Available online at www.sciencedirect.com
ScienceDirect
Journal of Magnetism and Magnetic Materials 310 (2007) e806–e808
www.elsevier.com/locate/jmmm

Inter-particle and interfacial interaction of magnetic nanoparticles

Che Jin Bae[a], Yosun Hwang[a], Jongnam Park[b], Kwangjin An[b], Youjin Lee[b], Jinwoo Lee[b], Taeghwan Hyeon[b], J.-G. Park[a,c,*]

[a]*BK21 Physics Division, Department of Physics and Institute of Basic Sciences, Sungkyunkwan University, Suwon 440-746, Republic of Korea*
[b]*National Creative Research Center for Oxide Nanocrystalline Materials and School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Republic of Korea*
[c]*Center for Strongly Correlated Materials Research, Seoul National University, Seoul 151-747, Republic of Korea*

Available online 15 November 2006

Abstract

In order to understand inter-particle as well as interfacial interaction of magnetic nanoparticles, we have prepared several Fe_3O_4 nanoparticles in the ranges from 3 to 50 nm. These nanoparticles are particularly well characterized in terms of size distribution with a standard deviation (σ) in size less than 0.4 nm. We investigated the inter-particle interaction by measuring the magnetic properties of the nanoparticles while controlling inter-particle distances by diluting the samples with solvents. According to this study, blocking temperatures dropped by 8–17 K with increasing the inter-particle distances from a few nm to 140 nm while the overall shape and qualitative behavior of the magnetization remain unchanged. It implies that most features observed in the magnetic properties of the nanoparticles are due to the intrinsic properties of the nanoparticles, not due to the inter-particle interaction. We then examined possible interfacial magnetic interaction in the core–shell structure of our Fe_3O_4 nanoparticles.

PACS: 75.50.Kj; 75.60.Ej

Keywords: Magnetic nanoparticle; Superparamagnetism; Inter-particle interaction; Interfacial interaction

Magnetic nanoparticles have recently been the focus of intensive research for various reasons. For example, they not only find possible applications in wide-ranging industry but also present a new way of understanding magnetism at reduced scales and dimensions. Despite this unprecedented opportunity in nanomagnetism, however, one of the biggest challenges has been how to prepare well-characterized nanoparticles, in particular with a fine control of size and shape. Thanks to efforts by several researchers, such fine control of size and shape of magnetic nanoparticles is now readily available [1,2], so opening the door for further thorough studies of their magnetic properties.

In the field of nanomagnetism, there are two basic questions of fundamental importance: one is the inter-particle interaction and another the surface state. These two problems are rather well known and there have been several reports on the subjects. For example, it was argued recently that some memory effects found in permalloy nanoparticles may be due to inter-particle interaction [3] although it was subsequently questioned and claimed to be instead the consequence of the distribution in the particle size [4]. This alone demonstrates that a simple question of inter-particle interaction is not trivial but still a live and important issue in nanomagnetism, requiring further systematic studies of well-characterized samples. On the other hand, the idea has been around for sometime of that the surface of magnetic nanoparticles may not have the same spin arrangement as that of the bulk because of broken bonds at the surface, leading to the concept of so-called surface states. This surface state or associated effect has indeed been observed in several magnetic nanoparticles such as NiO [5] and MnO [6], to name only a few.

Using well-characterized Fe_3O_4 nanoparticles prepared as described in Refs. [2,7]: all our samples are found to have standard deviations (σ) in size smaller than 0.4 nm, we

*Corresponding author. Department of Physics and Institute of Basic Sciences, Sungkyunkwan University, Suwon 440-746, Republic of Korea. Tel.: +82 31 2905955; fax: +82 31 2907055.
E-mail address: jgpark@skku.edu (J.-G. Park).

0304-8853/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2006.10.746

have tried to understand the two basic questions of nanomagnetism aforementioned. Since our samples are easily soluble in several solvents such as oleic acid and xylene, we could control the inter-particle distance precisely and measure the evolution of the magnetization as function of the inter-particle distance. While doing this, we have also investigated possible interfacial interaction between the surface state and the bulk state by measuring the field as well as temperature dependence of the magnetization. All our magnetization measurements have been carried out using a commercial SQUID magnetometer (MPMS-5XL, Quantum Design, USA).

In order to investigate the effects of the inter-particle interaction on the magnetic properties, in particular so-called blocking temperatures T_B, we have used mainly three nanoparticles with the sizes of 3, 5 and 7 nm. All these samples show that there are irreversible points: 45 K (3 nm), 75 K (5 nm) and 105 K (7 nm), in the magnetization data measured after zero-field cooling (ZFC) and field cooling (FC). We then dispersed the nanoparticles completely using two solvents: oleic acid and xylene, to find that their blocking temperatures dropped by 8–17 K with the largest effect found in the 3 nm particles. Nonetheless, the overall temperature dependence of the magnetization remains unchanged. To study the effects of inter-particle interaction more carefully, we have diluted the nanoparticle powder samples in a controlled manner using oleic acid and xylene. We measured the magnetization of all the diluted samples with applied field of 100 Oe; from which we could determine blocking temperatures as function of the inter-particle distance. As shown in Fig. 1 for the 7 nm sample, blocking temperatures drop rather quickly initially with small changes in the inter-particle distance and becomes easily saturated at the value of $T_B = 98$ K. In order to check the reproducibility of the results, we have repeated the measurements under similar conditions to find that they are more or less the same as shown in Fig. 1. The origin of the observed effects of the inter-particle interaction is revealed by our subsequent analysis using a formula with dipole–dipole interaction, $T_B(r) = T_B^0 + \Delta/r^3$, where T_B^0 is the blocking temperature of a single nanoparticle and Δ/r^3 a term of dipole–dipole interaction with r being a distance between the centers of two neighboring 7 nm nanoparticles (the line in Fig. 1). As one can see, all the observed behavior seems to follow the theoretical curve rather nicely, implying that a dominant interaction between particles is of dipolar nature. We have also made similar observations for 3 and 5 nm sized particles.

We also studied the field dependence of the magnetization of several nanoparticles at a number of temperatures. As summarized in Fig. 2, all our samples including a diluted one show coercive fields to decrease with increase in temperatures and disappear at the blocking temperatures. It is worth commenting that the temperature dependence of the coercive fields does not follow a theoretical prediction for classical single domain particles, $H_c = 1-(T/T_B)^{1/2}$ (dashed line in top figure). It is equally interesting to note that all our magnetization curves show horizontal

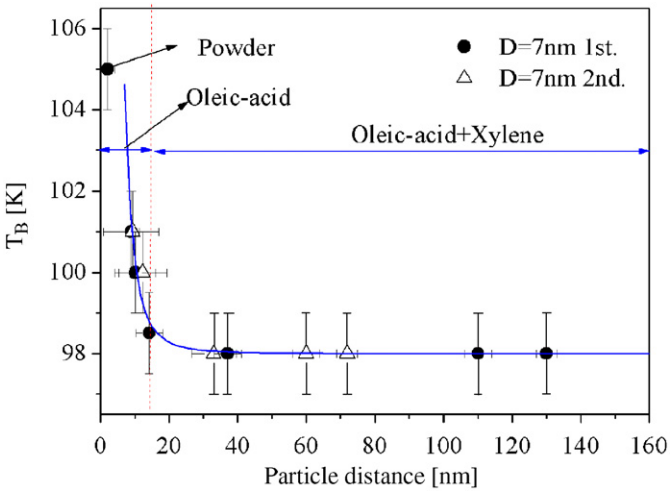

Fig. 1. It shows how blocking temperatures vary with increasing inter-particle distances (r) for the 7 nm sample. The line represents our curve fit using a formula of dipole–dipole interaction.

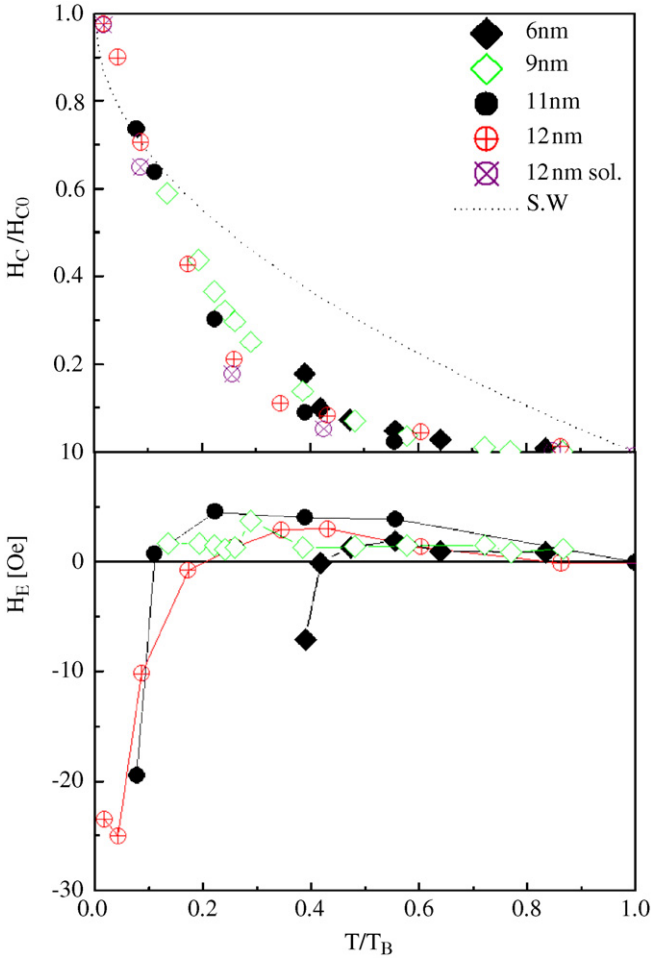

Fig. 2. (Top) Coercive field normalized with respect to the value extrapolated at $T = 0$ K is given as function of normalized temperature, T/T_B, where T_B is blocking temperature of each particle. (Bottom) Exchange bias, H_E, is plotted for the same compositions.

asymmetric shifts, which have clear temperature dependence as shown in the plot of H_E, defined as the amount of the horizontal shift in the coercive fields (see bottom figure of Fig. 2). Although similar shifts were previously reported and interpreted in terms of surface states of nanoparticles [5], however, we believe that there is a subtle but important difference between our case and that reported in Ref. [5]. A major difference lies in the fact that as our XMCD data revealed our nanoparticles form in a core–shell structure with Fe_3O_4 in the core part and α-Fe_2O_3 in the shell part [7]. According to our analysis, this core–shell structure gives rise to an additional term in magnetic interaction. This additional term, which we call interfacial interaction, describes interaction between the surface α-Fe_2O_3 and the core Fe_3O_4.

To summarize, we have investigated the two key questions of nanomagnetism using well-characterized Fe_3O_4 samples. Although our results support the generally held view of the nanomagnetism, nonetheless our finding of the experimental evidence for interfacial interaction begs better understanding of this interesting field.

Works at Sungkyunkwan University were supported by the Korea Research Foundation (Grant No. 2005-C00153) and the BAERI program.

References

[1] S. Sun, et al., Science 287 (2000) 1989.
[2] J. Park, et al., Angew. Chem. 44 (2005) 2872.
[3] Y. Sun, et al., Phys. Rev. Lett. 91 (2003) 167206.
[4] M. Sasaki, et al., Phys. Rev. Lett. 93 (2004) 139701.
[5] R.H. Kodama, et al., Phys. Rev. Lett. 79 (1997) 1393.
[6] J. Park, et al., J. Phys. Chem. B 108 (2004) 13594.
[7] J. Park, et al., Nat. Mater. 3 (2004) 891.