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Experimental observations of field-dependent activation of core and surface spins in Ni-ferrite nanoparticles

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Abstract

The magnetic behavior of Ni-ferrite ($NiFe_2O_4$) nanoparticles synthesized in a solid state reaction process has been investigated. The cooling field, H_{CF}, dependence of magnetization in a wide range of temperatures, from 5 to 300 K, has been examined for low and high field regimes. It has been observed that there is a transition region, ∼3–4 T, between different mechanisms that controls the magnetization. At low fields, <3 T, classical blocking–unblocking of small particles governs the magnetization whereas spin-glass like behavior prevails at high fields, >4 T, starting below a well defined freezing temperature of 50 K. The H_{CF} dependence of magnetic viscosity has shown that there is a significant jump in the relaxation rate of the particles around 4 T which appears as the boundary region for the temperature-dependent magnetization as well. These observations are interpreted as indicating that below the spin freezing temperature there is a boundary field (∼4 T) where the strongly pinned surface spins are enabled to be thermally activated while below this field only core spins participate in the magnetic relaxation.

1. Introduction

Nanocrystalline $NiFe_2O_4$ shows peculiar structural and magnetic properties. Small particle size promotes a mixed spinel structure whereas the bulk form is an inverse spinel. As far as the magnetic properties are concerned, spin-glass like behavior can be considered as the most interesting property that leads to a high field irreversibility, shift of the hysteresis loops, and anomalous relaxation dynamics. These features are attributed to the disordered spin structure that stems from broken exchange bonds due to missing oxygen and low coordination of cations at the surface of the particles. Spin canting has been suggested as the reason for the reduction of magnetization via Mössbauer spectroscopy in the ball-milled $NiFe_2O_4$ nanoparticles [1]. Kodama *et al* have proposed that those canted spins are present in a surface layer and freeze into a spin-glass like phase below a certain temperature, T_f. When not frozen, these surface spins have multiple minimum energy configurations for any orientation of the core magnetization [2]. Magnetic irreversibility and time-dependent magnetization in high fields are observed via cooling the samples, starting from above T_f to below T_f, both with and without an external field. Hysteresis loops performed at temperatures below T_f after field cooling exhibit loop shift due to unidirectional anisotropy resulting from the coupling between the disordered surface layer and core spins. Unidirectional anisotropy is also observed in magnetic systems where two different types of magnetic ordering, ferromagnetic (FM)/antiferromagnetic (AFM), exist [3]. Microscopic exchange interaction at the FM/AFM interface causes a horizontal shift of the hysteresis loop, generally in the opposite direction to the H_{CF}, when the FM/AFM system is field cooled below the Nèel temperature (T_N) of the AFM. Loop shift seen in FM/AFM coupled systems

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is due to the exchange interactions at a well defined interface, which can be observed by electron microscopy. However, in nanoparticle ferrites, there is no easily observable interface between the ordered core spins and disordered spins in the surface layer. The size of the ordered region can be varied by applying large enough fields to align interface spins in the direction of core spins at temperatures above T_f. The loop shift observed in ferrites disappears above T_f of the spin-glass like surface layer.

Another feature of spin-glass like structures is the observation of open hysteresis loops as a result of high local anisotropies in the magnetically disordered surface layer. Spin-glass like structure creates anomalies in the low temperature relaxation dynamics as well. The temperature dependence of the magnetic viscosity of organic coated $NiFe_2O_4$ particles showed a nonzero extrapolation of magnetic viscosity to zero temperature, indicating a non-thermal relaxation mechanism which was linked to macroscopic quantum tunneling via intrinsic surface anisotropy [4]. Kodama *et al* [2] have also studied time-dependent magnetization of a 2.5 nm $NiFe_2O_4$ particle by a numerical model and realized that relaxation is related to the reversal of particle magnetization directions as well as to the transitions between surface spin configurations.

The disordered nature of the oxide shell in an Fe–Fe oxide system has been shown by Fiorani *et al* to result in glassy dynamics where the increase in waiting time after application of a field at 50 K results in an increase in the exchange bias [5]. They interpret this as showing that with increasing waiting time the oxide phase evolves towards a lower energy configuration, resulting in a stronger interface exchange coupling with the Fe particle moment. They note that while there is a progressive freezing of the moments, the freezing is complete below 25 K, leading to a highly frustrated frozen state for the whole system, in low fields.

Since the glassy magnetic state can be homogenized by large enough applied field, it is therefore tempting to speculate that in such core–shell systems there may be a boundary field separating the two regions where the magnetic response, e.g. the relaxation rate, is dominated exclusively by the core while the shell region remains effectively frozen. There are relatively rare systematic field-dependent relaxation studies in such nanoparticles and to our knowledge such a 'critical field' has not been reported in the several similar core–shell structures that have been studied. It is, however, intuitively clear that lower cooling fields and their subsequent removal would lead to the relaxation effects associated with the weaker pinned moments while larger ones would subsequently select the remaining more strongly pinned ones. In the current study we show that this is indeed the case and there is a clear boundary field separating the response of the core moments (lower cooling fields) and that of the shell, at much higher fields.

In this paper, temperature and field dependencies of the magnetic behavior of $NiFe_2O_4$ nanoparticles synthesized by the solid state reaction are presented in terms of loop shift, blocking, and magnetic viscosity in a temperature range of 5–300 K using magnetic fields from 0.05 to 7 T. Our results clearly suggest that disordered spins at the surface layer of the particles become dominant below 50 K for magnetic fields below 3 T. However, external fields above 3 T significantly mitigate the influence of the spin-glass like surface region by reducing the number of disordered spins.

2. Experimental details

The inert gas condensation process was used to synthesize the precursor Ni:Fe (1:2) alloy nanoparticles, which were subsequently annealed to form $NiFe_2O_4$ nanoparticles. In our previous experiments, we have shown that it is possible to synthesize alloy nanoparticles of close melting point metals by simultaneously evaporating the metals to form an alloy and rapidly cooling the metal vapors to a metastable solid state phase [6]. The same idea has been used to synthesize Ni:Fe alloy particles in order to eventually obtain $NiFe_2O_4$ nanoparticles. Here, a controlled post-annealing in an oxidizing atmosphere is needed to oxidize the alloy particles and to obtain the ferrite structure. Therefore, as-synthesized Ni:Fe alloy nanoparticles were annealed at 450 °C for 12 h in ambient conditions. The temperature choice was based on an Ni–Fe binary alloy phase diagram. Different size $NiFe_2O_4$ nanoparticles are synthesized by annealing the as-synthesized samples at different temperatures above 450 °C, as described elsewhere [7].

Magnetic properties of the $NiFe_2O_4$ nanoparticles are examined by using a physical properties measurement system (PPMS) dc extraction magnetometer (Quantum Design Corporation). Investigation of magnetic properties is performed in a temperature range from 300 to 5 K using various operating fields for zero-field and field cooling conditions abbreviated as ZFC and FC, respectively. Relaxation measurements have been accomplished after cooling the sample from 300 K to the required temperature in the presence of different fields. Upon reaching the desired temperature and waiting 10 min, the applied field is removed and the remanent magnetization is monitored within a time interval of 50 min.

3. Results and discussion

Figure 1 summarizes the results from the structural analyses by electron microscopy and x-ray diffraction studies. The average particle size is measured to be 15 nm by transmission electron microscopy (TEM) (figures 1(a), (b)), whereas using x-ray diffraction (XRD) patterns (figure 1(c)) the grain size obtained from the (311) peak width using Scherrer's formula is about 9 ± 0.5 nm. The size difference is perhaps due to the fact that peak width is affected by various factors such as stress, compositional variations, etc. In fact, ferrite nanoparticles due to their small sizes are expected to have a structurally and magnetically disordered surface layer which gives rise to peculiar magnetic behaviors that are not observed in bulk ferrites [8]. A lattice image of a $NiFe_2O_4$ particle is presented to reveal polycrystalline structure and to demonstrate the differences between the average particle sizes obtained from the XRD pattern given in figure 1(c) and the TEM observations. A selected area diffraction pattern, figure 1(b),

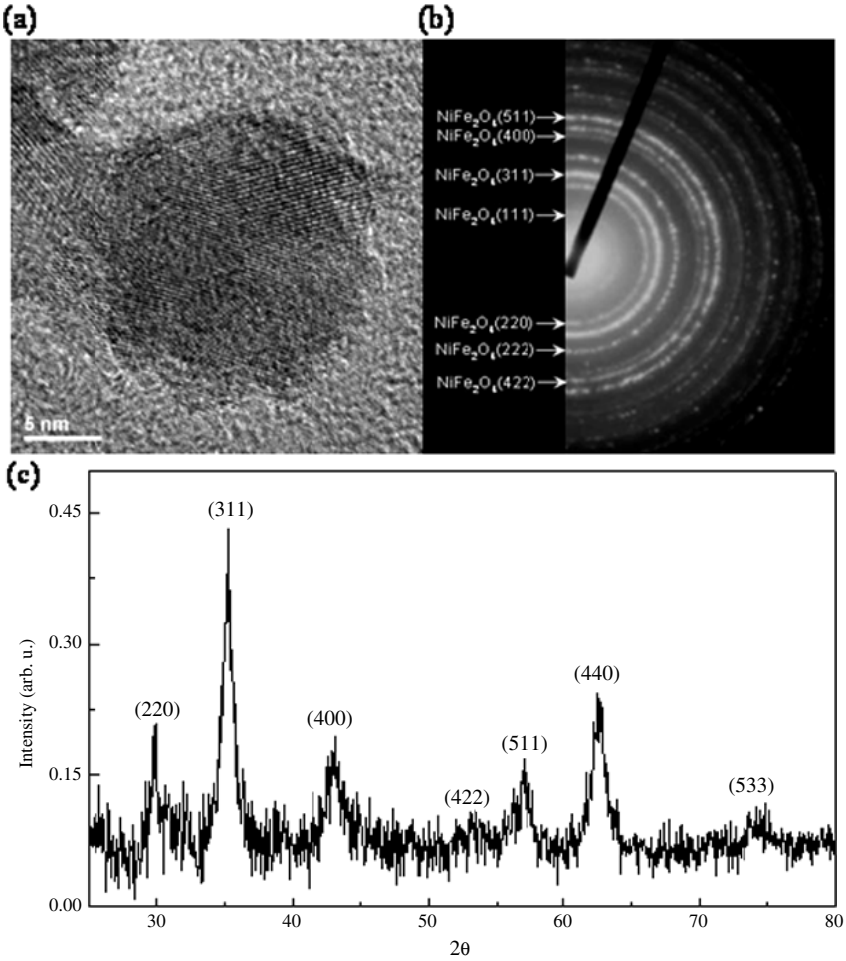

Figure 1. (a) Lattice image, (b) selected area diffraction pattern, and (c) x-ray diffraction pattern of $NiFe_2O_4$ nanoparticles.

which supports the XRD data is also included which confirms the $NiFe_2O_4$ structure.

Figure 2 shows the M–H loops obtained at the two ends of the temperature range studied in this work. At 300 K, the sample exhibits a clear superparamagnetic behavior with zero coercivity but does not seem to be saturated at 3 T. However, fitting the *law of approach to saturation* to the 300 K data allowed us to calculate saturation magnetization as 32.5 emu g^{-1} whereas the bulk saturation magnetization for $NiFe_2O_4$ is 52.4 emu g^{-1}.

It is understood that the difference between the saturation magnetization of nanoparticle ferrites and the bulk saturation values is due to the competition between the effects of spin canting and site exchange of cations in the disordered surface layer of the particles. While dominating cation disorder leads to the enhancement of the saturation magnetization, strong canted spin structure causes a reduction of the saturation magnetization [9, 10]. Therefore, the surface layer of the particles possesses a canted spin structure that is one of the ingredients for a spin-glass like system [11]. The M–H loop obtained at 5 K after field cooling the sample in 3 T field reveals unidirectional anisotropy indicated by the shifting of the loop towards the negative field direction. As previously discussed, this is a consequence of coupling between the collinear core spins and spin-glass like surface spins induced by field cooling the sample from a temperature above T_f. However, a hysteresis loop taken in the absence of the field during the cooling process, namely zero-field cooling, does not have the loop shift, as shown in the inset of figure 2. Notice that the FC loop at 5 K is open in the first quadrant, presumably due to the higher switching fields of some of the spin-glass like surface spins, as compared to the applied field. In fact, it can be observed that M–H loops are closed for the fields above 4 T whereas the loop shift persists at these fields. This is interpreted in the light of the fact that the open hysteresis loop and loop shift have different origins. The open hysteresis loop results from irreversible changes in the magnetically disordered spin configurations in the surface layer and the loop shift is an interface effect. It is understood that a 4 T field is enough to wash out the disorder in the bulk of the surface layer to a large extent but not high enough to completely overcome interface couplings.

In order to gain better insight into H_{CF} and temperature dependence of the loop shift, we obtained M–H loops at different temperatures for $H_{CF} = 0.5$, 1, and 3 T, as shown in figure 3. As expected, increasing temperature for a fixed H_{CF} decreases the loop shift while approaching T_f ($\sim$50 K) of the spin-glass like surface layer. The loop shift reduces as

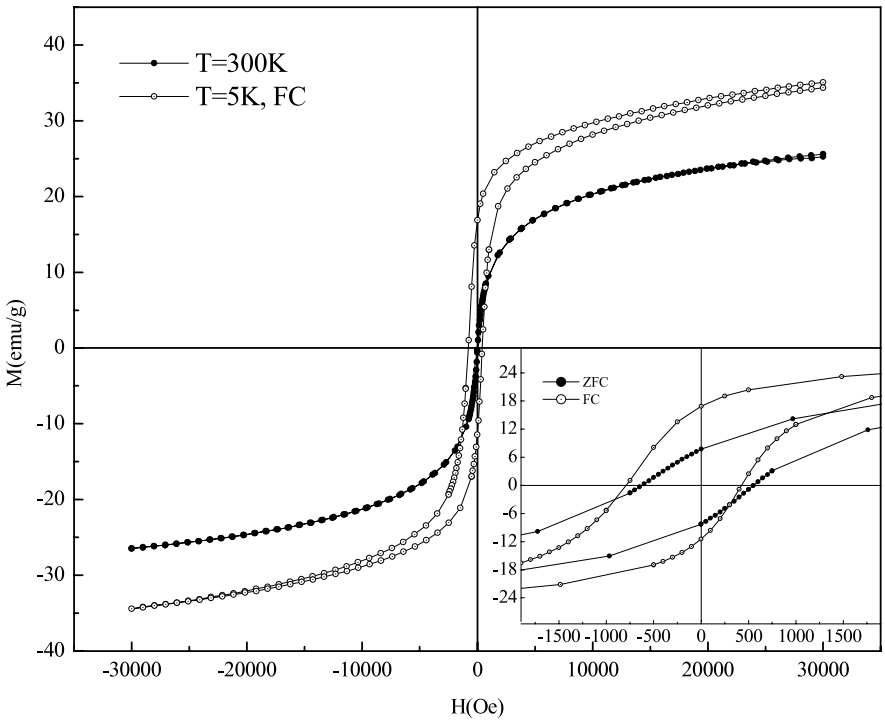

Figure 2. M–H loops at 300 and 5 K after field cooling the sample under 3 T applied field. Inset: expanded view of FC and ZFC M–H loops obtained at 5 K.

H_{CF} increases at a constant temperature. The decrease of the loop shift with increasing cooling fields has been seen in other core–shell structures as well [12]. The effect can be related to the competition between the Zeeman energy dominating at high fields and preventing the intra-particle exchange between the core and shell fully realizing itself. However, the decrease in the exchange bias in our case is unusually strong, varying exponentially with the cooling field applied, as shown in the inset of figure 3. We note that the dependence of the exchange bias on the ferromagnetic layer thickness in multilayers, $H_E\alpha$ $(1/t_{FM})$, is also well documented [13]. These observations seem to suggest that the very rapid decrease in the exchange bias may be a consequence of the increasing H_{CF} effectively increasing the size of the ferrimagnetic core by moving the interface towards the particle surface as it aligns the spins lying at the interface initially. Our conjecture about the movement of the interface or enlargement of the core will find substantiation in the other high field results that follow.

Disordered spins in the surface layer are expected to have an influence on the temperature dependence of the magnetization obtained under different applied fields for FC and ZFC conditions. For classical superparamagnetic nanoparticles, the temperature at which ZFC curve peaks is defined as the blocking temperature T_B, above which anisotropy fields are overcome by thermal energy. Blocking temperature is determined by particle size and magnetocrystalline anisotropy for non-interacting particles. T_B shifts to lower temperatures as applied field increases and irreversible magnetization (M_{FC}–M_{ZFC}) gets smaller and eventually vanishes. However, for spin-glass systems, one expects irreversible magnetization to be persistent below T_f due to competing exchange and random

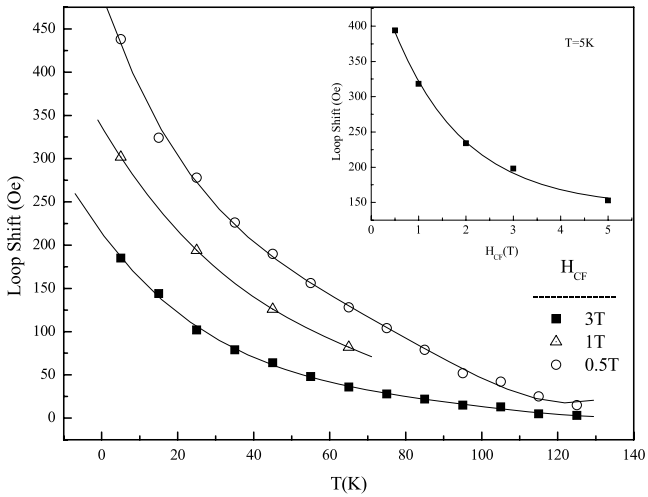

Figure 3. Temperature dependence of loop shift for different H_{CF}. Inset: loop shift as a function of H_{CF} at 5 K. Lines are to guide the eye.

anisotropies whose average energies are greater than that created by the applied field. As expected, our FC–ZFC measurements clearly indicate that for low enough fields, spin-glass like effects are suppressed while classical blocking/unblocking of the small particles dominates the magnetic irreversibility. However, the application of high fields manifested magnetic irreversibility below T_f due to the spin-glass like surface spins. It should be noted that similar behavior has been observed at mechanically alloyed $NiFe_2O_4$ nanoparticles [14]. Figure 4 presents FC–ZFC plots for various applied fields.

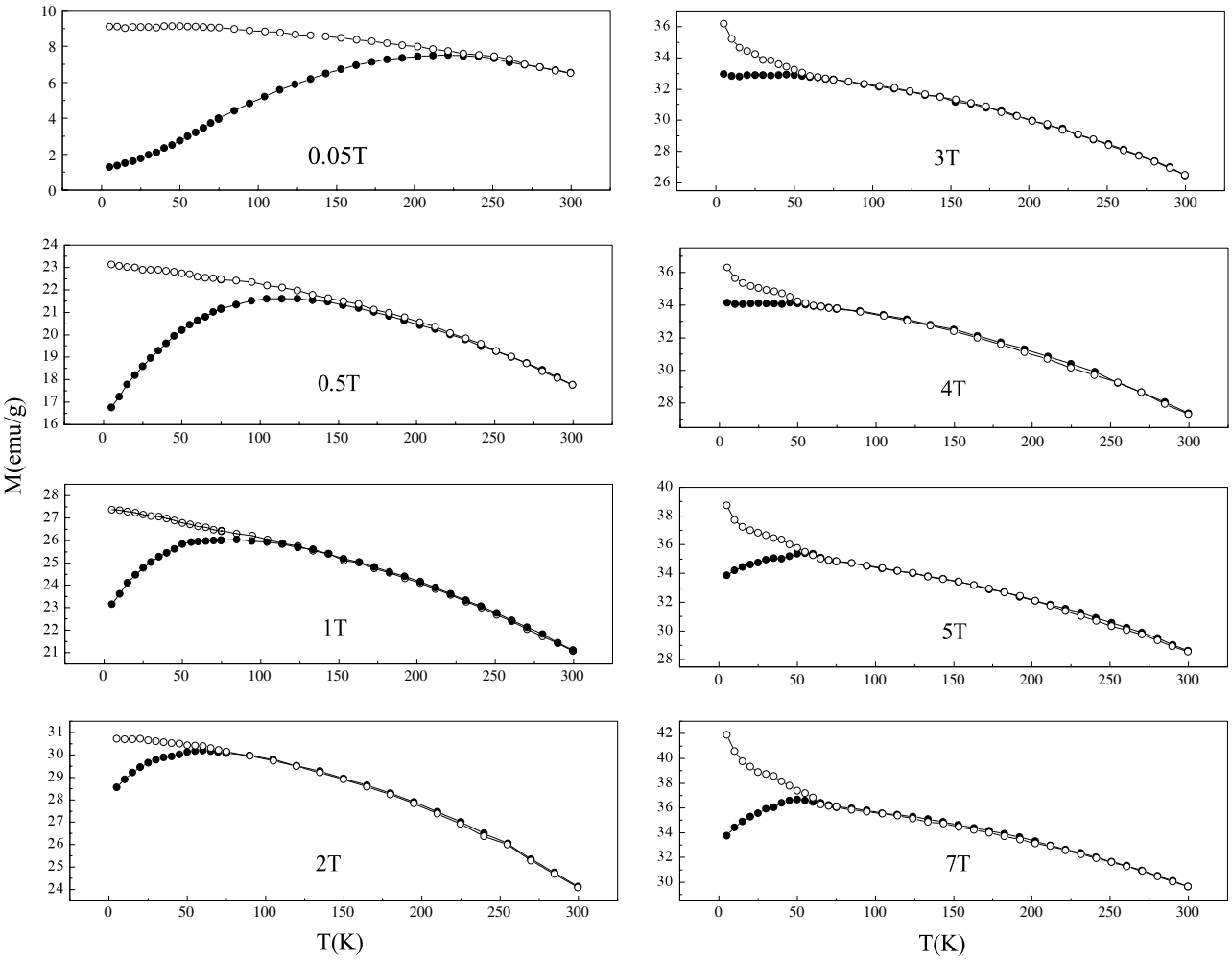

Figure 4. Temperature dependence of FC (open circles) and ZFC (solid circles) magnetizations for different applied fields.

Classical splitting between FC–ZFC curves due to competition between magnetocrystalline anisotropy related energy barriers and thermal energy is observed for the H_{CF} from 0.05 to 3 T with T_B exponentially decreasing from 232 to 55 K, respectively. Very significantly, however, from 3 to 7 T the irreversibility point (the temperature at which M_{FC}–$M_{ZFC} = 0$) does not move any further below 50 K. Furthermore, between 3 and 4 T the ZFC magnetization below 50 K remains constant, indicating that no further freezing of the core moments is occurring at these high fields. However, on increasing the field further, for $H = 5$ and 7 T, the ZFC moment again starts to increase (by 5% and 9% respectively) as the temperature is raised from 5 to 50 K. It is seen that while the ZFC magnetization becomes temperature independent at $\sim$34 emu g^{-1} for the 3 and 4 T fields, for both the higher fields it initiates at exactly the same value (34 emu g^{-1}) at 5 K and then proceeds to rise higher as T increases towards 50 K. However, for the FC magnetization measurements, application of fields higher than 4 T at 300 K starts aligning surface spins with the core spins. As the temperature is reduced below T_f, the FC magnetization of the system exceeds the saturation value 32.5 emu g^{-1} at room temperature, reaching 41.9 emu g^{-1} at 5 K for 7 T. The reason for the enhanced moment apparently is that the initially 'frozen' surface spins have become aligned with the core spins. In addition, the randomizing effect of temperature is also minimized. Above T_f, however, surface spins are not in their frozen state and due to their large effective local anisotropy fields and the randomizing effect of temperature they relax into one of the multiple equivalent minimum energy configurations and do not contribute to the magnetization of the system. The above observations can be summarized as suggesting that while the core moments become completely unblocked for fields of 3 T and above, there is another component of the magnetization that begins to get unblocked when applied fields exceed 4 T. We attribute this other component to arising from the contribution of the spin-glass like frozen shell that begins to become unfrozen above 4 T.

Another feature we notice is the upturn in the FC curves for $H_{CF} \geqslant 3$ T, explicit below 15 K. Similar behavior has been seen in the Fe–FeO core–shell systems [15]. We think that it results from the collinear rotation of small spin clusters that grow in the surface layer during the field cooling process. Notice that the upturn gets much more prominent as the field increases. In spin-glass systems, for $T > T_f$ short-range magnetic interactions are present and as

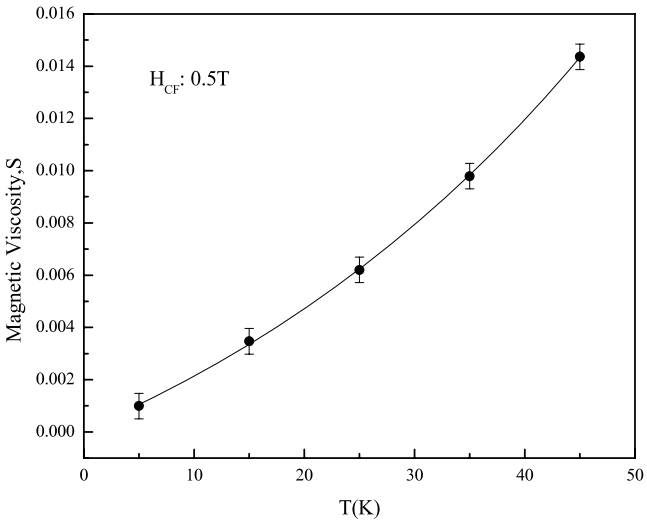

Figure 5. Magnetic viscosity versus temperature obtained after 0.5 T field cooling the sample. The line is only a guide to the eye.

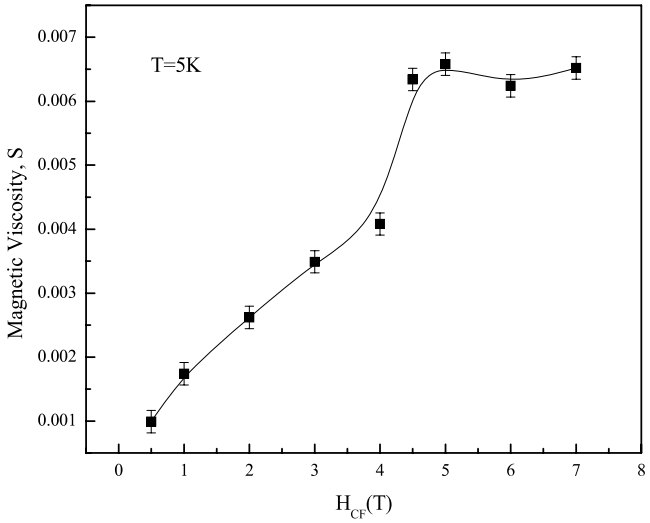

Figure 6. H_{CF} dependence of magnetic viscosity at 5 K. The line is only a guide to the eye.

the temperature approaches T_f the system gets divided into dynamically evolving magnetic clusters. A competition occurs between the short range exchanges, $J(r_{ij})$ and the disordering effect of temperature, k_BT. When $J(r_{ij}) > k_BT$ for a given group of spins, a cluster is formed. As T is decreased the clusters will grow in size and take on various shapes with respect to the distribution of the competing forces. The presence of a large field during cooling apparently stabilizes such cluster growth, leading to the observed sharp rise in the moments.

The most revealing of our measurements, in the context of the identification of a boundary field separating activation of the core–shell regions, is in the field dependence of the magnetic relaxation. Relaxation dynamics of the $NiFe_2O_4$ particles has been studied for $T < T_f$ using fields 0.05–7 T. In the first set of measurements, the time-dependent remanent magnetization at a fixed temperature was monitored after field cooling the sample in the presence of 0.5 T which was subsequently turned off. This field is not expected to be high enough to rotate an appreciable amount of surface spins. This measurement was performed for 5, 15, 25, 35, and 45 K. For small particle systems with a range of particle sizes and anisotropy energy barriers, the magnetization relaxation can be fitted to a logarithmic function of the form,

$$M(t) = M(t_0)\left[1 - S\ln\left(1 + \frac{t}{\tau}\right)\right] \qquad (1)$$

where S is the so-called magnetic viscosity and τ is the relaxation time [16, 17]. The data of magnetic relaxation at different temperatures are fitted to equation (1) and the values of S extracted from the fit are shown in figure 5. It is seen from the figure that as the temperature approaches T_f, the magnetic viscosity exponentially increases. A similar S–T trend at temperatures below T_B and with a peak at about T_B can be observed in magnetic nanoparticle systems that consist of particles with an average particle size of 15 nm [15]. However, the unique behavior of this system is depicted when we investigate the variation of magnetic viscosity with field at a fixed temperature by the application of high enough magnetic fields for which the activation of the surface spins has already been shown to be effective.

Figure 6 represents S–H behavior at 5 K where the disordered shell structure is expected to be completely frozen in the absence of large fields. As can be readily noticed, S shows a slowly increasing trend up to 4 T but then makes a very large jump, from 0.004 to 0.0065 at 4.5 T and levels off beyond this. This is obviously consistent with the previously discussed results. A high enough cooling field H_{CF} is able to rotate an appreciable amount of disordered surface spins during the cooling process. On removal of this applied field at a temperature below T_f those surface spins that have been rotated with the field also contribute to the relaxation while seeking a minimum energy configuration. Thus, consistent with the magnetization measurements, the relaxation data show very starkly that in the field region 4–4.5 T the surface spins are activated or depinned from their frozen state and enabled to participate in the dynamics, while below this field the response is dominated by the activation of the core moments of the different nanoparticles over their respective anisotropy barriers, which are effectively reduced by increasing external field.

The 3–4 T field required to activate the surface spins can be understood within the model for surface effects in ferrite nanoparticles proposed by Nunes and Yang [18]. They propose an ionic model for a ferrite lattice and calculate the expansion of small crystals due to an imbalance between the long range electrostatic forces and short range repulsion as a result of size reduction. They evaluate the resultant strain induced magnetic anisotropy fields for various ferrite structures based on this model. The effective anisotropy field value they obtained for $NiFe_2O_4$ is 2.6 T which is very close to our experimental field region and supports the idea that the crossover field observed has its origins in the activation of surface spins pinned due to the structural surface disorder in the nanoparticles.

4. Conclusions

The core–shell structure in magnetic nanoparticles is usually considered as being defined by a fixed interface, e.g. separating the Fe and FeO atoms in Fe nanoparticles. In the $NiFe_2O_4$ particles we have shown that this concept of the interface can be considered as a more flexible entity, where the boundary appears to shift with increasing applied fields, effectively enlarging the core at the expense of the shell. This appears to occur for fields in excess of 3 T at temperatures below the freezing temperature (∼50 K) of the surface or shell region. An important result that emerges from this study is that the temporal response of the particles appears to undergo a very sharp change at this boundary field (∼4 T) where the previously inactive or frozen surface spins become unfrozen and participate in the relaxation processes. It may appear that the very sharp increase in the relaxation at this field could arise from the breakdown of the interfacial exchange between core and surface spins, resulting in an overall decrease of the activation barriers. However, this possibility is ruled out by the observation of a very significant loop shift at the highest applied field (5 T, see inset in figure 3) which testifies that despite the depinning of a significant number of surface spins and a consequent shift of the interface to a larger radius, the exchange bias is still intact, albeit reduced significantly over the low field values. It is unclear at this point as to the extent that these observations can be generalized to other core–shell magnetic nanostructures where a rigid core–shell boundary exists. Such a generalization would require similar tests of the high field response of the relaxation below the spin freezing temperature of the shell.

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