Memory and aging effects in NiO nanoparticles

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Abstract
We report studies on magnetization dynamics in NiO nanoparticles of average size 5 nm. Temperature and time dependence of dc magnetization, wait time dependence of magnetic relaxation (aging) and memory phenomena in dc magnetization are studied with various temperature and field protocols. We observe that the system shows memory and aging in field-cooled and zero-field-cooled magnetization measurements. These experiments show that the magnetic behavior of NiO nanoparticles is similar to spin glasses. We argue that the spin glass behavior originates from the freezing of spins at the surface of the individual particles.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The slow dynamics shown by magnetic nanoparticles has been an active area of research for the past two decades because of numerous technological applications as well as for an understanding of the physics behind the exotic phenomena observed [1]. Ferro- and ferrimagnetic nanoparticles have been studied more than antiferromagnetic nanoparticles because of their technological potential as they have high magnetic moments [2]. Antiferromagnetic materials show a drastic change in their magnetic properties when the particle size goes to the nanoregime because of the uncompensated spins at the surface which give rise to a net magnetic moment. This leads to many interesting magnetic properties, e.g. a bifurcation between field-cooled (FC) and zero-field-cooled (ZFC) magnetization, a peak in ZFC magnetization, slow relaxation of magnetization and wait time dependence of magnetization relaxation (aging) and memory in FC and ZFC magnetization measurements [3–11]. If the particles are non-interacting, the magnetization dynamics is described by superparamagnetic relaxation as predicted by Néel–Brown theory [12, 13]. On the other hand, interactions can give rise to a spin-glass-like behavior (superspin glass) in interacting nanoparticles [3, 5–7, 14]. However, spin glass behavior can also arise in the nanoparticles due to spin frustration at the surface of individual particles [11, 15–18].

Bulk nickel oxide (NiO) is known to be antiferromagnetic with a Néel temperature T_N of 523 K. The temperature dependence of magnetization of NiO nanoparticles was first studied in 1956 by Richardson and Milligan and a peak in the magnetic susceptibility was found much below the bulk T_N [19]. It was observed that, on decreasing the particle size, the magnetization increases and the peak in susceptibility shifts to lower temperatures. Later in 1961 Néel suggested that small antiferromagnetic particles should exhibit superparamagnetism and weak ferromagnetism [20]. The observed particle moment of NiO nanoparticles is found to be much larger than that predicted by the two-lattice model of antiferromagnets and a multi-sublattice model has been proposed to explain it and also the observed high coercivities and loop shifts in these particles [21, 22]. There have been some reports on the magnetic properties of NiO nanoparticles which claim that they are superparamagnetic [23–28]. However, there are issues in considering them as superparamagnetic as their magnetization cannot be described by the modified Langevin function [21]. Tiwari *et al* have done a detailed study on the magnetic properties of NiO nanoparticles and have claimed, on the basis of scaling arguments, that NiO nanoparticles show spin glass behavior [15]. They have proposed that the surface spin disorder and frustration give rise to such behavior. Winkler *et al* have done magnetic measurements on both bare and polymer-dispersed NiO nanoparticles of 3 nm size and have found that they can be thought of as consisting of an antiferromagnetic core with an uncompensated moment and a disordered surface shell [17]. They have proposed that the interparticle interactions can increase the effective anisotropy energy of the core magnetic moments which results in shifting the freezing temperatures to higher values and in enhancing

the frustration of the spins at the surface. The behavior of NiO nanoparticles is also found to depend on the method of preparation, whether they are coated or not, and the nature of the coating [17, 23, 24, 29–32].

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 [5–8, 10, 14, 33–38]. Non-interacting particles are expected to show aging and memory effects only in FC magnetization measurements. These effects have been observed by various authors and their explanation is based on a simple superparamagnetic model where one assumes a distribution of anisotropy energy barriers and temperature-driven dynamics [6, 8, 10, 38]. In contrast, in interacting particles, the magnetization dynamics is spin-glass-like and so it is expected that they would show aging and memory effects in both FC and ZFC protocols like spin glasses. Indeed, this is the case and models based on canonical spin glasses have been used to explain these effects in such nanoparticle systems [5, 6]. Thus the presence of aging and memory in the ZFC protocol is like a litmus test for differentiating spin glasses and superparamagnets.

Most of the nanoparticles studied for aging and memory effects are ferro- or ferrimagnetic and there are very few studies on antiferromagnetic nanoparticles. We feel that it would be interesting to study these effects in NiO nanoparticles, an antiferromagnetic system in which surface effects are known to play a major role in determining the magnetic behavior. In fact, it has been claimed that these particles show spin glass behavior [15, 17]. In this work, we present a detailed study on aging and memory effects in 5 nm NiO particles with various temperature and field protocols and try to settle the issue of its spin glass nature.

2. Experimental details

NiO nanoparticles are prepared by the sol–gel method [15, 16, 21, 27]. A nickel hydroxide precursor is precipitated by reacting aqueous solutions of nickel nitrate (99.999%) and sodium hydroxide (99.99%) at pH 12, at room temperature. This precipitate is washed many times with distilled water to remove remnant nitrate and sodium ions. It is then dried at 100 °C for 6 h to get green colored nickel hydroxide powder. Nickel oxide nanoparticles are prepared by heating nickel hydroxide at 250 °C for 3 h in flowing helium gas. The sample is characterized by x-ray diffraction (XRD) using a Seifert diffractometer with Cu Kα radiation. The average particle size as determined by XRD using the Scherrer formula is 5 nm. All the magnetic measurements are done with a SQUID magnetometer (Quantum Design, MPMS XL5).

3. Results and discussion

3.1. Aging experiments

Temperature dependence of magnetization was done under FC and ZFC protocols at a field of 100 Oe (see figure 1). There is a bifurcation in FC and ZFC magnetizations which manifests
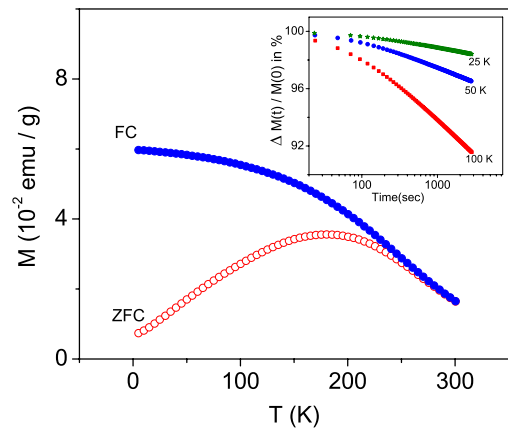

Figure 1. Temperature dependence of the dc magnetization in a 100 Oe field for both ZFC and FC protocols. The inset shows the decay of thermoremanent magnetization at temperatures 25, 50 and 100 K.

below 275 K and the ZFC magnetization has a broad peak at about 180 K. It can be seen that the FC magnetization increases with decreasing temperature, apparently tending to saturate. Time decay of thermoremanent magnetization (TRM) was done at temperatures 25, 50 and 100 K. For these measurements, we cool the sample in a field of 100 Oe to the temperature of interest and then switch off the field. Now the magnetization is measured as a function of time (see the inset of figure 1). It can be observed that the magnetization decays more or less logarithmically. This behavior is a characteristic of both superparamagnets and spin glasses. An experiment that can distinguish between the above two possibilities is the wait time dependence of magnetization relaxation (aging). We carried out aging experiments in both FC and ZFC protocols as follows: cool the sample in a field of 100 Oe for FC (or in zero field for ZFC) to the temperature of interest, wait for a specified time (wait time) and then switch the field off (or on in the case of ZFC). Now record the magnetization as a function of time. Superparamagnets are expected to show a weak wait time dependence of TRM and no wait time dependence in ZFC magnetization; in other words weak FC aging and no ZFC aging. Spin glasses are, however, known to show both FC and ZFC aging [6, 39]. Figure 2 shows the data for aging experiments in FC and ZFC protocols. A noticeable wait time dependence in both FC and ZFC protocols can be observed, which is evidence in support of spin glass behavior in NiO nanoparticles.

3.2. Memory experiments

We carried out memory experiments in both FC and ZFC magnetization measurements. In the ZFC protocol, we first record the ZFC magnetization in the standard way and call this the reference data. Now the sample is cooled in zero field to 5 K with a stop of one hour at 100 K. During subsequent heating the magnetization is recorded up to 300 K. In figure 3 we show the difference in magnetization between the ZFC data with the stop and the ZFC reference data. It is clear that there is a dip at 100 K, where the stop was taken during the cooling
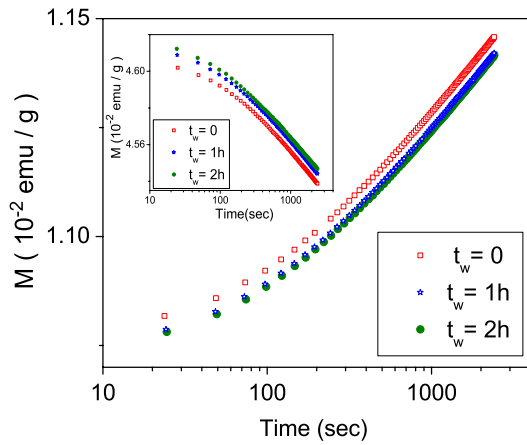
Figure 2. Wait time dependence of ZFC magnetization at 25 K. The inset shows the wait time dependence of TRM at 25 K.
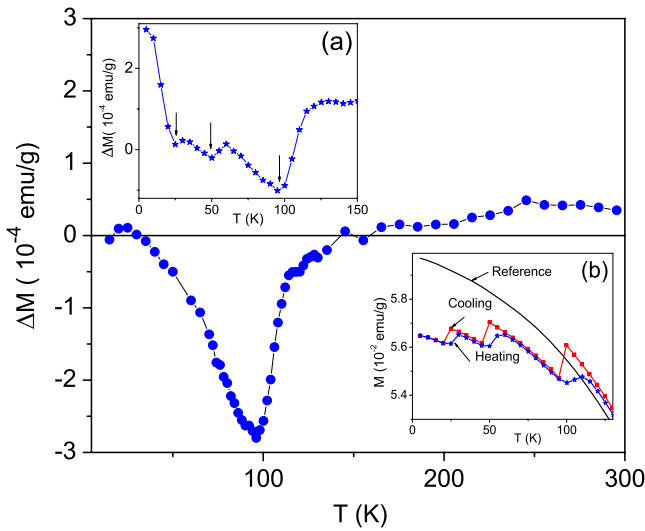

Figure 3. Memory experiments in the ZFC protocol. The difference in magnetization with a stop of one hour at 100 K in the cooling process and the reference data, plotted as a function of temperature. Inset: (a) memory experiments in the ZFC protocol with stops of one hour duration at 100, 50 and 25 K. (b) Memory experiments in the FC protocol with stops of one hour duration at 100, 50 and 25 K. The field is switched off during each stop. All the curves merge together above 200 K (not shown).

Figure 4. Magnetic relaxation with negative temperature cycling and a field change for (a) the FC protocol and (b) the ZFC protocol. The insets show that the relaxation during time t_3 is essentially a continuation of the relaxation during t_1, confirming that the system has the memory of earlier relaxations.

process, establishing the ZFC memory in the system. A ZFC memory experiment with multiple stops of one hour duration at 25, 50 and 100 K was also done and data has been shown in inset (a) of figure 3. The dips can be seen here at temperatures at which stops were taken but are less pronounced at 25 and 50 K. This may be due to the fact that multiple dips which are rather wide are interfering with each other. For doing FC memory experiments, the system is cooled in the presence of a magnetic field to 5 K with intermittent stops of one hour at 25, 50 and 100 K with the field switched off during the stops. The magnetization is measured while cooling and then during subsequent heating. The data is shown in inset (b) of figure 3. It can be observed that the system remembers the history of the
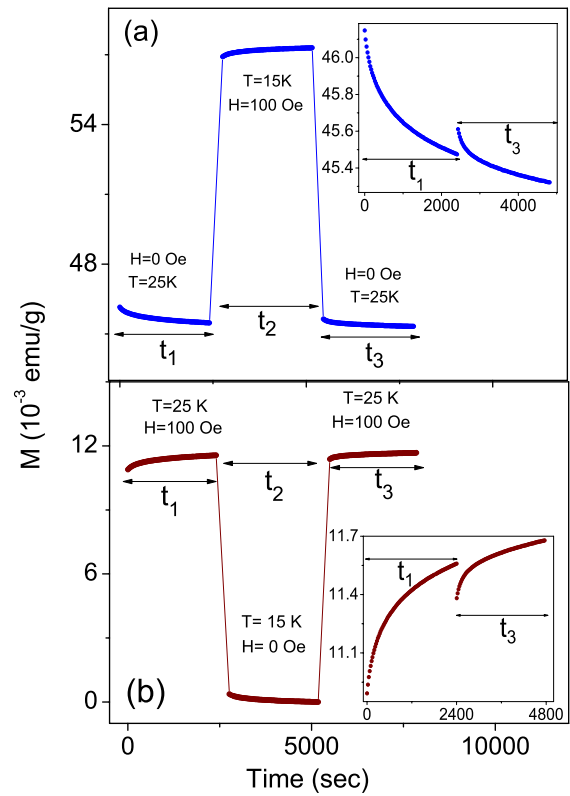
cooling process and the magnetization takes jumps close to the temperatures where the stops were taken.

Memory in FC magnetization has been observed for both interacting and non-interacting nanoparticles and it has been shown that a broad distribution of energy barriers is sufficient to produce memory effects in the FC protocol [6]. However memory in ZFC magnetization is a feature inherent to spin glasses and has not been observed in superparamagnets. Thus the memory observed in ZFC magnetization measurements provides conclusive evidence in favor of the spin glass nature of NiO nanoparticles. However, the width of the dip in figure 3 is rather large, about 100 K, the corresponding figure for canonical spin glasses being a few Kelvin [40].

To complement these memory experiments we have done negative temperature cycling experiments with field change in both FC and ZFC protocols, as suggested by Sun *et al* and adopted by many authors [5–9]. In the FC protocol, the system is cooled to 25 K in a field of 100 Oe, the field is then switched off and the magnetization is recorded for a time period t_1. Then the system is cooled to 15 K, a field of 100 Oe is applied and magnetization data is taken for a period t_2. Temperature is now changed back to 25 K, the field is switched off and magnetization is recorded again for a period t_3. Here $t_1 = t_2 = t_3 = 2800$ s (see figure 4(a)). It can be seen that, when the temperature is raised back to 25 K, the relaxation starts almost from the point at which it left off in the previous

relaxation at 25 K (please see the inset of figure 4(a)). This shows that the system has a memory of an earlier aging in spite of an intervening aging at a lower temperature. We have also done negative temperature cycling for ZFC magnetization relaxation in a similar manner (see figure 4(b) and its inset). The results again confirm the existence of memory in the ZFC protocol.

3.3. Discussion

The presence of aging and memory in ZFC magnetization of NiO nanoparticles confirms their spin glass behavior. There has been some work on other nanoparticle systems where the ZFC memory was observed [4–6, 34, 35, 40]. All those works were on ferrimagnetic and ferromagnetic materials and the interparticle interactions were said to be responsible for the observed glassy behavior. The dip in the ZFC memory in the present work (figure 3) is quite broad compared to those reported on other nanoparticle systems. This suggests that the origin of the spin glass behavior in NiO nanoparticles is, possibly, not interparticle interactions. In fact, the interactions between these particles are very weak and not sufficient to cause collective freezing of particle moments at such high temperatures as has been argued by Tiwari *et al* [15]. However, these interactions can enhance the frustration of spins at the surface of individual particles and shift the freezing temperatures to higher values [17]. The exchange bias effects observed in NiO nanoparticles indicate the presence of both ferro- and antiferromagnetic interactions at the surface, which can frustrate the spins leading to spin glass behavior [41, 42]. Thus the origin of the spin glass state in NiO nanoparticles seems to be the freezing of spins at the surface of the individual particles. The wide dip in ZFC memory of NiO nanoparticles as compared to canonical spin glasses can possibly be attributed to the finite size of the system.

4. Conclusion

We have done dc magnetic relaxation measurements on NiO nanoparticles with various temperature and field protocols. Our results show the presence of aging and memory effects in both FC and ZFC magnetizations, thus establishing the spin glass behavior of these particles. The origin of this behavior is possibly the surface spin freezing of individual particles rather than interparticle interactions. However, similar experiments with capped or dispersed nanoparticles are needed to further clarify the issue.

Acknowledgments

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