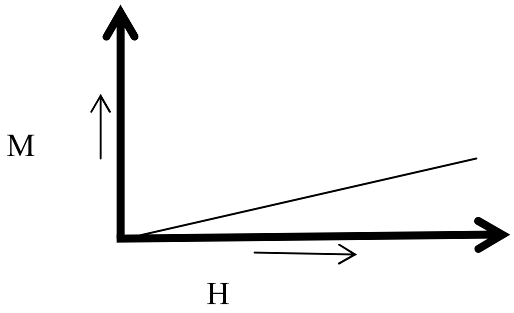


Figure 1.4: Magnetization as a function of applied field for paramagnetic materials.

1.1.3 Ferromagnetism

The ferromagnetic material shows spontaneous magnetization even in the absence of magnetic field. In ferromagnetic materials all the atomic magnetic moments are aligned parallel to each other due to strong exchange interaction among them. The exchange interaction is very strong but is short range in nature. Whereas the dipolar interaction is weak but is long range in nature. There is competition between these two types of interaction among atomic magnetic moments in any ferromagnetic material. The system minimizes its energy by dividing itself in large number of small regions called domains. In any domain all spins all parallel to each other. Between two domains the spins do not change their directions abruptly. In fact they change their directions gradually over some distance. This region is known as Bloch wall. In ordinary conditions all the domains are oriented randomly giving rise to zero magnetization. However the magnetization within each domain will still remain non zero.

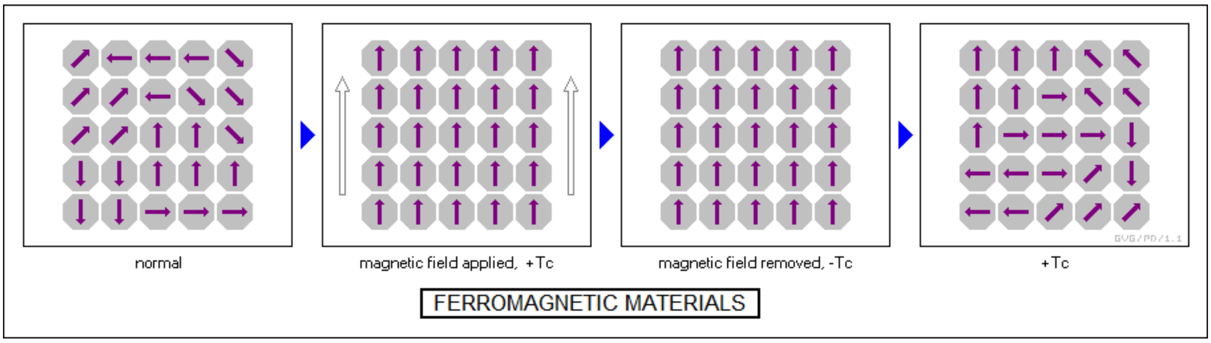


Figure 1.5: Arrangement of spins in ferromagnetic materials. [2]

At a critical temperature T_C, known as the Curie temperature, a ferromagnetic material becomes paramagnetic. At this temperature the thermal energy becomes larger than the exchange interaction energy between spins. Due to this reason the ferromagnetic ordering breaks and the material becomes paramagnetic. Above the Curie temperature the susceptibility of the system can be expressed by relation

$$\chi = \frac{C}{T - T_C}$$

Here C is material dependent constant.

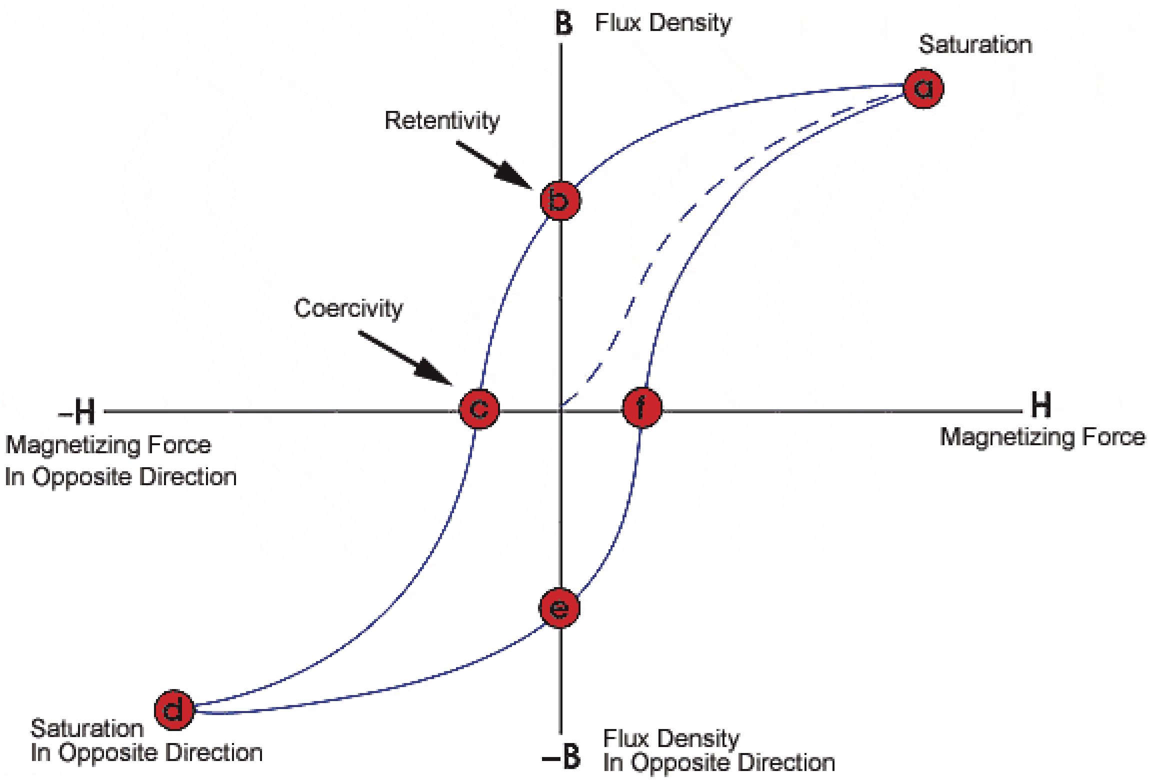


Figure 1.6: Hysteresis loop for ferromagnetic material. [3]

Figure 1.6 shows magnetization as a function of applied magnetic field for a ferromagnetic material below the Curie temperature T_c. The magnetic flux B increases with increasing strength of applied magnetic field. But at point ‘a’ magnetic flux density saturates i.e. if we further increase the magnetizing field there is no further increase in magnetic flux at this point, the reason for this is that at this point all the magnetic domains are aligned in same direction. Now when magnetizing field is decreases the magnetic flux density reaches from point ‘a’ to point ‘b’. Here at point ‘b’ magnetizing force is zero but magnetic flux remains present in the material. This residual magnetic flux is known as retentivity of the material. Now with further decrease in the applied magnetizing field, the magnetic flux density reaches to zero that is at point ‘c’. This negative applied magnetizing field corresponds to zero flux density is known as coercivity of the material. The reason for this is that due to reversing magnetic field flipped enough of domains to produce net flux zero. Further increasing the magnetization in negative direction produces increase in flux and become saturates at point ‘d’ but in opposite direction. When magnetizing field is again reduced to zero curve reaches at point ‘e’ which is residual magnetism. Now on further increasing magnetizing field in positive direction flux density again reaches zero value i.e. at point ‘f’.

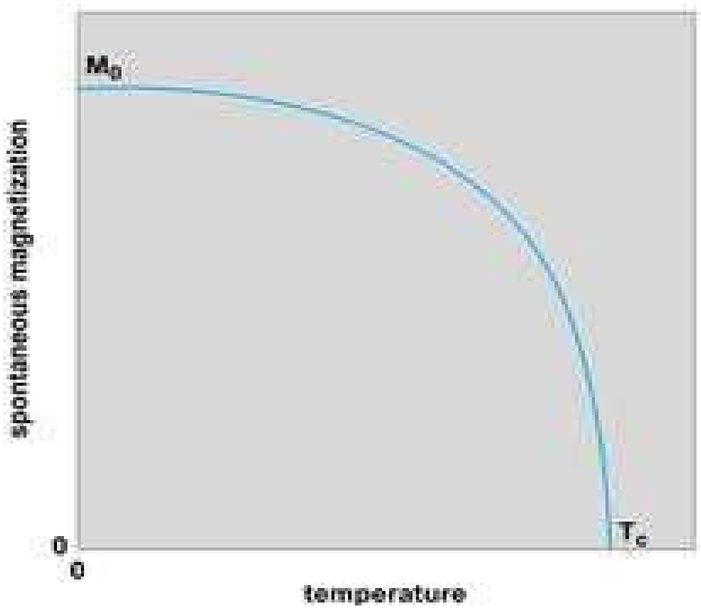


Figure 1.7: Magnetisation as a function of temperature for a ferromagnetic material. [4]

1.1.4 Antiferromagnetism

In antiferromagnetic materials the spins are arranged antiparallel to each other as shown in Figure 1.8. Because of this the material posses zero net magnetization. At a critical temperature, known as the Neel temperature T_N, the antiferromagnetic ordering breaks and the material becomes paramagnetic. Well above the Neel temperature the susceptibility of the material is described by relation

$$\chi = \frac{C}{T + T_N}$$

Here C is the material dependent constant.

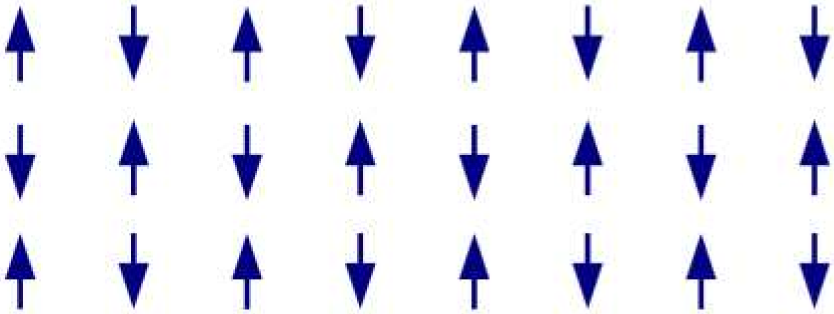


Figure 1.8: Arrangement of spins in antiferromagnetic materials. [5]

1.1.5 Ferrimagnetism

In ferrimagnetic materials the spin of atoms are arranged in opposite directions. But the magnitudes of neighboring moments do not equal to each other as in the case of antiferromagnetic materials. Due to this imbalance in magnitudes of spins the material posses a non zero magnetization. At a critical temperature the ferrimagnetic ordering breaks and the material becomes paramagnetic.

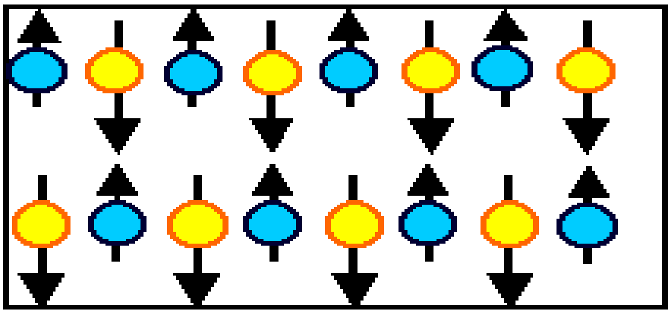


Figure 1.9: Arrangement of spins in Ferrimagnetic materials. [6]

1.2 Magnetic Anisotropy

Magnetization is anisotropic in nature. There are three main types of magnetic anisotropies described below.

1.2.1 Magnetocrystalline Anisotropy

Inside any crystal there is a preferred direction along which it is easiest to magnetize the crystal. This direction is known as easy axis. There is also a direction along which it is most difficult to magnetize the crystal. This direction is known as hard axis. For example Co has hexagonal structure and the c-axis is the easy axis. It is easiest to magnetize the Co crystal parallel or anti parallel to c-axis. In both orientations the system will have minimum energy. Let θ is angle between magnetization vector and c-axis at any instant. The magneto crystalline anisotropy energy increases with increasing θ and becomes maximum when $\theta = 90^0$. The magneto crystalline anisotropy energy starts decreasing for any further increase in the value of the angle θ and becomes minimum when $\theta = 180^0$. The variation of magneto crystalline anisotropy energy E_{an} as a function of the angle θ can be expressed by relation

$$E_{an} = K\ V\ \mathrm{Sin}^2\ \theta$$

Here K is anisotropy constant and V is the volume of the crystal. From this relation it is clear that the magneto crystalline anisotropy energy is directly proportional to the volume of the crystal [7].

1.2.2 Stress Anisotropy

The exchange energy depends on interaction between orbitals in neighboring atoms. If position of any atom changes then the interaction is affected. Thus if a strain is applied on a crystal then positions of atoms change and so magnetic behavior of the material also changes. When we apply a magnetic field then the crystal experiences strain which is function of the applied magnetic field. Due to this strain material changes its dimensions. This phenomenon is called magnetostriction. The magnetic energy density due to stress on a crystal is approximated given by

$$E_{an} = \frac{3}{2}\lambda_s \sigma sin^2\theta$$

Where θ is the angle between the magnetization and the direction of the stress, λ_s is constant and σ is stress [8].

1.2.3 Shape Anisotropy

This type of anisotropy depends upon the shape of the material. Although most materials show some magnetocrystalline anisotropy, a polycrystalline sample with no preferred orientation of its grains will not have an overall crystalline anisotropy. If the sample is spherical then same field magnetize it in same extent in every direction. On the other hand if sample is not in spherical shape it is easier to magnetize in particular direction. This phenomenon is known as shape anisotropy. When body is magnetized it produces magnetic charges at its surfaces, which act as a another source of magnetic field and this field is also known as demagnetizing field because it acts in opposite direction to the magnetizing field that produce it.

For example take a grain of needle shape. Now if the magnetization is along the long axis then the demagnetizing field is less than if it is along the small axis. This produces an easy axis of magnetization along the long axis. The magnitude of shape anisotropy is dependent on the saturation magnetization [9].

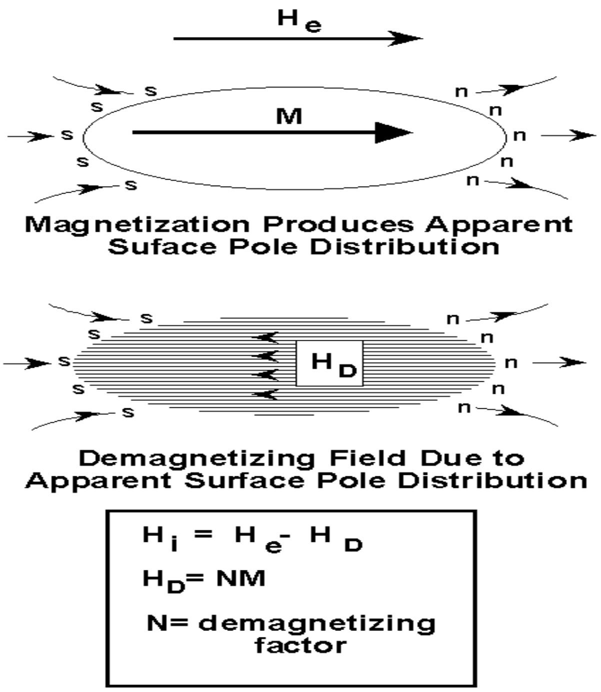


Figure 1.10: Shape anisotropy of prolate shaped grain. [9]

1.3 Superparamagnetism

Superparamagnetism occurs in those materials which are composed of very small crystallites of the order of nano meter in size. The magneto crystalline anisotropy energy is directly proportional to the volume of the crystal. In other words the magneto crystalline anisotropy energy decreases with decreasing size of the crystal. Let we have a collection of sufficiently small sized crystals and we are increasing the temperature of this system. Above a particular temperature when the thermal energy becomes larger than the magneto crystalline anisotropy energy then the orientation of the magnetization vector will not remain fixed and will change with time. This situation is similar to paramagnetism and is known as superparamagnetism. This phenomenon is usually observed in single domain particles. These single domain particles have a very large magnetic moments and show negligible remanence and coercivity with applied magnetic field.

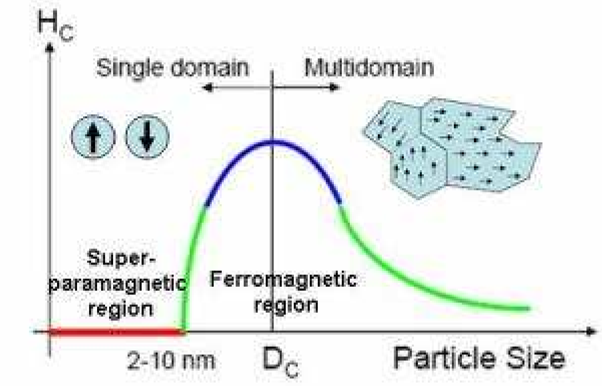
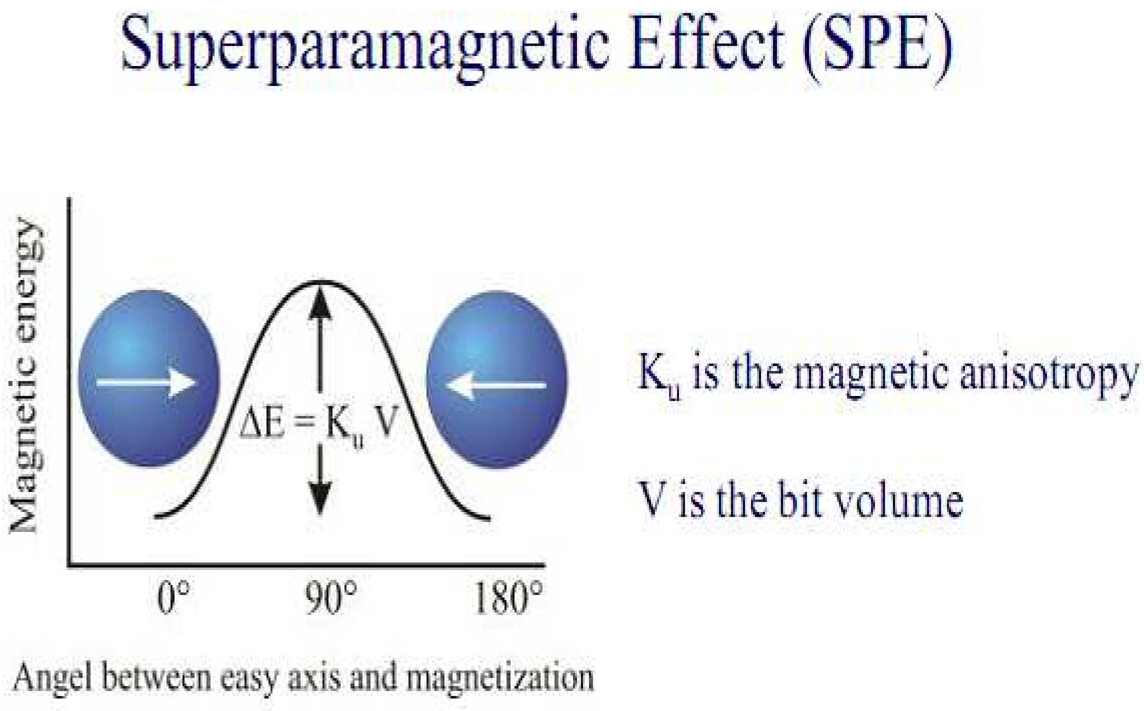


Figure 1.11: variation in magnetization of sample with the variation in size. [10]

The magnetic moment in single domain particles possess two stable orientations antiparallel to each other which are separated by an energy barrier. The stable orientation of nanoparticle is known as easy axis. But at finite temperature magnetization can flip and reverse its direction with time. The mean time between these two flips is known as Neel Relaxation time which is given by Neel-Arrhenius equation [11]

$$\tau_N = \tau_0 \exp\left(\frac{KV}{K_B T}\right),$$

where τ_0 is a constant.



Superparamagnetic Effect (SPE)

K_u is the magnetic anisotropy

V is the bit volume

Figure 1.12: Energy barrier diagram for Superparamagnetic effect. [12]

CHAPTER 2

Experimental Details

2.1 Synthesis

There are generally two methods to form nanoparticles. The first one is top down and the second one is bottom up method. In top down method a bulk material is broken into smaller particles using mechanical, chemical and other approaches. In bottom up method the nanoparticles are synthesized from atomic or molecular species by chemical reactions allowing the precursor particles to grow in size. The processes which are used in bottom up approach are sol gel, chemical vapor deposition, flame spraying, laser pyrolysis, atomic or molecular condensation etc.

In this work, nanoparticles of $Ni(OH)_2$ are synthesized by a sol gel route [13]. The $Ni(OH)_2$ is prepared by reacting aqueous solution of nickel nitrate and sodium hydroxide. The chemical reaction is given below.

$$NiNO_3 + 2NaOH \rightarrow Ni(OH)_2 + 2NaNO_3$$

In this method sodium hydroxide solution is added drop wise into aqueous solution of nickel nitrate with constant stirring until pH of the system reaches to 10. The resulting precipitate is filtered and washed several times. The precipitate is dried at 80 ^{0}C for 8 hours.

2.2 Characterization Techniques

The nanoparticles of nickel hydroxide are characterized by x- ray diffraction, thermo gravimetric analyzer and vibrating sample magnetometer.

2.2.1 X-Ray Diffraction

This technique is used to determine crystal structure, dimensions of unit cell, purity of sample etc. For this, a beam of x-rays is incident on the sample. This beam undergoes Bragg's diffraction as shown in Figure 2.1. The condition for maximum in the intensity of diffracted beam is given by relation

$$2\, d \operatorname{Sin} \theta = n\, \lambda,$$

Where d is interplaner spacing and λ is the wavelength of x-ray used. Here n = 1, 2…m. This is known as Bragg's law.

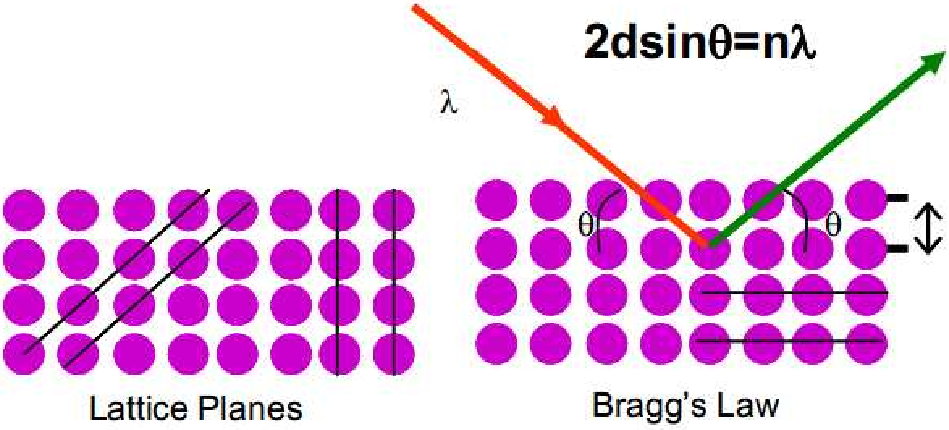


Figure 2.1: Diffraction of x-ray beam. [14]

2.2.2 Vibrating Sample Magnetometer (VSM)

VSM is used to measure the magnetization of given material. A Vibrating Sample Magnetometer is based on the principle of Faraday's law of induction which says that change in magnetic field causes production of electrical field. By measuring this electric field we can find the change in magnetic field.

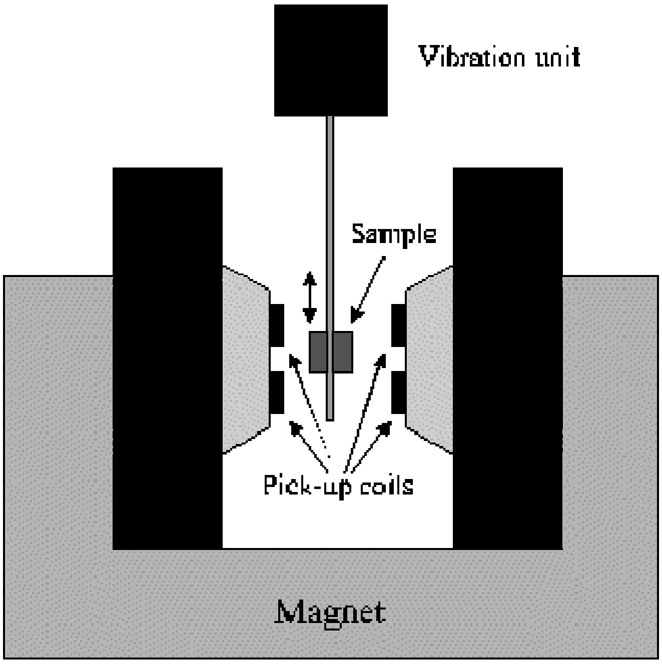


Figure 2.2: Vibrating Sample Magnetometer. [15]

An electromagnet is used to magnetize the sample. This magnetized sample is allowed to vibrate vertically inside a coil. Because of vibrating sample the magnetic field inside the coil changes with time. This changing magnetic field produces an electric field across the coil. Using appropriate electronic circuitry, this field is measured and the magnetization of the sample is estimated with the help of proper calibration [16].

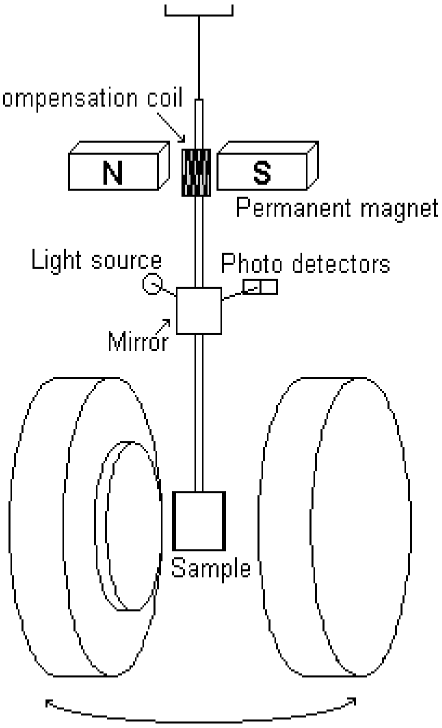


Figure 2.3: Systematic of Vibrating Sample Magnetometer. [17]

2.2.3 Thermogravimetric & Differential Thermal Analyzer

Thermo gravimetric analysis (TGA) is a technique used to examine the thermal decomposition of a material. It is used to measure the change in weight of material as a function of temperature. In this way the thermal stability of material can be examined.

Differential thermal analysis is used to detect any phase transition in the material. In this technique sample is heated continuously at a constant rate. DTA detects the release or absorption of heat when the sample is heated which is associated with chemical and physical changes in the material. In this method differential temperature is plotted against time or temperature.

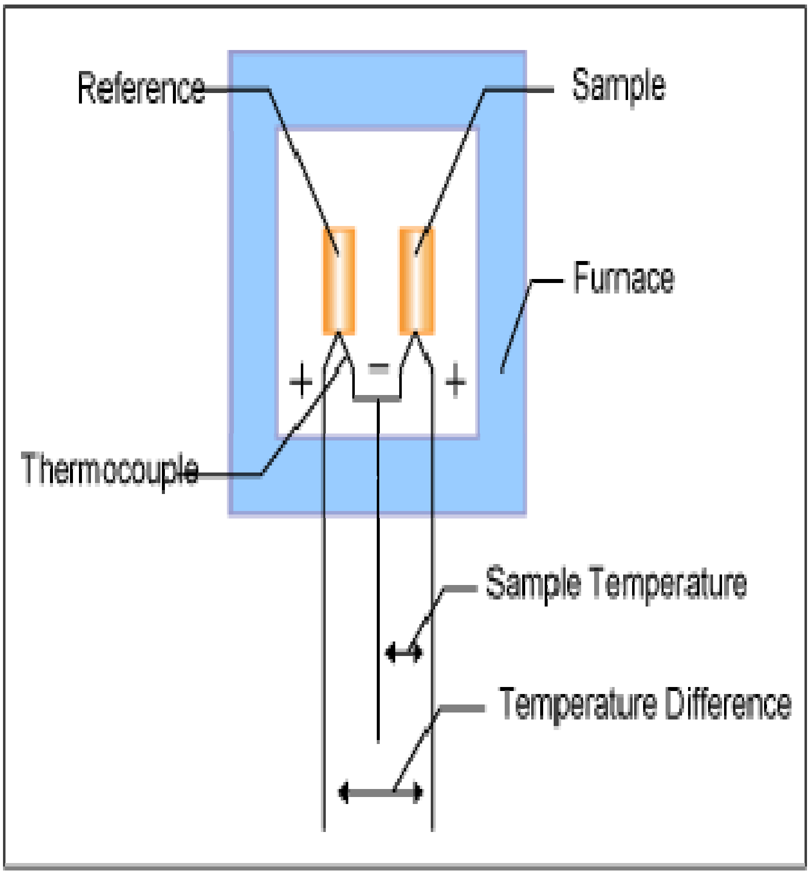


Figure 2.4: Block diagram of Differential Thermal Analyzer. [18]

CHAPTER 3

Results and Discussions

3.1 Structural Characterization

Room temperature x-ray diffraction patterns of the prepared green colored powder sample is obtained using Cu K_α radiation (wavelength $\lambda = 1.5418$ Å). This pattern is shown in Figure 3.1. From this pattern the green colored powder sample is found to be single phase $Ni(OH)_2$. This pattern also shows that the peaks are broadened. This indicates that the material is nano crystalline. The average crystallite size is calculated using the modified Scherrer formula

$$d = 0.9\ \lambda / \mathrm{Cos}\theta_B\ (B_M^2 - B_S^2)^{1/2}$$

where λ is the wavelength of the x-ray used, θ_B is the Bragg angle, B_M is the full width at half-maximum (FWHM) of a peak and B_S is the FWHM of the same peak of a standard sample. The use of $(B_M^2 - B_S^2)^{1/2}$ instead of B_M in the Scherrer formula takes care of instrumental broadening. Here the bulk NiO powder sample is used as the standard sample. Three most intense peaks in Figure 3.1 are used to calculate the average crystalline size using the modified Scherrer formula. This turns out to be about 7 nm.

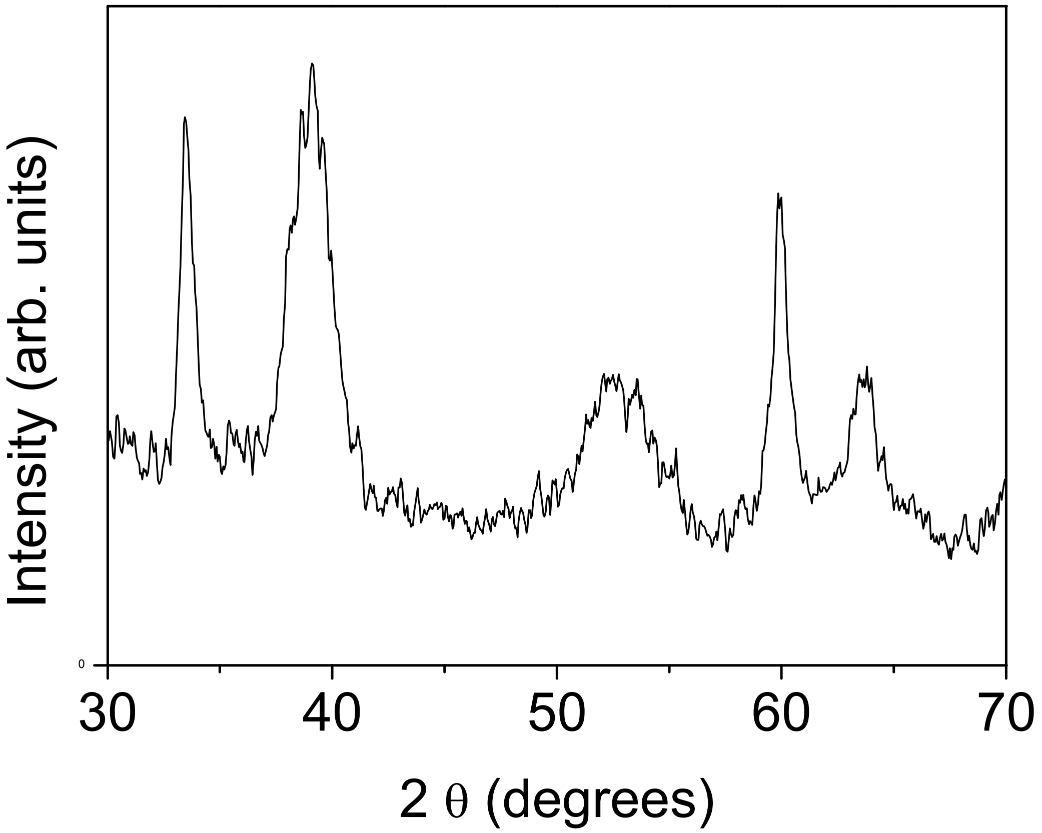


Figure 3.1: Room temperature x-ray diffraction pattern of $Ni(OH)_2$ nanoparticles.

3.2 Thermal Characterization

Many compounds decompose into other compounds on heating. Keeping this thing in mind the prepared green colored powdered sample is characterized with the help of a thermogravimetric and differential thermal analyzer.

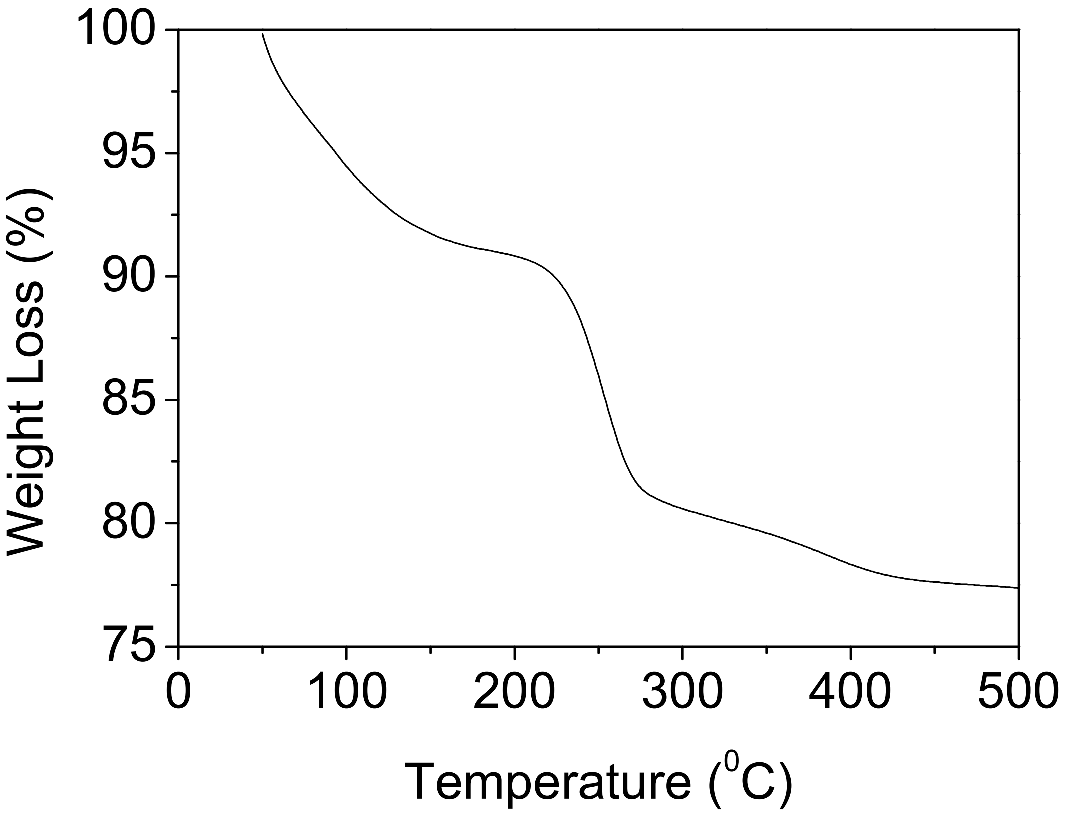


Figure 3.2: TGA curve for the nickel hydroxide sample.

In thermogravimetric analysis the mass of the material is recorded as a function of temperature. During this process the material is kept at a constant heating rate. For this the prepared green colored powder sample is heated at a rate of 10 ^{0}C per minute. The variation of mass of the sample as a function of temperature is shown in Figure 3.2. This figure shows that the mass of the sample decreases with increasing temperature continuously with a sudden change in mass at around 250 ^{0}C. After further heating the mass of the material becomes almost constant in some temperature range. This analysis indicates about the possibility of a phase change in the sample.

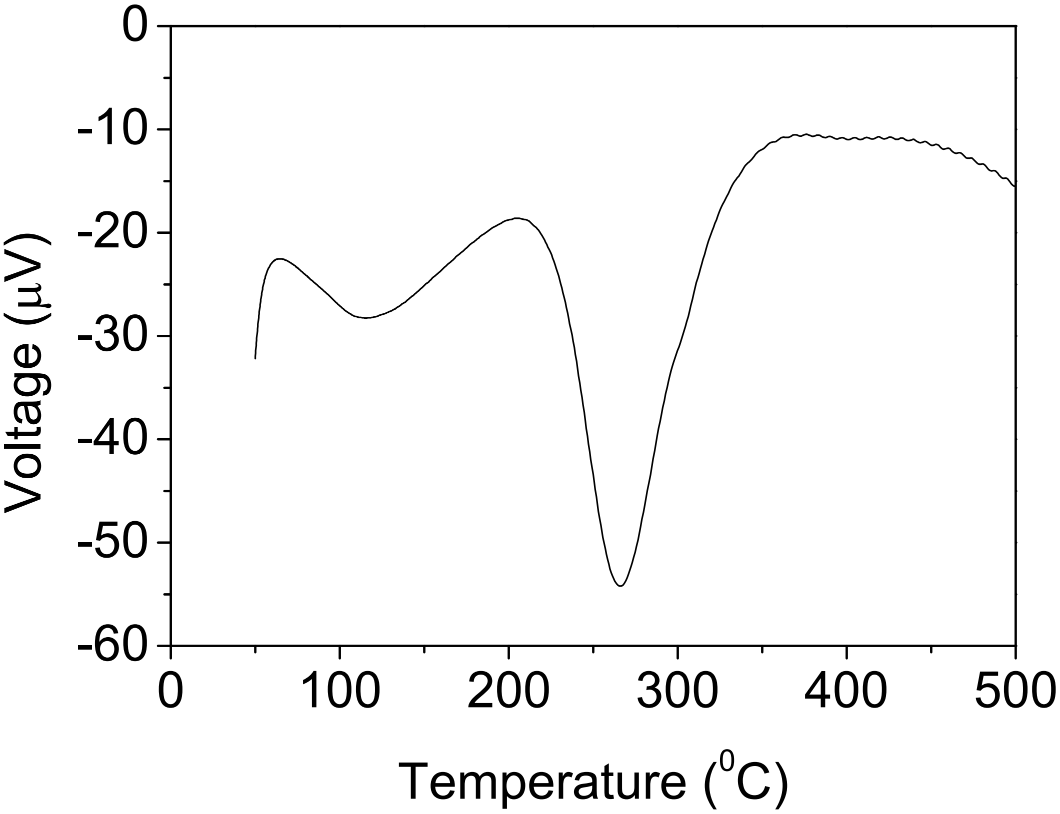


Figure 3.3: DTA curve for the nickel hydroxide sample.

In differential thermal analysis the temperature difference between a given material and a reference material is recorded as a function of temperature by keeping the material and the reference material at a constant heating rate. This variation, recorded at a constant heating rate of 10 ^{0}C per minute, is shown in Figure 3.3. This figure shows an intense endothermic peak at about 250 ^{0}C. This intense endothermic peak again indicates about the possibility of phase change in the material at about 250 ^{0}C. Thus the thermo gravimetric analysis and the differential thermal analysis indicate for a phase change in the material at about 250 ^{0}C. The prepared sample of $Ni(OH)_2$ is heated at 450 ^{0}C in air for three hours. The x-ray diffraction pattern of the resulting black colored powder sample is recorded. This pattern is shown in Figure 3.4 which is of NiO. It means that the $Ni(OH)_2$ nanoparticles decompose into NiO on heating in air at 450 ^{0}C.

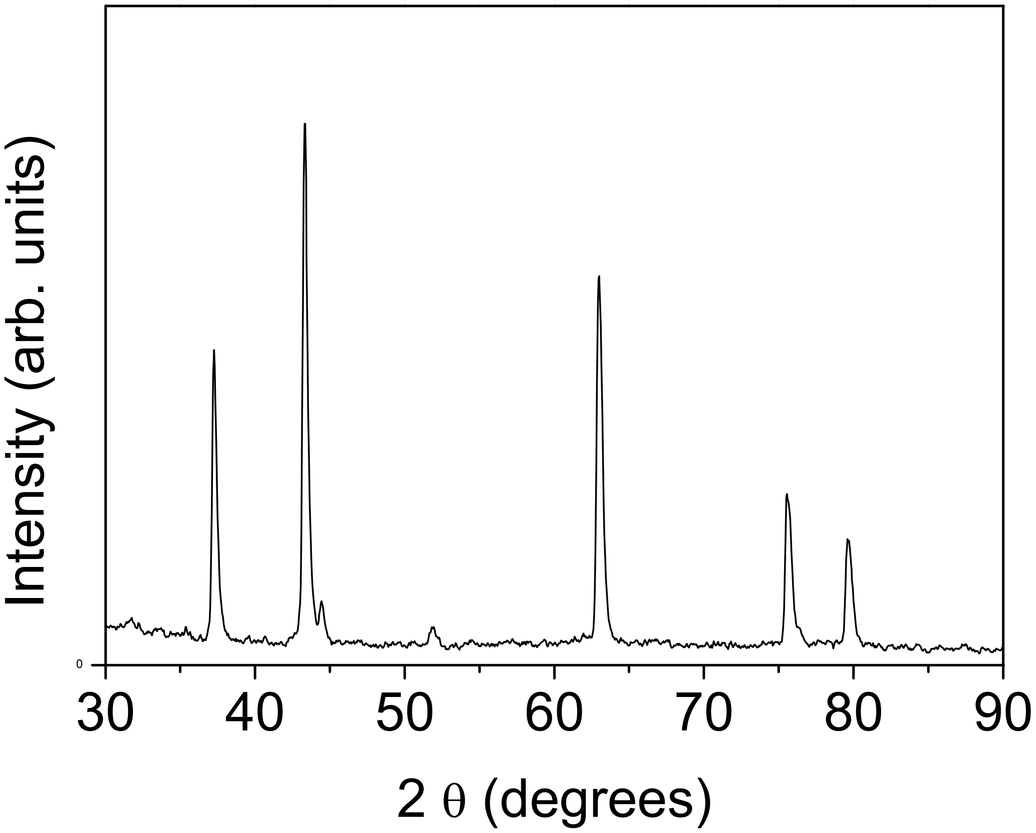


Figure 3.4: Room temperature x-ray diffraction pattern of NiO

3.3 Magnetization Measurements

Magnetization as a function of magnetic field measurement is done for $Ni(OH)_2$ nanoparticles at room temperature. This is shown in Figure 3.5. This figure shows that there is no hysteresis in the magnetization as a function of magnetic field curve. The magnetization of the sample increases with increasing magnetic field linearly throughout passing through the origin. These are characteristics of paramagnetic material. There is no sign of saturation of the magnetizations for this sample because paramagnetic materials usually require very high magnetic field to saturate.

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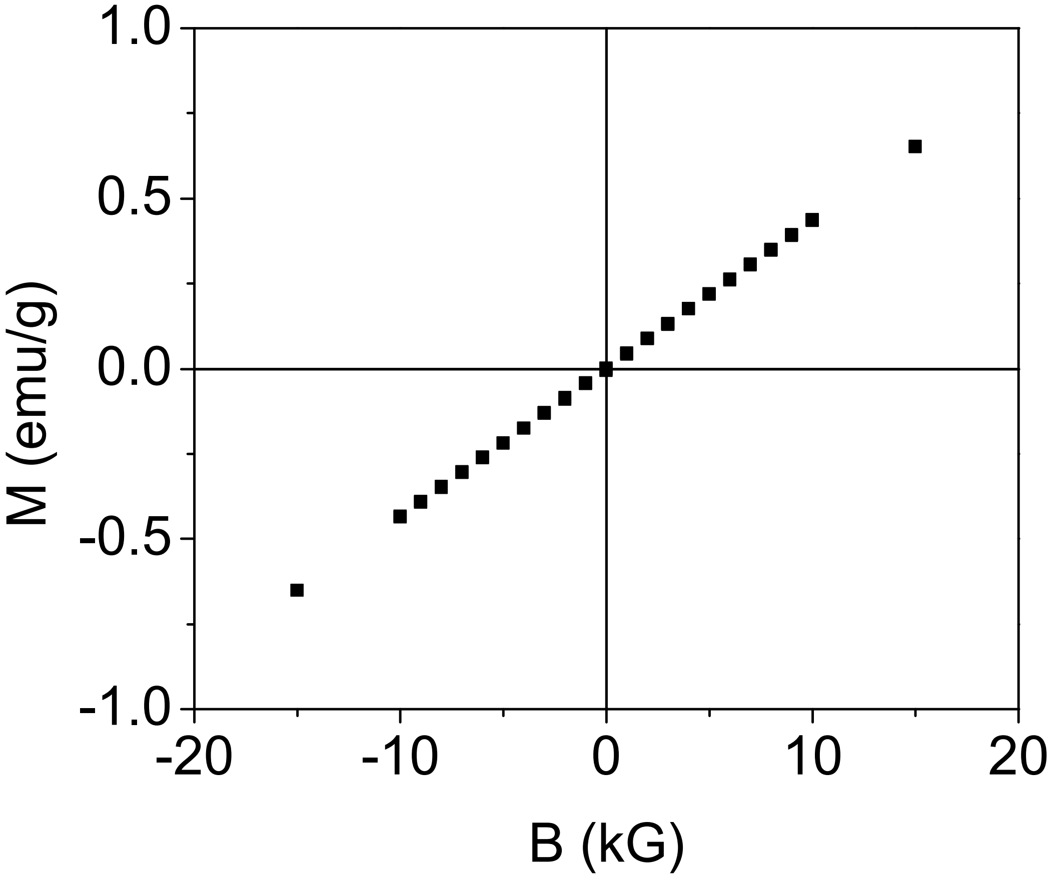

Figure 3.5: Magnetization as a function of applied magnetic field at room temperature for $Ni(OH)_2$ nanoparticles.

At high temperature the magnetization of a paramagnetic material is described by relation

$$M = (N \mu^2 / k_B T) B$$

where N is total number of ions, μ is ionic magnetic moment and k_B is the Boltzmann's constant. From this relation it is clear that the magnetization varies linearly with applied magnetic field. The slope of the line is $(N \mu^2 / k_B T)$. From Figure 3.5 the slope of the line turns out to be 4.34×10^{-5} emu / g Oe. Using this information the ionic magnetic moment of Ni^{2+} in $Ni(OH)_2$ turns out to be about 3.1 Bohr magnetons.

CHAPTER 4

Conclusions

In this work $Ni(OH)_2$ nanoparticles are synthesized by a sol gel method. The sample is characterized by x-ray diffraction, thermal analysis and vibrating sample magnetometer. The $Ni(OH)_2$ nanoparticles decompose in to NiO on heating at 450 ^{0}C in air. The $Ni(OH)_2$ nanoparticles are found to be paramagnetic at room temperature. The magnetic moment of Ni^{2+} ions turns out to be about 3.1 Bohr magnetons.

In this work the behavior of 7 nm $Ni(OH)_2$ particles is studied. One can further prepare nanoparticles of same material of different sizes and can study their behavior in details.

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