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Selective substitution in orbital domains of a low doped manganite: an investigation from Griffiths phenomenon and modification of glassy features

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Abstract
An effort is made to study the contrast in magnetic behavior resulting from minimal disorder introduced by substitution of 2.5% Ga or Al in Mn site of $La_{0.9}Sr_{0.1}MnO_3$. It is considered that Ga or Al selectively create disorder within the orbital domains or on its walls, causing enhancement of Griffiths phase (GP) singularity for the former and disappearance of it in the latter case. It is shown that Ga replaces Mn^{3+}, which is considered to be concentrated within the domains, whereas Al replaces Mn^{4+}, which is segregated on the hole-rich walls, without causing any significant effect on structure or ferromagnetic transition temperatures. Thus, it is presumed that the effect of disorder created by Ga extends across the bulk of the domain having correlation over a similar length scale, resulting in enhancement of the GP phenomenon. In contrast, the effect of disorder created by Al remains restricted to the walls, resulting in the modification of the dynamics arising from the domain walls and suppresses the GP. Moreover, contrasting features are observed in the low temperature region of the compounds; a re-entrant spin-glass-like behavior is observed in the Ga-doped sample, while the observed characteristics for the Al-doped sample are ascribed only to modified domain wall dynamics with the absence of any glassy phase. Distinctive features in third-order susceptibility measurements reveal that the magnetic ground state of the entire series comprises of orbital domain states. These observations bring out the role of the nature of disorder on the GP phenomenon and also reconfirms the character of self-organization in low doped manganites.

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

1. Introduction

The self-organized regimes of low doped manganites form one of the interesting areas to study the correlated behavior of spin, charge and orbitals [1]. Another appealing issue in condensed matter is the emerging similarities in the nature of self-organized structures in different transition metal oxides. Current investigation from NMR, neutron scattering and Raman spectroscopy have revealed an orbital ordered state comprising of ferromagnetic (FM) insulating domains separated by ferromagnetic metallic walls in a single crystal of $La_{0.8}Sr_{0.2}MnO_3$ [2] and $LaMnO_{3+\delta}$ [3]. Distinctive signatures

of such self-organized regimes, in the form of orbital domain (OD) states having hole-rich (metallic) walls separating the hole-deficient (insulating) regions, is also reflected in the bulk magnetic measurements of $La_{0.9}Sr_{0.1}MnO_3$ [4]. A similar type of phase separation in the form of stripes where the holes are collected in domain walls separating antiferromagnetic antiphase domains is observed in microscopic studies on cuprates [5]. Studies on nickelates have also revealed an ordering consisting of charged domain walls that form antiphase boundaries between antiferromagnetic domains due to microscopic segregation of doped holes [6]. One significant point in all these cases is that the nature of this

regime is different from the conventional FM domain which arises purely due to minimization of magnetostatic energy. Another important observation is that these self-organized arrangements seem to be destroyed at higher doping levels, as is observed in cuprates where the macroscopic phase separation between superconducting and non-superconducting phase vanishes with increase in doping [7]. Similarly, the OD state in $La_{0.9}Sr_{0.1}MnO_3$ is destroyed with the increase in self-doping. However, it changes the crystallographic structure as well [4]. Hence it would be interesting to probe the modification in the OD state by suitable quenched disorder within the same crystallographic structure.

An effective way to introduce disorder into manganite is through the Mn-site substitution. Earlier studies on various Mn-site substitutions have revealed that the induced physical properties depend both on the electronic configuration of the dopants as well as on the change in structure arising from ionic size mismatch [8]. Hence, incorporation of simple disorder without adding magnetic interactions and lattice distortion is a non-trivial task because of complexities in manganites. Moreover, another manifestation of disorder is the recent observation of Griffiths phase (GP)-like singularities [9–12]. Such GP regimes are defined in between the completely disordered high temperature paramagnetic (PM) region and the long range magnetic ordering temperature. The new temperature scale is called the 'Griffiths temperature' (T_G), where a clean system would have its transition in the absence of disorder [13]. Significantly, theoretical studies have shown the importance of correlated disorder in generating and enhancing the GP-like singularity [14, 15], particularly around low doping [16].

The OD of $La_{0.9}Sr_{0.1}MnO_3$ is supposed to be made of Mn^{3+}-rich domains separated by Mn^{4+}-rich walls. In this study, the Mn-site substitutions are selected in such a way that they will replace either of the Mn ions without changing the structure. Substitution of Al or Ga at the Mn site is expected to replace Mn^{4+} or Mn^{3+}, respectively, because of the matching of ionic radii [17]. Furthermore, for both these cases the resultant spin and orbital moment is zero, stressing the fact that no additional interaction in terms of spin–orbit coupling arises due to these substitutions. Though reports indicate that non-magnetic substitutions give rise to the same effect in the resulting compounds [8], we observe contrasting magnetic behavior in Al-or Ga-substituted (2.5% each) $La_{0.9}Sr_{0.1}MnO_3$ without change in structure. In the parent compound the GP phenomenon is observed and this feature is not unusual as it has also been detected in the corresponding single crystal [12]. Here we show that Ga substitution enhances the GP singularity, whereas it disappears in the Al-substituted sample. This is intriguing since these substitutions have an insignificant effect on the PM to FM transition temperature (T_C). This difference is attributed to the nature of the disorder created by Ga and Al substitutions. It will be argued that the disorder created by substitution of Ga has correlation within the Mn^{3+}-rich domains since it predominantly replaces Mn^{3+}. In contrast, correlation of the disorder does not extend to the bulk when Al is substituted since it selectively replaces Mn^{4+} in the hole-rich domain walls. Moreover,

Table 1. Structural and fitting parameters determined from Rietveld profile refinement of powder XRD pattern for the sample series. S is the goodness of fit. The percentage of Mn ions was determined by redox iodometric titration.

Samples	Parent	2.5% Al	2.5% Ga
a (Å)	5.5352(2)	5.5360(2)	5.5378(2)
b (Å)	5.5166(2)	5.5146(2)	5.5215(2)
c (Å)	7.7924(2)	7.7930(3)	7.7904(3)
V (Å)	237.94	237.91	238.21
S	1.25	1.27	1.19
Mn^{4+} (%)	11.3	9.6	10.7
Mn^{3+} (%)	88.7	87.9	86.8

the low temperature region of the Ga-substituted compound show re-entrant spin-glass-like features. In contrast, glassy characteristics are absent in the low temperature state of the Al-substituted compound. These contrasting magnetic states at low temperature in the substituted compounds also arise due to the selective substitution at the domains and at their walls. All these results also point to the intrinsic nature of the OD state where hole-rich walls separates the hole-poor regions and disorder can be selectively created by proper substitution.

2. Sample preparation and characterization

The $La_{0.9}Sr_{0.1}MnO_3$ sample (parent) is the same as used in [4]. The doped samples $La_{0.9}Sr_{0.1}Mn_{0.975}Ga_{0.025}O_3$ (2.5% Ga) and $La_{0.9}Sr_{0.1}Mn_{0.975}Al_{0.025}O_3$ (2.5% Al) are prepared under similar conditions. X-ray diffraction studies on the samples indicates that the entire series is crystallographically single phase and the pattern collected is analyzed by the Rietveld profile refinement [18]. Estimation of Mn^{3+}/Mn^{4+} is done by iodometric redox titration using sodium thiosulfate and potassium iodide. Homemade set-ups are used to measure ac susceptibility [19] and dc magnetization [20], along with a commercial 14 T vibrating sample magnetometer (VSM) from Quantum Design.

All the samples crystallize in orthorhombic structure (*Pbnm*). Table 1 summarizes the relevant structural parameters obtained by fitting the powder XRD data by Rietveld refinement which shows the changes in the lattice parameters a, b and c are, respectively, less than 0.04%, 0.08% and 0.02%. This illustrates that Al and Ga substitutions introduce insignificant changes in the structure. The percentage of Mn^{3+} and Mn^{4+} found from iodometry shows a preferential replacement of Mn^{4+} with Al^{3+} and Mn^{3+} with Ga^{3+}. Such preferential replacement of Mn^{4+} and Mn^{3+} by Al^{3+} and Ga^{3+}, especially around the lower percentage of Mn-site substitution has also been observed in other sample series like $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ [17] and $Pr_{0.5}Sr_{0.5}Mn_{1-x}Ga_xO_3$ [21].

3. Results and discussions

3.1. Distinctive magnetic features arising out of selective substitution at domains and walls by Ga and Al

Figure 1 shows the temperature dependence of the real part of ac susceptibility (χ_1^R). All samples undergo a paramagnetic to
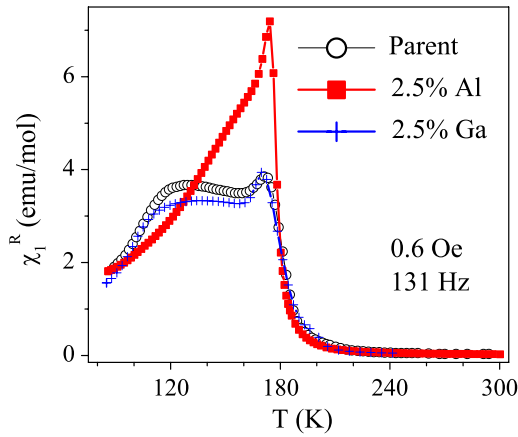
Figure 1. Temperature dependence of the real part of first-order ac susceptibility (χ_1^R) of the parent, 2.5% Al and 2.5% Ga compounds.

Figure 2. Thermal hysteresis (TH) of the imaginary part of first-order ac χ (χ_1^I) for 2.5% Al sample in 1 Oe ac field of 131 Hz. Inset shows the TH in χ_1^I in the same measurement condition for 2.5% Ga sample. The arrows point to the PM–FM transition temperature ($T_C \approx 178$ K) and the temperature of a peak above T_C, around 196 K.

ferromagnetic transition, around the same temperature, which is characterized by a sharp change in susceptibility near the T_C. The parent and the Ga-doped sample show another fall in χ_1^R at low temperature, which is absent for the Al-doped sample where a very sharp monotonic decrease is observed in χ_1^R below T_C. This shows the distinct behavior of the series having minimal non-magnetic disorder and similar structural parameters. Even though the nature of the χ_1^R curve of both the parent and the 2.5% Ga sample is qualitatively similar, the nature of the low temperature magnetic states is different. While the low temperature magnetic state of the parent shows glassy behavior arising from orbital domains, 2.5% Ga shows a re-entrant spin-glass-like behavior. In contrast, the 2.5% Al compound shows the absence of any glassy features in the low temperature region. The details of the low temperature behavior of the substituted compounds will be described in the later part of the paper. For the parent compound the self-organized regimes are of the form of orbital domains [4]. Generally for a phase-segregated hole-rich/poor system it is anticipated that the doped holes have to be concentrated at the walls [2] and hence for our case it is expected that Mn^{4+} has to be concentrated at the walls. To emphasize the fact that the wall dynamics is modified or suppressed by Al substitution, thermal hysteresis (TH) of ac susceptibility is measured for the Al- and Ga-substituted samples. Figure 2 shows the imaginary part of ac susceptibility (χ_1^I), as it is more sensitive to the domain wall dynamics compared to χ_1^R, which is dominated by the volume response of the domain. Such a measurement has also been previously used to probe the change in susceptibility behavior due to modification in the density of spins/holes at the domain walls [22]. The PM to FM transition is second order in nature, hence a TH immediately below T_C is ascribed to thermally irreversible domain wall dynamics due to low field irreversible domain wall pinning in the sample [4]. From the inset of figure 2, it is observed that a TH is present in χ_1^I for the Ga-doped sample below T_C (similar to that observed for the parent compound), while such a feature is absent for the Al-doped one. This indicates that in the latter compound the pinning potential of the walls disperses, leading to a reversible behavior in the thermal cycle. This highlights the fact that
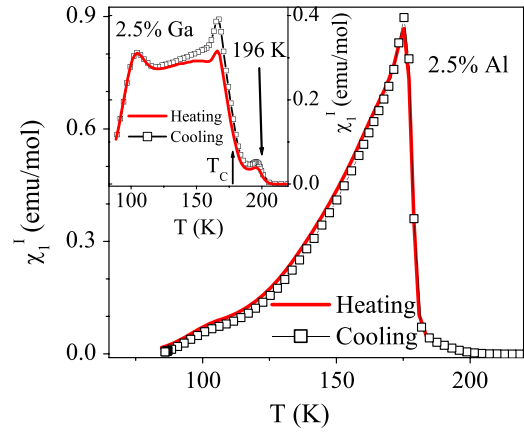
the wall dynamics is being modified by Al substitution. For the 2.5% Ga compound, the dynamics of the walls is similar to the parent as Ga preferentially replaces the Mn^{3+} of the domains. Hence, the above measurements clearly bring out the differences in the intrinsic nature of the magnetic state between the Al- and Ga-substituted samples, which arise from selective substitution of the domain walls and domains, respectively.

3.2. Enhancement and suppression of Griffiths phenomenon by Ga and Al substitution: role of correlation in disorder

An important and interesting feature observed in the inset of figure 2 is the presence of a peak around 196 K for the 2.5% Ga compound. Such a feature above T_C is absent for the 2.5% Al sample. Henceforth, we will concentrate on the observed contrasting feature above T_C for the two substitutions. Recent studies by De Teresa *et al* [23] have shown the presence of FM clusters in the PM phase. In the 2.5% Ga compound, the occurrence of the peak around 196 K suggests the presence of clusters above T_C. This peak remains unchanged with frequency of ac field (figure 5). However, the nature of the peak changes with the variation of amplitude of the ac field (H_{ac}), as is observed from the field dependence of χ_1^I (figure 3(a)). The peak in χ_1^I is associated with the magnetic losses and, in this case, the observed variation with H_{ac} can be ascribed to the variation of cluster size. The signature of the presence of these clusters is also observed when third-order susceptibility (χ_3^R) is probed, which also shows a peak around 196 K (inset figure 3(a)). To rule out a superparamagnetic (SPM) nature of these clusters, field dependence of this peak in χ_3^R is noted. This peak is seen to diverge with the decreasing amplitude of H_{ac} whereas in an SPM it does not diverge as $H_{ac} \rightarrow 0$ [24, 22]. Hence, this characteristic along with the absence in any shift in the temperature of this peak with frequency rules out the conventional SPM behavior of the clusters. Another interesting feature of this compound is observed when the real part of second-order
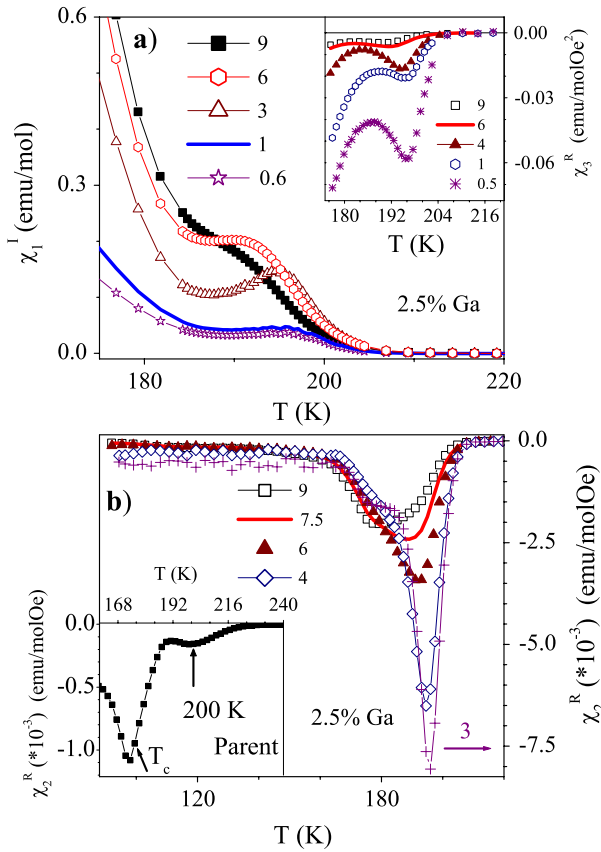
Figure 3. (a) Temperature dependence of imaginary part of first-order ac χ (χ_1^I) of 2.5% Ga compound in different ac fields of 131 Hz. The inset shows temperature dependence of real part of third-order ac χ (χ_3^R) for the same sample in different ac fields of 131 Hz. (b) Temperature dependence of the real part of second-order ac χ (χ_2^R) of 2.5% Ga sample in different ac fields of 131 Hz. The units of the field values in all the above cases are Oersteds. The inset shows temperature dependence of the χ_2^R of parent compound at 9 Oe ac field of 131 Hz. The arrows point to the transition temperature ($T_C \approx 179$ K) and the temperature of the hump above T_C, around 200 K.
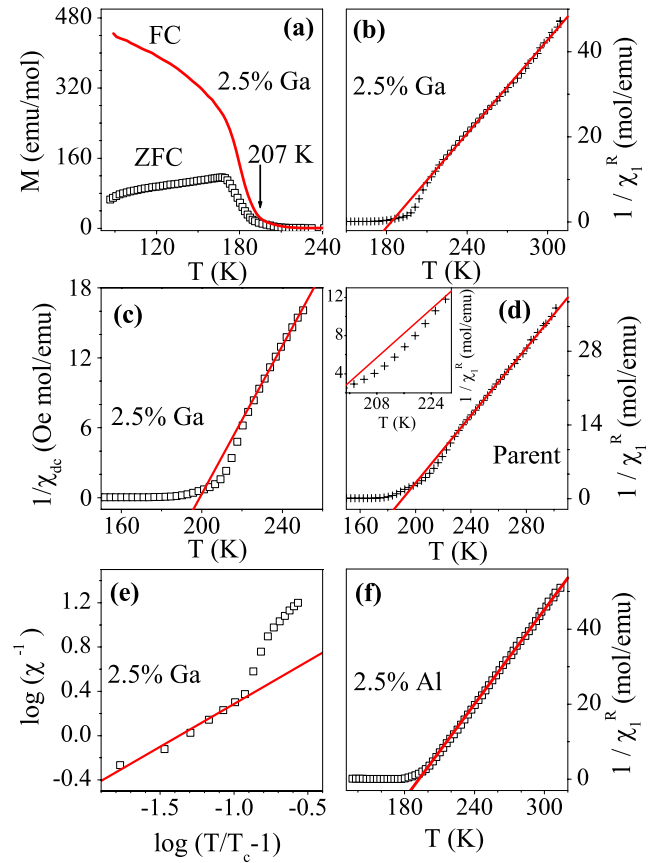
Figure 4. (a) Zero-field-cooled (ZFC) and field-cooled (FC) dc magnetization at 9 Oe for the 2.5% Ga sample. The arrow points to the bifurcation temperature, around 207 K, between ZFC and FC curves. (b) Temperature dependence of the inverse of the real part of first-order ac χ (χ_1^R) at 9 Oe ac field for 2.5% Ga sample. (c) Temperature dependence of the inverse dc susceptibility at 9 Oe dc field for 2.5% Ga sample. (d) Temperature dependence of the inverse of χ_1^R at 9 Oe ac field for the parent compound. The inset shows the magnified view around the inflection. (e) Log–log plot of the inverse of χ_1^R as a function of reduced temperature yielding susceptibility exponent $\lambda = 0.23$ for 2.5% Ga sample in 1 Oe ac field. (f) Temperature dependence of the inverse of χ_1^R at 9 Oe ac field for the 2.5% Al-doped sample. Solid lines in (b), (c), (d) and (f) are Curie–Weiss fits to the high-T behavior.

susceptibility (χ_2^R) is probed. Figure 3(b) shows the field dependence of the temperature response of χ_2^R, which shows a peak corresponding to a peak temperature of 196 K found in χ_1^I and χ_3^R. Even-order susceptibilities arise in systems in which the inversion symmetry of magnetization (M) with respect to the applied field is lost, i.e. $M(H) \neq -M(-H)$. The signature of the peak in χ_2^R above T_C ($\approx$178 K) of this sample clearly indicates the presence of clusters with short range ordering in the PM region. The local anisotropy within these clusters aligns the moments in a particular direction which give rise to the symmetry breaking field required for the experimental observation of χ_2^R. Hence the features in figure 3(b) strongly suggest that the nature of these clusters is FM-type. The peak broadens at higher fields which arises due to the existence of a diluted system of FM clusters, resulting in diffuse ordering above T_C. Such diffuse ordering is also present in the parent compound indicated by a broad hump in χ_2^R around 200 K, much above its T_C ($\approx$179 K) where a sharp peak in χ_2^R is observed (inset of figure 3(b)). Other

evidence of the presence of clusters above T_C comes from the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of the sample (figure 4(a)). It is observed that the bifurcation between the curves starts much above T_C, i.e. from 207 K whereas, in a typical ferromagnet, this bifurcation starts from T_C. This feature also demonstrates the presence of FM clusters in the PM phase which results in the bifurcation temperature being higher than T_C. Nevertheless, the presence of clusters above T_C is not the sufficient condition for GP. It may be noted that a non-GP-like clustered state above T_C has been observed in La$_{1-x}$Sr$_x$CoO$_3$ [25]. The fundamental feature which is typical for the GP is the observation of a downward deviation in inverse susceptibility (χ^{-1}) from the Curie–Weiss (CW) law [10, 11, 13, 26, 27]. Hence, to give a credible explanation for the fact that the clustered state in our system has the characteristic of a GP, inverse χ_1^R is plotted as a function of temperature (figure 4(b)). As
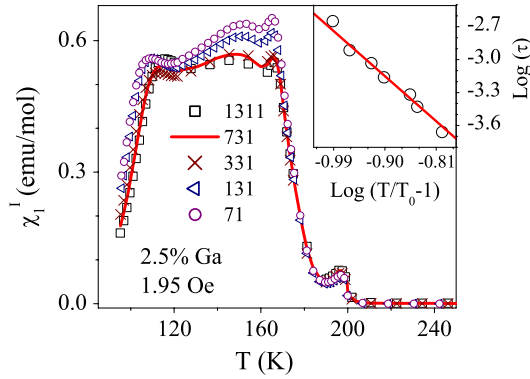
Figure 5. Temperature dependence of imaginary part of ac χ (χ_1^I) of 2.5% Ga sample at different frequencies. The units of frequencies are in hertz. Inset: dynamical scaling fit of relaxation time with reduced temperature.

expected, the curve shows a negative deviation from the CW law pointing to the fact that GP-like features are observed in the 2.5% Ga compound. The deviation starts from 208 K, which is also near to the bifurcation temperature (T) of ZFC and FC curves. In the typical PM regime ($T > 208$ K), the effective PM moment is $4.68\mu_B$, which agrees with the theoretical value and is also independent of the applied field value. Hence, the observed singularity in inverse χ_1^R below 208 K occurs due to the presence of FM clusters in the PM phase. It leads to an enhanced susceptibility compared to the normal PM susceptibility, resulting in the downward deviation in the temperature response of inverse susceptibility. Similar behavior is observed from the inverse dc magnetization data which is qualitatively identical to ac susceptibility data showing a downward deviation from CW behavior (figure 4(c)).

This feature in the Ga-substituted sample is not unusual since a GP-like feature is recently observed in the single crystal of the parent composition ($La_{0.9}Sr_{0.1}MnO_3$) by microscopic probes [12]. Moreover, the observation of a broad hump in χ_2^R around 200 K (inset of figure 3(b)) and a downward deviation from the CW law observed in the $1/\chi_1^R$ versus T plot (figure 4(d)) confirms the presence of GP-like features in the parent compound of the present series. Hence it can be said that addition of Ga enhances the disorder in the parent compound resulting in a more prominent deviation in the $1/\chi_1^R$ versus T behavior. This fact is substantiated from the value of the susceptibility exponent λ deduced from the power law [10] of the form $\chi^{-1} \propto (T/T_C - 1)^{1-\lambda}$, where $0 \leqslant \lambda < 1$ for GP. It is found that for the 2.5%Ga-doped compound, $\lambda = 0.23$ (figure 4(e)), while for the parent compound $\lambda = 0.17$ (not shown), clearly indicating that the Griffiths singularity is enhanced with Ga substitution. The values of λ are similar to those observed in a single crystal of $La_{0.7}Ba_{0.3}MnO_3$, indicating a weak singularity [27]. However, for the Al-substituted sample GP-like features are absent and it follows the CW law above T_C (figure 4(f)).

Hence the observed distinct behavior between Ga- and Al-substituted samples highlights the fact that the presence of correlated disorder is the cause of the observed Griffiths

phenomenon. Correlated disorder implies that, when disorder is introduced, its effect is distributed in the bulk of the system. The Mn^{3+} ions, which constitute a significant percentage of the domains, are favorably replaced by Ga, resulting in the effect of disorder being extended to larger length scales, into the bulk. Hence correlated disorder in the form of Ga results in an enrichment of the GP phenomenon in the 2.5% Ga compound. However, this correlation in the effect of disorder is suppressed by preferential replacement of Mn^{4+} by Al, which is in the majority at the walls. Such disorder simply modifies the wall and its dynamics. Consequently, no GP phenomenon is observed and we get a clean $1/\chi_1^R$ versus T behavior in the 2.5% Al compound.

3.3. Re-entrant spin-glass-like behavior with Ga and disappearance of the glassy features with Al substitution

In this section we concentrate on the low temperature phase of the substituted compounds. Even though some glassy dynamics were observed in the OD state of the parent compound, the behavior is not associated with conventional spin/cluster glasses or to any re-entrant systems. It is well known that the increase of disorder in FM or antiferromagnetic ground states can give rise to frustration, leading to the special behavior of spin-glass (SG)-like dynamics in the system [28]. Such features are observed when Ga is introduced into the system where the temperature of the peak appearing at low temperature in the imaginary part of the first-order ac χ (χ_1^I) is frequency-dependent and the peak around T_C does not shift with frequency (figure 5). The lower temperature peak is shifted downward in temperature with the decrease in frequency, which is a characteristic feature of SG dynamics arising from progressive freezing of spins. The shift of peak temperature with frequency is fitted to a power law (which follows from dynamic scaling theory) which is of the form

$$\tau = \tau^0 (T/T_0 - 1)^{-z\nu}$$

where τ^0 is the microscopic flipping time, T_0 is the characteristic temperature of SG freezing, ν is the critical exponent which describe the growth of spin correlation length and z is the dynamic exponent which describe the slowing down of relaxation (inset of figure 5). The fit yielded $z\nu = 5.04 \pm 0.35$, $\tau^0 = 2.5 \times 10^{-8}$ and $T_0 = 99$ K. The values of $z\nu$ and τ^0 do not match with those reported for SG (generally $z\nu$ lying between 7 and 10 and τ^0 of the order of 10^{-10}–10^{-13} for canonical SG) [29]. Thus it is observed that substitution of Ga in the compound introduces some characteristic features, as observed for SG dynamics, but it cannot be associated with any canonical SG systems.

To provide further evidence about the presence of the glassy phase, a memory effect similar to [4] is studied. The experiment is carried out in 4 Oe magnetic field with temporary stops (with the magnetic field switched off) at 110 and 95 K for a waiting time of 7200 s. As observed from figure 6, a decay in magnetization (ageing effect) is noted at the waiting temperatures in the cooling cycle, with the effect being significant at 110 K. During the warming cycle a distinct step-like feature is seen around 110 K, indicating that the system
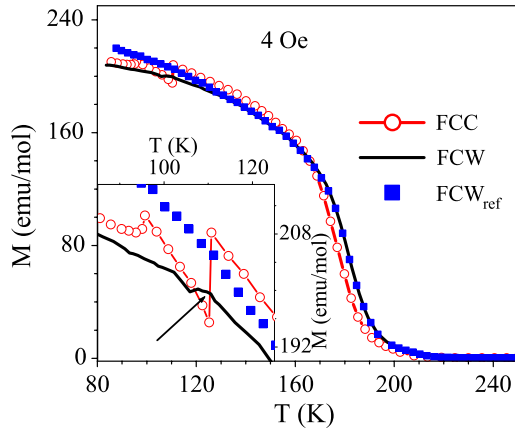
Figure 6. M–T curves during field cooling of 2.5% Ga sample. The field is switched off at two temperatures (110 and 95 K) for a waiting time of 7200 s (FCC). The M–T curve in warming mode (FCW) and normal FCW curve as FCW_{ref} are also shown. Inset shows the above graphs up to 125 K presenting an expanded view of the memory effect. The arrow points to a step-like feature observed in the warming cycle (FCW).

remembers its thermal history or the magnetic state reached by the system during the cooling cycle. Such memory effects are widely accepted as a signature of the freezing of spins [30]. Moreover, in our system it is expected that long range FM ordering will be present along with the freezing of spins at low temperature. Such a mixed phase is characteristic of a re-entrant spin glass (RSG) [31].

Hence to probe the nature of this glassy phase, the temperature response of χ_2^R is noted (figure 7(a)). This figure shows a peak around the PM to FM transition and a hump at lower temperatures. The presence of a significant χ_2^R signal in the low temperature region, even in the absence of a dc field supports the presence of a symmetry breaking field which is an essential feature for the FM ordering. It is to be noted that, for a canonical SG, χ_2^R is absent. Hence this measurement clearly indicates the presence of a mixed phase in the sample where FM ordering coexists with SG freezing. Therefore it can be said that the sample enters an FM phase from a random PM phase and on further lowering of temperature it once again re-enters into a new random phase where FM and SG ordering coexist, i.e. an RSG phase. Further, to give decisive proof about the presence of FM ordering in the low temperature region, Arrott's plot is done on the sample (figure 7(b)). Extrapolation of the high field data to H = 0 gives the non-zero values of spontaneous magnetization. The curves in the temperature range 85–105 K clearly show the presence of spontaneous magnetization which highlights the presence of FM ordering in the low temperature region of the compound.

The conclusive evidence about the RSG phase comes from the behavior of χ_3. This nonlinear ac χ is used as a probing tool as it is more sensitive to the subtle features which may remain undetected in the temperature response of the real part of the first-order ac χ. The real part of the third-order ac χ (χ_3^R) is usually employed to investigate and differentiate various metamagnetic states exhibited by different compounds [22, 24]. Figure 8 shows the field dependence of
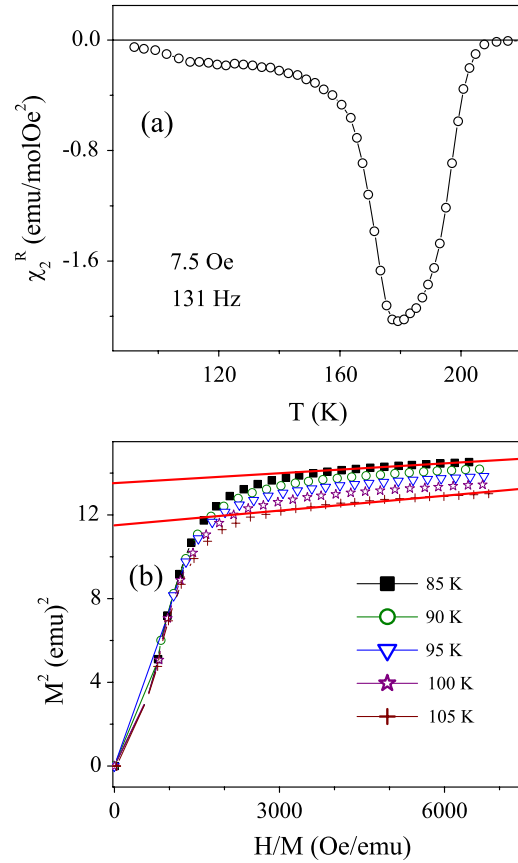

Figure 7. (a) Temperature dependence of real part of second-order susceptibility (χ_2^R) of 2.5% Ga sample. (b) Arrott's plot in the temperature range 85–105 K for the same. Solid lines are a linear fit to the M^2 versus H/M curve, indicating the presence of spontaneous magnetization.

χ_3^R which shows a peak corresponding to the characteristic temperature of SG freezing (T_0) at 9 Oe. As the amplitude of the ac field (H_{ac}) is decreased the peak is rounded up, unlike in typical SG, where the peak shows a negative divergence [24]. Such typical signatures of a non-divergent peak in χ_3^R are not uncommon and have also been observed in other re-entrant systems [31, 32]. Such contrasting behavior at the freezing temperature in the SG and RSG cases arises due to the fact that the transition is approached directly from the PM phase in the former while it is from the FM phase in the latter case. Hence the criticality observed in SG is not observed for RSG due to the existence of FM ordering.

However in the 2.5% Al sample, frequency dependence in χ_1^I observed below T_C vanishes in the low temperature region. Moreover no additional peak is observed at low temperature (figure 9), contrary to that observed in the 2.5% Ga compound. These features clearly rule out the presence of glassy features in the low temperature region of this compound. Hence the observation of this section also re-emphasizes the conclusion drawn in the previous sections which highlights the fact that, even though impurities are of a non-magnetic nature, the disorder effect arising out of these substituents is different. Ga preferentially replacing Mn^{3+} of the domains enhances both disorder and frustration in the compound which lead to an
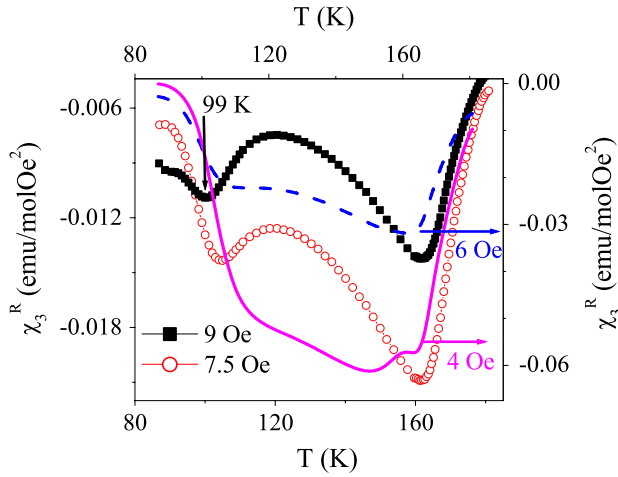
Figure 8. Temperature dependence of real part of third-order susceptibility (χ_3^R) of 2.5% Ga sample at different ac fields of 131 Hz. The black arrow points to the peak corresponding to characteristic temperature of SG freezing.
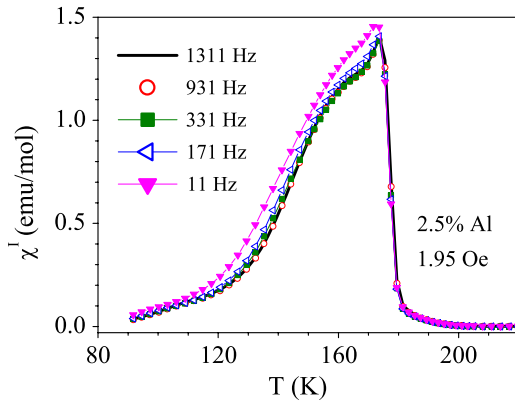

Figure 9. Temperature dependence of imaginary part of ac χ (χ_1^I) of 2.5% Al sample at different frequencies. The frequency dependence collapses in the low temperature region.

Figure 10. Temperature dependence of real part of third-order of ac χ (χ_3^R) at different frequencies for the (a) parent, (b) 2.5% Ga and (c) 2.5% Al compounds. All of them show crossover of χ_3^R in higher frequencies.

RSG-like behavior. On the other hand, Al favorably replacing the Mn^{4+} of the Mn^{4+}-rich walls introduces uncorrelated disorder, resulting in the suppression of glassy dynamics.

3.4. Similar frequency dependence in χ_3^R at low temperature: persistence of orbital domains

Finally an important feature is observed when the temperature response of χ_3^R of the entire series is studied (figure 10). It is observed that χ_3^R changes its sign from negative to positive at higher frequencies in the low temperature region of the compound. The changeover in χ_3^R is generally observed around T_C [33] and it arises due to the breaking of spatial magnetic symmetry. Additionally, the frequency-dependent crossover of χ_3^R implies that this behavior is also dependent upon intra- and inter-cluster effects [34]. Such a nonlinear magnetic response where the intra- and inter-cluster effects are separated has also been reported for other systems [35]. Generally the magnetization of each cluster will fluctuate and change direction with respect to each other in a certain
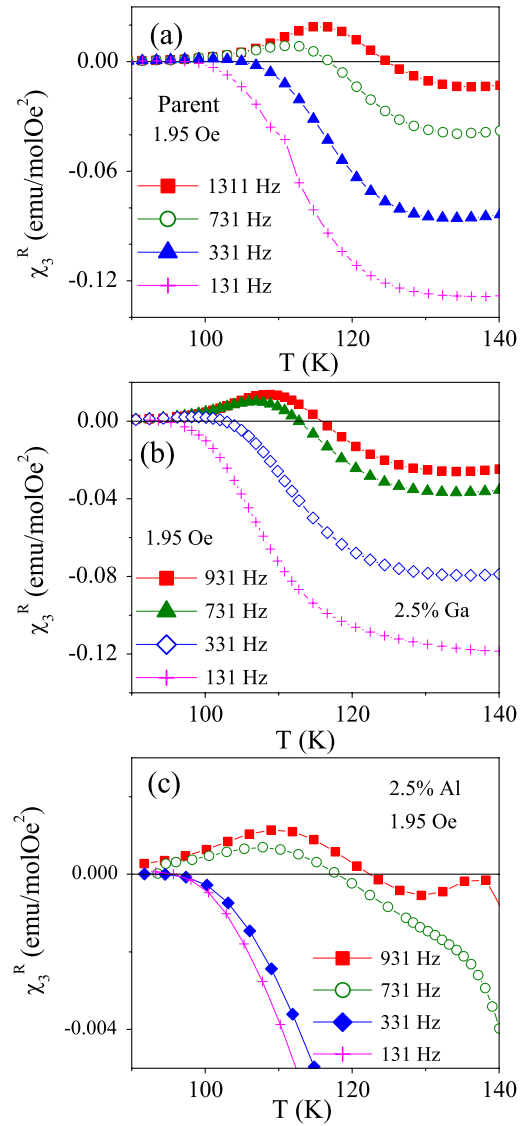
timescale, which is larger than the intra-cluster fluctuation. So, at higher frequencies where the probe time is less, the inter-cluster fluctuation cannot follow the excitation field and the temperature response of χ_3^R reflects the fluctuation inside each individual cluster.

In the parent compound, the presence of a low temperature structural transition [36] introduces an additional degree of freedom (orbital) owing to the change in occupancy of the orbitals by an e_g electron, which arises due to the change of lattice constant. This leads to the reformation of domains which results in a change in spin arrangement within the clusters. The intra-cluster ordering, which is formed below T_C, is affected by orbital ordering, resulting in a change of spatial magnetic symmetry leading to the frequency-dependent crossover of χ_3^R (figure 10(a)). This typical frequency-dependent crossover in χ_3^R is also observed in the substituted samples (figures 10(b) and (c)). Hence this measurement

clearly demonstrates that the intrinsic magnetic configuration of the substituted samples is of the form of orbital domains in analogy to the orbital domain state of the parent compound. Hence it can be said that in all these compounds at low temperature the intra-cluster ordering is similar. The observed contrasting magnetic features arise due to a difference in inter-cluster interactions which give rise to glassy FM behavior in the parent compound, RSG-like features in the 2.5% Ga compound and the absence of glassy characteristics in the 2.5% Al compound.

4. Conclusion

In summary, we show that it is possible to selectively introduce disorder either within the domains or at the walls of the orbital domain state in a low doped manganite ($La_{0.9}Sr_{0.1}MnO_3$), without introducing any significant change in the structure. Preferential replacement of Mn^{3+} ions by Ga introduces disorder within the Mn^{3+}-rich domains, having its effect extending over the dimension of the domain and is considered to be correlated on a similar length scale. This correlated disorder enhances the GP singularity, whereas the effect of disorder created by preferential replacement of Mn^{4+} by Al at the hole-rich domain wall is rather restricted. The correlation of such disorder remains confined to the walls; it only modifies the wall dynamics of the system and suppresses the singularity related to GP. In the low temperature region of the 2.5% Ga compound, RSG-like features are observed while glassy characteristics are absent in the 2.5% Al compound. χ_3^R measurements are done to highlight the fact that the magnetic state of the entire series is of the form of orbital domains.

These results are significant since it becomes possible from bulk magnetic measurement to reinforce the nature of self-organization in the low doped manganite and confirm that the hole-deficient domains (Mn^{3+}-rich) are separated by hole-affluent walls (Mn^{4+}-rich). It also shows the possibility to selectively create disorder in the self-organized structures in different systems. Moreover, this study may stimulate investigation of the relation between the nature of disorder and the GP in different systems.

Acknowledgments

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