Chapter 8

Magnetization Behaviour of Nanostructured Nickel Oxide
8.1 Introduction

Magnetism of materials in the nanosize regime is of extreme importance due to potential applications in diverse fields such as high density recording media, ferrofluid technology, spin valves, magnetic resonance imaging, magnetocaloric refrigeration, etc.\(^1-^3\) When the crystallite sizes are of the order of a few nanometers, energy considerations favour the formation of single domain particles, which could exhibit unique properties such as superparamagnetism.\(^4-^5\)

Numerous reports on the modified magnetic properties of single domain particles of ferromagnetic materials including the metals Fe, Co and Ni, and alloys such as Ni-P and Fe-Co have appeared in literature over the years.\(^6-^13\) More recently, magnetic properties of fine particles of transition metal oxides such as NiO, \(\gamma\)-Fe\(_2\)O\(_3\), NiFe\(_2\)O\(_4\), CoFe\(_2\)O\(_4\) and MgFe\(_2\)O\(_4\) with antiferromagnetic ordering of magnetic spins have gained renewed interest due to their interesting properties such as superparamagnetism, enhanced magnetic moments and field reversal due to quantum tunneling.\(^14-^23\) The modified magnetic properties of these nanostructured magnetic oxides with localized exchange interactions exhibit strong dependence on the average grain size emphasizing the importance of surface atoms and surface-driven spin rearrangements in determining their magnetic response.\(^14-^23\) This chapter presents the size dependent magnetization behavior of nanostructured nickel oxide having different average grain sizes studied using vibrating sample magnetometer.
8.2 Experimental

For the study of the static magnetization behaviour, nanostructured nickel oxide samples of three different average grain sizes were used. For reference, sample codes together with the average grain sizes are listed in Table 8.1. Magnetic hysteresis of the samples up to a field of 16 kOe were recorded using a Vibrating Sample Magnetometer (VSM - 5S. TOEI Industry Co Japan) at room temperature (297 K).

Table 8.1. Sample codes assigned to nanostructured nickel oxide samples used for the magnetization measurements.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Average grain size (nm)</th>
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<tbody>
<tr>
<td>N1</td>
<td>2-3</td>
</tr>
<tr>
<td>N4</td>
<td>12-13</td>
</tr>
<tr>
<td>N6</td>
<td>18</td>
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8.3 Results

Magnetization curves of the nanostructured nickel oxide samples at room temperature are shown in Figures 8.1 (a) and (b). The hysteresis curve for sample N1, with the smallest average grain size of 2-3 nm, is ‘S’-shaped with very low coercivity, \( H_c = 193.6 \) Oe, which is characteristic of superparamagnetism. For this sample, the saturation magnetization, \( M_s \), of \( \sim 2.5 \) emu/g is reached at an applied field of \( \sim 5 \) kOe. For samples N4 and N6, with average particle sizes of 12-13nm and 18 nm respectively, the dependence of magnetization on applied field is markedly linear and saturation magnetization is not reached even at the maximum applied field of 16 kOe. More importantly, it may be noted from Figures 8.1 (a) and (b) that the magnetization of the samples N4 and N6 at 16 kOe are respectively \( \sim 0.2923 \) emu/g and
- 0.3316 emu/g, both of which are about one order of magnitude smaller than the saturation magnetization of the sample N1. Also, the samples N4 and N6 have low values of coercivity (124.5 and 131.4 Oe respectively) as for sample N1.

![Figure 8.1. Magnetic hysteresis at room temperature for (a) sample N1 and (b) samples N4 and N6.](image)

### 8.4 Discussion

At temperatures lower than the Neel temperature (573 K), single crystalline nickel oxide is an antiferromagnet, with the magnetic ordering resulting from the super exchange interactions in which the electronic wavefunctions of the magnetic Ni$^{2+}$ ions overlap with those of the intermediate nonmagnetic O$^{2-}$ ions. Neutron diffraction studies on nickel oxide single crystals concluded that the magnetic spins of neighboring Ni$^{2+}$ ions are antiparallel to each other and the magnetic structure can be visualized as a two sublattice model in which each magnetic sublattice is constituted by the next nearest neighboring Ni$^{2+}$ ions with their magnetic spins aligned in the same direction. For an infinite lattice, the magnetic moments of the two magnetic sublattices cancel each other resulting in antiferromagnetism. However, when crystal lattice extends only over a few nanometers, the surface to volume ratio has a large value and the
uncompensated magnetic spins associated with the surface atoms become significant and may give rise to a net magnetization. Thus, for nanostructured nickel oxide samples, such as in the present study, the magnetic properties may be expected to depend strongly on the average grain size.

As seen from Figure 8.1 (a), the hysteresis curve of sample N1, with an average grain size of 2–3 nm, is ‘S’-shaped with very small coercivity, \( H_c = 193.6 \text{ Oe} \), which is characteristic of a superparamagnet. This is in agreement with the observations of Schelle and Deetscreek who had reported a similar hysteresis behavior for nickel oxide nanoparticles with an average particle size of \( \sim 2.2 \text{ nm} \). Nonlinear least square fitting of the initial magnetization curve of sample N1 was carried out using the Langevin equation,

\[
M(H) = M_s \left[ \coth \left( \frac{\mu H}{k_B T} \right) - \frac{k_B T}{\mu H} \right]
\]

where \( M(H) \) is the magnetization for an applied field \( H \), \( M_s \) the saturation magnetization, \( \mu \) the uncompensated magnetic moment, \( k_B \) the Boltzmann’s constant and \( T \) the absolute temperature.

![Figure 8.2. Initial magnetization curve of sample N1. Points show the measured data and line shows the results of nonlinear least square fitting using Langevin function.](image)
From the result of the curve fitting procedure shown in Figure 8.2, the values of the saturation magnetization, $M_s$ and the uncompensated magnetic moment, $\mu$ are obtained respectively as 2.544 emu/g and $\sim 1.68 \times 10^{19} \text{ J/T} \approx 1.8 \times 10^4 \mu_B$, where $\mu_B$ is the Bohr magneton.

The uncompensated moment of $\sim 1.8 \times 10^4 \mu_B$, estimated for sample N1 is much larger than that reasonably expected from uncompensated surface spins for nanoparticles of an antiferromagnetic material with a two sublattice magnetic structure, particularly for small particles with diameters less than $\sim 10 \text{ nm}$. Makhlof et al. had reported an uncompensated moment of $\sim 2 \times 10^3 \mu_B$ for nanostructured nickel oxide sample with an average particle size of $\sim 5.3 \text{ nm}$. The uncompensated moment of $\sim 1.8 \times 10^4 \mu_B$ estimated for sample N1 in the present study is almost nine times larger than that reported for nickel oxide nanoparticles with an average particle size of $\sim 5.3 \text{ nm}$. Kodama et al., had shown that the anomalously large values of uncompensated magnetic moments exhibited by nanoparticles of antiferromagnetic transition metal oxides with exchange interactions such as nickel oxide, when the particle size falls below a critical size is a finite size effect and cannot be understood on the basis of the two sublattice model valid for the corresponding bulk samples. It was shown that such anomalously large moments may arise from the multisublattice magnetic structure of these nanostructures with the number of magnetic sublattices increasing with decrease in the average particle size. This multisublattice spin configuration directly follows from the exchange interactions between the magnetic ions and the low coordination at the surface sites of nanostructures resulting in a fundamental change in the magnetic ordering throughout the particle. Also, according to this model, the number of magnetic sublattices and hence the magnetic properties of these nanostructures depend strongly on parameters such as surface roughness and density of broken exchange bonds at the surface (broken bond density).

Kodama et al., had theoretically calculated the equilibrium spin configurations in nanostructured nickel oxide with different average particle sizes ranging from 1 to 5 nm and investigated the effect of surface roughness and the broken bond density on the
magnetic structure. In these calculations, the broken bond density and surface roughness values were varied in the ranges 0.5 to 0.8 and 2 to 4 Å respectively. These calculations had shown that in the case of particles with average size < ~ 5 nm, the number of magnetic sublattices was close to 8 and it approached 2 with increase in particle size. The size threshold for this behavior was found to depend strongly on the parameters of the surface, i.e. the broken bond density and surface roughness. The results of these calculations indicate that for nanostructured nickel oxide with average grain size in the range 2–3 nm, the number of magnetic sublattices lie in the range 7–8 for a reasonably wide range of values of the parameters that characterize the surface. Thus, it seems reasonable to infer that the anomalously large value of uncompensated magnetic moment for the present sample N1 is a direct consequence of the multisublattice magnetic structure.

The magnetization of samples N4 and N6 with larger average particle sizes of 12-13 nm and 18 nm respectively show a more or less linear dependence on the applied field (Figure 8.1. (b)). This observation is in good agreement with the results of Schuele and Deetscreek who had reported a linear dependence of magnetization on the applied field for nickel oxide nanoparticles with an average particle size of ~ 21 nm. Also, from the reports of Makhlouf et al. who had measured the magnetization curves of nanostructured nickel oxide samples having different average particle sizes ranging from ~ 5.3 to ~ 31.4 nm, it can be noted that with increase in particle size the magnetization curve becomes more and more linear. Moreover, Kilcoyne and Cywinski had reported the existence of a linear contribution to the magnetization in addition to the superparamagnetic contribution (Langevin) for the iron storage protein, 'ferritin', which consist of a spherical protein shell of external diameter 13 nm, surrounding an antiferromagnetic iron oxyhydroxide core of diameter 7 nm. This linear component of the magnetization of nanoparticles of antiferromagnetic materials, which becomes more prominent than the superparamagnetic component (Langevin) with increase in particle size, has been identified as due to superantiferromagnetism in which the intrinsic antiferromagnetic susceptibility of the nanoparticles is enhanced over that of the corresponding bulk material.
Figures 8.3 (a) and (b) show the initial magnetization curves for sample N4 and N6 respectively. Comparing with the initial magnetization curve for sample N1, which exhibits a field dependence defined by the Langevin function as expected for a superparamagnet (Figure 8.2), the magnetization for both N4 and N6 varies linearly with the applied field.

From these curves, the susceptibility, $\chi$, for N4 and N6 are estimated to be $\sim 21.8 \times 10^{-6}$ and $\sim 22.4 \times 10^{-6}$ emu/g respectively. It may be noted that the susceptibilities of N4 and N6, which are almost identical, are about three times the antiferromagnetic susceptibility of bulk nickel oxide at room temperature which is reported to be $\sim 8 \times 10^{-6}$ emu/g.\textsuperscript{35-38} This means that, at room temperature, the magnetization of the samples N4 (12-13 nm) and N6 (18 nm) is dominated by the superantiferromagnetic component. Also, Schuele and Deetscreek had reported susceptibility values of $\sim 14.2 \times 10^{-6}$ and $\sim 11.6 \times 10^{-6}$ emu/g at 295 K for nickel oxide nanoparticles with average particle sizes of $\sim 21.6$ nm and $\sim 34.5$ nm respectively.\textsuperscript{15} From the results of the present study, it may be concluded that at room temperature, nickel oxide
nanoparticles with average grain size larger than ~ 10 nm may exhibit superantiferromagnetism with the magnetization curves showing a linear dependence on the applied field and with susceptibility values larger in comparison with the antiferromagnetic susceptibility of bulk nickel oxide.

From the foregoing discussion, it is clear that at room temperature, the magnetic properties of nanostructured nickel oxide with average grain sizes ranging from 2-3 to 18 nm, differ markedly from those of the corresponding bulk. More importantly, the magnetic response of nanostructured nickel oxide changes remarkably when the average grain size decreases from 12-13 nm for sample N4 to 2-3 nm for sample N1. One immediate explanation for the observed size dependence of magnetic properties of nanostructured nickel oxide may be the possible difference in the concentrations of Ni\(^{3+}\) and metallic Ni in the three samples studied. However, a detailed study by Richardson et al had established that the effect of valency of Ni on the magnetic response of nanostructured nickel oxide samples is negligible. Thus it seems reasonable to attribute the observed size dependence of magnetic behavior of nanostructured nickel oxide to the variation of the volume fraction of surface atoms with average grain size.

In Chapters 3 and 4, it was observed that the dc and ac conductivities of nanostructured nickel oxide samples with average particle sizes ≤ 7 nm is much varied from those of their counterparts with average particle sizes ≥ 10 nm. Also, it was shown that the size dependent variation of both dc and ac electrical conductivities of nanostructured nickel oxide (average particle sizes ranging from 2-3 nm to 16-17 nm), which was not a linear one, could be semi-quantitatively explained on the basis of calculations assuming a 14 sided tetrakaidecahedron geometry for the nanocrystallites. The choice of this complex yet symmetric geometry for the nanocrystalites was based on the reported crystallographic studies, which had concluded that growth of the nickel oxide crystallites occur in the tetrakaidecahedron shape. The volume fractions of the total interfacial region, (\(V_{\text{ir}}\)), constituted by both grain boundaries and triple junctions for the nanostructured nickel oxide samples N1 (2-3 nm), N4 (12-13 nm) and N6 (18 nm) were calculated assuming the grains to have a regular 14 sided
tetrahexahedron shape using Equation (3.3) of Chapter 3. Figure 8.4 (a) shows the variation of the volume fractions of the total interfacial region, $V_{if}$, with average grain size for the three samples. Also, the variation of coercivity, $H_c$ and the magnetization corresponding to the maximum applied field (16 kOe) with average particle size for the three samples are plotted in Figure 8.4 (b).

Figure 8.4. Variation of (a) $V_{if}$ and (b) $H_c$ and M at $H = 16$ kOe with average grain size.

The total interfacial volume fraction is maximum for sample N1 with the smallest average grain size of 2-3 nm and it decreases as the grain size increases. From Figure 8.4 (a), it may be noted that the interfacial volume fractions for samples N4 (12-13 nm) and N6 (18 nm) are respectively ~21% and ~15%, which are of comparable magnitude. This accounts for the more or less similar magnetic response of samples N4 and N6. However, it may be noted that for sample N1, with an average grain size of 2–3 nm, the interfacial volume fraction is about ~78%, which is about 4 to 5 times larger than those for samples N4 and N6. Also, from Figures 8.4 (a) and (b), it is evident that the size dependent variation of coercivity, $H_c$, and the magnetization corresponding to the maximum applied field (16 kOe) for the three samples is more or less similar to the variation of $V_{if}$, with average grain size. Thus it can be seen that the very large increase in the surface area to volume ratio explains the tremendous change
in the magnetic response of nanostructured nickel oxide when the average grain size is reduced from 12-13 nm for sample N4 to 2–3 nm for sample N1. The remarkable change in the magnetization behavior of sample N1 in comparison with that of samples N4 and N6 emphasizes the importance of the surface atoms and surface driven spin rearrangements in determining the magnetic response of nanostructured nickel oxide.

8.5 Conclusion

Magnetic hysteresis of nanostructured nickel oxide having three different average grain sizes were recorded at room temperature. The magnetic properties of nickel oxide nanoparticles in this size range are markedly different from that of the corresponding bulk. It was observed that sample N1 with an average grain size of 2-3 nm was superparamagnetic with the magnetization curve defined by the Langevin function. Anomalously large uncompensated magnetic moment associated with this sample has been attributed to the multisublattice magnetic structure. Samples N4 (12-13 nm) and N6 (18 nm) exhibited superantiferromagnetism with the magnetization curves varying linearly with applied field and susceptibility values larger than that of single crystalline nickel oxide. The remarkable change in the magnetization behavior of the sample N1 in comparison with that of samples N4 and N6 emphasizes the importance of the surface atoms and surface driven spin rearrangements in determining the magnetic property of nanostructured nickel oxide.

8.6 References

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