Effect of Distributed Particle Magnetic Moments on the Magnetization of NiO Nanoparticles

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Magnetization of nanoparticles of NiO are measured and analyzed taking into account a distribution in particle magnetic moment. We find that disregarding this distribution in the analysis is the reason for the many anomalous observations reported on this system in the literature.

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Studies on particles of a few nanometers in size have been attracting quite a lot of interest of late. For a physicist, the attraction is mainly due to the emergent properties that a particle or a collection of them shows when the particle size is made very small. According to Néel, tiny particles of an antiferromagnetic material exhibit magnetic properties such as superparamagnetism and weak ferromagnetism. If the surface to volume ratio, which varies as the reciprocal of particle size, of an antiferromagnetic particle is made sufficiently large then it can have a nonzero net magnetic moment because of an imperfect cancellation of elementary moments pointing in different directions near the surface of the particle. Recently, nanoparticles of antiferromagnetic materials have gained quite a lot of attention mainly because they show some surprising and unusual behavior unobservable in ferro or ferrimagnetic nanoparticles. Among different antiferromagnetic nanoparticles, NiO is a comparatively more interesting and well studied system. Long back, Richardson and Milligan reported magnetization measurements on NiO nanoparticles of different sizes and this has been followed by many more reports mostly by other workers. We also reported some work on NiO nanoparticles where we found that, at low temperatures, this system shows spin glass behavior. We also showed that the low temperature behavior of NiO nanoparticles is not superparamagnetic contrary to popular belief and expectation. After our work some other workers have also reached similar conclusions on NiO nanoparticles independently.

The magnetization of antiferromagnetic nanoparticles is expected to be described by a modified Langevin function. However, fitting the magnetization data of bare antiferromagnetic NiO nanoparticles as a function of magnetic field to the modified Langevin function results in unphysical fit parameters. For instance, the estimated particle magnetic moment turns out to be about 2000 $\mu_B$ for 5.3 nm particles. Such values for the particle magnetic moments are much larger than the expected value of about a few hundred Bohr magnetons from uncompensated spins on the surface of particles. Another method for the estimation of particle magnetic moment of NiO nanoparticles has also been used. Here the value of saturation magnetization at low temperature is divided by the estimated number of particles to get the particle magnetic moment. However, the moment estimated by this method has also been found to be larger than the expected value. A multisublattice model has been proposed to explain this large value of particle magnetic moment for NiO nanoparticles though there is no experimental support for this model yet.

The magnetization of nanoparticles of magnetic materials is expected to be only a function of the applied magnetic field $B$ and temperature $T$ and should scale with $T$ above the bifurcation temperature ($T_{bf}$) between low field cooled and zero field cooled magnetization. The magnetization of NiO nanoparticles is not found to show this scaling. These observations motivated us to revisit the antiferromagnetic NiO nanoparticles system once again. This work is an attempt to find the reason for getting unphysical numbers for the particle magnetic moment of NiO nanoparticles when the traditional methods are used to analyze the magnetization data above $T_{bf}$. The value of the bifurcation temperature $T_{bf}$ for the present system is about 295 K in 100 G applied magnetic field.

Here we present the magnetization measurements on 5 nm bare NiO particles as a function of applied magnetic field at sufficiently high temperatures, but well below the Néel temperature ($T_N$) of the system which is known to be about 523 K. We analyzed the data using the modified Langevin function without considering any distribution in particle magnetic moment and then repeated the analysis taking into account a distribution in the particle moment. We were pleasantly surprised by the results as it turned out that we can account for the anomalous observations reported on this system by the earlier workers.

NiO nanoparticles were prepared by a sol-gel method by reacting in aqueous solution nickel nitrate and sodium...
hydroxide at pH = 12 at room temperature as described elsewhere. We used nickel (II) nitrate hexahydrate (99.999%), sodium hydroxide pellets (99.99%), both from Aldrich, and triple distilled water to make nickel hydroxide. The sample of nickel oxide nanoparticles was prepared by heating the nickel hydroxide at 523 K for 3 hours in flowing helium gas (99.995%). The sample was characterized by x-ray diffraction and transmission electron microscopy. The average crystallite size as well as the particle size were found to be about 5 nm. The details of sample synthesis and structural characterization have been reported in one of our earlier works. All the magnetic measurements were done with a commercial SQUID magnetometer (Quantum Design, MPMS XL5).

We measured the magnetization $M$ of the 5 nm NiO particles as a function of external applied magnetic field $B$ at different temperatures $T$ ($T_{bd} < T < T_N$). These measurements are shown in Figure 1. Solid lines show fits to Equation (2). The inset shows a magnified view of the data along with the fits at lower magnetic fields which makes it clear that the fit quality is poor there.

![Figure 1](image-url)

**Figure 1:** (Color online) Magnetization as a function of applied magnetic field for 5 nm NiO particles at different temperatures. Solid lines show fits to Equation (2). The inset shows a magnified view of the data along with the fits at lower magnetic fields which makes it clear that the fit quality is poor there.

From Figure 1 we see that the fits to Equation (2) more or less pass through the measured data points which means the fit quality is quite good. A statistical measure of the goodness of a fit is the coefficient of determination $R^2$. The closer $R^2$ is to unity the better the fit. Values of the coefficient of determination $R^2$ for the fits are shown in Table I along with the fit parameters. The $R^2$ values are greater than 0.999 in all cases and this once again confirms the good quality of the fits.

From Table I we see that the particle magnetic moment $\mu_p$ is about two thousand Bohr magnetons and it decreases with increasing temperature. Somewhat similar results have been reported by others on NiO nanoparticles as well as on NiO nanorods. However there is a glaring inconsistency between the numbers we get for $M_0$ and $\mu_p$. In Equation (2) the fit parameters $M_0$ and $\mu_p$ should be related as $M_0 = N\mu_p$ where $N$ is the number of particles per unit mass of the sample. If we use this relation to estimate the average particle magnetic moment $\mu_p$ it turns out to be about 60 $\mu_B$ at 320 K which is very small compared to the value of $\mu_p$ presented in Table I. This fact invalidates the fit of experimental data to Equation (2). In the next paragraph we shall give another argument against the numbers presented in Table I.

Néel had discussed various ways by which a magnetic moment can appear on an NiO particles due to incomplete compensation of atomic moments in different sublattices. According to Néel the particle magnetic moment

\begin{equation}
M = M_0 L(x),
\end{equation}

where $L(x) = \text{coth}(x) - \frac{x}{4}$ is the Langevin function and $x = \frac{\mu_p B}{k_B T}$. Here $M_0$ is the saturation magnetization, $\mu_p$ is the particle magnetic moment and $k_B$ is the Boltzmann constant. However, magnetization of small particles of antiferromagnetic materials, even though they are superparamagnetic cannot be described by Equation (1). Rather, they are well described by an altered form known as the modified Langevin function, which contains an extra linear term in $B$ i.e.

\begin{equation}
M = M_0 L(x) + \chi_a B,
\end{equation}

where $\chi_a$ is the susceptibility of randomly oriented antiferromagnetic particle cores. We fitted the data shown in Figure 1 to the above equation and the resulting fits are shown as solid lines in the figure. Values of fit parameters $M_0$, $\mu_p$ and $\chi_a$ obtained are presented in Table I.

**Table I: Values of fit parameters $M_0$, $\mu_p$ and $\chi_a$ to Equation (2) and the corresponding values of the goodness of fit parameter $R^2$ for the 5 nm NiO nanoparticles at different temperatures.**

| $T$ (K) | $M_0$ (emu/g) | $\mu_p$ (µB) | $\chi_a$ (10^{-6} emu/g Oe) | $R^2$ |
|---------|--------------|--------------|------------------|------|
| 310     | 1.30         | 1967         | 34               | 0.9993 |
| 320     | 1.18         | 1841         | 32               | 0.9994 |
| 330     | 1.05         | 1825         | 31               | 0.9995 |
| 340     | 0.94         | 1734         | 29               | 0.9996 |
| 350     | 0.82         | 1621         | 27               | 0.9997 |

We use this relation to estimate the average particle magnetic moment $\mu_p$.

\[ \mu_p = \frac{M_0}{L(x)} \]
moment of an NiO nanoparticle can be written as

\[ \mu_p = p \mu_A \mu_B. \]  

(3)

Here \( p \) is a number which depends on the size, crystal structure and form or shape of the particle and \( \mu_A \) is the magnetic moment of \( \text{Ni}^{2+} \) ion which is known to be 3.2 \( \mu_B \) [17]. Néel proposed a total of five different possibilities for the origin of magnetic moment on an NiO particle of approximately cubic shape. Out of the five, two possibilities give the values of particle magnetic moment to be zero corresponding to \( p = 0 \). The other three possible values of \( p \) are about \( n^{\uparrow} \), \( n^\downarrow \) and \( n^{\pm} \) where \( n \) is the number of \( \text{Ni}^{2+} \) ions in the particle. Now, there can be many other possible set of values of \( p \) corresponding to shapes such as spheres, tetrahedrons or, more realistically, irregular shapes. But it seems safe to assume that the upper limit of \( p \) will be about \( n^{\uparrow} \) and the average will be considerably less. Making use of the fact that the crystal structure of NiO is face centered cubic with lattice constant 4.176 Å, the value of \( n \) for a 5 nm diameter spherical particle turns out to be about 3592. Using the information presented above along with Equation (3) we get the particle magnetic moment to be about 49 \( \mu_B \), 191 \( \mu_B \) and 750 \( \mu_B \) corresponding to \( p \) values of \( n^{\uparrow} \), \( n^\downarrow \) and \( n^{\pm} \) respectively. Thus according to Néel’s picture the maximum possible value of particle magnetic moment for a 5 nm NiO particle would be about 750 \( \mu_B \) which is much smaller than the values shown in Table II.

While using Equation (2) to fit the magnetization data we made a tacit assumption that all the particles have the same magnetic moment. But, this is not true. A sample of NiO nanoparticles has a distribution of particle magnetic moments not only due to distribution in size and shape but also due to the way in which the imbalance of spins arises in the particle as pointed out by Néel. We hazard the guess that disregarding the distribution in particle moments is perhaps the reason for the unphysical fit parameters obtained in Table I. Now we would like to carry out this fitting taking into account a moment distribution. Making our path easier is a precedent in this kind of analysis set by Silva et. al. in analyzing the magnetization of ferritin, a biological antiferromagnetic nanoparticle system [15].

In a sample that has a distribution in particle magnetic moments the low field magnetization is governed by the particles with larger magnetic moments. The contribution of particles of lower magnetic moments to the magnetization becomes important only at higher applied fields where the high field forces the moments to align with the field. The effect of a distribution in the particle magnetic moment on the magnetization of the system will show up in the Langevin or modified Langevin fit. To see this dependence let us take a look at the comparison of the measured magnetization to the modified Langevin fit at low fields in the inset of Figure 1. It is clear that the fits are no good at low fields while from the main panel one can see that the situation is much better at higher fields. This low field misfit is an indication of the role a distribution in the particle magnetic moment plays on the magnetization of a system. In this case the modified Langevin function has clearly underestimated the contribution of the larger moments.

Following Silva et. al. we assume that in a sample of nanoparticles the distribution in particle magnetic moment, \( \mu \), can be described by a log normal distribution function of the form [18]

\[ f(\mu) = \frac{1}{\mu s \sqrt{2\pi}} \exp \left(-\frac{[\ln(\frac{\mu}{\mu_0})]^2}{2s^2}\right), \]  

(4)

where \( n \) and \( s \) are parameters that characterize the distribution. The mean particle magnetic moment \( \mu_{\text{mean}} \) is equal to \( n\sqrt{\text{e}^{s^2}} \). Now, Equation (2) takes on the new form

\[ M(B, T) = N \int_0^\infty \mu L(x) f(\mu) d\mu + \chi_a B, \]  

(5)

where \( N \) is the total number of particles contributing to magnetization and \( L(x) \) is the Langevin function with \( x = \frac{\mu_B}{\mu_0} \). We used this equation to fit the magnetization data of Figure 1 and the fit parameters thus obtained along with the values of coefficient of determination \( R^2 \) are shown in Table II.

We see in Table II that the values of the coefficient of determination \( R^2 \) are surprisingly greater than 0.99999 in all the cases. These values of \( R^2 \) are much better than the values of the same shown in Table I. This means that the quality of the fits using Equation (5) is much better than that using Equation (2). In Figure 4 we show the new fits which clearly look good. The inset clearly shows that the fits are very good for lower values of applied magnetic fields also where the effect of distribution in the particle magnetic moment on the magnetization of the system is important as already discussed. We can now conclude that the fits of the magnetization data to Equation (5) are much better than that to Equation (2).

From Table II we find that the mean particle magnetic moments, which are equal to \( n\sqrt{\text{e}^{s^2}} \), turns out to

| \( T \) (K) | \( N \) \( (10^{12}) \) | \( s \) (\( \mu_B \)) | \( n \) (\( \mu_B \)) | \( \chi_a (10^{-6}) \) (emu/g Oe) | \( \mu_{\text{mean}} \) (\( \mu_B \)) | \( R^2 \) |
|--------|-----------------|-------------|---------|----------------|------------------|------|
| 310    | 8.7             | 1.34        | 116.5   | 21.4           | 287              | 0.999997 |
| 320    | 7.3             | 1.30        | 130.3   | 21.4           | 305              | 0.999998 |
| 330    | 6.5             | 1.27        | 136.8   | 20.9           | 308              | 0.999997 |
| 340    | 6.9             | 1.28        | 118.9   | 19.8           | 271              | 0.999998 |
| 350    | 6.8             | 1.26        | 114.4   | 18.9           | 254              | 0.999998 |
be about a few hundred Bohr magnetons, rather than a few thousand Bohr magnetons as found in the earlier fit, and are also well below the maximum possible value of about 750 $\mu_B$ according to the models proposed by Néel for the origin of magnetic moment in NiO particles.

In conclusion, we reported magnetization as a function of applied magnetic field for 5 nm NiO particles at different temperatures above the bifurcation temperature $T_{bf}$. Fitting the magnetization data to the modified Langevin function without considering any distribution in the particle magnetic moments yields very large and unphysical values for the particle magnetic moment. However we got reasonable values for the particle magnetic moment if the modified Langevin function is used to fit the magnetization data taking into account a distribution in the particle magnetic moment. The distribution in the particle magnetic moment arises from a distribution in particle size and form. This work clearly shows that the non consideration of a distribution in particle magnetic moment could be the reason for the anomalously large values of magnetic moment of NiO nanoparticles reported in the literature.

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