Size-dependent magnetization fluctuations in NiO nanoparticles

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The finite size and surface roughness effects on the magnetization of NiO nanoparticles is investigated. A large magnetic moment arises for an antiferromagnetic nanoparticle due to these effects. The magnetic moment without the surface roughness has a non-monotonic and oscillatory dependence on $R$, the size of the particles, with the amplitude of the fluctuations varying linearly with $R$. The geometry of the particle also matters a lot in the calculation of the net magnetic moment. An oblate spheroid shape particle shows an increase in net magnetic moment by increasing oblateness of the particle. However, the magnetic moment values thus calculated are very small compared to the experimental values for various sizes, indicating that the bulk antiferromagnetic structure may not hold near the surface. We incorporate the surface roughness in two different ways; an ordered surface with surface spins inside a surface roughness shell aligned due to an internal field, and a disordered surface with randomly oriented spins inside surface roughness shell. Taking a variational approach we find that the core interaction strength is modified for nontrivial values of $\Delta$ which is a signature of multi-sublattice ordering for nanoparticles. The surface roughness scale $\Delta$ is also showing size dependent fluctuations, with an envelope decay $\Delta \sim R^{-1/5}$. The net magnetic moment values calculated using spheroidal shape and ordered surface are close to the experimental values for different sizes.

Keywords: Antiferromagnetics; Fine-particle systems; Magnetic properties of nanostructures.

1. Introduction

Antiferromagnetic nanoparticles have been receiving a refreshed research attention over the last few years. These are considered as better candidates for exhibiting the magnetization reversal by quantum tunneling due to their small magnetic moment as compared to the ferromagnetic nanoparticles. The magnetic properties of nanoparticles are dominated by finite-size effects, and the surface anomalies such as surface anisotropy and roughness. As the particle size decreases, the fraction of the spins lying on the surface of a nanoparticle increases, thus, making the surface play an important role. The reduced coordination of the surface spins causes a symmetry lowering locally, and leads to a surface anisotropy, that starts dominating as the particle size decreases. Thus, an enhancement of surface and interface effects make the antiferromagnetic nanoparticles an interesting area.
Nickel Oxide (NiO) has been considered as a prototype for antiferromagnetism, as it is one of the first few materials in which antiferromagnetism was studied. One of the first serious concerns with NiO nanoparticle was, evidenced from the experimental study of Richardson and Milligan, that these nanoparticles show a large magnetic moment as the size becomes smaller than 100nm, apart from anomalous behavior of the magnetic susceptibility. It was also found that the exchange coupling between the surface spins and the antiferromagnetic core spins causes an exchange bias phenomenon in these finite-sized particles. This phenomenon is responsible for the observed shifted hysteresis loop after field cooling in NiO nanoparticles. This interface effect is very much size dependent. A large loop shift (>10KOE) and coercivities at low temperature has been reported for the intermediate sized particles (22nm – 31nm).

Winkler et al. reported that for 3nm particles the magnetization curves are reversible above $T \sim 170K$, but a hysteresis behavior is observed at lower temperatures. According to their observation, a large surface anisotropy is responsible for the anomalies in the shape of the hysteresis loop at low temperatures. They found that with a decrease in the temperature, a progressive blocking of the core particle moments starts off, and it is followed by a growth of spin clusters at the particle’s surface below $40K$, and finally their collective freezing in a cluster glass-like state at $15K$.

The net magnetic moment of antiferromagnetic nanoparticles has been a subject of research interest from a long time. Néel in 1961 suggested that fine particles of antiferromagnetic materials exhibit weak ferromagnetism and superparamagnetism. He argued that the permanent magnetic moment in these antiferromagnetic fine particles is due to incomplete magnetic compensation between the atoms on the two sublattices ‘A’ and ‘B’, which are identical in every respect, except that the atomic moments in B sublattice are antiparallel to that in A sublattice. Néel considered three general cases as shown in Ref. 18. If the uncompensation of spins occurs randomly in a particle, then the number of uncompensated spins $p$ will vary as $p \sim n^{\frac{1}{2}}$, where $n$ is the number of spins. If the spins are arranged in such a way that the ordered structure consists of odd number of ferromagnetic planes of A and B atoms, then $p \sim n^{\frac{1}{2}}$. Finally, if each plane consists of equal numbers of A and B atoms and the structure consists of incomplete top and bottom planes, then we would have $p \sim n^{\frac{1}{2}}$. Richardson et al. showed that $p \sim n^{\frac{1}{2}}$ from the size dependence of susceptibility in NiO nanoparticles. Thus, according to the Néel’s model, the magnetic moment $\mu$ for NiO nanoparticles varies as $\mu \sim n^{\frac{1}{2}} \mu_{N}^{^{2+}}$. Weak ferromagnetism was later confirmed by experiments on fine particles of NiO. However, Tiwari et al. argued that the NiO nanoparticles behave like a superspin glass, which is attributed to a surface spin disorder. Some authors accredited the large magnetic moment in NiO nanoparticle to nonstoichiometry, an existence of
small superparamagnetic metallic nickel clusters in NiO particle or the presence of
$Ni^{3+}$ ions within the NiO lattice. However Richardson et al. confirmed that the
presence of $Ni^{3+}$ in NiO do not contribute significantly to the magnetic moment of
NiO nanoparticles. More recently Yi et al investigated the size dependent mag-
netic properties of NiO nanostructures using experimental and first principle study.
They reported that NiO clusters with a size upto 1nm indicate ferromagneticlike
interactions with high magnetizations, and NiO nanocrystals with a particle size
over 2nm possess uncompensated magnetization.

The magnetic moment per particle for NiO has been investigated experimentally
by Kodama et al. From extrapolation of 5K magnetization curves from a large
magnetic field to zero field, they found 700 $\mu_B$ per particle for particles of size
15nm, while the Néel’s two-sublattice model predicts a magnetic moment of
about 80 $\mu_B$. For the particles of size 3nm, Winkler et al experimentally found
the magnetic moment per particle to be 500 $\mu_B$, whereas for this particle size, the
Néel’s model predicts a magnetic moment of 20 $\mu_B$.

This discrepancy, between the magnetic moments experimentally observed and
those predicted by the Néel’s two-sublattice model has been a serious question from
a long time. Kodama et al. have shown from numerical modeling that a reduced
symmetry on the surface of the nanoparticle actually causes a fundamental change
in the magnetic order which results in a multi-sublattice structure. Monte Carlo
studies for antiferromagnetic nanoparticles by Ziani et al also reveals a distinct
magnetic role of surface and core spins. Recently it has been pointed out that the
roughness at the surface layer gives rise to higher magnetic response for the surface
spins than the core spins.

In view of these studies, we investigate the large magnetic moment in NiO
nanoparticle by invoking a different ordering for surface spins than the bulk Néel
state ordering for core spins.

The outline of the present manuscript is as follows: In Sect. 2 we discuss a model
for bulk NiO, followed by a discussion on the finite-size effect in the magnetization
of NiO nanoparticles using spherical as well as spheroidal geometries in Sect. 3. We
will discuss surface effects and ordering of surface spins beyond Néel state ordering
for nanoparticles in Sect. 4 and Sect. 5 is devoted to conclusions.

2. The model

The crystal structure of bulk NiO has been comprehensively investigated in the
literature using x-ray diffraction method. It has been found to be face centered
cubic (fcc), with a Néel temperature of 523K. Each Ni atom has twelve nearest
neighbors and six next-nearest neighbors. The lattice parameter has been found
28 to be 4.1758Å at 297K and 4.1705Å at $T \rightarrow 0$ K.

The magnetic structure of NiO has been well established to be fcc-II by the
work of Shull et al and further by Roth et al. The atomic spins are stacked ferromagnetically in (111) plane but aligned antiferromagnetically in $<111>$
Fig. 1. The magnetic configuration of bulk NiO where closed-packed ferromagnetic sheets of spins are stacked antiferromagnetically along the direction perpendicular to the sheet which is \( \langle 111 \rangle \) direction for bulk NiO. The yellow (white) spheres denote up spins and the blue (black) spheres denote down spins.

The direction of alignment of the spin moments has been found to be \( \langle 11\bar{2} \rangle \) directions. The magnetic configuration of bulk NiO is shown in Fig. 1.

The neutron diffraction studies by Hutchings et al.\textsuperscript{32} confirmed that the predominant interaction in NiO is a large next-nearest neighbor antiferromagnetic exchange interaction \( J_{nnn} = 221K \) linked by \( 180^0 \) superexchange path \( Ni^{2+} - O^{2-} - Ni^{2+} \). The nearest-neighbor interaction is linked by \( 90^0 \) path \( Ni^{2+} - O^{2-} - Ni^{2+} \), which is much smaller in strength. Due to the lattice contraction, there is a slight difference in the exchange interaction between the nearest neighbors in the plane, \( J_{nn}^- = 16.1K \), and between nearest neighbors out of the plane, \( J_{nn}^+ = 15.7K \). Hutchings et al.\textsuperscript{32} also used an orthorhombic form for the anisotropy \( E_i^A = K_1(\vec{s}_i \cdot \hat{x})^2 + K_2(\vec{s}_i \cdot \hat{z})^2 \) with \( \hat{x} \) is the easy axis direction \( \langle 112 \rangle \) and \( \hat{z} \) is the hard axis direction \( \langle 111 \rangle \), where \( \vec{s}_i \) is the atomic spin at site \( i \). The anisotropy constants are gives as \( K_1 = 1.13K \) and \( K_2 = .06K \). Since \( K_2 \) is much smaller than \( K_1 \), we use \( K_1 \) as anisotropy constant and \( \hat{z} \) as anisotropy axis.

The spins in the NiO interact via Heisenberg exchange interaction. The Hamil-
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Fig. 2. A portion of (111) plane of the bulk NiO is shown. A circle, whose centre is one of the lattice points itself is drawn. The circle shown is a cross section of NiO nanoparticle. The lattice points on the perimeter of the circle are highlighted. Some of the lattice points are lying just inside the perimeter and some just outside. These lattice points are responsible for the fluctuations.

The Hamiltonian of the system in the presence of an external magnetic field $H$ is

$$
\mathcal{H} = J_{nnn} \sum_{\langle ij \rangle} \vec{s}_i \cdot \vec{s}_j - J_{nn} \sum_{\langle ij \rangle} \vec{s}_i \cdot \vec{s}_j + J_{n+} \sum_{\langle ij \rangle} \vec{s}_i \cdot \vec{s}_j
$$

$$
- K_1 \sum_i (\vec{s}_i \cdot \hat{z})^2 - \vec{H} \cdot \sum_i \vec{s}_i. \tag{1}
$$

The first term represents the dominant antiferromagnetic next-nearest neighbor exchange energy. These next-nearest neighbors lie in the adjacent planes just above and just below the plane consisting the spin $s_i$, e.g. for each spin in the plane B in Fig. 1 three of the six next-nearest neighbors lie in plane A while other three lie in plane C. The second term represents the ferromagnetic nearest neighbor exchange energy which determines the interaction of $s_i$ with six of the twelve nearest neighboring spins lying in the same plane as spin $s_i$. The third term is antiferromagnetic nearest neighbor interaction energy which represents the antiferromagnetic interaction of $s_i$ with six nearest neighbors lying in the planes other than the plane containing spin $s_i$, e.g. each spin in the plane B, has three nearest neighbors in plane A and three in plane C. The fourth term represents the uniaxial anisotropy energy and the last term is the Zeeman energy.

The most dominant term in the above Hamiltonian is the first term which supports antiferromagnetic order. Thus, in the bulk we have a Néel state ordering where spins are stacked ferromagnetically in (111) plane but aligned antiferromagnetically in ⟨111⟩ directions. Though the Néel state in the bulk has zero magnetization, however, as the size of the particle becomes smaller, the Néel state ordering shows a
3. Finite-size effects in the Néel state

We consider various geometries for antiferromagnetic NiO nanoparticles. The crystal structure of NiO nanoparticles is the same as that of bulk NiO, except that the unit cell is slightly enlarged. The spherical geometry of NiO nanoparticle consists of circles stacked with decreasing radius on both sides of the equatorial great circle. These circles are circular cross-sections of (111) planes of NiO. The lattice sites in these circular planes are arranged in a triangular lattice structure. We show a part of a (111) plane in Fig. 2. The separation between two neighboring planes is \( \delta = 2a/ \sqrt{3} \), where \( a \) is the triangular lattice parameter which is related to the cubic lattice parameter \( a_0 \) as \( a = a_0/ \sqrt{3} \). These circular planes in a NiO nanoparticle are stacked in a sequence A-B-C-A-B-C \( \cdots \) as shown in Fig. 1, where A, B, C planes are distinguished from each other by a shift of their centers from the origin. We label 0, 1, 2 to the lattice points in the successive planes A, B, C. The position vectors of the center of planes A, B, C can be given (using cartesian unit vectors \( \hat{i}, \hat{j}, \hat{k} \)) as \( \vec{r}_0 = 0 \), \( \vec{r}_1 = a(\frac{1}{2} + \frac{1}{2\sqrt{3}} \hat{j}) \), and \( \vec{r}_2 = a(\frac{1}{2} - \frac{1}{2\sqrt{3}} \hat{j}) \) respectively. We can write the three-dimensional position vector of the lattice sites in \( l^{th} \) plane labelled by integers \( m, n \) and \( l \) (using the cartesian unit vectors \( \hat{i}, \hat{j}, \hat{k} \)) as

\[
\vec{r}_{mnl} = (m + \frac{n}{2})a\hat{i} + \frac{\sqrt{3}n}{2}a\hat{j} + l\delta\hat{k}. \tag{2}
\]
If $N_0$, $N_1$ and $N_2$ are the total number of lattice sites, counting from the planes of type A, B and C respectively, then the total number of lattice sites within a sphere of radius $R$ will be given as,

$$N_{\text{sphere}}(R) = \sum_{I=0}^{2} N_I(R), \quad (3)$$

where,

$$N_I(R) = \sum_{\vec{r}_{mn} \in I \mod 3} \Theta (R - |\vec{r}_{mn} - \vec{r}_I|), \quad (4)$$

$\Theta$ represents Heaviside step function and $\vec{r}_I$, ($I = 0, 1, 2$), has been discussed above. We transform the above equation using the Poisson sum formula as

$$N_I(R) = \frac{1}{a^3} \sum_{p,q,w} \int e^{2\pi i \left( x' p + y' q + z' w \right)} \times \Theta \left( R - |\vec{r}' - \vec{r}_I| \right) \, d^3 r'. \quad (5)$$

Thus, the total number of spins can be written as

$$N_{\text{sphere}}(R) = \frac{16\pi}{3} \left( \frac{R}{a_0} \right)^3 \sum_{I=0}^{2} \sum_{\{\vec{G}\}} \cos (\vec{G}, \vec{R}_I) \frac{j_1(GR)}{GR}, \quad (6)$$

where $\vec{G} = \frac{4\pi}{\sqrt{3}} \left[ p\frac{\sqrt{3}}{2} \hat{i} + (q - \frac{p}{2}) \hat{j} + \frac{w}{2\sqrt{2}} \hat{k} \right]$ is a three dimensional reciprocal lattice vector, labeled by three integers $p$, $q$ and $w$, and $\vec{R}_I = \vec{r}_I + I\delta \vec{k}$. $j_1$ is a spherical Bessel function of order one.

Due to the oscillatory behavior of the Bessel function, $N_{\text{sphere}}(R)$ varies non-monotonically with the particle size $R$, and the wavelength of oscillations goes as $1/G$. Thus, the longest wavelength mode $\vec{G} = 0$ in the above gives the smooth contribution as $N_{\text{sphere}}^{\text{Bulk}} = \frac{16\pi}{3} \left( \frac{R}{a_0} \right)^3$, while the terms with $\vec{G} \neq 0$ represent oscillatory fluctuations. The fluctuation $N_{\text{sphere}}^{\text{fluc}}$ in the total number of spins in the sphere of radius $R$ can be obtained from

$$N_{\text{sphere}} = N_{\text{sphere}}^{\text{Bulk}} + N_{\text{sphere}}^{\text{fluc}}. \quad (7)$$

From Eq. (6), and the asymptotic behavior of the spherical Bessel function, $j_1(x) \sim 1/x$, we can see that the amplitude of oscillatory fluctuations varies as,

$$N_{\text{sphere}}^{\text{fluc}} \sim R. \quad (8)$$

Hence the next to leading order term in the number of spins within a sphere goes as $R$ rather than $R^2$, which we could have expected from a random-walk argument, viz. the amplitude of the fluctuations is proportional to the square root of the the number of points on the boundary, here the spherical surface. The amplitude of
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The bulk two-sublattice Néel magnetic structure of NiO requires us to assign all the spins in a circular plane of the NiO nanoparticle to be either +1 or -1. Thus we assign the circular planes to be +1 and -1 alternately, corresponding to ferromagnetic sheets of spins with alternating polarization stacked along ⟨111⟩ direction in the FCC lattice. Since, we have three different types of circular planes, and the circular planes are stacked as A-B-C-A-B-C · · ·, as shown in Fig. 1, all the spins in each of A (or B or C) type of planes will have either +1 or -1 value depending on the location of the plane along the stacking direction. The total magnetic moment $M_{\text{sphere}}(R)$ of NiO spherical particles of size $R$ can be found by summing the magnetic moment of all the circular planes. Following Hutchings et al.,32 we assume that each $Nt^{2^+}$ spin has a magnetic moment of $2\mu_B$. Thus, we can write the total magnetic moment for the spherical particle as

$$M_{\text{sphere}}(R) = 2\mu_B \sum_{l=0}^{2} M_l(R),$$

(9)
where,

\[ M_I(R) = \sum_{R_{mnlt} \text{ odd}} (-1)^l \Theta (R - |\vec{r}_{mlt}|). \]  (10)

Applying the Poisson sum formula and proceeding analogously as we did above,

\[ M_I(R) = \frac{4}{3\sqrt{3}a_0^3} \sum_{\{\vec{g}, w\}} \cos (\vec{g} \cdot \vec{r}_I) \cos \left(\frac{2I\pi w}{3}\right) \int e^{i\vec{G} \cdot \vec{r}} e^{i\pi z \delta} \Theta (R - r') d^3 r', \]  (11)

we evaluate \( M_I(R) \) and thus the total magnetic moment in the units of Bohr magneton (\( \mu_B \)) as

\[ M_{\text{sphere}}(R) = \frac{32\pi}{3} \frac{R^2}{a_0^3} \sum_{l=0}^2 \sum_{\{\vec{g}, w\}} \cos (\vec{g} \cdot \vec{r}_I) \]
\[ \times \cos \left(\frac{2I\pi w}{3}\right) \left(G^2 + 3\pi^2 + 2\sqrt{3}\pi G_z\right)^{-\frac{1}{2}} \]
\[ \times j_1 \left\{ R \left(G^2 + 3\pi^2 + 2\sqrt{3}\pi G_z\right)^{\frac{1}{2}} \right\}, \]  (12)

where \( \vec{G} = \vec{g} + G_z \hat{k} \) and \( G_z = \frac{2\pi}{3} w \). The total magnetic moment \( M_{\text{sphere}} \) displays oscillations as a function of the particle size, and the wavelength of oscillations goes as \( 1/ (G^2 + 3\pi^2 + 2\sqrt{3}\pi G_z)^{\frac{1}{2}} \). Unlike \( N_{\text{sphere}} \), which had a smooth part (\( \vec{G} = 0 \)) and oscillatory terms (\( \vec{G} \neq 0 \)) (see Eq. (6)), all the terms in the above Eq. (12) for the total magnetic moment display oscillations. In fact, all the terms have a similar asymptotic behavior. Using the asymptotic behavior of the Bessel function, the amplitude of the fluctuations in \( M_{\text{sphere}} \) can be shown to vary as,

\[ M_{\text{sphere}} \sim R. \]  (13)

The contribution from the longest wavelength mode \( \vec{G} = 0 \) to the magnetic moment can be written as

\[ M_{\vec{G}=0} = \frac{32}{\sqrt{3}} \frac{\left(\frac{R}{a_0}\right)^2}{j_1 \left(\sqrt{3}\pi \frac{R}{a_0}\right)} \]  (14)

The terms with \( (\vec{G} \neq 0) \) represent the fluctuations in the total magnetic moment on various length scales. The magnetic moment, as obtained from Eq. (12) for the terms up to \( |\vec{G}| = 400 \) and as obtained from exact numerical counting is plotted with particle size in Fig. 4. We find that the net magnetic moment is not as large as seen from experiments. For example, for the particles of diameter 3nm, we find the magnetic moment to be \( 26\mu_B \), which is too small compared to experimental value \( 500\mu_B \). Also, for the particles of diameter 15nm, we find the magnetic moment to be \( 112\mu_B \), whereas experimental investigation reports \( 700\mu_B \). Thus,
a net magnetic moment due to Néel-state does not quantify the large magnetic moment experimentally observed in NiO nanoparticles.

In a realistic situation the shape of NiO nanoparticles is not a perfectly spherical. An oblate spheroid (with high oblateness) or a platelet-shaped geometries has been reported by experiments. Thus we again calculate magnetization for an spheroidal geometry of nanoparticles. The result of calculation for an oblate spheroid with polar radius $R/\epsilon$ and equatorial radius $R$, shown in the Appendix, is

$$M_{\text{spheroid}}(R) = \frac{32\pi}{3\epsilon} \frac{R^2}{a_0^3} \sum_{I=0}^{2} \sum_{(\tilde{g}, w)} \cos (\tilde{g} \cdot \tilde{r}_I) \times \cos \left( \frac{2I\pi w}{3} \left( G^2 + \frac{3\pi^2}{\epsilon^2} + 2\sqrt{3}\pi G_z \frac{\epsilon}{\epsilon} \right) \right)^{-\frac{1}{2}} \times j_1 \left( R \left( G^2 + \frac{3\pi^2}{\epsilon^2} + 2\sqrt{3}\pi G_z \frac{\epsilon}{\epsilon} \right)^{-\frac{1}{2}} \right),$$

and the magnetic moment for the longest wavelength mode $\tilde{G} = 0$ can be written as

$$M_{\tilde{G}=0} = \frac{32}{\sqrt{3}} \left( \frac{R}{a_0} \right)^2 j_1 \left( \frac{\sqrt{3}\pi R}{\epsilon a_0} \right).$$

Using this geometry, we find that the net magnetic moment value increases a little bit but again it is not comparable to experimental values. For 3nm particles, the magnetic moment improves to 34$\mu_B$ for $\epsilon = 2$; 40$\mu_B$ for $\epsilon = 3$; and 70$\mu_B$ for $\epsilon = 4$. These values are still very small as compared to experimental value 500$\mu_B$ for 3nm particles. Similarly, for the particles of diameter 15nm, we find the magnetic moment to be 153$\mu_B$ for $\epsilon = 2$, 258$\mu_B$ for $\epsilon = 3$, and 308$\mu_B$ for $\epsilon = 4$. Thus we see that increasing the oblateness increases the net magnetic moment of the nanoparticle. But the experimental value is still beyond our reach within the present model. In order to improve the model, we need to invoke a different ordering for surface spins than the bulk Néel-state ordering. We analyze the effects of roughness on the surface of nanoparticle and introduce a surface anisotropy and a ferromagnetic exchange interaction term for the surface spins in the Hamiltonian. The modified model is discussed in the following section and a variational approach is used to find the optimal thickness of surface roughness.

4. Surface effects and variational approach

The surface effects dominate the magnetic properties of nanoparticles. The breakdown of the dominant next-nearest neighbor antiferromagnetic interaction on the surface of the nanoparticle leads to uncompensated spins. These uncompensated spins play a vital role in determining the magnetic behavior of NiO nanoparticles. The magnetization reversal study for antiferromagnetic nanoparticles by Zianni et al.
al using Monte Carlo simulation also reveals a distinct magnetic role of surface and core spins. The broken bonds and defects at the surface layer gives rise to high magnetic response of the disordered surface spins than the core spins. This surface effect can be incorporated in two different ways; viz. an ordered surface with surface spins ordering owing to internal field due to core spins, and a disordered surface with spins oriented randomly at the surface which cancel out thus giving zero contribution to the total magnetic moment. Due to the surface roughness, the uncompensated surface spins can be more easily polarized by a small magnetic field.

For an ordered surface, we take that the spins inside a surface roughness shell of thickness $\Delta$ are aligned by a field due to a net core magnetic moment though small. This would enhance the net magnetic moment of nanoparticles. In this scenario, the core spins within a sphere of size $R - \Delta$ have the bulk antiferromagnetic structure, carrying a magnetic moment of order $R$, as we calculated in Sect. 3, and the spins within a shell of size $\Delta$ are all polarized, carrying a magnetic moment of order $R^2$.

For a nanoparticle of radius $R$, we can write the total magnetic moment $M_{\text{ordered}}(R, \Delta)$ as

$$M_{\text{ordered}}(R, \Delta) = \left| M_{\text{sphere}}(R - \Delta) \right| + 2\mu_B \left( N_{\text{sphere}}(R) - N_{\text{sphere}}(R - \Delta) \right).$$

In the above, the first term is due to the core Néel-state magnetic moment, and the second term represents the surface roughness effect. Here, the core spins within a sphere of radius $R - \Delta$ have the bulk magnetic structure. The spins within the shell of thickness $\Delta$ are aligned, each spin contributing a magnetic moment of $2\mu_B$. Since $M_{\text{sphere}}$ in the Eq. (17) goes as $R$ while surface roughness terms as a whole is proportional to $R^2$, the total magnetic moment has a leading term going as $R^2$, if the shell thickness is independent of the size.

We take a variational approach to establish the behavior of $\Delta$ with the particle size. In the variational approach, we modify the Hamiltonian (Eq. (1)) for nanoparticle, by including a ferromagnetic exchange interaction term $-J_s \sum_{\langle ij \rangle} \vec{s}_i \cdot \vec{s}_j$ with coefficient $J_s$ for spins lying in the roughness shell $\Delta$ and a ferromagnetic exchange interaction term like $-J_{cs} \sum_{i \in \text{core}, j \in \text{surface}} \vec{s}_i \cdot \vec{s}_j$ with coefficient $J_{cs}$ between core and surface spins lying at the interface of core and surface. Moreover we introduce surface anisotropy term $-K_s \sum_i (\vec{s}_i \cdot \hat{z})^2$ with coefficient $K_s$ for the surface spins which prevails over the uniaxial core anisotropy with coefficient $K_1$. Hence we can ignore the core anisotropy term. Taking all the interactions into account exactly, we can write energy of the system as

$$E(\Delta) = (\beta - \alpha)N_{\text{sphere}}(R - \Delta) - \beta N_{\text{sphere}}(R) - \sum_{i \in \text{core}, j \in \text{surface}} \langle \vec{s}_i \cdot \vec{s}_j \rangle,$$

where $\alpha = z_c + \frac{3J^+_{\text{nnn}}}{4J_{\text{nnn}}} + \frac{3J^-_{\text{nnn}}}{4J_{\text{nnn}}}$ and $\beta = z_s J_{\text{nnn}} + \frac{K_s}{J_{\text{nnn}}}$. $z_c$ and $z_s$ are the coordination numbers of core spins and surface spins. We use the value of $J_{cs}$ same as that of
Fig. 5. The surface roughness thickness $\Delta$ is plotted with the particle size. Dotted line shows the optimized $\Delta$ obtained from Eq. (18). The fluctuations in $\Delta/R$ show an envelope decay, $\Delta/R \sim 26R^{-6/5}$, shown as a solid line.

In the above equation, we find that the first term and the last term explicitly contain the variational parameter $\Delta$. The energy is minimized with respect to $\Delta$ to get the optimal thickness of the surface roughness shell. We choose the parameters to be $\alpha = 6.2a_0/R$ and $\beta = 6a_0/R$, such that we have a nontrivial $\Delta$ and the total magnetic moment per particle for an assembly of particles with lognormal distribution is close to the experimental value for the corresponding sizes. This indicates a modification in the core interaction strength in nanoparticles, which signifies a deviation from a two-sublattice ordering. For large enough sizes, $\Delta$ becomes zero and only contribution to the net magnetic moment is the first term in Eq. (17).

In Fig. 5 the optimal $\Delta/R$ which minimizes energy $E$ in Eq. (18) is plotted with particle size $R$. We find that $\Delta/R$ shows an oscillatory behavior and the amplitude of oscillations is decreasing with increasing particle size. The best fit of the curve shows that $\Delta \sim 26R^{-6/5}$. In Fig. 6 we have plotted net magnetic moment for corresponding particle sizes using Eq. (17). The total magnetic moment displays size-dependent fluctuations, whose amplitude shows a peak at $R \approx 12a_0$. Further increasing the size of the particle lowers the magnetization which occurs due to the lowering of the surface roughness effect i.e., less availability of ordered spins near surface. A similar behavior has been observed in experiments by Yi et al. where the magnetization of NiO powder increases with the annealing temperature (grain size) and shows a peak at an annealing temperature 170°C. Annealing at higher temperature than 170°C leads to a lower magnetization.

In the case of a disordered surface, we take a disordered spin structure inside the shell of thickness $\Delta$. In this situation, the net contribution from the disordered
surface will be zero and magnetic moment will solely be due to the core spins inside the sphere of radius $R - \Delta$.

$$M_{\text{disordered}} = M_{\text{sphere}}(R - \Delta).$$  \hfill (19)

Since $M_{\text{sphere}}$ shows nonmonotonic oscillatory dependence on particle size $R$, $M_{\text{disordered}}$ should also show the same behavior with particle size. In Fig. 7(a) we plot coarse-grained $M_{\text{disordered}}$ with particle size $R$ using spherical as well as spheroidal particles. Averaging is done over a window size of $2.8a_0$. In the same curve we have also shown ordered surface case. The net magnetic moment increases with increasing oblateness of the spheroidal nanoparticles. In the same Fig. 7(a) we have shown ordered surface case for both geometries, spherical ($\epsilon = 1$) and spheroidal with $\epsilon = 4$. In both the geometries, the coarse-grained magnetic moment shows nonmonotonic oscillating behavior as a function of the size. Though the peak value in spheroid case is more than the sphere, we see a sharp rise and fall of magnetic moment just before and just after the peak ($\approx 9a_0$) in spheroid case which is different than sphere where the magnetic moment slowly increases with particle size, a plateau is seen for intermediate range, and for bigger sizes it starts decreasing with size.

The systems of magnetic nanoparticles in experimental studies are in general polydisperse. The shape and size of the particles are not well known but the particle size distribution is often found to be lognormal. We consider the system consisting of lognormally distributed, widely dispersed nanoparticles, hence non interacting among each other. The weight of a given size (radius $R$) of nanoparticles is given...
by a lognormal distribution,

\[ P(R/a_0) = \frac{1}{\sigma(R/a_0)\sqrt{2\pi}} e^{-\frac{(\ln(R/a_0) - \mu)^2}{2\sigma^2}}. \] (20)

The characteristic parameters of the distribution are chosen to be \( \mu = \ln(\bar{R}/a_0) \) and \( \sigma = 0.5 \). Using this distribution, the magnetic moment for ordered-surface spherical nanoparticle of diameter 3nm works out to be 510\( \mu_B \) which is quite close to the experimental value 500\( \mu_B \). For the ordered-surface oblate spheroidal nanoparticle (oblateness \( \epsilon = 4 \)) of same size this value is 297\( \mu_B \), which is a little less than the experimental value. Using the same size distribution for disordered-surface spherical nanoparticle and spheroidal nanoparticle, we find net magnetic moment 18\( \mu_B \) and 40\( \mu_B \) respectively, which is very small as compared to experimental value. Similarly, for a distribution of particles with mean size 15nm, our calculation of net magnetic moment for ordered-surface spherical particle is 820\( \mu_B \), and for order-surface spheroidal particle is 703\( \mu_B \). For disordered case, calculated value for spherical and spheroidal geometries are 68\( \mu_B \) and 122\( \mu_B \), respectively. Thus for 15nm size particles, magnetic moment calculations using ordered surface and spheroidal geometry is very close to the experimental value 700\( \mu_B \). The experimental value of magnetic moment for 8.5nm particle size has also been shown in the Fig. 7(b). For a spherical particle magnetic moment has peak value around 12\( a_0 \) whereas for spheroid case it is around 9\( a_0 \). As we can see from Fig. 5, the surface roughness effect is stronger only for particles of intermediate sizes, which confirms the greater role of surface roughness for these sizes. But for the nanoparticles of sizes greater than 12\( a_0 \), the surface roughness shell \( \Delta \) becomes very small and a net magnetic moment arises largely due to the uncompensation of bulk Néel-state ordering which will tend to zero for large enough sizes showing the bulk character. Thus Fig. 7(b) reflects a trend for ordered surface particles, where the net magnetic moment is very small for smallest size particles. Increasing the size, magnetic moment increases and reaches a maximum due to the greater role of surface, and again decreases towards the bulk value. In the same figure Fig 7(b), we have shown total magnetic moment for a disordered case averaged over the same distribution as discussed above. The magnetic moment in disordered case is showing an increasing trend with particle size,
Fig. 7. (a) Coarse-grained magnetic moment versus particle size where coarse-graining is done over a window of size $2.8a_0$. (b) Averaged magnetic moment versus size where averaging is done over a lognormal size distribution, shown in Eq. (20), with a width of the distribution $\sigma = 0.5$. In both figures (a) and (b), two different cases ordered and disordered surfaces has been shown. For both cases two different geometries of nanoparticles, a sphere ($\epsilon = 1$) and a spheroid with $\epsilon = 4$ has been shown. An increase in oblateness $\epsilon$ results an enhanced magnetic moment in disordered case, but for ordered surface, magnetic moment for spheroidal particle is less than that of spherical particle.

but the value is small as compared to ordered case. The magnetic moment values calculated here depends on the model parameters the core interaction parameter $\alpha$, and the surface roughness parameter $\beta$, and the width of the size distribution $\sigma$. Adjusting these parameters for a given size distribution and varying oblateness leads to the net magnetic moment value comparable to the experimental values. Tuning of the parameters $\alpha$ and $\beta$ are directly related to the multi-sublattice ordering for nanoparticles as predicted by Kodama et al.3

5. Conclusions

We have investigated finite-size and surface roughness effects in NiO nanoparticles. We have found that the net magnetic moment due to finite-size fluctuations is nonmonotonic, oscillatory and proportional to the particle size $R$, hence magnetization goes as $1/R^2$. The geometry of the particle also plays an important role in net magnetic moment. An oblate spheroid shape particle shows an increase in net magnetic moment by increasing oblateness of the particle. The experimental magnetic moments for various sizes are quite large compared to the magnetic moments that arise as a finite-size fluctuation. The surface effects become very important in nanoparticles. We have incorporated surface effects in two different ways; an ordered surface where all the spins lying in the surface roughness shell are aligned due to internal field from the core spins, and a disordered surface where spins are randomly oriented in the surface roughness shell. Due to roughness of the surface and structural disorders, the uncompensated surface spins can be more easily deviated from
the antiferromagnetic alignment by a magnetic field. We have introduced a surface
anisotropy term and a ferromagnetic exchange interaction term for the surface spins,
and a ferromagnetic exchange interaction term between core and surface spins lying
at the interface of core and surface along with the bulk model in the Hamiltonian.
A variational approach has been taken to find the dependence of the shell thickness
on the size of particle. We have found that for nontrivial values of $\Delta$, the core in-
teraction strength is modified which shows a signature of multi-sublattice ordering
rather than two-sublattice ordering for smaller sizes. $\Delta$ is showing size dependent
fluctuations, with an envelope decay $\Delta \sim R^{-1/5}$. We have shown that the total
magnetic moment calculated with ordered as well as disordered surfaces displays
size dependent fluctuations. For an ordered surface case, smoothening these fluctu-
ations by a window-averaging, using a lognormal size distribution of nanoparticles,
results a magnetic moment per particle which is very close to observed experimen-
tal values of various sizes. We have also found that due to surface roughness effect,
the net magnetic moment shows a trend where magnetic moment is very small for
smallest size particles. Increasing the size, magnetic moment increases and reaches
a maximum at $R \sim 12a_0$ (depending upon the distribution of sizes and oblateness
of the particles), and again decreases towards the bulk value.

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Appendix A. Spheroidal nanoparticles

In this appendix, we calculate the total number of spins and net magnetic moment
of a nanoparticle using spheroid geometry with polar radius $R/\epsilon$ and equatorial
area $R$. We can write the three-dimensional position vector of the lattice sites in $l^{th}$
plane labelled by integers $m$, $n$ and $l$ is (using the cartesian unit vectors $\hat{i}, \hat{j}, \hat{k}$) as

$$\vec{r}_{mnl} = (m + \frac{n}{2})a\hat{i} + \frac{\sqrt{3}n}{2}a\hat{j} + l\delta\hat{k}. \quad (A.1)$$

The spheroidal geometry implies that only those spins whose locations satisfy $x^2 + $nnl + $\epsilon^2y^2nnl \leq R^2$, should be counted.

If $N_0$, $N_1$ and $N_2$ are the total number of lattice sites, counting from the planes
of type A, B and C respectively following section 3 then the total number of lattice
sites within a spheroid of equatorial radius $R$ will be given as,

$$N_{\text{spheroid}}(R) = \sum_{l=0}^{2} N_l(R), \quad (A.2)$$
where,
\[ N_I(R) = \sum_{l\equiv l(I\text{Mod}3)} \Theta \left( R^2 - (x_{mnl} - x_I)^2 - (y_{mnl} - y_I)^2 - \epsilon^2 z_{mnl}^2 \right), \quad (A.3) \]

and \( x_0 = 0, y_0 = 0; x_1 = a/2, y_1 = a/2\sqrt{3}; \) and \( x_2 = a/2, y_2 = -a/2\sqrt{3}. \) We transform the above equation using the Poisson sum formula as
\[ N_I(R) = \frac{1}{a^3} \sum_{p,q,w} \int e^{2\pi i (x'p + y'q + z'w)} \Theta \left( R - \sqrt{(x'_{mnl} - x_I)^2 - (y'_{mnl} - y_I)^2 - \epsilon^2 z_{mnl}^2} \right) dx' dy' dz'. \quad (A.4) \]

Thus, the total number of spins can be written as
\[ N_{\text{spheroid}}(R) = \frac{16\pi}{3} \left( \frac{R}{a_0} \right)^3 \sum_{l=0}^{2} \sum_{\{\vec{G}\}} \cos \left( \vec{G}.\vec{R}_I \right) \frac{j_1(\vec{G}R)}{GR}, \quad (A.5) \]

where \( \vec{G} = \frac{4\pi}{\sqrt{3}} \left[ p\frac{\sqrt{3}}{a} \hat{i} + q \hat{j} + w \frac{2\sqrt{3}}{a} \hat{k} \right] \) is a three dimensional reciprocal lattice vector, labeled by three integers \( p, q \) and \( w, \) and \( \vec{R}_I = \vec{r}_I + I\epsilon\hat{k}. \) \( j_1 \) is a spherical Bessel function of order one.

We can write the total magnetic moment for the ellipsoidal particle as
\[ M_{\text{spheroid}}(R) = 2\mu_B \sum_{l=0}^{2} M_I(R), \quad (A.6) \]

where,
\[ M_I(R) = \sum_{\vec{r}_{mnl} \text{Mod}3} (-1)^l \Theta(R_l), \quad (A.7) \]

and \( R_l = \sqrt{R^2 - l^2\delta^2 \epsilon^2}. \) Applying the Poisson sum formula and proceeding analogously as we did above, we calculate \( M_I(R) \) and thus the total magnetic moment in the units of Bohr magneton (\( \mu_B \)) as
\[ M_{\text{spheroid}}(R) = \frac{32\pi}{3 \epsilon} \left( \frac{R^2}{a_0} \right)^2 \sum_{l=0}^{2} \sum_{\{\vec{g},\vec{w}\}} \cos \left( \vec{g}.\vec{r}_I \right) \]
\[ \times \cos \left( \frac{2I\pi w}{3} \right) \left( G^2 + \frac{3\pi^2}{\epsilon^2} + 2\sqrt{3}\pi G_z \right)^{-\frac{1}{2}} \]
\[ \times j_1 \left( R \left( G^2 + \frac{3\pi^2}{\epsilon^2} + 2\sqrt{3}\pi G_z \right)^{\frac{1}{2}} \right), \quad (A.8) \]

where \( \vec{G} = \vec{g} + G_z \hat{k} \) and \( G_z = \frac{2\pi}{\sqrt{3}} w. \)

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