

SUPERPARAMAGNETISM AND MAGNETO-CALORIC EFFECT (MCE) IN FUNCTIONAL MAGNETIC NANOSTRUCTURES

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Abstract. Magnetic nanoparticles exhibit superparamagnetic and ferromagnetic behaviors controlled by the particle size and interactions. While monodisperse nanoparticles are of interest from fundamental science perspective, functional nanostructures involve dispersion of particles in host matrices such as polymers. We discuss synthesis and magnetism of polymer nanocomposites based on PMMA with embedded Fe_3O_4 nanoparticles. An interesting application of nanoparticle assemblies is in magneto-caloric effect (MCE) that has the potential for local cooling/heating of NEMS and MEMS devices. We have studied MCE in CoFe_2O_4 nanoparticles by measuring family of M-H curves at set temperature intervals and calculated the entropy change (ΔS) for this system.

1. INTRODUCTION

Magnetic nanoparticles behave very differently from bulk or thin film systems. When the size of the particles is reduced below the single domain limit (~15 to 20 nm for iron oxide), they exhibit superparamagnetism at room temperature followed by a spin-glass like transition at low temperature [1]. Superparamagnetism is essentially a result of non-interacting, thermally fluctuating nanoparticle moments where the particle volume dependent effective anisotropy energy (KV) of each particle is easily overcome by the thermal energy ($k_b T$). The effect of this is that the nanoparticles have a large moment with high saturation magnetization (as expected in ferromagnets) but a non-hysteretic M-H curve with zero remanence and coercivity. Superparamagnetic particles have a number of applications in fields as varied as biomedical technol-

ogy, electromagnetic devices [2,3]. For example, the lack of magnetic hysteresis coupled with high saturation magnetization is highly desirable in RF and microwave magnetic applications as the magnetic losses are considerably reduced. In addition, the granular and disconnected nature of nanoparticle assemblies prevents eddy current losses too.

For device applications, since particles are generally dispersed in a non-magnetic (conducting or non-conducting) matrix, it is important to investigate the collective magnetic response and possible influence of the matrix itself. It is well known that in polymer host matrices, nanoparticle agglomeration and magnetic interactions can affect the overall properties to a great extent [4-6]. Many attractive properties of polymers like non-corrosiveness, light weight, mechanical strength and dielectric tunability can be utilized along with novel magnetic and opti-

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cal properties of nanoparticles to make multifunctional materials. Inclusion of ferromagnetic or superparamagnetic nanoparticles in polymers is especially important as magnetic nanoparticles have shown promise in various potential applications like spin-polarized devices, carriers for drug delivery, magnetic recording media, high-frequency applications, etc.

Another area where there is relatively little work is in exploring the possibility of refrigeration using the magneto-caloric effect (MCE) in nanoparticle clusters or assemblies [7]. While the concept of magnetic refrigeration has been around for a long time, lack of easily processable materials have limited the effectiveness of this approach to very low temperatures. MCE is an inherent property of all magnetic materials and is due to the coupling of the magnetic sublattice with the external applied field. The discovery of giant MCE in $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys [8] with promising refrigeration characteristics in the intermediate temperature (40K to 200K) range has revived interest in the search for new MCE materials. Recently, the importance of nanoscale inclusions of Fe in this alloy has been discussed by Provenzano *et al.* [9]. Their results indicate that the magnetic entropy change is enhanced and also pushed to near room temperature in Fe containing systems in addition to reduction in hysteretic losses. There have also been investigations of MCE in nanoparticle-based systems as it has been theoretically predicted that the entropy change could be enhanced in these systems [10].

In this paper we report on two functional aspects of magnetic nanostructures currently being explored in our laboratory. The first is a demonstration of controlled nanoparticle dispersion in polymer nanocomposites exhibiting superparamagnetism and the second is an analysis of MCE in the vicinity of the blocking temperature for chemically synthesized Co-ferrite nanoparticles containing small and large size distribution.

2. SUPERPARAMAGNETIC POLYMER NANOCOMOSITES

Nanoparticles of Fe_3O_4 were synthesized using a standard chemical co-precipitation method and characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Analysis of the particle size distribution showed a mean size of 11 nm with a standard deviation of 4 nm. We have also further improved the size distribution using an ultracentrifuge and reduced the standard deviation to 2 nm. After confirming their magnetic nature by test-

ing their attraction to a bar magnet, the particles in solution were coated with oleic acid. The surfactant-coated nanoparticles were suspended in hexane and further centrifuged to separate any agglomerated clusters and/or particles of larger size out. To prepare polymer nanocomposite thin films, 5% poly-methyl-methacrylate (PMMA) by weight was dissolved in chlorobenzene and vigorously stirred for a few hours, until it is all dissolved. The Fe_3O_4 nanoparticles coated with oleic acid were added and sonicated to facilitate uniform dispersion. The solution was spun coat onto substrates at 4000 rpm which yielded films of about 2 microns thickness. One of our goals was to spin coat a layer of conducting polymer (polypyrrole) on top to form a bi-layer. The reason for a conducting polymer sheath was to develop all-polymer layered structures that integrate electromagnetic interference (EMI) suppression capabilities for RF applications. The polypyrrole layer is non-magnetic and does not interact with the PMMA based nanocomposite film in any way interfering with its magnetic response. The top panel of Fig. 1 shows a cross-sectional TEM image of the bi-layer. The uniform dispersion of Fe_3O_4 nanoparticles is clearly evident in the bottom PMMA layer and it is important to note that individual particles are clearly resolved with very little clustering observed. This is quite significant as it is a challenging task to control the nanoparticle diffusion and avoid agglomeration during the polymerization process [11]. Our contention is that the solvent-based technique that we employed with individual nanoparticles coated by fatty acid and the overall polymerization process assisted by vigorous sonication may be responsible for the nearly cluster-free dispersion inside the polymer matrix. Molecular Dynamics (MD) simulations have been particularly successful in investigating the dispersion of nanoparticles in polymers [4, 12]. When the polymer-polymer interaction strength is stronger than the polymer-particle interaction strength, the system potential energy is lowered by clumping the particles. If the interaction between the particles and the polymer can be increased, the particles will then disperse throughout the polymer. In our case, the oleic acid surfactant coating on the particles increases the interaction with the polymer and thus favors the process of uniform dispersion.

Fig. 1 also shows the magnetization vs field (M-H) measurements on the sample done using a commercial Physical Property Measurement System (PPMS) from Quantum Design. M-H curves taken at two temperatures (300K and 10K) are shown and

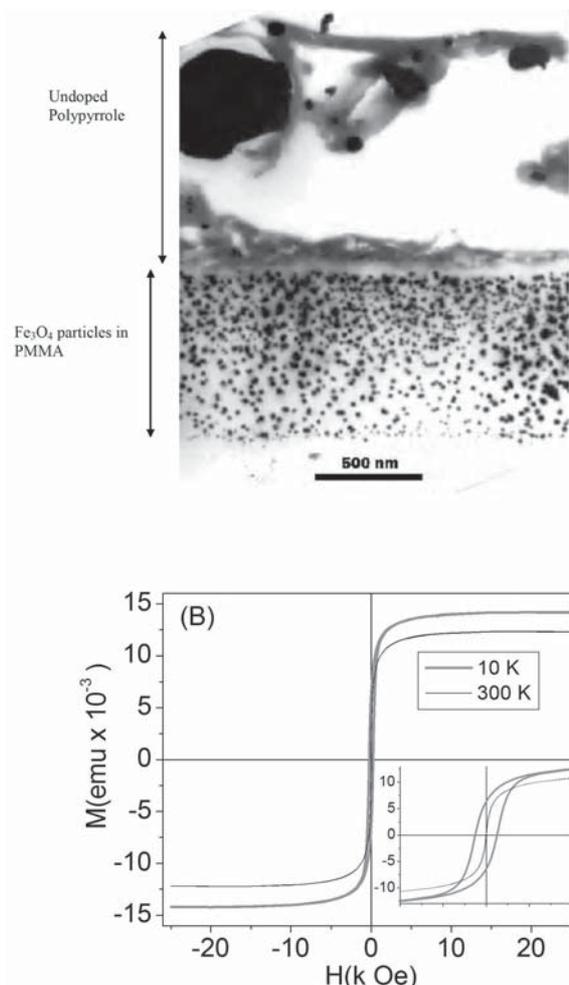


Fig. 1. (Top) Cross-sectional TEM image of spun coat PMMA/Polypyrrole bilayer films showing the dispersion of Fe_3O_4 nanoparticles in the PMMA layer. (Bottom) Magnetization vs Field at room temperature and 10K. Inset shows the low-field region indicating the presence of hysteresis at low temperature.

both of them display a strong non-linear behavior with saturation magnetization. The inset shows the expanded view of the low-field region. The M-H curve at 300K does not show any hysteresis whereas the loop at 10K shows a clear hysteresis with a coercivity of around 150 to 200 Oe. This is characteristic of the sample being superparamagnetic at room temperature and entering a blocked state at low temperature which results in opening up of the hysteresis loop. The cross-sectional TEM image along with this magnetic response provides evidence that we have indeed obtained superparamagnetic polymer nanocomposites at room temperature.

3. MAGNETO-CALORIC EFFECT (MCE) IN FERRITE NANOPARTICLES

MCE in conventional ferromagnetic materials is limited to the entropy change associated with the spin disorder-order states achieved across the paramagnetic to ferromagnetic transition as one cools the sample below the Curie temperature (T_c). The entropy change in a magnetic system can be calculated from the thermodynamic Maxwell relation:

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \quad (1)$$

or integrating over the field,

$$\Delta S = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH.$$

From measurements of $M(H, T)$, the magnetic entropy change can be calculated. Typical values of the entropy change range in the 0.1 to 1 J/kg-K over a field of 1 or 2 Tesla. In systems exhibiting metamagnetic transitions and close coupling between the magnetic and structural degrees of freedom (such as the manganites), giant MCE with one or two orders of magnitude bigger entropy change have been reported in the vicinity of Curie temperature. However these changes do not persist over a broad temperature range. As indicated before, it is somewhat cumbersome to systematically tune the ferromagnetic Curie temperature in materials through solid state chemistry and doping. It is precisely for this reason that magnetic nanoparticles have a unique advantage. In nanoparticles there is a versatile order-disorder transition associated with the superparamagnetic-blocked states referred to as the blocking transition (T_B). Unlike the Curie temperature, T_B can be varied by adjusting the particle size, shape, dispersion and inter-particle interactions. While it is unlikely that simple elemental and oxide nanoparticles will exhibit giant magnetic entropy changes, the advantages lie in the ease of synthesis, tunability of T_B and also the dispersion of nanoparticles in other host matrices that themselves can be good MCE materials. MCE in several nanoparticle systems have been investigated by a number of groups over the years. It has been theoretically predicted [10] that nanocomposite superparamagnetic nanoparticles have the potential to exceed the performance of garnets and other commonly used magnetic refrigerants particularly at low fields generated by simple electromagnets

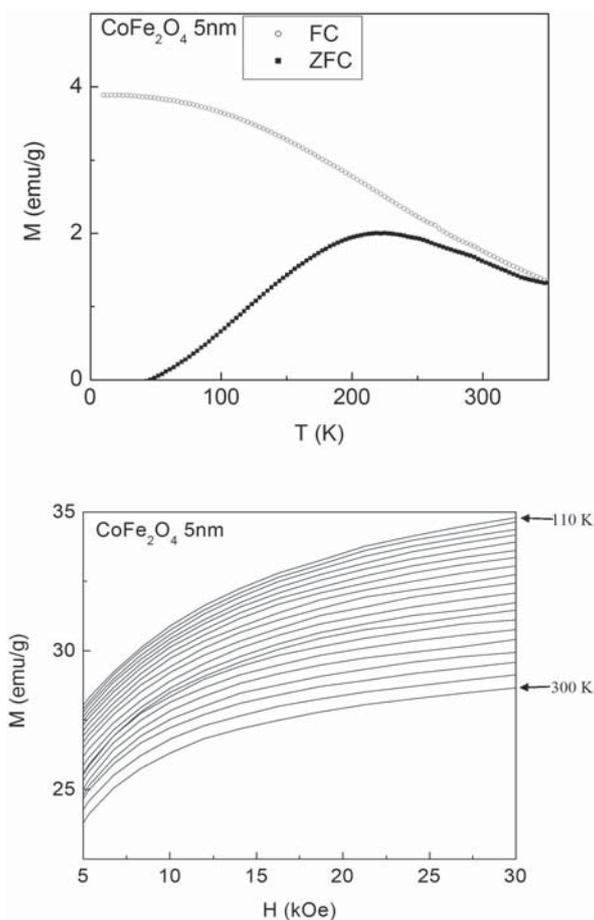


Fig. 2. (Top) Zero-field cooled (ZFC) and Field-cooled (FC) magnetization data with 100 Oe applied field for CoFe_2O_4 nanoparticles. (Bottom) Family of M-H curves at various temperatures from which the entropy change is extracted.

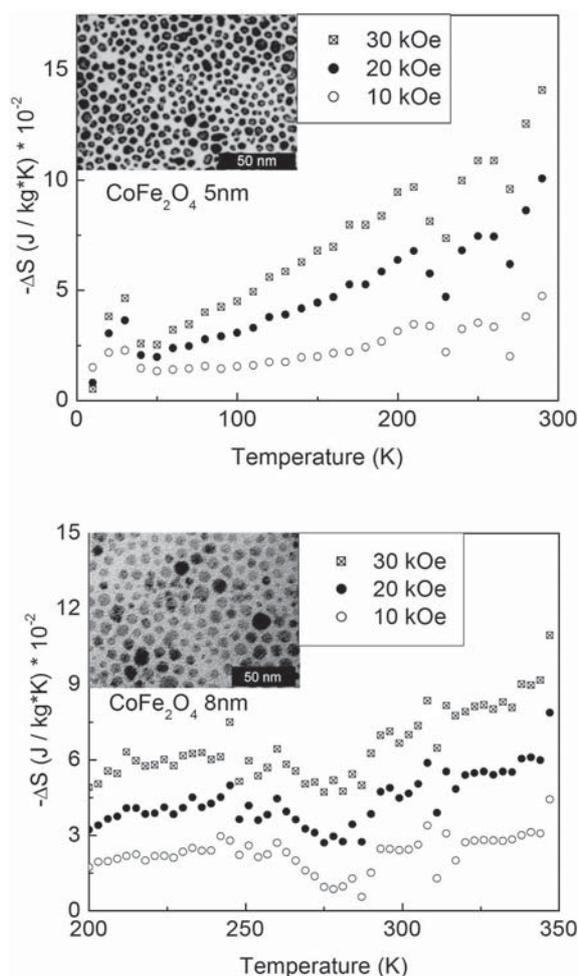


Fig. 3. Magnetic entropy change for CoFe_2O_4 nanoparticles of mean size 5 nm (top) and 8 nm (bottom). Insets show TEM images of as-synthesized particles.

(1 to 2 T range as opposed to 5 – 10 T or higher which are only attainable in superconducting or pulsed magnets).

In this work, we have measured and calculated the magnetic entropy change using the standard Maxwell method in CoFe_2O_4 nanoparticles prepared by chemical methods.

To make CoFe_2O_4 nanoparticles, a mixture of cobalt(II) acetylacetonate, phenyl ether, 1,2-hexadecanediol, oleic acid, and oleylamine are mixed and heated to 156 °C. At this point iron(III) acetylacetonate mixed in phenyl ether was added and heated to reflux (260 °C) for 1 hour. The particles precipitated upon addition of excess ethanol and centrifuging. They were then washed several times using deionized water and magnetic decantation. After that, they were dried and used in pow-

der form at this stage for magnetic measurements or suspended in hexane for further size selection. We were able to isolate two sets of nanoparticles with mean size distribution centered around 5 nm and 8 nm. The TEM images for these two sets are shown in the insets of Fig. 3 and the magnetic characterizations for the 5 nm particles are plotted in Fig. 2. The top panel in Fig. 2 shows the zero-field cooled and field-cooled magnetization with a broad peak seen in ZFC curve characteristic of the blocking transition followed by a slow decrease in magnetization at low temperature. Our goal was not to have a sharp blocking transition (expected for a monodisperse system with a very tight size distribution) but rather have a broad transition which is realized in polydisperse nanoparticles with a large size distribution. The reasoning behind this is based on the simple

conjecture that if the magnetic entropy change (ΔS) is maximum in the vicinity of the blocking transition, then having a broad transition would retain a nearly constant ΔS over a broader temperature range. Such characteristics would be desirable for field-driven small scale refrigeration applications such as cooling MEMS devices. The bottom panel of Fig. 2 shows the M-H curves over a field range of 0.5 to 3 T taken at temperature intervals of 10K from 110 to 300K which spans a sizeable region covering the blocking peak. The ΔS were numerically calculated from these data sets using the Maxwell equation and the results for the two CoFe_2O_4 nanoparticle samples are plotted for three field values in Fig. 3. The values for the entropy change are quite small as reported in several other nanoparticle systems and comparatively slightly higher [13,14]. This is consistent with models that indicate that introducing some amount of inter-particle interactions could lead to higher entropy change in comparison to strictly non-interacting superparamagnetic particles [13]. Currently we are in the process of doing systematic MCE experiments on a single ferrite system by varying parameters such as the overall particle size, dispersion and inter-particle interactions.

While the expected trend of large ΔS is observed for higher applied fields, there is one aspect to the data in Fig. 3 that needs to be mentioned. In both the systems, it is observed that the ΔS increases uniformly as a function of temperature (up to 300 to 350K which is the limit of our PPMS) and does not follow the shape of the blocking peak which is centered around 220K for the 5 nm particles and higher for the 8 nm particles (not shown in this paper). A similar trend was also observed in our studies on other ferrite nanoparticles with much lower blocking peak ($\sim 40\text{K}$) where a broad maximum in ΔS was seen around a temperature about 4 to 5 times larger than blocking temperature. This is quite promising as it would imply that reasonably high ΔS can be maintained at temperatures well above the blocking transition which makes it different from conventional ferromagnets where ΔS drops off sharply away from T_c . The origin of this behavior of ΔS is unclear at this time. In nanoparticles, there is another characteristic temperature above the blocking temperature (T_B) which is the irreversibility point (i.e. the temperature below which the ZFC and FC curves deviate and above which they lie on top of each other). It remains to be seen if this temperature is relevant in any way for the ΔS dependence and more experiments are needed to further explore these issues.

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