Mater.Phys.Mech. 4 (2001) 1-4

MAPPING OF SWITCHING AND ANISOTROPY FIELDS IN MAGNETIC NANOPARTICLES

Srikanth Hariharan

Materials Physics Laboratory, Department of Physics, University of South Florida, Tampa, FL 33620, USA

Received: July 3, 2001

Abstract. Magnetic nanostructures hold tremendous potential as basic building blocks in spin-electronic devices and high-density data storage. Precise mapping of fundamental parameters like the anisotropy and switching fields over a wide range in temperature and magnetic fields, is essential to understand the influence of the relaxation, interactions and other phenomena that govern the dynamic magnetic properties in these systems. Dynamic radio-frequency transverse susceptibility (χ_T) experiments provide a very sensitive and unique way to probe these features. We present and discuss the field-dependent transverse susceptibility in two nanoparticle systems: (i) polymer-coated Fe particles and (ii) γ-Fe_2O_3 particles synthesized by micelle method. Systematic χ_T scans at different fixed temperatures reveal variation of the switching and anisotropy fields. Our experiments provide a unique and powerful way to precisely probe the dynamic magnetization in the presence of thermal relaxation and interactions.

Spin electronics is rapidly emerging as the technology of choice for next generation electromagnetic devices [1]. Development of thin film multilayers exhibiting giant magnetoresistance (GMR) and magnetic nanostructures have already revolutionized the data storage industry. There is a concerted effort by researchers to produce periodic assemblies of nanoparticles that have the potential to increase data storage capabilities to > 50 Gigabits/inch^2. Thermal stability of the stored information at room temperature is still a bottleneck that needs to be addressed in magnetic nanostructures. Novel synthetic routes to produce magnetic nanoparticles, size control, and self-assembly are all desirable aspects and researchers are actively pursuing avenues leading to improvements in these areas. Typical morphologies consist of assemblies of nanograins, powders, particles dispersed in a binding material, such as colloids or polymers, and embedded in a matrix. Due to granular texture and the small size of the grains, the physical properties of such systems are strongly modified in comparison to the properties exhibited by their bulk counterparts. For example, some of the exciting developments arising from research on single-domain magnetic nanoparticles include achievement of promising large coercivities in ferromagnetic (FM) and ferrite nanoparticles [2].

The incorporation of magnetic nanoparticles into devices requires fundamental understanding of the collective dynamic magnetic response. Magnetic anisotropy is one of the most fundamental properties that determines important parameters like the switching field distribution and shape of the hysteresis loop. Several important field scales like the switching (H_{sw}) and anisotropy (H_K) fields depend on the particle size distribution, intra- and inter-particle interactions, thermal relaxation effects etc. So in magnetic nanopowder samples, it is important to be able to map the variation of these field scales in the *H-T* plane to get an idea of the systematic influence of material parameters on the magnetic response. Moreover, high-speed switching, magnetic recording and microwave applications all require high frequencies (MHz to GHz) of operation and it is useful to probe the dynamic properties particularly when the materials are subject to high frequency electromagnetic fields.

To address this issue, we have developed a novel radio-frequency (RF) resonant technique based on transverse magnetization measurements to accu-

Corresponding author: Srikanth Hariharan, e-mail: sharihar@chuma1.cas.usf.edu

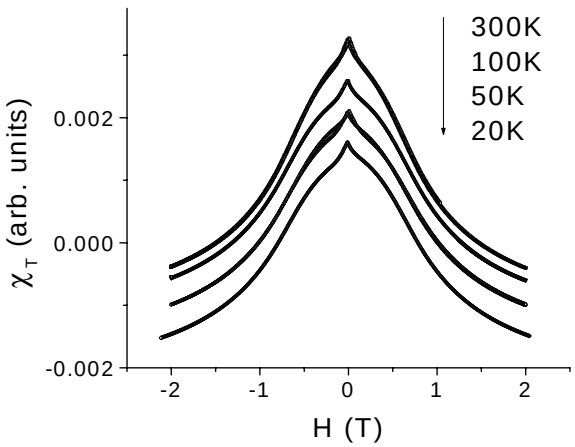

Fig. 1. The RF transverse susceptibility of polystyrene-coated Fe nanoparticles at different temperatures. The data are plotted as % change and arbitrarily shifted along the vertical axis for clarity.

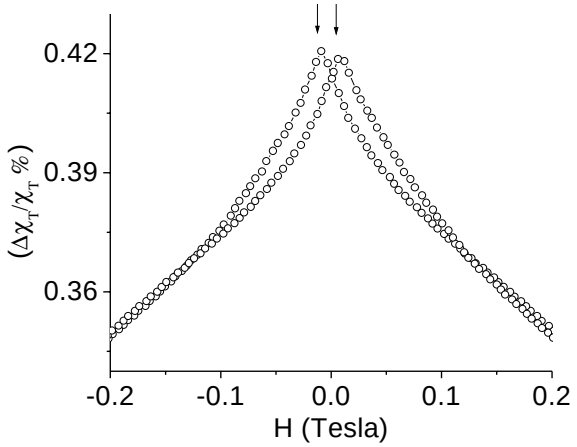

Fig. 2. Low field χ_T scan at T = 300K for polymer-coated Fe. The switching field peaks are marked by arrows.

rately track the variation of dynamic magnetic susceptibility [3]. This system has been used to study nanoparticles in powder form (Fe, γ-Fe_2O_3) and magnetic thin films (CrO_2) [4,5]. The resonant method is based on a tunnel-diode oscillator (TDO) operating at around 8 MHz. The material is placed in an inductive coil that forms part of an LC-tank circuit driven by a tunnel diode biased in its negative resistance region. In the experiment, the shift in resonance frequency is tracked as a function of static field (H) and temperature (T). This is proportional to the change in transverse susceptibility (χ_T). These experiments provide a novel way to measure the anisotropy (H_K) and switching (H_{sw}) fields directly as singular peaks in χ_T are observed at these characteristic fields. The key advantage of our method is the fact that a large number of field-dependent χ_T scans can be done at fixed temperatures and it is possible to accurately track the characteristic fields as the nanoparticle system undergoes a transition from the superparamagnetic to the blocked state.

We have used the TDO method to study a variety of nanoparticle systems. In this paper, to illustrate the effectiveness of this technique and demonstrate the potential for mapping the switching and anisotropy fields, we present and discuss the results on two systems: (i) polystyrene coated Fe nanopowder samples synthesized by microwave plasma method and (ii) γ-Fe_2O_3 nanoparticles synthesized by reverse-micelle method.

Polymer-coated magnetic nanoparticles are of great technological interest as the coating provides a matrix for binding of the particles and also prevents grain growth and agglomeration. A microwave plasma system was used for the synthesis of iron nanopowders and subsequent in-situ encapsulation with polystyrene using plasma polymerization technique [6]. Iron pentacarbonyl and styrene monomer were the starting chemical precursors injected into the plasma reaction zone. The styrene monomer, under the intense heat of the plasma, breaks down forming free radicals. The free radicals recombine (polymerize) on the surface of the iron nanoparticles as they descend down the water-cooled reaction column and polymer encapsulated iron nanopowder was collected in a special filter bag assembly. The average estimated size of isolated particles inferred from TEM image was around 15 – 20 nm with some amount of agglomeration present.

Fig. 1 shows the transverse susceptibility (χ_T) data for different temperatures. The curves are relatively shifted along the vertical axis for clarity. The variation is representative of the change in susceptibility with field for a collection of magnetic nanoparticles with randomly oriented anisotropy axes. Fig. 2 shows the data around zero field for T = 300K. The peaks (marked by arrows) occur at $\pm H_{sw}$ ~ 60 Oe and give a direct measure of the switching fields. From the transverse susceptibility calculations based on the Stoner-Wohlfarth model, the presence of broad shoulders at higher fields (Fig. 1) is indicative of a large distribution in H_k [7,8]. In general this is due to the distribution in particle size and easy axis directions in individual uniaxial particles. In Fig. 1, a careful inspection reveals a gradually asymmetry in the shoulders setting in as the temperature is lowered below 300K. This is quite pronounced and noticeable for the scan at T = 20K.

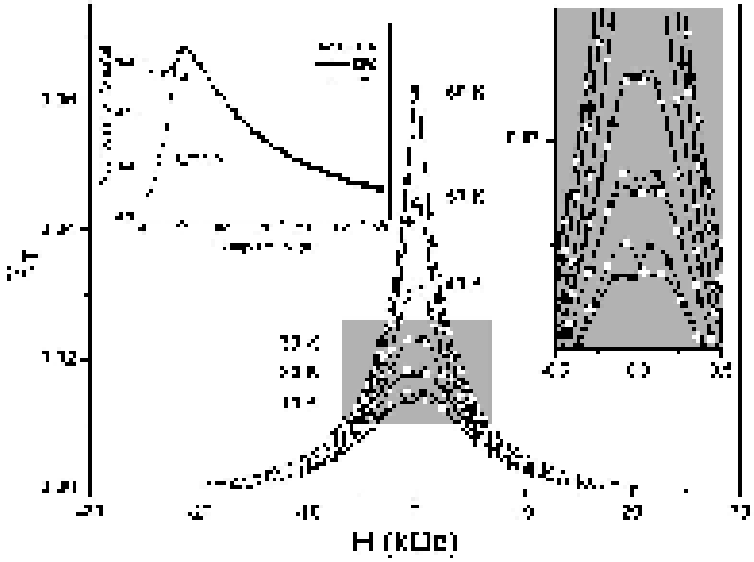

Fig. 3. Field-dependent RF transverse susceptibility of γ-Fe_2O_3 nanoparticles at various temperatures (main panel); zero-field cooled (ZFC) and field cooled (FC) magnetization (left panel); expanded view of (χ_T, *H*) data marked by the shaded region (right panel).

This trend in the temperature dependence of χ_T is observed only in polymer-coated nanoparticles and not in uncoated nanopowders of Fe or γ-Fe_2O_3 that we have measured before synthesized using the same method. Systematic experiments on other polymer-coated nanoparticles are needed to understand the precise origin of this onset of asymmetry. In general, we believe that these features may be a consequence of altered inter-particle interactions introduced by the polymer medium. Interactions have been studied in the past and it has been suggested that this would result in spin re-orientation or disorder at the surface of the particles different from the core and thus introducing a surface anisotropy term in the total magnetic anisotropy [9]. Another possibility is the existence of van der Waal's forces in the composite system that would effectively introduce magnetostriction contributions to the anisotropy. Such effects are common in ferrofluids and polymer-matrix composite materials where domain level processes couple the mechanical and magnetic energies.

As a second example, we now present the results on spherical uniaxial γ-Fe_2O_3 nanoparticles with an average size distribution peaked around 6 nm, prepared using the reverse-micelle method [10]. Unlike the microwave plasma generated particles where larger particles are always produced, the micelle method provides much better control in size distribution. In this system, a clear sharp blocking temperature is seen around 50K and this gives us the opportunity to use TDO experiments to study the variation of the switching peaks in more detail as the system undergoes a transition from ferromagnetic to superparamagnetic state as a function of temperature.

The main panel of Fig. 3 shows the χ_T data at six different temperatures covering the region from 10K to 60K that is just below the blocking temperature. The shaded region around zero field is blown up in the right panel to clearly depict the peak structure exhibited by the transverse susceptibility. Bipolar field scans are represented by open symbols (–20 kOe to 20 kOe) and filled symbols (20 kOe to –20 kOe). A prominent feature that can be distinguished clearly (as seen in right inset of Fig. 3), is that for low temperatures (below ~40K) the curves show two peaks having different heights but located symmetric about the origin of the field axis. As the temperature is increased, the peak heights become equal and eventually the double-peak structure becomes less pronounced and merges into a single central peak. This trend is consistent with a gradual transition from a blocked state toward a superparamagnetic one. At low temperature almost all the particles of the system have a relaxation time much greater than the experimental time (blocked state), which determine the irreversible behavior and the two peaks in the field dependence of the χ_T. Increasing the temperature, the relaxation time of the particles decreases leading to a thermal equilibrium of the system (superparamagnetism). We

notice also an increasing of the zero field values, $\chi_T(H_{DC}=0)$, as the temperature is increasing, followed by a decreasing for temperatures greater than 65K. This implies that the temperature variation of the initial transverse susceptibility $\chi_T(H_{DC}\rightarrow 0)$, for this experimental time, $\tau_m=1/f=1.25\cdot 10^{-5}$ s, has a maximum around 65K. As it was mentioned before, for DC magnetic measurements, where the experimental time is usually around $\tau_m=10^2$ s the blocking temperature is around T_B=53K. This is consistent with an increasing of the blocking temperature, T_B, as the experimental time decreases, as it is typically observed experimentally in magnetic nanoparticle systems [11].

In conclusion we have presented a novel experimental approach based on a resonant RF method that can be effectively used for mapping the switching and anisotropy field distributions in magnetic nanoparticles. Two case studies of typical materials obtained used different synthetic routes are presented to provide an overall demonstration of the effectiveness of this method when compared to conventional magnetization experiments.

ACKNOWLEDGEMENTS

The author acknowledges a DARPA/AMRI subcontract from grant MDA 972-97-1-0003. Stimulating discussions with L. Spinu and his experimental contributions are gratefully acknowledged. We also thank A. Sampath and T. S. Sudarshan for providing the polymer-coated Fe samples and J. Fang and S. Li for providing the γ-Fe_2O_3 nanoparticles in this study.

REFERENCES

[1] G. Prinz and K. Hathaway // *Physics Today* **48** (1995) 58.

[2] *Nanophase Materials: Synthesis –Properties – Applications,* ed.by G. C. Hadjipanayis and R. W. Siegel (Kluwer, Dordrecht, 1994).

[3] H. Srikanth, J. Wiggins and H. Rees // *Rev. Sci. Intrum*. **70** (1999) 3097.

[4] L. Spinu, H. Srikanth, E. E. Carpenter and C. J. O'Connor // *J. Appl. Phys*. **87** (2000) 5490.

[5] L. Spinu, H. Srikanth, A. Gupta, X. W. Li and Gang Xiao // *Phys. Rev. B* **62** (2000) 8931.

[6] R. K. Kalyanaraman, M. S. Krupashankara, T. S. Sudarshan and R. Dowding // *Nanostruct. Mater.* **10** (1999) 1379.

[7] A. Aharoni, E. H. Frei, S. Shtrikman and D. Treves // *Bull. Res. Counc. of Israel* **6A** (1957) 215.

[8] L. Spinu, C. J. O'Connor and H. Srikanth // *IEEE Trans. Magn.* **37** (2001) 2188.

[9] J. L. Dormann, D. Fiorani and E. Tronc // *Adv. Chem. Phys.* **XCVIII** (1997) 283.

[10] C.T. Seip, E.E. Carpenter, C.J. O'Connor, V.T. John and S. Li // *IEEE Trans. Magn.* **34** (1998) 1111.

[12] J. L. Dormann, L. Spinu, E. Tronc, J. p. Jolivet, F. Lucari, F. D'Orazio and D. Fiorani // *J. Magn. Magn. Mater.* (1998) L255.