Investigating Negative Magnetization and Blocking Temperature in Aggregates of Ferrite Nanoparticles

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Abstract. Blocking temperatures of aggregates of Mn$_{0.5}$Zn$_{0.5}$Gd$_x$Fe$_{2-x}$O$_4$ ferrite nanoparticles, with $x = 0.02$, 0.05, 0.11, 0.15, and 0.2, were obtained from the zero-field-cooled (ZFC) magnetization measurements. We found a nonmonotonic behavior of the blocking temperature with increasing size of the particles. The effective magnetic anisotropy was calculated and found to have two distinct rates of increase with decreasing the size of the particles. These results were attributed to the strong inter-particle interactions in the aggregated nanoparticles and the enhanced role of surface anisotropy with the decrease of the size of the particles. In three samples, the ZFC magnetization was found to exhibit a significant negative magnetization in a considerable part of the low temperature region. To our knowledge, this is the first time that negative magnetization is reported in such nanoparticles. These peculiar results are discussed and are currently under investigation.

1. Introduction

It is well-established that, due to large surface-to-volume ratio, surface effects of magnetic nanoparticles (MNPs) strongly influence their magnetic properties [1-3]. The magnetic surface effects could result of several factors such as the expansion or contraction of the lattice structure near the surface [4, 5], the missing of crystallographic symmetry at the surface [6], roughness, reduction in coordination number, charge transfer, and other factors [7-9]. The impact of each of these surface effects cannot be separated from that of the other effects, and hence all of these effects contribute to the surface anisotropy of the NPs. Technological applications of MNPs demand their thermal stability [10]. If thermal energy ($k_BT$, where $k_B$ is Boltzmann’s constant) exceeds the magnetic anisotropy energy (magnetic energy barrier) between stable magnetic directions, the nanoparticles (NPs) relax from the blocked state to the superparamagnetic state, where the magnetic moment of the NP starts flipping randomly and will not be fixed in a specific direction. The blocking temperature, $T_b$, is the temperature at which the magnetization direction starts flipping. The blocking temperature of MNPs depends on the magnitude of the energy barrier which is determined by several factors such as the size, shape and magnetic anisotropy of MNPs, and inter-particle interactions. Exchange-bias effect can also impact the energy barrier of MNPs [7, 11, 12]. For single-domain particles with small inter-particle interactions, the relaxation time of the magnetic moment of the NPs is given by [13]
\[
\tau = \tau_0 e^{\Delta E / k_B T}
\] (1)

where \(\tau_0\) is an attempt time \((10^{-9} - 10^{-13})\) s, \(\Delta E\) is the magnetic energy barrier of spin reorientation the MNPs, and \(T\) is the absolute temperature. At the blocking temperature, \(T_b\), the NPs become superparamagnetic where the relaxation time, \(\tau\) becomes equal to the measurement time, \(\tau_m\). In a typical magnetization experiment, \(\tau_m = 100\) s. Hence, \(\ln \tau_m / \tau_0 = \Delta E / k_B T = 25\). Thus the magnetic energy barrier, \(\Delta E = 25k_B T_b\). For single-domain MNPs with uniaxial anisotropy, \(\Delta E\) is given by

\[
\Delta E = K_{\text{eff}} V
\] (2)

where \(V\) is the average volume of the NPs, and \(K_{\text{eff}}\) is the effective anisotropy energy density constant of the NPs. Thus for NPs with small inter-particle interactions, the effective anisotropy constant, \(K_{\text{eff}}\) is given by \([14, 15]\)

\[
K_{\text{eff}} = 25k_B T_b / V
\] (3)

The effective anisotropy constant of MNPs, \(K_{\text{eff}}\) is usually given by the phenomenological formula \([16]\),

\[
K_{\text{eff}} = K_V + \frac{K_S}{d}
\] (4)

where \(K_V\), is the bulk anisotropy energy density constant, \(K_S\), is the surface anisotropy constant, and \(d\), is the diameter of the MNP.

Reversal magnetization or negative magnetization effect appears when the direction of magnetization (in the FC or ZFC branches) in a material becomes opposite to the direction of the applied magnetic field to that material. The temperature at which magnetization becomes zero and changes sign (from negative to positive in the ZFC branch and from positive to negative in the FC branch) is called the compensation temperature, \(T_{\text{comp}}\). Reversal magnetization is a challenging field of research and has a potential applications in magnetic devices \([17 - 21]\). This effect was first observed by Néel in ferrimagnets that consist of two magnetic ions coupled antiferromagnetically each other \([22]\). The cause of negative magnetization was suggested to be due to the difference in the temperature dependent magnetization of two magnetic ions. Negative magnetization has been observed in several magnetically ordered materials, such as intermetallic alloys and multilayers, perovskites, spinel ferrites, molecular magnets, and garnets \([21]\). However, the origin of the observed negative magnetization in some materials is not well-known yet \([21, 22]\).

In this paper we show interesting results about the blocking temperature behavior as function of size of the NPs. We also show the occurrence of negative magnetization in some of these NPs.

1. **Experimental Methods**

The ferrite nanoparticles with several Gd\(^{3+}\) concentrations were obtained via chemical co-precipitation and feritization. Details on the synthesis method can be found in \([24]\). The X-ray diffraction (XRD) was performed using Agilent/Oxford Gemini Diffractometer using molybdenum (Mo) \(K\alpha\) radiation. The magnetic measurements were conducted using Quantum Design Superconducting Quantum Interference Device (SQUID).

2. **Results and Discussion**

As reported in \([25]\), the XRD diffraction patterns for MNPs nanoparticles with \(x = 0.02, 0.05, 0.11, 0.15,\) and 0.2 indicate a single-phase FCC spinel structure for the samples with no
detectable impurity phases. From the XRD patterns and using Scherrer’s formula [26, 27], the sizes of
the particles were estimated to be in the range 4 - 10 nm indicating a single domain structure. For $x = 0.02, 0.05, 0.11, 0.15,$ and 0.2, the diameters are 9.2, 7.4, 7.1, 5.0, and 4.2 nm respectively. Using a
SQUID, the measurements of magnetization versus temperature ($M$-$T$) were conducted on all samples
from 5 K to 400 K in an applied magnetic field of magnitude 100 Oe.

![Figure 1: ZFC magnetization curve for $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Gd}_x\text{Fe}_{(2-x)}\text{O}_4$ nanoparticles with $x = 0.05, 0.11,$ and 0.15.](image)

Figure 1 displays the zero-field-cooled (ZFC) magnetization measurements as function of temperature
for $x = 0.05, 0.11,$ and 0.15. In the ZFC branch, the samples were cooled down to the lowest
temperature (5 K) in zero applied field. A magnetic field of magnitude 100 Oe was then applied, and
the magnetic measurements were performed during the heating process up to 400 K. It can be seen that
the peaks of the ZFC curves occur at large temperatures, indicating large particle-particle interactions
[28]. On the other hand, the broad peaks indicate large size distribution of the NPs. The blocking
temperature $T_b$ is obtained from the peaks of the ZFC curves. An arrow in figure 1 shows $T_b$ for $x = 0.11,$ the other values were obtained similarly. Figure 2 displays the blocking temperature as function
of the NPs sizes. For MNPs, $T_b$ is expected to increase with increasing the size of particles [29, 30].
However, figure 2 displays a nonmonotonic behavior of $T_b$ with the size of NPs. This behavior could
be attributed to large inter-particle interactions. In [25], the SEM images show large aggregates of
these NPs which supports the idea of large inter-particle interactions. It was reported that decreasing
the inter-particle spacing (increasing inter-particle interactions) leads to an increase in the blocking
The blocking temperature, $T_b$, and the compensation temperature, $T_{\text{comp}}$, as function of the diameter of the NPs. The dashed lines are guide for the eye.

This result was also reported using Monte Carlo simulations [34]. It is well-known, but not well-understood, that the magnetic properties of MNPs are sensitive to particle-particle interactions. Not only intrinsic properties, but also the extrinsic properties play significant roles in determining the blocking temperature. Thus, $T_b$ not only depends on the size of NPs but also on the magnetic inter-particle interactions. Hence, the nonmonotonic behavior of $T_b$ as function of the size in our ferrite NPs could be explained by assuming different strength of the inter-particle interactions among the aggregated samples.

There are several experimental methods that could be used to obtain the effective anisotropy constant, $K_{\text{eff}}$ [35]. One of these methods is to use the Zero Field Cooled (ZFC) magnetization measurements. $K_{\text{eff}}$ for a particular MNP with volume $V$, and the blocking temperature, $T_b$, was calculated using equation (3) [36]. Any experimental sample contains large numbers of NPs with different sizes, shapes, surface effects, and particle-particle interactions. Hence, $K_{\text{eff}}$ is a result of many effects. Figure 3 displays the effective anisotropy constant as function of the size of the NPs. In obtaining this figure we used equation (3) as an approximation (knowing that it might not yield accurate results in the case of our aggregated samples). As can be seen in this figure, $K_{\text{eff}}$ increases with two distinct rates as the size of NPs decreases.
For NPs with diameters above 7 nm, $K_{eff}$ increases slowly with decreasing the diameter. However, for diameters smaller than 7 nm, $K_{eff}$ increases steeply with decreasing diameter. This behavior could be attributed to the enhanced role of surface anisotropy with decreasing the size of NPs.

![Graph showing the effective anisotropy constant as function of the diameter of the NPs. The dashed line is a guide for the eye.]

As can be seen in figure 1, for the samples with $x = 0.05, 0.11, \text{ and } 0.15$, the initial magnetization (at 5 K) starts with significant negative values and increases monotonically upon heating the samples up the compensation temperatures. Reversal magnetization was not observed in the ZFC branches of the samples with $x = 0.02, \text{ and } 0.2$ (not shown in figure 1). For the samples with $x = 0.05, \text{ and } 0.15$ the negative magnetization persists up to temperatures above 150 K while for the sample with $x = 0.11$, the magnetization direction flips positive at nearly 74 K. An arrow in figure 1 shows $T_{comp}$ for $x = 0.11$, the other values were obtained similarly. This indicates a dependence of the compensation temperature, $T_{comp}$ on the composition of the samples (among other possible factors). In figure 2, $T_{comp}$ (for $x = 0.05, 0.11, \text{ and } 0.15$) is plotted as function of the size of NPs, where is evident that $T_{comp}$ has a nonmonotonic behavior that is opposite to the behavior of $T_m$. Several parameters are suggested to play roles in the appearance of negative magnetization, these include, temperature dependence of sublattice magnetization, magnetic anisotropy, magnetic exchange interactions, and crystal structure [21]. In [37], the negative magnetization was observed in polycrystalline Co$_2$CrAl compound (in both bulk and thin films) in the ZFC branch at fields below 100 Oe. The compensation temperature decreases with the increase of magnetic field. This behavior was suggested to be initiated by Landau diamagnetism, and then preserved by the peculiar electronic structures of the compound. In [38], negative magnetization was observed in the ZFC branch in polycrystalline SrRuO$_3$ at low applied fields.
Several factors such as high magnetocrystalline anisotropy constant, intrinsic negative spin polarization, and random orientation of easy axis were suggested to be key points in this behavior. Negative magnetization in the ZFC branch, in low applied field, was observed at low temperatures in CoCr$_2$O$_4$ nanoparticles of sizes 30 - 40 nm [39]. The origin of the negative magnetization in those CoCr$_2$O$_4$ nanoparticles is not well-known.

It is important to state that to our knowledge, this is the first time that negative magnetization is observed in such ferrite NPs. We believe that these results are not due to experimental errors. We are aware of the fact that residual field of the SQUID magnetometer during the cooling process could cause negative magnetization. However, in our study, the applied field was 100 Oe and the negative magnetization persists up to more than 150 K in some samples, making the possibility of residual field very small. The origin of the negative magnetization observed in our samples could be attributed to the difference in temperature dependence of the magnetic moments at the tetrahedral and octahedral sites coupled with surface spin structures which change with the $x$ value. However, detailed investigation is needed to understand this effect in our NPs.

3. Conclusions
Blocking temperatures of aggregates of Mn$_{0.5}$Zn$_{0.5}$Gd$_{2-x}$Fe$_{2-x}$O$_4$ ferrite nanoparticles (with several Gd$^{3+}$ cations concentrations) were obtained from the ZFC magnetic measurements. The blocking temperature was found to have nonmonotonic behavior as function of the size of NPs. This behavior was attributed to significant inter-particle interactions between the NPs. Reversal magnetization was observed in the low temperature ZFC branches of some samples while it did not appear in other samples. This behavior was attributed to the difference in temperature dependence of the magnetic moments at the tetrahedral and octahedral sites coupled with surface spin structures which change with the Gd$^{3+}$ cations concentrations. The steep increase of the effective anisotropy with decreasing the size of NPs is suggested to be due to the enhanced role of surface effects as the NPs become smaller.

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References
1. D. Fiorani (ed) Surface Effects in Magnetic nanoparticles, Springer. New York, 2005.
2. I. M. Obaidat, B. Issa, and Y. Haik, Nanomaterials 5, 63 (2015).
3. B. Issa, I. M. Obaidat, B. A. Albiss, and Y. Haik, Int. J. Mol. Sci. 14, 21266 (2013).
4. F. Dorbauer, R. Evans, M. Kirschner, O. Chubykalo-Fesenko, R. Chantrell, T. Schrefl, J. Magn. Magn. Mater. 316, E791 (2007).
5. R. Evans, F. Dorbauer, O. Chubykalo-Fesenko, T. Schrefl, R.W. Chantrell, IEEE Trans. Magn. 43, 3106 (2007).
6. M. Jamet, W. Wernsdorfer, C. Thirion, V. Dupuis, P. Mélino, A. Pérez, D. Mailly, Phys. Rev. B 69, 24401 (2004).
7. R.F.L. Evans, R. Yanes, O. Mryasov, R.W. Chantrell, O. Chubykalo-Fesenko, Europhys. Lett. 88, 57004 (2009).
8. F. Garcia-Sanchez, O. Chubykalo-Fesenko, O. Mryasov, P. Asselin and R.W. Chantrell, J. Appl. Phys. 103, 07F505 (2008).
9. G.R Aranda, O. Chubykalo-Fesenko, R. Yanes, J. Gonzalez, J.J. del Val, R.W. Chantrell, Y.K. Takahashi, K. Hono, J. Appl. Phys. 105, 07B514 (2009).
10. S. Sun, C.B. Murray, D. Weller, L. Folks, A. Moser, Science 287, 1989 (2000).
11. R. Yanes, O. Chubykalo-Fesenko, R.F.L. Evans, and R.W. Chantrell, J. Phys. D: Appl. Phys. 43, 474009 (2010).
12. V. Skumryev et. al., Nature 423, 850 (2003).
13. L. Néel, Ann. Geophys. 5, 99 (1949).
14. P. Guardia, B. Batlle-Brugal, A. G. Roca, O. Iglesias, M. P. Morales, C. J. Serna, A. Labarta and X. Batlle, J. Magn. Magn. Mater. 316, e756 (2007).
15. R. Venugopal, B. Sundaravel, W. Y. Cheung, I. H. Wilson, F. W. Wang and X. X. Zhang, Phys. Rev. B 65, 014418 (2001).
16. F. Bodker, S. Mörup and S. Linderoth, Phys. Rev. Lett. 72, 282 (1994).
17. Y. Ren, T. T. M. Palstra, D. I. Khomskii, E. Pellegrin, A. A. Nugroho, A. A. Menovsky, and G. A. Sawatzky, Nature (London) 396, 441 (1998).
18. K. Yoshii and A. Nakamura, J. Solid State Chem. 155, 447 (2000).
19. S. M. Yusuf, A. Kumar, and J. V. Yakhmi, Appl. Phys. Lett. 95, 182506 (2009).
20. B. Sarkar, B. Dalal, and S.K. De, Appl. Phys. Lett. 103, 252403 (2013).
21. A. Kumar, and S.M. Yusuf, Physics Reports 556, 1 (2015).
22. S. Gu, W. He, M. Zhang, T. Zhuang, Y. Jin, H. ElBidweihy, Y. Mao, J. H. Dickerson, M. J. Wagner, E. D. Torre, and L. H. Bennett, Scientific Reports 4, 6267 (2014).
23. L. Néel, Ann. Phys. (Leipzig) 3, 137 (1948).
24. I. M. Obaidat, B. Issa, and Y. Haik, J. Nanosci. Nanotech. 11, 3882 (2011).
25. I. M. Obaidat, B. Issa, B. A. Albiss, G. Qabaja, N. E. Al Khaili, Z. A. Karam, A. M. Hefaity, S. Qadri, A. Al-Okour, and Y. Haik, J. Nanoeng. Nanomanuf. 2, 325 (2012).
26. P. Scherrer, Nachr. Ges. Wiss. Göttingen 26, 98 (1918).
27. A. Patterson, Phys. Rev. 56, 978 (1939).
28. D. Predoi, V. Kuncser, G. Filoti, G. Schinteie, J. Optoelectron. Adv. Mater. 5, 211 (2003).
29. M Hanson, C Johansson, M S Pedersen and S Mørup, J. Phys.: Condens. Matter 7, 9269 (1995).
30. T.C. Monson, E.L. Venturini, V. Petkov, Y. Ren, J.M. Lavin, D.L. Huber, J. Magn. Magn. Mater. 331, 156 (2013).
31. H. T. Yang, D. Hasegawa, M. Takahashi, and T. Ogawa, J. Appl. Phys. 94, 013103 (2009).
32. J. Dai, J-Q. Wang, C. Sangregorio, J. Fang, E. Carpenter, and J. Tang, J. Appl. Phys. 87, 7397 (2000).
33. K. Rumpf, P. Granitzer, P. M. Morales, P. Poelt, and M. Reissner, Nanoscale Res. Lett. 7, 445 (2012).
34. J. Garcia-Otero, M. Porto, J. Rivas, and A. Bunde, Phys. Rev. Lett. 84, 167 (2000).
35. S. Yoon, J. Korean Phys. Soc. 59, 3069 (2011).
36. T. Hyeon, Y. Chung, J. Park, S. S. Lee, Y-W. Kim and B. H. Park, J. Phys. Chem. B 106, 6831 (2002).
37. K.W. Kim, J.Y. Rhee, Y.V. Kudryavtsev, V.G. Prokhorov, J.M. Kim, and Y.P. Lee, J. Korean Phys. Soc. 59, 3064 (2011).
38. B. Sarkar, B. Dalal, and S.K. De, Appl. Phys. Lett. 103, 252403 (2013).
39. D.P. Dutta, J. Manjanna, and A.K. Tyagi, J. Appl. Phys. 106, 043915 (2009).