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Memory effect versus exchange bias for maghemite nanoparticles

K. Nadeem [a,*], H. Krenn [b], D.V. Szabó [c]

[a] Materials Research Laboratory, Department of Physics, International Islamic University, Islamabad, Pakistan
[b] Institute of Physics, Karl-Franzens University Graz, Universitätsplatz 5, A-8010 Graz, Austria
[c] Karlsruhe Institute of Technology, Institute for Applied Materials, 76344 Eggenstein-Leopoldshafen, Germany

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ABSTRACT

We studied the temperature dependence of memory and exchange bias effects and their dependence on each other in maghemite (γ-Fe_2O_3) nanoparticles by using magnetization studies. Memory effect in zero field cooled process in nanoparticles is a fingerprint of spin-glass behavior which can be due to i) surface disordered spins (surface spin-glass) and/or ii) randomly frozen and interacting nanoparticles core spins (super spin-glass). Temperature region (25–70 K) for measurements has been chosen just below the average blocking temperature (T_B=75 K) of the nanoparticles. Memory effect (ME) shows a non-monotonous behavior with temperature. It shows a decreasing trend with decreasing temperature and nearly vanishes below 30 K. However it also decreased again near the blocking temperature of the nanoparticles e.g., 70 K. Exchange bias (EB) in these nanoparticles arises due to core/shell interface interactions. The EB increases sharply below 30 K due to increase in core/shell interactions, while ME starts vanishing below 30 K. We conclude that the core/shell interface interactions or EB have not enhanced the ME but may reduce it in these nanoparticles.

1. Introduction

The magnetic memory effect in nanoparticles has been investigated intensively due to its complex behavior [1–3]. Memory and aging effects are considered as finger prints for spin-glass behavior in magnetic systems [4–8]. Spin-glass arises in magnetic systems due to randomness and frustration of magnetic spins. There can be two kinds of spin-glass behavior in nanoparticles, one is the super spin-glass [9–11] which arises in interacting nanoparticles due to random freezing of the huge core spin (super spin) of individual nanoparticles, while second is the surface spin-glass in core/shell nanoparticles due to disordered surface spins [12,13]. The memory effect (ME) is reported also for non-interacting superparamagnetic nanoparticles due to distribution in their relaxation times which arises through particle size distribution [14]. Differentiation of ME due to particle size distribution and spin-glass can be done by using zero field cooled (ZFC) and field cooled (FC) magnetic measurements. The ME due to particles size distribution of superparamagnetic nanoparticles can be found only in FC, while spin-glass nanoparticles show ME in both ZFC and FC protocols. De et al. [15] studied the ME in nanocrystalline superparamagnetic $Fe_{50}Ni_{50}$ alloy embedded in silica matrix and observed ME in FC only, which arises due to particle size distribution. Khan et al. [16] reported memory effect in ZFC process for $La_{0.9}Sr_{0.1}CoO_3$ single crystal and attributed it to spin-glass behavior. Therefore in this article we have done ME in ZFC process to exclude the possibility of ME due to particle size distribution albeit the microwave plasma synthesis provides the most narrow size distribution among other preparation methods.

For interacting nanoparticles, the ME increases with increasing nanoparticle concentration (dipolar interactions) [17]. Peddis et al. [18] reported ME in super spin-glass ferromagnetic (FM) Co nanoparticles in antiferromagnetic (AFM) Mn matrix and found that the ME increases with increasing nanoparticle concentration and interface interactions (between nanoparticles and matrix). Domingo et al. [19] reported exchange bias (EB) phenomena in the same super spin-glass system (Co nanoparticles in Mn matrix). Malik et al. [20] reported ME in FC process for nickel ferrite/polymer composites and found suppression of ME with increasing magnetic nickel ferrite component in the composite. Vasilakaki et al. [21] did Monte Carlo simulation of the ME of an assembly of FM core/AFM shell nanoparticles and found good comparison with the experimental results of system containing FM Co nanoparticles dispersed in AFM Mn matrix. They concluded that both dipolar interactions and interface interactions increase the ME. ME has been also reported for non-interacting core/shell nanoparticles which signifies the presence of surface spin-glass freezing in them due to disordered spins at the nanoparticle's surface. Bisht et al. [12] reported ME in both ZFC and FC processes for nickel oxide nanoparticles and attributed it to surface spin-glass behavior.

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* Corresponding author.
E-mail address: kashif.nadeem@iiu.edu.pk (K. Nadeem).

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Unlike FM nanoparticles dispersed in AFM matrix, the interface interactions in bare ferrite nanoparticles are between surface spins and core spins. Core/shell interface interactions are dominate in fine sized nanoparticles due to large surface to volume ratio. These core/shell interactions in nanoparticles lead to the EB effect, which is well known for FM layers on AFM substrates [22–24]. Cabreira-Gomes et al. [25] reported the presence of EB in core/shell $MnFe_2O_4/\gamma\text{-}Fe_2O_3$ and $CoFe_2O_4/\gamma\text{-}Fe_2O_3$ nanoparticles and attributed it to core/shell interactions. Therefore in this article, we have chosen fine 6 nm maghemite ($\gamma\text{-}Fe_2O_3$) spinel ferrite nanoparticles to extract possible correlation between memory and exchange bias effects by using temperature dependent magnetic measurements.

2. Experimental

$\gamma\text{-}Fe_2O_3$ nanoparticles were prepared by microwave plasma synthesis. The complete synthesis process and structural evaluation of the materials (made by the same synthesis process) is reported elsewhere [26,27]. Average particle size and size-distribution statistics were determine from an image analysis of transmission electron micrographs (TEM, model number CM20 from FEI with 200 kV acceleration voltage and LaB6 cathode). Magnetic measurements were taken by using superconducting quantum interference device (SQUID)-magnetometry (Quantum Design, MPMS-XL-7). The AC susceptibility measurements were performed by the same magnetometer.

3. Results and discussion

Fig. 1 shows the transmission electron microscopy (TEM) image of maghemite nanoparticles at 10 nm scale. It is observed that the nanoparticles are nearly of spherical shape. Average particle size as calculated from log-normal distribution function fit was 6.1 nm with a normalized standard deviation $(\sigma_D)=0.22$ [28].

Fig. 2(a) shows the ZFC/FC magnetization curves taken under applied field of 50 Oe. The ZFC curve exhibits peak at 75 K which corresponds to average blocking temperature (T_B) of the nanoparticles. Below T_B, the nanoparticles spins are blocked in their anisotropy (easy) axes and are in blocked state. Above T_B, nanoparticles spins get de-blocked due to enough thermal energy and will be in superparamagnetic state [29]. The FC curve gets separated from ZFC and flattens below T_B. The flatness of the FC curve is an indication for the presence of spin-glass behavior and/or interparticle interactions in these nanoparticles. In fine core/shell maghemite nanoparticles, the surface effects are more dominant due to large surface-to-volume ratio. The surface atoms have coordination bonds on the inner side only and thus contribute to surface disorder and magnetic frustration. Due to randomly frozen surface spins, the surface anisotropy is different as compared to core anisotropy of ferrimagnetically aligned core spins. The surface disorder and frustration are main ingredients for surface spin-glass behavior. As core/shell interactions are usually dominant below T_B, we have chosen a region just below this temperature for ME and EB experiments.

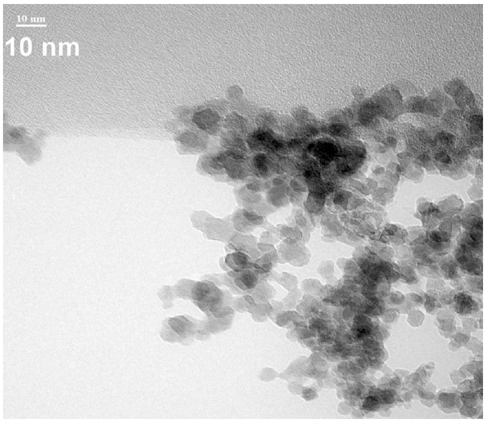

Fig. 1. Transmission electron microscopy image of fine 6 nm maghemite nanoparticles at 10 nm scale.

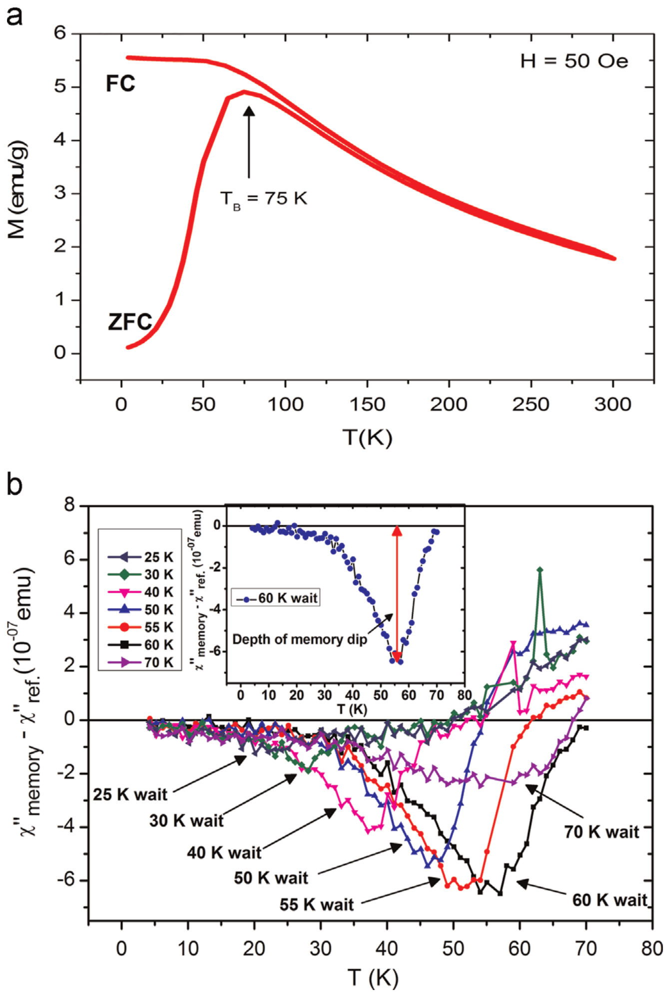

Fig. 2. (a) ZFC/FC magnetization curves of maghemite nanoparticles. Arrow indicates the average blocking temperature of the nanoparticles, (b) ME measured for different halted temperatures. The sample was halted at 25 K, 30 K, 40 K, 50 K, 55 K, 60 K, and 70 K for 2 h during the ZFC process to get χ''_{memory}, whereas the $\chi''_{ref.}$ is determined without any halting temperature. Inset shows that how the ME dip was calculated and vertical arrow indicates the depth of the ME dip.

The ME in ZFC magnetic measurement is a finger print for the spin-glass behavior. Although we observed the ME in both in-phase (see Fig. S1) and out-of-phase AC susceptibility, it appeared more pronounced in out-of-phase part. Therefore we have taken the out-of-phase AC susceptibility here. We adopted the ME measurement protocol as described in detail elsewhere [30]. To investigate the ME, one needs two curves, (i) the reference curve and (ii) the memory curve (for which the system is halted at particular temperature for a specified time). The difference between ZFC memory and ZFC reference curves shows a dip at the halting temperature which indicates the presence of ME as known from spin-glass systems [30]. For the reference curve, the sample is continuously ZFC from room temperature to 4.2 K and then immediately the out-of-phase AC susceptibility is recorded on increasing temperature up to 70 K. For the memory curve, the