2006

Magnetic and structural properties of nanoparticles of nickel oxide

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Magnetic and Structural Properties of Nanoparticles of Nickel Oxide

DISSERTATION

Submitted to the Eberly College of Arts and Sciences

at

West Virginia University

In Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

in Physics

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2006

Keywords: Nickel Oxide, Nanoparticles, Magnetism

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ABSTRACT

In this dissertation, magnetic properties of NiO nanoparticles (NP) prepared by the sol-gel method in the size range $D = 5$ nm to 20 nm, with and without oleic acid (OA) coating, are reported. Transmission electron microscopy (TEM) studies show the morphology of the smaller particles to be primarily rod-like, changing over to nearly spherical shapes for $D > 10$ nm. Average sizes D of NP determined by x-ray diffraction (XRD) are compared with the results from TEM. From the analysis of the XRD line intensities, the particle size dependence of the Debye-Waller factors for Ni and O atoms are derived. It is found that the Debye-Waller factors of nickel and oxygen atoms in smaller particles are larger than those in bulk NiO.

For the coated and uncoated NiO nanorods of 5 nm diameter, variations of the magnetization M with temperature T (5 K to 370 K) and temperature variations of the EMR (electron magnetic resonance) spectra were measured to determine the respective blocking temperatures $T_B(m)$ and $T_B(EMR)$. The following differences are noted: (1) $T_B(m)$ is reduced from 230 K (uncoated) to 85 K (coated) for $H = 25$ Oe; (2) Decrease of $T_B(m)$ with H is weaker and the ratio $T_B(EMR)/T_B(m)$ is smaller for the uncoated particles. These differences are due to stronger interparticle interaction present in the uncoated particles.

Temperature variation (5 K-300 K) of the AC magnetic susceptibilities (χ' and χ'') at various frequencies f (0.1-10,000 Hz) are reported for the coated and uncoated 5 nm diameter nanorods of NiO. Using the peak in χ' as the blocking temperature T_B , it is observed that T_B increases with increasing f . The data for the two samples fit the Vogel-Fulcher law: $f = f_0 \exp[-E_a/k(T_B - T_0)]$ with $f_0 = 9.2 \times 10^{11}$ Hz, $E_a/k = 1085$ K and $T_0 = 162$ K (0 K) for the uncoated (coated) particles. This shows that T_0 provides a good measure of the effects of interparticle interactions on magnetic relaxation and that these interactions are essentially eliminated with the OA coating.

For all the particles, measurements of M versus T (5 K–370 K) in the zero-field cooled (ZFC) and field-cooled (FC) modes are used to determine the average blocking temperature T_P . For the OA coated particles, T_P increases with increase in size D as expected for superparamagnetic particles. However for the uncoated NP, T_P decreases initially with increase in size for $D < 10$ nm; but for $D > 10$ nm, T_P follows the same

trend as for the coated NP. These differences are interpreted in terms of significant interparticle interaction. The data of M vs. the applied field H for $T > T_p$ are fit to the modified Langevin function: $M = M_0 \mathcal{L}(\mu_p H / k_B T) + \chi_a H$, to determine the magnetic moment μ_p per particle as a function of size D . The variation of μ_p with size D is interpreted in terms of the fraction of spins on the surface layer of the particles which contribute to μ_p . It is observed that this fraction varies as $1/D$ reaching nearly 100 % for the 5 nm particles. From the temperature dependence of M_0 and extrapolating to $M_0 \rightarrow 0$, the Néel temperatures T_N for various sizes are determined. T_N for NiO nanoparticles is found to decrease rapidly with decrease in size for $D < 10$ nm.

ACKNOWLEDGEMENTS

It is my pleasure to acknowledge the following people for their invaluable support during my years of study at West Virginia University.

First, I would like express my sincere gratitude and many thanks to my research advisor, Prof. M.S. Seehra, for suggesting the problem, for his fruitful guidance, assistance and encouragement throughout my research project and for his assistance in personal matters.

Thanks to each of my committee members, Dr. Larry E. Halliburton, Dr. Martina Bachlechner, Dr. Sergei Urazhdin, and Dr. Lloyd Carroll for spending time out of their insanely busy schedules to fit me in so I could finish.

I wish to thank Dr. A. Manivannan for his generous help in the X-ray diffraction, TEM, and SQUID measurements. I also wish to thank Dr. Nancy Giles, Dr. Thomas H. Myers, Dr. David Lederman and Dr. Art Weldon for their wonderful lectures and generosity with their time. I thank Dr. J. Bonevich for carrying out the TEM studies reported in this work. My gratitude and sincere thanks to Dr. Jagadeesh S. Moodera, Dr. Wooyoung Lee, Dr. Jung -Bum Choi, and Dr. Yang-Ki Hong, for their fruitful advice.

My sincere thanks goes to Prof. Seehra's post-doctoral associates Dr. Prasant Dutta (2003-present) and Dr. Alex Punnoose (2002) for their professional help and friendship and Dr. Halliburton's post-doctoral associate, Dr. Nelson for his professional help in computer programming. I wish to thank the people in my lab, Aashish, Vivek, Sukanaya, Susmita, and Jeremy. My special thanks to Siobhan, Sherry, and Sandy for their friendship and timely help during various occasions. Technical assistance provided by Phil and Tom is greatly acknowledged. I wish to thank my colleagues, Chunchuan, Jorge, Zhang, and everyone else I have forgotten to mention. I express my sincere thanks to my friends, Sungho, Dr. Yang and his family, Pastor Kim and his family. I also wish to acknowledge, my aunt and her family in Chicago, my relatives, uncles, aunts and their family, grand mother and grand father in Korea.

Finally, I have a deep sense of gratitude towards my mother for her constant support and understanding. I would like to thank my brothers, Youngyoon and Youngjun for their invaluable understanding and encouragement.

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CHAPTER I

INTRODUCTION

1.1 Magnetic properties of Bulk NiO

The magnetic properties of bulk NiO have been studied for several years and are reasonably well understood. NiO is crystallized in the NaCl structure and below its Néel temperature $T_N \approx 523$ K, Ni^{2+} ions in the ferromagnetic (111) planes are stacked antiferromagnetically along the $\langle 111 \rangle$ direction [Shull et al, 2000, Barbier et al, 2004 and Milano et al, 2004]. The antiferromagnetic (AF) order in NiO originates from the superexchange coupling of Ni atoms in alternating (111) planes through oxygen 2p electronic orbitals. NiO is the 3d transition metal (TM) mono-oxide. The orbital moment of the 3d TM ion is usually quenched in solids because atomic 3d orbitals are greatly deformed in solids by crystal field. However, the spin-orbit interaction in 3d TM mono-oxides can restore some of the orbital moment of localized 3d electrons by reducing crystal field effect. Thus, the experimental magnetic moment / Ni atom = $2.2 \pm 0.2 \mu_B$ is observed with the unquenched orbital moment contribution about 17 % [Neubeck et al, 1999 and Kwon et al, 2000]. The magnitudes of the nearest-neighbor and next-nearest neighbor exchange constants J_1 and J_2 are calculated as 34 K and 202 K respectively using the random-phase-approximation Green's-function theory [Srinivason et al, 1984, Seehra et al, 1988]. The above values are close to the experimental results, from the fit to the experimental spin-wave dispersion curves [Hutchings et al, 1972] and from the Raman scattering data [Dietz et al, 1971].

1.2 Magnetic properties of NiO Nanoparticles

In contrast to bulk NiO, the magnetic properties of NiO in reduced dimensions such as in the nanoparticle (NP) from for sizes $D < 30$ nm are not well understood. Since the magnetic nanoparticles have disordered arrangement, particle size distribution,

random orientation of magnetization, these make their behavior more complex and difficult to understand. Early work [Richardson et al, 1956] investigated the magnetic properties of colloidal NiO for particle size $D < 200$ nm and particularly, observed peaks in susceptibility measurements for $T < T_N$ for crystal sizes 10 to 20 nm. This led Néel to propose the model of superparamagnetism [Néel, 1961] in which large residual moments can occur in AF-NP due to the uncompensated spins especially, on the surface. For the size-range $D \geq 5$ nm, the magnetic properties of NiO-NP have been studied [Makhlouf et al, 1997]. Although their magnetization curves above the blocking temperatures could not be fit into one single curve with a Langevin function, they showed that at $T = 293$ K, the magnetic moment per particle $\mu_p \approx 2000 \mu_B$ determined from the Langevin fit is larger by an order of magnitude than the expected value from the two-sublattice model which is applied to bulk NiO. In follow up studies [Kodama et al, 1997 and 1999], numerical modeling of spin configurations yielded 8-, 6-, or 4-sublattice configuration to explain the finite size effects and the observed high coercivities and loop shifts. However they did not address the variation of μ_p with particle size in their experimental and modeling studies. Also neutron diffraction studies to verify the proposed departures from the two sublattice magnetic ordering have not yet been reported. Recently, Rubinstein et al [2001] have reported on the temperature dependence of the electron magnetic resonance (EMR) spectra of 6 nm NiO particles. Similar to the observations reported in ferrihydrite NP [Seehra et al. 2001], the resonance line was observed to shift to lower fields with decrease in temperature. However, the observed line shapes were very complex and distorted so that the line-width ΔH and the resonance field H_r could not be measured accurately and hence their temperature variations could not be compared with the predictions for nanoparticle system [Nagata et al. 1992].

1.3 Motivation for the present work

Currently, nature of materials in reduced dimensions (thin films, wires, nanoparticles (NP)) has become a very interesting area of study due to their unique magnetic properties as well as their numerous technological applications [Dormann et al. 1992, Kluwer et al. 1994, Speliotis, 1999, and Kodama et al. 1999]. Especially, interest in

spin ordering at antiferromagnetic (AF) interfaces with ferromagnetic (F) layers [Mocuta et al. 2003, and Ohldag et al. 2001], has strongly increased since the exchange bias at a F/AF interface can be applied to lots of fields which rely on exchange bias and spin electronics. Exchange bias at a F/AF interface provides an unidirectional magnetic anisotropy resulting a hysteresis loop shift. This property is a key feature in modern magnetic field spin-valve devices. AF NiO can be a good candidate as T_N of NiO is above room temperature. It is of special interest in spin-valve devices which require an AF/F (ferromagnet) interface to produce exchange bias at room temperature [Berkowitz et al. 1999 and references therein]. Thus, it is worthy to study the magnetic properties of NiO NP.

This thesis is divided into seven chapters and the contents are as follows. In the second chapter, I discuss magnetic properties of bulk NiO with the Molecular Field theory which is the simplest effective field approximation [Smart, 1966]. Using this theory, I show the three types of antiferromagnetic orderings and ferromagnetic ordering in the face-centered cubic lattice. Curie-Weiss temperature θ and Néel temperature T_N are calculated in terms of exchange constants J_1 (J_2) for the nearest neighbor (for the next nearest neighbor) and compared with experimental results. In the third chapter, the synthesis procedures of NiO NP are specifically introduced. To reduce interparticle interaction, oleic acid (OA) coating is employed. The morphology and structure of the obtained various sized particles are studied through the x-ray diffraction (XRD) and transmission electron microscopy (TEM). Comparison of the sizes determined from the broadening of the x-ray diffraction (XRD) lines and TEM studies shows that TEM studies of NP are important for understanding their structural/magnetic properties. In the fourth chapter, the general properties of superparamagnetism are explained for ferromagnetic and antiferromagnetic systems. In the fifth chapter, one of the important issued in NP magnetism, the effect of interparticle interaction, is focused on to explain the various measured properties with our OA coated and uncoated NiO NP, especially, for the smallest particle with nominal size 5 nm. The coated particles are expected to have much weaker interparticle dipolar interaction vs. the uncoated particles. In the sixth chapter, I focus on the changes in the magnetic properties and morphology of the NiO-NP with increase in the nominal size D from 5 nm to about 20 nm. To investigate the

effect of interparticle interaction, I also provide a comparison between the magnetic properties of the OA coated vs. the uncoated particles. And in the seventh chapter, a summary of the major results of this work is given.

CHAPTER II

Molecular Field Theory of Magnetic Ordering

2.1 Introduction

A magnetic ion in a crystal experiences exchange interactions with other magnetic ions. In molecular field theory, these interactions are replaced by an effective field or a molecular field. This discussion of the molecular field theory is based on the information given in the book [Smart, 1996]. Let the two-sublattices consist of “a” and “b” atoms which are ordered antiferromagnetically and the Heisenberg exchange Hamiltonian is given by

$$H_{\text{ex}} = -2 \sum_{a \neq b} J_{ab} S_a \cdot S_b \quad (2.1)$$

where J_{ab} is the exchange constant and S_a and S_b are the spins on atoms a and b.

The total fields acting on “a” and “b” atoms are

$$H_a = H_0 + H_{\text{eff}} = H_0 + \gamma M_b \quad (2.2)$$

$$H_b = H_0 + H_{\text{eff}} = H_0 + \gamma M_a \quad (2.3)$$

where γ is the molecular field coefficient and H_0 is applied field. Let J_{ab} be non-zero only for the nearest-neighbors which number z .

Then

$$\langle H_{\text{ex}} \rangle = -2 J_{ab} \langle S_a \rangle \cdot \sum \langle S_b \rangle \quad (2.4)$$

The expectation values of H_{ex} can be written as

$$\langle H_{\text{ex}} \rangle = -g \mu_B H_{\text{eff}} \cdot \langle S_a \rangle \quad (2.5)$$

By substituting Eq. (2.4) into (2.5), we have

$$H_{\text{eff}} = 2z J_{ab} \langle S_b \rangle / g \mu_B = \gamma M = \gamma g \mu_B N_a \langle S_b \rangle \quad (2.6)$$

where N_a is the number of atom in “a” sublattice, μ_B is the Bohr magneton and g is the Landé g-factor.

So, we have

$$\gamma = 2 J_{ab} z / N_a g^2 \mu_B^2. \quad (2.7)$$

Eq. (2.7) shows that γ is proportional to the exchange constant J_{ab} . The transition metal oxides, MnO, NiO, CoO, and FeO crystallize in the NaCl (FCC) structure. Since there are four (4) magnetic ions (e.g. Ni^{2+}) per unit cell, the two sublattice model is inadequate. In comparison, the SC lattice has only one atom/cell and BCC lattice has two atoms per unit cell. When a material orders antiferromagnetically (AF) below its Néel temperature, T_N , the size of the magnetic unit cell becomes double that of the chemical unit cell because of AF ordering. Therefore, the magnetic unit cell of the corresponding SC, BCC, and FCC chemical unit cells have two, four, and eight magnetic ions respectively. Thus, in describing ordering in SC, BCC, and FCC cells, we need to consider 2, 4, and 8 sublattices respectively. For discussing ordering in NiO, the Ni^{2+} ions are divided into eight sublattices as shown in Fig.2.1.

2.2. The secular equation

We begin with the general equation of the exchange Heisenberg Hamiltonian

$$H = -2 \sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (2.8)$$

where J_{ij} is the exchange interaction between an i atom and one of its j neighbors.

The total field acting on one atom of the i^{th} sublattice is

$$H_i = H_0 + \sum_{\substack{j=1 \\ i \neq j}}^n \gamma_{ij} M_j \quad (2.9)$$

where γ_{ij} is the molecular field coefficient, M_j is the magnetization of the j^{th} sublattice and n is the number of sublattices.

Following the Eq. (2.7), we have

$$\gamma_{ij} = 0 \quad \text{for } i = j \quad (2.10)$$

$$\gamma_{ij} = n (2 J_{ij} z_{ij}) / N g^2 \mu_B^2 \quad \text{for } i \neq j \quad (2.11)$$

where z_{ij} is the number of j neighbors of an i atom and N is the total number of atoms.

Eq. (2.10) and Eq. (2.11) state that atoms interact with atoms on the other sublattices only. For NiO, a given atom has 12 nearest neighbors at a distance of $a/\sqrt{2}$ on six different lattices and six next-nearest neighbors on the cubic edges at a distance of a .

Fig. 2.1 The face-centered cubic lattice divided into eight sublattices.

Thus, from the Fig.2.1, let $\gamma_{12} = \gamma_{13} = \gamma_{14} = \gamma_{16} = \gamma_{17} = \gamma_{18}$ be γ_1 for the nearest neighbors (nm) and γ_{15} be γ_2 for the next-nearest neighbors (nnm). For each H,

$$\begin{aligned}
 H_1 &= H_0 + 8/6 \gamma_1 M_2 + \dots + 8 \gamma_2 M_5 + \dots + 8/6 \gamma_1 M_8 \\
 H_2 &= H_0 + 8/6 \gamma_1 M_1 + \dots + 8 \gamma_2 M_6 + \dots + 8/6 \gamma_1 M_8 \\
 &\dots\dots\dots \\
 H_8 &= H_0 + 8/6 \gamma_1 M_1 + \dots + 8 \gamma_2 M_4 + \dots + 8/6 \gamma_1 M_7
 \end{aligned} \tag{2.12}$$

The relation of M and H is represented by the Curie law,

$$\begin{aligned}
 M_i &= C / nT H_i \\
 &= C / nT (H_0 + \sum \gamma_{ij} M_j)
 \end{aligned} \tag{2.13}$$

where the Curie constant, $C = N/8 g^2 \mu_B^2 S(S+1)/3k_B$.

So, $H_1, H_2, \dots$, and H_8 in Eq. (2.12) can be replaced by $8T/C M_1, 8T/C M_2, \dots$, and $8T/C M_8$. We can rewrite Eq. (2.12) as

$$\begin{aligned}
 8T/C M_1 - 8/6 \gamma_1 M_2 - \dots - 8 \gamma_2 M_5 - \dots - 8/6 \gamma_1 M_8 &= H_0 \\
 - 8/6 \gamma_1 M_1 + 8T/C M_2 - \dots - 8 \gamma_2 M_6 - \dots - 8/6 \gamma_1 M_8 &= H_0 \\
 &\dots\dots\dots \\
 - 8/6 \gamma_1 M_1 - 8/6 \gamma_1 M_2 - \dots - 8 \gamma_2 M_4 - \dots + 8T/C M_8 &= H_0
 \end{aligned} \tag{2.14}$$

Eq. (2.14) can be represented by the matrix with the applied field $H_0 = 0$ and the determinant of the secular equation is (with $a_0 = 8T/C$, $a_1 = -4/3 \gamma_1$, $a_2 = -8\gamma_2$),

$$\begin{vmatrix}
 a_0 & a_1 & \dots & a_2 & \dots & a_1 \\
 a_1 & a_0 & \dots & a_2 & \dots & a_1 \\
 \vdots & \vdots & \dots & \vdots & \dots & \vdots \\
 a_2 & a_1 & \dots & a_0 & \dots & a_1 \\
 \vdots & \vdots & \dots & \vdots & \dots & \vdots \\
 a_1 & a_1 & \dots & a_2 & \dots & a_0
 \end{vmatrix} = 0 \tag{2.15}$$

The eight solutions of Eq. (2.15) yield the transition temperatures. To solve this Eq. (2.15), the standard procedure of subtracting rows and columns is employed (without affecting the solutions), leading to only three independent solutions due to degeneracy. The first factor leads to quadruple degeneracy, $(a_0 - a_2)^4 = 0$ or $a_0 = a_2$.

These yield

$$T_{N2} = -C \gamma_2 \quad (2.16)$$

In the remaining determinant, add row 1 to row 5. This changes the determinant 8×8 to 7×7 . Repeat this step until the determinant becomes 4×4 . Thus we finally get a 3×3 matrix,

$$-A \begin{vmatrix} -A & -A & A + 4a_1 \\ A & 0 & 2a_1 \\ 0 & A & 2a_1 \end{vmatrix} = 0 \quad (2.17)$$

where $A \equiv (a_2 + a_0 - 2a_1)$

So, we have the results of Eq. (2.17) as

$$A^3 = 0, \quad \text{triple roots} \quad (2.18)$$

$$\text{And } A = -8a_1, \quad \text{single root} \quad (2.19)$$

From Eq. (2.18) and Eq. (2.19) respectively

$$T_N = C (-1/3 \gamma_1 + \gamma_2) \quad (2.20)$$

$$T_N = C (\gamma_1 + \gamma_2) \quad (2.21)$$

The eigen vectors for each transition temperature can be obtained by substituting each solution of the matrix into original matrix. For the first case of $a_0 = a_2$, the result is

$$a_0 (M_1 + M_5) + a_1 (M_2 + M_3 + \dots + M_8) = 0 \quad (2.22)$$

This means

$$M_1 = -M_5$$

Similarly

$$M_2 = -M_6, M_3 = -M_7, M_4 = -M_8 \quad (2.23)$$

For the solution, $a_2 + a_0 - 2a_1 = 0$,

$$\begin{aligned} & a_0 (M_1 + M_2 + M_3 + M_4) - a_1 (M_5 + M_6 + M_7 + M_8) \\ & + a_1 \{3(M_1 + M_2 + M_3 + M_4) + 5(M_5 + M_6 + M_7 + M_8)\} = 0 \end{aligned}$$

The eigen vectors of this equation are

$$\begin{aligned} & M_1 = M_5, M_2 = M_6, M_3 = M_7, M_4 = M_8 \\ & \text{and } M_1 + M_2 + M_3 + M_4 = M_5 + M_6 + M_7 + M_8 = 0 \end{aligned} \quad (2.24)$$

And for the last case, $a_2 + a_0 + 6a_1 = 0$,

$$a_0 (M_1 - M_5) + a_1 (M_2 + M_3 + M_4 - 6M_5 + M_6 + M_7 + M_8) = 0$$

So,

$$M_1 = M_2 = M_3 = M_4 = M_5 = M_6 = M_7 = M_8 \quad (2.25)$$

In summary, the solutions are

First case, $T_{N2} = -C \gamma_2$, where $J_2 < 0$

$$M_1 = -M_5, M_2 = -M_6, M_3 = -M_7, \text{ and } M_4 = -M_8 \quad (2.26)$$

This is what is observed in NiO and represents the AF ordering of type II.

Second case, $T_{N1} = C (-1/3 \gamma_1 + \gamma_2)$, where $J_1 < 0$ and $J_2 > 0$

$$\begin{aligned} & M_1 = M_5, M_2 = M_6, M_3 = M_7, M_4 = M_8 \\ & \text{and } M_1 + M_2 + M_3 + M_4 = M_5 + M_6 + M_7 + M_8 = 0 \end{aligned} \quad (2.27)$$

This one shows the AF ordering for type I

And the last case, $T_C = C (\gamma_1 + \gamma_2)$, where $J_1 > 0$ and $J_2 > 0$

$$M_1 = M_2 = M_3 = M_4 = M_5 = M_6 = M_7 = M_8 \quad (2.28)$$

This case is the ferromagnetic state.

2.3. Three types of ordering and equations for T_N and θ

Eq. (2.27) describes the antiferromagnetic ordering of magnetic atoms. Atoms are ordered ferromagnetically in $x - y$ plane and the direction of spins is changed alternately as shown in Fig. 2.2 (a) choosing $M_1 = M_2 = -M_3 = -M_4$. This arrangement can also occur in $y - z$ plane and $x - z$ plane. The number of nearest neighbor pairs ordered antiferromagnetically is the largest among the other orderings. So this is called the antiferromagnetic ordering of type I. The feature of ordering in Eq. (2.26) also represents antiferromagnetic ordering. The atoms within planes perpendicular to a particular cube diagonal are ordered ferromagnetically and the directions of these atoms are antiparallel with adjacent planes as shown in Fig.2.2 (b). This is called antiferromagnetic ordering of type II. There is another type of antiferromagnetic ordering called antiferromagnetic ordering type III. This ordering is similar to type I with the only difference being the change in the direction of one spin at the cube edge followed by the same sublattice. This is shown in Fig. 2.2 (c). And in the last case shown in Eq. (2.28), $M_1, M_2, \dots$, and M_8 , all have same magnitude and direction, leading to the ferromagnetic state.

The Curie-Weiss temperature θ and the Néel temperature T_N for the NiO system can be represented in terms of exchange constants J_1 and J_2 . Eq. (2.14) can be written as

$$\begin{aligned} M_1 &= C/8T \{H_0 + 4/3 \gamma_1 (M_2 + \dots + M_8) + 8 \gamma_2 M_5\} \\ M_2 &= C/8T \{H_0 + 4/3 \gamma_1 (M_1 + \dots + M_8) + 8 \gamma_2 M_6\} \\ &\dots\dots\dots \\ M_8 &= C/8T \{H_0 + 4/3 \gamma_1 (M_1 + \dots + M_7) + 8 \gamma_2 M_4\} \end{aligned} \quad (2.29)$$

In the paramagnetic region,

$$\begin{aligned} M &= \sum M_i \\ &= C/8T \{8H_0 + 4/3 \gamma_1 6 (M_1 + \dots + M_8) + 8 \gamma_2 (M_1 + \dots + M_8)\} \\ &= C/T \{H_0 + (\gamma_1 + \gamma_2) M\} \end{aligned} \quad (2.30)$$

$$M = C/T H_0 / \{1 - C/T (\gamma_1 + \gamma_2)\} \quad (2.31)$$

And

$$\chi = \partial M / \partial H_0 = C / \{T - C(\gamma_1 + \gamma_2)\} = C / \{T + |\theta|\} \quad (2.32)$$

where the paramagnetic transition temperature, $\theta = -C(\gamma_1 + \gamma_2)$.

Fig. 2.2 Antiferromagnetic types in FCC lattice.

This FCC system has 12 nearest neighbors and 6 next nearest neighbors. From Eq. (2.11),

$$\begin{aligned} \gamma_1 &= (2 \times 12) J_1 / (N/8 g^2 \mu_B^2), \\ \text{and} \quad \gamma_2 &= (2 \times 6) J_2 / (N/8 g^2 \mu_B^2) \end{aligned} \quad (2.33)$$

Thus, the transition temperature θ has the form,

$$\theta = 2S(S+1)(12 J_1 + 6J_2) / 3k_B \quad (2.34)$$

Similarly, the transition temperatures for each ordering type, determined for $H_0 = 0$, are also given by J_1 and J_2 .

$$\begin{aligned} \text{In Eq. (2.28),} \quad T_C &= C (\gamma_1 + \gamma_2) \\ &= 2S(S+1)(12 J_1 + 6J_2) / 3k_B \end{aligned} \quad (2.35)$$

$$\begin{aligned} \text{In Eq. (2.27),} \quad T_{N1} &= C (-1/3 \gamma_1 + \gamma_2) \\ &= 2S(S+1)(-4 J_1 + 6J_2) / 3k_B \end{aligned} \quad (2.36)$$

$$\begin{aligned} \text{And in Eq. (2.26),} \quad T_{N2} &= - C \gamma_2 \\ &= - 2S(S+1)(6J_2) / 3k_B \end{aligned} \quad (2.37)$$

For the antiferromagnetic ordering of type III, P.W. Anderson [1950] proposed the magnetic structure given by the transition temperature T_{N3} .

$$\begin{aligned} T_{N3} &= C/3 (-\gamma_1 + \gamma_2) \\ &= 2S(S+1)(-4 J_1 + 2J_2) / 3k_B \end{aligned} \quad (2.38)$$

The results for the transition temperatures show that, in ferromagnetic ordering, the real transition temperature, T_C , and the paramagnetic transition temperature, θ , are the same in Eq. (2.34) and Eq. (2.35). But the transition temperatures, T_N , for the antiferromagnetic ordering are different depending on the magnetic ordering.

2.4. The J_1 - J_2 diagram for FCC systems

In a paper in 1988, Seehra and Giebultowitz investigated the relationship between the magnetic structures of FCC systems and the exchange constants J_1 and J_2 . Using the values of J_1 and J_2 which are known accurately from experiments, they drew the phase diagram shown in Fig. 2.3. The exchange constants J_1 and J_2 are dominant in systems where magnetic ions occupy the FCC lattice sites and there exists four types of orders in magnetic structure for the values of J_1 and J_2 except where $J_1 > 0$ and $J_2 = 0$. The three antiferromagnetic orderings and ferromagnetic ordering are possible as calculated in previous section.

In Fig. 2.3, phase boundaries are shown determined by making the differences in the transition temperatures in Eq. (2.35), Eq. (2.36), Eq. (2.37), and Eq. (2.38) to equal zero. For Eq. (2.35) and Eq. (2.36), the difference is

$$T_C - T_{N1} = 2S(S+1)(16J_1) / 3k_B \quad (2.39)$$

Thus, the boundary of these regions, $J_1 = 0$ is obtained by allowing Eq. (2.39) to equal zero.

Similarly, for Eq. (2.35) and Eq. (2.37), $J_1 = -J_2$
for Eq. (2.37) and Eq. (2.38), $J_1 = 2J_2$
for Eq. (2.36) and Eq. (2.38), $J_2 = 0$

That is,

$$\begin{array}{ll} J_1 = 0 & \text{between AFI and F} \\ J_1 = -J_2 & \text{between F and AFII} \\ J_1 = 2J_2 & \text{between AFII and AFIII} \\ J_2 = 0 & \text{between AFIII and AFI} \end{array} \quad (2.40)$$

These authors suggested that the closer a magnetic structure gets to the boundary, the more unstable it becomes. For instance, EuSe is located close to the boundary and experimentally shows that magnetic ordering is changed from AFII to F even in small difference of temperature. And the materials in AFII are quite stable since they all are further away from the boundaries. Thus, if J_1 and J_2 are known accurately among the FCC systems, transition can be predicted.

Fig.2.3 Phase diagram of FCC systems with J_1 and J_2 [Seehra et al, 1988].

2.5 J_1 and J_2 for the FCC system

In section 2.3, equations for T_N and θ are derived using the molecular field theory. Many experiments show the values of T_N and θ for particular materials [Smart, 1996] and J_1 and J_2 can be calculated by substituting these values into the equations for T_N and θ . Table 2.1 shows the calculated values of J_1 and J_2 for the FCC systems.

For NiO with $S = 1$, Eq. (2.34) and Eq. (2.37) are

$$\begin{aligned}\theta &= 2S(S + 1)(12 J_1 + 6J_2) / 3k_B = -1310 \text{ K} \\ T_{N2} &= - 2S(S + 1)(6J_2) / 3k_B = 523 \text{ K}\end{aligned}\tag{2.41}$$

Thus, we obtain $J_1 / k_B = - 81.9$ and $J_2 / k_B = - 65.4$ for NiO from Eq. (2.41). J_1 and J_2 for the other compounds are calculated in a similar way for each magnetic ordering type.

The above calculated values of J_1 and J_2 for NiO are quite different from the experimental values obtained in neutron scattering experiments. Experimental value estimates that J_1 is approximately zero and J_2 has a value much bigger than J_1 . It shows that the molecular field theory does not always agree with the actual exchange values since this theory neglects higher order interactions. In the paper [Srinivasan et al, 1983], the authors solved this difficulty using Green's function analysis which is discussed in the next section.

Compound	Type of ordering	T_N (°K)	θ (°K)	$-J_1 / k_B$	$-J_2 / k_B$
MnO	AFII	116	- 610	7.1	3.3
FeO	AFII	198	- 570	7.8	8.3
CoO	AFII	292	- 330	1.3	19.5
NiO	AFII	523	-1310	81.9	65.4
α - MnS	AFII	154	- 465	4.4	4.4
MnS ₂	AFIII	60	- 592	5.5	5.9
MnTe ₂	AFI	100	- 528	6.7	1.6

Table. 2.1. The summary of the values of J_1 and J_2 calculated by the Molecular Field theory for AF materials.

2.6 Results of the Green's Function Theory for J_1 and J_2

There is another method to evaluate J_1 and J_2 , the nearest neighbor and next-nearest neighbor exchange constants, in the molecular field theory. In the previous section, J_1 and J_2 are determined from the transition temperature T_N and paramagnetic transition temperature θ . However, for some materials, it is difficult to measure exact θ experimentally. Thus, susceptibility χ is used instead of θ . In Eq. (2.32), susceptibility χ is $\chi(T) = C / \{T - C(\gamma_1 + \gamma_2)\}$, where $C = (N/8)g^2 \mu_B^2 S(S+1)/3k_B$. For the case of antiferromagnetic type II, the transition temperature T_N is

$$T_N = -4S(S+1)(J_2) / k_B. \quad (2.42)$$

And at this transition T_N , susceptibility χ is

$$\chi(T_N) = -N g^2 \mu_B^2 / 16 \{12(J_1 + J_2)\}. \quad (2.43)$$

In the paper [Srinivasan et al, 1984], the authors calculate the values of J_1 and J_2 for NiO, with the values of $\chi(T_N) = 8.8 \times 10^{-6} \text{ cm}^3/\text{g}$, $S=1$, $g = 2.23$ and $T_N = 524\text{K}$. From the Eq. (2.42) and Eq. (2.43), they came up with

$$J_1 / k_B = -51.5\text{K} \text{ and } J_2 / k_B = -65.5\text{K} \quad (2.44)$$

It is well known that the molecular field theory is not always a good approximation. Thus, the authors attempt to estimate J_1 and J_2 using the random-phase-approximation Green's function theory. Bartel and Morosin [1971] calculated the relation of $k_B T_N / J_2$ versus J_1 / J_2 for $S = 1$. This figure is shown in Fig. 2.4 which used two times larger values of J_1 and J_2 as the authors start from Hamiltonian $H = - \sum J_{ij} S_i \cdot S_j$ to obtain J_1 and J_2 . First they assume $J_1 = 0$ which leads $k_B T_N / J_2 = 2.67$ and J_2 / k_B is calculated to -196 K yielding to half reduced $J_2 / k_B = -98 \text{ K}$ in our notation. From Eq. (2.43), $(J_1 + J_2) = -117 \text{ K}$ for $\chi(T_N) = 8.8 \times 10^{-6} \text{ cm}^3/\text{g}$ and $J_2 / k_B = -98 \text{ K}$ yield $J_1 / k_B = -19 \text{ K}$. This in turn represents the ratio, $J_1 / J_2 = 0.19$, yielding $k_B T_N / J_2 = 2.626$. Thus, again $J_2 / k_B = -99.6\text{K}$ and $J_1 / k_B = -17.4\text{K}$ are obtained. If this step is repeated, J_1 and J_2 converge to constant values for J_1 and J_2 . The last values are $J_1 / k_B = -17 \text{ K}$ and $J_2 / k_B = -101 \text{ K}$. Here, J_1 and J_2 , according to Green's function theory are different from the results according to the molecular field theory. However, Green's function approximation agrees well with the experimental

values from the spin-wave dispersion curve, and Raman scattering. Fig. 2.4 shows the relations of $k_B T_N / J_2$ vs. J_1 / J_2 which calculated by Green's function theory for FCC antiferromagnetic ordering of type II and $S = 1$ case [Bartel et al, 1971]. This calculation is only valid for FCC antiferromagnetic ordering type II and $S = 1$ case such as NiO. Although Green's function is complicated for the $S \neq 1$ case, many people have already solved J_1 and J_2 for the other compounds using Green's function approximation. The results are shown in Table 2.2.

	By Molecular field theory		By Green's function theory	
Compounds	$-J_1 / k_B$	$-J_2 / k_B$	$-J_1 / k_B$	$-J_2 / k_B$
MnO	7.1	3.3	5	5.5
FeO	7.8	8.3	-0.9	8.0
CoO	1.3	19.5	2.8	13.7
NiO	81.9	65.4	17.0	101.0
α – MnS	5.5	5.9	3.5	6.4

Table 2.2 shows the difference between J_1 and J_2 , determined by the molecular field theory and Green's function theory.

Fig. 2.4 shows the relation between $k_B T_N / J_2$ and J_1 / J_2 calculated by Green's function theory for the FCC antiferromagnetic ordering of type II and the $S = 1$ case [Bartel et al, 1971].

2.7 Measurement of J_1 and J_2 for NiO by other methods

There are several ways to measure J_1 and J_2 experimentally such as measurement of spin – wave dispersion by Inelastic Neutron Scattering techniques [Hutchings et al, 1972] and Raman scattering data [Dietz et al, 1971].

Experiment	- J_1 / k_B	- J_2 / k_B
Neutron work	-8.0	111
Raman Scattering	small	107
Molecular field theory (from θ and T_N)	82	65
Molecular field theory (from T_N and χ)	52	66
Green`s function theory	17	101

Table 2.3 shows the difference of J_1 and J_2 determined by several methods to compare with the molecular field theory.

CHAPTER III

Synthesis and Structural Properties

3.1 Synthesis

The NiO nanoparticles were synthesized chemically through the sol-gel technique [Pierre et al. 1998], which is used to produce metal oxides. The synthesis procedure consisted of four steps: the reaction of the precursor to form sol, gelation, drying, and annealing. The first step is to make a nickel hydroxide Ni(OH)_2 precursor called a sol. To get this, a completely dissolved nickel nitrate $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution and an aqueous sodium hydroxide NaOH are mixed, making $\text{pH} = 12$. The reaction is

The reason for the $\text{pH} = 12$ is that for this pH only, the XRD (x-ray diffraction) pattern of the product has no impurities, except the pattern of powder Ni(OH)_2 . This means that when the $\text{pH} = 12$, the two chemicals have completely reacted. The Ni(OH)_2 precursor was centrifuged to remove any liquid. During this activity, the sample was washed many times with distilled water to remove any impurities. It is called gelation. The gel was left at room temperature overnight to dry the gel. It yielded powder form of Ni(OH)_2 by grinding the dried gel. Ni(OH)_2 was determined to decompose to NiO at 200°C using thermogravimetric measurements according to the equation,

To obtain NiO particles with different sizes, the obtained powder samples are annealed at various temperatures. Using X-ray diffraction (in section 3.3), it was found that particles with the sizes of 5, 7, 8, 12, 16, 20, and 41 nm were obtained by annealing at the temperatures of 523, 573, 623, 673, 723, 773, and 873 K respectively. Here, each sample will be known by its nominal size, determined by XRD.

NiO nanoparticles have been studied by several groups [Jacobs et al, 1963, Richardson et al, 1991 and references therein]. Although NiO nanoparticles are strongly aggregated, these authors did not consider the effect of interparticle interactions which affect magnetic properties. Bødker et al [Bødker et al, 2000] proposed methods to reduce the interparticle interactions by particle coating. We employed this coating method to

verify the effect of interparticle interactions. Each size of NiO powder was milled using a ball mill with a tungsten carbide vial and four 7/16 inch tungsten carbide balls made by Spex. These particles, when ground into a fine powder, were dispersed in 0.01M HNO₃, given ultrasonic treatment, and centrifuged to get dispersed particles. To fix this dispersion, a small amount of Oleic Acid was added. The samples were air dried overnight. These coated samples were investigated in many experiments such as XRD, TEM, and SQUID for magnetic analysis and their properties compared with those of uncoated samples.

3.2. Transmission Electron Microscopy (TEM)

We investigated the particle size distribution and morphology through the use of Transmission Electron Microscopy (TEM) for various sized particles of both uncoated and coated NiO nanoparticles. The particles here are labeled according to the average size determined by XRD. TEM studies reported here were kindly done by Dr. John Bonevich (National Institute of Standards and Technology, Gaithersburg, MD) on samples prepared by us for the TEM studies.

A TEM is capable of providing crystallographic information and also produce images of nanoparticle surfaces. In a TEM, the electrons from a source enter the sample and are scattered as they pass through it. These particles are then focused by an objective lens and are amplified by a magnifying lens, finally producing the desired image [Poole et al. 1990]. The results from the TEM micrographs are really important and interesting since for $D < 10$ nm, the particles are primarily in the form of nanorods. However for $D > 10$ nm, the particle shapes become more rounded. In none of the earlier studies of NiO nanoparticles prepared by the sol-gel methods, such features have been reported [Bødker et al. 2000, and Tiwari et al. 2005].

Fig. 3.1 shows the results of TEM measurements for the particle size, $D = 5$ nm of both the uncoated (a) and coated (b) cases. In Fig. 3.1 (a), the overall shape of the particles looks like entangled hair and the rods are very strongly aggregated. Thus, efforts were made to figure out the diameter of all rods. The coated nanorods of particle size 5 nm tend to be less entangled and more straight and so were easier to measure. We picked

rods as many as we could to measure the diameter and the obtained average diameter was approximately 1.7 nm for both the uncoated and coated nanorods.

For the samples of nominal XRD sizes of 7 (7) nm and 8 (11) nm, there are mixed shapes of ellipses and rods in uncoated (coated) cases. The uncoated cases shown in Fig 3.2 (a), (b) and Fig. 3.3 (a), (b) were so hazy that the exact size could not be read, especially for the 7 nm cases since the rods lay one upon another. In Table 3.1, we have summarized the sizes of the particles as determined from TEM and XRD measurements. It is noted that the diameters of the nanorods for different particles are smaller than the sizes measured by the XRD. However, it turns out that volume of the nanorods nearly equals the volume of an equivalent sphere with diameter equal to the size of particles determined by XRD. For the ellipse, the obtained sizes were 7 and 9 nm, which were closer to the XRD results, similar to the coated 7 and 11 nm particles. The typical particle size distribution for the coated 7 nm particles is shown in Fig. 3.3 (e). Through the TEM pictures of the uncoated 8 nm and the coated 11 nm particles, we can see that fewer particles are in the form of nanorods compared to the 5 and 7 nm samples. Fig. 3.2 (c) represents the uncoated 12 nm particles showing the reduced quantity of the nanorods and rods that look like a pill with uniform sides. For the uncoated 16 nm particles and coated 17 nm particles, their TEM show that the spheres and ellipses are mixed, but there are no rods. It is shown in Fig. 3.2 (d) and Fig. 3.3 (c). For the uncoated 20 nm and 41 nm particles and the coated 20 nm sample, TEM pictures are shown in Fig. 3.2 (e), (f) and Fig. 3.3 (d) respectively. As the particle size becomes larger, the shape of the particles changes to a near sphere and, so it is much easier to measure the particle size, now that the particles are much more dispersed. Thus, we could determine the particle size distribution statistically. These bar graphs are shown in Fig 3.2 (g) and Fig. 3.3 (f) for the uncoated 20 nm and coated 27 nm samples.

It is evident that the shape of nanoparticle is transformed from a rod to a sphere by using a higher annealing temperature. For the particle size $D > 10$ nm, most of the rods have disappeared and are replaced by nearly spherical particles. The particle sizes are estimated from these spheres and ellipses which are very close to the size obtained by XRD.

(a) uncoated

(b) coated

Fig. 3.1 TEM pictures of particle size $D = 5$ nm for uncoated (a) and coated (b) cases.

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 3.2 Transmission electron microscopy (TEM) images of NiO 7, 8, 12, 16 20 and 41 nm samples represented in (a), (b), (c), (d), (e) and (f) respectively.

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 3.3 Transmission electron microscopy (TEM) images for coated 7, 8, 17, and 27 nm samples represented in (a), (b), (c) and (d) respectively.

3.3 X-ray Diffraction (XRD)

X-ray diffraction analysis was performed on all the samples using a Rigaku Diffractometer and monochromatic radiation $\text{CuK}\alpha$. This diffractometer was used to determine the unknown spacing of the crystal planes with the known wavelength ($\lambda = 1.5418 \text{ \AA}$) of X-rays using a powder sample. In our experiments on NiO, voltage applied to the target was 40 kV, filament current was set to 30 mA and the scan range of 2θ was 20° to 100° at the speed $0.06^\circ/5 \text{ sec}$. Small amounts of sample annealed at various temperatures were placed in the middle of glass sample holder and pressed gently by hand to make a smooth surface. Then, one to two drops of ethanol were added onto the spot which the sample was located and dried in air. The sample holder with the sample was placed vertically in the diffractometer. Fig. 3.4 shows the results for each sample. With these results, we matched the phase of each sample to the phase of the pure NiO using the software JADE and JCPDC data base. There were no significant impurities. Any line shift for different annealing temperatures is negligible and the Bragg lines of small particle are broadened due to the small crystalline size. These results are discussed next.

Fig. 3.4 shows XRD patterns for all particle size annealed at various temperatures for uncoated and coated samples.

3.4 Particle size broadening from XRD

XRD patterns contain significant information about the material: the Miller indices, the unit cell dimensions and especially the particle size and strain and so on. In the previous section, we identified the patterns by comparing with the standard NiO phase in JADE. The identified phase in JADE gives us basic information of indices and structure of materials directly. The NiO indices and structure observed from JADE were (111), (200), (311), (222), and (400) and a sodium chloride structure. Important information from XRD patterns is the determination of particle size and strain. For the powder sample, the analysis of XRD patterns were fit to the modified Scherrer equation,

$$\beta \cos \theta = 0.9\lambda/D + \eta \sin \theta \quad (3.3)$$

where D is the particle size, η is the strain and β is full-width at half maximum of a diffraction peak at the angle 2θ .

To understand the broadening due to particle size D , we follow the procedure outlined in Klug et al. [1974]. First the Bragg's law for X-ray diffraction is given by (Figs. 3.5 and 3.6):

$$2d \sin \theta_B = n\lambda. \quad (3.4)$$

According to Eq. (3.4), at $\theta = \theta_B$, the path difference between rays refracted from consecutive planes is λ whereas at all other angles, the phases of the scattered rays are such as to cancel out completely for an infinite crystal. This leads to a δ -function at $\theta = \theta_B$.

When a crystal is of finite size $t = md$ with $m+1$ plains (Fig. 3.6), then for some angles near θ_B complete cancellation of the beam only occurs at $2\theta_1$ and $2\theta_2$ slightly different from $2\theta_B$. We define the width B as

$$B = \frac{1}{2} (2\theta_1 - 2\theta_2) = \theta_1 - \theta_2 \quad (3.5)$$

where $(\theta_1 - \theta_2)$ is the angular spread which gives rise to the width. Then the equations for the angles θ_1 and θ_2 are

Fig. 3.5 indicates the diffracted beam for actual case (a) and ideal case (b).

Fig. 3.6 Diagram shows the effect of crystal size on diffraction. [Klug et al].

$$\begin{aligned} 2t \sin \theta_1 &= (m + 1) \lambda \\ 2t \sin \theta_2 &= (m - 1) \lambda \end{aligned} \quad (3.6)$$

By subtraction in Eq (3.6),

$$\begin{aligned} t (\sin \theta_1 - \sin \theta_2) &= \lambda \\ 2t \cos \{(\theta_1 + \theta_2)/2\} \sin \{(\theta_1 - \theta_2)/2\} &= \lambda \end{aligned} \quad (3.7)$$

As θ_1 and θ_2 are both very close to θ_B , approximately, $\theta_1 + \theta_2 = 2\theta_B$ and $\sin \{(\theta_1 - \theta_2)/2\} = \{(\theta_1 - \theta_2)/2\}$. Therefore,

$$\begin{aligned} 2t \{(\theta_1 - \theta_2)/2\} \cos \theta_B &= \lambda, \\ t &= \lambda / (B \cos \theta_B) \end{aligned} \quad (3.8)$$

A more accurate form is,

$$t = 0.89\lambda / (B \cos \theta_B) \quad (3.9)$$

Eq (3.9) is the Scherrer formula. Here t represents the particle size D . The accurate width B can be obtained by taking into account the instrument error due to separation of the $K\alpha$ doublet. At the low angle, the separation of α_1 and α_2 is negligible. But at high angle, it becomes more important. The corrected width β will be

$$\beta_{\text{corr}}^2 = B^2 - b^2 \quad (3.10)$$

where b is instrumental width and depends on angle θ .

When the Bragg peak of XRD is considered, we also should take into account the broadening due to strain. The effect of strain is two fold, line shift and broadening. If strain is uniform, the line is shifted from where it should be and if strain is non – uniform, there is a shape distortion resulting in the broadening of the line. The peak of metal oxide can be broadened due to stress or due to smaller particle size. Although it is not always possible to know whether the observed broadening is due to stress or to smaller particle size, through our XRD pattern and TEM studies, we found that the XRD peaks are broadened as the particle size is reduced and when we compare two TEM pictures of 5

nm coated and uncoated samples, the coated sample is more straight than twisted uncoated one. Thus, the uncoated particle has a more broadened peak due to non – uniform stress. This comparison is shown in Fig. 3.7. Therefore the width β should include strain factor. The total width β is

$$\beta_{\text{tot}} = \beta_{\text{corr}} = \beta_{\text{crystalline}} + \beta_{\text{strain}} \quad (3.11)$$

To calculate the broadening due to strain, let $2d = \lambda/\sin\theta$ and differentiate both sides to yield $2\Delta d = -d/\tan\theta (2\Delta\theta)$. Thus β_{strain} is

$$\beta_{\text{strain}} = 2\Delta\theta = -2(\Delta d/d)\tan\theta \approx \eta \tan\theta \quad (3.12)$$

where η is strain constant.

Thus the total breadth β_{tot} is

$$\begin{aligned} \beta_{\text{tot}} &= 0.9 \lambda / D \cos \theta + \eta \tan \theta \\ \beta_{\text{tot}} \cos \theta &= 0.9 \lambda / D + \eta \sin \theta \end{aligned} \quad (3.13)$$

Eq (3.13) is the modified Scherrer relation. From the graph $\beta_{\text{tot}} \cos \theta_B$ vs. $\sin \theta$ (Fig. 3.8), the intercept at $\sin \theta = 0$, yields $D = 0.89\lambda/(\beta_{\text{tot}} \cos \theta_B)$ and the slope of the lines yields η . Thus, for the uncoated samples, the resulting particle sizes are 4.8, 7.0, 8.5, 12.0, 16.0, 20.0, and 41.0 nm annealed at temperatures 523, 573, 623, 673, 723, 773 and 873 K respectively. Similarly for the coated particles, sizes 5.3, 7.0, 11.0, 17.0 and 27.0 nm are obtained for the annealing temperature 523, 573, 623, 673 and 773 K. These results are shown in Table 3.1.

From the plot of strain η vs. particle size D shown in Fig. 3.9, there are large error bars for particle sizes < 10 nm. Above 10 nm, the strain for both uncoated and coated particles does not show any particle size dependence. This corresponds to the pattern of transition of the shape of the particles from rods to spheres. Significant reduction of the strain for the coated particles for $D < 10$ nm, is observed as compared to the values of the uncoated particles. Note that sizes here are average sizes determined by XRD in terms of diameter of a sphere with equivalent volume.

Fig. 3.7 The comparison of the XRD patterns broadening for the coated and uncoated 5 nm particles.

Fig. 3.8 Plots of $\beta \cos \theta$ vs. $\sin \theta$ for different samples annealed at the various temperatures and the analysis for the uncoated and coated particles.

Fig. 3.9 Plot of the strain η versus particle size for the coated and uncoated particles.

In Table 3.1, we summarize the results of the particle sizes obtained from TEM and XRD analysis. For the smaller particles, the majority of the particles are in the form of nanorods, as shown in TEM pictures. For annealing temperature $T_a \geq 673$ K, nanorods change into particles with rounded morphology. This can be understood in terms of lowering of the surface energy with higher annealing temperatures. This also explains why the data in Fig.3.9 has high degree of scatter for smaller particles since the particles have a varied morphology and hence wider distribution of strain. From Table 3.1, it is evident that agreement between the sizes determined from XRD and TEM is generally good for the larger rounded particles. For the smaller particles with nanorod shapes, the calculated volume of the nanorods is quite close to the volume of a sphere of diameter D determined by XRD so that XRD measures average diameter of an equivalent sphere. Consequently, we have used the size D determined from XRD for labeling the figures.

Sample	TEM (Rod)		TEM (Sphere)	XRD (nm) (uncoated)
	Diameter (nm)	Length (nm)	Diameter (nm)	
NiO 523 K	1.7±0.5	25±8	5 ± 1	5 ±0.4
NiO 573 K	2.0±0.7	20±5	7 ± 2	7 ± 1.4
NiO 623 K	3.0±0.8	20±5	9 ± 2	8 ± 2.0
NiO 673 K	-	-	13 ± 3	12 ±1.1
NiO 723 K	-	-	16 ± 3	16 ±1.2
NiO 773 K	-	-	23 ± 5	20 ±1.5

Table 3.1 The summary of the particle size calculated from TEM analysis comparing the results derived by XRD measurements.

3.5 Structure Factor for NiO

The scattering of x-rays occurs due to the interaction of x-ray photons with electrons in solids. Therefore there are two factors affecting the scattering of x-ray beam: the atomic form factor f which depends on the density of electrons in the scatterer, and the geometrical structure factor S_K whose form is determined by the basis of the scatterer. The phase difference between the incident and scattered beam is represented by $\exp\{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}\} = \exp\{i\mathbf{K} \cdot \mathbf{r}\}$ where $\mathbf{K}$ is the reciprocal lattice vector and $\mathbf{r}$ is the position vector within the cell. In the case of a polyatomic crystal, the atomic form factor becomes f_j for each atom j of the cell. Thus the structure factor has the form,

$$S_K = \sum f_j \exp\{i\mathbf{K} \cdot \mathbf{r}_j\} = \sum f_j \exp\{2\pi i (hx_j + ky_j + lz_j)\} \quad (3.14)$$

For the NiO structure of sodium chloride, the basis consists of Ni^{2+} at (000) , $(\frac{1}{2} \frac{1}{2} 0)$, $(0 \frac{1}{2} \frac{1}{2})$, and $(\frac{1}{2} 0 \frac{1}{2})$ and O^{2-} at $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$, $(0 0 \frac{1}{2})$, $(\frac{1}{2} 0 0)$, and $(0 \frac{1}{2} 0)$. Let f_1 and f_2 be the atomic form factors of O^{2-} and Ni^{2+} ions respectively. Then Eq. (3.14) becomes,

$$\begin{aligned} S &= 4 (f_{\text{Ni}} + f_{\text{O}}), & \text{for } hkl \text{ all even} \\ &= 4 (f_{\text{Ni}} - f_{\text{O}}), & \text{for } hkl \text{ all odd} \end{aligned} \quad (3.15)$$

Thus, for hkl all even, NiO has the lines (200) , (220) , (222) , and (400) , and the lines (111) and (311) for hkl all odd. Note that the scattered intensity is proportional to $|S|^2$ so that all the observed lines in NiO have contributions from both the Ni and O atoms.

The position displacement of reflected lines can also occur due to the effect of temperature. The atoms in solids are vibrating as the temperature increases, leading to a change in their position. But the width of the diffracted line is not affected since the phonon frequency ($\nu \sim 10^{13}$ Hz) is negligible compared to the x-ray frequency ($\nu \sim 10^{18}$ Hz). This temperature dependence of reflection lines is explained by the Debye–Waller Factor. If we assume that thermal vibrations are isotropic, for small displacement u_j , the structure factor of a cubic structure can be written as [Warren, 1996],

$$[S_{hkl}]_T = S_{hkl} \exp(-B \sin^2 \theta / \lambda^2) \quad (3.16)$$

where Debye – Waller temperature factor, $B = 8\pi^2/3 \langle u_j^2 \rangle$

or Intensity has the form,

$$[I_{hkl}]_T = I_0 \exp(-2B \sin^2 \theta / \lambda^2) = m (LP) |S|^2 \exp(-2B \sin^2 \theta / \lambda^2) \quad (3.17)$$

where m is the multiplicity factor, and Lorentz polarization factor $(LP) = \{(1 + \cos^2(2\theta)) / \sin^2 \theta \cos \theta\}$ [Warren, 1990].

We need to have a different B for Ni and O atoms from Eq (3.15). Thus, we let intensity $I = m (LP) \{f_{Ni} \exp(-B_{Ni} \sin^2 \theta / \lambda^2) + f_O \exp(-B_O \sin^2 \theta / \lambda^2)\}^2$ for hkl all even and $I = m (LP) \{f_{Ni} \exp(-B_{Ni} \sin^2 \theta / \lambda^2) - f_O \exp(-B_O \sin^2 \theta / \lambda^2)\}^2$ for hkl all odd. To reduce the symbols, let $Q_{even} = (I / m (LP))^{1/2}_{even}$ and $Q_{odd} = (I / m (LP))^{1/2}_{odd}$ for each case. Now we can determine B_{Ni} and B_O by combining these relations,

$$\begin{aligned} \ln \{(Q_{even} + Q_{odd}) / 2f_{Ni}\} &= -B_{Ni} (\sin^2 \theta / \lambda^2) \\ \ln \{(Q_{even} - Q_{odd}) / 2f_O\} &= -B_O (\sin^2 \theta / \lambda^2) \end{aligned} \quad (3.18)$$

Here, an example of how to calculate the B_{Ni} and B_O for NiO 5nm uncoated sample is given. Table 3.2 shows the calculation of each line from the x-ray data and the atomic scattering factors f_{Ni} and f_O which depend on the angle θ . Using this data, we draw the graph $Q = (I/mLP)^{1/2}$ vs. $\sin \theta / \lambda$ for hkl all even and odd each.. In Fig. 3.10, the linear equation represents the Q_{even} and Q_{odd} for each $\sin \theta / \lambda$. This calculation is shown in Table 3.3. Now we let $(Q_{even} + Q_{odd}) / 2f_{Ni}$ be Q^+ and $(Q_{even} - Q_{odd}) / 2f_O$ be Q^- and finally we can get the B_{Ni} and B_O from the slopes of the relation $\ln(Q^+)$ and $\ln(Q^-)$ respectively which is shown in Fig. 3.11.

We summarize the Debye–Waller Temperature Factor for all uncoated particles in Table 3.4 and make a graph of the results in Fig. 3.12. Through the graph, we know that the thermal vibrations of nickel increase for small particle size less than 12 nm and in case of oxygen, B_O decreases as particle size decreases.

hkl	θ	m	I	LP	$(I/mL P)^{1/2}$	f_{Ni}	f_O	$\sin\theta/\lambda$
(111)	18.56	8	305	15.74	1.556	18.55	4.83	0.2065
(200)	21.61	6	601	11.32	2.975	17.55	4.46	0.2389
(220)	31.25	12	374	5.09	2.474	14.73	3.34	0.3365
(311)	37.50	24	113	3.58	1.146	13.32	2.78	0.3948
(222)	39.40	8	81	3.31	1.749	12.88	2.53	0.4117
(400)	47.40	6	46	2.74	1.672	11.87	2.16	0.4774

Table 3.2 shows the information about each Bragg peak in the x-ray pattern of 5 nm uncoated NiO.

Fig. 3.10 Plot of $Q = (I/mL P)^{1/2}$ vs. $\sin\theta/\lambda$ for hkl all even and odd.

$(\sin\theta/\lambda)^{1/2}$	Q_{odd}	Q_{even}	Q^+	Q^-	$\ln(Q^+)$	$\ln(Q^-)$
0.0426	1.556	3.16	0.1271	0.0432	-2.0628	-3.1419
0.0571	1.485	2.987	0.1269	0.0423	-2.0644	-3.1630
0.1132	1.273	2.392	0.1244	0.0380	-2.0843	-3.2702
0.1559	1.146	2.048	0.1199	0.0339	-2.1211	-3.3843
0.1695	1.109	1.949	0.1187	0.0326	-2.1312	-3.4234
0.2279	0.966	1.561	0.1064	0.0251	-2.2405	-3.6849

Table 3.3 summarizes the results of the calculation from Fig 3.10.

Fig. 3.11 Plots of $\ln Q^+$ ($\ln Q^-$) against $(\sin\theta/\lambda)^2$, the slopes give directly the values of B_{Ni} (Ni) and B_O (O).

Particle size (nm)	B_{Ni}	B_O
5	0.88 (0.18)	0.79 (0.36)
7	1.24 (0.19)	0.81 (0.31)
8	0.69 (0.17)	0.68 (0.38)
12	0.73 (0.19)	1.39 (0.39)
16	0.10 (0.18)	0.80 (0.33)
20	0.48 (0.18)	0.97 (0.34)
41	0.33 (0.19)	1.32 (0.40)
bulk	0.12 (0.18)	0.53 (0.32)

Table 3.4 shows the Debye – Waller Temperature Factor for all particle sizes (uncoated).

The Debye-Waller factor takes into account the effect of lattice vibrations on the diffracted-beam amplitudes. From Table 3.4, it is noted that there is some particle size dependence of the Debye-Waller factors. For smaller size samples below 10 nm, the Debye-Waller factors of nickel and oxygen becomes larger than the values of the bulk NiO although there is considerable experimental uncertainty due to scatter of the data. As particle size increases, the value for nickel tends to decrease close to the bulk value whereas the value of oxygen tends to increase. There are several theoretical models proposed for sodium chloride structure. One of those models, a so-called shell model (SM) was proposed [Dick et al, 1958], in which the atom is represented by a core consisting of the nucleus and inner electrons and a shell with the outer electrons. In this SM model at $T = 293$ K, the calculated Debye-Waller factors are $B_{Ni} = 0.2624$ for Ni and $B_O = 0.3567$ for O. These values are comparable with the result of our bulk sample.

Fig. 3.12 Plots of Debye-Waller factor vs. D using the results from Table 3.4.

CHAPTER IV

Review of Superparamagnetism

4.1. Superparamagnetic Particles

Néel's pioneering work for the magnetic properties of single-domain particles was followed by many investigations of these nanoparticles because these nano-sized magnetic particles have applications in technology such as, magnetic recording media, ferrofluids, magnetic refrigeration, catalysts, and soft magnetic materials [Dormann et al, 1992 and references in]. However, the magnetic properties are not easily understood because there are complex things to take into account such as particle size distributions, magnetic interparticle interactions, and magnetic anisotropy. In this chapter, I present a review of the basic properties of the magnetic nanoparticles, based in part on the material in the book by Morrish [Morrish, 2001]. This review will be important for discussing the magnetic properties of NiO nanoparticles presented in Chapters V and VI.

When particles have a magnetization which changes spontaneously due to the thermal agitation, similar to the paramagnetic atoms, with the exception that magnetic moment is very large, these particles are said to exhibit superparamagnetism, first introduced by Néel [Néel, 1962]. This phenomenon is investigated in single-domain size with uniaxial anisotropy which has an easy direction along the z-axis. Here, we assume that the particle's magnetization (M) remains constant for the applied field to simplify the analysis.

Consider a prolate ellipsoidal particle in a magnetic field as shown in Fig. 4.1. The applied field makes magnetization, M , to lie in the plane at the angles of, α , ϕ respect to the polar axis and the field respectively. The shape anisotropy produces demagnetization energy per unit volume given by

$$F_D = \frac{1}{2} \{ (M \cos \alpha)^2 D_a + (M \sin \alpha)^2 D_b \} \quad (4.1)$$

where D_a and D_b are the demagnetization coefficients along the polar axis a and the equatorial axis b direction. For simplicity, we assume that the exchange energy $F_{ex} = 0$.

Fig. 4.1 This diagram shows the prolate ellipsoidal particle with an applied magnetic field H .

In Chapter II, we treated a $\mathbf{S} \cdot \mathbf{S}$ term of the Heisenberg exchange interaction energy as a scalar product, assuming coordinate symmetry. In reality, there is a preferred direction for the magnetization due to the lack of the symmetry. This effect is called, crystalline anisotropy. For an ellipsoidal particle, the demagnetization energy acts as anisotropy energy. This anisotropy energy is a minimum if $\mathbf{M}$ lies along the polar axis, called the easy direction whereas if $\mathbf{M}$ lies along an equatorial axis, called the hard direction, the energy is a maximum. Eq. (4.1) can be modified into the form,

$$F_D = \frac{1}{2} M^2 D_a + \frac{1}{2} M^2 (D_b - D_a) \sin^2 \alpha. \quad (4.2)$$

So, for a particle with volume V , the variable part of the energy in the above equation is

$$\begin{aligned} F_T &= \frac{1}{2} M^2 (D_b - D_a) V \sin^2 \alpha \\ &= \frac{1}{2} CV \sin^2 \alpha \end{aligned} \quad (4.3)$$

where $C = M^2 (D_b - D_a)$, for $C = 2K$, where K here corresponds to the magnetocrystalline anisotropy constant. Fig. 4.2 shows the energy F_T vs. α in Eq. (4.3). There are two minimum energy states at $\alpha = 0$ and π with the opposite directions and these states are separated by an energy barrier of height $\frac{1}{2} CV$ at $\alpha = \pi/2$. This means that to switch the state from the parallel direction, $\alpha = 0$, to the antiparallel direction, $\alpha = \pi$, we have to overcome the energy barrier of $\frac{1}{2} CV$. Thus, the magnetization is stable if there are no perturbations such as a thermal agitation. For small particles, as the energy barrier is lowered due to the small volume, thermal energy is sufficient to change the magnetization between $\alpha = 0$ and $\alpha = \pi$ making the average of the remanence $\langle M_r \rangle$ equal to zero. The magnetization flips up or down states due to thermal energy as in a paramagnetic particle but here the magnetic moment is very large. This phenomenon is called superparamagnetism.

One important characteristic of superparamagnetism is the superparamagnetic relaxation time τ which is the average time the magnetization spends in the minima of the anisotropy energy. Now, consider an assembly of particles with a uniaxial anisotropy along z -axis. In a large field H along the z direction, all the particles are magnetized to saturation M . And if the field is removed, magnetization will decay due to thermal agitation according to the relation,

$$M_H = M \exp(-t / \tau). \quad (4.4)$$

If τ is very large, and $M_H = M$, the system is stable. The relaxation rate $1/\tau$ must be proportional to the Boltzmann factor $\exp(-\Delta E / k_B T)$ since ΔE is the energy barrier ($\frac{1}{2}CV$) between the two energy minima. Thus, we can write the relaxation rate as,

$$1/\tau = 1/\tau_0 \exp(-\Delta E / k_B T) = f_0 \exp(-CV / 2k_B T) \quad (4.5)$$

where k_B is Boltzmann's constant and f_0 is the attempt frequency typically in the range 10^9 to 10^{12} sec. According to Eq. (4.5), $f = 1/\tau$ is a strong function of temperature T and f decreases as T decreases. At a certain temperature T_B , the relaxation rate f will become equal to f_m , the frequency of measurement. This leads to

$$f_m = f_0 \exp(-\Delta E / k_B T_B) \quad (4.6)$$

or
$$T_B = (\Delta E / k_B) / \ln(f_0 / f_m). \quad (4.7)$$

According to Eq. (4.7), T_B depends on the frequency of measurement, f_m . The higher the f_m , the higher the T_B . For magnetization measurements, if we assume that the experimental measuring time $\tau = 1/f_m \approx 10^2$ sec, $f_0 \approx 10^9$, Eq. (4.7) will have the relation,

$$\Delta E = \frac{1}{2} CV = 25 k_B T_B. \quad (4.8)$$

For each particle with size V , there is a corresponding temperature T_B , above which the particles behave like a superparamagnet. I will use the above equations to interpret our results in Chapter V.

The existence of this superparamagnetism (SP) can be tested experimentally. No remanence in the experiment of M vs. H is observed for SP for $T > T_B$. SP can be destroyed by cooling as the relaxation time varies exponentially with temperature. The temperature below which the system is stable or blocked is called the blocking temperature T_B . Therefore, through measuring the remanence, we can see the increase of remanence proportional to the amount of the particles which are superparamagnetic as temperature decreases. In another experiment, magnetization M vs. H at different temperatures above blocking temperature is measured. If the particle is superparamagnetic, the experimental results have to follow the Langevin function which is valid for single domain superparamagnetic nanoparticles. This means that the plots of normalized magnetization vs. H/T measured at various temperatures should collapse into one single graph. Here, we obtain very large magnetic moments μ_P estimated from the Langevin function,

$$M_H(T) = M(0) L(x) = M(0) \{ \coth(x) - 1/x \} \quad (4.9)$$

where x is $\mu_p H / k_B T$. In the limit of very small x , $L(x) \approx x/3$ and then the magnetization is

$$M_H(T) = M(0) \mu_p H / 3 k_B T = C / T \quad (4.10)$$

Eq (4.10) is the Curie law for paramagnetism, with the Curie constant $C = M(0) \times \mu_p / 3 k_B$ for superparamagnetism.

Fig. 4.2 For a single particle, the energy with an angle, α is separated by the energy barrier $\frac{1}{2} CV$ at $\alpha = \pi/2$ between the two equivalent state at $\alpha = 0$ and $\alpha = \pi$ [Morrish, 2001].

4.2 Critical size for single domain particles in ferromagnets

A ferromagnetic material, as described in Chapter II, has a magnetic moment, even in the absence of a magnetic field. This is explained by a spontaneous magnetization. In spite of this property, a ferromagnetic material may exhibit no magnetic moment without applying a field. These results can be explained using the concept of small region, called domain postulated by Weiss [1907]. Generally, ferromagnetic particles consist of many domains all oriented in different directions in $H = 0$ so that the total magnetization is zero. If the particle size is small or a single domain, then for such particles, the magnetization is large even in $H = 0$, giving rise to superparamagnetism. Thus, when we treat the SP-NP, it is important to know the critical size for a single-domain in zero applied fields. To estimate the critical size, we need to consider a domain wall, often called Bloch wall (Bloch, 1932) which separates two domains in a bulk ferromagnet.

A Bloch wall in a ferromagnet is a transition region which separates adjacent domains having different directions of magnetization. Exchange energy of this region has the form,

$$F_{EX} = \langle H_{EX} \rangle = -2J_e S^2 \cos \varphi \quad (4.11)$$

where φ is the angle between neighboring spins. For small φ , we can let $\cos \varphi$ be $(1 - \varphi^2/2)$ and hence Eq. (4.11) is divided into constant part and φ dependant part which need to be considered. In a Bloch wall, the total change in angle is π since the magnetization is reversed between up and down sides. If the total change of π occurs in N steps, the angle φ between spins is π/N . Thus, the variable part of the exchange energy is $J_e S^2 \pi^2/N$ for N atoms. If all spins are parallel to the easy axis, the anisotropy energy, F_K will be minimized. However, because of the domain wall, F_K is not in the minimum and so the thickness of the wall is limited by this crystalline energy. If we let “a” be the lattice constant, then the wall thickness δ is Na . Therefore the wall energy F_{WALL} per unit area of the wall is

$$F_{WALL} = F_{EX} + F_K = J_e S^2 \pi^2/a\delta + K\delta. \quad (4.12)$$

By minimizing this energy with respect to δ , we obtain the wall thickness $\delta = (J_e S^2 \pi^2 / Ka)^{1/2}$. We substitute δ into Eq. (4.12) leading to minimum wall energy as

$$F_{WALL} = 2\pi S (J_e K/a)^{1/2} \quad (4.13)$$

Now we calculate the critical size below which a ferromagnetic material will exist as a single domain particle. For a spherical particle with diameter d , the magnetic energy of the uniform state is $M_S^2 d^3$ for the volume d^3 , and there exist Bloch wall energy separating the domains. Thus, the critical size is calculated by letting the magnetic energy for the volume equal to wall energy for area,

$$M_S^2 d_C^3 = F_{WALL} d_C^2 \quad (4.14)$$

So, we obtain the critical size for single domain particles in ferromagnets,

$$d_C (\text{cm}) = F_{WALL} / M_S^2 = 1/M_S^2 \times \{2\pi S (J_e K/a)^{1/2}\} \quad (4.15)$$

Note if M_S is small, d_C is large. That is why usually ferrimagnets are used for applications. For example, if $M_S \approx 1700$ Oe and $F_W = 3$ ergs/cm² for Fe, then from Eq. (4.15), $d_C \approx 10^{-6}$ cm ≈ 100 Å. That is particles with size less than $d_C \approx 100$ Å will be single domain.

4.3 Superparamagnetism in Antiferromagnetic Nanoparticles

Néel described the magnetic structure of antiferromagnetic (AF) nanoparticles as an exchange-coupled spherical bilayer composed of an inner antiferromagnetic core and an outer shell of uncompensated spins [Néel et al, 1962]. As a particle size becomes smaller, the percentage of surface spins becomes much larger compared to that in bulk materials. Thus, for small particles, the effect of the surface spins is significant. The spins in the interior are governed by the normal exchange and anisotropy terms. However, the surface spins have only exchange interactions with interior spins. The exchange interaction between these two layers creates a unidirectional anisotropy which may cause superparamagnetism due to uncompensated spins. This can produce a ferromagnetic/antiferromagnetic (F/AF) interface, leading to a shift of hysteresis loop, the so-called exchange bias phenomenon [Berkowitz et al, 1999 and Nogues et al, 1999]. Therefore, nanoparticles of AF material have important applications in devices which use the exchange bias, such as spin valves.

For NiO, Néel considered a two-sublattice model with A and B as the sublattices. If the number of atoms, n_A and n_B , are equal, the usual antiferromagnetic state follows. But if not, a net magnetic moment is proportional to $p = n_A - n_B$. Néel considered three cases as shown in Fig. 4.3, with details given in later papers [Richardson et al, 1991 and Mangin et al, 1999]. In case I, atoms are randomly ordered and the probability to find atom A without B is proportional to the square root of the number of atoms leading $p = (n)^{1/2}$. In case II, ordered pairs are occupied on complete sublattices. For case IIa and IIb, they are completely compensated in their ordering resulting in p being zero. For case IIc, the atoms on the top and bottom layers have the same orientation and this case yields $p = (n)^{2/3}$. And in last case III, the pairs have incomplete ordered sublattices with $p = (n)^{1/3}$. For each case, the magnetic moment μ_p is represented by $\mu_p = p\mu_A\mu_B$ where μ_A is the atomic spin moment and μ_B is the Bohr magneton.

In this work, we show that the above 2-sublattice model cannot explain our experimental observations. Kodama et al. [Kodama et al, 1997] proposed that the multi-sublattice ordering may be necessary to explain the large magnetic moment and large coercivities observed in NiO nanoparticles. Their calculation predicted the nature of ordering as the particle size is changed.

For AF materials, the Langevin function in Eq. (4.9) has to be modified to

$$M = M_0 L(\mu_p H / k_B T) + \chi_a H \quad (4.16)$$

where M_0 is the saturation magnetization and χ_a is the susceptibility of the antiferromagnetically ordered nanoparticle core. This modified Langevin function is used to determine μ_p by fitting $(M - \chi_a H) / M_0$ against H/T for temperatures between the blocking temperature T_B and the Néel temperature T_N .

Fig. 4.3 shows the origin of particle magnetic moments for antiferromagnetic NiO particles proposed by Néel.

4.4 The behavior of M vs. H (Stoner-Wohlfarth Model)

Here, I summarize how the magnetization of a single-domain particle will respond to applied field. Consider the same case for single domain particle as shown in Fig. 4.1. If we take into account the applied field part in Eq. (4.3), the total energy will be,

$$F_T = \text{const} - \frac{1}{4} M^2 (D_b - D_a) V \cos 2\alpha - HMV \cos \varphi \quad (4.17)$$

where φ is the angle between M and H. To find the equilibrium state, we minimize F_T with respect to φ and obtain

$$\partial F_T / \partial \varphi = \frac{1}{2} M^2 (D_b - D_a) V \sin 2\alpha + HM \sin \varphi = 0. \quad (4.18)$$

This equation satisfies a minimum with condition of $(\partial F_T / \partial \varphi)^2 > 0$. Since $M \times H = MH \sin \varphi$ is the torque acting on the magnetization due to applied field, Eq. (4.18) means that when the torque by demagnetization and applied field are the same, the system is stable. Eq. (4.18) can be represented as this,

$$\frac{1}{2} \sin 2(\varphi - \theta) + h \sin \varphi = 0 \quad (4.19)$$

where $h = H / M(D_b - D_a) = H / H_A$, and here H_A is the shape anisotropy. However, Eq. (4.19) is difficult to solve analytically. Thus, we just look at particular cases.

For $H = 0$, Eq. (4.19) indicates $\alpha = 0$ and this means M lies along the polar axis. An applied field then rotates M toward H. The component of M along H is $M \cos \varphi = M_H$. If H is applied perpendicular to the polar axis ($\theta = \pi/2$), $h = \cos \varphi = H / H_A$ from Eq. (4.19). Therefore, magnetization M_H changing linearly with field until $h = 1$ (or $H = H_A$) means that there is no hysteresis because the rotation of the moment is reversible for this single domain particle. This relation is shown in Fig. 4.4 (a). Fig. 4.4 (b) shows H applied opposite to the polar axis ($\theta = \pi$) leading the relation $\cos \varphi = -H / H_A$. If field is applied opposite to the magnetization, some perturbation causes very small rotation of the magnetization, but the anisotropy will force M to remain close to original orientation. Changes in magnetization can occur by jumps in a small field which will favor the magnetization to be in the field direction. Here, the coercivity H_C is H_A .

(a)

(b)

Fig. 4.4. (a) represents the case of a field applied perpendicular to the polar axis. There is a reversible rotation leading to no hysteresis, and (b) is the case of that a applied field is parallel with the polar axis. No reversible rotation occurs.

In the case of $\theta = 45^\circ$, the $\sin 2(\varphi - \theta)$ term of Eq. (4.19) equals $\cos 2\varphi$ and hence double values of $\sin \varphi = \{-h \pm (h^2 + 2)^{1/2}\}/2$ are calculated. Thus, there are jumps from $\varphi = 30^\circ$ to $\varphi = -90^\circ$ at $h = 0.5$. This allows us to guess that the remanence and coercivity of an assembly of randomly oriented particles will be $M_H/M = 0.5$ and $h_C = H/H_C = 0.5$ respectively since the coercivity field of the individual particles range from $h = 0$ to $h = 1$. These values are comparable to the numerical calculation yielding $h_C = 0.479$ and $M_H/M = \langle \cos \varphi \rangle = 0.5$ [Stoner et al. 1948]. This is shown in Fig. 4.5.

4.5 Relaxation and Magnetic Viscosity

If a system is disturbed by an external perturbation, the time τ which it requires to return to the equilibrium state is the relaxation time. For magnetic nanoparticles, studies of relaxation time have been reported by a number of research groups. The relaxation time is determined by the interaction of the magnetic moment of the particles with its environment [Dormann et al 1980, 1983 and Fiorani et al 1981, 1983, 1986].

For isolated particles, the relaxation time is written as (Eq. (4.5)),

$$\tau = \tau_0 \exp (\Delta E / k_B T) \quad (4.20)$$

where $\Delta E = \frac{1}{2} CV = KV$. This equation is called Néel-Arrhenius law which is valid only for non-interacting particles. However, in a real system, this relation has to be changed by including the effect of the influence of magnetic interactions on the relaxation time. In calculation of relaxation time for interacting particles, Shtrikman and Wohlfarth proposed one possible derivation which consisted of two cases, weak and strong coupling, respectively [Shtrikman et al, 1981]. For weak-coupling regime, they considered an energy barrier as $V(K + H_i M)$ where K is the magnetocrystalline anisotropy constant and $VH_i M$ is the contribution of the interaction energy to the barrier. Using a statistical mean value, H_i is replaced by $(H_i^2 MV)/k_B T$. This leads above relaxation time to a Vogel-Fulcher law,

$$\tau \approx \tau_0 \exp [VK / k_B (T - T_0)] \quad (4.21)$$

where T_0 is proportional to H_i^2 and increases with the interaction strength. If Eq. (4.21) is valid, then following the earlier arguments, it follows that

$$T_B = T_0 + (KV/k_B)/\ln(f_0/f_m) \quad (4.22)$$

Fig 4.5 shows hysteresis curves of randomly oriented particles calculated by Stoner and Wohlfarth [Stoner et al. 1948].

Thus, the effect of the interaction represented by T_0 is to enhance T_B by T_0 since the second term on the right hand side of Eq. (4.22) is T_B of the non-interacting system at the measuring frequency f_m (see Eq. (4.7)). A similar result was derived by Dormann et al. [Dormann et al. 1988].

The effect of an applied field H on T_B of a non-interacting nanoparticle system for H applied along easy axis is to lower the energy barrier $\Delta E = KV$ to

$$\Delta E \rightarrow \Delta E - \mu_p H + \mu_p^2 H^2 / 4(\Delta E) \quad (4.23)$$

where μ_p is the magnetic moment of the particle [Bean and Livingston, 1959]. Ibrahim et al. [1995] have shown that the effect of Eq. (4.23) is to lower T_B in the presence of an applied field H . However, in real systems, the particles are oriented randomly with respect to H and the interaction of the particles has to be taken into account. I will discuss these issues in Chapter V when the experimental results are presented on NiO nanoparticles.

For the theoretical simple case, if we consider particles which have identical barriers, it will be easy to solve the problem of relaxation. When we apply a magnetic field to the particles, all the particles are aligned in one direction with the field direction. Then, as the field is removed, the magnetic moment of the particles will simply decay following Eq. (4.4). In reality, however, there is a broad distribution of energy barriers. In this case, the magnetization has been shown to decay as [Street et al, 1949],

$$M(t) = M(t_0) - S(H, T) \ln(t/t_0) \quad (4.24)$$

where $S(H, T)$ is the magnetic viscosity that depends on both the magnetic field H and the temperature T . A computer simulation study of the magnetic viscosity has been reported by Gonzalez et al. [Gonzalez et al. 1994] on a system with a distribution of barriers. This study showed that $S(H, T)$ peaks at a temperature $\approx T_B$. Experimental verification of this result has been observed in ferrihydrite nanoparticles [Ibrahim et al. 1995].

CHAPTER V

Experimental Results in 5 nm NiO Nanoparticles.

In this chapter, I focus on our results for the smallest particles of NiO with 5 nm nominal XRD size and examine the effect of OA coatings on the magnetic properties.

5.1 Electron Magnetic Resonance (EMR)

In 5 nm NiO nanoparticles, we observed an EMR signal at room temperature near $g \approx 2$ at the EMR frequency $f = 9.28$ GHz following the resonance condition $hf = g\mu_B H_r$. This is a surprising result since in bulk antiferromagnets, the EMR signal above T_N disappears below T_N because of the energy gap $\approx (2H_E H_A)^{1/2}$ in the energy spectrum which appears for $T < T_N$ [e.g. Seehra et al. 1970]. This EMR signal becomes weaker and unobservable for larger particle size. Although no definite explanation of the origin of the signal is known, there have been several suggestions such as the size effects [Kenning et al, 1987, Tang et al, 1991, and Sako et al, 1995], the uncompensated surface spins [Néel, 1962], the presence of a spin-glass-like shell on the particle surface [Martinez et al, 1998] and so on. Among these suggestions, the effect of uncompensated surface spins is regarded as the more likely possibility.

Recently, the temperature dependence of the EMR spectra of 6 nm NiO particles was first reported by Rubinstein et al. [2001]. They showed that the resonance line was shifted to lower fields with decreasing temperature similar to ferrihydrite NP as reported by Seehra et al. [2001]. In the studies by Rubinstein et al [2001], the line width ΔH and the resonance field H_r were difficult to measure because line shape was very complex and distorted. So interpretation of the data could not be given.

We performed the measurements of EMR signal with varied temperature and magnetic field for all the particles. EMR measurements reported here were done by Dr. P. Dutta of our research group [Seehra et al. 2004]. Our observations show that the strength of the EMR signal decreases significantly as particle size increases. Only the uncoated and coated 5 nm samples have sufficiently well defined signals. Therefore, for 5 nm

samples, the EMR studies were carried out by measuring various EMR parameters, such as line width ΔH , resonance field H_r and intensity I_0 as a function of temperature.

The EMR measurements were done at 9.28 GHz using a standard reflection – type cavity, a Varian magnet and an Oxford Instruments cryostat for variable temperature studies. The EMR measurements were done with decreasing temperature, starting from room temperature to 4 K. For each temperature, the magnetic field was scanned from 100 to 10,100 Oe mimicking the field – cooled (FC) case.

The behavior of the EMR signal with temperature is shown in Fig. 5.1 for the uncoated 5 nm particles. From this graph, we can see that the lines broaden and shift to lower fields as temperature decreases. By analyzing each signal for both the uncoated and the coated samples, the comparative temperature dependences of the three EMR parameters, ΔH , H_r and I_0 are measured, as plotted in Fig. 5.2. First, it is noted that at each T , ΔH for the coated NP is reduced by almost a factor of two compared to that in the uncoated NP. This can be explained by the reduction of interparticle interaction due to the OA coating since any anisotropic interaction such as the dipolar interaction broadens the EMR signal [Castner et al, 1971 and references therein]. For the calculation of EMR intensity, ideally the intensity should be calculated by measuring the surface area under the curve by double integration of the derivative signals. In our case, however, as there is large zero-field absorption, this procedure will lead a wrong estimation while the equation $I_0 = (\Delta H)^2 \ell$, ℓ being peak-to-peak height, provides a more reliable estimate of the intensity [Poole Jr. C.P, 1983].

For the experimental determination of $T_B(\text{EMR})$ from the I_0 vs. temperature plot, we can expect that for $T > T_B(\text{EMR})$, the intensity I_0 will vary as $1/T$ expected for superparamagnetism. For $T < T_B(\text{EMR})$, there will be a rapid decrease in magnitude of intensity with decreasing temperatures due to spin freezing. Following this criterion, we can easily estimate the blocking temperatures. Each sample shows two peaks regarded as blocking temperatures, $T_B(m)$ measured by magnetization studies and $T_B(\text{EMR})$ measured by EMR studies. $T_B(m)$ is at lower temperature than $T_B(\text{EMR})$ as EMR signal is measured in high frequency. These two blocking temperatures for the uncoated sample vs. the coated sample are shifted to a higher temperature region by a temperature difference ≈ 140 K presumably due to strong interparticle interaction. The field

dependence of the blocking temperature and the ratio of these two blocking temperatures are more specifically discussed later.

Fig. 5.1 Plots of the EMR derivative line for several temperatures for the uncoated NiO.

Fig. 5.2 Plots of the resonance field H_r , linewidth ΔH , and intensity I_0 of the EMR line against temperature for the coated and uncoated NiO.

5.2 Temperature Variation of the low-field magnetic susceptibility

The susceptibility χ versus T was measured in zero-field-cooled (ZFC) condition and field-cooled (FC) for both the coated and uncoated nanorods. Each sample is cooled from room temperature to 5 K with $H = 0$ and then the magnetization M was measured at $H = 100$ Oe. This is the ZFC measurement. The FC measurements used a similar procedure except the samples were cooled to 5 K in $H = 100$ Oe. Prior to the SQUID measurements, we made a small sample holder using a white plastic drinking straw. The magnetization data were corrected to remove the background effect of the sample holder with $\chi = M/H = -2.3 \times 10^{-8}$, independent of T .

The plots of the variation of χ vs. T for the uncoated (a) and the coated cases (b) are shown in Fig. 5.3 with T_p as the temperature at which χ (ZFC) peaks. In the temperature regions above T_p , the ZFC and FC curves are nearly identical and approximately follow the Curie-law. However, the curves are not identical due to the particle size distribution observed in our TEM analysis. Comparing the data for the two samples, we note two differences. The first is that the average blocking temperature T_B , proportional to T_p in χ (ZFC) shifted to lower T for coated NP. The temperature difference is around 140 K and similar to the difference in EMR data between the uncoated and the coated samples. The second point is that for the uncoated NP, the FC curve is flattened out at lower T . These two results are interpreted in terms of reduction of the interparticle dipolar interaction upon OA coating [Bødker et al. 2000, Chantrell et al. 2000, and Mørup 1994], as discussed in further detail later.

In Chapter IV, we derived the equation for T_B as

$$T_B = (\Delta E/k_B)/\ln(f_0/f_m) \quad (5.1)$$

For our SQUID measurements, the measuring frequency $f_m \approx 1$ Hz and for previous EMR, $f_m \approx 9.28 \times 10^9$ Hz was used. Using these two frequencies and above equation, we can calculate the theoretical ratio of $T_B(\text{EMR})/T_B(\text{m})$ as 5.9 (4.3) for $f_0 = 10^{12}$ (10^{13}) Hz for non-interacting SPM particles. It is known theoretically that the ratio $T_B(\text{EMR})/T_B(\text{m})$ decreases as the strength of the interparticle interaction increases [Mørup, 1994]. In our experiments, the obtained the ratio, $T_B(\text{EMR})/T_B(\text{m}) \approx 3.1$ (1.5) for the coated (uncoated)

NP. These values are in line with the theoretical estimates discussed above [Mørup, 1994].

5.3 Field Dependence of Blocking Temperatures

To study the effects of interparticle interactions further, we measured the blocking temperatures in ZFC for different measuring fields, from 25 Oe through 1,000 Oe. The shift in $T_B(m)$ with applied field H is shown in Fig. 5.4 for uncoated and coated NP. Normalized plots of $T_B(H)/T_B(25 \text{ Oe})$ versus H are shown in Fig. 5.5 indicating a decrease of the $T_B(H)$ with increasing field. As discussed in Chapter IV, the applied field reduced the energy barrier for relaxation and hence T_B is reduced. It is evident that decrease for coated NP is more pronounced for smaller H than that for uncoated NP. Therefore we can expect that for non-interacting NP, the change in the energy barrier with field is much larger than that for interacting NP. This phenomenon is theoretically discussed by El-Hilo et al. [1992] through a computer simulation taking into account the effect of interparticle interaction. In Fig. 5.4, we also notice that a second peak is observed for the coated NP in the lower temperature region around $T \approx 13 \text{ K}$. This peak may be from the OA coating since it does not change with applied H . Therefore no further discussion of this peak is presented here.

Several measurements have been reported on the field dependence of T_B for a fine particle system. Using Brown's equation, Wenger and Mydosh showed that for a constant value of τ , the dependence of T_B on H is of the form, $T_{BH} \propto H^\nu$, where $\nu = 2$ for low fields and $\nu = 2/3$ for high fields [Wenger et al, 1984]. For low fields, they derived the following equation,

$$T_{BH} = T_{B0}[1 - I_{sb}VH^2/k_B H_K T_{B0}] \quad (5.2)$$

where T_{BH} and T_{B0} are the characteristic blocking temperatures in an applied field and zero field, indicating the H^2 dependence. For high fields, they derived $H^{2/3}$ variation, although an analytical expression for all H was not possible. Similar results were derived by Dormann.

Fig. 5.3 Temperature dependence of the magnetic susceptibility for FC (field-cooled) and ZFC (zero-field cooled) cases showing reduction in blocking temperature by coating.

Fig. 5.4 Plot of χ / χ_{max} (χ_{max} is the value at $T = T_B$ defined by the maximum) in various applied fields against temperature for coated and uncoated NP.

Fig. 5.5 Plots of the blocking temperature $T_B(H)$ at a magnetic field H normalized by its value at $H = 25$ Oe vs. H . The dotted lines are visual guides.

In a more recent paper, El-Hilo et al. [1992] have calculated the effect of interparticle dipolar interaction on the variation of T_B with applied field H . They compared the results of computer simulation data with experimental data for a weakly interacting fine particle system, Fe_3O_4 . Fig. 5.6 shows that the variation of the normalized blocking temperature, T_{RH} is proportional to $H^{2/3}$. Their data have a good agreement with the theoretical prediction showing $T_{RH} \propto H^{2/3}$ at high fields and $T_{RH} \propto H^2$ at low fields and the effect of interaction is to weaken the field dependence.

Tiwari and Rajeev [Tiwari et al. 2005] have used the observed $H^{2/3}$ variation of T_P as evidence that T_P in NiO represents spin-glass freezing temperature. However, as discussed earlier, it has been shown theoretically that the $H^{2/3}$ variation is valid not only for the mean-field models of spin-glasses but also for superparamagnetic particles, although for the latter cases, the variation is expected to change to H^2 in the limit $H \rightarrow 0$ [Wenger et al. 1989 and Dormann et al. 1987]. Furthermore, it has been shown that the effect of dipolar interparticle interaction is to weaken the H dependence [El-Hilo et al. 1992] and this has been verified in nanoparticles of Fe_3O_4 [El-Hilo et al. 1992] and in our studies of the 5 nm NiO nanorods [Seehra et al. 2005]. To check the H^q dependence in our 5 nm NiO-NP, we have fit the data to the Eq: $T_P(H) = T_P(0) [1 - CH^q]$ where C is a constant. The results are shown in Fig. 5.7 as plots of $\ln [T_P(0) - T_P(H)]$ vs. $\ln H$ as well as $[T_P(0) - T_P(H)]$ vs. $H^{2/3}$. For lower fields, q is larger but the magnitudes of q are clearly smaller than the theoretically expected values of $q = 2$ ($2/3$) for lower (higher) H . Interestingly, in the plot of $H^{2/3}$ variation in Fig. 5.7, one might infer that the variation is linear for larger $H^{2/3}$. However, this is misleading since $\ln [T_P(0) - T_P(H)]$ vs. $\ln H$ plot yields entirely different magnitudes of q . It is evident that H dependence of T_P in our samples is quite different form that reported by Tiwari and Rajeev [Tiwari et al. 2005].

Fig. 5.6 The measured variation of the normalized temperature, T_{RH} vs. $H^{2/3}$. The dotted line and solid lines are interacting and non-interacting cases respectively [El-Hilo, 1992].

Fig. 5.7 (a) Plot of the shift in the peak temperatures $[T_p(0) - T_p(H)]$ against $H^{2/3}$ for the 5 nm NiO particles. The lines connecting the points are for visual aid. (b) Plot of $\ln [T_p(0) - T_p(H)]$ against $\ln H$ to check the H^q variations.

5.4 Magnetization M vs. Field H

In the AF superparamagnetic system, the magnetization M above the blocking temperature is expected to follow the modified Langevin function shown as in Eq. (4.16). From the dc susceptibility measurement in the previous section, we know T_B for the coated and uncoated NP are 65 K and 210 K respectively, at the measuring field $H = 100$ Oe. The measurements of the magnetization M are performed with field $H = 0$ through 55 kOe at various temperatures of 230 to 370 (300) K for uncoated (coated) samples. Fig. 5.8 shows the experimental data. Following Eq. (4.16), the data fit well to the Langevin function giving one single curve for all the measured temperatures as shown in Fig. 5.9. From this fitting, we obtained magnetic moments per particle, $\mu_P \approx 1000$ (1240) μ_B for coated (uncoated) NP of nominal XRD size ≈ 5 nm.

Below the blocking temperature T_B , the system is expected to be in the blocked (ordered) state having a hysteresis feature. The hysteresis loops for both coated and uncoated NP were measured at 5 K using ZFC and FC methods up to $H = \pm 55$ kOe respectively. For the FC case, the samples were cooled to 5 K in $H = 20$ kOe, followed by the hysteresis loop measurements. Fig. 5.10 shows the hysteresis curves of the FC in an expanded scale to compare the coercivity H_C and exchange bias H_E for both the uncoated and the coated particles. For the uncoated NP, there is reduction of H_C vs. the coated NP. It may be explained in terms of the effect of interparticle interaction. Kechrakos et al. [1998] using Monte Carlo computer simulation have shown that for a weakly dipolar interacting system at low temperature, there is a reduction of the coercivity with increasing interparticle interaction. Qualitatively, the interparticle interaction averages out the anisotropy H_A and thus reduces the coercivity H_C which is proportional to H_A .

Fig. 5.8 Isothermal plots of the magnetization M against applied field H at temperatures shown.

Fig. 5.9 Fitting of the M vs. H data to Eq. (4.16) yielding the plot of $(M - \chi_a H)/M_0$ vs. H/T . The solid line is the Langevin variation with $\mu_p = 1240$ (1000) μ_B for uncoated (coated) NP.

Fig. 5.10 Plot of M vs. H measured at $T = 5$ K shows that the coercivity H_C is smaller for the uncoated particles vs. the coated particles.

5.5 Frequency Dependence of Blocking Temperatures

Here, I present the results of the AC measurements of the magnetic susceptibilities, χ' and χ'' , using the frequencies $f_m = 0.1$ Hz to 10^4 Hz. Interpretation of these results discussed later shows that the relaxation rates are governed by the Vogel-Fulcher law,

$$f = f_0 \exp\{-E_a/k_B(T_B - T_0)\} \quad (5.3)$$

where $T_0 = 162$ (0) K for the uncoated (coated) particles. Measurements of the AC magnetic susceptibilities χ' and χ'' were carried out using commercial SQUID magnetometers in 7 Oe amplitude of the AC field but zero DC magnetic field. The data above 1 kHz were taken using the physical property measurement system (PPMS) at Bose State University whereas the data at the lower frequencies were taken using the magnetic property measurement system (MPMS) at West Virginia University [Shim et al. 2006].

Fig. 5.11 shows the plots of χ' and χ'' against temperature for the uncoated 5 nm NP. The plot of χ' versus temperature for the coated NP is shown in Fig. 5.12. The χ'' vs. T plot had large scatter because of small magnitudes and so this data are not shown here. We can see that the temperature position of the peak of χ' is much higher than that of χ'' and from a closer examination, the position of the peak of χ'' agrees with the peak position of $d(\chi')/dT$. Similar observations have been reported in other NP systems [Dormann et al, 1996, Jonsson et al, 1998, and Vincent et al, 1996]. For both NP, the peak positions of χ' and χ'' shift to higher temperatures with increasing frequency as we expect from the above VF law. Note that the second peak is observed again for the coated NP in the lower temperature region, near $T \approx 13$ K, similar to the case of the measurements of the field dependence of blocking temperature. These second peaks in the coated NP might be due to the OA coating.

From Eq. (5.3), it follows that

$$\ln f = \ln f_0 - (E_a/k)/(T_B - T_0). \quad (5.4)$$

For $T_0 = 0$, Eq. (5.3) reduces to the Néel-Arrhenius (NA) relation, with

$$\ln f = \ln f_0 - (E_a/k)/T_B. \quad (5.5)$$

First, in order to check the validity of NA relation for our coated and uncoated NP, we plot $\ln f$ vs. $1/T_B$ in Fig. 5.13 using the peak position in χ' to be T_B and the value of T_B obtained from the EMR studies at $f = 9 \times 10^9$ GHz [Seehra et al, 2005]. The data fit linear lines as expected from Eq. (5.8), with the following magnitudes for the attempt frequency and the energy barrier E_a/k : $f_0 = 9.2 \times 10^{11}$ Hz and $E_a/k \approx 1085$ (45) K for the coated NP and $f_0 = 1.4 \times 10^{39}$ Hz and $E_a/k \approx 18250$ (1585) K for the uncoated NP. For the coated NP, the above results are in line with the theoretical estimates for AF NP and the observed values for other systems [Kilcoyne et al, 1995, Ibrahim et al, 1995 and Dickson et al, 1993]. However, for the uncoated NP, the above magnitudes of f_0 and E_a/k_B are too large and unphysical, leading us to conclude that the NA relation is not valid for the uncoated NP as expected.

The differences observed in the variation of $\ln f$ vs. $1/T_B$ for coated and uncoated NP are interpreted in terms of the presence of interparticle interaction in the uncoated NP and its absence in the coated NP. In order to check the validity of the VF law, we plot $\ln f$ vs. T_B with fitting curves in the VF law (Eq. (5.7)) shown in Fig. 5.14. In the theoretical fitting, we used the values of $E_a/k = 1083$ K and $f_0 = 9.2 \times 10^{11}$ Hz derived from the NA relation for the coated NP and from this fitting, we obtained $T_0 = 162$ K for the uncoated NP and $T_0 = 0$ K for the coated NP. Here, the values of T_0 represents a measure of the interparticle interaction on magnetic relaxation and these magnitudes of T_B are comparable to the difference in the values of blocking temperatures for uncoated and coated NP shown in Fig. 5.3 for DC measurements. The fit of the data to Eq. (5.5) is very good, except for a slight difference at $f = 9.28 \times 10^9$ Hz for the uncoated NP. This may be related to the fact that the VF law is valid only for weak interparticle interaction and at higher f , deviations from the VF law are expected for stronger interparticle interaction [Dormann et al, 1988 and 1996, Shtrikman et al, 1981, and Zhang et al, 1996].

Fig. 5.11 Temperature variation of χ' and χ'' in uncoated NiO NP at different frequencies is shown. The lines through the points are for visual aid.

Fig. 5.12 Temperature dependence of χ' vs. T for the coated NP.

Fig. 5.13 Plot of $\ln f$ against $1/T_B$ for the coated and uncoated NiO NP. The solid lines are fits to Eq. (5.8) with parameters given in the plot. The size of error bars for the uncoated sample is within the size of the symbols.

From Eq. (5.5), it also follows that

$$T_B = T_0 + (E_a/k)/\ln(f_0/f) \quad (5.6)$$

Eq. (5.6) shows that interparticle interaction enhances the T_B by T_0 so that the theoretical fits in Fig. (5.14) for uncoated NP are simply shifted by T_0 . This enhancement of T_B by interparticle interaction is in agreement with more explicit calculations for the dipolar interparticle interaction [Chantrell et al, 2000]. Another view of this enhancement of T_B is that the interactions enhance correlation and so effectively increase the particle volume V [Allia et al, 2001, Vargas et al, 2005 and Denardin et al, 2002]. This enhances T_B since $E_a = KV$, and hence T_B is proportional to V ,

In summary, comparing the changes in T_B as a function of applied field H and measuring frequency f_m in the coated and uncoated 5 nm NP of NiO, the effect of the presence of the interparticle interaction in the uncoated particles and its absence in the coated particles has been demonstrated.

Fig. 5.14 Plot of $\ln f$ against T_B for the coated and uncoated NiO 5 nm NP. The solid lines are fits to Eq. (5.5) with $T_0 = 162 \text{ K}$ for the uncoated and $T_0 = 0 \text{ K}$ for the coated NiO NP. The magnitudes of E_a/k and f_0 used in the fit are the same as in Fig. 5.13.

CHAPTER VI

Size Dependence of the Magnetic Properties in NiO Nanoparticles

6.1 Introduction

The structure and morphology of NiO-NP were investigated through the analysis of XRD and TEM in Chapter III. TEM studies show that the shapes of the NiO-NP change with increasing particle sizes. For the smaller particles, more of the particles are in the form of nanorods whereas for the larger particles produced by annealing temperatures, $T_a \geq 673$ K, nanorods change to particles with rounded morphology. Also there is a high degree of scatter in XRD data for smaller particle sizes due to the rod like morphology. Results of our magnetic studies on nominal 5 nm NiO NP [Seehra et al. 2004, 2005 and Shim et al. 2006] were described in chapter 4 where the differences between the magnetic properties of oleic-acid (OA) coated and uncoated particles were explained in terms of the interparticle interaction (negligible for coated particles).

In this chapter, I focus on the changes in the magnetic properties of the NiO-NP with increase in the nominal XRD size D from 5 nm to about 20 nm. To investigate the effect of interparticle interaction, for all the particles, comparisons between the magnetic properties of the OA coated and the uncoated particles are provided. The variations of the magnetization M with temperature T (0 K to 370 K) for the uncoated and coated samples, are measured by employing the ZFC and FC modes. From these measurements, blocking temperature T_B is determined for each particle size. Fits of the magnetization M vs. applied H at different temperatures $T > T_B$ to the modified Langevin function (Eq. (4.16)) is used to determine μ_p as a function of size D . Analysis of these data shows that the fraction f of spins in the surface layer of the NP, which contribute a moment of $2.2 \mu_B$ to μ_p changes with D . It is observed that this fraction f varies as $1/D$ reaching nearly 100 % for the 5 nm particles. The Néel temperature T_N decreases rapidly for $D < 10$ nm.

6.2. Magnetization vs. Temperature

The measurements of M vs. T were carried out under the zero-field-cooled (ZFC) and field-cooled (FC) modes following the same procedure as in section 5.2. For ZFC, the sample is cooled to 5 K in zero magnetic field, a magnetic field $H = 100$ Oe is then applied at 5 K followed by measuring M with increasing T after stabilizing the temperature at each temperature till $T = 370$ K is reached. For the FC case, the data are then taken with decreasing T in a similar fashion. The data so taken for different samples are shown in Fig. 6.1 for the uncoated particles and in Fig. 6.2 for the coated particles. Note that the temperatures T_P at which the magnetic susceptibility $\chi (= M/H)$ peaks for the ZFC cases are also indicated. T_P represents the average blocking temperature for each particle. The temperatures at which the ZFC and FC data bifurcates are generally higher than T_P , most likely due to the wide particle size distribution, especially for large D . The plot of T_P vs. particle size D is shown in Fig. 6.3 for both the coated and the uncoated particles. A noteworthy feature of this plot is that for $D < 10$ nm, T_P for the uncoated particles continues to increase with decrease in D whereas the trend for the coated particles is just the opposite. Note that T_P for non-interacting particles is expected to be proportional to the particle volume V (Eq. (4.8)) in line with the observations for the coated particles. The results for the uncoated particles can be interpreted in terms of the interparticle interaction. The reason is explained as below.

Following the discussion on the magnetic relaxation in the 5 nm NiO nanorods [Shim et al. 2006] in Chapter V, the relaxation rate f for the magnetization for $T > T_P$ follows the Vogel-Fulcher law [Shtrikman et al. 1981, Dormann et al. 1988, and Zhang et al. 1996]. The second term on the right-hand side of Eq. (5.8) represents the blocking temperature for non-interacting NP's ($T_0 = 0$) at the measuring frequency f_m . Using the data of the variation of T_P with measuring frequency f from $f = 0.1$ Hz to 10^4 Hz in the 5 nm NiO nanorods, it was shown that $T_0 = 162$ (0) K for the uncoated (coated) nanorods with $E_a/k = 1083$ K and $f_0 = 9.2 \times 10^{11}$ Hz [Shim et al. 2006]. The relevance of the above results for the data presented here is that it also provides an explanation for the data of Fig. 6.3 in that the enhanced T_P for the uncoated particles is simply due to the interparticle interaction (Note that in general $T_P = \beta T_B$ where β takes into account the particle size distribution, with $\beta = 1.5 - 2.0$ depending on the distribution [Gittleman et al.

1974 and El-Hilo et al. 1992]). Since $E_a = KV$ where K is the anisotropy constant and V is the volume of the particles, the increase in T_B with increase in size D is expected as observed in Fig. 5.3 for the coated particles. Another view of this enhancement of T_B by interparticle dipolar interaction is that the interactions enhance correlations and this effectively increases the particle volume V [Chantrell et al. 2000, Allia et al. 2001, Denardin et al. 2002, and Vargas et al. 2005]. The question of why the effects of interparticle interaction become negligible for larger particles is addressed later.

In a recent paper on the uncoated NiO nanoparticles with sizes $D = 5.1, 6.2$ and 8.5 nm, Tiwari and Rajeev [Tiwari et al. 2005] reported somewhat similar behavior of the decreases of T_P with increase in particle size. Although their particles were prepared by the similar sol-gel method, TEM studies were not included in this paper so that it is not possible to compare the morphological features. They argue that the T_P in their samples really represents spin-glass freezing and not the effect of interparticle dipole-dipole interaction. Their argument is partly based on their assumption that $\mu_P \approx 100 \mu_B$ (although no Langevin-type analysis of the data to determine μ_P was presented). On the other hand, our analysis presented here shows that $\mu_P \geq 10^3 \mu_B$ for $D \approx 5$ nm, making the interparticle interaction more important. Spin-glass freezing of the surface spins has been observed in NP of ferrihydrite [Punnoose et al. 2005] and $\gamma\text{-Fe}_2\text{O}_3$ [Martínez et al. 1998 and Koksharov et al 2000] but in these cases, the spin-glass freezing temperature T_S is considerably lower than T_P . Analysis of our AC susceptibility data for the coated and uncoated NiO nanoparticles also shows that in coated particles, the interparticle interaction is negligible whereas in uncoated 5 nm particles, an effective interparticle interaction temperature $T_0 \approx 162$ K in Eq. (5.6) is needed to fit the relaxation data [Shim et al. 2006]. Further evidence that OA coating essentially eliminates the interaction is evident from the increase of T_P with size D for the coated particles, as expected for superparamagnetic particles (Fig.6.3).

Fig. 6.1 Temperature variation of the magnetic susceptibility χ of the uncoated NiO-NP measured in $H = 100$ Oe (10^4 Oe = 1 Tesla) for the FC and ZFC modes. The arrows indicate the location of T_P , the temperatures at which χ (ZFC) peaks for each case.

Fig. 6.2 Same as Fig. 6.1 except for the OA coated NiO-NP.

Fig. 6.3 Variation of T_p with particle size for the uncoated and coated NiO-NP. The dotted lines through the points are a guide to eye.

6.3 Magnetization vs. Magnetic Field

For $T > T_p$ where the particles are expected to be in the superparamagnetic (SPM) state, The magnetization M is measured in field H up to 55 kOe in the temperature range of 230 (200) to 370 (300) K for uncoated (coated) particles. These plots of M vs. H are shown in Fig. 6.4 for the uncoated particles and in Fig. 6.5 for the coated particles. It is evident that M does not saturate even at $H = 55$ kOe and there is a high field magnetic susceptibility χ_a . For the larger particles with wider size distributions ($D = 17$ nm and 27 nm coated), a small remanence at $H = 0$ was observed probably because the larger particles are still unblocked at these temperatures as attested by the data in Fig. 6.2. This remanence was subtracted out in fitting the data to the Langevin function [Resnick et al. 2006].

In order to figure out the parameters M_0 , μ_p , and χ_a from the Langevin function fitting, first in the experimental data measured in each temperature in Fig. 6.4 and Fig. 6.5, χ_a and M_0 are estimated from measuring the slope of linear part in high field of M vs. H plot and reading the value of intersection point with y-axis in the plot of $(M - \chi_a H)$ vs. $1/H$ as H goes to infinity respectively. These estimated values of χ_a and M_0 have temperature dependence as shown in Fig. 6.6 and Fig. 6.7. For the smaller particles, larger slopes are observed.

Using these estimated parameters, χ_a and M_0 , the variation of M vs. H for $T > T_p$ is fitted to the modified Langevin function in a manner similar to the one used in earlier studies of doped ferrihydrite [Punnoose et al, 2004] and ferritin NP [Makhlouf et al, 1997]. The plots of $(M - \chi_a H)/M_0$ against H/T are shown in Fig. 6.8 for the uncoated and coated particles with the solid lines as the fits with the μ_p as shown in the figures. To see whether there is some temperature dependence to μ_p , the variation of μ_p with temperature is estimated by fitting the data in Fig. 6.4 and Fig. 6.5 using non-linear fitting in program ORIGIN at each temperature. The magnitudes of μ_p vs. temperature so determined are plotted in Fig. 6.9 for both the uncoated and coated particles. For the smaller particles, there is no significant temperature dependence to μ_p as the fits in Fig. 6.8. However for the larger particles, μ_p increase until one temperature point around 280 (350) for coated (uncoated) samples and after that point, μ_p decreases.

Recently, the topic of how μ_P in AF-NP varies with temperature has received considerable attention. Partly based on the experimental results of Seehra et al. [2000] in ferrihydrite nanoparticles where μ_P was found to increase with temperature, Mørup et al [2004] proposed a theory which predicted increase of μ_P with temperature in AF-NP. However, Silva et al. [2005] have recently argued that a wide particle-size distribution can mimic μ_P increasing with temperature. Our studies also show that for larger particles (e.g. $D \approx 20$ nm) with wider size distribution, μ_P apparently shows an increase with increase in temperature. For smaller particles, μ_P is essentially temperature independent. In our analysis, we have not taken into account the particle size distribution since the size distribution in most of our cases does not follow any simple distribution function such as lognormal or Gaussian. Nevertheless for the smaller particles, our data show that μ_P is temperature independent or decreases slowly with increase in temperature.

Fig. 6.4 Plots of measured magnetization M vs. applied field H (10^4 Oe = 1 Tesla) for the uncoated NiO-NP at several temperatures above T_P . The lines joining the points are for visual aid.

Fig. 6.5 Same as in Fig. 5.4 except the data are for the OA coated NiO-NP.

Fig. 6.6 Plots of χ_a vs. T show the linear decrease of χ_a with temperature.

Fig. 6.7 Temperature dependence of M_0 (Eq. (4.16)) for the uncoated and coated NiO-NP for $T > T_p$. The solid lines through the data points represent linear variations whereas the dotted lines are extrapolations to $M_0 \rightarrow \text{zero}$ to estimate the Néel temperature T_N .

Fig. 6.8 Plots of $(M - \chi_a H)/M_0$ against H/T for selected coated and uncoated NiO-NP. The solid lines are fits to Eq. (4.16) with μ_p (magnetic moment/particle) values shown on the figures.

Fig. 6.9 μ_P determined at different temperatures by fitting the data of M vs. H to Eq. (4.16). For the smaller coated and uncoated NiO-NP, μ_P so determined is essentially temperature independent.

6.4 Size dependence of μ_P

The variation of μ_P with size D is addressed next. Néel suggested that μ_P depends on the total number of atoms n_D , the crystal structure and particle morphology [Richardson et al. 1956, 1991 and Neel, 1961]. This model leads to $\mu_P = p\mu_B$ where p is the difference in the numbers of atoms in the two sublattices A and B of the antiferromagnet ($p = n_A - n_B$ and $n_D = n_A + n_B$) and μ_B is Bohr magneton. How the atoms on the surface of the NP are arranged determines the dependence of p on n_D . For random ordering $p = n_D^{1/2}$ but $p = n_D^{2/3}$ if surface atoms all belong to the same sublattice. Of course dependence of μ_P on size D comes through n_D , the number of magnetic atoms per particle. In the case of NiO, we consider Ni^{2+} ions on a FCC lattice with lattice constant of 4.1795 Å to determine n_D for each size D assuming spherical particles of diameter D . Using the above information, we calculate $n_D = 3,586$ for $D \approx 5$ nm. This n_D yields $\mu_P = 515 \mu_B$ for $p = n_D^{2/3}$ and $\mu_P = 132 \mu_B$ for $p = n_D^{1/2}$. These magnitudes are considerably smaller than the experimental value of $\mu_P \approx 1250 \mu_B$. Clearly this analysis does not describe the experimental result satisfactorily, a situation also noted in earlier studies [Makhlouf et al. 1997].

Assuming a core – shell model where a fraction $f = n_C/n_A$ of the Ni^{2+} spins on the surface layer (shell) contribute to μ_P and the spins in the core are antiferromagnetically ordered, we can calculate f by comparing the experimental μ_P with the calculations (see Table 5.I). This fraction f is plotted as a function of D in Fig. 6.11, with the dashed line representing the $1/D$ variation ($\ln f$ vs. $\ln D$ plot yielded the slope of negative one). There is a slight departure for this variation for the $D = 5$ nm particles in such a way that not only all the spins in the top surface layer are contributors to μ_P for this size, but some additional spins perhaps in the second adjacent layer at the surface are also contributing to μ_P (sizes D for which is μ_P temperature dependent in Fig. 5.9 are not included in Fig. 6.11). The model that emerges from this analysis is that with decrease in D , a larger fraction of surface spins contribute to μ_P as a result of their decoupling from the core spins. This model is physically appealing since surface spins have lower coordination and hence weaker exchange coupling to the spins in the core. Therefore it is likely that for $D < 5$ nm, the long range AF order will eventually break down as D is decreased. In a recent work, Tang et al. [Tang et al. 2003] in antiferromagnetic CoO layers have reached a

similar conclusion in that layers with thickness ≈ 1 nm were found to have T_N approaching 0 K.

From the comparison shown in Fig. 6.3, it is evident that the effect of interparticle interaction decreases with increase in size D . The interparticle dipolar interaction between two particles varies approximately as μ_p^2/D^3 . From Table 6.1, although μ_p increases by a factor about 3 from $D = 5$ nm to $D = 20$ nm, the magnitude of μ_p^2/D^3 decreases by a factor of 9/64. In addition, the fraction n_C/n_D goes down as D increases approaching nearly zero for the largest particles. The effect of these factors is to lower the effects of interparticle interaction for larger particles quite significantly as observed experimentally.

6.5. Size dependence of T_N

In the plot of M_0 vs. T in Fig. 6.7, M_0 decreases linearly with increasing temperature. To explain this temperature dependence of M_0 , Makhoul et al. [1997] suggested that M_0 originates from surface moments and surface moments should vary linearly with $T_N - T$ near T_N . Thus, we can write this in the form [Seehra et al. 2000 and Punnoose et al. 2004],

$$M_0 = M^* [1 - (T/T_N)] \quad (6.1)$$

where M^* is the magnitude of M_0 extrapolated to $T = 0$ K. This can be used to determine T_N for the NiO-NP by assuming that linear extrapolation to $M_0 \rightarrow 0$ yields T_N . T_N 's so determined are plotted against particle size D in Fig. 6.12. This result shows that for $D < 20$ nm, T_N begins to decrease slowly and for $D < 10$ nm, it decreases rapidly from T_N of bulk NiO. This is somewhat similar to results reported by Tang et al. [2003] and Ambrose et al. [1996] for thin films of CoO, although they offered slightly different explanations. Tang et al. showed that the Néel temperature of the CoO layers decreases slightly with decreasing CoO layer thickness from 100 to 30 Å, but then exhibits a sharp decrease for CoO layer thickness below 20 Å. They suggested that this dramatic decrease below 20 Å is due to the structural change of CoO from crystalline to

amorphous rather than a finite size effect. And this structural change also leads to an increased number of weakly coupled uncompensated spins causing a significant change in temperature dependence of the magnetization. Whereas Ambrose et al explained the decrease of T_N for thin films of CoO in terms of a finite size effect, where T_N was found to decrease as

$$\{T_N(\infty) - T_N(t)\}/T_N(\infty) = (\xi_0/t)^\lambda \quad (6.2)$$

where ξ_0 is the extrapolated correlation length at $T = 0$ K and $\lambda = 1/\nu$ is the shift exponent for the finite-size scaling as the thickness of the film is lowered ($\nu = 2/3$ for 3d systems).

In NiO NP, our TEM studies show the morphology for the smaller particles to be rod-like, changing over to nearly spherical shapes for $D > 10$ nm. Thus this structural change can also be the reason for the sharp decrease of NiO T_N below 10 nm. The fitted curve for the parameters, $\xi_0 = 3.17$ (0.2) nm and $\lambda = 3.24$ (0.5), is also shown in Fig. 6.12, suggesting $\nu \approx 1/3$ for our NiO-NP system, although the limited number of data points makes it difficult to more accurately determine $\lambda = 1/\nu$.

Table 6.1: Calculated values of the Ni^{2+} spins for a sphere of diameter D : n_A = # spins on the surface layer; n_D = total number of spins; n_C = number of spins contributing to μ_P evaluated from the Langevin fits. Also listed are the ratios n_C/n_A and n_C/n_D .

D (nm)	n_A	n_D	μ_P / μ_B (uncoated)	$(\mu_P / \mu_B)/2.2$ = n_C	n_C/n_A	n_C/n_D
5	468	3,586	1,250	568	1.21	0.158
7	881	9,840	1,115	507	0.58	0.051
8	1,151	14,689	1,250	568	0.49	0.039
12	2,590	49,577	1,780	809	0.31	0.016
16	4,640	117,516	2,500	1,136	0.24	0.010
20	7,193	229,523	3,000	1,364	0.19	0.006

D (nm)	n_A	n_D	μ_P / μ_B (coated)	$(\mu_P / \mu_B)/2.2$ = n_C	n_C/n_A	n_C/n_D
5	468	3,586	1,000	455	1.03	0.13
7	881	9,840	900	409	0.46	0.042
11	2,176	38,187	1,500	682	0.31	0.018
17	5,197	140,956	4,000	1,818	0.35	0.013
27	13,110	564,712	8,000	3,636	0.28	0.006

Fig. 6.10 Plot of μ_P vs. particle size D shows that μ_P increases with increase in D .

Fig. 6.11 Plot of the fraction f of the surface layer spins contributing to μ_p against D for the coated and uncoated NiO-NP. The dashed line is the fitted $1/D$ variation for the uncoated particles only.

Fig. 6.12 Plots of estimated T_N (Fig. 6.7) against particle size D for the coated and uncoated NiO-NP. The dashed line is a theoretical fit with the parameters given in the text.

6.6. Hysteresis loop measurements

We performed the measurements of the hysteresis loops for all the particles. Following the procedure as described in section 5.4, the hysteresis loops were measured at 5 K using ZFC and FC cases up to $H = \pm 50$ kOe. For the FC case, the samples were cooled from 390 K to 5 K in $H = 20$ kOe, followed by the hysteresis loop measurements. The loops for each particle are shown in Fig. 6.13 for the uncoated particles and in Fig. 6.14 for the coated particles. The hysteresis loop parameters, viz., coercivity H_C and exchange bias H_E for both the uncoated and coated particles are summarized in Table 6.2.

For all the particles, H_E values are larger for the FC measurement than the ZFC. For the uncoated samples, the loops are narrow for the smaller particles but the loops are larger for the larger particles leading to increase in the values of H_E and H_C . However, for the coated samples, the loops are narrow even in 27 nm particles. This is an interesting result since several hysteresis loops measurements for AF-NP [Makhlouf et al. 1997a and 1997b, Kodama et al, 1999, and Punnoose et al. 2001] show that most AF-NPs below their blocking temperatures show significant increase in the loop width with strong exchange bias when field-cooled from $T > T_p$. The magnitudes of H_C for the coated samples decrease because of the absence of interparticle interaction.

An interesting result observed here is the appearance of steps in the hysteresis loops in the low-field region for the uncoated particles. These step-like features are dramatically reduced by increasing particle size. Such steps in the hysteresis loops have been observed for Ferrihydrite NP [Punnoose et al. 2004] and for single-domain Ni nanomagnets [Grundler et al. 1999]. The recent theoretical studies of Fraerman and Sapozhnikov [2002] for one dimensional NP system, explained that the nature of the steps is determined by the competing effects of coercivity, interparticle interactions, and thermal energy. Punnoose et al. explained that the steps in the hysteresis loops in the low-field region could be due to the dipolar interparticle interaction. Our data support their interpretation from the reduction of the step-like features for our coated samples compared to the uncoated samples.

To explain the hysteresis loops for NiO-NP, more experiments are needed, especially temperature dependence of the loops parameters below the blocking temperatures with the change in particle size.

Fig. 6.13 Hysteresis loops for the various particle sizes are measured in zero – field cooled (ZFC) and field cooled (FC) cases at $T = 5$ K for uncoated.

Fig. 6.14 Hysteresis loops for the various particle sizes are measured in zero – field cooled (ZFC) and field cooled (FC) cases at $T = 5$ K for coated samples.

(ZFC)		5nm	7nm	8nm	12nm	16nm	20nm
$-H_E$	Uncoated	0	85	235	50	250	1,470
	Coated	0	50	0	40	-	30
H_C	Uncoated	115	1,030	1,490	560	3,020	5,610
	Coated	640	2,510	600	860	-	440

(FC)		5nm	7nm	8nm	12nm	16nm	20nm
$-H_E$	Uncoated	0	210	1010	85	1750	4540
	Coated	105	1070	170	855	-	160
H_C	Uncoated	180	630	1,010	405	2,970	6,560
	Coated	670	2790	460	1270	-	580

Table 6.2 The hysteresis loop parameters observed in the ZFC and FC modes are summarized for each particle and here field unit is Oe.

(a) Field – cooled

(b) Zero Field - cooled

Fig. 6.15 Plot of the variations of loop shift H_E and coercivity H_C on each particle size under FC and ZFC condition.

CHAPTER VII

CONCLUSION

7.1 Structure and Morphology of NiO-NP

Studies reported in this dissertation have shown the changing morphology of the NiO-NP prepared by the sol-gel technique with increase in size D . For $D < 10$ nm, the particles have primarily rod-like features observed in TEM studies whereas for $D > 10$ nm the rod-like features give way to more sphere shaped particles. However, for the smaller particles with nanorods features, it turns out that the volume of the nanorods is quite close to a sphere of diameter D determined by XRD so that XRD measures average diameter of an equivalent sphere. This comparison between XRD and TEM showed the importance of both TEM and XRD studies for investigating nanoparticles. The particles coated with oleic acid to reduce interparticle interaction show similar change in morphology with change in size.

The intensities (area under the peaks) of the XRD lines were analyzed in terms of the Debye-Waller factors B for the Ni and O atoms. A general trend of the increase of B with decrease in size D is observed suggesting that the atoms in the nanoparticles are more loosely bound than those in bulk materials.

7.2 Effects of interparticle interaction on 5 nm NiO-NP

The blocking temperatures T_B are measured at different measuring frequencies f_m by magnetization and EMR studies for both coated and uncoated NiO 5 nm nanorods. The dc and ac measurements show that blocking temperature T_B decreases as field H increases and increases as frequency f increases, respectively.

The Vogel-Fulcher law describes well the magnetic relaxation of the 5 nm particles, T_B being enhanced by T_0 in the uncoated particles. Also, it has been shown that T_0 provides a good measure of the effect of interparticle interactions on magnetic relaxation. Oleic acid coating of NiO 5 nm NP essentially eliminated these interparticle interactions.

7.3. Size dependence of the magnetic properties of NiO-NP

The blocking temperature, T_P for non-interacting particles is expected to be proportional to the particle volume V in line with the observations for the coated particles. However, for $D < 10$ nm, T_P for the uncoated particles continues to increase with decrease in D due to interparticle interaction.

Unlike previous studies on NiO-NP, we were able to fit the M vs. H data for $T > T_P$ for most sizes with the modified Langevin function and determine μ_P and its (very weak) temperature dependence. Further analysis showed that μ_P is determined by a fraction f of the surface-layer spins, with f varying as $1/D$ such that for $D = 5$ nm, all the Ni^{2+} in the surface layer contribute a moment of $2.2 \mu_B$ to μ_P . Additionally, comparison of the data for the OA-coated and uncoated NP provided clear evidence for the presence (absence) of interparticle interaction in the uncoated (coated) nanoparticles. Finally, the decrease of the Néel temperature T_N with decrease in D , as expected for reduced dimensionality, was observed.

7.4. Hysteresis loop measurements of NiO-NP

We measured the hysteresis loops of NiO-NP at 5 K below the blocking temperature. The step-like features observed in the low-field regions of the hysteresis loops might be due to interparticle interaction since the features are quite reduced by OA coating. The temperature dependence of the hysteresis loop parameters (exchange bias, coercivity, remanence) for the different particles and the nature of the magnetic state for $T < T_P$ requires additional studies.

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