Non-equilibrium effects in the magnetic behavior of Co$_3$O$_4$ nanoparticles

Vijay Bisht and K.P.Rajeev
Department of Physics, Indian Institute of Technology Kanpur 208016, India

We report detailed studies on non-equilibrium magnetic behavior of antiferromagnetic Co$_3$O$_4$ nanoparticles. Temperature and field dependence of magnetization, wait time dependence of magnetic relaxation (aging), memory effects and temperature dependence of specific heat have been investigated to understand the magnetic behavior of these particles. We find that the system shows some features characteristic of nanoparticle magnetism such as bifurcation of field cooled (FC) and zero field cooled (ZFC) susceptibilities and a slow relaxation of magnetization. However, strangely, the temperature at which the ZFC magnetization peaks coincides with the bifurcation temperature and does not shift on application of magnetic fields up to 1 kOe, unlike most other nanoparticle systems. Aging effects in these particles are negligible in both FC and ZFC protocol and memory effects are present only in FC protocol. We estimate the Néel temperature by using Fisher’s relation as well as directly by measurement of specific heat, thus testing the validity of Fisher’s relation for nanoparticles. We show that Co$_3$O$_4$ nanoparticles constitute a unique antiferromagnetic system which develops a magnetic moment in the paramagnetic state because of antiferromagnetic correlations and enters into a blocked state above the Néel temperature.

PACS numbers: 75.50.Tt, 75.20.-g, 75.75.Jn, 75.50.Lk
Keywords: Co$_3$O$_4$ nanoparticles, magnetic properties, superparamagnetism, memory, aging, antiferromagnetic correlations, Fisher’s relation, FC-ZFC.

I. INTRODUCTION

In the past two decades, magnetic nanoparticles have attracted much attention due to (a) their potential uses in various areas such as data storage and biomedicine and (b) the challenge to understand the physics underlying the various exotic phenomena exhibited by them. Most of such work has focused on ferromagnetic and ferrimagnetic nanoparticles because of their high magnetic moments that make them industrially valuable. However, there have been a few studies on antiferromagnetic nanoparticles and interestingly, their magnetic behavior is found to be more complex and intriguing.

Below a critical size, particles of a ferromagnetic or ferrimagnetic material consist of a single domain and each particle carries a magnetic moment, which can reverse its direction due to thermal agitation. In these particles, the magnetic dynamics is thermally activated leading to paramagnetic behavior above a particular temperature, called blocking temperature. This phenomenon is known as superparamagnetism as instead of atomic spins, particle moments (‘superspins’) are involved. Below this temperature, the moments appear frozen in a particular direction, on the time scale of the measurement. Antiferromagnetic nanoparticles can also develop a net moment due to uncompensated spins and can exhibit superparamagnetism as proposed by Néel. Thus magnetic nanoparticles are expected to show superparamagnetism, though, interparticle interactions can complicate matters leading to spin glass like behavior. In addition to interparticle interactions, spin glass behavior can arise within a particle due to freezing of spins at the surface.

Magnetic nanoparticles show some characteristic features which are common to both spin glasses and superparamagnets. These include irreversibility in the field cooled (FC) and zero field cooled (ZFC) magnetizations, a peak in ZFC magnetization, slow magnetic relaxation and hysteresis at low temperature. However, some important features that distinguish these two are: (1) FC magnetization goes on increasing as the temperature is decreased in superparamagnets while it tends to saturate below the peak temperature in particles showing spin glass behavior. (2) In systems showing spin glass like behavior, wait time dependence of relaxation (aging) and memory effects are present in both FC and ZFC magnetizations. In contrast, in superparamagnetic particles, these effects are present in FC magnetization only. (3) The field dependence of temperature at which the ZFC magnetization peaks ($T_p$) is known to behave differently in the two cases.

There have been studies on various antiferromagnetic nanoparticles in both bare and coated forms in the past several years. It has been noticed that there is a lot of variation in the magnetic behavior of the nanoparticles of different materials. For example, NiO nanoparticles have been reported to show spin glass like behavior. CuO nanoparticles show an anomalous magnetic behavior that cannot be described as superparamagnetic or spin glass like. Ferritin shows superparamagnetic behavior, etc. Co$_3$O$_4$ is an antiferromagnetic material and in the bulk form, its Néel temperature has been reported to lie between 30 K and 40 K. There have been some reports on hysteresis, time dependence of magnetization, exchange bias and finite size effects in bare, coated and dispersed Co$_3$O$_4$ nanoparticles and various claims have been made in support of spin glass like and superparamagnetic behavior in these particles. It will be, therefore, worthwhile to investigate their magnetic behavior carefully. In the present work, we present a de-
tailed study on non-equilibrium features such as temperature, time and field dependence of magnetization, aging and memory effects. We also report specific heat measurements to find the Néel temperature ($T_N$) of Co$_3$O$_4$ nanoparticles. Usually $T_N$ is estimated in nanoparticles using the Fisher’s equation that relates specific heat ($C$) and magnetic susceptibility ($\chi$) of antiferromagnetic materials$^{33,34}$. We determine $T_N$ using both methods and are able to test the validity of Fisher’s relation in these nanoparticles.

II. EXPERIMENTAL DETAILS

Co$_3$O$_4$ nanoparticles are prepared by a sol gel method. Aqueous solution of sodium hydroxide is mixed with that of cobalt nitrate till the pH of the solution becomes 12. At this stage cobalt hydroxide separates from the solution forming a gel that is centrifuged to obtain a precipitate which is washed with water and ethanol several times and dried to obtain a precursor. This precursor is heated at 250 °C for 3 hours to obtain Co$_3$O$_4$ nanoparticles. The sample is characterized by X-ray diffraction (XRD) using a Seifert diffractometer with Cu Kα radiation and Transmission electron microscopy (TEM) using FEI Technai 20 U Twin Transmission Electron Microscope. All the magnetic measurements are done with a SQUID magnetometer (Quantum Design) and specific heat measurements are done with a PPMS (Quantum Design).

III. RESULTS AND DISCUSSION

A. Particle size

The XRD pattern of the sample (Figure 1) corresponds to that of Co$_3$O$_4$. The average particle size as estimated from the broadening of XRD peaks using the Scherrer formula turns out to be 12.5 nm. TEM image is shown in Figure 2 (a). Parts (b) and (c) of this figure show the corresponding selected area diffraction (SAD) pattern and the particle size distribution of the sample. It can be seen that the particles are more or less spherical in shape and the average particle size estimated comes out to be about 18 nm with a standard deviation of 1.5 nm. The SAD pattern consists of concentric diffraction rings with different radii. The diameter of a diffraction ring in 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..., rings correspond to (220), (311), (222)... planes, respectively, in agreement with the XRD pattern.

B. Temperature and field dependence of magnetization

The temperature dependence of magnetization was done under field cooled (FC) and zero field cooled (ZFC) protocols at fields 100 Oe, 300 Oe and 1000 Oe. See Figure 3. We note that the FC magnetization in this case is increasing with decrease in temperature down to the lowest temperature of measurement without any sign of saturation, a feature characteristic of superparamagnets$^8$. However, the temperature at which the ZFC magnetization peaks (31 K) i.e. $T_P$ is also the temperature of bifur-
A peak at 26 K, which should correspond to the Néel contribution, is noticeable between 15 K and 40 K with a peak at 28 K. We calculated the magnetic specific heat by subtracting a linear contribution from the total specific heat and this data is shown in the inset of Figure 4. It will be interesting to check the validity of this relation for the present nanoparticle sample. In Figure 4, we have also shown the plot of $d(\chi T)/dT$ as a function of $T$, which has a peak somewhere in between 20 K to 25 K, giving an estimate of the Néel temperature. Thus the value of $T_N$ extracted from the specific heat is somewhat greater than the value obtained from the Fisher relation.

**D. Aging and memory effects**

Nanoparticles that show spin glass like behavior are expected to show aging and memory effects in both FC and ZFC protocols while those showing superparamagnetic behavior show these effects only in FC protocol. Further the effects in FC protocol are weaker in superparamagnetic particles than in the systems showing spin glass like behavior. These experiments can thus give valuable information about the nature of magnetic behavior of a system.

For doing aging experiments in FC protocol, the sample is cooled to a particular temperature in a field of 100 Oe, the field is switched off after waiting for a specified period and magnetization is recorded as a function of temperature. Inset shows the plot of specific heat as a function of temperature. The line (red) shows the linear part of specific heat which is subtracted from the total specific heat to get the magnetic contribution.

\[ C \propto d(\chi T)/dT \] (1)
of time. In the corresponding ZFC case, the sample is cooled to the temperature of interest in zero field and the field is switched on after a certain wait time and subsequently magnetization is recorded as a function of time. We show the results of aging experiments at 20 K in Figure 5. It can be seen that aging effects are negligible in both FC and ZFC measurements.

For carrying out FC memory experiments, the system is cooled in the presence of a magnetic field to 20 K and a stop of one hour is taken at this temperature. Magnetic field is switched off for the duration of the stop and is turned on before cooling it further to 10 K. The magnetization is measured while cooling and then during subsequent heating. These data have been taken at 300 Oe field. See Figure 6. It can be observed that there is some indication of memory as the heating curve meets the cooling curve just above the temperature at which the stop was taken. We have also done memory experiments in ZFC protocol with a stop of one hour at 20 K. For doing these measurements, we first cool the sample continuously down to 10 K in zero field and applying a field of 300 Oe to record the magnetization data as the temperature is increased in steps up to 100 K. We call this data as the ZFC reference. Now the sample is cooled in zero field down to 10 K with a stop of one hour at 20 K and during subsequent heating the magnetization is recorded with an applied field of 300 Oe as the temperature is increased to 100 K. In the inset of Figure 4, we show $\Delta M$, the difference in magnetization between the ZFC data with the stop and the ZFC reference, as a function of temperature. We observe that there is no indication of memory at the temperature at which stop was taken in the cooling process and $\Delta M$ is less than 0.05%. This is in contrast to canonical spin glasses or nanoparticle systems that show spin glass like behavior where a clear dip in $\Delta M$ vs $T$ curve is observed at the temperature where the halt was made during the cooling process and in the vicinity of the dip $\Delta M$ is of order 1% or more. From these experiments, it is clear that below the peak temperature, the irreversibility in FC and ZFC magnetization is due to superparamagnetic blocking.

E. DISCUSSION

We have seen that Co$_3$O$_4$ nanoparticles show some features characteristic of nanoparticle magnetism. Some of these are due to finite size effects viz. a net magnetic moment due to uncompensated surface spins and a decrease in Néel temperature. Some are manifestations of non equilibrium in magnetic nanoparticles viz. irreversibility in FC and ZFC magnetization and a slow magnetic relaxation at low temperature. However there are several unusual features observed in this system, that deserve a closer look.

![Figure 5: (Color online) Aging experiments in ZFC protocol at 20 K with waiting times 30 s, 300 sec and 3000 sec. Inset shows the corresponding experiments in FC protocol.](image1)

1. Behavior above $T_P$

In ferromagnetic and ferrimagnetic nanoparticles, the ZFC magnetization generally shows a peak at a particular temperature, above which the behavior is superparamagnetic. This behavior is characterized by the superposition of magnetization curves taken at various temperatures above $T_P$ when plotted against $H/T$ [43]. However, Makhlouf et al. have shown that in Co$_3$O$_4$ nanoparti-

![Figure 6: (Color online) Memory experiments in FC protocol with a stop of one hour duration at 20 K at a field of 300 Oe. The field is switched off during the stop as indicated by the arrow. Inset shows the corresponding data for ZFC memory experiment. The difference in magnetization with a stop of one hour at 20K in the cooling process and the reference data is plotted as a function of temperature.](image2)
cles, magnetization vs $H/(T+\theta)$ curves taken at temperatures above 50 K superpose with ($\theta = 85$ K), a feature characteristic of antiferromagnetic materials. Our data (50 K-300 K) also fits well to Curie-Weiss law, $\chi \propto 1/(T+\theta)$, with $\theta = 107$ K and coefficient of determination, $R^2 = 0.9992$. See Figure 7. Thus, the system is not in a superparamagnetic state above $T_P$. It may be noted that $T_N$ as found by specific heat measurements is 5 K less than $T_P$ and the Fisher relation gives an even lower estimate of $T_N$.

2. Behavior below $T_P$

There have been some reports of spin glass like features in Co$_3$O$_4$ nanoparticles coated with organic surfactants and those dispersed in amorphous matrices at low temperature. However, in the present work and in other studies on bare nanoparticles, no such features have been found. Absence of aging and memory effects in ZFC protocol confirms that the behavior of Co$_3$O$_4$ nanoparticles is not spin glass like. Thus below $T_P$, observation of a bifurcation in FC and ZFC magnetization and a slow magnetic relaxation seems to correspond to a blocked state as observed in superparamagnetic particles. Presence of memory effects in FC protocol also support this inference.

At $T_P$, there also occurs a bifurcation between FC and ZFC magnetization and this change looks abrupt as at this point a slope change in the FC magnetization can be seen. Thus even before the actual transition to an antiferromagnetic state, the particles get blocked as indicated by the FC and ZFC bifurcation. We propose that this is due to the short range antiferromagnetic correlations which are known to persist above the Néel temperature. These short ranged correlations can give rise to a net magnetic moment when the correlation length becomes comparable to the particle size and thus the particles can get blocked above $T_N$.

IV. CONCLUSION

We have done a detailed study of non-equilibrium magnetic behavior of Co$_3$O$_4$ nanoparticles. We find that their behavior is unique among antiferromagnetic nanoparticles. There is a peak in ZFC magnetization and at this temperature ($T_P$), a sudden bifurcation between FC and ZFC magnetization occurs, strangely, above the Néel temperature. There is a sudden slope change in FC magnetization at the bifurcation temperature and the magnetization keeps on increasing on decreasing the temperature, a feature characteristic of superparamagnetic nanoparticles. However, the behavior of susceptibility above the peak temperature is paramagnetic rather than superparamagnetic. Aging and memory effects are not observed in ZFC magnetization measurements which show the absence of spin glass like behavior in this system. However observation of memory in FC protocol supports superparamagnetic blocking below $T_P$. Thus, above $T_P$, Co$_3$O$_4$ nanoparticles are paramagnetic with antiferromagnetic correlations and below $T_P$, they get blocked in the paramagnetic state itself even before the transition to an antiferromagnetic state at $T_N$.

Acknowledgments

VB thanks the University Grants Commission of India for financial support. Authors thank Prof. C.V. Tomy, IIT Bombay for specific heat measurements.

---

* Electronic address: vijayb@iitk.ac.in
† Electronic address: kpraj@iitk.ac.in
1 J. L. Dormann, D. Fiorani, and E. Tronc, Advances in Chemical Physics 98, 283 (1997).
2 Steen Mørup, Daniel E Madsen, Cathrine Frandsen, Christian R H Bahl and Mikkel F Hansen, J. Phys.: Condens. Matter 19, 213202 (2007).
3 Q A Pankhurst, J Connolly, S K Jones and J Dobson, J. Phys. D: Appl. Phys. 36, R167 (2003).
4 L. Néel, Ann. Geophys. C.N.R.S. 5, 90 (1949).
5 W. F. Brown Jr., Phys. Rev. 130, 1677 (1963).
6 Vijay Bisht and K P Rajeev, J. Phys.: Condens. Matter 22, 016003 (2010).
7 X. Batlle and A. Labarta, J. Phys. D 35, R15 (2002).
M. Sasaki, P. E. Jonsson, H. Takayama, and H. Mamiya, Phys. Rev. B 71, 104405 (2005).
9 Y. Sun, M. B. Salamon, K. Garnier and R. S. Averback, Phys. Rev. Lett. 91, 167206 (2003).
10 Malay Bandyopadhyay and Sushanta Dattagupta, Phys. Rev. B 74, 214410 (2006).
11 S. Sahoo, O. Petracic, W. Kleemann, P. Nordblad, S. Cardoso and P. P. Freitas, Phys. Rev. B 67, 214422 (2003).
12 S. D. Tiwari and K. P. Rajeev, Phys. Rev. B 72, 104433 (2005).
13 K. Nadeem, H. Krenn, T. Traussing, and I. Letofsky-Papst, Journal of Applied Physics 109, 013912 (2011).
14 B. Martinez, X. Obradors, Ll. Balcells, A. Rouanet, and C. Monty, Phys. Rev. Lett. 80, 181 (1998).
15 Malay Bandyopadhyay and Sushanta Dattagupta, Phys. Rev. B 74, 214410 (2006).
16 S. Sahoo, O. Petracic, W. Kleemann, P. Nordblad, S. Cardoso and P. P. Freitas, Phys. Rev. B 67, 214422 (2003).
17 S. D. Tiwari and K. P. Rajeev, Phys. Rev. B 72, 104433 (2005).
18 K. Nadeem, H. Krenn, T. Traussing, and I. Letofsky-Papst, Journal of Applied Physics 109, 013912 (2011).
19 B. Martinez, X. Obradors, Ll. Balcells, A. Rouanet, and C. Monty, Phys. Rev. Lett. 80, 181 (1998).
20 Some authors have observed a \( T_b \) which lies a few Kelvins above \( T_P \) and some others have found it even below \( T_P \).
21 R. K. Zheng, Hongwei Gu, Bing Xu, and X. X. Zhang Phys. Rev. B 72, 014416 (2005).
22 T. Bitoh, K. Ohba, M. Takamatsu, T. Shirane, and S. Chikazawa, J. Phys. Soc. Jpn. 64, 1305 (1995).
23 R. K. Zheng, Hongwei Gu, Bing Xu, and X. X. Zhang, J. Phys.: Condens. Matter 18, 5905 (2006).
24 Vijay Bisht, K. P. Rajeev and Sangam Banerjee, Solid State Communications 150, 884 (2010).
25 S. H. Kilcoyne and R. Cywinski, Journal of Magnetism and Magnetic Materials 140, 1466 (1995).
26 D. A. Resnick et al. Journal of Applied Physics 99, 08Q501 (2006).
27 Yuko Ichiyanagi and Saori Yamada, Polyhedron 24, 2183 (2005).
28 Syozo Takada et al., Nano Letters 1, 379 (2001).
29 Y. Ichiyanagi, Y. Kimishima and S. Yamada, Journal of Magnetism and Magnetic Materials 272, e1245 (2004).
30 Salah A. Makhlouf, Journal of Magnetism and Magnetic Materials 246, 184 (2002).
31 Lin He, Chinpeng Chen, Ning Wang, Wei Chou and Lin Guo, Journal of Applied Physics 101, 103911 (2007).
32 Michi Sato et al. Journal of Applied Physics 88, 2771 (2000).
33 T. Mousavand et al., Physical review B 79, 144411 (2009).
34 Shandong Li et al., Journal of Applied Physics 95, 7420 (2004).
35 Some authors have observed a \( T_b \) which lies a few Kelvins above \( T_P \) and some others have found it even below \( T_P \).
36 H. Kachkachi, W. T. Coffey, D. S. F. Crothers, A. Ezzir, E. C. Kennedy, M. Nogués and E. Tronc., J. Phys.: Condens. Matter 12, 3077 (2000).
37 R. Sappey, E. Vincent, N. Hadacek, F. Chaput, J. P. Boilot and D. Zins, Phys. Rev. B 56, 14551 (1997).
38 J. A. Mydosh, Spin Glasses: An Experimental Introduction, p89 (Taylor & Francis, 1993).
39 Y. Ichiyanagi, Y. Kimishima and S. Yamada, Journal of Magnetism and Magnetic Materials 272, e1245 (2004).
40 A. Punnoose, H. Magnone, M. S. Seehra and J. Kumar, J. Phys.: Condens. Matter 20, 015218 (2008).
41 M. E. Fisher, Philos. Mag. 7, 1731 (1962).
42 Salvatore A. Makhlouf, Journal of Magnetism and Magnetic Materials 246, 184 (2002).
43 Some authors have observed a \( T_b \) which lies a few Kelvins above \( T_P \) and some others have found it even below \( T_P \).
44 K. H. J. Buschow and F. R. de Boer, Physics of Magnetism and Magnetic Materials, p93 (Kluwer Academic Publishers, 2004).