Temperature Dependence of Saturation Magnetization and Coercivity in Mn_{0.5}Zn_{0.5}Gd_{0.02}Fe_{1.98}O_{4} Ferrite Nanoparticles

I. M. Obaidat\textsuperscript{1},* B. Issa\textsuperscript{1}, B. A. Albiss\textsuperscript{2}, and Y. Haik\textsuperscript{3,4}

\textsuperscript{1}Department of Physics, United Arab Emirates University, Al-Ain 17551, United Arab Emirates
\textsuperscript{2}Superconductivity & Magnetic Measurements Laboratory, Physics Department, Jordan University of Science and Technology, Irbid 22110, Jordan
\textsuperscript{3}Center for Research Excellence in Nanobiosciences, University of North Carolina-Greensboro, NC 27412, USA
\textsuperscript{4}Department of Mechanical Engineering, Qatar University, Qatar

*e-mail:iobaidat@uaeu.ac.ae

Abstract. The influence of temperature on coercivity, $H_c$ and saturation magnetization, $M_s$, were investigated experimentally in Mn$_{0.5}$Zn$_{0.5}$Gd$_{0.02}$Fe$_{1.98}$O$_4$ ferrite nanoparticles (average size 35 nm). Isothermal magnetization curves $M(H)$ were obtained in the field range from -5 kOe to +5 kOe at different temperatures after the zero field cooling (ZFC) process. The temperature dependence of the coercivity, $H_c(T)$ deviated slightly from the classical Kneller’s law. The temperature dependence of saturation magnetization, $M_s(T)$ was found to have an excellent agreement with the Bloch’s law. These results are discussed in terms of several factors such as the size and size distribution of the particles, inter-particle interactions and the surface spin.

1. Introduction

When the radius of the magnetic nanoparticles (MNPs) decreases, larger fraction of the atoms resides on the surface compared to those in the core of the particle. This is because of the increase in the ratio of the surface area to the volume of the particle. This gives the nanoparticles (NPs) interesting properties that could be different from those of the bulk material. At very small sizes, nanoparticles display superparamagnetic behavior above the so-called blocking temperature, $T_B$ [1]. Superparamagnetic particles (at temperatures above the blocking temperature) show a quick response to the variations in the applied magnetic field. In the typical case, these responses occur with zero remnant magnetization, $M_R$ and coercivity, $H_c$.

Ferrimagnetic nanoparticles such as Mn$_{0.5}$Zn$_{0.5}$Gd$_{0.02}$Fe$_{1.98}$O$_4$ are attractive because of their biomedical applications as contrast agents in magnetic resonance imaging (MRI) and their promising application in self-controlled magnetic hyperthermia [2, 3]. Although many interesting studies were conducted on ferrite nanoparticles, many investigations are being conducted to understand their magnetic behavior [4-17].

Due to finite size effects, surface spin effects (such as spin canting, spin freezing, spin disorder), the saturation magnetization of nanoparticles was found to be different from that of the corresponding bulk material. In ferromagnetic particles, these effects become more important because of the superexchange interaction [18, 19]. Surface spin disorder can occur at the surface of the nanoparticle because of the existence of impurities such as oxygen ion vacancy at the surface of the nanoparticle.
which could lead to the breaking of superexchange bonds between the magnetic cations [20]. Hence, the saturation magnetization in ferrite nanoparticles is noticeably small compared with that of bulk material [21, 22]. The decrease of saturation magnetization in nanoparticles becomes more pronounced with the decrease of the size of nanoparticles where the surface to volume ratio becomes larger [23]. On the other hand, the temperature dependence of coercivity and saturation magnetization in nanoparticles [24] showed the importance of surface spin and finite size effects in nanoparticles. The temperature dependence of coercivity is described by Kneller’s law [25, 26]

\[ H_c(T) = H_0 \left[ 1 - \left( \frac{T}{T_B} \right)^\alpha \right] \]  

(1)

Here \( T_B \) is the superparamagnetic blocking temperature of the nanoparticles and \( H_0 \) is the coercivity at \( T = 0 \) K. Kneller law was derived in the temperature range \((0 - T_B)\), where the nanoparticles were considered to be single-domain, non-interacting and with uniaxial anisotropy. For such system, \( \alpha \) was found be equal to \( \frac{1}{2} \).

For bulk ferromagnetic or ferrimagnetic materials at low temperatures, the saturation magnetization, \( M_s \) as function of temperature is governed by the Bloch’s law [27]

\[ M_s(T) = M(0) \left[ 1 - \left( \frac{T}{T_o} \right)^\alpha \right] \]  

(2)

Here \( M(0) \) is the saturation magnetization at 0 K and \( T_o \) is the temperature at which the \( M_s \) becomes zero. The exponent \( \alpha \) is known as the Bloch’s exponent where \( \alpha = 3/2 \) for bulk materials. Bloch derived the \( T^{3/2} \) law by considering the magnon excitation of long wave-length spin-waves at low temperatures. However, in nanoparticles and due to finite size effects, magnons could have wavelengths larger than the size of the particle. The confinement of the wavelength of the spin wave by the size of the magnetic nanoparticle results in a gap in the spin-wave energy spectrum [24]. On the other hand, at temperatures larger than the spin-wave energy gap, Bloch’s law seems to be applicable in nanoparticles. Several studies [28-42] reported the deviation of the saturation magnetization from Bloch’s law in nanoparticles at low temperatures. The modified Bloch’s law for nanoparticles was shown to have similar form to the Bloch’s law for bulk materials but with Bloch’s exponent \( \alpha \) which could have values larger and smaller than 3/2 [34, 35] at intermediate temperatures and decays exponentially at low temperatures [31]. Various interpretations were proposed for the deviation from the Bloch’s law in nanoparticles [24, 31-40]. For example, the additional magnetization due to shell spins was suggested to induce the deviation from the Bloch law [38]. In [40], the deviation of the saturation magnetization from the Bloch law at temperatures below 50 K was suggested to be due to the canted surface spins which freeze into a disordered state.

In this paper we studied the role of temperature on the coercivity and saturation magnetization in Mn\(_{0.5}\)Zn\(_{0.5}\)Gd\(_{0.02}\)Fe\(_{1.98}\)O\(_4\) ferrite nanoparticles in temperatures between 5 and 300 K. We compare our data with Bloch’s and Kneller’s laws.

2. Experimental Methods

The aim of this synthesis process is to produce Gd-substituted Mn-Zn ferrite nanoparticles of the desired stoichiometry, exhibiting the form \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Gd}_x\text{Fe}_{2-x}\text{O}_4 \) with controlled values for the Gd concentration. Chemical co-precipitation and ferritization (formation of ferrite) method was used here. In order to obtain Fe\(^{3+}\), Gd\(^{3+}\), Mn\(^{2+}\) and Zn\(^{2+}\) ions in aqueous form different metal solutions were prepared in the synthesis process. Solutions such as Fe\(_2\text{O}_3\), \( \text{MnCl}_2 \), \( \text{ZnSO}_4\), \( \text{GdCl}_3\), \( \text{ZnSO}_4\), and Fe\(_2\text{SO}_4\) were mechanically stirred in deionized water. Controlled Argon pressure was implemented. A thick crystalline precipitate which is formed after addition of the co-precipitating base (sodium hydroxide base), was stirred at room temperature for half hour, and then heated for one hour at 90 °C. Ferritization of this precipitate is ensured by heating in the precipitation alkaline solution. The synthesized nanoparticles then were filtered and washed several times with doubly distilled water and acetone. The nanoparticles then were filtered and dried at room temperature. Finally, the nanoparticles were prepared as powders or colloids. The magnetic measurements were conducted
using Superconductor Quantum Interference Device (MPMS SQUID VSMdc Magnetometer). The average size of the nanoparticles and their size distribution were extracted using scanning electron microscopy (SEM) analysis (EDX, Jeol Model JSM-5600).

3. Results and Discussion

Tunnelling electron microscopy (TEM) image of the nanoparticles is displayed in figure 1. It is seen that there are some agglomerations of the particles. In figure 2, the size histogram of the nanoparticles obtained from SEM image is displayed. The histogram revealed a non-uniform dispersion of nanoparticles with average diameter of 35 nm. The magnetization hysteresis measurements were conducted at several temperatures from 5 K up to room temperature 300 K. For each hysteresis measurement, the sample was cooled to the specific temperature and the magnetization measurement was done under the applied magnetic field from -5 kOe to +5 kOe.

Figure 3 displays the magnetization hysteresis loops at several temperatures (5, 50, 100, 200, and 300 K). We can see that the saturation magnetization at 200 and 300 K was achieved while it was not fully achieved at temperatures below 200 K. This could be a result of surface effects where disordered surface spins of nanoparticles are not easily aligned along the direction of the applied magnetic field leading to the incomplete saturation magnetization. The value of the magnetization at the largest applied field of 5 kOe is referred to as the saturation magnetization. In figure 4(a), we plotted the coercive fields, $H_c(T)$ as a function of temperature. $H_c(T)$ which were obtained from the magnetization hysteresis loops. It is clear that the coercivity decreases monotonically with increasing temperatures.
Figure 3. $M(H)$ hysteresis curves of the ferrite nanoparticles obtained at 5, 50, 100, 200, and 300 K in the field range from -5 to +5 kOe. The inset of the figure is a magnification of curves at very low fields. This behavior is understood since thermal energy will enhance thermal fluctuations of the pinned magnetic moments and hence minimizing the effect of anisotropy barriers. We have fitted the $H_c(T)$ data with the Kneller’s law (equation 1). $H_c$ is estimated by extrapolating the $H_c(T)$ curve towards the magnetic field axis (at $T = 0$ K). The blocking temperature for our nanoparticles is predicted to be larger than 200 K. This prediction is based on earlier measurements of blocking temperature (determined from the peak of zero field cooled magnetization) of other smaller Mn$_{0.5}$Zn$_{0.5}$Gd$_{0.02}$Fe$_{1.98}$O$_4$ nanoparticle samples that were similarly synthesized [43, 44]. The solid line in figure 4(b) shows the fitting of our $H_c(T)$ data with the Kneller’s law. We can see the good fitting of the data to the above relation but with $\alpha = 0.57$, $T_B = 223$ K and $H_o = 274$ Oe. Due to fluctuations that occurred at $T = 300$ K near $H = 0$ Oe, it was not possible to include $H_c$ value for $T = 300$ K in the fitting.

Figure 5(a) displays the saturation magnetization, $M_s$ as a function of temperature. We can see that $M_s(T)$ decreases monastically with temperature. However, at temperature below 100 K, $M_s$ decreased...
slowly with increasing temperature after which, $M_s$ dropped sharply. We have fitted the $M_s(T)$ data for our nanoparticles with the Bloch’s law (equation 2). The solid line in figure 5(b) shows the fitted curve.

![Graph](image)

(a) Coercivity as function of temperature, $H_C(T)$ for the ferrite nanoparticles. The dashed line is a guide for the eye. (b) Coercivity as function of temperature $H_C(T)$ for the ferrite nanoparticles. The solid line represents the fitting to the modified Kneller’s law.

![Graph](image)

Figure 4. (a) Coercivity as function of temperature, $H_C(T)$ for the ferrite nanoparticles. The dashed line is a guide for the eye. (b) Coercivity as function of temperature $H_C(T)$ for the ferrite nanoparticles. The solid line represents the fitting to the modified Kneller’s law.

![Graph](image)

Figure 5. (a) Saturation magnetization as function of temperature, $M_s(T)$ for the ferrite nanoparticles. The dashed line is a guide for the eye. (b) Saturation magnetization as function of temperature, $M_s(T)$. The solid line represents the fitting to the modified Bloch’s law.

We can see the excellent fitting of the data with the above relation with $\alpha = 1.514$. $M(0)$ was determined from the fit to be 23.3 emu/g and $T_o$ is nearly 490 K. The dependence of the saturation magnetization, $M_s$ of these ferrite particles on temperature is well described by Bloch’s law over the whole temperature range.

We suggest that the excellent fitting of our data to Bloch’s law and the good fitting to Kneller’s and are due to the large volume of our nanoparticles where the bulk properties are nearly recovered. The slight deviation from Kneller’s law could be attributed to several factors such as the size distribution of
the particles, significant inter-particle interactions [41, 42] and the disordered surface spins which influence the surface anisotropy and hence the effective anisotropy in the particles. We believe that the smaller the particles are the larger is the influence of surface effects and the larger is the deviation from Kneller’s and Bloch’s laws. The size at which a crossover between the nanoparticle properties and bulk properties occurs is currently under investigation.

4. Conclusions
The coercivity, $H_c$ as function of temperature was found to have good agreement with the classical Kneller’s with small deviations. The temperature dependence of saturation magnetization, $M_s(T)$ was found to have excellent agreement with Bloch’s laws. The good fitting of our data with these laws is suggested to be due to the large size of the particles where bulk properties might be significant. The small deviation from Kneller’s law is suggested to be due the volume distribution, strong inter-particle interactions and enhancement of the effective anisotropy of these nanoparticles due to the disordered surface spins.

ACKNOWLEDGMENT
This work was financially supported by the UAEU Program for Advanced Research (UPAR) under the Grant no. 31S162.

References
[1] V. Skumryev, S. Stoyanov, Y. Zhang, G. Hadjipanayis, D. Givord, and J. Nogues, Nature 423, 850 (2003).
[2] B. Issa, I. M. Obaidat, B. A. Albiss, and Y. Haik, Int. J. Mol. Sci. 14, 21266 (2013).
[3] I. M. Obaidat, B. Issa, and Y. Haik, Nanomaterials 5, 63 (2015).
[4] R. H. Kodama, A.E. Berkowitz, E.J. McNiff Jr., S. Foner, J. Appl. Phys. 81, 5552 (1997).
[5] R. H. Kodama, A.E. Berkowitz, Phys. Rev. B 59, 6321 (1999).
[6] F. Gazeau, E. Dubois, M. Hennion, R. Perzynski, Yu.Raikher, Europhys. Lett. 40, 575 (1997).
[7] M. Hennion, C. Bellouard, I. Mirebeau, J.L. Dormann, M.Nogues, Europhys. Lett. 25, 43 (1994).
[8] C. Bellouard, I. Mirebeau, M. Hennion, Phys. Rev. B 53, 5570 (1996).
[9] L. Del Bianco, A. Hernando, M. Multigner, C. Prados, J.C. Sanchez-Lopez, A. Fernandez, C.F. Conde, A. Conde, J. Appl. Phys. 84, 2189 (1998).
[10] A. Millan, A. Urtizberea, N. J. O. silva, F. Palacio, V. S. Amaral, E. Snoeck, V. Serin, J. Magn. Magn. Mater. 312, L5 (2007).
[11] A. K. Gaharwar, J. E. Wong, D. Müller-Schulte, D. Bahadur, and W. Richtering, J. Nanosci. Nanotechnol. 9, 5355 (2009).
[12] P. V. Hendriksen, F. Bodker, S. Lenderoth, C. A. Oxborrow, S. Wells, and S. Morup, J. Phys: Condens. Matter 6, 3081 (1994).
[13] D. Lin, A. C. Nunes, C. F. Majkrzak, A. E. Berkowitz, J. Magn. Magn. Mater. 145, 343 (1995).
[14] S. Lenderoth, P. V. Hendriksen, F. Bodker, S. Wells, K. Davies, S. W. Charles, S. Morup, J. Appl. Phys. 75, 6583 (2004).
[15] Y. Xuan, Q. Li, and G. Yang, J. Magn. Magn. Mater. 312, 464 (2007).
[16] J. Wang, C. Zeng, Z. Peng, and Q. Chen, Physica B 349, 124 (2004).
[17] P. Mathur, A. Thakur, M. Singh, J. Magn. Magn. Mater. 320, 1364 (2008).
[18] C. Caizer, M. Stefanescu, C. Muntean, I. Hrianca, J. Adv. Mater. 3, 919 (2001).
[19] C. Caizer, Appl. Phys. A 80, 1745 (2005).
[20] A. E. Berkowitz, R. H. Kodama, S. A. Makhlof, F. T. Parker, F. E. Spada, E. J. McNiff Jr., S. Foner, J. Magn. Mater. 196–197, 591 (1999).
[21] L. Zhang, G. C. Papaefthymiou, R. F. Ziolo, J. Y. Ying, Nano Structur. Mater. 9, 185 (1997).
[22] B. Martinez, A. Roig, X. Obradors, E. Molins, P. Claret, C. Monty, J. Appl. Phys. 79, 2580 (1996).
[23] C. Caizer, M. Stefanescu, J. Phys. D: Appl. Phys. 35, 3035 (2002).
[24] K. Maaz, A. Muntaz, S. K. Hasanain, M. F. Bertino, J. Magn. Magn. Mater. 322, 2199 (2010).
[25] E. F. Kneller, F. E. Luborsky, J. Appl. Phys. 34, 656 (1963).
[26] X. Battle, M. Garcia del Muro, J. Tejada, H. Pfeiffer, P. Goand, E. Sinn, J. Appl. Phys. 74, 3333 (1993).
[27] F. Bloch, Z. Phys. 61, 206 (1930).
[28] E. Della Torre, L. H. Bennett and R. E. Watson, Phys. Rev. Lett. 94, 147210 (2005).
[29] V. Senz, R. Röhlsberger, J. Bansmann, O. Leupold, K. –H. Meiwes-Broer, New J. Phys. 5, 47 (2003).
[30] P. V. Hendriksen, S. Linderoth, P. A. Lindgard, J. Magn. Magn. Mater. 104–107, 1577 (1992).
[31] P. V. Hendriksen, S. Linderoth, P. A. Lindgard, Phys. Rev. B 48, 7259 (1993).
[32] S. Linderoth, L. Balcells, A. Labarta, J. Tejada, P. V. Hendriksen, S. A. Sethi, J. Magn. Magn. Mater. 124, 269 (1993).
[33] A. S. Eggeman, A. K. Petford-Long, P. J. Dobson, J. Wiggins, T. Bromwich, R. Dunin-Borkowski and T. Kasam, J. Magn. Magn. Mater. 301, 336 (2006).
[34] D. Ortega, E. Vélez-Fort, D. A. García, R. García, R. Litrán, C. Barrera-Solano, M. Ramírez-del-Solar and M. Domínguez, Phil. Trans. R. Soc. A 368, 4407 (2010).
[35] Y. A. Koksharov, In “Magnetic Nanoparticles”, S. P. Gubin (Ed.), Wiley-VCH, Berlin, 2009.
[36] C. R. Alves, R. Aquino, M. H. Sousa, H. R. Rechenberg, G. F. Goya, F. A. Tourinho, J. Depeyrot, J. Met. Nanocrys. Mater. 20–21, 694 (2004).
[37] K. Mandal, S. Mitra, P. A. Kumar, Europhys. Lett. 75, 618 (2006).
[38] L. D. Tung, V. Kolesnichenko, D. Caruntu, N.H. Chou, C.T. O Connor, L. Spinu, J. Appl. Phys. 93, 7486 (2003).
[39] S. Morup, Europhys. Lett. 77, 27003 (2007).
[40] C. R. Alves, R. Aquino, J. Depeyrot, T. A. P Cotta, M. H. Sousa, F. A. Tourinho, H. R. Rechenberg, G. F. Goya, J. Appl. Phys. 99, 08M905 (2006).
[41] S. P. Gubin, Yu. A. Koksharov, G. B. Khomutov, G. Yu. Yurkov, Russian Chemical Reviews 74, 489 (2005).
[42] A. K. Giri, J. Appl. Phys. 81, 1348 (1997).
[43] I. M. Obaidat, B. Issa, and Y. Haik, J. Nanosci. Nanotech. 11, 3882 (2011).
[44] I. M. Obaidat, B. Issa, B. A. Albiss, G. Qabaja, N. E. Al Khaili, Z. A. Karam, A. M. Hefaity, S. Qadri, A. Al-Otouur, and Y. Haik, J. Nanoeng. Nanomanuf. 2, 325 (2012).