Magnetic properties of the self-doped lanthanum manganites $La_{1-x}MnO_3$

C. Raj Sankar and P. A. Joy*
Physical and Materials Chemistry Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India
(Received 3 February 2005; revised manuscript received 21 April 2005; published 1 July 2005)

The magnetic properties of different compositions in the self-doped lanthanum manganites, $La_{1-x}MnO_3$, have been studied by ac susceptibility and dc magnetization measurements in the temperature range 10–300 K. All compositions with $x<0.125$ show an anomalous decrease in the ac susceptibility and zero field cooled (ZFC) dc magnetization at low temperatures, below the ferromagnetic ordering temperature. The temperature below which this anomalous behavior is observed, T_a, varies with the degree of La vacancy in the series where the Mn^{4+} concentration decreases with increasing x. Moreover, T_a varies with the Mn^{4+} content for a given composition. However, in both cases, this temperature levels off when the concentration of Mn^{4+} is above 23%. The magnetic-transition-like feature broadens and shifts to further lower temperatures with increasing magnetic fields and vanishes when measured above a certain field. A small but drastic increase in the coercivity is observed below T_a. There is a direct correlation between the shapes of the curves of the inverse of the coercivity as a function of temperature and ac susceptibility, indicating the influence of magnetic anisotropy on the characteristics of the ac susceptibility and zero field cooled magnetization curves of the self-doped compounds. The direct correlation between the changes in the coercivity and ac susceptibility as well as ZFC magnetization when measured at low magnetic fields give evidence to the role of domain wall pinning effects, which varies with the degree of self-doping or Mn^{4+} concentration.

DOI: 10.1103/PhysRevB.72.024405 PACS number(s): 75.30.−m, 75.50.−y, 75.60.−d

I. INTRODUCTION

The self-doped perovskite manganite compositions $La_{1-x}MnO_3$ exhibit magnetic and electrical properties very similar to that of the divalent cation doped colossal magnetoresistive (CMR) manganites.[1,2] These similarities in the properties are attributable to the Zener-type of double-exchange[3] interactions between the Mn^{3+} and the Mn^{4+} ions through the intervening oxygen anions that are present in the crystal lattice of both the systems. Jahn-Teller distortion and electron-phonon interactions also play important roles in determining the properties of these mixed valent oxides.[4] Thus, perovskite manganites generally constitute a system in which orbital, charge, and spin interactions are highly important. Since the amount of Mn^{4+} and the concentration of doping or vacancy are critical factors in determining the structural, magnetic, and conducting properties of these materials, their distribution in the lattice must be an important factor controlling the properties. A systematic study of the variation in the ferromagnetic transition temperature (T_c) of a series of self-doped compositions, $La_{1-x}MnO_3$, was made in the recent past and a maximum value for x was established as 0.125.[5,6]

Some anomalous magnetic behavior at low temperatures is observed in the ferromagnetic regime of the CMR oxides $La_{1-x}A_xMnO_3$ (A=Ca, Sr, Ba), for low concentrations of the substituted ions. This is observed in the form of a decrease in the ac susceptibility or zero field cooled (ZFC) dc magnetization measured using very low magnetic fields, at temperatures much below the paramagnetic to ferromagnetic ordering temperature of the specific compositions.[7–13] This is generally explicated as due to the glassy-spin configuration or spin frustration, the presence of a mixed state of ferromagnetic and antiferromagnetic phases in the sample, the ferromagnetic to antiferromagnetic transition, and is sometimes attributed to the effect of charge ordering. However, sufficient evidence for the existence of long-range magnetic order in such samples has been obtained from the neutron diffraction studies even at temperatures below the magnetic anomaly.[14–16]

Initial studies on the evolution of a low-temperature magnetic anomaly in the self-doped manganite system indicated that the anomaly is observed for $x<1/8$ and the temperature at which the anomaly is observed in the ac susceptibility increases upon decreasing the doping level.[17] Since it was found that the Mn^{4+} concentration also increases upon decreasing the doping level, it was not clear whether the La vacancy or Mn^{4+} concentration is driving the low-temperature behavior. The observations were attributed to nonuniform distribution of the vacancies or Mn^{4+} content, which affects the movement of domain walls in low magnetic fields. In this paper we report detailed studies on the dc magnetization and ac susceptibility measurements on different compositions in the self-doped series, by varying the Mn^{4+} concentration of fixed La-vacancy systems. Different behavior is observed with the changes in the Mn^{4+} concentration when the extent of self-doping is varied.

II. EXPERIMENT

Generally it is very difficult to synthesize $La_{1-x}MnO_3$ compositions with reproducible magnetic properties, as the Mn^{4+} content is highly affected by the atmospheric conditions and other parameters during the synthesis.[18] Therefore, polycrystalline samples of different compositions of $La_{1-x}MnO_3$ in the range $0.031 \leqslant x \leqslant 0.125$ were synthesized in a single batch, by the conventional ceramic method, as reported earlier.[5] The vacancy concentrations x are selected as fractions of whole numbers. La_2O_3 and MnO_2 were mixed

well in the required stoichiometric proportions and heated first at 1273 K for 48 h and then at 1473 K for 48 h with several intermediate grindings. The powders were then pressed into pellets and heated for a further 12 h at 1473 K. The Mn^{4+} content was varied by annealing the selected samples at 1173 K in a flowing oxygen or nitrogen atmosphere. The samples were characterized using a Philips PW 1830 powder x-ray diffractometer. The Mn^{4+} content of the samples was estimated by the iodometric titration method.[5] dc magnetic measurements were done on an EG&G PAR vibrating sample magnetometer in the temperature range 10–300 K. Magnetization as a function of magnetic field (maximum field of 15 kOe) was made at different temperatures after cooling the samples in zero applied field to the required temperature. Zero field cooled and field cooled magnetizations were made in the temperature range 12–300 K. Temperature variation (15–300 K) of the ac susceptibility of the samples was measured at different ac fields and frequencies by the mutual inductance method.

III. RESULTS AND DISCUSSION

Previous studies showed that the limit of self-doping possible in $La_{1-x}MnO_3$ is $x=1/8$.[5,6] Although the Mn^{4+} content is expected to increase upon increasing the amount of self-doping, assuming complete Mn and O stoichiometry, the opposite trend was observed for the compositions processed under identical conditions. Moreover, the Mn^{4+} concentration was found to be larger than the expected values for $x<0.07$ and smaller for higher doping concentrations in $La_{1-x}MnO_3$. Based on the Mn^{4+} concentrations, the actual compositions were identified as Mn deficient ($La_{1-x}Mn_{1-y}O_3$) for $x<0.07$ and oxygen deficient ($La_{1-x}MnO_{3-\delta}$) above this value of x. For small values of x, the Mn deficiency y is larger than the La vacancy x. All the compositions were found to be having the rhombohedral perovskite structure, with the rhombohedral distortion decreasing with the increasing degree of self-doping.[5] Although some of the compositions are Mn deficient and others O deficient, for convenience, the self-doped compositions are denoted as $La_{1-x}MnO_3$, where x is the degree of self-doping.

The ac susceptibility curves for some of the self-doped compositions are shown in Fig. 1. All compositions show a ferromagnetic transition, with the highest T_c of ~240 K for $x=1/8$. The Curie temperature decreases with decreasing amount of self-doping in $La_{1-x}MnO_3$. The variation of the Curie temperature, obtained as the temperature at which a minimum in the temperature dependence of the derivative of the susceptibility $d\chi/dT$ is observed, as a function of x as well as Mn^{4+} concentration is shown in Fig. 2. In both the plots, the T_c variation shows three distinct regions. In the first region, at larger values of x, T_c decreases linearly with x down to $x=0.077$ and then drops drastically. Another linear region is observed between $x=0.05$ and 0.071 and a third region is observed below $x=0.05$. The interesting observation is that the first linear region corresponds to oxygen-deficient compositions, the second to Mn-deficient compositions wherein the Mn vacancy is smaller than La vacancy, and the third region to Mn-deficient compositions wherein the Mn vacancy is larger than the La vacancy.[5]

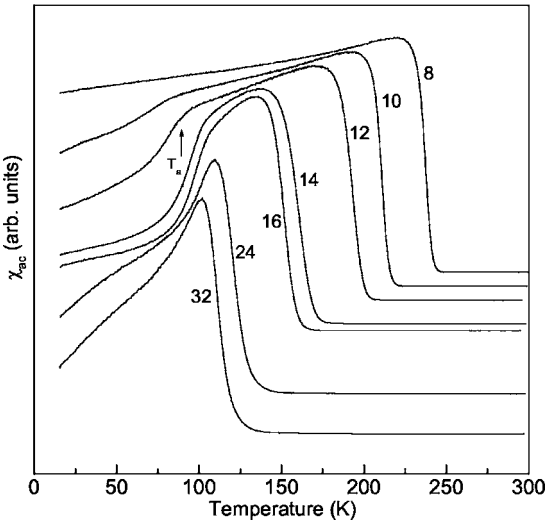

FIG. 1. ac susceptibility (measured at $h=2$ Oe and $f=210$ Hz) curves for different compositions in $La_{1-x}MnO_3$. The numbers indicate $n=1/x$. The curves are shifted along the y axis for clarity.

For $x=0.125$, the susceptibility decreases continuously, down to the lowest temperature, as the temperature is decreased. An interesting feature observed is the appearance of a drop in the susceptibility at low temperatures in the ferromagnetic regime, for compositions with $x<0.125$. The temperature at which the anomalous drop in the susceptibility is observed (T_a), as well as the drop in the susceptibility below T_a, increases with decreasing amount of doping. The variation of T_a as functions of x and Mn^{4+} concentration is shown in Fig. 2. T_a increases almost linearly with decreasing x in the oxygen-deficient compositional region and becomes constant (≈105 K) for Mn-deficient compositions. Another way of looking at the variation is with respect to the Mn^{4+} concentration. T_a remains constant when the Mn^{4+} concentration is more than 23% and decreases with decreasing Mn^{4+} content. Since the compositions for $x<0.07$ are both La and Mn

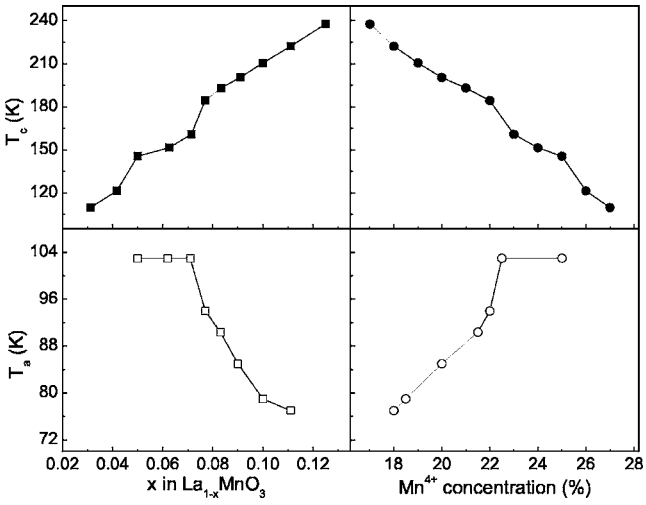

FIG. 2. Variations of T_c and T_a as functions of x in $La_{1-x}MnO_3$ and the Mn^{4+} concentration.

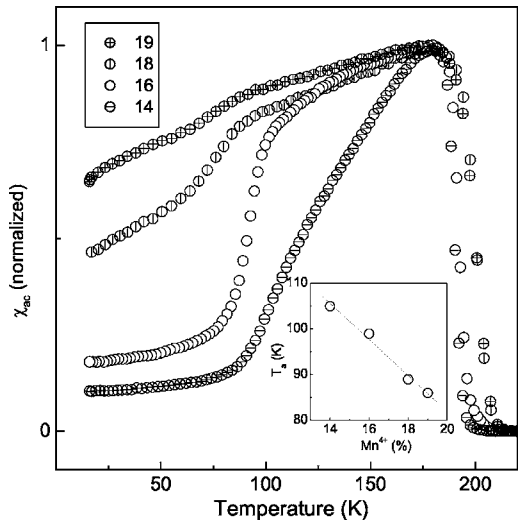

FIG. 3. ac susceptibility curves of $La_{0.909}MnO_3$ for different Mn^{4+} concentrations. The numbers indicate percentage Mn^{4+} concentrations. Inset: T_a as a function of Mn^{4+} concentration.

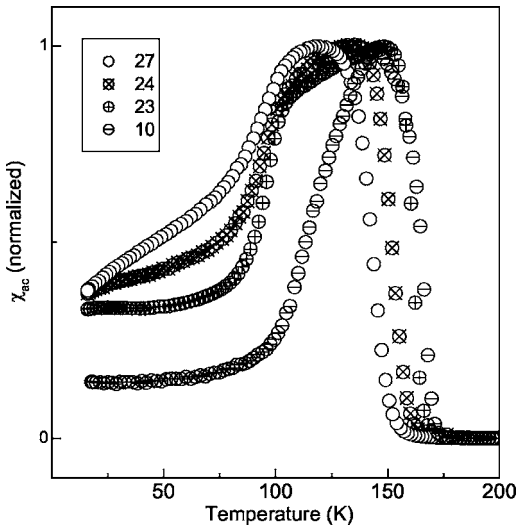

FIG. 4. ac susceptibility curves of $La_{0.937}MnO_3$ for different Mn^{4+} concentrations. The numbers indicate percentage Mn^{4+} concentrations.

deficient, it is not clear whether the factor responsible for the low-temperature decrease in the susceptibility is La deficiency, Mn deficiency, oxygen deficiency, Mn^{4+} concentration, or a combination of all these factors.

However, as shown in Fig. 3, for a given La-vacancy concentration in the oxygen-deficient region of the compositions ($x=0.091$), both T_a as well as the slope of the decrease in the susceptibility below T_a increases with decreasing Mn^{4+} concentration. T_c is found to be slightly decreased with decreasing Mn^{4+} content, from 201 to 190 K, for the decrease in the Mn^{4+} concentration from 19% to 14%. This amounts to a decrease in the oxygen stoichiometry in $La_{0.91}MnO_{3-\delta}$ from 2.96 to 2.93. An interesting observation is that the value of T_a approaches towards the constant value of ~105 K, as observed for higher Mn^{4+} content or for lower vacancy concentrations in the series. Similarly, the shape of the ac susceptibility curve also approaches that of the lower La-vacancy compositions where the susceptibility drops off immediately below T_c and a sharp peak is observed. Such sharp peaks in the ac susceptibility curves are generally observed for compounds with large magnetocrystalline anisotropy.[19] When the magnetic field used for the measurements is much smaller than the anisotropy field, which increases with decreasing temperature, the response of the magnetic moments to the ac field decreases with temperature. Therefore, it may be assumed that there is a corresponding increase in the anisotropy field when the Mn^{4+} concentration is decreased considerably. Troyanchuk *et al.* have observed such an increase in the anisotropy field with decreasing Mn^{4+} concentration for $La_{0.88}MnO_{3-\delta}$.[20] However, similar ac susceptibility behavior is observed for the compositions with larger Mn^{4+} compositions (smaller La vacancies) also in the series (see Fig. 1), making it difficult to arrive at a particular conclusion on the specific role of Mn^{4+} concentration.

On the other hand, for the Mn-deficient compositions, where T_a is in the maximum range, there is no considerable effect on T_a upon decreasing the Mn^{4+} concentration, as shown in Fig. 4 for $La_{0.937}MnO_3$. The samples with Mn^{4+} content of 27%, 24%, and 23% were obtained by repeatedly heating the sample at 1473 K in air, and the one with low Mn^{4+} concentration is obtained after annealing in nitrogen atmosphere. Theoretically, the maximum possible Mn^{4+} content for this value of x in $La_{1-x}MnO_3$ is 18.9%, assuming there are no Mn vacancies. A value larger than this automatically assumes Mn vacancies. The composition $La_{0.937}Mn_{0.984}O_3$ is calculated for 24% Mn^{4+} concentration. Based on this, the composition with 27% Mn^{4+} should have excess oxygen. Since the perovskite structure is a close packed structure with the oxygen sites fully occupied,[21] it will not be possible to accommodate more oxygen in the structure. In addition, if the oxygen stoichiometry is maintained, then increasing the Mn^{4+} concentration implies a decrease in the overall Mn content in the compositions for a given La deficiency, $La_{0.937}Mn_{0.975}O_3$ for 27% Mn^{4+}, which is not feasible. Hence, the only possible way to accommodate excess Mn^{4+} in the otherwise oxygen stoichiometric compositions is to assume that even these compositions are initially oxygen deficient to some extent, so that the actual composition is $La_{1-x}Mn_{1-y}O_{3-\delta}$ for all La-deficient compositions. In this case, it is possible to further decrease or increase the oxygen stoichiometry to accommodate a larger or smaller amount of Mn^{4+}. It is not possible to obtain the values of both y and δ at the same time from the Mn^{4+} content estimations.

For $La_{0.875}MnO_3$, though no drop in the susceptibility is observed at low temperatures (see Fig. 2), based on the above observations it is expected that the anomaly can be induced on decreasing the Mn^{4+} content. Figure 5 shows the ac susceptibility curve of a nitrogen annealed sample with lower Mn^{4+} concentration. A sharp magnetic transition is observed at a lower temperature for the sample with 9% Mn^{4+} content. A decrease in the susceptibility is observed after going through a maximum below T_c. In addition, a slope change with a faster drop in the susceptibility is observed below ~110 K, close to the maximum value of T_a observed

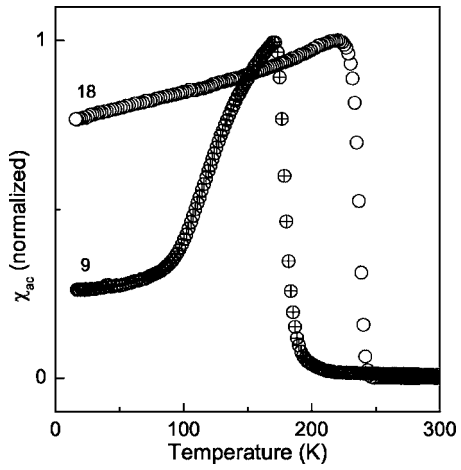

FIG. 5. ac susceptibility curves of $La_{0.875}MnO_3$ for two different Mn^{4+} concentrations. The numbers indicate percentage Mn^{4+} concentrations.

for other compositions. The shape of the curve of the sample with lower Mn^{4+} concentration, at low temperatures, is similar to that observed for the compositions with $x=0.091$ and 0.063 having the Mn^{4+} concentrations close to 13%. Thus, the Mn^{4+} content is found to have serious effects on the magnetic properties of the self-doped manganites in the ferromagnetic region also apart from the effect on the magnetic transition temperatures. However, a large decrease in Mn^{4+} content in such manganites causes structural distortion, which may affect the magnetic characteristics. All the compositions with the lower Mn^{4+} concentrations were found to be orthorhombic, compared to the rhombohedral perovskite structure of the other compositions.

For $La_{0.937}MnO_3$, T_a is already the limiting larger value obtained for the series ($\sim$105 K) and therefore there is no further increase in the value of T_a with decreasing Mn^{4+} content. Although T_a is unchanged on decreasing the Mn^{4+} concentration, larger drop in the susceptibility is observed when Mn^{4+} concentration is decreased. Interestingly, in this case T_c increases with decreasing the Mn^{4+} content, opposite to the trend observed for $La_{0.909}MnO_{3-\delta}$ (see Figs. 3 and 4). This is attributable to the increasing strength of the double-exchange interactions with increasing the concentration of Mn^{3+} or that Mn^{3+}-O-Mn^{3+} ferromagnetic exchange interactions become more predominant when the Mn^{4+} concentration is lower. Assuming that the actual composition is $La_{0.937}Mn_{0.975}O_3$ for 27% Mn^{4+}, the oxygen stoichiometry will be decreased from 3 to 2.98, corresponding to the decrease in the Mn^{4+} concentration from 27% to 23%. When the Mn^{4+} concentration is as low as 10%, the composition becomes more oxygen deficient as $La_{0.937}Mn_{0.975}O_{2.92}$. This is equivalent to the composition having no Mn deficiency as $La_{0.953}MnO_3$ and for this composition, the susceptibility decreases sharply below the T_c, almost similar to that observed for $La_{0.909}MnO_{2.93}$ with 14% Mn^{4+}, as shown in Fig. 3.

The above observations imply that there is no specific trend in the variation of the Curie temperature with Mn^{4+} concentration in the self-doped (La-deficient) manganites. The magnetic transition temperature varies in both directions with increasing Mn^{4+} concentration when there is no Mn deficiency in the structure and increases with increasing Mn^{4+} concentration for Mn-deficient compositions. This is based on the assumptions of the estimated Mn^{4+} concentrations and the compositions derived from these values, assuming that the La deficiency is same as that in the starting composition. It is possible that this discrepancy is due to the assumed compositions of the self-doped manganites, where the compositions are derived from the Mn^{4+} content. A uniform tendency for the variation of T_c with Mn^{4+} content for all compositions in the self-doped series might be possible assuming Mn and O deficiencies in all cases and that the general composition is $La_{1-x}Mn_{1-y}O_{3-z}$. The difficulty to obtain both y and z values hinder the calculation of the actual composition. In general, it can be concluded that the magnetic behavior of the self-doped manganites below the magnetic transition temperature is determined by the Mn^{4+} concentration rather than the La vacancy. A sharp decrease in the susceptibility below T_c is obtained for compositions with very low Mn^{4+} content, irrespective of the La deficiency. There exists a limiting maximum value for T_a, which is independent of the Mn^{4+} concentration. In addition, T_a varies with Mn^{4+} concentration for a given composition only when it is less than a maximum possible value.

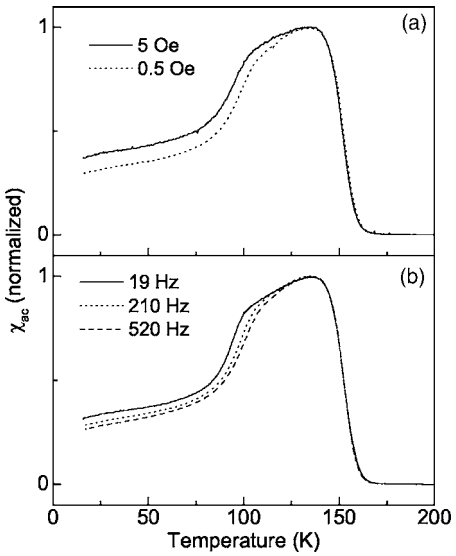

FIG. 6. ac susceptibility curves of $La_{0.937}MnO_3$ recorded at (a) two different ac fields at a frequency of 210 Hz and (b) at different frequencies in a field of 0.5 Oe.

Figure 6(a) shows the ac susceptibility curves of the $x=0.063$ composition recorded at two different ac magnetic fields, at the ac frequency of 210 Hz. Although the transition temperature and the broad maximum below T_c are not affected by this change in the ac field, large difference is observed in the region of the anomalous drop in the susceptibility. T_a is decreased from 103 to 99 K, when the ac field is increased from 0.5 to 5 Oe. A similar effect is observed when the measurement frequency is varied at a constant ac field, as shown in Fig. 6(b). T_a is decreased from 106 to 99 K when the ac frequency is decreased from 520 to 19 Hz, whereas the T_c and the broad maximum are unaffected. The ac field and frequency dependence of the features in the susceptibility curves are typical of spin glass

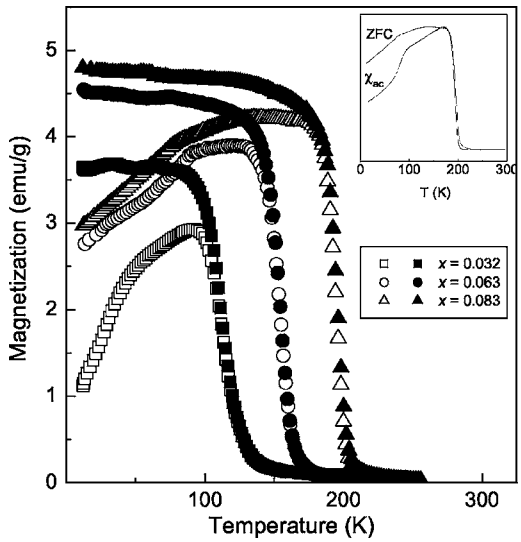

FIG. 7. Field cooled (closed symbols) and zero field cooled (open symbols) magnetization curves of three different compositions in $La_{1-x}MnO_3$. Inset: normalized ZFC and ac susceptibility curves of $x=0.083$.

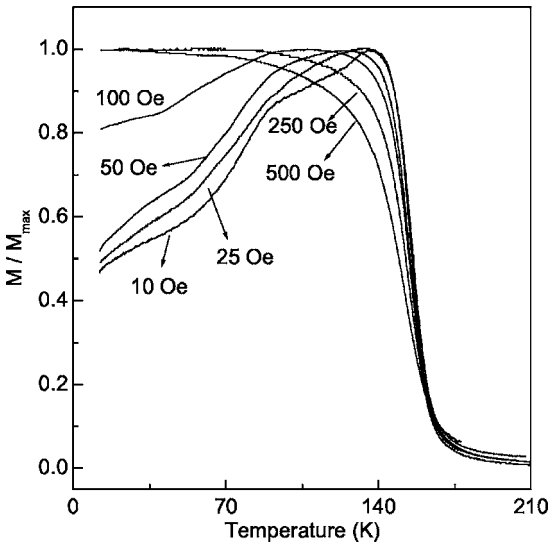

FIG. 8. Zero field cooled magnetization curves of $La_{0.937}MnO_3$, measured in different dc magnetic fields.

systems.[22,23] Therefore, such systems showing a ferromagnetic transition and a drop in the susceptibility at a lower temperature associated with frequency dependence are termed as reentrant spin glass systems,[24,25] where the low-temperature drop in the susceptibility is ascribed to a ferromagnetic to spin glass transition.

The signatures of the ac susceptibility curves are usually observed in the dc magnetization curves also when measured under zero field cooled conditions in the presence of sufficiently low magnetic fields.[19] Zero field cooled and field cooled magnetizations recorded in a dc magnetic field of 50 Oe, for three different self-doped compositions, are shown in Fig. 7. Characteristic features observed in the ac susceptibility curves are found in the ZFC magnetization curves also. However, as shown in the inset of Fig. 7, the anomaly is shifted to lower temperatures and the feature is broadened in the ZFC curve. This is expected because, as shown in Fig. 6, T_a decreases with decreasing the frequency towards the dc limit and moreover, a field of 50 Oe is used in the dc measurement which is comparatively larger than the ac fields used for the typical ac susceptibility measurements (T_a decreases with increasing ac field). Thermomagnetic irreversibility (divergence of FC and ZFC magnetizations) is observed below T_c for all three compositions. A drastic decrease in the magnetization observed in the ZFC magnetization curve is not observed in the FC case. Thermomagnetic irreversibility is a common feature observed for ferromagnetic and ferrimagnetic systems,[26–30] which were earlier thought to be characteristic features of spin glasses.

There are studies on well-defined ferromagnetic or ferrimagnetic systems showing frequency dependence of the features in the ac susceptibility below the ferromagnetic transition temperature. For example, the recent neutron diffraction studies on the ferrimagnetic oxide $YFeMnO_5$ show magnetic ordering down to 2.9 K, whereas a frequency dependence of the susceptibility is observed below $T_c=165$ K.[31] Similarly, in the case of $La_{0.83}Sr_{0.17}MnO_3$, which exhibits a feature similar to the self-doped manganites studied here, only a ferromagnetic component is observed down to low temperatures.[8] However, a structural transition was observed at the temperature where an anomaly is observed. $La_{0.85}Ca_{0.15}MnO_3$ was also found to exhibit similar behavior from ac susceptibility and neutron diffraction studies.[32] De Brion *et al.* observed a similar behavior in the ac susceptibility and ZFC magnetization curves in the case of $La_{0.93}MnO_3$.[33] Magnetic saturation was observed at very low temperatures, with no time dependence of the magnetization, indicating the absence of any spin glass behavior. Fe_3O_4, the well known ferrimagnetic oxide, exhibits a frequency dependence of a low-temperature anomaly of single crystals in the ac susceptibility, and this has been ascribed to freezing out of domain wall motion due to the rearrangements of the electron states within the domain wall.[34] Similarly, studies on single crystals of ferrimagnetic $FeCr_2S_4$ suggest that domain wall pinning effects are responsible for similar features.[35] High driving fields are required to overcome the pinning forces, and the origin of the relaxation processes can be due to temperature variation of the magnetocrystalline anisotropy. There are also other causes for the relaxation arising from the changes in the domain structure due to structural transformation, domain wall pinning due to nonuniform distribution of magnetic ions, presence of antiphase boundaries, etc.

It was found that in the ac susceptibility curve, increasing the measuring field decreases T_a, accompanied by an increase in the susceptibility. A similar behavior is observed in the ZFC magnetization also, with increasing the dc field, as shown in Fig. 8. For $La_{0.937}MnO_3$, a systematic change in the ZFC magnetization behavior is observed when the applied field strength is increased and no anomaly at low temperatures is observed when the applied field is increased from 100 to 250 Oe. The magnetization increases continuously with decreasing temperature, when measured using higher magnetic fields. The difference (or feature) between the ZFC

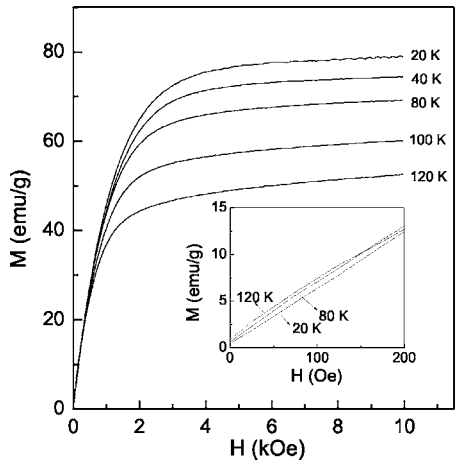

FIG. 9. Initial magnetization curves of $La_{0.937}MnO_3$, recorded at different temperatures. Inset: Initial magnetization curves in small magnetic fields.

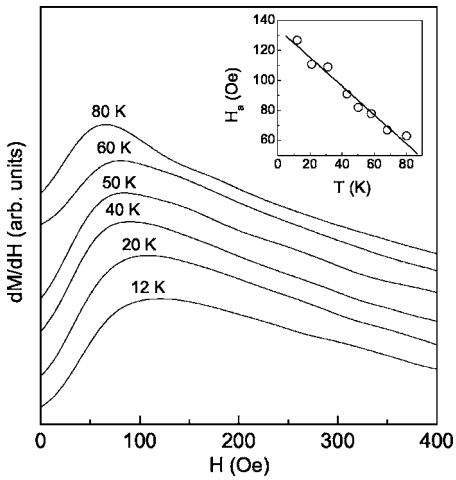

FIG. 10. Variation of dM/dH as a function of field at different temperatures, for $La_{0.937}MnO_3$. The field H_a at which a maximum is observed in dM/dH vs H as a function of temperature.

magnetizations, measured at field strengths of 50 and 250 Oe decreases continuously with increasing temperature. This indirectly indicates that there may exist a critical field, and if the ZFC magnetization measurements are made at or above this field, no anomaly could be observed in the ZFC magnetization below T_c. That is, the anomaly appears to be originating from some feature whose effect can be canceled by sufficient activation energy in the form of larger magnetic fields at lower temperatures or by thermal activation in the presence of lower magnetic fields. This is true if the domain wall pinning effect is responsible for the anomaly where higher magnetic fields can depin the walls at lower temperatures when magnetic fields larger than the pinning fields completely destroy the pinned state.

Previous studies have shown that the features in the ZFC magnetization curves, measured at a given low magnetic field, are directly related to the initial magnetization at this field at different temperatures.[36] Since the initial magnetization behavior at low magnetic field strengths is dominated by domain wall motion, the characteristic features of the ZFC magnetization curves recorded at different magnetic fields are a reflection of the domain structure of the individual material. Figure 9 shows the initial magnetization curves of $La_{0.937}MnO_3$ measured at different temperatures. Though the magnetization is saturated above 5 kOe and the magnetization continuously decreases with increasing temperature at larger magnetic fields, the reverse trend is observed at lower magnetic fields at temperatures below 100 K. The magnetization is lower at lower temperatures at low magnetic fields, as shown in the inset of Fig. 9. Such behavior in multidomain particles is known to be a characteristic feature of domain wall pinning.[37]

The indication for the existence of a critical field, as observed from the ZFC measurements, suggests that the pinning of domain walls is responsible for the anomalous behavior at low temperatures. Hence, we have attempted to trace the critical field by studying the isothermal magnetization processes at moderately low magnetic fields. In the initial magnetization curve of a virgin sample, the first part of the curve at low magnetic fields corresponds to reversible domain wall motion followed by irreversible movement of the walls due to unpinning, and this corresponds to a steep rise in the magnetization. The domain wall unpinning field is obtained by differentiating the magnetization with respect to the magnetic field. Figure 10 shows the dM/dH curves as a function of field, at different temperatures. A broad maximum is observed in each curve at a certain field, and this field decreases with increasing temperature. The maximum of the curve corresponds to the steepest part of magnetization curve in which the change in M is due mainly to irreversible domain wall motion in a polycrystalline sample, as observed in several magnetic systems,[37–39] and can be identified as domain wall unpinning field H_a. It can otherwise be defined as the threshold field required in order to unpin the domain walls. Understandably, this must vary with the rate at which field is applied and the temperature.[38] In the present study, the rate of variation of the field was kept constant as 1.6 Oe s^{-1}. It was found that no maximum is observed in the differential magnetization curves above 100 K matching with the maximum value of T_a observed in ac susceptibility curve for $La_{0.937}MnO_3$. This is in accordance with the finding that there is no magnetic anomaly due to domain wall pinning beyond 105 K. In addition, the inset in Fig. 10 shows that H_a decreases upon increasing temperature at the rate of approximately 1 Oe/K, and the intercept on the y axis is 135 Oe. This is in agreement with the observation made from ZFC magnetization curves obtained using different applied field strengths. The anomalous drop of magnetization in the ZFC magnetization curves, as shown in Fig. 8, is observed when the applied field $H < H_a$, and disappeared when $H > H_a$. The above results imply that the temperature above which the domain walls are depinned (T_{dw}) will be decreased upon increasing the field used for the ZFC magnetization measurements, and no anomaly is expected down to lowest temperatures when the magnetic field is larger than 135 Oe, supporting the results shown in Figs. 8 and 9. That is, there is a direct correlation between the nature of M_{ZFC} curves and the domain structure of a material.

A large magnetic relaxation effect is usually observed at a temperature where the domain walls become unpinned.[36]

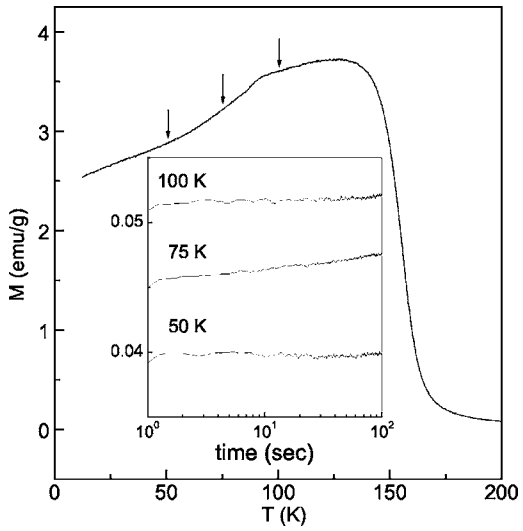

FIG. 11. Time dependence of the zero field cooled magnetization of $La_{0.937}MnO_3$ recorded at three different temperatures, as indicated by arrows in the ZFC magnetization curve; $H=50$ Oe.

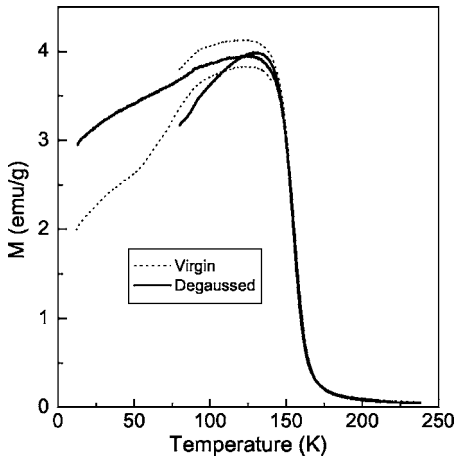

FIG. 12. Comparison of the temperature variation of the magnetization of $La_{0.937}MnO_3$ recorded after zero field cooling (broken lines) and after applying a field and degaussing the ZFC sample (solid lines).

This argument directly supports the conclusion that the frequency dependence of the low-temperature feature observed in the ac susceptibility curve is associated with domain wall pinning effects. In fact, relaxation of the ZFC magnetization is observed in the temperature region where the anomaly is observed. Figure 11 shows the time dependence of the ZFC magnetization of $La_{0.937}MnO_3$, measured at three different temperatures as indicated in the figure: (i) where the ac susceptibility becomes almost constant after the anomalous decrease below T_a, (ii) where maximum slope change is observed, and (iii) slightly above T_a. For each measurement, the sample was cooled through the T_c in zero field, to the required temperature, and the magnetization was recorded as a function of time immediately after applying a magnetic field of 50 Oe. It may be seen that there is no appreciable variation in the magnetization for cases (i) and (iii), whereas the magnetization continuously increases with time in the temperature region where the anomaly is observed.

Another important observation supporting the conclusion that the anomalous low-temperature behavior is not because of any antiferromagnetic transition or impurity and that it is due mainly to some domain wall effects comes from degaussing experiments.[12] The sample after cooling to the lowest temperature in zero field is exposed to a field for magnetic saturation, and the remnant magnetization was reduced to zero by degaussing. The magnetization was then continuously monitored on warming in a field of 50 Oe, the same way as in the case of the ZFC magnetization measurement. The virgin ZFC magnetization curve measured after cooling to 12 K and the corresponding curve obtained after degaussing are compared in Fig. 12. The magnetization at low temperatures is increased considerably and the anomalous behavior is almost vanished after degaussing the sample. On the other hand, if the sample is cooled only to the temperature region where a large drop in the magnetization is observed, the virgin and degaussed ZFC magnetization curves show different behavior. Here, although the anomalous drop in the magnetization is almost vanished, the magnetization after degaussing is lower than that when the sample is not degaussed. The behavior of the degaussed sample is as if there is a hindrance to the alignment of the magnetic moments in the direction of the field. This is possible if the moments are locked in certain regions and directions. This implies that the anomalous drop in the magnetization below 100 K is associated with domain wall pinning effects. If this was due to any other magnetic phases present in the sample or any other magnetic transition, this would not have been destroyed on degaussing.

If the low-temperature anomalous feature in the ac susceptibility as well as ZFC magnetization is due to domain wall motion effects, due to the pinned domain walls, this should be reflected in the coercivity of the material also.[40] Figure 13 shows a comparison of the ac susceptibility and the variation of coercivity as a function of temperature for $La_{0.917}MnO_3$ and $La_{0.937}MnO_3$. For both the samples, the coercivity initially increases almost linearly below T_c and a small jump in the coercivity is observed below T_a. This correlation between the changes in the coercivity and the ac susceptibility can be seen clearly in Fig. 14. Figure 14 compares the shapes of the inverse of the coercivity and ac susceptibility curves, normalized at a certain temperature, for four compositions, $x=0.031$, 0.063, 0.083, and 0.091, in $La_{1-x}MnO_3$. In all cases, there is a direct comparison of the changes in the ac susceptibility as well as the coercivity with temperature, especially in the temperature region where the drop in the susceptibility is observed. Moreover, as shown in Fig. 15 for $La_{0.909}MnO_3$ and $La_{0.937}MnO_3$, when the susceptibility drops drastically below T_a, as the Mn^{4+} concentration is decreased (see Figs. 3 and 4), a corresponding increase in the coercivity at low temperatures is observed. As long as T_a is unaffected for Mn^{4+} concentration $>22\%$, the coercivity also remains almost the same and the increase in the coercivity is observed only for a decrease in the Mn^{4+} concentration below 22%. This tells about the increasing anisotropy on decreasing the Mn^{4+} concentration, likely due to the increased domain wall pinning effects. It is possible that the distribution of Mn^{4+} ions, at lower concentrations, in the lat-

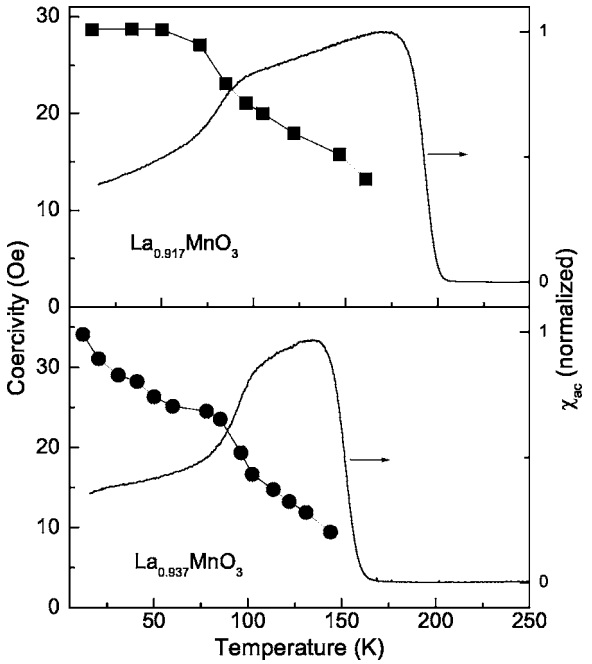

FIG. 13. Temperature variation of the coercivity and ac susceptibility of $La_{0.917}MnO_3$ and $La_{0.937}MnO_3$.

tice, is responsible for the effect of increased anisotropy.

In fact, Troyanchuk *et al.* have recently reported the magnetic properties of $La_{0.88}MnO_{3-\delta}$ with different Mn^{4+} concentrations.[20] The sample with 22% of Mn^{4+} shows a similar behavior in the zero field cooled magnetization curve measured at a field strength of 100 Oe, as in the case of the ac susceptibility curve of the $La_{0.875}MnO_{3-\delta}$ sample studied in this work. Decreasing the Mn^{4+} concentration from 22% to 18% gives rise to a small decrease in the ZFC magnetization below 100 K. This drop is enhanced and the temperature at which this drop is observed is increased to slightly above 100 K upon further decreasing the Mn^{4+} concentration.

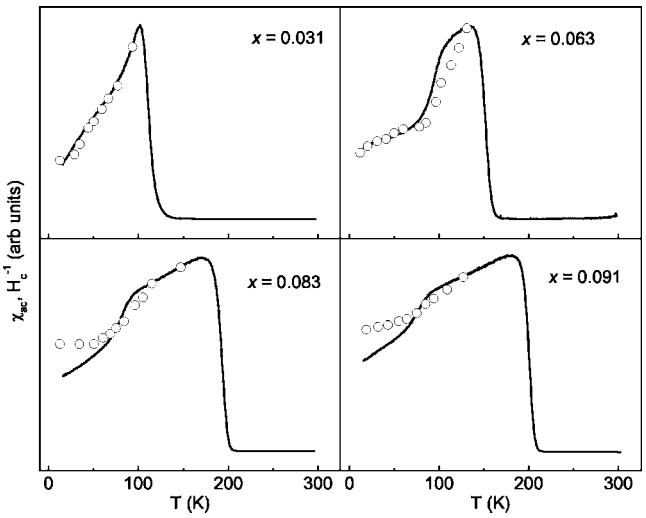

FIG. 14. Normalized ac susceptibility and $H_c^{-1}(T)$ curves of four different compositions.

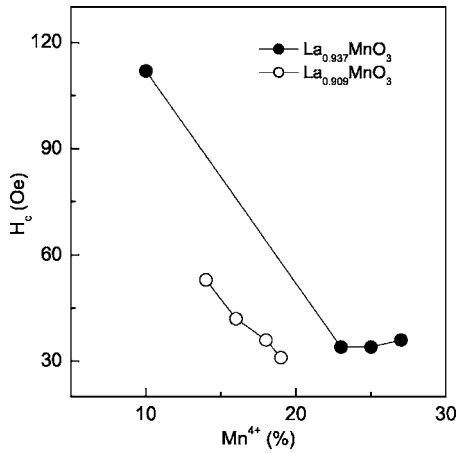

FIG. 15. Coercivity, measured at 12 K, as a function of Mn^{4+} concentration for $La_{0.909}MnO_3$ and $La_{0.937}MnO_3$.

Moreover, the magnetic transition temperature decreases continuously and the transition becomes broad with decreasing Mn^{4+} concentration.

Thus, the studies on different compositions in the self-doped lanthanum manganite series $La_{1-x}MnO_3$ show some interesting features in the ferromagnetic regime. A drop in the ac susceptibility and ZFC magnetization observed at low temperatures is influenced by the Mn^{4+} concentration. Irrespective of the degree of La vacancy, the temperature below which the anomalous drop is observed never exceeds a maximum value of ~105 K. There is a direct correlation between the magnetic anisotropy and the decrease in the susceptibility, as evidenced from the variation in the coercivity at low temperatures as a function of Mn^{4+} concentration as well as temperature for different compositions. The larger changes in the zero field cooled magnetization as a function of time in the temperature region where the anomaly is observed, the disappearance of the anomaly in the ZFC magnetization measurements at larger fields, the absence of the anomaly in the FC magnetization measurements, the dependence of the anomalous feature with ac field and frequency in the ac susceptibility measurements, etc., point to the role of domain wall pinning effects as the origin of the anomaly, rather than due to other magnetic transitions or spin glass or reentrant spin glass behavior. As to the cause for the domain wall pinning effects, the likely contributions are the inhomogeneous distribution of Mn^{4+} ions in the lattice. However, there is a more possible chance for a structural phase transition at the temperature where the anomaly is observed, as reported by Kawano *et al.*[8] This minor structural change affects the Mn-O-Mn bond angle which may cause a small canting of the spins so that the applied field is not sufficient to orient the moments in lower magnetic fields. The fact that the anomaly is not observed when measured in larger magnetic fields supports this conclusion.

Further, for the self-doped composition with Mn^{4+} content less than 15% a structural change from rhombohedral to orthorhombic symmetry is observed. This may be attributed to the large structural distortion due to strong Jahn-Teller effect prevailing in the "Mn^{3+} rich" lattice. The nature of the magnetization curves of these samples are almost identical,

with no apparent flat region immediately below T_c but with a sharp decrease in susceptibility. The structural change which is highly susceptible to the amount of Mn^{4+} in the lattice suggests that a structural phase transition is a probable cause of the low-temperature anomalous magnetic behavior observed in $La_{1-x}MnO_3$. Moreover, a large value of coercivity is observed at 12 K for the orthorhombic perovskite with $x=0.063$ and $Mn^{4+}=13\%$. This is in consistency with the observations made in $LaMnO_{3+\delta}$ by Pavlov *et al.*,[41] where the coercivity of the sample is found to undergo a drastic increase when the amount of Mn^{4+} is decreased below 15% which is accompanied by a structural phase transition. Thus, a structural rearrangement involving a change from rhombohedral to orthorhombic geometry that might hinder the domain wall motion can be thought to have such a magnetic hardening effect on the manganites under investigation similar to La-Sr-Mn-O compositions, as stated by Kawano *et al.*[8]

However, this is not a definite conclusion, and another factor that is worth mentioning in this context is the role of ordered and disordered local structural distortions in defining the domains and domain walls. Shibata *et al.* have observed the tendency for local structural inhomogeneity in lightly doped $La_{1-x}Sr_xMnO_3$ and they presumed this might have serious effects on the magnetic and electronic properties of manganites.[42] In $La_{1-x}MnO_3$ also, due to the presence of La-site vacancies, there might be a change in local structure since the crucial parameters determining the properties such as Mn-O distance and Mn-O-Mn bond angles would undergo certain changes in the vicinity of vacancies. When such vacancies are homogeneously distributed about the lattice as in the case of $x=0.125$ composition, the local distortions may become globally ordered. As soon as the vacancies are inhomogeneously distributed when $x<0.125$, the global ordering is destroyed and the local distortions may act as impurity centers for the pinning of domain walls. It can be assumed that as the vacancy ordering deviates from 1/8, distribution of vacancies becomes more and more inhomogeneous, ultimately resulting in the formation of strong domain wall pinning centers when the values of x become sufficiently small. It may be for a similar reason that such a low-temperature magnetization anomaly has been observed in lightly doped calcium and strontium manganites.

Another factor to be considered as domain wall pinning centers in the manganites generally is the Mn deficiency in the structure especially since strong pinning is observed in self-doped compositions when manganese vacancy is increased. It is known that[2] lanthanum calcium manganites have a tendency to form compositions with excess oxygen stoichiometry. This may create vacancies at the cationic site, probably both at La (and/or Ca) and Mn sites leading to domain wall pinning at Mn-vacancy defect centers. A detailed investigation is required to probe the exact compositional/structural features that provide centers for domain wall pinning.

Another important observation is that the magnetic transition temperatures of different compositions is not directly related to the Mn^{3+} to Mn^{4+} ratio. The magnetic transition temperature increases with Mn^{4+} content for certain compositions, whereas the reverse is observed for some other compositions. These compositional regions are marked by the degree of vacancies at the cationic and anionic sites of the perovskite structure and need to be studied in detail.

IV. CONCLUSIONS

Studies on different ferromagnetic compositions in the self-doped manganites, $La_{1-x}MnO_3$ show that there is no direct correlation between the magnetic ordering temperature and the Mn^{4+} concentration. The variation of Curie temperature with Mn^{4+} content show opposite trends in the low La-vacancy and the high La-vacancy compositional regions. Moreover, the Mn^{4+} concentration decreases upon increasing the deficiency of La, which is opposite to that expected, whereas the Curie temperature is increased. ac susceptibility measurements show that a decrease in the susceptibility in the ferromagnetic region, below the Curie temperature, is directly linked with the concentration of Mn^{4+} ions. The temperature below which the decrease in the susceptibility is observed varies with the Mn^{4+} concentration for different compositions. In general, more pronounced effects are observed at lower Mn^{4+} content for each composition. There is an associated increase in the coercivity linking the anomalous behavior to contributions from magnetic anisotropy. The observation of relaxation of magnetization in the temperature region where the anomalous behavior is observed, disappearance of the anomalous behavior when higher dc magnetic fields are used for the ZFC magnetization measurements, the absence of the feature in the FC magnetization measurements, lower initial magnetization at lower magnetic field strengths and lower temperatures (although the magnetization continuously decreases with increasing temperature at higher fields), etc., point to the contribution from domain wall pinning effects in determining the low-field magnetic behavior. The likely origin of the domain wall pinning effects is either from a nonuniform distribution of the Mn^{4+} ions that form as pinning centers or from mild structural distortions at lower temperatures so that the magnetic moments are canted at certain regions in the structure. Other possibilities such as vacancies of manganese ions, local structural distortions, etc. may also form as pinning centers. Relatively higher temperatures at lower magnetic fields or higher fields at lower temperatures are required to overcome the influence of the pinning effects.

ACKNOWLEDGMENTS

C.R.S. is grateful to CSIR, India, for financial support. Financial assistance from DST, Government of India, in the form of a project (SP/S2/M-17/99) is gratefully acknowledged.

*Electronic address: pa.joy@ncl.res.in; URL:http//www.ncl-india.org

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