Effect of Ga doping for Mn on the magnetic properties of $La_{0.67}Ca_{0.33}MnO_3$

S. M. Yusuf*
Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

M. Sahana, K. Dörr, U. K. Rößler, and K.-H. Müller
IFW Dresden, Postfach 270016, D-01171 Dresden, Germany
(Received 25 April 2002; published 12 August 2002)

The effect of Ga substitution for Mn in the ferromagnetic manganite $La_{0.67}Ca_{0.33}MnO_3$ has been studied by preparing a series of $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ ($x=0$, 0.10, 0.25). Magnetic properties have been investigated by means of macroscopic ac susceptibility and dc magnetization, mesoscopic neutron depolarization, and microscopic neutron-diffraction probes. The substitution of Mn^{3+} by nonmagnetic Ga^{3+} allows one to study the effect of a reduction of the number of lattice sites participating in the itinerant ferromagnetic double exchange interaction, i.e., a dilution of the magnetic Mn sublattice. In contrast to other Mn site substitutions, changes of the electronic band structure by structural effects are small due to similar ionic size of Mn^{3+} and Ga^{3+}. Experimental results show that the ferromagnetism at low temperature is suppressed and the system is driven into a randomly canted ferromagnetic state for $x=0.10$ and a cluster spin-glass state for $x=0.25$.

DOI: 10.1103/PhysRevB.66.064414 PACS number(s): 75.50.Lk, 75.60.Ch

I. INTRODUCTION

Rare-earth manganite perovskites of the type $R_{1-x}A_xMnO_3$, where R is the trivalent rare-earth ions and A is the divalent alkali-earth ions, have recently been the focus of a large number of experimental and theoretical studies. This is because they exhibit a range of extraordinary magnetic, electronic, and structural properties including colossal negative magnetoresistance,[1–3] charge ordering,[4–7] and magnetic-field-induced changes in structure[8,9] and transport properties,[10] and also because of potential technological applications. When a divalent ion (A) is doped in the rare earth site a proportional number of Mn^{3+} is converted into Mn^{4+} and mobile e_g electrons are introduced, which mediate a ferromagnetic interaction between Mn^{3+} and Mn^{4+} according to the double exchange (DE) interaction model.[11] In these systems the ferromagnetic interaction between Mn^{3+} and Mn^{4+}, caused by the hopping of e_g electrons between two partially filled d orbitals of neighboring Mn^{3+} and Mn^{4+} ions via the orbital overlap $e_g(\mathrm{Mn})-2p_\sigma(\mathrm{O})-e_g(\mathrm{Mn})$, and a strong on-site Hund's coupling between the t_{2g} core spins and mobile e_g electrons (known as DE interaction) plays an important part in determining the magnetic behavior.[12] These ferromagnetic interactions must compete with coexisting $t_{2g}(\mathrm{Mn})-2p_\pi(\mathrm{O})-t_{2g}(\mathrm{Mn})$ antiferromagnetic interactions.

Recently, the important role of the intrinsic disorder in these mixed-valent systems was recognized[13] in connection with inhomogeneous states found on various scales from the formation of polaronic clusters or clustered magnetic regions[14] up to large-scale phase separation.[15,16] Disorder effects appear necessary to understand magnetic ordering and transport properties in these compounds.[16] Far-reaching scenarios were discussed, where ''colossal'' or ''giant'' effects were caused by inhomogeneities in such metal oxides due to a competition between different ordered phases linked by a first-order transition in the ''clean limit.'' [17] Therefore, studies are of high interest where disorder in colossal magnetoresistive manganites can be extrinsically introduced and varied. Experimentally, this can be achieved by a suitable substitution for R and/or Mn sites. Extensive research on metallic, ferromagnetic manganites of the type $La_{0.7}Ca_{0.3}MnO_3$, where the Ca concentration is close to an optimum value in relation to the ferromagnetic interaction, was done through doping the La sites with rare earths (Y,[18,19] Pr,[19] Dy,[20] Tb,[21,22] etc.) of different sizes. The lattice distortions introduced by La-site disorder influence the ferromagnetic DE couplings by changing the Mn-O-Mn angle. The competition with antiferromagnetic superexchange interactions, that are less affected by lattice effects, may give rise to magnetically disordered states. Thus this type of disorder indirectly affects the magnetic couplings between the Mn sites. Phenomenologically, changes in the magnetic behavior can be understood in terms of the tolerance factor for the perovskite structure, i.e., the average ionic size of the La site (r_A),[19] and the La-site size-disorder, i.e., the width σ of the distribution of the ions on the La site.[23] A decreasing (r_A) and/or an increasing σ reduce the transition temperature T_C. Beyond critical values, the lattice disorder brings about glassy magnetic states. In these insulating or metallic states, evidence of ferromagnetic clustering has been found.[18,22]

Direct substitution of Mn sites yields another probe for the magnetism in these systems. Since the early studies,[24–26] various investigations have been made;[27–31] however, the aspect of effects due to the introduced disorder in the Mn-O-Mn subsystem did not play a prominent role. Many studies focused on the overall properties of the magnetic system, e.g., by shifting the average balance between ferromagnetic and antiferromagnetic couplings in the magnetic sublattice. It is interesting to note that only recently a substantial enhancement of T_C by partial Ru substitution in a layered ferromagnetic manganite was found. But this effect seems related to a particular itinerant ferromagnetic double exchange by delocalized t_{2g} electrons and to a ferromagnetic superexchange.[32] Generally it was found that the possible substitutions by various other ions such as the $3d$ metals,[24–26,30,33–37] or In, Al, Ga, or Ge,[28,29,38–41] drastically lower the critical temperature

T_C of the paramagnetic-ferromagnetic transition and eventually lead to insulating states and/or spin-glass-like properties for higher substitutions.[31,34–36,38–40] Responsible for this are the combined effects of Mn-site substitution: (i) a shifting of the effective valency in the remaining Mn-O-Mn network; and (ii) changes of the band-structure for the conduction electrons mediating the DE exchange,[42] i.e., band filling and bandwidth, for the e_g electrons. These band-structure effects imply disorder and therefore influence the ferromagnetic double exchange. Immobile defect ions on Mn sites cause an electrostatic potential on neighboring Mn ions,[42] which introduces attractive sites for mobile e_g-band electrons or holes in the Mn lattice where the average charge is between three and four elementary charges. For example, a substituted divalent atom like Zn^{2+}[43] will strongly attract holes in its vicinity. Further Mn-site substitution may cause (iii) lattice distortions due to changed ionic size, (iv) magnetic dilution for nonmagnetic ions like Al^{3+},[37,28,38–40] In^{3+},[40] and Ti^{4+},[35,36] or (v) additional magnetic couplings by introduction of magnetic ions like Cr,[33] Fe,[25,41,44–46] Co,[27,31] Ni,[27] or Cu.[37] These effects may be interrelated, and all of them can influence the magnetic behavior.

Most investigations of Mn-site substitution show a combination of these microscopic effects even for nonmagnetic (diamagnetic) dopant ions. For example, Blasco *et al.*,[39] from a detailed study on $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_{3-d}$ compounds, reported a drastic decrease of the Curie temperatures and the temperature of the associated metal-insulator transition with Al^{3+} doping up to $x=0.05$. Magnetic inhomogeneities were found for $x \geqslant 0.1$. The macroscopic results obtained for this $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_{3-d}$ series are very similar to those obtained for $(La_{1-y}Tb_y)_{2/3}Ca_{1/3}MnO_3$,[21] which shows a cluster spin glass state for $y \sim 1/4$.[22] Similarly, from a study on magnetic properties and magnetoresistance of $La_{2/3}Ca_{1/3}Mn_{1-x}In_xO_3$ compounds, Sanchez *et al.*[40] reported that In^{3+} destroys long-range ferromagnetic order and induces a cluster-glass behavior and the absence of metal-insulator transition for $x \geqslant 0.05$ substitution. It should be noted that in both studies on trivalent diamagnetic dopants a possibly interrelated effect of size mismatch with respect to Mn^{3+} and induced oxygen vacancies might have played a role for the magnetic properties. Liu *et al.*[35] concluded from magnetization, resistivity, and electron-spin resonance studies that for more than 10 at. % doping of Ti for Mn in $La_{0.7}Ca_{0.3}MnO_3$, a cluster spin-glass state occurs at low temperatures with combined effects of the size and the valence of Ti^{4+} ion.

Substitution of Mn sites with magnetic ions was also intensely studied. Cr substitution[24,47] at the Mn site only slightly decreases T_C, which may indicate that this dopant does not strongly modify the ferromagnetic double exchange. On the other hand, substitution by Fe (Refs. 25, 26, 30, 34, 41, and 43) or Ni (Ref. 27) yielded drastic reductions of the Curie temperature. Iron substitution[25,26,30,33,34,41,44–46] provided the best-studied and simplest case of a magnetic dopant ion on Mn sites. From Mössbauer spectroscopy studies[25,41] it is proved that the Fe^{3+} ($S=5/2$) moments are antiferromagnetically coupled to the ferromagnetic Mn-O network. One assumes that the Fe cannot take part in the double-exchange mechanism involving the Mn e_g bands, because the Fe^{3+} e_g up states are completely filled, and the energies of t_{2g} down states are about 2 eV above these levels.[25,34] Therefore, the magnetic coupling in Mn-O-Fe must be due to weaker antiferromagnetic superexchange. Because Fe-O-Fe superexchange pairs should also be antiferromagnetic, pairs of Fe in the ferromagnetic manganites will experience magnetic frustration which can yield spin canting for the Fe spins and surrounding Mn spins, as described already by Leung, Morrish and Evans for $La_{1-x}Pb_xMn_{1-y}Fe_yO_3$ compounds.[25] This may explain cluster-glass-like properties at higher Fe substitution[30,43] and the randomly canted, weakly ferromagnetic spin-structures within mesoscopic clusters in $La_{0.7}Ca_{0.3}Mn_{0.9}Fe_{0.1}O_3$.[45]

Considering the complex influences incurred by Mn-site doping, it is desirable to study the effect of a direct replacement of Mn^{3+} by a nonmagnetic (diamagnetic) ion without the effect of static lattice distortion and/or introducing any additional magnetic exchange interaction due to the replacement. The change of the effective Mn valency cannot be avoided; however, substitution by a trivalent ion starting from a compound with $Mn^{4+}/Mn^{3+} \sim 0.3$ allows one to remain well within the range of the ferromagnetic phase with $Mn^{4+}/Mn^{3+} < 1$.

Substitution of Ga^{3+} ions on Mn sites can fulfill these requirements. Ga^{3+} has no magnetic moment and an ionic size very similar to Mn^{3+}. Thus lattice effects are not introduced by Ga^{3+} substitution.[29] Also Ga^{3+} has a filled-shell configuration; the orbitals are not available for the exchange interactions. Recently, Sun *et al.*[29] investigated the effects of Ga doping (limited to 10 at.%) in the Mn site of $La_{0.67}Ca_{0.33}MnO_3$ by low field (50 Oe) dc magnetization and resistivity (under zero external field) studies. The Curie temperature and the associated metal-insulator transition temperature were reported to decrease drastically with the Ga doping as also found in $Pr_{1-x}(Ca,Sr)_xMn_{1-y}Ga_yO_3$.[38] Cao *et al.* studied $La_{0.70}Ca_{0.30}Mn_{1-x}Ga_xO_3$ with Ga substitution also up to $x=0.1$, and concluded from x-ray-absorption fine-structure data that the substitution promotes the formation of clusters.[48]

As remarked upon above, disorder in the mixed-valent manganites is interesting for the fundamental understanding of the mechanisms underlying their particular magnetic and magnetoresistive properties. Substitutional disorder without the complications due to lattice effects are now being studied theoretically. Upon completion of the experimental work reported in this paper, we became aware of a numerical study[42] of a disordered double-exchange model with competing superexchange interactions, where Ga- and Fe-doped $La_{0.67}Ca_{0.33}MnO_3$ was considered. A quantum critical point behavior is predicted for Ga substitution with $x \sim 0.1-0.2$, where the paramagnetic state may reach down to zero temperature. Above $x=0.2$, the calculation points toward a complicated situation with different, nearly degenerate phases that might look somehow glassy experimentally, as suggested by the authors. The predicted phase diagram is similar to the scenario described by Burgy *et al.*[17]

In this paper, we present results on the effects of the substitution of Mn by Ga (10% and 25 at.%) in

$La_{0.67}Ca_{0.33}MnO_3$ from a study of macroscopic magnetic properties by detailed ac susceptibility and dc magnetization measurements which is combined with investigations of the magnetic order at microscopic and mesoscopic length scales from neutron diffraction and neutron depolarization, respectively. In these compounds, where magnetic frustration and disorder are present, the nature of the magnetic correlation cannot be determined by bulk magnetic measurements unequivocally. Neutron diffraction has been employed in order to characterize the long-range magnetic order and its gradual suppression by the substitution. Neutron depolarization probes magnetic inhomogeneity on a length scale of several 10 nm up to few μm and, thus, allowed to probe the existence of magnetic clusters for 25% of Ga. The results provide a strong indication of the cluster spin glass state of $La_{0.67}Ca_{0.33}Mn_{0.75}Ga_{0.25}O_3$. Since Ga^{3+} is a nonmagnetic, size-matching substitution for Mn^{3+}, our experimental results essentially reflect how the random dilution of the Mn sublattice influences the magnetic order on the different length scales.

II. EXPERIMENTS

Polycrystalline $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ ($x=0$, 0.10, and 0.25) samples were prepared through a conventional solid-state reaction route. Stoichiometric amounts of La_2O_3, $CaCO_3$, $MnC_2O_4\cdot 2H_2O$, and Ga_2O_3 were ground well, and the homogeneous mixture was heated at 900 °C for 24 h, cooled to room temperature, reground and heated at 1250 °C for 24 h. The black powder thus obtained was pelletized and sintered at 1500 °C for 12 h. The sintered samples thus obtained were powdered. X-ray-diffraction patterns for all three samples were recorded at room temperature using a Siemens system with Cu K-α radiation.

The real part of ac susceptibility data were obtained on all the samples in an ac field of 0.5 Oe and at a frequency of 80 Hz, using an APD closed cycle helium refrigerator with Meissner coil assembly in conjunction with an EG & G Model 5208 lock-in amplifier. The frequency dependence of the in-phase ac-susceptibility in the frequency range 10 Hz $\leqslant$ f $\leqslant$ 10 kHz and in an ac field of 1 Oe was measured using a Lakeshore 7000 Series susceptometer.

The magnetization measurements were carried out with $x=0$, 0.10, and 0.25 samples as a function of temperature and magnetic field using either a Quantum Design SQUID (superconducting quantum interference device) magnetometer or an Oxford Instruments design vibrating sample magnetometer. All measurements were carried out on compacted powder samples. Compacting ensures that rotation of the crystallites does not take place. In zero field cooled (ZFC) measurements the sample was cooled from ~300 to 5 K in zero field. A field of preset magnitude was applied at 5 K, and then the ZFC magnetization measurements were carried out in the heating cycle. For the field-cooled (FC) case, on the other hand, the sample was first cooled from ~360 to 5 K in the presence of the preset field value and measurements were then carried out in this field during the heating cycle, as in the ZFC case.

The one dimensional (z-z) neutron-depolarization measurement, which is a sensitive tool to probe the magnetic inhomogeneity on a mesoscopic length scale,[49–53] was carried out using the neutron-polarization analysis spectrometer (PAS) at Dhruva reactor, Trombay ($\lambda = 1.205$ Å). A detailed description of the spectrometer was given in earlier papers.[54,55] The temperature of the sample was varied between 15 and 300 K in a closed-cycle helium refrigerator and controlled to better than 0.1 K. Measurements were performed in the heating cycle in the presence of a 7-Oe external field after cooling the sample in the same field of 7 Oe from 300 to 15 K. The incident neutron beam was polarized along the $-z$ direction (vertically down) with a beam polarization of 98.60(1)%. The transmitted neutron beam polarization was measured along the $+z$ direction, as described in detail in Ref. 54. The powder sample used for the depolarization study was in the form of a pellet of cylindrical shape. The sample was placed in the neutron beam in such a way that the flat surface of the cylindrical sample remains perpendicular to the propagation direction of the polarized neutron beam. The beam passed through an effective sample thickness of 9.8 mm. The beam size was restricted with a cadmium slit, which is within the size of the sample. An external magnetic field of 7 Oe (on the sample) was applied parallel to the incident neutron beam polarization direction ($-z$) using a small electromagnet.

The unpolarized neutron diffraction patterns were recorded for all the three samples at 15 and 297 K on the PAS in its unpolarized mode over the lower 2θ angular range of ~11°–33° where magnetic Bragg scattering intensities are predominantly expected (if any). The temperature variation of diffracted intensity of the (110) and (002) Bragg peaks was studied from 15 to 200 K for the $x=0.25$ sample. The diffraction measurements were carried out on the polycrystalline sample with no external magnetic field.

III. RESULTS AND DISCUSSION

X-ray diffraction patterns of polycrystalline samples of $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ with $x=0$, 0.10, and 0.25 are presented in Fig. 1. It shows clean single-phase patterns of orthorhombic crystalline structure with space group *Pbnm* for all samples. No noticeable change in the lattice parameter is found for the Ga-doped samples. Figure 2 shows the temperature dependence of the ac susceptibility (χ_{ac}) curve for all the three samples. Magnetic transition temperatures (defined as the point of steepest slope in the χ_{ac} vs T curve) are found to be ~238.6, ~122.8 K and ~48 K for $x=0$, 0.10, and 0.25 samples, respectively, indicating that the substitution of Ga for Mn leads to a strong decrease in the magnetic ordering temperature. The onset of magnetic ordering for the $x=0$ sample is found to be ~252 K, in accordance with the reported value in literature.[56] With increasing Ga substitution, the transition is broadened and eventually the χ_{ac} curve shows a cusplike peak at 41.5 K for the $x=0.25$ composition. A similar peak was found to occur at ''the spin-glass-like'' transition in $La_{2/3}Ca_{1/3}MnO_3$ doped with Al (Ref. 39) and Fe (Ref. 44) for higher degree of substitution. The transition broadening has also been observed in other perovskite materials substituted by tetravalent Ti ions for Mn sites.[35,36]

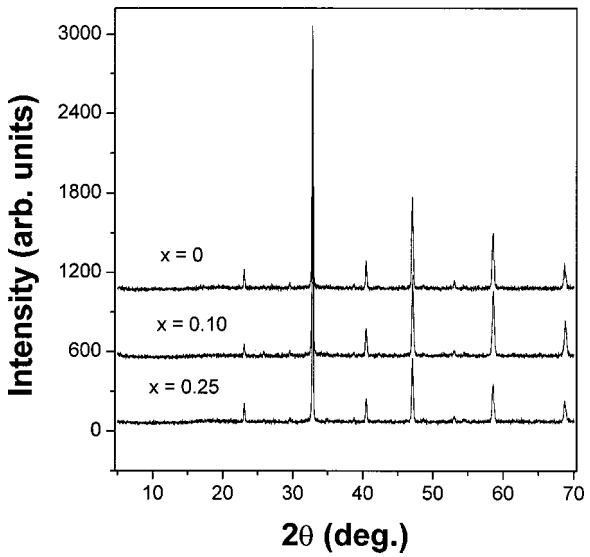

FIG. 1. Powder x-ray-diffraction patterns for $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ with $x=0$, 0.10, and 0.25.

In Fig. 3 an irreversibility between the ZFC and FC magnetization curves is clearly seen for the $x=0.25$ sample at temperatures below about 30 K. The irreversibility is found to persist even under a field of 20 kOe. The branching temperature is found not to change with the applied magnetic field up to 20 kOe. This implies that the anisotropy field is very large in the $x=0.25$ compound. For the $x=0.10$ sample an irreversibility is found only at low applied field (Fig. 3). For the parent $x=0$ sample no such irreversibility is found (not shown). Such an irreversibility in the M-T data for the FC and ZFC measurements was observed in several manganite systems, and it was suggested that this irreversibility arises possibly due to the canted nature of the spins or due to the random freezing of spins.[19,57,58]

In Fig. 4, the magnetic-field dependence of virgin magnetization is shown for the $x=0$, 0.10, and 0.25 samples at 15 K with a maximum magnetic field of 48 kOe. It is clearly seen that for the $x=0.25$ sample, the saturation of magnetization is not achieved even under a 48-kOe field. The value of magnetization at 15 K under a 48-kOe field is found to be 96.38 emu g^{-1} ($\sim 3.61\mu_B$ per formula unit), 83.99 emu g^{-1}

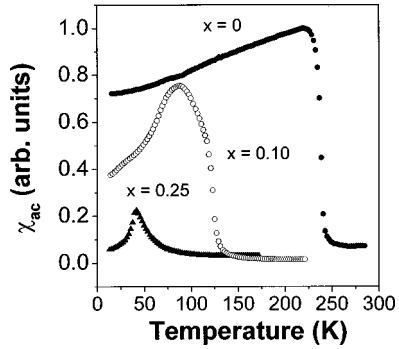

FIG. 2. Temperature dependence of the real part of the ac susceptibility for $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ ($x=0$, 0.10, and 0.25) compounds measured in an ac field of 0.5 Oe and a frequency of 80 Hz.

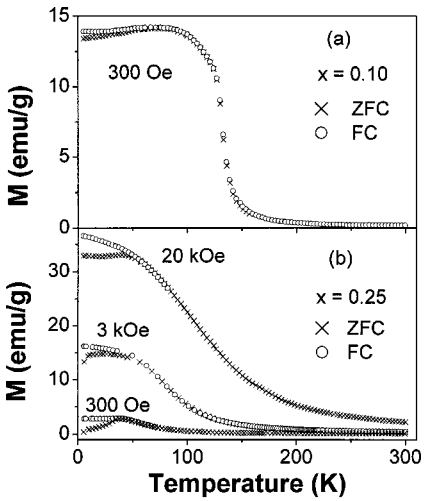

FIG. 3. ZFC and FC magnetization (a) at a 300- Oe field for $La_{0.67}Ca_{0.33}Mn_{0.9}Ga_{0.1}O_3$ and (b) at 300-, 3000-, and 20000-Oe fields for $La_{0.67}Ca_{0.33}Mn_{0.75}Ga_{0.25}O_3$.

($\sim 3.17\mu_B$ per formula unit), and 48.29 emu g^{-1} ($\sim 1.84\mu_B$ per formula unit) for $x=0$, 0.10 and 0.25 samples, respectively. Because La^{3+}, Ca^{2+}, Ga^{3+}, and O^{2-} ions have no magnetic moment, the moment of $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ originates from the moments of Mn^{3+} and Mn^{4+} ions. The nominal numbers of Mn^{3+} and Mn^{4+} ions per formula unit are 0.67 and 0.33 for the $x=0$ sample, 0.57 and 0.33 for the $x=0.10$ sample, and 0.42 and 0.33 for the $x=0.25$ sample, respectively. High-spin manganese gives spin only (orbital contribution quenched) ordered moment $\mu=gs\mu_B$ where Mn^{3+} and Mn^{4+} carries $4\mu_B$ and $3\mu_B$, respectively, with g (the gyromagnetic ratio) $=2$. Assuming a complete ferromagnetic order of the manganese spins, maximum spin-only ordered moments of $3.67\mu_B$, $3.27\mu_B$, and $2.67\mu_B$ per formula unit are expected for the $x=0$, 0.10, and 0.25 samples, respectively. For the $x=0$ sample the observed value of ordered moment is in good agreement with this expected spin-only value and, for the $x=0.10$ sample, the observed moment is marginally lower (~3%). However, for the $x=0.25$ sample, the observed moment is significantly lower than the

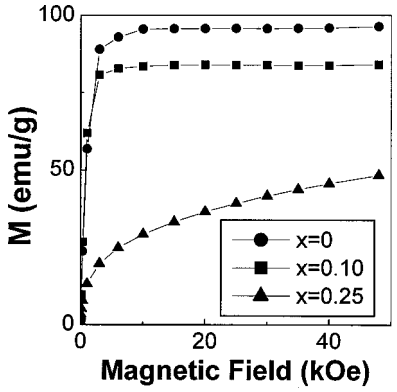

FIG. 4. Virgin magnetization curves for $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ at 15 K. Solid lines are drawn to guide the eyes.

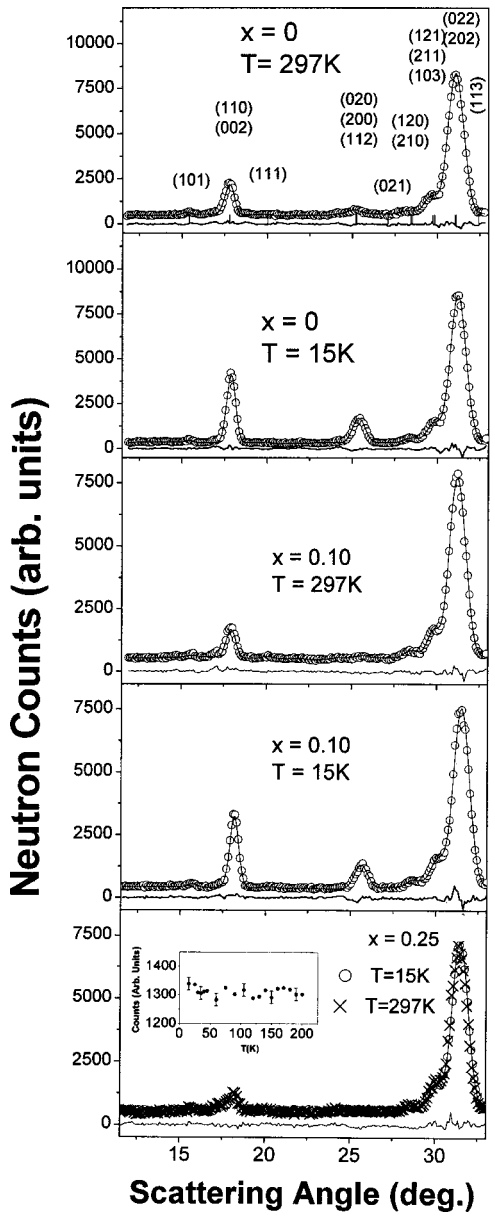

FIG. 5. Neutron-diffraction patterns for $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$, with $x=0$, 0.10, and 0.25 at 297 and 15 K recorded over the lower angular range of $\sim 11°-33°$ where magnetic Bragg scattering intensities are predominantly expected (if any). Open circles and crosses show the observed data. The solid lines represent the Rietveld refined patterns. The difference patterns between the observed and calculated patterns are also shown at the bottom of each curve by solid lines. The vertical lines indicate the position of allowed Bragg peaks. The *hkl* values are marked above the respective scattering angles. For the $x=0.25$ sample the observed patterns at 297 and 15 K are shown on the same scale. The inset shows the combined peak intensity of (110) and (002) Bragg peaks as a function of temperature for the $x=0.25$ sample.

expected spin-only value. We recall that this value of magnetization is still far from saturation at 48 kOe.

Figure 5 shows the observed and Rietveld refined (using the FULLPROF program[59]) neutron powder diffraction patterns recorded at 15 and 297 K (i.e., well above and below the magnetic transition temperatures) without any external magnetic field for all the three samples. The refinement shows an orthorhombic perovskite structure (sp. gr. *Pbnm*) for all samples at all temperatures. The stoichiometric nature of the samples is confirmed from the analysis. The refinement for the $x=0$ sample at 15 K shows a ferromagnetic ordering of Mn moments with a net site averaged ordered moment of $3.4(1)\mu_B$ per Mn ion (oriented along the crystallographic *c*-direction) as reported in the literature.[56] For the $x=0.10$ sample, the corresponding value is found to be $3.2(1)\mu_B$ per Mn ion (i.e., $2.88\mu_B$ per formula unit). These values are in good agreement with the results obtained in our dc magnetization measurements. However, for the $x=0.25$ sample, the refinement shows the complete absence of a ferromagnetically ordered moment. In fact no trace of ferromagnetic ordering was found over the entire temperature range down to 15 K, as peak intensities do not vary with temperature indicating magnetic scattering (see the inset in Fig. 5). It may be stressed that no additional Bragg peaks was found either indicating the absence of any other ordered magnetic phase (antiferromagnetic, spiral, etc.) in the $x=0.25$ compound. The reduction of observed site averaged ordered moment for Mn ion in the $x=0.10$ sample (as compared to the parent $x=0$ sample) suggests that the spins are randomly canted at an average angle of $\sim 20°$ with respect to the [001] crystalline axis in the $x=0.10$ compound. A canted ferromagnetic behavior has been reported for other perovskites.[46,60] Such a behavior for mixed-valent manganites was theoretically predicted by de Gennes[61] within a model for competing ferromagnetic double-exchange and antiferromagnetic superexchange interactions (also see Ref. 62). Due to the random nature of substitution of Mn^{3+} with Ga^{3+} this mechanism can cause a random (local) canting of spins.[46] A higher degree of the substitution which leads to a random distribution of the ferromagnetic and antiferromagnetic exchange interactions may cause the formation of ferromagnetic spin clusters with randomly canted spins.

In order to obtain more clues regarding the nature of spin ordering in the $x=0.25$ sample, here we present the results of dc magnetization and neutron depolarization. Before presenting the experimental results of our neutron depolarization study on the $x=0.25$ sample, we briefly recall the theory of neutron depolarization in various magnetic systems.[49,50,52] The neutron depolarization technique is a mesoscopic probe. It can measure the spatial magnetic inhomogeneity on a length scale, say from 10 nm to several microns. In an unsaturated ferromagnet or ferrimagnet, the magnetic domains exert a dipolar field on the neutron polarization and depolarize the neutrons owing to the Larmor precession of the neutron spins in the magnetic field of domains. As the neutron depolarization technique probes the magnetic inhomogeneity on a mesoscopic length scale, a magnetic inhomogeneity on an atomic scale—as in a true spin-glass state—has no effect on the neutron polarization. In a true spin-glass phase (in a zero-field-cooled state), the atomic spins are randomly frozen in space on a microscopic length scale and, as a result, the magnetic induction averages out to zero on a mesoscopic length scale. Hence no depolarization is found in true spin-glass systems. Similarly no depolarization is expected in the paramagnetic state because the temporal spin fluctuation is

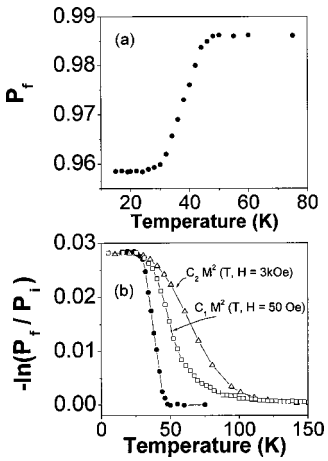

FIG. 6. (a) Temperature dependence of transmitted neutron beam polarization measured at 7 Oe applied field for the $x=0.25$ sample. (b) Comparison of $-\ln[P_f(T)/P_i]$ and C $[M(T)]^2$ at various fields applied during M vs T measurements for the $x=0.25$ sample (see the text).

too fast (10^{-12} s or faster) for the neutron polarization to follow the variation in the magnetic field **B** acting on the moving thermal neutrons. However, one would expect depolarization for the case of clusters of spins (at least of mesoscopic length scale) with net moments. During the passage of polarized neutrons through such a spin cluster if the Larmor precession time of neutron spins is shorter than the relaxation time τ for the clusters, the neutron spins will effectively ''see'' a nonzero precession field, and a depolarization of neutron spins occurs. If the Larmor precession angle of the neutron spin is a small fraction of 2π over a cluster length, the observed depolarization can be represented by the expression[49,51]

$$P_f = P_i \exp\left[-\alpha\left(\frac{d}{\delta}\right)\langle\Phi_\delta\rangle^2\right], \tag{1}$$

where P_i and P_f are the initial and final neutron beam polarization, α is a dimensionless parameter $\approx 1/3$, d ($=9.8$ mm) is the effective thickness of the sample, δ is the average cluster size, and $\Phi_\delta = (4.63\times10^{-10}\ \mathrm{G}^{-1}\ \text{Å}^{-2})\ \lambda B\delta$ is the precession angle. $B = 4\pi M_S \rho$ (in G), denotes the internal mean induction within a spin cluster, λ the neutron wave length, M_S the spontaneous magnetization in emu g^{-1} and ρ the density of the material in g cm^{-3}. The temperature dependence of the neutron beam polarization for the $x=0.25$ sample is shown in Fig. 6(a). The procedure for obtaining P_f values from the measured flipping ratios for the transmitted polarized beam is described elsewhere.[54] P_f starts to decrease right from 48 K. At $T>48$ K, the value of P_f is the same as the incident beam polarization. This implies that the sample is in its paramagnetic phase above 48 K where no change of neutron polarization is expected. The magnetic ordering temperature for this sample is thus estimated to be 48 K in accordance with the ac susceptibility data in Fig. 2. At lower temperatures, the presence of clusters of spins with net magnetic moments is thus confirmed from the occurrence of significant depolarization down to 15 K,

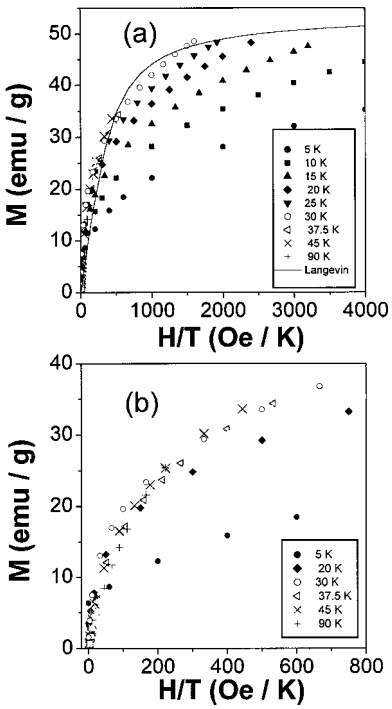

FIG. 7. Virgin magnetization M vs H/T for the $x=0.25$ perovskite, under ZFC conditions. The solid curve in (a) represents the calculated Langevin function as described in text. The superposition of curves for $T>30$ K is shown separately in (b) for better clarity.

the lowest temperature of measurement. In order to compare the temperature dependence of P_f with the temperature dependence of the low-field magnetization we plot-ln$[P_f(T)/P_i]$ and $C[M(T)]^2$ (where C is a normalization factor) in Fig. 6(b). It is interesting to note that a temperature independent behavior of M and P_f is evident at $T<30$ K, indicating a temperature-independent cluster size δ below this temperature. A deviation between the temperature dependence of magnetization and P_f is evident above $T\sim30$ K, where $M(H,T)$ shows a clear field dependence. Variation of the observed temperature dependence of magnetization with fields indicates a field-induced magnetic ordering on magnetization.

In order to obtain the cluster moment, the temperature and magnetic-field behaviors of magnetization of these spin clusters were analyzed by plotting the magnetization as function of H/T (Fig. 7). When the thermal energy becomes higher than the anisotropy energy, the cluster moments will exhibit a Boltzmann distribution of orientations with respect to applied magnetic field H at thermal equilibrium. The effective magnetization is then given by the classical Langevin expression

$$M = M_O[\coth(\mu H/k_\mathrm{B}T) - k_\mathrm{B}T/\mu H], \tag{2}$$

where M/M_o refers to the component of magnetization in the field direction; μ refers to the magnetization of the magnetic cluster, comprising a large number of magnetic Mn ions; and k_B is the Boltzmann constant. At higher temperatures ($T>30$ K), the superposition of data at various temperatures can be seen. The Langevin curve [shown in Fig. 7(a)], com-

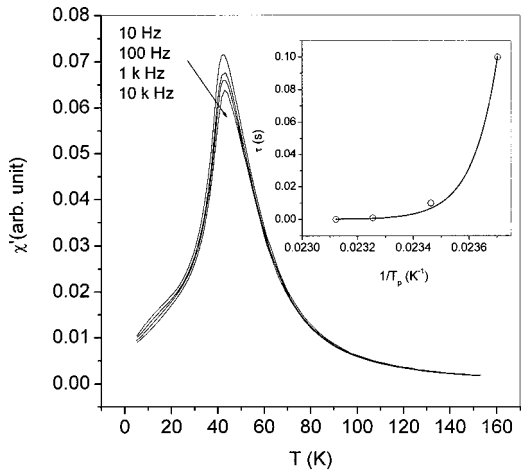

FIG. 8. Temperature dependence of in-phase ac susceptibilities at different frequencies for the $x=0.25$ sample. The inset shows the relaxation time τ as a function of the inverse peak temperature. The solid line is the fit to the Néel-Arrhenius equation explained in the text.

puted using a saturation magnetization of 53.9 emu/g ($\sim 2.0\mu_B$/f.u.) and an effective cluster moment of $\sim 82\mu_B$, is found to represent the magnetization behavior at temperatures >30 K. At temperatures below 30 K, the curves in Fig. 7 deviate from superposition, indicating the freezing of cluster moments at these temperatures.

It is well known[63] that often it is difficult to distinguish between a superparamagnet and a cluster spin glass experimentally. In particular, the H/T scaling of the static magnetization above the freezing temperature (Fig. 7) is no positive proof for independent superparamagnetic clusters, i.e., the absence of magnetic interactions. An attempt has been made to distinguish the two by measuring the frequency dependent ac susceptibility as a function of temperature, $\chi(f,T)$ (Fig. 8) for the $x=0.25$ sample. A frequency-dependent shift of the susceptibility peak temperature can be seen in Fig. 8. Assuming thermally activated relaxation, it is possible to describe the ac susceptibilities for independently relaxing magnetic clusters by the Néel-Arrhenius law with a relaxation time τ given by[64]

$$\tau = \tau_0 \exp(KV/k_B T). \tag{3}$$

In this expression K is the magnetic anisotropy energy per unit volume, T is the temperature, and V is the volume of the cluster. The value of τ_o depends on the gyromagnetic precession time and is usually $\sim 10^{-10}$–10^{-13} s for superparamagnetic relaxation.[64] Now $\chi(f,T)$ at any given frequency f is sensitive to magnetic entities having a range of relaxation times (τ) of the order of that frequency.[65] At $T=T_B$, where T_B is the blocking temperature, the relaxation time τ can be equated to the observation time $t_{obs}=1/f$.[65,66] From the peak temperature $T_p(f)$ obtained from the ac susceptibility we may estimate the characteristic freezing or blocking temperatures seen within the observation time. Therefore, fitting τ vs $T_p^{-1}(f)$ according to Eq. (3) should yield the Arrhenius prefactor. However, from the fit (inset of Fig. 8) we find an unphysically small $\tau_0 \sim 10^{-100} \ll 10^{-12}$ s. This indicates that interactions exist[67] among the relaxing magnetic entities, and that the magnetic transition for the $x=0.25$ sample should be described as a collective freezing. Combining this observation with our conclusions about ferromagnetic correlations on a mesoscopic length scale from neutron depolarization, we conclude that the $x=0.25$ sample shows a transition into a cluster-spin glass state at low temperature. A detailed study on the glassy dynamical properties will be published elsewhere.[68]

A cluster spin-glass state was already found in several doped manganites such as in $(La_{1-x}Tb_x)_{2/3}Ca_{1/3}MnO_3$,[21,22] $(La_{1-x}Dy_x)_{0.7}Ca_{0.3}MnO_3$,[20] $La_{0.7-x}Y_xCa_{0.3}MnO_3$,[18] $La_{2/3}Ca_{1/3}Mn_{1-x}In_xO_3$,[40] $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$,[35] etc. However, the difference in the present work is that Ga has been used to substitute the Mn, and Ga is both nonmagnetic and very similar in size to Mn. The microscopic mechanisms responsible for the observed cluster spin-glass behavior in the present $La_{0.67}Ca_{0.33}Mn_{0.75}Ga_{0.25}O_3$ compound is, thus, exclusively due to random magnetic dilution caused by Ga^{3+} ions at the Mn sites. The present work also includes the results of a neutron depolarization study that gives a robust demonstration of a cluster spin glass at 25% of Ga substitution. Comparing with the detailed study on $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_{3-d}$,[39] we find somewhat similar tendencies. However, still a sizeable ferromagnetically ordered moment of 2.5 ($1.86\mu_B$) was found for $x=0.15$ (0.25) of Al, respectively. Higher Al substitution seems to cause also a much more smeared magnetic freezing at low temperatures.[39] This effect may be caused by the different Al^{3+} radius and the reported oxygen understoichiometry in these compounds, which may yield more heterogeneous magnetic states. The magnetic Fe^{3+} substitution seems to have a stronger tendency than the diamagnetic Ga^{3+} to destabilize ferromagnetic long-range order as in Ref. 46 no ordered magnetic moment was found from neutron diffraction for $La_{0.67}Ca_{0.33}Mn_{0.9}Fe_{0.1}O_3$. This can be understood as a consequence of the sizable frustrated antiferromagnetic superexchange involving Fe^{3+} ions. However, the transition temperature for the randomly canted ferromagnetic state in that compound is 108 K, which is rather similar to the transition temperature of 123 K found here for the less canted ferromagnetic state in $La_{0.67}Ca_{0.33}Mn_{0.9}Ga_{0.1}O_3$.

In their theoretical study, Alonso *et al.* did not treat the Fe substitution in $La_{0.67}Ca_{0.33}MnO_3$ in a model with disorder, and, thus, could not describe the important difference between Fe and Ga,[42] which may involve strong, locally random spin-canting and noncollinearly distorted Mn-spin moments near Fe. Some general aspects of the double-exchange-model and predictions for Ga-diluted $La_{0.67}Ca_{0.33}MnO_3$ by Alonso *et al.*[42] are confirmed by our experiments, i.e., the drastic suppression of ferromagnetic order and the occurrence of a glassy behavior with increasing substitution. However, their prediction of magnetic glassiness at higher dilution is based on the competition between a multitude of different *antiferromagnetic* orderings with small coexistence regions between them in the phase-diagram of their theoretical model. This prediction does not agree with the observed cluster glass with ferromagnetic short-range order at $x=0.25$ in our experiment. A more general phase-

separation scenario with competing ferromagnetic and possibly antiferromagnetic order[17] ruled by a quantum critical point in the range $x=0.1-0.2$ Ga substitution remains to be explored experimentally.

IV. SUMMARY AND CONCLUSIONS

The present study on $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ with $x=0$, 0.10, and 0.25 has shown that all the samples have orthorhombic crystallographic structure with *Pbnm* space group; no change of lattice parameters was noticeable. Therefore, structural effects on the electronic band structure should be small. With the substitution of Mn^{3+} by Ga^{3+} the following changes of the magnetic behavior are observed: (i) The magnetic ordering temperature decreases quite drastically. (ii) An irreversibility between the ZFC and FC magnetization vs *T* curves occurs which increases with the increase of Ga substitution. (iii) As detected by neutron diffraction and depolarization measurements, the collinear ferromagnetic state of the parent compound transforms to a locally canted ferromagnetic state for $x=0.10$ and to a cluster-spin glass state for $x=0.25$. Microscopically, the effects of the Ga substitution can be understood as follows: nonmagnetic Ga^{3+} ions do not participate in the ferromagnetic double-exchange interaction, as well as in the antiferromagnetic superexchange interaction. Thus both interactions should be weakened by the substitution. However, the suppression of the itinerant ferromagnetic exchange appears to be more pronounced. This might be related to the effect of an additional electrostatic attraction the Ga^{3+} sites have on the hole charge carriers, as pointed out by Alonso *et al.*[42] The appearance of a randomly canted ferromagnetic phase for the $x=0.10$ sample can be attributed to the shifted balance of both magnetic interactions (toward the antiferromagnetic side) and the random nature of the substitution. For higher degree of Ga substitution ($x=0.25$) the ferromagnetic long-range order is fully lost. Random and competing interactions result in the occurrence of spin clusters with a net magnetic moment. Remaining magnetic coupling of the clusters leads to a cluster-spin glasslike behavior. A broad distribution of cluster size is probable in the $x=0.25$ compound. However, in the present analysis no attempt has been made to take into account any such possibility. Small-angle neutron scattering[45] and wavelength-dependent neutron depolarization study[49,50] may give a quantitative measure of the presence of different sizes for magnetic clusters in the present system, if any.

Summarizing the effect of Ga substitution observed in our experiments one might state that the magnetic properties of Ga substituted $La_{0.67}Ca_{0.33}MnO_3$ are qualitatively similar to those obtained by other substitutions on the Mn site. The significance lies in the fact that these properties are caused by the dilution of the Mn sublattice. Neither a change of the crystal structure has been observed, nor additional magnetic interactions of Mn with the substituted element are involved. Therefore, these experimental results should be useful for a direct comparison with recently established theoretical models.

ACKNOWLEDGMENTS

S.M.Y. is grateful to Dr. S.K. Sikka and Dr. M. Ramanadham for their encouragement and support in this work. M.S. thanks M.S. Hedge for providing the sample preparation facilities and the Alexander von Humboldt Foundation for a fellowship.

*Author to whom correspondence should be addressed. FAX: +91 22 5505151. Electronic address: smyusuf@apsara.barc.ernet.in

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