Evidence of ferromagnetic domains in the La$_{0.67}$Ca$_{0.33}$Mn$_{0.9}$Fe$_{0.1}$O$_3$ perovskite

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The nature of the low-temperature magnetic state of polycrystalline La$_{0.67}$Ca$_{0.33}$Mn$_{0.9}$Fe$_{0.1}$O$_3$ has been studied by magnetization, neutron diffraction, and neutron depolarization measurements. Neutron depolarization measurements indicate the existence of ferromagnetic domains with low net magnetic moments below 108 K. The substitution of Mn^{3+} by Fe^{3+} reduces the number of available hopping sites for the Mn e_g (up) electron and suppresses the double exchange, resulting in the reduction of ferromagnetic exchange. The competition between the ferromagnetic double-exchange interactions and the coexisting antiferromagnetic superexchange interactions and its randomness due to random substitutions of Mn^{3+} with Fe^{3+} drive the system into a randomly canted ferromagnetic state at low temperatures.

I. INTRODUCTION

In recent years there has been a growing interest in ferromagnetic rare-earth manganese perovskites due to the importance of potential technological applications and the fascinating physics involved.[1–6] When a divalent ion (A) is doped in the La site of antiferromagnetic LaMnO$_3$, it introduces mobile e_g electrons that mediate the ferromagnetic interaction between Mn^{3+} and Mn^{4+} within the framework of the double-exchange interaction model.[7] The ferromagnetic interaction is dependent on the on-site Hund's coupling between the t_{2g} core spins and mobile e_g electrons and on the hopping integral t between e_g(Mn)-$2p_\sigma$(O)-e_g(Mn) orbitals.[8] These ferromagnetic interactions must compete with coexisting t_{2g}(Mn)-$2p_\pi$(O)-t_{2g}(Mn) antiferromagnetic interactions. The long-range ferromagnetic and antiferromagnetic interactions can be perturbed when a nonmagnetic or noninteracting ion is partially substituted for manganese ions. There are several such recent studies on magnetic properties of Mn-site substituted La$_{1-x}$A$_x$MnO$_3$ manganese perovskite oxides.[9–15] Such a substitution may introduce disorder and frustration in the system that may eventually lead to a spin-glass-type of behavior. The La$_{0.67}$Ca$_{0.33}$MnO$_3$ compound is a ferromagnet with $T_C=250$ K (Ref. 16) and 275 K (Ref. 17). In a recent study of (i) the irreversibility between zero-field-cooled (ZFC) and field-cooled (FC) magnetization, with a field-dependent branching temperature, (ii) the frequency and field dependence of the ac susceptibility anomaly, and (iii) the magnetoresistance, a spin-glass-type of behavior with a spin freezing temperature of 42 K has been reported by Cai *et al.*,[18] for the La$_{0.67}$Ca$_{0.33}$Mn$_{0.9}$Fe$_{0.1}$O$_3$ compound. Ahn *et al.*[12] have shown that for this amount of Fe a direct replacement of Mn^{3+} by Fe^{3+} occurs. The similar ionic radii of Fe^{3+} and Mn^{3+} mean that lattice distortion effects of the substitution may be ignored. It is a general practice to characterize a spin glass by such characteristic

behaviors in ZFC-FC magnetization and ac susceptibility curves.[19] However, Wang *et al.* have shown for the La$_{0.7}$Ca$_{0.3}$MnO$_3$ ferromagnetic compound that such features can arise from freezing of domains.[20] Among others, in local (randomly) canted spin systems such characteristic behaviors have also been interpreted in terms of kinetic freezing of magnetic domains.[21–23] An inconsistency of the result of Cai *et al.*[18] was the fact that they correlated the peak in resistivity around 42 K (where the metal-to-insulator transition and CMR effect have been found) with the spin-glass freezing temperature. A true double-exchange-mediated spin-glass should be insulating as observed, e.g., in (La$_{2/3}$Tb$_{1/3}$)$_{2/3}$Ca$_{1/3}$MnO$_3$ with $\rho=10^{13}\,\Omega$ cm.[24,25] In this compound, a size of spin clusters of around 18 Å was determined by small-angle neutron-scattering measurements.[26]

In order to identify the magnetic nature that the present material possess, some further clues are needed. Microscopic neutron diffraction and mesoscopic neutron depolarization results provide help. The nature of the sample cannot be determined by bulk magnetic measurements unequivocally. In the present study, we have, therefore, carried out neutron diffraction, polarized neutron transmission (neutron depolarization), and magnetization measurements on La$_{0.67}$Ca$_{0.33}$Mn$_{0.9}$Fe$_{0.1}$O$_3$ in order to know the nature of magnetic ordering in this Fe substituted perovskite.

II. EXPERIMENTAL DETAILS

The sample was synthesized by dissolving stoichiometric amounts of La$_2$O$_3$, CaCO$_3$, MnC$_2$O$_4$·2H$_2$O, and FeC$_2$O$_4$·2H$_2$O in nitric acid. The nitrate solution of metal ions is evaporated to dryness at 300 °C. The black powder is then heated at 800 °C for 24 h. The powder thus obtained was ground well and annealed at 1250 °C for 24 h. Room-temperature powder x-ray diffraction pattern confirmed the single phase formation of orthorhombic perovskite structure

with Pbnm space group for the $La_{0.67}Ca_{0.33}Mn_{0.9}Fe_{0.1}O_3$ compound, as reported for the $La_{0.7}Ca_{0.3}Mn_{1-x}Fe_xO_3$ compounds with $x=0.0$, 0.02, 0.04, 0.06, 0.08, 0.10, and 0.12.[14] The lattice parameters are found to be $a=5.488(1)$ Å, $b=5.469(3)$ Å, and $c=7.790(3)$ Å.

ZFC and FC dc magnetization measurements in dependence on temperature and magnetic field were carried out on a polycrystalline sample of $La_{0.67}Ca_{0.33}Mn_{0.9}Fe_{0.1}O_3$ in a vibrating sample magnetometer in the temperature range of 3.8–300 K and the field range of 80 kOe. All measurements were carried out on compacted powder samples. Compacting ensures that rotation of the crystallites does not take place. In ZFC measurements the sample was cooled from room temperature to 3.8 K in zero field. A field of 100/3000 Oe was applied at 3.8 K, and then the ZFC magnetization measurements were carried out in the heating cycle. For the FC case, on the other hand, the sample was first cooled from room temperature to 3.8 K in the presence of 100/3000 Oe field (the measuring field used afterwards). The measurements were then carried out (keeping the field on) in the heating cycle, as in the ZFC case.

Neutron-depolarization study, a good tool to probe the magnetic inhomogeneity on a mesoscopic length scale,[27–31] was carried out using the neutron-polarization analysis spectrometer (PAS) at Dhruva reactor, Trombay ($\lambda=1.205$ Å). The detailed description of the spectrometer has been given in earlier papers.[32,33] 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. The one-dimensional neutron-depolarization measurements were carried out in the heating cycle in presence of 10 Oe external field after cooling the sample in the same field of 10 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 an earlier paper.[32] The powder sample used for the depolarization study was in the form of a pellet of cylindrical dimension. The sample was placed in the neutron beam in such a way that its plane surface (xz) remains perpendicular to the propagation direction (y) of the polarized neutron beam. The beam passed through an effective sample thickness of 6 mm. The beam size was restricted with a cadmium slit, which is within the size of the sample. The external magnetic field of 10 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 at 15, 125, and 300 K on the PAS in its unpolarized mode over the lower 2θ angular range of $\sim12°-33°$ where magnetic Bragg scattering intensities are predominantly expected (if any). The temperature variation of diffracted intensity at the peak positions of the (110) and (002) Bragg peaks was studied from 15 to 150 K. The diffraction measurements were carried out on the polycrystalline sample with no external magnetic field.

III. EXPERIMENTAL RESULTS AND DATA ANALYSIS

Figure 1 shows the temperature dependence of the ZFC and FC magnetization at 100 and 3000 Oe. Irreversibility
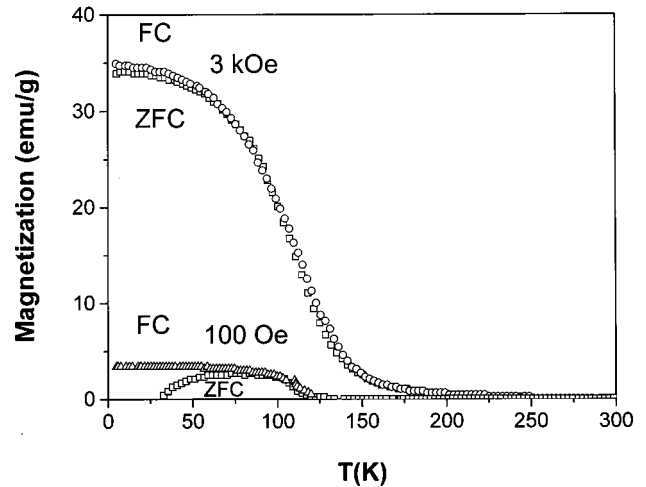

FIG. 1. Magnetization vs temperature measured during warming in applied fields of 100 and 3000 Oe, after the sample had been zero-field cooled (ZFC) or field-cooled (FC), respectively.

between the ZFC and FC magnetization curves is clearly seen at low temperatures. The irreversibility decreases with the increase of field value as reported by Cai *et al.*,[18] and found to persist even under a field of 3000 Oe. The ZFC data show a broad maximum around 80 K at 100 Oe field. No down turn in the FC curve at any temperature is found, which indicates that there is no loss of magnetization at low temperatures (down to 3.8 K) even at low applied fields. If the transition temperature is taken as the inflection point in the magnetization vs T curve, the magnetic ordering temperature clearly increases as the applied magnetic field increases similar to what was reported in Ref. 11.

Figure 2 shows the magnetic hysteresis loop recorded at 3.8 K. It is clearly seen that the saturation of magnetization is not achieved even under 80 kOe field. The value of magnetization at 3.8 K under 80 kOe field is found to be 54.6 emu g^{-1} ($\sim2.0\mu_B$ per Mn/Fe site). This value of moment is appreciably below the expected free ion value for $57\%\,Mn^{3+}$, $33\%\,Mn^{4+}$, and $10\%\,Fe^{3+}$. The inset in Fig. 2, depicting the low-field magnetization data over ±5 kOe at
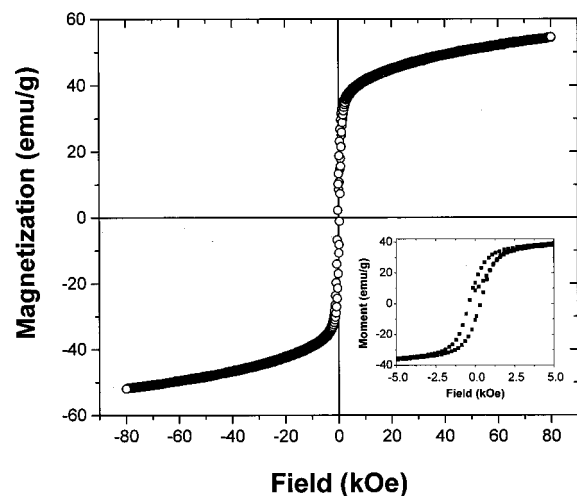

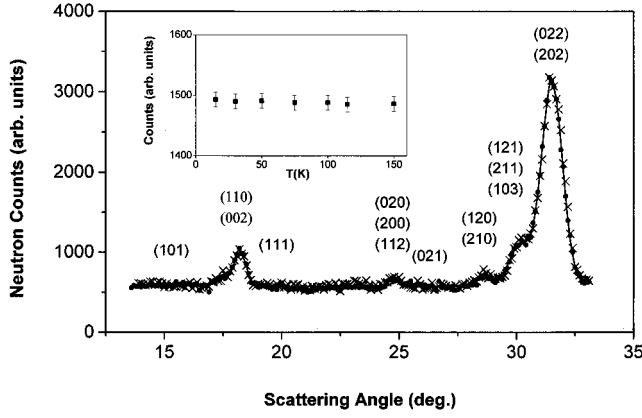FIG. 2. Hysteresis loop recorded at 3.8 K. The inset enlarges the low field range of ±5 kOe.

FIG. 3. Neutron diffraction patterns at 125 K (crosses) and 15 K (solid circles) recorded over the lower angular range of ~ 12–$33°$ where magnetic Bragg scattering intensities are predominantly expected (if any). The *hkl* values are marked above the respective scattering angles. The solid line represents the calculated pattern only with nuclear scattering. The inset shows the combined peak intensity of (110) and (002) Bragg peaks as a function of temperature.

FIG. 4. Temperature dependence of the transmitted neutron beam polarization P, measured at 10 Oe applied field.

3.8 K, shows the presence of hysteresis with a low coercive field of $H_c \sim 350$ Oe. From this curve, a magnetization of about 35 emu g^{-1} at technical saturation can be estimated.

Figure 3 shows neutron powder diffraction patterns recorded at 125 and 15 K (well above and below the magnetic ordering temperature of 108 K, obtained from the neutron depolarization study). At 15 K, no extra Bragg intensity to the nuclear (fundamental) peaks is observed as compared to the 125 K pattern. The neutron diffraction data recorded at 15 K were analyzed by the Rietveld method using the FULL-PROF program.[34] The refinement shows no ferromagnetic ordered magnetic moment present in the compound. It may be stressed that no additional Bragg peaks are also found, indicating the absence of any other long-range-ordered magnetic phase (antiferromagnetic, spiral, etc.) in this compound. It is estimated using the FULLPROF program that an ordered moment of $\sim 0.6 \mu_B$ per (Mn/Fe) site sets the lower limit of the measurable ordered moment using the present neutron-diffraction technique. The absence of a magnetic contribution to the (110) and (002) nuclear Bragg peaks is evident from the inset shown in Fig. 3.

Before presenting the experimental results of our neutron-depolarization study, we briefly recall the theory of neutron depolarization in various magnetic systems.[27,28,30] Neutron depolarization is a mesoscopic probe. It can measure the spatial magnetic inhomogeneity on a length scale, say, from 100 Å 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 true spin-glass state—has no effect on the neutron polarization. In a true spin-glass phase, the 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
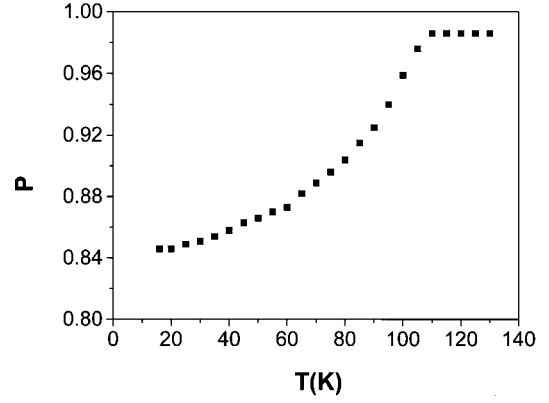
length scale. Hence no depolarization is found in true spin-glass systems. Similarly no depolarization is expected in the paramagnetic state because the temporal spin fluctuation is too fast (10^{-12} s or faster) for the neutron polarization to follow the variation in the magnetic field B acting on 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. The advantages of neutron depolarization technique are that the domain size information can be obtained (as an average over the entire sample), and there are essentially no resolution restrictions on the size of the domains, which can be measured.

The temperature dependence of the transmitted neutron beam polarization P for an applied field of 10 Oe is depicted in Fig. 4. The procedure of obtaining P values from the measured flipping ratios for the transmitted polarized beam is described elsewhere.[32] P shows a continuous decrease right from 108 K and the tendency to attain a constant value below about 20 K. At $T > 108$ K, the value of P is the same as the incident beam polarization. This implies that the sample is in its paramagnetic phase above 108 K where no change of neutron polarization is expected. The magnetic ordering temperature for this sample is thus estimated to be 108 K. The presence of domains or clusters of spins with net magnetic moments is confirmed from the occurrence of significant depolarization down to 15 K, the lowest temperature of measurement. From the observed depolarization an estimate of the average size of domains/clusters was made using the expression[27,29]

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

where P_i and P_f are the initial and final neutron beam polarization, α is a dimensionless parameter $\approx \frac{1}{3}$, $d (= 6$ mm) is the effective thickness of the sample, δ is the average domain size, and $\Phi_\delta = (4.63 \times 10^{-10}$ G^{-1} Å^{-2})$\lambda \delta B$ the precession angle. The internal mean induction $B(G) = 4\pi M_S \rho$ within a domain at low temperature was estimated from the bulk magnetization measurements. Here M_S is the spontaneous magnetization in emu g^{-1} and ρ is the density of the material in g cm^{-3}. The magnetization value of 35 emu g^{-1}, obtained from the technical saturation of magnetization at 3.8 K, can be used for a first estimate of B. The mean B of ~ 2600 G is

obtained using the average sample density of 5.95 g cm^{-3}. Equation (1) is valid with the assumption that the Larmor precession angle of the neutron spin due to the internal magnetic fields of the sample is a small fraction of 2π over a typical domain/cluster length. The value of Φ_δ for a 1.205 Å neutron in a 10 μm Fe domain ($B \sim 20$ kG) is ~ 1.1 rad. In the compound we are studying, the value of B is only ~ 2600 G and allows Eq. (1) to be valid up to large domain sizes of about 100 μm. Using the above expression, as used in the literature,[35] an average domain/cluster size of ~ 0.4 μm is obtained at 20 K. The estimate of the domain size could be improved by measuring the wavelength dependence of transmitted neutron beam polarization $P(\lambda)$.[28,29] Another factor, which probably introduces an error to the estimated value of δ is the internal mean induction B. In a well-behaved ferromagnet, B is well represented by the saturation magnetization. However, in systems where spins are canted, the applied field may suppress the domain walls but it could simultaneously align the spins on a microscopic length scale, so that B increases with the applied field. This effect is revealed, for our sample, by the increasing magnetization measured in high fields (Fig. 2). Magnetization shows a knee around 2.6 kOe, which locates the onset of technical saturation and is attributed to the suppression of the Bloch walls. The microscopic spin alignment is clearly evident above 2.6 kOe by the residual slope of the technical saturation plateau up to 80 kOe. The magnetization at technical saturation gives an overestimated B. This is reflected by the fact that a spontaneous magnetization of 35 emu g^{-1} ($\sim 1.3\mu_B$ per Mn/Fe site) should be clearly visible in the neutron diffraction data, which is not the case. It is, therefore, evident that the actual spontaneous magnetization of the compound is lower. Since the field-cooled magnetization corresponds to the magnetization at thermodynamic equilibrium state, Abdul-Razzac and Kouvel[36] deduced a value of the spontaneous magnetization in some reentrant spin-glass system by cooling the sample from above the ordering temperature in several applied fields and extrapolating to zero value of the cooling field. It was found that the obtained M_S was considerably lower than the magnetization measured at the onset of technical saturation. We have also estimated M_S following this method and obtained a value of 15 ± 5 emu g^{-1}. The corresponding low magnetic moment of $0.56\mu_B$ per Mn/Fe site is below the detection limit of the neutron diffraction experiment. The estimate of the average domain size, thus, gives 2 μm. Further sources of uncertainty in the domain size cannot be ruled out now: (i) The calculation of B is done assuming a homogeneous magnetic state. However, a phase segregation in the present system, as observed in other perovskites[37,38] cannot be ruled out. If the ferromagnetic domains represent only a certain volume percentage of the sample, the estimate of B will again be influenced. (ii) Inaccuracy (if any) arising from the assumption of the presence of only one type of domain size can be handled by performing the wavelength dependence of the neutron depolarization.[28,29] (iii) Further uncertainty in the δ value could arise from the assumptions of the domain structure model used here, and a full three-dimensional polarization analysis[30] would be useful in this regard. It seems that model-dependent corrections will in-

crease the derived domain size. Hence, the obtained domain size of about 2 μm is expected to reflect the correct order of magnitude.

Depolarization data do not reveal any transition at low temperature (around 42 K). No evidence of breakdown of domain structure at low temperatures (which results in a recovery of the transmitted neutron beam polarization P (Ref. 29) is found. The temperature dependence of P is typical for a system with ferromagnetic domains. For instance, the wavelength dependence study of $P(\lambda)$ at various temperatures in Ref. 29 showed that the observed temperature variation of polarization with decreasing temperature comes from the thermal increase of the mean induction within a domain and that the domain size is temperature independent. For our sample, the temperature dependence of P is correlated with the temperature dependence of the magnetization at technical saturation, M_S^*, like $\ln[P_f(T)/P_i] = F[M_S^*(T)]^2$, with a constant factor F. A deviation from this behavior only appears above 90 K, near the magnetic ordering temperature, where the ratio of M_S/M_S^* will be increasingly larger. Referring to Eq. (1), this result indicates a temperature-independent domain size.

IV. DISCUSSION

Our depolarization study confirms that domains with net magnetic moments exist in the La$_{0.67}$Ca$_{0.33}$Mn$_{0.9}$Fe$_{0.1}$O$_3$ perovskite compound. The domains are found to be quite large (~ 2 μm). However, the neutron diffraction study does not show the presence of any magnetic Bragg intensity. It is therefore suggested that the spins are highly canted in this compound.[39] The possibility of uniform canting of spins is ruled out from the absence of any observed magnetic Bragg peak intensity. The canting of Mn/Fe site moments is, therefore, assumed to be random (local) from site to site so that the ordered component of moments that gives a long-range ferromagnetic ordering over the domain is quite less in magnitude ($< 0.6\mu_B$ per Mn/Fe site). Since Fe^{3+} replaces Mn^{3+}, doping with Fe reduces the Mn^{3+}/Mn^{4+} ratio. In the electron hopping mechanism between the Mn^{3+} and Mn^{4+} only the Mn e_g (up) electron (responsible for the double-exchange mechanism) is active. The Fe e_g (up) band is completely filled and electron hopping from Mn^{3+} to Fe^{3+} is forbidden. Thus the doping of Fe at the Mn site reduces the number of available hopping sites and suppresses the double exchange, resulting in the reduction of ferromagnetic exchange, and metallic conduction. The antiferromagnetic superexchange interaction prevails between Fe^{3+} and its neighboring Mn^{3+} or Mn^{4+} or Fe^{3+} (if there is any) along with coexisting t_{2g}(Mn)-$2p_\pi$(O)-t_{2g}(Mn) antiferromagnetic interactions. These antiferromagnetic interactions compete with coexisting ferromagnetic interactions. It is highly probable that the random substitutions of Mn^{3+} with Fe^{3+} lead to a randomness of the signs of the local exchange coupling (ferromagnetic or antiferromagnetic) being responsible for the random (local) canted spin canting in the present compound. The continuous drop of the transmitted neutron beam polarization P right from 108 K down to about 20 K (below which temperature P shows a tendency to attain almost a constant value) indicates no breakdown of domain structure at any temperature below the ordering temperature ($= 108$ K). Fur-

thermore, the smooth variation of P rules out any abrupt change in the magnetic ordering process as a function of temperature. We have estimated the ordering temperature (~ 108 K) from the low-field depolarization study as it varies with the applied magnetic fields in the magnetization measurements (Fig. 1), similar to what was reported by Pissas et al.[11] for the $La_{0.75}Ca_{0.25}Mn_{0.98}Fe_{0.02}O_3$ compound that shows a ferromagnetic cluster behavior (with a size distribution) in the Mössbauer spectroscopy experiment.[11]

The observed irreversibility between the ZFC and FC magnetization curves (Fig. 1 and Ref. 18), as well as the characteristic dependency of ac susceptibility on frequency and amplitude of the ac field[18] seem to indicate the kinetic freezing of these domains of randomly canted spins, which strongly depends upon the cooling process of the sample. Some of us have shown (in a different class of systems) that all the features in ac susceptibility, ZFC, and FC magnetization that are mimics to a spin-glass phase transition can occur from kinetic freezing of magnetic domains.[22,23,40] The nonsaturation behavior of magnetization, reduced magnetization, irreversibility between the ZFC and FC magnetization curves, the field-dependent branching temperature of ZFC-FC magnetization, etc., support the presence of a canted spin state. The broad peak in ZFC magnetization has previously been observed in many other types of systems[22,23,40,41] and explained in the following way. Owing to reduced spin fluctuations, a higher value of magnetization is expected at lower temperatures. If magnetic hardness also shows a higher value at lower temperatures these two will have opposite effects on the temperature dependence of magnetization. This can produce a peak in the ZFC curve with the peak temperature shifting to a lower value as the applied magnetic field increases.

It seems worth mentioning that the low net magnetic moment observed for the ferromagnetic domains in $La_{0.67}Ca_{0.33}Mn_{0.9}Fe_{0.1}O_3$ indicates the proximity of a critical Fe concentration where ferromagnetic long-range order will vanish. Neutron depolarization measurements would provide a sensitive tool to determine the magnetic nature of samples near such a critical concentration.

V. SUMMARY AND CONCLUSION

We have carried out magnetization, neutron diffraction, and neutron depolarization measurements in order to know the nature of the low-temperature magnetic state of polycrystalline $La_{0.67}Ca_{0.33}Mn_{0.9}Fe_{0.1}O_3$ perovskite. The neutron diffraction study does not show any ferromagnetic Bragg contribution to the nuclear peaks or extra Bragg peaks at low temperatures. However, the neutron depolarization study confirms the presence of ferromagnetic domains with low net moments below the ordering temperature ($=108$ K). The substitution of Mn^{3+} by Fe^{3+} reduces the number of available hopping sites for the Mn e_g (up) electron and suppresses the double exchange, resulting in the reduction of ferromagnetic exchange. Due to the competition of this ferromagnetic exchange interaction with coexisting antiferromagnetic superexchange interactions and the random substitution of Mn^{3+} with Fe^{3+}, a randomly canted ferromagnetic phase with very low net domain moment seems to occur.

ACKNOWLEDGMENTS

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