Spin glass behavior of gelatin coated NiO nanoparticles

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We report magnetic studies on gelatin coated NiO nanoparticles of average size 7 nm. Temperature and time dependence of dc magnetization, wait time dependence of magnetic relaxation (aging), memory effects in the dc magnetization and frequency dependence of ac susceptibility have been investigated. We observe that the magnetic behavior of coated NiO nanoparticles differs substantially from that of bare nanoparticles. The magnetic moment of the coated particles is highly enhanced and the ZFC magnetization data displays a sharp peak \((T_{p1} \approx 15 \text{ K})\) at a low temperature in addition to a usual high temperature peak \((T_{p2} \approx 170 \text{ K})\). We observe that this system exhibits various features characteristic of spin glass like behavior and \(T_{p2}\) corresponds to the average freezing temperature. We argue that this behavior is due to surface spin freezing within a particle. The nature of the low temperature peak is however ambiguous, as below \(T_{p1}\) some features observed are characteristic of superparamagnetic blocking while some other features correspond to spin glass like behavior.

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I. INTRODUCTION

There has been a renewed interest in magnetic nanoparticles in the past several decades because of the promise of various possible technological applications they hold as well as from the perspective of fundamental understanding. Below a certain size, a ferromagnetic particle consists of a single domain and behaves as a giant magnetic moment. Néel proposed that just as a ferromagnetic particle, a tiny antiferromagnetic particle can also develop a net magnetic moment due to uncompensated spins at its surface. The behavior of an ensemble of non-interacting particle moments is expected to be superparamagnetic. On the other hand if the particles interact with each other they can give rise to superspin glass behavior. Further, surface effects are also important in nanoparticles because of their large surface-to-volume ratio. For instance it has been shown recently that spin glass behavior can arise within an individual nanoparticle due to the freezing of spins at its surface.

Nickel oxide (NiO) is an antiferromagnetic material with Néel temperature \((T_N)\) 523 K. There have been a large number of studies on NiO nanoparticles and indeed it is the most well studied among the antiferromagnetic nanoparticles. These studies include temperature dependence of dc and ac susceptibility, their field and frequency dependence, hysteresis and exchange bias, time dependence of magnetization and related dynamic effects. Certain features shown by NiO nanoparticles are characteristic of both superparamagnetism and spin glass behavior viz. a bifurcation in FC and ZFC magnetization, a peak in ZFC magnetization and slow magnetic relaxation. As a result there have been claims of superparamagnetism as well as spin glass behavior in this system. However, it has been shown that the temperature dependence of magnetization of this system above the bifurcation temperature cannot be described by the Langevin function or a modified version of the same tailored for antiferromagnetic particles. We note that this is contrary to what is expected of a superparamagnetic system.

Below the bifurcation temperature, spin glass or spin glass like features have been observed in this system. In a recent paper, we reported aging and memory effects in bare NiO nanoparticles and the results show that this system indeed shows spin glass like behavior. Tiwari et al. have argued that such behavior arises due to freezing of surface spins on individual particles as the interactions between the particles are too weak to give rise to the observed large freezing temperatures. The origin of spin glass behavior in NiO nanoparticles is still somewhat controversial as there is no universal agreement on whether it is due to interparticle interactions or due to surface spin frustration within individual particles. A possible way to settle this issue would be through a study of the magnetic behavior of non-interacting particles. We can reduce the inter-particle interactions by increasing the distance between them. One way of doing this would be to coat the particles or disperse them in some medium. There have been some works on coated and dispersed NiO nanoparticles and nanorods and widely varying results have been reported. In these works, the upper broad peak is generally associated with superparamagnetic blocking. Further it has been observed that the coating tends to decrease the interactions which manifests as a lowering of the blocking temperature. Another sharp peak at a much lower temperature is seen in some reports and the origin of this peak has not been accounted for in most of the works. However some authors...
Figure 1: XRD pattern of the sample heated at 350°C for 15 hours. All the peaks correspond to those of NiO.

The XRD pattern of the sample shown in Figure 1 corresponds to that of pure NiO which has FCC structure. The average particle size was estimated to be 7 nm from the width of XRD peaks (111), (200) and (220) using the Scherrer formula. TEM image of the sample is shown in Figure 2 and the insets (a) and (b) of this figure show the particle size distribution and the selected area diffraction (SAD) pattern. It can be seen that the particles are more or less of spherical shape and the particle size was estimated to be 9.3 nm with a standard deviation 2.8 nm. The SAD pattern consists of concentric diffraction rings with different radii. The diameter of a diffraction ring in the SAD pattern is proportional to \( \sqrt{h^2 + k^2 + l^2} \), where \((hkl)\) are the Miller indices of the planes corresponding to the ring. Counting the rings from the center 1st, 2nd, 3rd, 4th and 5th rings correspond to (111), (200), (220), (311) and (222) planes respectively, as would be expected in the case of a material with FCC crystal structure.

### II. EXPERIMENTAL DETAILS

Gelatin coated NiO nanoparticles are prepared by a sol gel method as described in detail by Meneses et al.\(^26\). In brief, 2.5 g of gelatin was dissolved in 100 ml distilled water while stirring continuously at 60°C. 100 ml of aqueous solution of 2.5 g of NiCl\(_2\).6H\(_2\)O (99.99%) was added at the same temperature to the above solution. An aqueous solution of NaOH was added to this mixture till the pH became 12. This mixture was then cooled at room temperature to form a gel, which was heated at 80°C for 36 hours to obtain a precursor. Nickel oxide nanoparticles were prepared by heating this precursor at 350°C for 24 hours. The sample was characterized by X-ray diffraction (XRD) using a Seifert diffractometer with Cu Kα radiation and Transmission electron microscopy (TEM) using FEI Tecnai 20 U Twin Transmission Electron Microscope. The percentage of gelatin by mass was estimated using thermo-gravimetric analysis (TGA) to be 42% and the average thickness of gelatin shell estimated turned out to be 5 nm. All the magnetic measurements were done with a SQUID magnetometer (Quantum Design, MPMS XL5).

### III. RESULTS AND DISCUSSION

#### A. Particle size

To further complicate matters, some authors observe only the low temperature peak with the upper broad peak missing in coated particles and in one report this peak has been seen even in a bulk sample.\(^7,16\) We, therefore, felt that it will be worth our while to carry out a systematic study on the magnetic behavior of coated NiO nanoparticles to clear the air.

#### B. Temperature and field dependence of magnetization

The temperature dependence of magnetization is done under field cooled (FC) and zero field cooled (ZFC) protocols at 100 Oe. See Figure 3. It can be seen that...
the FC and ZFC magnetization curves bifurcate slightly below 300 K and the magnetization data taken during heating (FCW) and that taken while cooling (FCC) in the FC protocol are essentially the same. Further it can be observed that there are two peaks in the ZFC magnetization; the first ($T_{p1}$) is a sharp one at about 14 K and the second ($T_{p2}$) is a broad one around 170 K. The FC magnetization shows a steep low temperature rise starting at about 30 K and keeps on rising till the lowest temperature of measurement, a characteristic feature seen in superparamagnets.

In bare nanoparticles, usually a single broad peak, corresponding to $T_{p2}$, is observed in the magnetization vs. temperature plot. However, there are some reports on bare, dispersed and coated nanoparticles where two peaks have been observed. Some workers report a single peak at low temperature in coated nanoparticles with the upper broad peak missing and to confound matters even further, some authors have observed $T_{p1}$ even in bulk samples. Winkler et al. have observed two peaks in ZFC magnetization for NiO nanoparticles of size 3 nm; occurring at 17 K and 70 K for bare particles and at 15 K and 60 K for dispersed particles. They found that the high temperature peak in the $ac$ susceptibility data follows the Arrhenius law like superparamagnets while the lower peak follows a power law similar to spin glasses. Further the shape of virgin curve in the hysteresis loop below the low temperature peak is S-shaped, a feature seen in canonical spin glasses while well above the lower peak temperature, this feature is absent. Thus they associate the upper peak with superparamagnetic blocking of core moments and the lower peak to surface spin glass freezing. However Tiwari et al. have reported a single broad peak in the ZFC magnetization as well as in $ac$ susceptibility in 5 nm bare nanoparticles at about 150 K and they have shown that the system shows spin glass features. For instance, the value of relative shift of $ac$ susceptibility peak per decade of frequency lies in a range expected for spin glasses, field dependence of peak temperature follows Almeida-Thouless (AT) line and the high field data obeys $dc$ scaling law for spin glasses.

We carried out hysteresis measurements in the field range $-2.2$ kOe to $+2.2$ kOe at temperatures 10 K and 100 K. The results are shown in the inset of Figure 3 and it can be seen that the system shows hysteresis at both 10 K and 100 K with a larger coercivity at 10 K. In contrast to what Winkler et al. got, the virgin curve in this case is not S-shaped either at 10 K or at 100 K. An S-shaped virgin curve is a feature observed in canonical spin glasses, but we do not see it in our system.

To investigate the field dependence of ZFC magnetization, we carried out experiments at various fields in the field range 100 Oe to 10 kOe. These data are shown in Figures 4 and 5. It can be observed that both the peaks ($T_{p1}$ and $T_{p2}$) shift to lower temperatures with increasing field; the dependence being weaker for the lower peak. $T_{p2}$ disappears above an applied field of 750 Oe while $T_{p1}$ disappears only above 2 kOe. For superparamagnets the field dependence of peak temperature, $T_p$, is expected to be given by

$$T_p \propto V \left(1 - \frac{H}{H_K}\right)^2, \quad 0 \leq H \leq H_K$$

(1)

where $V$ is the volume of a particle and $H_K$ is a positive constant depending on anisotropy of the system. Coming to the case of spin glasses we note that the stability limit of spin glasses is defined by the AT line in the $H-T$ phase diagram, below which the spin glass state is stable. Indeed in many spin glass systems, the field dependence of peak temperature is known to follow the AT line given by the equation.
where \( T_f \) is the spin glass transition temperature in zero applied field. Thus, in a superparamagnetic system \( T_p^2 \) should be linearly related to \( H \) whereas in spin glasses \( T_p \) should decrease linearly with \( H^{1/2} \). In the insets of Figures 4 and 5 we show the plots of \( T_p \) vs \( H^{1/2} \) and \( T_p^2 \) vs \( H \) for both peaks. The goodness of the fits can be judged by the coefficient of determination \( (R^2) \) which are shown in the corresponding plots. It can be seen that for the lower peak the superparamagnetic fit is better while for the upper peak, the AT line fit is better. Thus from these experiments, one can hazard the guess that the lower peak arises due to superparamagnetic blocking while the upper one corresponds to spin glass behavior.

We note that the broad peak, \( T_{p2} \), in coated nanoparticles appears at about 170 K at low field (Figure 6) which is quite close to the corresponding value 150 K seen in bare particles of comparable size as reported by Tiwari et al.\(^6\) Apparently interparticle interactions have little influence on \( T_{p2} \) and thus cannot be contributing to spin glass behavior. Indeed Tiwari et al. estimate that the dipolar interactions between bare particles can give rise to freezing temperatures at most a few Kelvins.\(^6\) Thus we conclude that in NiO nanoparticles, whether bare or coated, the interparticle interactions are quite small and cannot give rise to spin glass like behavior.

\[
H \propto \left(1 - \frac{T_p}{T_f}\right)^{\frac{3}{2}}, \quad 0 \leq T_p \leq T_f
\]  

(2)

Figure 5: (Color online) Field dependence of ZFC magnetization data for various fields at higher temperatures in the vicinity of \( T_{p2} \). Insets show plots of (a) \( T_{p2}^{1/2} \) vs \( H \) and (b) \( T_{p2} \) vs \( H^{1/2} \).

Figure 6: (Color online) Temperature dependence of the real part of ac susceptibility for various frequencies with an ac field of 3 Oe. Insets: (a) Temperature dependence of the imaginary part of the susceptibility. (b) A magnified view of low temperature peak of real part shown in the main panel. Lines have been drawn to guide the eyes.

C. Particle moment

Néel proposed that small particles of antiferromagnetic materials can possess a net magnetic moment due to incomplete compensation of spins between atoms on two sublattices.\(^{25}\) The number of uncompensated spins, \( p \), is roughly proportional to \( n^x \) where \( n \) is the total number of atoms in the particle and \( x \) can be 1/3, 1/2 or 2/3 depending on the shape of the particle and the arrangement of atoms in it.\(^{25}\) The particle moment depends on \( p \) and thus on the particle size. Kodama et al. have estimated a magnetic moment \( 80 \mu_B \) per particle for bare 15 nm NiO particles using Néel’s two sublattice model and found that this value is too small compared to 700\( \mu_B \), a value estimated from experimental data.\(^{33}\) They proposed the existence of a multi-sublattice ordering in NiO nanoparticles to account for the anomalously high magnetic moment.

A linear extrapolation of the high field magnetization data at 10 K (shown in the inset of Figure B) gives an estimated moment of about 1350 \( \mu_B \) for the gelatin coated 9 nm particles. We see that the particle magnetic moment increases roughly by 2.5 times on coating bare nanoparticles with gelatin.\(^{34}\) A similar enhancement in the particle moment was observed by Winkler et al. on dispersing 3 nm particles in a non magnetic matrix.\(^{34}\) This observation is puzzling because it is unclear how a non-magnetic coating leads to an enhancement of magnetic moment of a particle. Winkler et al. have argued that the absence of demagnetizing character of interparticle interactions is responsible for the increase in magnetization in coated nanoparticles. We disagree with this argument.
because as we had discussed earlier (section III B), the interparticle interactions are quite small and hence cannot give rise to such an enormous decrease in the magnetic moment of bare particles as opposed to coated particles.

D. ac susceptibility

We measured the temperature dependence of ac susceptibility at several frequencies: 33, 90, 330 and 1000 Hz. The sample is cooled from room temperature to 5 K in a zero magnetic field and a probing ac magnetic field of amplitude 3 G is applied to measure the susceptibility as the temperature is increased to 300 K. In Figure 6, the real part, $\chi'$, of the ac susceptibility is shown and the inset (a) displays the imaginary part, $\chi''$. Inset (b) shows a magnified view of the low temperature peak. We note that the real part ($\chi'$) has a sharp peak near 16 K and a broad high temperature peak between 200 K and 300 K. This broad high temperature peak can be observed more clearly in the imaginary part. As the frequency is raised the value of $\chi'$ decreases and the peaks shift slightly to higher temperatures. A quantitative measure of the variation of peak temperature with frequency is the relative shift in peak temperature, $\Delta T_\text{p}/T_\text{p}$, per decade of frequency. This quantity lies between 0.0045 and 0.06 for many canonical spin glasses. For ferritin, a known superparamagnet, its value is approximately 0.13 and for another superparamagnet a-(Ho$_2$O$_3$)(B$_2$O$_3$) it is 0.28. In the present case, for the lower peak, using the real part of susceptibility, this value comes out to be 0.046 and using the imaginary part, its value is 0.067. For the upper peak, using the imaginary part, this value turns out to be 0.0553. Thus for both the peaks, the relative shift lies in the range

observed in spin glass and spin glass like systems and provides an empirical evidence in support of spin glass like behavior.

E. Memory and Aging Experiments

In the past several years, aging and memory effects have been investigated in many nanoparticle systems using ac susceptibility and low field dc magnetization measurements with various temperature and field protocols. It has been seen that superparamagnets
as well as spin glasses show these effects in FC protocol. However only spin glasses show aging and memory in ZFC protocol. We have reported memory effects in bare NiO nanoparticles in both FC and ZFC protocols in a previous work. Therefore, it will be interesting to investigate these effects in coated nanoparticles where interactions between the particles should be negligible.

We carried out memory experiments in both FC and ZFC protocols with stops of one hour taken at 8 K, 15 K and 150 K. The procedure of these experiments is as follows. In the FC protocol, the system is cooled in the presence of a magnetic field (100 Oe) to 5 K with intermittent stops of one hour at 8 K, 15 K and 150 K, with the field switched off during the stops. The magnetization is measured while cooling and then during subsequent heating. The results of memory experiments in FC protocol are shown in Figure 4. We found that at 150 K, there are no indications of memory but at 8 K and 15 K, memory is present as is evident from a small jump in the magnetization at these temperatures. However, these effects are much weaker than those observed in bare NiO nanoparticles. In the ZFC protocol, to begin with we record the ZFC magnetization data normally and then with stops of one hour at 8 K, 15 K and 150 K while cooling. We observed that there is no significant difference between these two data and this shows that the system has no ZFC memory.

These experiments indicate that the lower peak can correspond to superparamagnetic blocking as the memory is present only in FC measurements and not in ZFC measurements. On the other hand absence of memory at 150 K in both FC and ZFC protocols is quite unusual as it does not correspond to either spin glass like or superparamagnetic behavior. However this apparent absence of memory could be because of some transition associated with the lower peak $T_{p1}$ which can wipe out the memory of stops taken at higher temperatures.

In addition to memory effects, aging has been used as a tool to distinguish superparamagnets and spin glasses. We recall that aging is seen in FC protocol in both superparamagnets and spin glasses while in ZFC protocol it is seen only in spin glasses. We investigated aging at three different temperatures 5 K, 20 K and 150 K in both FC and ZFC protocols. To check for FC aging the sample is cooled in a field of 100 Oe to the temperature of interest, and after waiting for a specified duration (wait time, $t_w$) the field is switched off. Subsequently the magnetization data is recorded as a function of time. These data are presented in Figure 5. Similarly, in the corresponding ZFC aging experiment, the sample is cooled in a zero field to the temperature of interest, and after waiting for a specified wait time the field (100 Oe) is switched on; magnetization as a function of time is recorded subsequently. The ZFC aging data are presented in Figure 6. We note that a good amount of aging is discernible in both FC and ZFC magnetizations at 5 K and 150 K but not at 20 K. The presence of aging in ZFC protocol at 5 K and 150 K is a strong evidence which supports the thesis that the system is spin glass like.

![Figure 10: (Color online) Linear scaling plot of the dc nonlinear susceptibility. The scaled curve is obtained using $T_f = 170$ K, $\gamma = 140$ and $\beta = 2.5$. ($H$ is in units of Oe and $\chi_{NL}$ is in units of emu/gOe.)](image)

**F. Static Scaling**

Static critical scaling has been widely used as an evidence for phase transition in spin glasses and an appropriate quantity to examine the critical behavior is the nonlinear susceptibility, $\chi_{NL}$, given as:

$$\chi_{NL} = \chi_0 - \frac{M}{H} = -(\chi_3H^2 + \chi_4H^4 + ...). \quad (3)$$

It should be noted that $\chi_{NL}$ should diverge in the critical region as $\chi_3$, $\chi_4$, ... are divergent in that region. To describe $\chi_{NL}$ in the critical region, the following scaling equation has been proposed:

$$\chi_{NL} \propto H^{2\beta/(\beta+\gamma)}G(t/H^{2/(\beta+\gamma)}), \quad (4)$$

where $t$ is the reduced temperature $(T-T_c)/T_c$, $\beta$ and $\gamma$ are critical exponents of the spin glass order parameter and $G$ is the scaling function.

To demonstrate scaling, the parameters $\beta$, $\gamma$ and $T_c$ are selected so that all the data points taken at various fields are judged to fall on a single master curve on a plot of $\chi_{NL}/H^{2\beta/(\beta+\gamma)}$ vs. $t/H^{2\gamma+\gamma}$. Figure 10 shows the scaling plot of our data using Equation (4). It is clear that four data sets taken at different magnetic fields are falling well on a master curve. It has been seen that several sets of $\beta$, $\gamma$ and $T_c$ can give reasonably good plots. In Figure 10, we used $T_c = 170$ K, $\gamma = 140$ and $\beta = 2.5$. The values of critical exponents $\beta$ and $\gamma$ should be unity according to mean field theory. However it has been seen that the values determined from experiments can be much larger than unity. Thus the magnetization data follows scaling laws confirming spin glass behavior in this system. It can
be however noted that the non linear susceptibility does not diverge in contrast to canonical spin glasses and the reasons for this could be the finite size of the system and the distribution of freezing temperatures due to particle size distribution as has been discussed by Tiwari et al. 5

IV. CONCLUSION

We find that the behavior of gelatin coated NiO nanoparticles is more intriguing than that of bare particles. The particle magnetic moment is enhanced several times on coating and the reasons for this phenomenon are not clear. An additional peak ($T_{p1}$) is observed in the ZFC magnetization data at 14 K which is usually not present in bare nanoparticles. The field dependence of $T_{p2}$ in ZFC magnetization follows the AT line as one would expect in the case of a spin glass. Further, $\Delta T_p/T_p$, per decade of frequency in $ac$ susceptibility lies in the range seen in spin glasses. Strong aging effects have been observed at 150 K in both FC and ZFC protocols, again a feature characteristic of spin glass like systems. The $dc$ scaling analysis presents conclusive evidence in support of spin glass behavior with $T_1 = 170$ K. Thus it is clear that the system goes into a spin glass state with an average freezing temperature, 170 K. Since the particles are coated with gelatin it is clear that the spin glass behavior cannot be due to interparticle interactions. Rather it has to have its origins within a particle.

Below $T_{p1}$, the behavior of this system shows some features characteristic of superparamagnetic blocking viz. increase in the FC magnetization on decreasing the temperature, $H^2$ dependence of $T_{p1}$ and presence of memory in FC magnetization without a corresponding effect in ZFC magnetization. However certain features observed correspond to spin glass like behavior viz. frequency dependence of susceptibility with a value of $\Delta T_p/T_p$, per decade of frequency in the range of spin glasses and aging effects in ZFC protocol in addition to those in FC protocol. Thus the nature of the low temperature peak is ambiguous.

We have shown that this system shows spin glass behavior in contrast to most of the earlier reports which claimed superparamagnetism. Further we have argued convincingly that the reason for this behavior is surface spin freezing and not interparticle interactions. At low temperature, below $T_{p1}$, the behavior shows features of both superparamagnetism and spin glasses thus making its nature equivocal.

Acknowledgments

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To compare the magnetic moment of 9 nm coated nanoparticles with bare nanoparticles, we estimated the moment of 5 nm particles taking M-H data from Tiwari et al. and this value turns out to be $385\mu_B$. A rough estimate of the average particle moment of 9 nm bare particles can be taken as the arithmetic mean of that of 5 nm and 15 nm particles which gives the value $530\mu_B$. 

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