Evidence of electronic phase arrest and glassy ferromagnetic behaviour in (Nd$_{0.4}$Gd$_{0.3}$)Sr$_{0.3}$MnO$_3$ manganite: comparative study between bulk and nanometric samples

S Kundu and T K Nath

Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur, West Bengal 721302, India

E-mail: souravphy@gmail.com and tnath@phy.iitkgp.ernet.in

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Abstract
The effect of the doping of rare earth Gd$^{3+}$ ions replacing Nd$^{3+}$ in Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ is investigated in detail. Measurements of resistivity, magnetoresistance, magnetization, and linear and nonlinear ac magnetic susceptibility on chemically synthesized (Nd$_{0.7-x}$Gd$_x$)Sr$_{0.3}$MnO$_3$ show various interesting features with doping level $x = 0.3$. A comparative study has been carried out between a bulk and a nanometric sample (grain size $\sim$60 nm) synthesized from the same as a prepared powder to maintain an identical stoichiometry. The resistivity of the samples shows strong dependence on the magnetic field–temperature history. The magnetoresistance of the samples also shows strong irreversibility with respect to sweeping of the field between the highest positive and negative values. Moreover, the resistivity is found to increase with time after field cooling and then switching off the field. All these phenomena have been attributed to phase separation effects and the arrest of phases in the samples. Furthermore, the bulk sample displays a spin glass like behaviour as evident from the frequency dependence of linear ac magnetic susceptibility and critical divergence of the nonlinear ac magnetic susceptibility. The experimentally obtained characteristic time $\tau_0$ after dynamical scaling analysis of the frequency dependence of the ac susceptibility is found to be 10$^{-17}$ s which implies that the system is different from a canonical spin glass. An unusual frequency dependence of the second harmonic of ac susceptibility around the magnetic transition temperature led us to designate the magnetic state of the sample to be glassy ferromagnetic. On reduction of the grain size low field magnetoresistance and phase arrest phenomena are found to enhance but the glassy state is observed to be destabilized in the nanometric sample.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The manganites with a perovskite ABO$_3$ structure have attracted enormous research interest over the years because of their very rich and unusual physical properties which are easily tunable through various ways like substitution/doping, external pressure, change in grain size, etc [1]. Firstly, it has been found that the appropriate substitution of the A-site trivalent elements with divalent materials (like Sr$^{2+}$ and Ca$^{2+}$, etc) introduces ferromagnetism and metallicity...
accompanied by a colossal magnetoresistance effect governed mainly by the so called double exchange mechanism [2]. Furthermore, it has also been found that substitution of the trivalent A-site with a different trivalent ion (like the rare earth elements) in a double exchange ferromagnetic manganite introduces many other fascinating effects on the angetic and electronic properties [3–5]. Such A-site substitution has some fundamental effects on the system as mentioned below. For instance, substitution by an ion with different ionic radius changes the average A-site ionic radius \( \langle r_A \rangle \) of the parent manganites effecting directly the band width of the material [3, 6]. This type of substitution also promotes A-site disorder due to random distribution of the A-site cations with different size and is generally estimated by the variance \( \sigma^2 = \sum y_{i} r_{i}^2 - \langle r_A \rangle^2 \), \( y_i \) is the fractional occupancy of the \( i \)-th ion in the A-site [4, 7]. It has been observed that the above mentioned doping has a profound influence on the magnetic transition temperature as well as on other magnetic and electronic properties [3, 8–10]. Moreover, if the dopant has a magnetic moment then an additional magnetic coupling takes place between the Mn-site and the dopant apart from the Mn\(^{3+}/\text{Mn}^{4+}\) double exchange interaction [11, 12]. Ultimately, the phase separation effect which plays a significant role in most of the behaviour of manganites, is enhanced on such substitution [10]. A large amount of study has been carried out on doping of rare earth elements in the A-site of La based manganites (La–Sr/Ca–Mn–O). These parent compounds are known to be an excellent double exchange system with a non-magnetic \( \text{La}^{3+} \) cation which plays a significant role in most of the behaviour of the system. The present study found to have a strong influence on both the electronic and magnetic properties of the system. The present study also includes a detailed comparative study of the observed properties in bulk and nanometric samples with the same stoichiometry.

2. Experimental details

Polycrystalline samples of \( \text{Nd}_{0.4}\text{Gd}_{0.3}\text{Sr}_{0.3}\text{MnO}_3 \) have been synthesized through a chemical pyrophoric reaction route [14]. High purity \( \text{Nd}_2\text{O}_3, \text{Gd}_2\text{O}_3, \text{Sr(NO}_3)_2 \) and \( \text{Mn(CH}_3\text{COO})_2 \) were dissolved in water with the appropriate amount of \( \text{HNO}_3 \). Triethanolamine was then added to this solution and stirred continuously while heating the mixture at 180 °C. Finally, combustion takes place producing a black fluffy powder which, on calcination, produces polycrystalline samples of \( \text{Nd}_{0.4}\text{Gd}_{0.3}\text{Sr}_{0.3}\text{MnO}_3 \). To synthesize nanometric as well as bulk samples of the same stoichiometry we have calculated one part of the as prepared sample at 750°C and the remaining at 1150°C. The former produces nanometric samples of \( \text{Nd}_{0.4}\text{Gd}_{0.3}\text{Sr}_{0.3}\text{MnO}_3 \) (NGSMO_N), while the latter produces the bulk sample of \( \text{Nd}_{0.4}\text{Gd}_{0.3}\text{Sr}_{0.3}\text{MnO}_3 \) (NGSMO_B).

Structural characterization of the samples has been carried out through high resolution x-ray diffraction (HRXRD) from Pananalytical, high resolution transmission electron microscopy (HRTEM) from JEOL Ltd, Japan and field emission scanning electron microscopy (FESEM) from Carl Zeiss, Germany. The electronic-transport properties of the samples was measured employing a standard linear four probe technique on pellets (approximate dimension \( \sim 8 \text{ mm} \times 3 \text{ mm} \times 0.3 \text{ mm} \)) of the samples down to a lowest temperature of 2 K and under a highest magnetic field of 8 T. We have employed a conductive silver paint for making contacts on the sample surface. Measurement of the resistivity and magnetoresistance has been carried out by applying a low dc current (employing Keithley-6221 current source) of magnitude 10 μA for NGSMO_B and 1 μA for NGSMO_N sample to avoid Joule heating in the samples. A closed cycle helium refrigeration cryostat attached with an 8 T superconducting magnet from Cryogenics Ltd, UK was employed to perform these measurements. The static (dc) magnetizations, \( M(T) \) and \( M(H) \), were measured in a superconducting quantum interference device (SQUID) from Quantum Design. The linear and nonlinear ac susceptibility was measured down to 2 K employing a homemade ac susceptibility coil fitted inside the Helium refrigeration cryostat. A lock-in-amplifier (SR830) was used to measure the induced signal. Temperature of the sample was controlled by high precision PID temperature controllers from Lakeshore Cryotronics, USA (model 325 and 340) with a temperature stability better than \( \pm 50 \) mK.

3. Results

3.1. Structural properties

The HRXRD data shown in figure 1(a) reveal that the samples are of single phase with no detectable impurity phase present. For further structural analysis we have performed Rietveld refinement of the experimental data using the Maud programme. Both the nanometric and the bulk samples are found to crystallize in the orthorhombic \( \text{Pnma} \) space group. The refined lattice parameters are 5.4401(8) Å (a),
Figure 1. (a) Plot of experimental HRXRD data of the samples (dots) with the fitted curve (line) and the difference on Rietveld refinement. (b) HRTEM image of the NGSMO_N sample. (c) Distribution of grain size of the NGSMO_N sample with the fitted curve with a log-normal distribution function. (d) FESEM image of the NGSMO_B sample. (e) Selected area diffraction pattern of the NGSMO_N sample.

7.6841(4) Å (b) and 5.4630(5) Å (c) for the NGSMO_B sample. The lattice parameters for the NGSMO_N sample are 5.4584(3) Å (a), 7.6551(6) Å (b) and 5.4341(10) Å (c). The unit cell volume of NGSMO_B sample (228.3 Å³) is found to reduce slightly in the NGSMO_N sample (227.1 Å³). Hence, we see that the structural change is not significant with the change of grain size. The HRTEM (figure 1(b)) image of the NGSMO_N sample displays that the grain size of the sample is in the nanometric regime (less than 100 nm). The average grain size is about 60 nm as determined from the plot of distribution (figure 1(c)). On the other hand, the FESEM image of NGSMO_B (figure 1(d)) shows micrometre (µm) size grains and the sample is expected to show bulk properties. The spotty rings in the SAED (selected area electron diffraction) pattern in figure 1(e) of the NGSMO_N sample indicate the polycrystalline nature of this sample.

3.2. Transport properties

A detailed analysis of the electronic- and magneto-transport properties of both the samples has been carried out. The resistivity as a function of temperature of the samples has been measured at zero magnetic field and shown in figure 2. Both the samples show a metal to semiconductor/insulator transition followed by a resistivity minima and resistivity upturn in the low temperature regime. The striking difference between these two samples is the presence of a huge upturn of resistivity for NGSMO_N (figure 2(a)). In the case of the NGSMO_B sample this upturn is not so prominent (figure 2(b)). This indicates a strong influence of grain size on the observed low temperature minima of polycrystalline manganites. The temperature dependent resistivity in the low temperature regime has been analyzed in more detail. Such observation of the resistivity minimum is generally explained in terms of Coulomb blockade [15], Kondo effect [16, 17] or electron–electron (e–e) interaction [16, 17]. Due to the Coulomb blockade effect resistivity goes as exp(√(1/T)) in the low temperature regime. Here Δ is equivalent to charging energy. The Kondo effect, which is generally observed in low resistive magnetic alloys exhibits ln(T) dependence of resistivity in the low temperature regime. In a disordered, high resistive system the elastic type e–e scattering occurs when the mean free path of the electrons becomes small and the resistivity shows T¹/² dependence. With an increase of temperature inelastic scattering of electrons increases and gives rise to the resistivity minimum. This inelastic scattering is assumed here to have a Tⁿ dependence, in general. The Coulomb blockade type model is found to produce very poor fitting of the resistivity data in the low temperature regime of the NGSMO_B sample (at H = 0 T). Then we employ equations like ρ = ρ₀ – ρ₁ ln T + ρ₂ τ² assuming Kondo effect.
or $\rho = \rho_0 - \rho_c T^{-1/2} + \rho_n T^n$ assuming e–e interaction to fit the low temperature resistivity data of the NGSMO_B sample as shown in the inset of figure 2(b). One can easily observe that the resistivity minimum in this sample is best described through the e–e interaction process as the latter equation gives a better fit. The obtained parameters $\rho_0$, $\rho_c$, $\rho_n$, and $n$ are found to be $563 \ \Omega \ cm$, $72.5 \ \Omega \ cm \ K^{-1/2}$, $7.3 \times 10^{-4} \ \Omega \ cm \ K^{-n}$ and 3.4, respectively. We employ a similar approach to fit the low temperature resistivity data of the NGSMO_N sample. However, none of the above mentioned models are found to fit the experimental data satisfactorily. This indicates that the mechanism behind the huge low temperature upturn and minima in the resistivity of the NGSMO_N sample is more complicated and different from that in the NGSMO_B sample. We primarily attribute this complication in the NGSMO_N sample to the presence of an enhanced grain boundary where the actual nature of the electron transport is not understood so far. Interestingly, the NGSMO_N sample shows a thermal hysteresis around the metal–insulator transition as shown in the inset of figure 2(a). This thermal hysteresis is a generic feature of first order phase transition [18, 19].

During the measurement of resistivity of the samples under magnetic field/without magnetic field, we adopted mainly four different protocols.

(1) The resistivity was measured during heating at zero magnetic field after cooling the sample without the application of field (ZFC_W resistivity).

(2) The sample was cooled in zero magnetic field and data were taken during heating at specific selected magnetic field (ZFC_FW).

(3) The sample was cooled under selected magnetic field and data were taken during heating at the same field (FC_FW).

(4) The sample was cooled under selected magnetic field and data were taken during heating at zero applied field (FC_W).

In all these cases the cooling is always started from a temperature much above the metal–insulator transition temperature.

The methods described in (2) and (3) are similar to what is generally followed in field cooled and zero field cooled magnetization measurements, magnetization being replaced by resistivity of the sample. The method described in (4) is possible as a magnetic field is not necessary for the measurement of resistivity.

Figure 3(a) displays the ZFC_FW and FC_FW resistivity curves for the NGSMO_N sample. One can observe that the resistivity versus temperature curves following these two methods at a particular field tend to bifurcate from each other at a very low temperature (< 20 K). At the lowest applied field (0.1 T) the bifurcation is not prominent. However, at 1 T field the bifurcation seems to be the maximum and decreases with increasing field thereafter. As a consequence, the bifurcation point shifts to a lower value of temperature in the high field regime. The FC_FW curve remains below the ZFC_FW curve at all applied fields. This precisely implies that the sample remembers the history even during heating at the same field which is reflected in the bifurcation. A history dependence of resistivity of a sample is not a very common phenomenon and not commonly reported in the literature especially in the case of manganites with an optimally doped regime. Even for the parent compound Nd_{0.7}Sr_{0.3}MnO_3, no such history dependence of resistivity is reported to the best of our knowledge. So, the observed effects can be attributed to the doping of Gd^{3+} in the A-site of the system under study. A similar measurement has been carried out on the NGSMO_B sample to compare the effects with the nanometric counterpart. A similar bifurcation between the ZFC_FW and FC_FW curves has been found as shown in figure 3(b). Obviously, in case of NGSMO_B the bifurcation is small compared to that in the NGSMO_N sample. We, hence, can conclusively state that the thermo-magnetic history dependence of resistivity is enhanced due to the decrease of grain size.

The resistivity of both the samples has also been measured following a slightly different protocol namely FC_W as mentioned earlier. It has been found from figures 3(c) and (d) that the measured resistivity at zero field is strongly dependent on the magnetic field at which the samples were cooled before the measurement. There is a huge difference observable for the NGSMO_N sample between the FC_W, 8T curve and the ZFC_W curve (figure 3(c)). Even at low field the FC_W, 1 T curve differs significantly with the ZFC_W curve. The difference increases with increasing field. The NGSMO_B sample shows similar behaviour as depicted.
in figure 3(d). The only difference is that the bifurcation between the FC_W and ZFC_W curves is smaller compared to that of the NGSMO_N sample. These measurements elaborate the fact that the electronic phase of the sample is frozen or arrested during field cooling (a low resistive state) and does not come back to the original state even when the magnetic field is removed. Importantly, the reduction of grain size enhances this phenomenon.

At this point, the obvious question arises as to whether the frozen or arrested phase evolves with time and tries to come back to the original state as soon as the field is switched off. To have a clear picture about this, we have performed the time dependence of resistivity of both the bulk and nanometric samples. The samples were first cooled from a high temperature greater than the ferromagnetic (FM)–paramagnetic (PM) (as well as metal–insulator) transition temperatures under a highest magnetic field of 8 T down to the desired measuring temperature. After reaching the desired temperature the field was switched off and the resistivity of the samples was measured as a function of time for a sufficiently long period. This experiment has been performed at several temperatures for the NGSMO_N sample. Quite interestingly, it is found from the inset of figure 4 that the resistivity of the NGSMO_N and NGSMO_B samples increases with time. The resistivity shows a sharp rise initially and a slow variation thereafter for the NGSMO_N sample at all temperatures. At an intermediate temperature (30 K) the change of resistivity is observed to be maximum indicating a non-monotonic dependence of the relaxation rate with...
Figure 5. (a) Plot of magnetoresistance (MR) of the samples as a function of temperature at $H = 1$ and $8$ T. Panels (b)–(e) show the MR of the NGSMO$_N$ sample as a function of magnetic field ($-8$ T–$0$ T–$8$ T) at different temperatures. Panel (f) displays the variation of MR with magnetic field of the NGSMO$_B$ sample at $3$ K.

Comparing the data at $3$ K we find that the increment of resistivity is higher for the NGSMO$_N$ sample compared to the NGSMO$_B$ sample within the measured time span. These measurements confirm that the arrested electronic phase actually has a dynamic character and evolves with time. Thereafter, we try to find out a possible functional form of this time dependence of resistivity. Interestingly, we have observed that the relaxation is of logarithmic type similar to the relaxation of magnetization found in many magnetic systems (spin glasses and magnetic nanoparticle systems) as evident from the linear nature of the curves in figure 4. The curves are fitted assuming an empirical relation, $\rho(t) = \rho(0) + C \log(t)$ ($C$ is a constant), successfully except the initial fluctuating part as shown in figure 4. Only at high temperature ($60$ K) we see some deviation from this law.

The magnetoresistance (MR) of the samples have been measured as a function of temperature as well as field. From figure 5(a) it is evident that the MR reaches nearly $100\%$ in the low temperature regime at the highest applied field ($8$ T) for both the samples and decreases as the temperature
is increased. At 1 T field there is a marked difference between the MR versus $T$ curves of the samples at the low temperature regime. The NGSMO$_N$ sample shows a higher MR which can be considered as an improvement of MR in the low temperature regime at low applied fields as an outcome of the reduction of grain size. One can also notice a mutual crossover of the MR versus $T$ curves of the samples at both the applied fields below a certain temperature. In the low temperature regime the nanometric sample shows higher MR, whereas, above a certain temperature (nearly the metal–insulator transition temperature) the bulk sample shows higher MR. The field dependence of MR and the effect of field cycling at different temperatures of the nanometric and bulk samples are shown in figures 5(b)–(f). The main observed feature of these measurements is that the resistive state after application of the field does not return to the zero field state even when the field is swept to the negative highest value through zero. This is nothing but the similar arrest of the phase on application of the field as mentioned earlier. Noticeably, with an increase of temperature from 3 to 70 K in the case of the NGSMO$_N$ sample this phenomenon is gradually weakened as the final value of resistance comes closer to the initial value. At 70 K we do not see any irreversibility at all. It is also found that the phenomenon is stronger in the nanometric sample when we compare the results with the bulk counterpart at 3 K (figures 5(b) and (f)). In order to have an insight about the mechanism of observed MR we have tried to fit our experimental virgin MR versus $H$ data with different available models. Firstly, the spin dependent hopping model [20] has been employed to both the samples. According to this model the MR in the FM regime is proportional to $B(x)$, whereas MR is proportional to $B^2(x)$ in the PM regime. $B(x)$ is the Brillouin function. By tentatively assuming a mixture of FM and PM phases in the sample the total MR can be expressed as $MR = F(T)B(x) + P(T)B^2(x)$, where, $F(T)$ and $P(T)$ are the FM and PM phase fractions in the sample, $x = g\mu_B J(T)/k_BT$. The symbols have their usual significance. The MR versus $H$ curve of the NGSMO$_B$ sample is found to fit satisfactorily with this model. From the obtained values of $J(T)$, the average value of total spin of a magnetic cluster, we have calculated the size of the cluster in terms of the perovskite lattice unit (l.u.) as a function of temperature and this is shown in figure 6(a). This model is found to provide a very poor fitting in the case of the NGSMO$_N$ sample and is not discussed here. Even if the fitting seems good for the NGSMO$_B$ sample one can observe very large error bars in the values of calculated cluster size. This indicates that the above mentioned model is not sufficient to account for the magneto-transport mechanism in this sample entirely. Furthermore, we have applied a second model namely spin polarized tunnelling model proposed by Raychaudhuri et al [21]. According to this phenomenological description of MR, low field MR is mainly due to the spin polarized tunnelling between adjacent grains and known as spin polarized tunnelling MR (MR$_{SPT}$). MR at a higher field comes from the double exchange mechanism and is known as the intrinsic MR (MR$_{INT}$). The total MR at field $H$ is given by, $MR = −\int_0^H [A \exp(−Bk^2) + CK^2 \exp(−DK^2)] dk (^\prime MR_{SPT}) − JH − KH^3 (^\prime MR_{INT})$ where, $A, B, C, D, J$ and $K$ are adjustable fitting parameters. This equation too, seems to fit well to the experimental data of NGSMO$_B$ sample. From the obtained values of the parameters we have calculated the spin polarized tunnelling MR and the intrinsic MR as a function of temperature and plotted in figure 6(b). The spin polarized tunnelling MR is found to be the maximum near the metal–insulator transition and decreases as the temperature is increased. Intrinsic MR follows an opposite nature to the former. In the case of the NGSMO$_N$ sample we again see a poor fitting. This clearly indicates that the magneto-transport mechanism is much more complicated for the NGSMO$_N$ sample compared to its bulk counterpart.

3.3. Magnetic properties

In order to probe the magnetic properties of the samples dc magnetization has been measured with the temperature at very low dc applied fields following zero field cooled (ZFC)–field cooled (FC) protocols. The dc magnetic susceptibility ($\chi_{dc} = M/H$) is plotted as a function of temperature in figure 7(a) for both the samples. The NGSMO$_B$ sample shows a sharp transition at around 100 K, similar to an FM–PM transition. The FM–PM transition temperature as well as the metal–insulator transition temperature in
the NGSMO_B sample is much lower than that in the parent compound Nd_{0.7}Sr_{0.3}MnO_3 [1]. However, below the transition temperature a huge bifurcation between the ZFC–FC susceptibility is observed. This indicates that the FM phase is not like a usual long range ordered FM one, rather there could be a sufficient amount of frustration and disorder originating from antiferromagnetic coupling between Mn and Gd moments in this FM state [8, 11]. It is also noticeable that the ZFC curve of NGSMO_B shows a sharp increase in value with the increase of temperature in the lowest temperature regime. This is possibly originating from the ordering of the Nd^{3+} moments [22]. The NGSMO_N sample shows an overall feature similar to that of its bulk counterpart. However, the PM–FM transition is found to broaden and flattened, whereas the low temperature rise of moment is not found to be prominent. The destabilization of the FM phase around the disorder surface region of the nanograins and the distribution of grain size can be attributed to the broadening of the magnetic transitions in NGSMO_N. The magnetization of both the samples has also been measured as a function of magnetic field at different temperatures and shown in figure 7(b). All the samples show a slightly non-saturating nature of the magnetization even up to 7 T field indicating an incomplete and progressive alignment of the magnetic moments of magnetic species in the samples. We have theoretically calculated the effective magnetic moment of the sample by adding the spin only moments \( g/[S(S + 1)] \) \( \mu_B \) \( (g = 2) \) of the magnetic ions. Firstly, assuming that the magnetism is only coming from B-site (Mn ions), the effective moment of our sample should be 4.6 \( \mu_B \)/formula unit (f.u.). From the \( M–H \) data of the NGSMO_B sample at the lowest temperature (5 K) it is quite clear that the A-site magnetic ions (Nd^{3+} and Gd^{3+}) contribute to the sample magnetization, the saturation magnetization \( M_s = 6.65 \mu_B/\text{f.u.} \), calculated from approach to saturation model, \( M = M_s - a/H + b/H^2 \) being higher than this theoretical value. This observed moment \( (6.65 \mu_B/\text{f.u.}) \) is also higher than the experimentally observed moment of Nd_{0.7}Sr_{0.3}MnO_3 [22]. This clearly indicates that the dopant Gd^{3+} moment contributes to the magnetism of the sample and all the magnetic moments are in a partially aligned state. This observation is consistent with some earlier reports which showed that a small amount of doping with magnetic rare earth material in the A-site actually enhances the net saturation moment of the sample [9]. The Curie–Weiss plot \( (1/\chi \text{ versus } T) \) shows a straight line in the PM regime for the NGSMO_B sample (inset of figure 7(a)). From the fitting of the equation \( \chi = C/(T - \theta) \) \( (C \text{ is the Curie–Weiss constant and } \theta \text{ is the PM Curie temperature}) \) to the experimental data we have calculated the value of \( C = 9.0 \text{ emu mol}^{-1} \text{ Oe}^{-1} \text{ K} \) and \( \theta = 111 \text{ K} \). This experimental value of \( C \) corresponds to an effective moment of the PM sample \( (p_{eff}) \) of 8.46 \( \mu_B \) for the sample. Now assuming that all the magnetic ions in the sample \( (\text{Nd}^{3+}, \text{Gd}^{3+}, \text{Mn}^{3+}, \text{Mn}^{4+}) \) are free in the PM regime, the theoretically calculated effective PM moment of this sample is \( \sqrt{\sum \mu^2} = 6.74 \mu_B \) \( (c = \text{fractional occupancy of the magnetic ions}) \) [11, 23]. This value is lower than the experimental value. Such a high value of experimental \( p_{eff} \) can be explained in terms of the presence of FM clusters in the PM regime of the sample. This indicates that the FM–PM phase transition is not absolutely sharp and the presence of FM clusters, which have a higher spin moment than those of the individual ions, in the PM regime, gives rise to a higher value of effective PM moment [23]. Furthermore, we have tested the FM ordering in the light of Rhodes–Wohlfarth criteria [24]. In the localized model, \( q_c/q_s = 1 \), where \( p_{eff} = \sqrt{[q_c(q_c + 2)]} \). Here 1/2q_c is the effective spin number and \( q_s \) is the average spontaneous moment (in \( \mu_B \)) calculated from \( M–H \) measurement. In the itinerant model, \( q_s \) may be less than \( q_c \) and \( q_c/q_s \) \( (>1) \) gives a measure of the degree of itinerancy. We see, in our case, that \( q_c = 7.52 \mu_B \) and is greater than \( q_s = 6.65 \mu_B \). This conforms to the fact that this system is an itinerant ferromagnet (due to the double exchange mechanism). The NGSMO_N sample, on the other hand, always shows a smaller value of magnetization at all measured temperatures compared to the bulk sample (figure 7(b)). It is expected as the magnetically disordered surface of the nanograins will contribute less to the total magnetization.
Figure 8. (a) The variation of the real part of linear ac susceptibility ($\chi^R_1$) of the NGSMO\_B sample with respect to temperature at different frequencies and at ac applied field ($h_{ac}$) of 3 Oe. The top right inset shows the magnified version of the main plot around the transition region. The top left inset shows the fitted curve to the experimental data under the scheme of the critical slowing down model. (b) Plot of $\chi^R_1$ versus temperature of the NGSMO\_N sample at different frequencies at $h_{ac} = 3$ Oe. The most striking difference observable from the $M$–$H$ data is the change in coercivity with the change of grain size. At the lowest temperature (5 K), the coercivity of the NGSMO\_B sample is found to be 160 Oe, whereas, it is as high as 1100 Oe for the NGSMO\_N sample at the same temperature as shown in the inset of figure 7(b). This effect can be attributed to the extraordinarily enhanced surface anisotropy due to the presence of defects, broken bonds, non-stoichiometry, etc. which produces a number of pinning centres for the spins around the surface regime in the nanometric sample [25].

In order to obtain a clearer picture about the magnetic state of the system, we have performed ac magnetic susceptibility (linear and nonlinear) measurements on both the samples as shown in figures 8(a) and (b). The frequency dependent real part of the linear susceptibility ($\chi^R_1$) of the bulk sample is shown in figure 8(a). The $\chi^R_1$ versus $T$ curves for the NGSMO\_B sample show similar features like the ZFC magnetization versus $T$ behaviour with an FM–PM like transition at around 100 K. However, it is evident that below the transition the susceptibility shows a sharp drop unlike a conventional FM. More interestingly, the peaks of the $\chi^R_1$ versus $T$ curves are clearly frequency dependent as evident from the top right inset of figure 8(a). The magnitude of the susceptibility gradually decreases and the position of the peak shifts to high temperature with an increase of frequency. These collectively signify a spin glass like behaviour. To further investigate this feature we have measured the second and third harmonics (nonlinear susceptibility) of ac susceptibility as a function of temperature. The real part of the second harmonic susceptibility ($\chi^R_2$) of the NGSMO\_B sample measured at different frequencies is shown in figure 9(a). The $\chi^R_2$ versus $T$ curves show a sharp peak at around the FM–PM transition. The second harmonic (and other even harmonics) is generally observed when symmetry breaking spontaneous magnetization is present in the sample [26]. The observed peak in $\chi^R_2$ signifies the presence of ferromagnetism in this sample. Interestingly, the peak in $\chi^R_2$ also shows a frequency dependence like the linear susceptibility (the peak shifts to higher temperature with the increase of frequency as shown in the inset of figure 9). This can be regarded as a very unconventional feature as in a canonical spin glass $\chi^2$ is not present but $\chi_1$ shows frequency dependence at the freezing temperature of the sample. In our NGSMO\_B sample, on the other hand, a spin glass like frequency dependent peak in $\chi_1$ has been observed, whereas, $\chi^R_2$ is also found to be present and exhibits a peak at the same transition temperature with similar
frequency dependence. Keeping in mind these behaviours in the ac susceptibility (ferromagnetism along with glassiness) of the NGSMO_B sample, we label the FM state of this sample as a glassy ferromagnet (GFM). A strong test for a spin glass like behaviour in a system is the measurement of third order susceptibility (χ₃) which shows a sharp negative peak at around the freezing temperature and diverges in the low field limit (hₑ → 0) [27]. In this regard, a thorough measurement of χ₃ and its analysis has been carried out on our samples. The temperature dependent real part of the third order susceptibility (χ₃R) of the NGSMO_B sample is shown in figure 10(a) at different ac magnetic fields (hₑ). In the low field regime χ₃R shows a sharp peak at around the GFM–PM transition temperature supporting the glassy behaviour of the system. Now we plot the peak/maximum values of χ₃R after normalizing it with respect to that at hₑ = 15 Oe, as a function of magnetic field (hₑ) as shown in figure 10(b). Interestingly, χ₃R for the NGSMO_B sample shows a diverging nature as the ac field is reduced showing a spin glass like feature. One noticeable fact is that an increase of hₑ changes the nature of variation of χ₃R versus T considerably. As the ac field is increased χ₃R shows a crossover nature (clearly visible for hₑ = 5 Oe), precisely, a positive peak below the transition temperature and a negative peak above it, unlike a single negative peak in the low hₑ regime. This crossover nature is a characteristic feature of a long range ordered magnetic system and generally observed near the FM–PM transition temperature of a conventional FM [28]. It is possible that when the magnetic field is high enough all the spins in a grain are forced to respond to the field coherently and display a long range ordered behaviour instead of exhibiting a spin glass like criticality. So, on the basis of features observed from the measurement of χ₃R it is clear that the system (NGSMO_B) has an FM character accompanied with glassiness. Finally, we try to analyse the frequency dependence of χ₃R employing known models. Application of the Arrhenius law of the form τ = τ₀ exp(Ea/k_BT) [29, 30] yields unphysical values of Ea and τ₀ showing the inapplicability of this law to the observed phenomena. It also hints at the fact that the system is not a non-interacting particle system. However, the relaxation process could not be explained by the Vogel–Fulcher law either. Finally, application of the critical slowing down model of the form τ = τ₀(Tf/Tg – 1)−zυ [29, 30] produces a physically meaningful set of parameters. Here, τ = 1/f, Tg = spin glass transition temperature, zυ = critical exponent, τ₀ = the characteristic time and Tf = frequency dependent peak of χ₃R versus T curves. On application of this model (as shown in the inset of figure 8(a)) we get Tg = 86 K, zυ = 3 and τ₀ = 10⁻¹² s. The value of zυ falls on the lower side of the observed values (4–12) for the spin glass materials [29]. However, the value of τ₀ is smaller than the reported values of this parameter (10⁻¹¹–10⁻¹⁴ s) in spin glasses [29]. This signifies that in spite of having spin glass like signatures, our system is different from a canonical spin glass.

In a similar manner, we have also measured the linear and nonlinear ac susceptibility of the nanometric NGSMO_N samples. The linear susceptibility (χ₁R) of the sample at different frequencies as a function of temperature is plotted in figure 8(b). There is clearly no observable shift of the peaks with frequency. The FM–PM transition is found to be very broad compared to the bulk sample. The variation of χ₄R in the inset of figure 9(b) and χ₃R in the inset of figure 10(a) with temperature show peaks around the FM–PM transition. All the higher order susceptibilities are found to be frequency independent. A comparative study of the divergence of χ₃R (figure 10(b)) around the transition temperature with the bulk shows that unlike the NGSMO_B sample, χ₃R tends to saturate as the magnetic field hₑ is reduced towards zero for the nanometric NGSMO_N sample. From the above mentioned study on the ac susceptibilities of the NGSMO_N sample it is quite clear that the glassy phase is destabilized in it due to the reduction of grain size.

4. Discussion

Now we turn to describe the possible scenario behind the observed features of the system. It has been mentioned earlier that introducing Gd³⁺, replacing Nd³⁺, decreases the average A-site ionic radii, increases the A-site disorder and induces extra magnetic coupling with the Mn-site. A decrease of

![Figure 10](image-url)

**Figure 10.** (a) Variation of the real part of the third harmonic of ac susceptibility (χ₃R) of the NGSMO_B sample as a function of temperature at different ac fields. The inset of (a) shows the variation of the same for the NGSMO_N sample with temperature at a particular field (2 Oe) and frequency (555.3 Hz). (b) Plot of the normalized peak value of χ₃R (with respect to the peak value of χ₃R at hₑ = 15 Oe) of both the samples as a function of ac field.
(ρ_M) can directly be related to the decrease of the FM–PM transition temperature of \( \text{Nd}_0.4\text{Gd}_0.3\text{Sr}_0.3\text{MnO}_3 \) compared to the parent compound \( \text{Nd}_0.7\text{Sr}_0.3\text{MnO}_3 \). The above mentioned effects on the doping of Gd collectively enhance the phase separation of the system. Though it is almost impossible to get an idea of the actual microscopic nature of the phase separated state, one can easily put forward a possible picture of the magnetic and electronic state in the sample. Keeping in mind the observed metal–insulator transition and FM as well as antiferromagnetic interactions in the system we can divide the system in broadly two classes of phase. One of them is the low resistive metallic phase which magnetically should have an FM character allowing double exchange to operate. The other one is a high resistive insulating phase and possibly has a less FM or antiferromagnetic character and may even be a canted spin state. Previously, the possibility and possibly has a less FM or antiferromagnetic character and may even be a canted spin state. Previously, the possibility of a separate spin glass phase coexisting with the FM state was reported [10]. Even though our system shows a spin glass like behaviour, we believe that a separate spin glass phase is not possible because the system (NGSMO_B) does not show any other spin glass transition except the FM–PM transition. Rather the magnetic state of the system is itself glassy in nature as a whole. However, as the temperature of the system is increased, PM clusters (insulating in nature) develop, grow in size and the sample undergoes the FM–PM transition. Similarly, the metal–insulator transition can be explained. In the low temperature regime the metallic phase dominates and as the temperature is increased insulating phases grow in size leading to an insulating nature of the system above a certain temperature (metal–insulator transition temperature). With such an assumption of a two component system the resistivity/conductivity can be conveniently described through effective medium approximation [31, 32].

The effective resistivity (ρ_{eff}) of the system is given by

\[ f(T, H) \left[ \frac{\rho_{FM} - \rho_{eff}}{2\rho_{FM} + \rho_{eff}} \right] + [1 - f(T, H)] \left[ \frac{\rho_{AFI} - \rho_{eff}}{2\rho_{AFI} + \rho_{eff}} \right] = 0. \]

Here \( f \) represents the volume fraction of the FM metallic phase whose resistivity is \( \rho_{FM} \) and \((1 - f)\) is the volume fraction of the antiferromagnetic insulating phase whose resistivity is \( \rho_{AFI} \). Obviously, \( \rho_{FM} \) is less than \( \rho_{AFI} \). In a simpler approach where these two phases are connected in series the effective resistivity can be written as

\[ \rho_{eff} = f(T, H)\rho_{FM} + (1 - f(T, H))\rho_{AFI} = 0. \]

So an increase of \( f \) (or decrease of \((1 - f)\)) will decrease the resistivity of the system and vice versa. Necessarily, we take the phase fraction \( f \) as a function of temperature and field. This naturally explains the observed properties of our system.

It is a well known issue that the large MR of manganites (\( r \)) can directly be related to the decrease of the FM–PM transition temperature of \( \text{Nd}_0.4\text{Gd}_0.3\text{Sr}_0.3\text{MnO}_3 \) compared to the parent compound \( \text{Nd}_0.7\text{Sr}_0.3\text{MnO}_3 \). The above mentioned effects on the doping of Gd collectively enhance the phase separation of the system. Though it is almost impossible to get an idea of the actual microscopic nature of the phase separated state, one can easily put forward a possible picture of the magnetic and electronic state in the sample. Keeping in mind the observed metal–insulator transition and FM as well as antiferromagnetic interactions in the system we can divide the system in broadly two classes of phase. One of them is the low resistive metallic phase which magnetically should have an FM character allowing double exchange to operate. The other one is a high resistive insulating phase and possibly has a less FM or antiferromagnetic character and may even be a canted spin state. Previously, the possibility of a separate spin glass phase coexisting with the FM state was reported [10]. Even though our system shows a spin glass like behaviour, we believe that a separate spin glass phase is not possible because the system (NGSMO_B) does not show any other spin glass transition except the FM–PM transition. Rather the magnetic state of the system is itself glassy in nature as a whole. However, as the temperature of the system is increased, PM clusters (insulating in nature) develop, grow in size and the sample undergoes the FM–PM transition. Similarly, the metal–insulator transition can be explained. In the low temperature regime the metallic phase dominates and as the temperature is increased insulating phases grow in size leading to an insulating nature of the system above a certain temperature (metal–insulator transition temperature). With such an assumption of a two component system the resistivity/conductivity can be conveniently described through effective medium approximation [31, 32].

The effective resistivity (ρ_{eff}) of the system is given by

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\[ \rho_{eff} = f(T, H)\rho_{FM} + (1 - f(T, H))\rho_{AFI} = 0. \]

So an increase of \( f \) (or decrease of \((1 - f)\)) will decrease the resistivity of the system and vice versa. Necessarily, we take the phase fraction \( f \) as a function of temperature and field. This naturally explains the observed properties of our system.

It is a well known issue that the large MR of manganites cannot be explained on the basis of double exchange alone. One has to incorporate the phase separation scenario [33]. It is quite obvious that the effect of phase separation has an important role to play in our system showing a high negative MR even in a low magnetic field. On the application of a magnetic field the volume fraction of the low resistive metallic phase \( f \) is increased (and \((1 - f)\) is decreased) and gives rise to negative MR. Moreover, when the field is switched off the latest phase separated state tends to persist (with only a slow evolution with time). This is reflected in the huge bifurcation between the ZFC–W and FC–W resistivity curves. It seems that the electronic phase gets arrested when the sample is field cooled. A similar bifurcation in the resistivity of manganite showing first order phase transition has been reported [18, 34]. We note that our nanometric NGSMO_N sample, in which the maximum history dependence is found, exhibits a prominent first order phase transition. Recently, similar phenomena have been observed in some other manganite materials and the effect is attributed to a more commonly used terminology called kinetic arrest [18, 34–36]. When we look at the ZFC–FW and FC–FW curves, the maximum bifurcation is found at an intermediate field. When the field is high both the ZFC–FW and FC–FW states tend to saturate to the high field low resistive state (saturation of \( f \)) reducing the bifurcation with the increase of the magnetic field.

The observed time dependence of FC resistivity can be explained taking the thermal energy into account. On switching off the field, the insulating clusters start growing in size, increasing the overall fraction of the insulating state in the sample and a simultaneous increase in the resistivity with time. At the lowest temperature, obviously the stability of the individual phases is very high through their individual barrier energies. As the temperature is increased, thermal energy comes to play, competes with the energy barriers and enhances the time rate of change of resistivity. At a much higher temperature, however, thermal energy dominates and disturbs the individual character of the phases and is reflected in a lower rate of change of resistivity. The reduction of the irreversibility in the MR versus \( H \) curves on an increase of temperature (figure 5) can be attributed to the thermal instability of the phases in a similar fashion. All these observations of the thermo-magnetic irreversibility of resistivity in the system indicate that \( f(T, H) \) and \( [1 - f(T, H)] \) are not only functions of temperature and field but also depend on field–temperature history.

To explain the magnetic behaviour of the system, one has to incorporate the role of Gd^{3+} necessarily. We know that the bulk parent compound \( \text{Nd}_0.7\text{Sr}_0.3\text{MnO}_3 \) does not show any kind of glassy behaviour. However, the presence of Gd^{3+} in the sample creates the extra antiferromagnetic exchange interaction between Gd and Mn ions. We also know that the exchange between Mn^{3+} and Mn^{4+} is FM in nature. So, the presence of two types of exchange bonds as well as the random distribution of these bonds provide two necessary ingredients, frustration and disorder, for a sample to display spin glass like behaviour. However, our system (NGSMO_B) is different from a canonical glass and exhibits comparatively faster dynamics evidenced from the smaller value of \( \tau_0 \).

On reduction of grain size the phase separation scenario discussed will be modified. The nanograins can be visualized as a crystallographically ordered core with a shell or surface where defects, broken bonds, etc, may exist in large numbers. Moreover, the surface to volume ratio increases when the size is reduced. We believe that with such a background (nanosize grains) the spatial extent of the individual phases will be reduced which in turn enhance the phase separation
in the sample. Effectively, we observe the enhanced MR, time dependence of resistivity and thermo-magnetic irreversibility in the NGSMO$_N$ sample. However, due to the destabilization of the phases, ultimately the glassy phase ceases to exist in NGSMO$_N$. The lack of the required number of interacting spins over a certain region in NGSMO$_N$ destabilizes the glassy behaviour which is necessarily a collective behaviour of a spin system via multiple exchange interaction.

5. Conclusions

In summary, the effect of doping of Gd$^{3+}$ in Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ has been investigated in terms of the measurement of the electronic and magnetic properties. We have observed that the system shows thermo-magnetic history dependence in its electronic- and magneto-transport properties. Both the bulk and nanometric samples show high magnetoresistance even in low field. The temporal dependence of resistivity is investigated after a field cooling and resistivity is found to increase with time when the field is switched off. Magnetically, the bulk system shows a spin glass like behaviour along with a ferromagnetic nature. We have designated this magnetic state as a glassy ferromagnetic state. The observed phenomena have been explained through the phase separation scenario in manganites. The reduction of grain size is found to enhance the history dependence in transport properties but destabilizes the glassy behaviour. This work clearly reveals the strong influence of doping as well as size reduction on manganite material.

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