Memory, relaxation and aging effect in Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ nanoparticles

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Abstract. The low temperature dynamics of Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ nanoparticles is studied through magnetic memory, relaxation and aging measurements. These nanoparticles are prepared through chemical method with an average size of 15 nm. This system shows memory effect in dc magnetization. The measured magnetic relaxation exhibits logarithmic dependence with time. These results are in favor of interparticle interactions which induce the collective behavior in these nanoparticles. The aging experiments show that magnetic relaxation does not depend on given wait time prior to application of field, thus distinguishing the dynamics of this system from that of spin glass. However, the magnetic relaxation measured with positive and negative temperature cycle shows asymmetric response. This suggests that dynamics of these nanoparticles can be explained invoking hierarchical model rather than droplet model, commonly used in describing the dynamics of glassy systems, which is quite intriguing.

1. Introduction
The dynamics of magnetic nanoparticles at low temperature (T) has been a subject of intense research for the last several decades [1, 2]. Usually, ferromagnetic (FM) nanoparticles consist of single domain structure of FM spins having random anisotropy. For noninteracting assembly of nanoparticles, dynamics is described by Néel-Brown theory predicting superparamagnetic (SPM) behavior where thermal fluctuation overcome the anisotropy energy of individual particle and magnetization spontaneously flip from one easy direction to another [3]. Such particles will have relaxation time ($\tau$) of the form $\tau = \tau_0 \exp(KV/k_BT)$, where $\tau_0$ is microscopic relaxation time, K is anisotropy constant, V is volume and $k_B$ is Boltzmann constant. With decreasing T, $\tau$ increases exponentially and at particular temperature $T_B$, magnetic moment is blocked along the easy direction. However, situation becomes complicated if there exists interparticle interactions which induces collective behavior giving rise to rich variety of magnetic configurations. This collective behavior often manifest itself through various experimental observations, i.e., slow magnetic relaxation, memory, aging, etc. which are usually observed for spin glass (SG) systems.

We have investigated the dynamics of Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ (PSMO) nanoparticles at low T. PSMO is a medium bandwidth half doped manganite. Bulk PSMO shows paramagnetic (PM) to FM transition followed by FM to A-type antiferromagnetic (AF) transition on cooling from room temperature [4]. However, PSMO nanoparticles exhibit SPM behavior showing broad peak in T variation of magnetization (M) measurement [5]. Moreover, due to presence of dipolar interactions [5], these nanoparticles are expected to exhibit experimental signatures which are related to collective phenomenon. We have observed slow magnetic relaxation and memory
effect in PSMO nanoparticles. However, these nanoparticles do not exhibit aging phenomenon, implying their dynamics is different from that of SG system. By measuring the magnetic relaxation with positive and negative T cycle, we show that dynamics of present nanoparticles could be explained with hierarchical model rather than droplet model in SG.

2. Experimental details

PSMO nanoparticles are prepared by chemical (pyrophoric) method using materials Pr$_6$O$_{11}$, SrCO$_3$ and Mn(CH$_3$COO)$_2$ with purity more than 99.99% [5, 6]. Room temperature x-ray diffraction (XRD) pattern shows sample is in single phase and crystallize in tetragonal structure with I4/mcm symmetry [5]. The particle size is calculated from XRD data exploiting Scherrer formula [7] and transmission electron microscope (TEM) (model: Tecnai 20 G2). Figure 1(a) shows TEM image of particles and Figure 1(b) shows the particle size distribution obtained from TEM image. The average particle size obtained from both XRD and TEM is around 15 nm. Mn ionic concentration is obtained from Iodometric Redox titration with the values Mn$^{3+}$ = 48.5 % and Mn$^{4+}$ = 51.4 %. Magnetization is measured with home made vibrating sample magnetometer [8] and SQUID (MPMS) made by Quantum Design.

3. Results and discussions

Figure 2 shows the T variation of M measured in 10 Oe following zero field cooled (ZFC) and field cooled (FC) protocols. $M_{ZFC}$ shows peak around 202 K ($T_B$), and huge bifurcation is observed between $M_{ZFC}$ and $M_{FC}$ below $T_B$. The behavior of M(T) is typical characteristic feature of SPM system. Moreover, $M_{FC}$ in Figure 2 continues to increase with decreasing T similar to SPM particles, whereas for SG system $M_{FC}$ remains flat below the peak in $M_{ZFC}$ [1].

Magnetic state of these nanoparticles is probed through history dependent magnetic relaxation measurements. Usually, SPM particles with single energy barrier show an exponential magnetic relaxation. However, for distribution of relaxation times which can arise due to polydisperse nature of particles and/or interparticle interactions, magnetization relaxes slowly following stretched exponential function or logarithmic function. We have measured magnetic relaxation for PSMO nanoparticles where the system is cooled in zero field to 166 K (below $T_B$), and after proper thermal stabilization, 10 Oe field (H) is applied and M is measured as a function of time (t) up to $10^4$ s. Inset of Figure 3 shows that M relaxes following the function $M(t) = M_0 + S \log(t)$, where $M_0$ is parameter and S is magnetic viscosity. This is an indication in favor of interparticle interactions. Furthermore, we have looked into the aging effects on these nanoparticles, where in above experiment field is applied after a certain wait time ($t_w$) and subsequently M(t) is measured. For the systems with nonequilibrium dynamics, like SG, aging effect is prominent and magnetic relaxation depends on $t_w$ [1]. We have used $t_w = 10^2, 10^3$ and $10^4$ s, and data are plotted in Figure 3 after normalizing them by M(t=20 s). It is evident
The selected correlation of spins having spatial order more than ℓ spins [10]. At particular T, these droplets grow infinitely with t. With the change in T by ∆T, theoretical models. One is droplet model which assumes the distribution of droplets of correlated effect. This observation clearly shows the presence of interactions among these nanoparticles. The collective dynamics often gives rise to magnetic memory effect. To test this, FC memory effect is measured following Ref. [2, 9] which have attributed this to interparticle interactions. This measurement starts with cooling the sample in field where intermittent stop is given at temperature T_i (below T_B) with the field is switched off, allowing the system to relax for certain amount of time t_i, and then FC cooling is resumed. Magnetization measured in this process is called FC_{wait}. After reaching to low T, the sample is warmed and the measured magnetization is called FCW. For the system which exhibits memory effect, FCW shows distinct upturn around each T_i and regains its FC_{wait} value above T_i. The applied field is 30 Oe and we selected T_i = 164 and 120 K, and t_i = 2 h. The data are presented in Figure 4 along with FC_{Ref}. It is evident in figure that measured FCW exhibits distinct upturn at each T_i showing the magnetic memory effect. This observation clearly shows the presence of interactions among these nanoparticles.

Usually, collective dynamics in SG is qualitatively explained within the framework of two theoretical models. One is droplet model which assumes the distribution of droplets of correlated spins [10]. At particular T, these droplets grow infinitely with t. With the change in T by ∆T, correlation of spins having spatial order more than ℓ(∆T) breaks and new relaxation starts at temperature T ± ∆T. However, this process is symmetric with the sign of ∆T. The another one is hierarchical model which considers that an infinite number of metastable states separated by barriers are hierarchically organized in free energy landscape at a particular T [11]. With a decrease in T by ∆T, each metastable state splits into new substates and with the increase in T by ∆T these states merge into new state showing an asymmetrical behavior. Thus, the measured magnetic relaxation with positive and negative T cycle would show symmetric and asymmetric behavior for droplet and hierarchical model, respectively.

To identify the model accounting the dynamics of these nanoparticles we have collected the magnetic relaxation data with cycling T. For this purpose, sample is cooled in zero field from the room temperature to 151 K. After stabilization of T, 15 Oe field is applied and M is measured as a function of t for t_1 s. Then without changing the field, we cooled the sample to 135 K and measured M(t) for t_2 s, and then sample is heated back to 151 K and M(t) is measured for t_3 s. The selected t_1 = t_2 = t_3 = 4000 s. In Figure 5, M(t) increases continuously at 151 K, but at 135 K relaxation is almost halted. However, system resumes its relaxation again at 151 K. It is observed in figure that magnetic relaxation during t_3 is nearly a continuation of that during

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M(t) = M(0) e^{-t/\tau}
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cooled back to 151 K, relaxation is almost halted and $M(t)$ during of Figure 5. It is observed that $M$ relaxes both at 151 K and 166 K but when the system is intermittent stop for 2 h at 164 K and 120 K.

$t_1$. Again the same protocol is followed for positive $\Delta T$ (at 166 K) and data are plotted in inset of Figure 5. It is observed that $M$ relaxes both at 151 K and 166 K but when the system is cooled back to 151 K, relaxation is almost halted and $M(t)$ during $t_3$ is not a continuation of $t_1$. This asymmetric behavior of relaxation in Figure 5 can be explained with the hierarchical model as at lower T relaxation occurs only within newly born substates. So, when heated back to original T, $M(t)$ is a continuation of earlier value as the relative occupation in each state remains unchanged. On the contrary, during relaxation at higher T, relative occupation of states are changed because they are merged into new state. As a result, when cooled back to original T, $M(t)$ does not match with the earlier value. Nonetheless, these results indicate that interparticle interactions are present in these nanoparticles which influence the low-T dynamics significantly.

4. Conclusion
Magnetic relaxation, aging and memory measurements are done to study the low T dynamics in Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ nanoparticles. System shows slow magnetic relaxation following logarithmic dependence on time and memory effect in dc magnetization. These are due to collective behavior induced by interparticle interactions. However, aging effect is found to be absent, thus distinguishing the dynamics of this system from that of SG. Further, asymmetric response of magnetic relaxation measured with positive and negative T cycle suggests that dynamics of these nanoparticles can be explained by hierarchical model rather than droplet model. These results are intriguing on the perspective of nanoparticles in manganite.

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