Synthesis and Characterization of Nickel Oxide Nanoparticles

A Dissertation submitted

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BY
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July 2011

Dedicated to my

Parents

Certificate

This is to certify that the dissertation entitled "Synthesis and Characterization of Nickel Oxide Nanoparticles" submitted by Sakshi Gupta is in partial fulfillment for the degree of Master of Science in Physics in this university. This work has been done under my supervision. She 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 Oxide Nanoparticles" is the work carried out by me under the supervision of Dr. S. D. Tiwari. The matter embodied in this dissertation has not been submitted anywhere else for the award of any degree.

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Sakshi Gupta

Abstract

Nanoparticles of NiO are prepared by thermal decomposition of freshly prepared nickel hydroxide by a sol gel route at 300 ^{0}C. This sample is characterized by x-ray diffractometer and vibrating sample magnetometer. The average crystallite size is found to be about 5 nm. The prepared nanoparticles of NiO are found to be antiferromagnetic at room temperature.

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CHAPTER 1

Introduction

1.1 Magnetism

All matters consist of atoms and the atom consists of positively charged nucleus surrounded by negatively charged electrons. In atom the electron has two types of motions i.e. the orbital motion and the spin. These two types of motions are responsible for the magnetic moment of the electron. The magnetic behavior of any material is decided by the relative arrangement of atomic magnetic moments inside the material. Depending on the behavior of materials in external magnetic field, all the materials can be classified into following main categories [1-3].

1.1.1 Diamagnetism

In diamagnetic materials all the electrons are paired and so the net electronic spin magnetic moment is equal to zero. Magnetization of diamagnetic material is always opposite to the applied magnetic field direction. In other words the susceptibility of the diamagnetic material is always negative. Also the susceptibility of the diamagnetic material is independent of temperature.

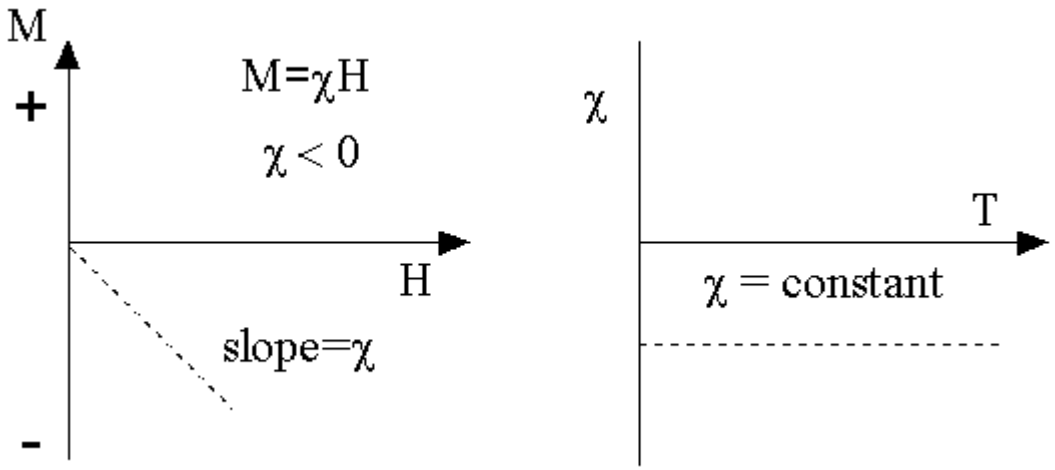

Figure 1.1: Variation of magnetization M as a function of applied magnetic field H and variation of susceptibility χ as a function of temperature T for diamagnetic material. [4]

1.1.2 Paramagnetism

Paramagnetism is shown by a collection of non interacting magnetic moments. Such materials consist of unpaired electron spins. Magnetization of paramagnetic material is zero in absence of any external magnetic field. In presence of external applied magnetic field the moments try to align themselves along the field direction giving rise to a positive value for the magnetic susceptibility. The magnetization in paramagnetic materials is seen as long as the external magnetic field is present.

The magnetization of paramagnetic materials varies with external applied magnetic field according to relation

$$M = N \mu^2 H / 3 k_B T.$$

Here N is the atomic concentration. The susceptibility of a paramagnetic material varies with temperature according to relation

$$\chi = N \mu^2 / 3 k_B T.$$

This relation is called the Curie law.

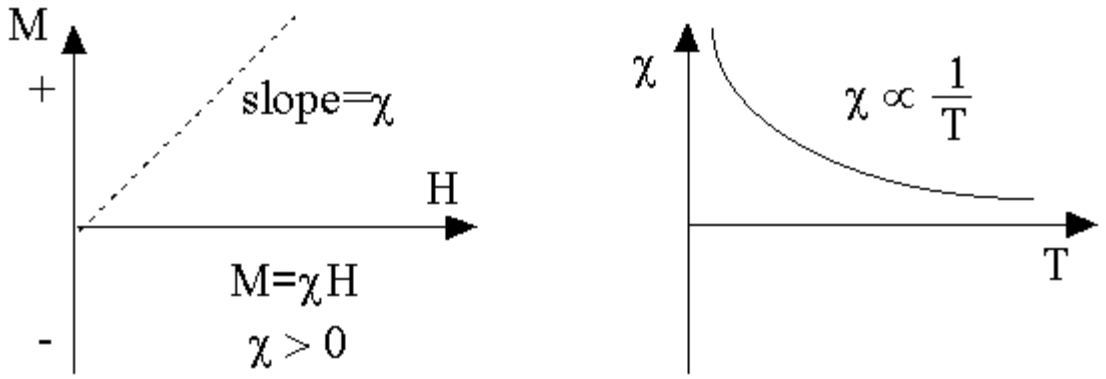

Figure 1.2: Variation of magnetization M as a function of applied magnetic field H and variation of susceptibility χ as a function of temperature T for a paramagnetic material. [4]

1.1.3 Ferromagnetism

In ferromagnetic materials all the magnetic moments are aligned in same direction due to exchange interaction. These moments try to minimize the energy of the system by having their neighboring atomic dipole moments aligned in the same direction. But if whole of the dipoles align in the same direction then the magnetic field would be very high and energy also would be very high. So, the system makes the microscopic regions in which billions of dipoles are aligned but the alignment directions of the separate regions are random giving net magnetic moments equal to zero. These microscopic regions are called domains.

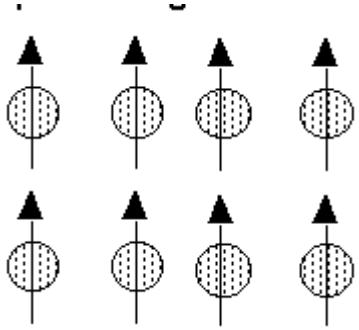

Figure 1.3: Arrangement of spins for ferromagnetic material. [4]

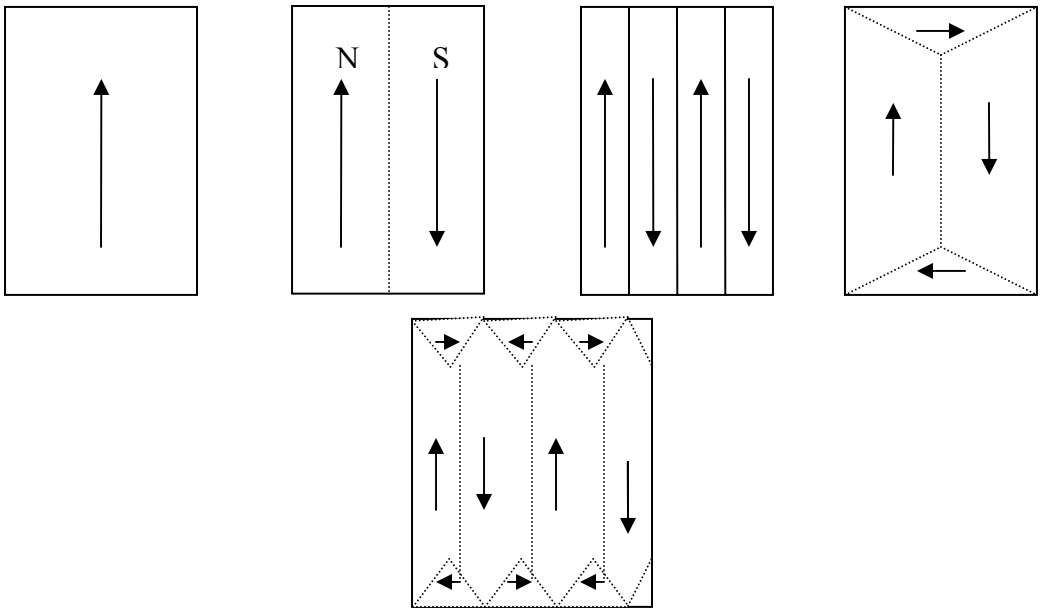

Figure 1.4: The origin of domains in ferromagnetic materials.

The subdivision cannot take place indefinitely because, the region within the domains called transition region needs energy to be produced and maintained. This transition region is also called domain wall. Within wall the magnetization changes direction from that in one domain to that in the other domain.

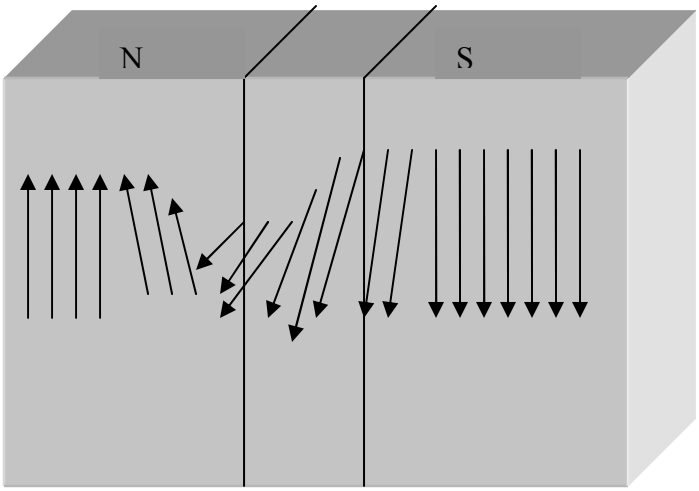

Figure 1.5: The Structure of Bloch Wall separating domains.

The Curie temperature can be defined as the value of temperature above which the ferromagnetic material becomes paramagnetic. Graph between temperature and magnetization can be drawn to show how the magnetization of sample decreases with increase in temperature. Ferromagnets can retain a memory of an applied field after the removal of field.

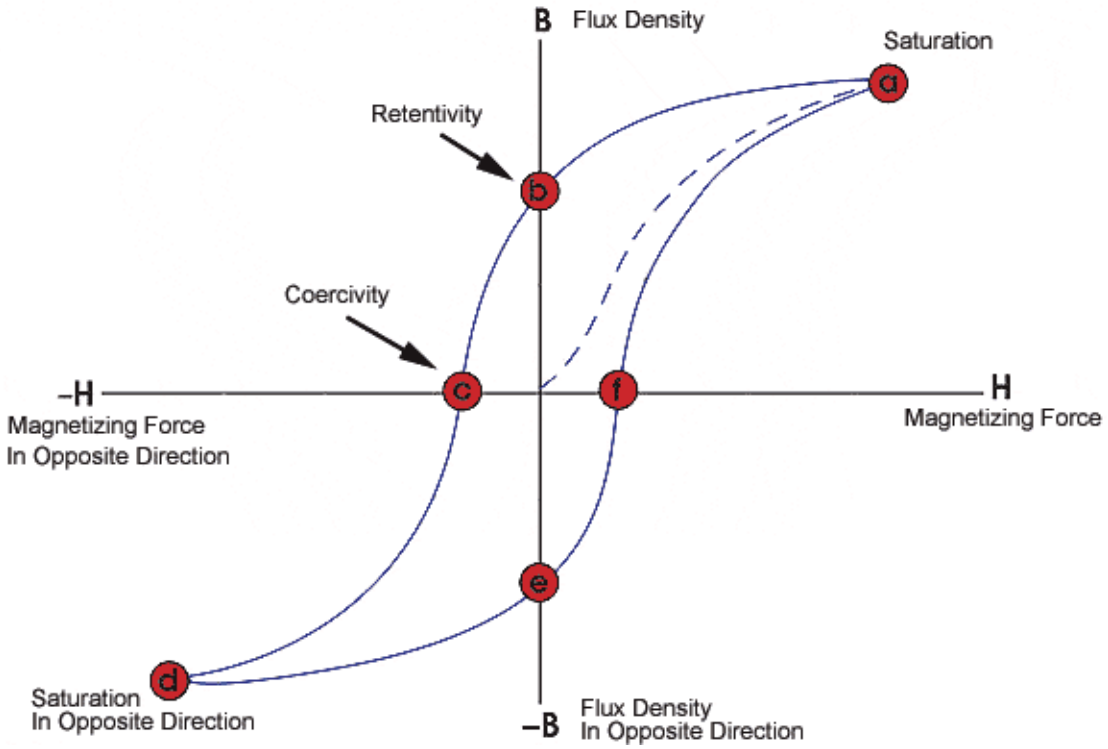

Figure1.6: Hysterisis loop for ferromagnetic material. [5]

1.1.4 Antiferromagnetism

Antiferromagnetism arises when the two sublattices of a lattice are having net magnetic moment equal to zero. Both sublattices are having the magnetic moments equal in magnitude but opposite in direction. Above a particular temperature, called the Neel temperature, a given antiferromagnetic material becomes paramagnetic.

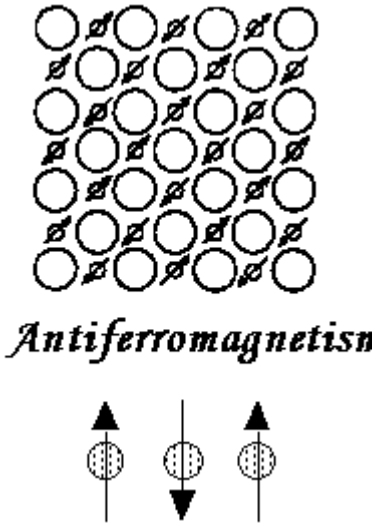

Figure 1.7: Arrangement of spins for antiferromagnetic material. [4]

1.1.5 Ferimagnetism

Ferrimagnetism arises when the two sublattice of a lattice are having some net magnetic moment. Here the magnetic moments of each sub lattices are opposite in directions but not equal in magnitude. Above a critical temperature, known as the Curie temperature, a given ferrimagnetic material becomes paramagnetic.

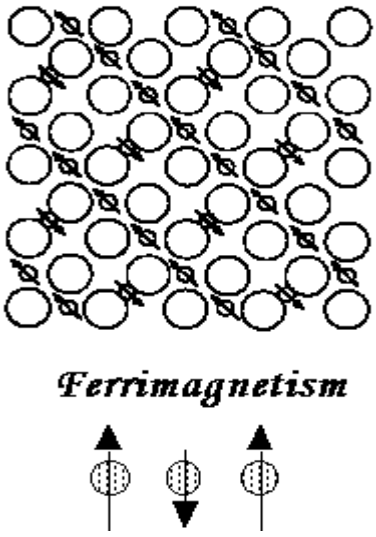

Figure 1.8: Arrangement of spins for ferrimagnetic material. [4]

1.2 Magnetic Anisotropy

The magnetization of any crystal is anisotropic in nature. There are three main types of magnetic anisotropies.

1.2.1 Magnetocrystalline Anisotropy

In a crystal there is a direction along which it is easiest to magnetize the material. This axis is known as the easy axis. In similar manner there is also a direction along which it is most difficult to magnetize the material. This direction is known as the hard axis. Magnetocrystalline anisotropy energy is given by relation

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

where K is the anisotropy constant, V is the volume of the crystal and θ is the angle that the magnetization vector makes with the easy axis. This relation shows that the anisotropy energy has minima when the angle θ is either 0^0 or 180^0.

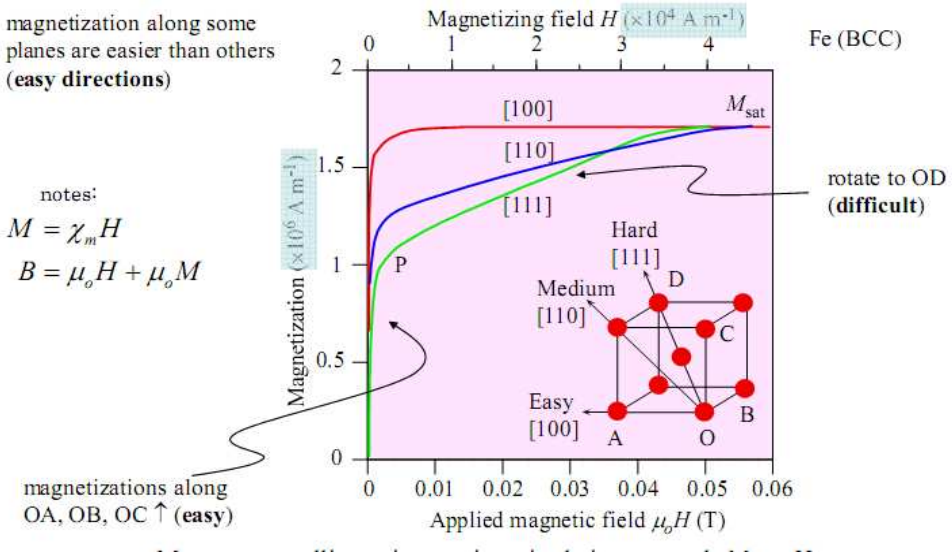

Figure 1.9: Magnetization of iron along the different crystallographic axes in the presence of applied magnetic field. [6]

1.2.2 Stress Anisotropy

If a crystal is placed in an external magnetic field then the crystal elongates in one direction and compresses in another direction. This effect is known as magnetostriction. This arises due to spin orbit coupling. It is clear that because of magnetostriction effect the anisotropy also depends on strain. Whenever a demagnetized sample is magnetized then the sample experiences a strain. This strain is function of applied magnetic field along crystallographic axes. The reverse effect can also be seen. The change in magnetization of the sample can also be observed with the application of stress on the sample.

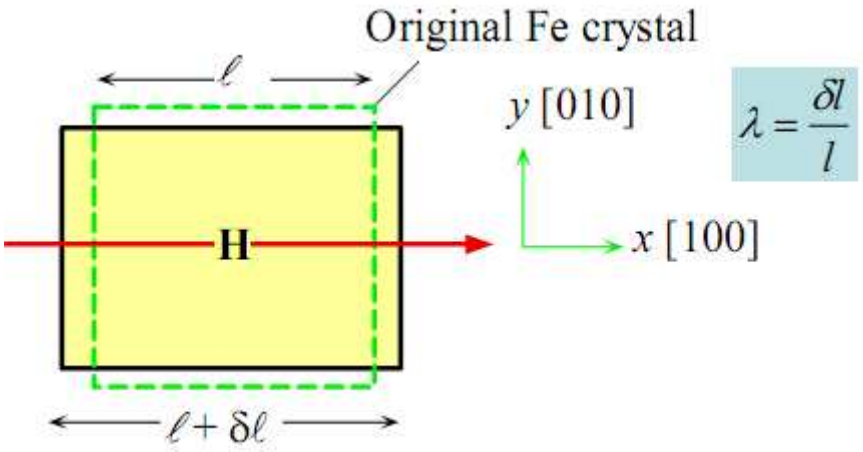

Figure 1.10: Demonstration of change in dimensions with the application of magnetic field. [6]

1.2.3 Shape Anisotropy

The anisotropy arising due to the shape of the crystal is called shape anisotropy. When a sample is magnetized then it produces magnetic charges or poles at its surface. These poles produce new magnetic field which is in a direction opposite to that of the applied field. This induced field is called demagnetizing field. The value of this field changes with the change in the direction of the applied magnetic field.

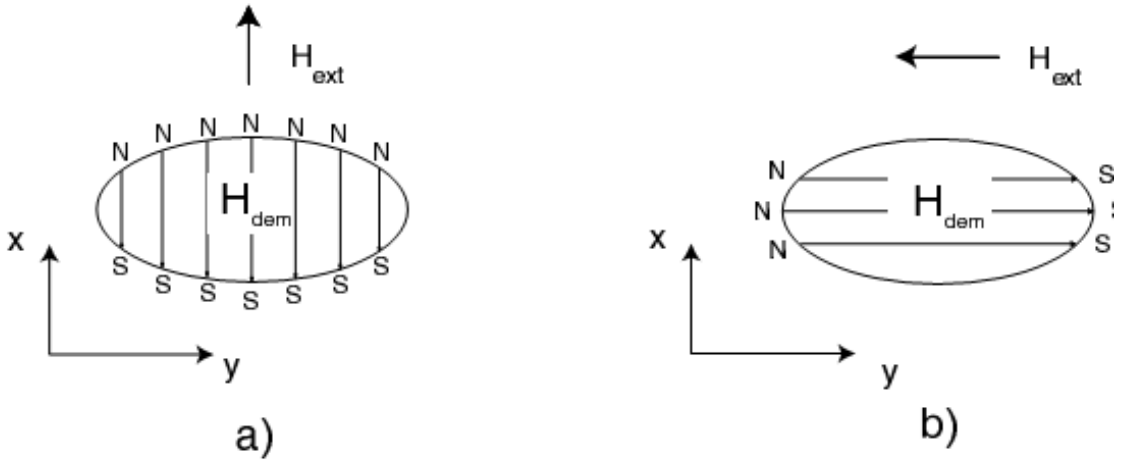

Figure 1.11: Demonstration of demagnetizing field. [7]

1.3 Superparamagnetism

Superparamagnetism is observed in a collection of nanometer sized particles of magnetic materials. The magnetocrystalline anisotropy energy is directly proportional to the volume of the crystal. In other words the magnetocrystalline anisotropy energy of a crystal decreases with decreasing volume of the crystal. For a sufficiently small size crystal the magnetocrystalline anisotropy energy becomes smaller than the thermal energy and the orientation of the magnetization vector will flip with time. This situation is similar to paramagnetism. This is called the superparamagnetism. The time between two flips is called Néel relaxation time. The magnetization of a superparamagnetic sample depends on temperature. If $k_B T << E_{an}$ then a non zero magnetization as well as hysterisis loop are observed. However if $k_B T >> E_{an}$ then the particle magnetic moments will be oriented randomly giving rise to zero magnetization. This is the situation of superparamagnetism.

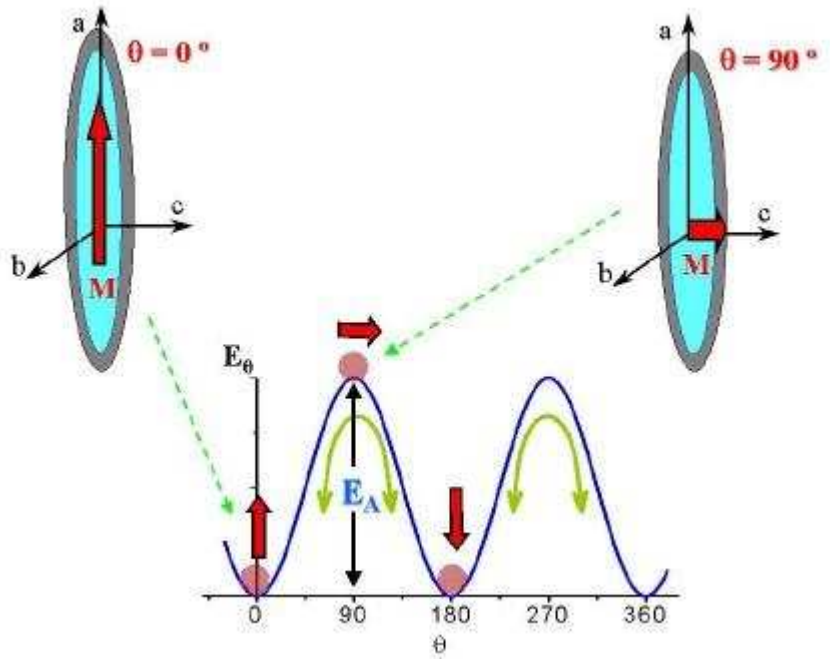

Figure 1.12: Energy barrier diagram for a superparamagnetic particle. [8]

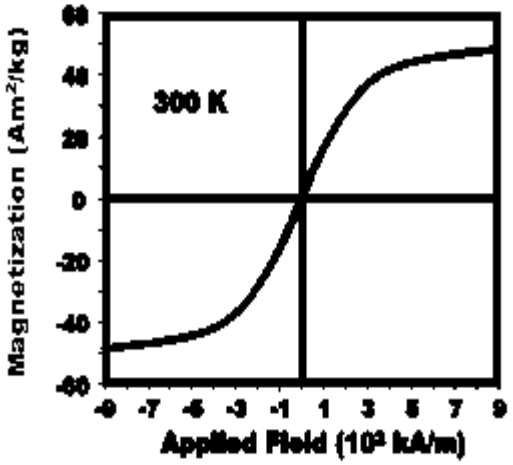

Figure 1.13: Magnetization as a function of applied magnetic field curve for a superparamagnetic sample. [9]

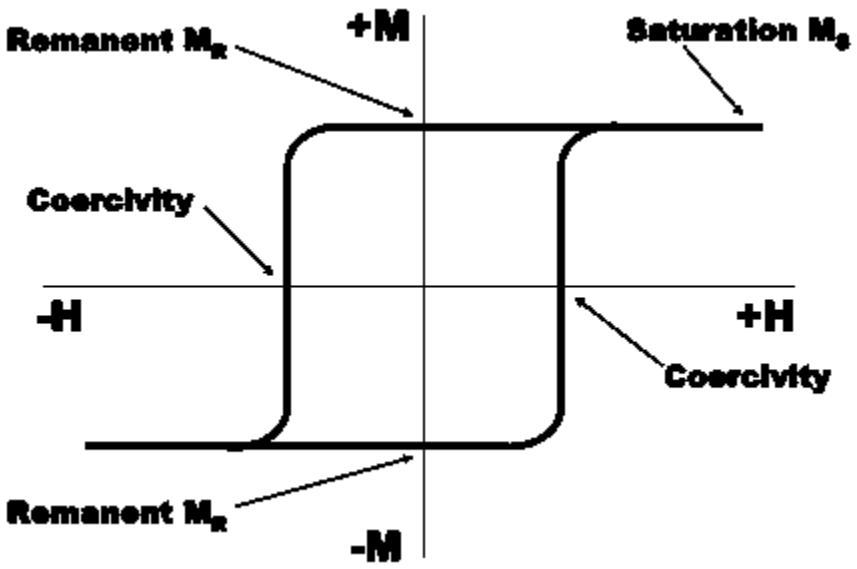

Figure 1.14: Magnetization as a function of applied magnetic field curve for ferromagnetic sample. [9]

The magnetization as a function of applied magnetic field curve for a superparamagnetic sample and for a ferromagnetic sample is shown in Figures 1.13 and 1.14 respectively. It is clear that superparamagnetic sample does not have ramenance and coericive field whereas for a ferromagnetic sample they are non zero.

CHAPTER 2

Experimental Details

2.1 Synthesis

There are various physical and chemical methods for the preparation of nano crystalline materials. In the present work nanoparticles of NiO are synthesized by a sol gel method. This process involves the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The starting materials are processed to form a sol in water or dilute acid. Removal of the liquid from the sol yields the gel.

Nanoparticles of NiO are prepared by thermal decomposition of freshly prepared $Ni(OH)_2$ as described elsewhere [10]. The $Ni(OH)_2$ is prepared by reacting aqueous solutions of 0.1 M nickel nitrate and 0.5 M sodium hydroxide. For this NaOH solution is added drop wise with constant stirring until the pH of the system reaches to 12. The chemical reaction between nickel nitrate and sodium hydroxide solutions is as follows.

$$Ni(NO_3)_2 + 2\ NaOH \rightarrow Ni(OH)_2 + 2\ NaNO_3$$

The resulting green gel is washed several times with distilled water. Finally the gel is dried by heating at 100 ^{0}C for 10 hours. Nickel hydroxide decomposes into nickel oxide on heating as follows.

$$Ni(OH)_2 \rightarrow NiO + H_2O$$

In this work nanocrystalline NiO sample is prepared by heating the nickel hydroxide in air for 3 hours at 300 ^{0}C.

2.2 Experimental Techniques

2.2.1 X- Ray Diffraction

Figure 2.1 shows a beam of x-ray falling on a set of parallel atomic planes at an angle θ. The reflected x-ray beam undergoes a constructive interference if

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

where d is separation between atomic planes, λ is the wavelength of the x-rays and n = 1, 2, ……This is Bragg's law. The x-ray diffraction pattern of a powder sample gives plot of intensities of diffraction peaks as a function of angle 2θ. Using this plot possible values of d are calculated. In this way the given material is characterized.

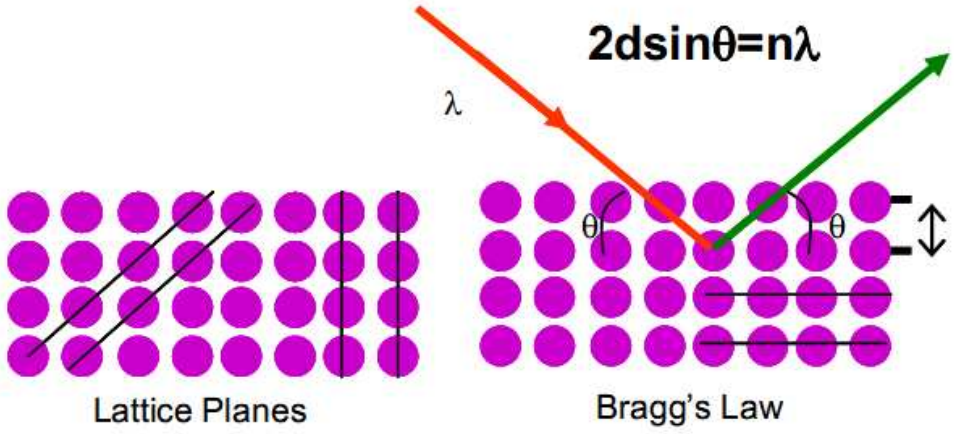

Figure 2.1: X-ray beam reflected by the set of parallel planes. [11]

2.2.2 Thermal Analysis

Thermal analysis is an experimental method in which thermal stability of a given material is examined as a function of temperature [12]. In differential thermal analysis the temperature difference between the given sample and an inert sample is measured as a function of temperature. During this process the system is heated at a constant rate. This technique detects the release or absorption of heat when the sample is heated or cooled

which is associated with chemical and physical changes in material. In this method differential temperature is plotted against time or temperature.

In thermo gravimetric analysis the mass of the sample is measured as a function of temperature. During this process the sample is heated at a constant rate. This technique is useful to know about the thermal stability of the material and to know whether the sample is inert or oxidizing. Both organic and inorganic samples can be characterized with this technique.

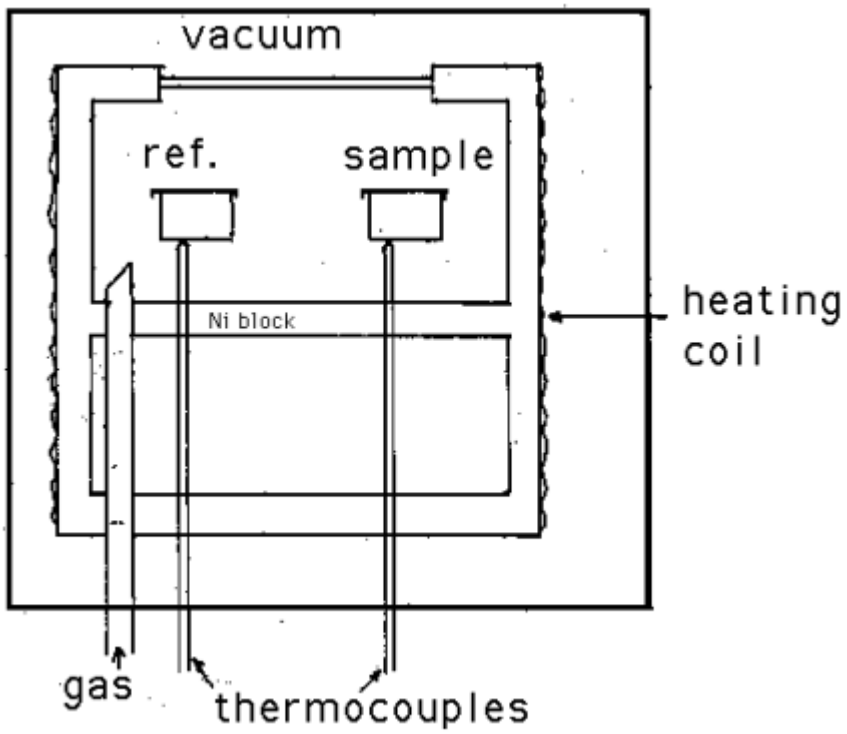

Figure 2.2: Schematic diagram of a DTA cell. [12]

2.2.3 Vibrating Sample Magnetometer

A vibrating sample magnetometer (VSM) is used to measure the magnetization of a given sample. This magnetometer is based on the Faraday's Law. According to this law a time varying flux induces an emf. In VSM, a magnetic field is applied to

magnetize the sample. This sample is allowed to vibrate vertically inside a pickup coil. Because of this an emf is induced across the coil. This emf can be measured with the help of proper electronic circuitry. In this way the magnetization of the sample can be estimated with the help of proper calibration.

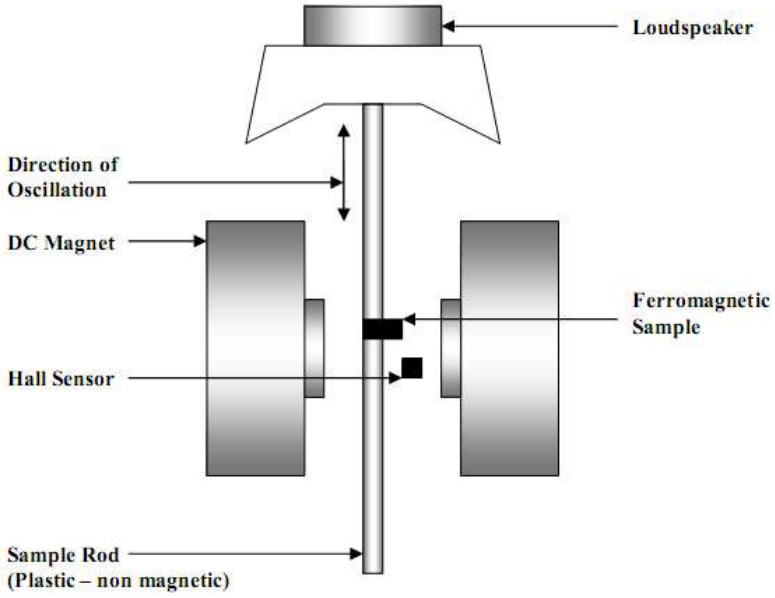

Figure 2.3: The vibrating sample magnetometer. [13]

CHAPTER 3

Results and discussion

3.1 Structural characterization

Structural characterization of the prepared sample is done using a x-ray diffractometer and Cu K_α radiation (wavelength λ = 1.5418 Å) at room temperature. Intensity of the diffracted x-ray beam is recorded as a function of the angle 2θ. The X-ray diffraction pattern of the prepared green colored powder sample at room temperature is shown in Figure 3.1. From this pattern it is found that the prepared green Colored powder sample is nickel hydroxide.

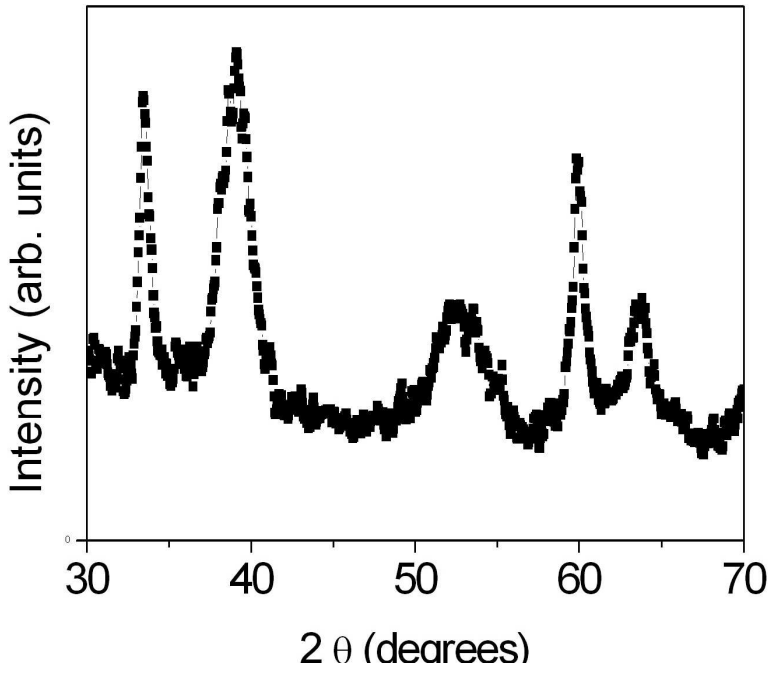

Figure 3.1: Room temperature x-ray diffraction pattern of nickel hydroxide.

The nickel hydroxide decomposes into nickel oxide on heating. Details of this are discussed in Section 3.2. Keeping this thing in mind the synthesized green colored

powder is heated at 250 ^{0}C for 3 hours. Because of this heating the color of the sample changes from green to black. Room temperature x-ray diffraction pattern of this sample is shown in Figure 3.2. From this pattern it is clear that the black colored sample is NiO.

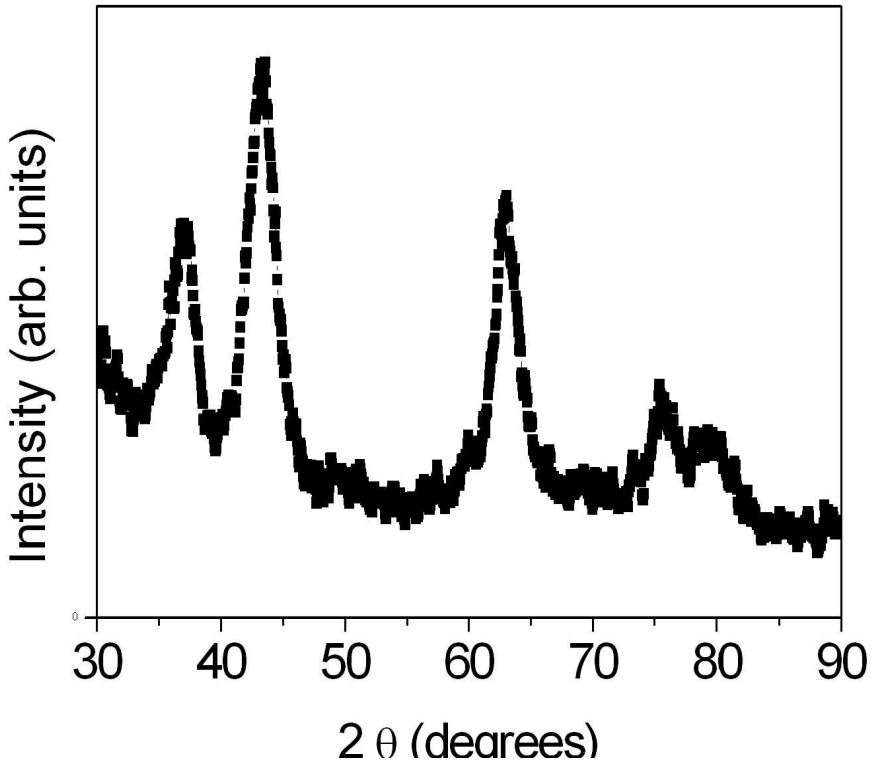

Figure 3.2: Room temperature x-ray diffraction pattern of NiO nanoparticles.

From Figure 3.2 it is also noticed that the peaks are broadened. This indicates that the sample is nanocrystalline. The average crystallite size is calculated using the modified Scherrer formula [14]

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

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 in radians and B_S is the FWHM of the same peak of a standard sample. Here the bulk NiO powder sample from Aldrich is used as the standard sample. The room temperature x-ray diffraction pattern of the bulk NiO sample is shown in Figure 3.3. Two most intense peaks in Figure 3.2 are used to calculate the average crystalline size using the modified Scherrer formula. This turns out to be about 5 nm. The use of $(B_M^2 - B_S^2)^{1/2}$ instead of B_M in the Scherrer formula takes care of instrumental broadening.

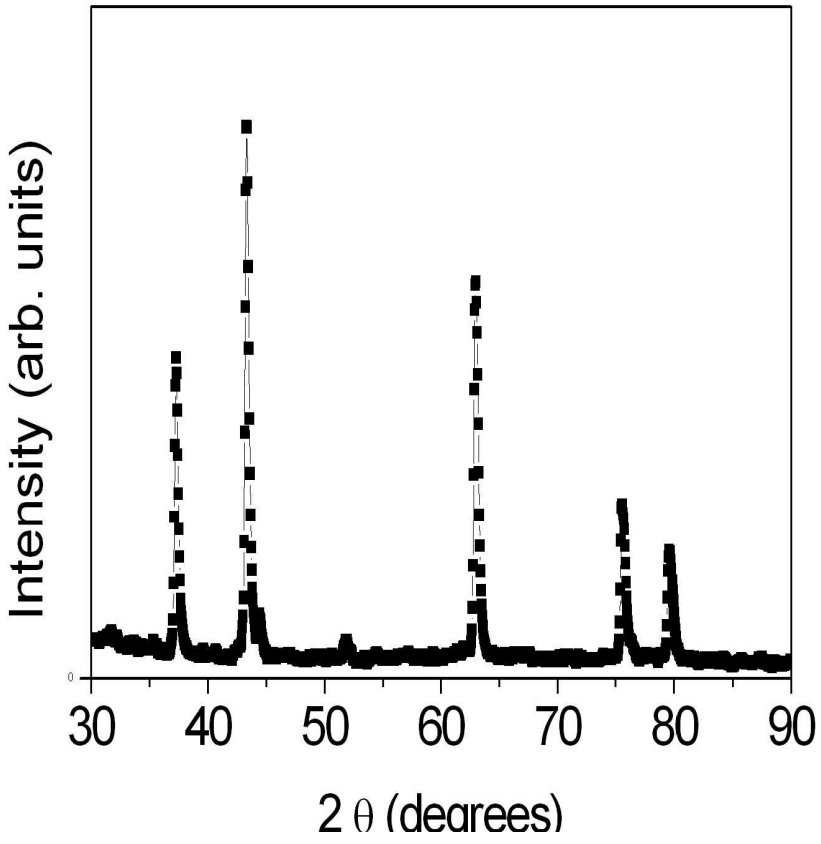

Figure 3.3: Room temperature x-ray diffraction pattern of bulk NiO.

3.2 Thermal characterization

Many compounds are not stable and decompose into some other compounds on heating. The prepared sample of nickel hydroxide is characterized with the help of thermogravimetric analyzer to check its thermal stability. For this the sample is heated at a constant rate of 10 ^{0}C per minute and the weight loss is recorded as a function of temperature. The resulting curve is shown in Figure 3.4.

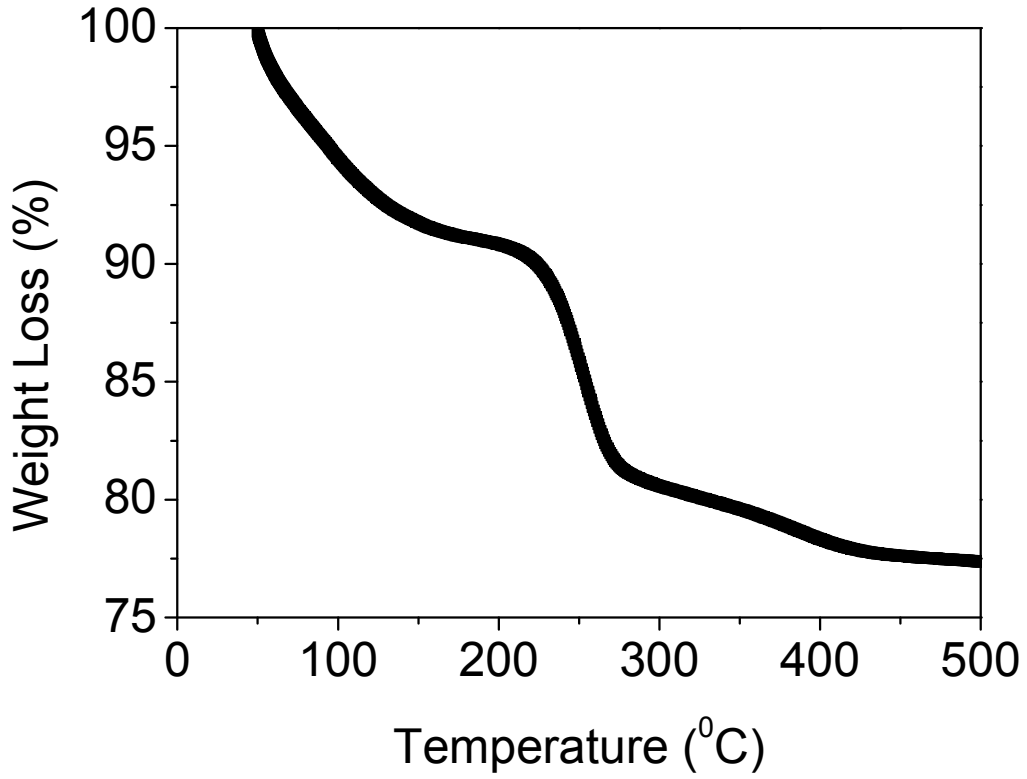

Figure 3.4: TGA curve for nickel hydroxide sample.

From Figure 3.4 it is noticed that the mass of sample decrease slowly with increasing temperature. At about 200 ^{0}C, the mass of the sample starts decreasing suddenly. This indicates for a possible phase transition around this temperature. Figure 3.5 shows DTA curve for the nickel hydroxide sample. This curve shows an intense endothermic peak at about 240 ^{0}C. This observation again indicates for a possible phase transition. The green

colored powder sample of nickel hydroxide is heated at 300 ^{0}C for three hours. The structural characterization of the resulting black colored powder sample is done with the help of x-ray diffractometer. Figure 3.2 shows the x-ray diffraction pattern of the sample. From this pattern it is confirmed that the nickel hydroxide is converted into NiO nanoparticles on heating at 300 ^{0}C.

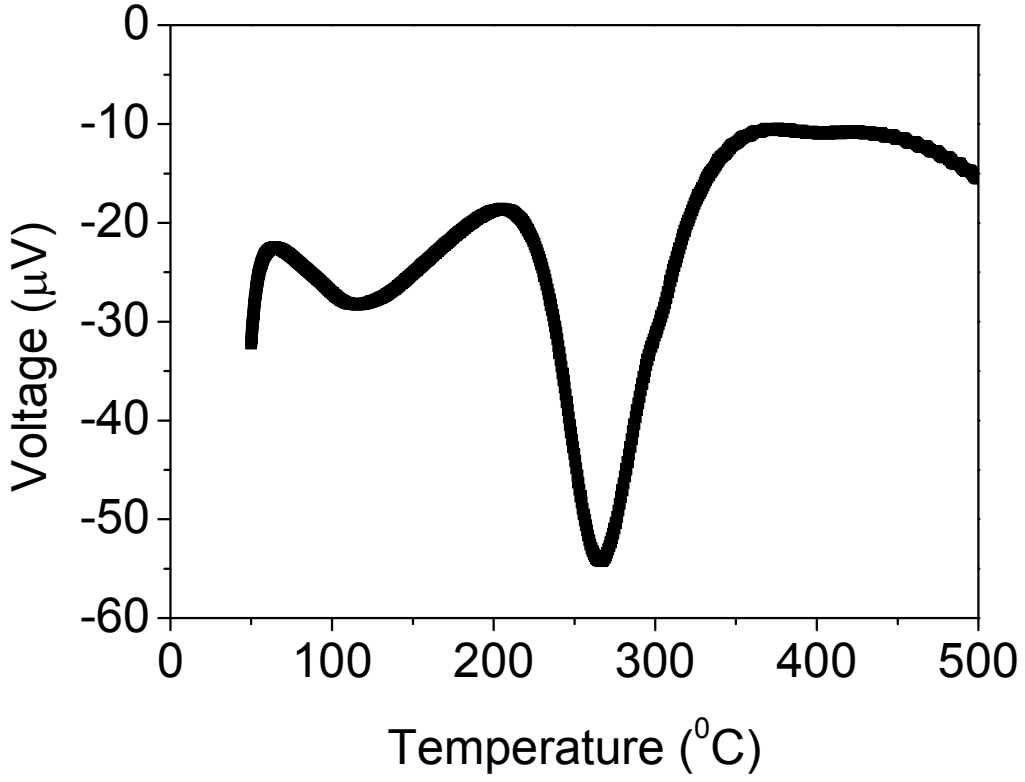

Figure 3.5: DTA curve for nickel hydroxide sample.

3.3 Magnetization measurements

Magnetization as a function of magnetic field measurements is done for nanocrystalline and bulk NiO samples using a vibrating sample magnetometer at room temperature. These measurements are shown in Figures 3.6 and 3.7 respectively.

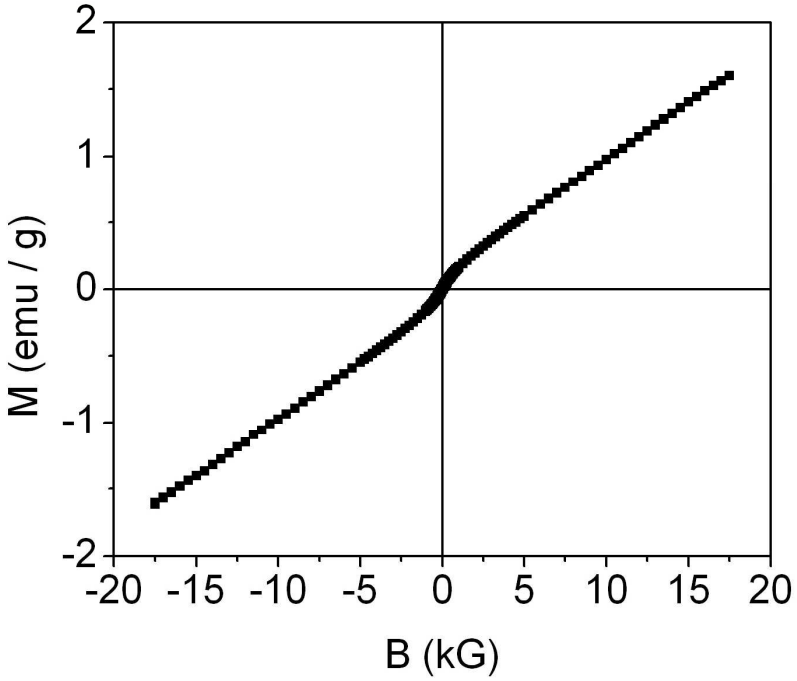

Figure 3.6: Magnetization M as a function of applied magnetic field B at room temperature for NiO nanoparticles.

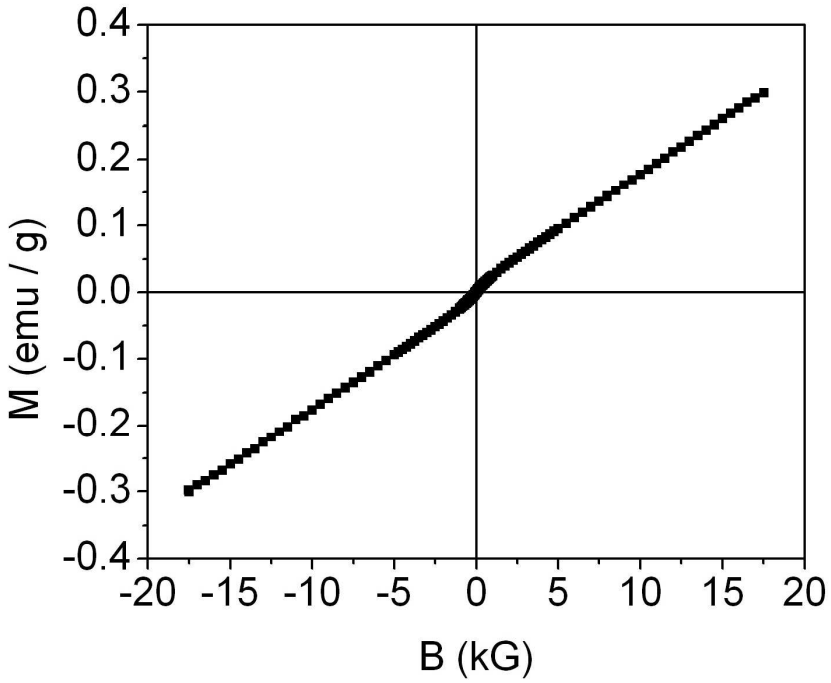

Figure 3.7: Magnetization M as a function of applied magnetic field B at room temperature for bulk NiO.

From Figures 3.6 and 3.7 it is found that there is no hysteresis in all the *M* vs. *H* curves. The magnetizations of the two samples increase with increasing magnetic field strength. It is also observed that at smaller magnetic fields the magnetization increases with magnetic field nonlinearly whereas at relatively higher magnetic fields the magnetization increases with magnetic field almost linearly. These are characteristics of antiferromagnetic materials. There is no sign of saturation of magnetizations for these samples because antiferromagnetic materials usually require very high magnetic field to saturate.

Magnetic susceptibility is defined as ratio of the magnetization to the applied magnetic field. For this the linear portion of the magnetization versus magnetic field curve is used. The magnetic susceptibilities of the samples are calculated at room temperature using Figures 3.6 and 3.7. The results are shown in Table I.

Sample	Susceptibility (emu / g Oe)
NiO nanoparticles	8.07×10^{-5}
Bulk NiO	1.58×10^{-5}

If Figures 3.6 and 3.7 are compared then it is found that the magnetization of nanocrystalline NiO is higher than that of bulk NiO. The fraction of spins lying on the surface of antiferromagnetic particles increases with decreasing particle size. Because of this reason the magnetization of antiferromagnetic particles increases with decreasing particle size [10].

CHAPTER 4

Conclusions

In this work NiO nanoparticles are synthesized by thermal decomposition of $Ni(OH)_2$ at 300 ^{0}C in air. The sample is characterized by x-ray diffraction, thermal analyzer and vibrating sample magnetometer. The magnetization of NiO nanoparticles is compared with that of bulk NiO. In this study the NiO nanoparticles are found to be antiferromagnetic at room temperature. The magnetization of NiO is also found to increase with decreasing crystallite size. Uncompensated spins on the surface of particles are responsible for this.

In literature comparatively little work on $Ni(OH)_2$ is found. There is still possibility for detailed magnetic study of $Ni(OH)_2$ system by someone in future.

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