Influence of B-site disorder in La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$B$_x$O$_3$ (B = Fe, Ru, Al and Ga) manganites

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Abstract
We have investigated the influence of B-site doping on the crystal and magnetic structure in La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$B$_x$O$_3$ (B = Fe, Ru, Al and Ga) compounds using neutron diffraction, small angle neutron scattering, magnetization and resistivity techniques. The B-site doped samples are isostructural and possess an orthorhombic structure in the $Pnma$ space group at 300 K. A structural transition from orthorhombic to monoclinic is found to precede the magnetic transition to the CE-type antiferromagnetic state in a few of these samples. On doping with Fe, the charge and orbitally ordered CE-type antiferromagnetic state is suppressed, followed by growth of the ferromagnetic insulating phase in $0.02 \leq x \leq 0.06$ compounds. At higher Fe doping in $x > 0.06$, the ferromagnetic state is also suppressed and no evidence of long range magnetic ordering is observed. In Ru doped samples ($0.01 \leq x \leq 0.05$), the ferromagnetic metallic state is favored at $T_C \approx 200$ K and $T_{MI} \approx 125$ K and no significant change in $T_C$ and $T_{MI}$ as a function of Ru doping is found. In contrast, with non-magnetic Al substitution for $0.01 \leq x \leq 0.03$, the charge ordered CE-type antiferromagnetic state coexists with the ferromagnetic metallic phase. With further increase in Al doping ($0.05 \leq x \leq 0.07$), both CE-type antiferromagnetic and ferromagnetic phases are gradually suppressed. This behavior is accompanied by the evolution of an A-type antiferromagnetic insulating state. Eventually, at higher Al doping ($0.10 \leq x \leq 0.13$), this phase is also suppressed and the signature of a spin glass like transition is evident in $M(T)$. Likewise, substitution with Ga is observed to induce similar effects to those described for Al doped samples. The presence of short range ferromagnetic ordering has been further explored using small angle neutron scattering measurements in a few of the selected samples.

1. Introduction

Perovskite manganites $R_{1-x}A_xMnO_3$ ($R$: trivalent rare earth ion and $A$: divalent alkaline earth ion, Ca, Ba or Sr) have been widely studied due to the presence of a variety of phenomena, namely colossal magnetoresistance, charge, orbital, and spin ordering and phase separation behavior. In particular, the nature of charge, orbital and spin ordering is strongly influenced by various perturbations such as disorder effects at the rare earth ($A$) site and transition metal ($B$) site, hydrostatic pressure, magnetic and electric field, and by varying the particle size [1–5].

Several experimental and theoretical studies have been devoted to investigating substitutional disorder effects in charge ordered manganites. Generally, two sources of substitutional disorder have been described in charge ordered manganites: $A$-site and $B$-site disorder. The magnetic and transport properties in several systems are observed to be systematically influenced by structural distortions and lattice disorder associated with the average $A$-site ionic radii ($\langle r_A \rangle$).
and variance ($\sigma^2$) due to size mismatch between the A-site cations [6–10]. The B-site substitution, as against A-site, induces disorder directly in the Mn–O network, leading to much stronger impact on the magnetic and transport properties. The high sensitivity of the charge and orbitally ordered antiferromagnetic state to B-site disorder has been studied in several half-doped $\text{R}_0.5\text{A}_0.5\text{MnO}_3$ manganites [5, 11–13]. These studies show that a few per cent of Mn-site doping brings about drastic changes in the magnetic and transport properties, without significantly influencing the crystal structure. B-site dopants such as Cr, Ru, Ni, or Co in low bandwidth $\text{R}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ($R = \text{Nd}, \text{Pr}, \text{and Sm}$) manganites are able to suppress the robust charge ordered state and effectively induce ferromagnetic tendencies [14–31]. Among these, Ru doping is found to rapidly suppress the antiferromagnetic phase and stabilize the long range ordered ferromagnetic metallic phase. Hebert et al [14] have shown that the elements with d^9 or d^10 configuration and those without d orbitals do not induce ferromagnetism, whereas those with d electrons cause suppression of the antiferromagnetic phase at the expense of the ferromagnetic state. However, Fe^{3+} ions, despite having the d^3 electronic configuration, are shown to belong to the former category, displaying no evidence of the ferromagnetic state in the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ sample. In contrast, the magnetization and transport studies on intermediate bandwidth $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ compounds show the favoring of the ferromagnetic phase for $x < 0.05$, while for higher Fe doping the ferromagnetic transition temperature decreases, leading the system toward a spin glass like state [32–35]. Recent investigations show that the systems with non-magnetic dopants (d^9 or d^10), such as $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$, may also favor ferromagnetic tendencies [40]. In contrast, in the Ga substituted $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ system, the gradual emergence of a charge ordered phase at the expense of the ferromagnetic phase is observed [41]. In the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ and $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Ga}_x\text{O}_3$ series, the contrasting magnetic behavior with Al and Ga doping is ascribed to preferential substitution of Mn^{3+} with Al^{3+} and Mn^{3+} with Ga^{3+} ions due to their similar ionic radii. Most of these studies carried out using magnetization and transport techniques highlight the transition from charge ordered insulating to ferromagnetic metallic state. The phase separation behavior as a result of low temperature decreases, leading the system toward a spin glass like state [32–35]. Recent investigations show that a few per cent of Mn-site doping brings about drastic changes in the magnetic and transport properties, while the one with smaller distortion increases. Neutron diffraction analysis in the $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ compound reveals the suppression of orthorhombic to charge and orbitally ordered monoclinic structural transition upon doping with Cr or Ni and favors the ferromagnetic phase [46]. The role of B-site substitution on the charge and spin structure in half-doped manganites has also been theoretically investigated [47–50]. The phase separation behavior observed in these B-site doped compounds has been attributed to a small valence change driven variation in the carrier density. These studies also show that the non-magnetic dopants also favor the stabilization of the ferromagnetic state. This behavior is ascribed to lattice defects and e_g carrier density. The destabilization of the charge and orbitally ordered CE-type antiferromagnetic state is followed by the evolution of a ferromagnetic state with or without the C-type antiferromagnetic or spin glass like phases. Although the previously reported studies have established the destabilization of the charge and orbitally ordered state by non-magnetic and magnetic dopants, very few neutron diffraction studies exist which reproduce the theoretically postulated magnetic structures.

In the present work, we have investigated the influence of B-site disorder on the crystal and magnetic structure in the $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ system primarily using neutron diffraction and small angle neutron scattering techniques. The $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ compound undergoes successive ferromagnetic metallic transition at $T_C \approx 230$ K and CE-type antiferromagnetic insulating transition at $T_K \approx 170$ K [51, 52]. We have studied the polycrystalline $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{B}_x\text{O}_3$ ($B = \text{Fe}, \text{Ru}, \text{Al}$, and Ga) compounds. The choice of dopants is due to the contrasting magnetic ground states these are expected to induce. Destabilization of the charge and orbitally ordered antiferromagnetic state against B-site disorder is observed. Depending on the dopants, these are found to induce a long range ordered ferromagnetic metallic or insulating state, or a short range ordered ferromagnetic phase with or without coexisting antiferromagnetic phases. In compounds with magnetic doping of Fe and Ru, no signature of magnetic phase coexistence behavior is found. Interestingly, we have found that non-magnetic substitution (Al or Ga) in the $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ compound leads to a coexistence of a CE-type state and ferromagnetic ordering for $x \leq 0.03$ and favors A-type antiferromagnetic structure in $0.05 \leq x \leq 0.07$ samples. For higher Al and Ga concentrations the system evolves into a magnetically disordered state. This behavior is in contrast to the magnetic dopants where the evolution of an A-type antiferromagnetic phase is not found. In this study, we also do not observe C-type antiferromagnetic structure following the melting of the CE-type state shown in the theoretically proposed phase diagram [47].

2. Experimental method

The polycrystalline samples were synthesized by a conventional solid-state reaction method. The starting materials $\text{La}_2\text{O}_3$, $\text{Mn}_2\text{O}_3$, $\text{CaCO}_3$, $\text{Fe}_2\text{O}_3$, $\text{Ru}_2\text{O}_3$, $\text{Al}_2\text{O}_3$, and $\text{Ga}_2\text{O}_3$ were mixed in proper stoichiometric ratio and fired at 1250 °C for 48 h. The samples were then repeatedly ground and heat treated at 1400 °C for 48 h. Finally, the samples were pelletized and sintered at 1450 °C for 48 h. Initial values
of cell parameters and phase identification of all the samples at 300 K were obtained from their x-ray powder diffraction patterns recorded on a Rigaku diffractometer of rotating anode type using Cu Kα radiation. Neutron diffraction patterns were recorded on a multi-PSD based powder diffractometer \( (\lambda = 1.249 \text{ and } 1.2443 \text{ Å}) \) at Dhruva Reactor, Bhabha Atomic Research Centre, Mumbai, at selected temperatures between 5 and 300 K, in the \( 5^\circ \leq 2\theta \leq 140^\circ \) angular range. The powdered samples were packed in a cylindrical vanadium container and attached to the cold finger of a closed cycle helium refrigerator. Rietveld refinement of the diffraction patterns was performed using the FULLPROF program [53]. The magnetization measurements were carried out using a SQUID (Quantum Design, USA) or VSM magnetometer (Oxford Instruments). The standard four point probe technique was used to measure the dc resistivity between 3 and 300 K. Small angle neutron scattering (SANS) measurements \( (\lambda = 4.52 \text{ and } 7.03 \text{ Å}) \) as a function of temperature between 15 and 300 K in the \( Q \) range \( 0.007 \text{ Å}^{-1} \leq Q \leq 0.3 \text{ Å}^{-1} \) were carried out on the SANS-II instrument at the Swiss Spallation Neutron Source, Paul Scherrer Institute, Switzerland [54].

3. Results and discussion

3.1. Crystal structure

All the B-site doped compounds studied here in the series \( \text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{B}_{x}O_{3} \) \( (B = \text{Fe } (0.01 \leq x \leq 0.1), \text{Ru} (0.01 \leq x \leq 0.05), \text{Al} (0.01 \leq x \leq 0.13), \text{and } \text{Ga} (0.01 \leq x \leq 0.07)) \) are isostructural, possessing orthorhombic structure (space group \( \text{Pnma} \)) at 300 K. These compounds crystallize in \( O' \) orthorhombic symmetry characterized by \( b/\sqrt{2} \leq a \leq c \) [55, 56]. The refinement of x-ray diffraction patterns at 300 K reveals that the volume as a function of doping \( (x) \) with \( B = \text{Fe, Ru, Al, and Ga} \) does not change appreciably or show any systematic behavior. This could be due to the small concentration of dopants and very small difference in the value of ionic radii between the Mn ions and the dopants [57].

Figure 1 shows the neutron diffraction pattern of the \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_{3} \) \( (x = 0) \) compound. On lowering the temperature below the charge ordering temperature, \( T_{CO} \approx 200 \text{ K} \) (on heating), structural transition to a lower symmetry monoclinic structure in \( \text{P2}_1/m \) space group is found, as has been reported earlier in similar systems exhibiting the charge ordering behavior [51]. A signature of this in the form of splitting of the nuclear Bragg reflections \( (0 0 4) (4 4 2) \) in the \( \text{Pnma} \) space group to \( (0 0 8) (4 4 2) \) and \( (4 4 2) \) in the \( \text{P2}_1/m \) space group is observed below \( T_{CO} \). The patterns displayed in the inset to figure 1 show the structural transformation of the orthorhombic phase in the \( \text{Pnma} \) space group to the charge and orbitally ordered monoclinic phase in the \( \text{P2}_1/m \) space group. In the \( \text{P2}_1/m \) space group, the Mn\(^{3+}\) and Mn\(^{4+}\) ions occupy two distinct sites, in accordance with the charge order scenario proposed in the Goodenough model [58]. Nevertheless, the Goodenough model has been challenged by experiments, which have presented evidence for charge disproportion in several half-doped manganites. Studies reveal that this ionic picture proposed in the Goodenough model of the Mn\(^{3+}\) and Mn\(^{4+}\) ions may not be true, and the Zener polaron model [59, 60] has been proposed, in which all the Mn sites become equivalent with a valence of +3.5. Herrero-Martín et al have probed the local structure around Mn ions in charge ordered systems using resonant scattering of a synchrotron x-ray beam and show the presence of fractional charge segregation [61]. This disagreement between the two models is still not settled in the literature. We find, in the absence of high resolution data, similar values of \( \chi^2 \) and \( R \)-factors on fitting the diffraction data in both the \( \text{Pnma} \) and \( \text{P2}_1/m \) space groups. Additionally, lowering of the symmetry to the \( \text{P2}_1/m \) space group requires the refinement of 29 positional parameters as against 7 in the \( \text{Pnma} \) space group. This reduces the reliability of the obtained positional parameters. Therefore, the low temperature crystal structure is refined in the \( \text{Pnma} \) space group, which yields an average structure. Similar refinement of the neutron diffraction pattern has been performed in the \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) compound, which is in agreement with Radaelli et al [51]. The obtained values of the structural parameters are in agreement with the previously reported studies on the \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) compound [51].

For comparison the selected portion of the neutron powder diffraction patterns between \( 53^\circ \leq 2\theta \leq 56.5^\circ \) for the \( \text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.96}\text{B}_{0.04}O_3 \) \( (B = \text{Fe, Ru, Al, and Ga}) \) samples is shown in figure 2. In the \( \text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.96}\text{Fe}_{0.04}O_3 \) (Fe 1% doping) sample an orthorhombic to monoclinic structural transition (figure 2(a)), similar to the \( x = 0 \) compound, is observed. In samples with higher Fe doping (0.02 \( \leq x \leq 0.10 \)) this splitting is suppressed. This indicates the
suppression of charge and orbital ordering with increasing Fe doping. In contrast, a similar doping concentration of Ru (1%) is found to suppress the monoclinic structural transformation and the orthorhombic structure in the \( Pnma \) space group is retained down to the lowest temperature of 22 K, as shown in figure 2(b). On substitution with Al and Ga (\( x \leq 0.03 \)), the signature of structural transformation from orthorhombic to charge and orbitally ordered monoclinic structure is observed, as shown in figures 2(c) and (d). On increasing the doping level in \( x \geq 0.03 \) samples, the signature for the presence of monoclinic structure gradually disappears. This behavior is similar to that observed in Ni and Cr doped \( La_{0.5}Ca_{0.5}MnO_3 \) compounds by Martinelli et al using a neutron diffraction technique [46].

The cell parameters as a function of temperature in the 1% Fe doped sample are shown in figure 3. On reducing the temperature below 300 K, the lattice parameters exhibit an anomalous behavior, while the volume displays a nearly linear temperature dependence. The lattice parameter \( b \) shows a drastic decrease while \( a \) and \( c \) expand on lowering the temperature. As a consequence, in the neutron diffraction pattern the \((2\ 0\ 2)\) and \((0\ 4\ 0)\) nuclear Bragg reflections which merge at 300 K exhibit splitting when cooling below \( T \leq 225 \) K in the 1% Fe doped compound. This anomalous behavior is associated with ordering of \( d_{z^2} \) orbitals in the \( a\)-\( c \) plane, which is in agreement with other similar charge ordered systems [51]. The temperature at which orbital ordering occurs is found to coincide with the charge ordering temperature. The charge ordering transition is the temperature below which the resistivity shows a steep rise. The transition to a charge and orbitally ordered state is accompanied by an increase of strain in the \( a\)-\( c \) plane, as evidenced in the \( La_{0.5}Ca_{0.5}MnO_3 \) compound [52]. Also, Ahn et al have reported the importance of uniform strain in stabilization of the charge ordered phase [62]. To describe the orthorhombic strains, Meneghini et al defined \( OS_{||} = 2(\frac{\sqrt{2}a}{c+a}) \) distortions in the \( ac \) plane and \( OS_{\perp} = 2(\frac{\sqrt{2}a\sqrt{2}}{c+a+b}) \) along the \( b \) axis [63]. The charge and orbital ordering transition is accompanied by a sharp increase in the orthorhombic strain parameters \( OS_{||} \) and \( OS_{\perp} \) [52].

![Figure 2](https://example.com/figure2.png)  
Figure 2. A selected portion \((53^\circ \leq 2\theta \leq 56.5^\circ)\) of the neutron diffraction patterns collected around the orthorhombic to monoclinic structural transition for \( La_{0.5}Ca_{0.5}Mn_{0.99}B_{0.01}O_3 \) samples with (a) \( B = Fe \), (b) \( B = Ru \), (c) \( B = Al \) and (d) \( B = Ga \).

![Figure 3](https://example.com/figure3.png)  
Figure 3. Temperature dependence of the lattice parameters and the unit-cell volume for the \( La_{0.5}Ca_{0.5}Mn_{0.99}Fe_{0.01}O_3 \) (Fe 1%) sample. The inset to the figure shows the temperature dependence of the orthorhombic strains \( OS_{\perp} \) and \( OS_{||} \) in the \( La_{0.5}Ca_{0.5}Mn_{0.99}Fe_{0.01}O_3 \) sample. The continuous lines are a guide for the eye.
The orthorhombic strains $O_{3,⊥}$ increases below 100 K, as shown in the inset to figure 3. The strain observed. A minimum in $T_{\text{La}}$ has been reported previously in neutron diffraction studies on $\text{Os}$ As a consequence, no significant change in cell parameters exhibit nearly linear reduction while cooling. With the onset of the ferromagnetic transition temperature $T_{\text{C}} \sim$ is observed at 225 K, both $O_{3,⊥}$ and $O_{3,∥}$ increase and become nearly constant below 100 K, as shown in the inset to figure 3. The strain increases below $T_{\text{C}}$ and, therefore, favors the stabilization of the charge ordered phase. Figure 4 shows the variation of the cell parameters as a function of the temperature for the 2% Fe doped compound. In contrast to the 1% Fe doped sample, here the cell parameters $a$, $b$, and $c$ decrease on lowering of the temperature. However, below 100 K, an anomalous behavior is observed. A minimum in $b$ is found at 100 K, which coincides with the onset of the ferromagnetic transition temperature ($T_{\text{C}}$). This plausibly indicates that the onset of ferromagnetic ordering is accompanied by the reorientation of orbitals. The temperature dependence of the lattice parameters in the 4% Fe doped samples exhibits a similar decrease on lowering the temperature and a minimum in the lattice parameter $b$ at 125 K, coinciding with $T_{\text{C}}$. A similar temperature dependence of the lattice parameters, with a minimum in $b$ close to $T_{\text{C}}$, has been reported previously in neutron diffraction studies on $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ for $\text{B = Ni and Cr doped systems}$ [46]. The orthorhombic strains $O_{3,∥}$ and $O_{3,⊥}$, for 2% (shown in the inset to figure 4) and 4% Fe doped samples exhibit a maximum close to the ferromagnetic transition temperatures of 100 and 125 K, respectively. Such a behavior may indicate that with the onset of the long range ordered ferromagnetic phase below $T_{\text{C}}$ the orthorhombic strains in the lattice are reduced, accompanied by suppression of charge and orbital ordering. At higher Fe doping in $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1−x}\text{Fe}_x \text{O}_3$ with $x \geq 0.06$, the cell parameters exhibit nearly linear reduction while cooling. As a consequence, no significant change in $O_{3,∥}$ and $O_{3,⊥}$ is observed.

In the $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1−x}\text{Ru}_x \text{O}_3$ with $0.01 \leq x \leq 0.03$ samples, the cell parameters as a function of temperature display behavior similar to that described for the 2% Fe doped sample. A minimum in the lattice parameter $b$ is observed at $\sim 200$ K, coinciding with the ferromagnetic transition temperature. This is accompanied by the $O_{3,∥}$ and $O_{3,⊥}$ showing a maximum at a temperature close to $T_{\text{C}}$. On increasing the Ru doping in the $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.95}\text{Ru}_{0.05} \text{O}_3$ (Ru 5% doping) sample no anomalous behavior in the lattice parameters as a function of temperature is observed and they display an almost linear reduction on lowering the temperature below 300 K. Consequently, the orthorhombic strain parameters exhibit no significant change as a function of temperature.

With Al doping in $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1−x}\text{Al}_x \text{O}_3$ (0.01 $\leq x \leq 0.07$) compounds, the temperature evolution of the cell parameters exhibits behavior typical of charge and orbital ordering, as observed in the $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.95}\text{Fe}_{0.05} \text{O}_3$ sample (figure 3). The variation of the orthorhombic strain parameters shows an increase below the charge and orbital ordering temperature. This indicates that the ordering of $d_{z^2}$ orbitals in the $ac$ plane is accompanied by an increase in strain [51, 52]. Additionally, in the 3% Al doped sample, a broad minimum in the lattice parameter $b$ accompanied by a maximum in orthorhombic strains close to the ferromagnetic transition temperature ($T_{\text{C}} \approx 125$ K) is observed. In contrast with Fe and Ru substituted $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ compounds, the signatures of charge and orbital ordering in Al doped systems are retained up to a much higher doping level with $x = 0.07$. However, the transition temperature of the charge and orbital ordering continuously reduces with increasing Al doping. Finally, in $0.10 \leq x \leq 0.13$ samples, the charge and orbital ordered state is fully suppressed. Similarly, with Ga doping of 1%, the signature of charge and orbital ordering is evident in the temperature dependence of the cell parameters. At 3% Ga doping, a minimum in the lattice parameters is seen at $T \approx 125$ K. This behavior is similar to 2–4% Fe and 1–3% Ru doped samples. At higher Ga substitution, the charge and orbitally ordered state is fully suppressed.

Therefore, doping with magnetic ions (Fe and Ru) causes suppression of charge and orbital ordering much more rapidly than with non-magnetic dopants (Al and Ga). In samples exhibiting ferromagnetic ordering, anomalous behavior of the cell parameters is observed, which coincides with the onset of the ferromagnetic transition. These results indicate that with induced disorder at the B-site the homogeneous strain field is collapsed into an inhomogeneous one, which is accompanied by the gradual suppression of the charge ordered phase. Theoretical studies have shown that long range homogeneous strain plays a crucial role in stabilization of the charge and orbitally ordered state in half-doped manganites [64]. Experimentally, the presence of phase coexistence behavior in manganites is correlated with different lattice strains, wherein their interplay with temperature leads to stabilization of one phase at the expense of the other [23, 43–45]. Structurally, a more distorted phase would favor an insulating state, whereas the less distorted one would exhibit ferromagnetic metallic behavior.

### 3.2. Magnetization and transport behavior

The temperature dependence of magnetization, $M(T)$, measured under zero field cooled (ZFC) and field cooled (FC) conditions for $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1−x}\text{Fe}_x \text{O}_3$ (0.01 $\leq x \leq 0.10$) samples, is shown in figure 5(a). The 1% Fe doped sample...
undergoes multiple magnetic transitions as a function of temperature, displaying behavior similar to the $x = 0$ compound [52]. On lowering of the temperature to $\sim 230$ K, a hump in magnetization is observed (not visible on the present scale in figure 5(a)). This coincides with the onset of the charge ordered insulating state and $T_C$, as observed for the $x = 0$ compound [52]. On further reducing the temperature, another broad hump in the magnetization is observed at $\sim 100$ K, which is identified with an antiferromagnetic transition temperature ($T_N$) obtained from neutron diffraction measurements. The variation of magnetization with field, $M(H)$, of the 1% Fe doped sample at $T = 10$ K is shown in the inset to figure 5(a). In the region $T < T_N$, coexistence of ferromagnetic clusters in the charge and the orbitally ordered antiferromagnetic matrix is evident from the narrow hysteresis loop in the $M(H)$ behavior. However, the moment value is considerably lower than the expected value. In addition, anomalous behavior in the form of a virgin curve lying outside the envelope curve and a step like behavior in the virgin curve is visible in the $M(H)$ data. Previous reports on high resolution neutron diffraction studies in the presence of a magnetic field show that the steps in the $M(H)$ of charge ordered systems with CE-type antiferromagnetic structure are accompanied by a change in the cell parameters [65, 66]. In the Ga substituted Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.975}$Ga$_{0.025}$O$_3$ compound, a magnetic field as high as 6 T is observed to favor the ferromagnetic phase, without significantly influencing the CE-type antiferromagnetic state. A similar description based on a martensitic like scenario on the strain accommodation in phase separated manganites has been proposed to explain the step like behavior in $M(H)$ [66, 67]. At higher Fe doping in La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Fe$_x$O$_3$ with $0.02 \leq x \leq 0.06$, the magnetic nature appears to be modified. On cooling below 300 K, the $M(T)$ exhibits an increase below the respective ordering temperatures and displays no significant change thereafter, which indicates the onset of the ferromagnetic state. The ferromagnetic transition temperatures, $T_C$, for 2%, 4%, and 6% Fe doped samples are 100, 150 and 75 K, respectively. In these Fe doped samples, a large bifurcation between the ZFC and FC curves arises below 50 K, as shown in inset (ii) to figure 5(a) for the 2% Fe doped sample, indicating the coexistence of ferromagnetic and spin glass phases. The presence of a spin glass phase in B-site substituted compounds has been brought out in some of the recent theoretical studies [50]. The ferromagnetic behavior is progressively suppressed with increase in Fe doping and in the 10% Fe doped sample no evidence of long range magnetic ordering is observed. This is also confirmed by neutron diffraction measurements described later. However, the extremely narrow hysteresis loop evident in $M(H)$ suggests the presence of short range ferromagnetic ordering.

The variation of resistivity with temperature, $\rho(T)$, in La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Fe$_x$O$_3$ ($0.01 \leq x \leq 0.10$) samples is shown in figure 5(b). The resistivity data were collected during heating and cooling cycles. In these samples, the temperature dependence of resistivity exhibits an insulating behavior over the entire measured temperature range between 5 and 300 K. In comparison to the Li$_{0.5}$Ca$_{0.5}$MnO$_3$ compound ($\rho(T)$ shown in inset (ii) to figure 5(b)), in Fe doped samples with $0.01 \leq x \leq 0.06$, a reduction in resistivity at 5 K by nearly two orders of magnitude is found. Besides, with Fe doping the point of inflection ($\approx T_{CO}$) below which the $\rho(T)$ exhibits a steep rise is absent. This indicates the suppression of charge ordering in these samples, which is in agreement with the suppression of the structural transition from the orthorhombic phase in the $Pnma$ space group to the monoclinic phase in the $P2_1/m$ space group observed in the low temperature neutron diffraction study. Additionally, a broad hump accompanied by a thermal hysteresis between the heating and cooling cycles is evident near $T_C$ and is shown in inset (i) to figure 5(b). The gradual suppression of the anomalous behavior and reduction in the width of thermal hysteresis with increasing Fe doping is also evident in this figure. The thermal hysteresis behavior in $\rho(T)$, observed in phase separated manganites, has been
explained as arising from the formation of metal clusters and their size distribution across the metal–insulator transition [68].

The magnetization data, $M(T)$, of La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Ru$_x$O$_3$ (0.01 $\leq x \leq 0.05$) samples is shown in figure 6(a). As a function of Ru doping, the increase in $M(T)$ at 200 K ($\sim T_C$) indicates an onset of ferromagnetic ordering. The broad nature of the transition indicates an inhomogeneous nature of the ferromagnetic state. The $M(T)$ data for the 1% Ru doped sample are shown in the inset to figure 6(a). This figure is representative of the Ru doped samples with 0.01 $\leq x \leq 0.05$. The signature of a typical ferromagnetic behavior is evident in the $M(T)$ curve. At low field, the magnetization $M$ shows a sharp rise and saturates thereafter. The saturation value of the magnetization ($\sim 3.3$ $\mu_B$/f.u.) is close to the expected value of $\sim 3.5$ $\mu_B$/f.u. In figure 6(b), the temperature dependence of the resistivity, $\rho(T)$, of Ru doped La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Ru$_x$O$_3$ (0.01 $\leq x \leq 0.05$) samples is displayed. With Ru doping of 1% the charge ordered insulating state is destabilized and the insulator to metal transition is induced at $T_{MI}$ $\approx$ 125 K. Similar behavior in $\rho(T)$ is observed for the Ru doped sample with $x = 0.05$. No significant change in $T_C$ and $T_{MI}$ as a function of Ru doping is observed. Similar behavior has been recently reported in Ru doped Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ compounds, attributed to the coexistence and competing nature of double exchange and superexchange interactions [69, 70]. Also, it is observed that there is a large difference between $T_C$ and $T_{MI}$ in Ru substituted samples: $\Delta T = T_C - T_{MI} = 75$ K. The observed difference indicates the percolative nature of ferromagnetic regions.

In figure 7(a) the magnetization as a function of temperature in La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Al$_x$O$_3$ (0.01 $\leq x \leq 0.13$) samples is displayed. In the 1% Al doped sample, a shallow hump in $M(T)$ at $\approx$200 K is observed. The SANS study described later shows the onset of short range ordered ferromagnetic correlations below 200 K. On further lowering of temperature the magnetization saturates below 75 K. From the magnetization studies transition to an antiferromagnetic state is not clear. The neutron diffraction study on the 1% Al doped sample shows evidence of antiferromagnetic ordering with $T_N$ $\approx$ 150 K. The resulting competing nature of the ferromagnetic and antiferromagnetic interactions describes the magnetization behavior. The value of magnetization at 5 K increases with increase in Al concentration, exhibiting a maximum for 3% Al doping, and decreases subsequently for higher Al doping. In the 3% Al doped sample a transition to a ferromagnetic state occurs at $T_C$ $\approx$ 200 K and from the neutron
diffraction study we find the presence of an antiferromagnetic phase below $T_N \approx 120$ K. In La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Al$_x$O$_3$ with $0.05 \leq x \leq 0.07$ compounds, similar behavior of transition to antiferromagnetic and ferromagnetic states is observed. The nature of the antiferromagnetic ordering in these compounds obtained from neutron diffraction measurements is discussed below. Likewise, in Al doped samples with $0.10 \leq x \leq 0.13$, $M(T)$ increases below 100 K and a maximum at 50 K is observed. At 50 K, $M(T)$ displays a drop accompanied by bifurcation in the FC and ZFC curves, as shown in inset (i) to figure 7(b) in the 13% Al doped sample. Such a behavior has been reported in other charge ordered manganites and is ascribed to a transition to a spin glass like state [71, 72]. Both randomness and frustration of spins are necessary to produce a spin glass state. The competing antiferromagnetic and ferromagnetic interactions could lead to such frustrations in the system, leading to the growth of a spin glass or cluster glass state. The nature of spin glass phases in manganites is still a topic of discussion [72, 73].

The resistivity data, $\rho(T)$, of Al doped samples in La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Al$_x$O$_3$ ($0.01 \leq x \leq 0.13$) are displayed in figure 7(b). In La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Al$_x$O$_3$ with ($0.01 \leq x \leq 0.03$) samples, while cooling from 300 K an insulator to metal transition, accompanied by thermal hysteresis (inset (ii) to figure 7(b)), is observed at $T_{MI} \approx 100$ K. The origin of the thermal hysteresis is similar to that described in the case of Fe doped samples. In higher Al doped compounds with $0.05 \leq x \leq 0.13$, the temperature dependence of the resistivity again shows an insulating behavior over the entire measured temperature range between 50 and 300 K. Below 50 K the resistivity is too high to be measurable. Also, the thermal hysteresis between the heating and cooling cycles is diminished.

In La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Ga$_x$O$_3$ ($0.01 \leq x \leq 0.07$), the $M(T)$ shown in figure 8(a), displays behavior similar to Al doped samples. In the 1% Ga doped sample, a transition correlated with the charge and orbitally ordered state at $\approx 180$ K and magnetic transitions at $T_N \approx 150$ K (obtained from neutron diffraction data) and $T_C \approx 60$ K are observed. At 3% Ga doping, the ferromagnetic transition is evident at $\approx 125$ K, with no bifurcation in the ZFC and FC curves. At higher Ga doping of 7%, a sharp increase in magnetization occurs below 100 K, exhibiting a maximum at 50 K. Below 50 K, the sharp drop in magnetization is accompanied by a bifurcation between the ZFC and FC curves. Also, the typical features of metamagnetic transition and phase coexistence are evident in the $M(H)$ curves of Ga doped samples. With Ga doping in La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Ga$_x$O$_3$ ($0.01 \leq x \leq 0.07$), the resistivity as a function of temperature displays behavior similar to the Al doped sample, as observed in figure 8(b). The Ga doped $0.01 \leq x \leq 0.03$ samples undergo an insulator to metal transition at $\approx 100$ K, while the $x = 0.07$ sample remains insulating down to 50 K. Both Al and Ga doping exhibit similar magnetic behavior, though based on their ionic radii they are expected to selectively substitute Mn$^{3+}$ and Mn$^{4+}$ ions, respectively.

3.3. Magnetic structure

The neutron diffraction pattern in the angular range $5^\circ \leq 2\theta \leq 80^\circ$ of the La$_{0.5}$Ca$_{0.5}$Mn$_{0.99}$Fe$_{0.01}$O$_3$ (Fe 1% doping) sample at 300 and 22 K is shown in figure 9. This neutron diffraction pattern is a representative of the samples displaying CE-type antiferromagnetic spin structure at low temperatures. In the 1% Fe doped sample, on lowering of temperature, below the antiferromagnetic ordering temperature superlattice reflections are observed similar to those of the La$_{0.5}$Ca$_{0.5}$Mn$_{0.99}$O$_3$ compound (figure 1). This suggests the antiferromagnetic nature of the sample below the transition temperature ($T_N$). The superlattice reflections are marked with an asterisk (*) symbol in figure 9. In particular, the strong reflections $(0, 1, 1)$ and $(\frac{1}{2}, 1, \frac{1}{2})$ are shown and these characterize the onset of CE-type antiferromagnetic ordering [51]. These superlattice reflections are indexed on a $2a \times b \times 2c$ cell in the space group $P2_1/m$. In the CE-type antiferromagnetic spin structure the Mn$^{3+}$ and Mn$^{4+}$ ions occupy two distinct sites and are associated with the propagation vectors $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$, respectively. The CE-type model used for refinement describes the low temperature phase as one-dimensional zigzag chains with ferromagnetically aligned spins in the $ac$ plane, while the interchain coupling is antiferromagnetic. This is the checkerboard pattern and the model was first proposed by
The temperature dependence of the Mn-site moment for Mn$^{3+}$ and Mn$^{4+}$ ions in the 1% Fe doped compound is shown in the inset to figure 9. In the 1% Fe doped compound $T_N \approx 150$ K is deduced from the temperature dependence of the refined Mn-site magnetic moment. Rietveld refinement of the neutron diffraction pattern at 22 K indicates that the magnetic moments for Mn$^{3+}$ and Mn$^{4+}$ sites are predominantly oriented along either the $a$ or $c$ axis and their values are 1.9(2) $\mu_B$ and 2.1(1) $\mu_B$, respectively. These values are in closer comparison to the values obtained in the case of an $x = 0$ sample of 2.8(3) $\mu_B$ and 2.6(3) $\mu_B$, reported by Radaelli et al. [51] for Mn$^{3+}$ and Mn$^{4+}$ sites, respectively. The lowering of both the site moments indicates that Fe$^{3+}$ is distributed randomly over both the sites. Fe$^{3+}$ is a non-JT ion like Cr$^{3+}$. However, unlike Cr$^{3+}$, the number of $e_g$ electrons increases with Fe doping. Our observations are again different from the incommensuration of Mn$^{3+}$ observed in the case of Ni$^{2+}$ doping [46]. From the present neutron diffraction data no significant change in $\chi^2$ and magnetic $R$-factor is observed on changing the orientation of spins between the $a$ and $c$ axes. Therefore, the spins were constrained to be oriented along the $a$ axis. Similarly, the $x$ and $z$ axis components of the magnetic moments of Mn$^{4+}$ ions could not be refined separately and therefore the orientation was constrained to be along the $a$ axis. Additionally, no enhancement in intensity of the low angle fundamental Bragg reflections was visible, which indicates the absence of ferromagnetic ordering observable from the present neutron diffraction experiment. This is further corroborated by SANS data where no signature of ferromagnetism is observed.

In figure 10, the neutron diffraction pattern of La$_{0.5}$Ca$_{0.5}$Mn$_{0.99}$Fe$_{0.01}$O$_3$ (Fe 1%) at 22 and 300 K is displayed. The data at 22 K have been shifted vertically for clarity. The continuous lines are the fitted lines to the indexed nuclear and CE-type antiferromagnetic phases, respectively. The curve at the bottom is the difference between the observed and calculated intensities at 22 K. The inset shows the variation of the antiferromagnetic site moments of Mn$^{3+}$ and Mn$^{4+}$ ions with temperature for the 1% Fe doped sample. The continuous lines are a guide for the eye.
of evolution of superlattice reflections, is observed. The ferromagnetic phase at low temperature is refined in the orthorhombic structure in the Pnma space group, as described for the 2% Fe doped compound. The refined ferromagnetic moments at 22 K for the 1% and 5% Ru doped samples are 2.64(5) and 3.19(6) μB, respectively. The value of the antiferromagnetic moment value at 5 K is 2.18(6) μB for the 1% Fe doped sample. The ferromagnetic moment value at 5 K is 1.1(1) μB, in comparison to the 1% Al doped compound. The temperature dependence of the antiferromagnetic moment is shown in inset (i) to figure 11. This reduction in CE-type antiferromagnetic moment is accompanied by the favoring of ferromagnetic ordering with TC ≈ 150 K. The ferromagnetic moment as a function of temperature in the 3% Al doped sample is displayed in inset (ii) to figure 11. The refined ferromagnetic moment value at 5 K is 2.18(6) μB, which is in agreement with the M(H) study. Therefore, in samples with x ≤ 0.3, CE-type antiferromagnetic ordering coexists with the ferromagnetic ordering. This is not very evident from M(T, H) studies alone. In the 5% Al doped compound, a CE-type antiferromagnetic state with considerable reduction in moment value is still evident, whereas the ferromagnetic phase is fully suppressed. In addition, new distinct superlattice reflections indicated by (+) in figure 12 are observed. However, the antiferromagnetic moment values at the respective Mn+ and Mn4+ sites are reduced to 1.2(1) and 1.5(1) μB, respectively. The continuous lines through the data points are fitted lines to the chemical and magnetic structure described in the text. The * symbol indicates reflections corresponding to the A-type antiferromagnetic spin structure. The tick marks in the first and second rows correspond to positions of Bragg reflections in nuclear and A-type antiferromagnetic phases, respectively. The curve at the bottom is the difference between the observed and calculated intensities at 5 K.
the CE-type and emergence of the A-type antiferromagnetic state observed in these systems is similar to that observed in previously reported neutron diffraction studies on A-site doped compounds [9, 8]. On increasing the Al doping to 7%, both the CE-type antiferromagnetic and ferromagnetic phases are suppressed, while the superlattice reflections corresponding to an A-type antiferromagnetic state are still visible below \( T_\text{N} \approx 125 \text{ K} \). The obtained value of magnetic moment at 5 K is 3.12(6) \( \mu_B \). Eventually, with increasing Al doping between 10 and 13%, the A-type antiferromagnetic state is also suppressed and no signature of long range magnetically ordered phases is seen from neutron diffraction measurements.

With Ga doping in \( \text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Ga}_x\text{O}_3 \) (0.01 \( \leq x \leq 0.07 \)), the results obtained from the present temperature dependent neutron diffraction study exhibit behavior similar to those in Al doped samples. In low Ga doping of 1%, the CE-type antiferromagnetic state is observed below \( T_\text{N} \approx 150 \text{ K} \), accompanied by ferromagnetic ordering below \( T_\text{C} \approx 60 \text{ K} \). The refinement of the diffraction pattern at 5 K yields the antiferromagnetic moment values at Mn\(^{3+}\) and Mn\(^{4+}\) sites as 2.3(3) and 2.3(2) \( \mu_B \), respectively, while the ferromagnetic moment value is 1.0(1) \( \mu_B \). At 3% Ga doping also, the CE-type antiferromagnetic phase is accompanied by the ferromagnetic state having \( T_\text{C} \approx T_\text{N} \approx 125 \text{ K} \). However, in comparison to the 1% Ga substituted compound, the CE-type antiferromagnetic phase is significantly weakened, indicated by the reduced moment values at Mn\(^{3+}\) and Mn\(^{4+}\) sites of 1.4(2) and 1.2(1) \( \mu_B \). The obtained ferromagnetic moment value at 5 K is 2.74(6) \( \mu_B \), in agreement with the \( M(H) \) study. Finally in the 7% Ga doped sample, both CE-type antiferromagnetic and ferromagnetic states are suppressed, whereas the A-type antiferromagnetic state persists below \( T_\text{N} \approx 75 \text{ K} \). The obtained moment value at 5 K is \( \approx 1.5(1) \mu_B \). The A-type antiferromagnetic spin structure has been analyzed in a manner similar to that described for Al doped compounds.

Therefore, the present neutron diffraction measurements together with magnetization and transport measurements reveal the evolution of various complex magnetic structures as a function of temperature and different B-site dopants. Specifically, we find the emergence of an A-type antiferromagnetic spin structure accompanied by the gradual suppression of both CE-type antiferromagnetic and ferromagnetic phases, on substituting with non-magnetic dopants in \( \text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{B}_x\text{O}_3 \) with \( B = \text{Al} \) and \( \text{Ga} \) compounds, which has not been observed before. This is unlike the behavior reported in the \( \text{Fe}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) compound, wherein doping with non-magnetic ions such as \( \text{Al} \), \( \text{Ga} \) or \( \text{Ti} \) leads to the development of a pseudo-CE-type antiferromagnetic state at the expense of the CE-type antiferromagnetic ground state [42, 44, 65].

### 3.4. Small angle neutron scattering

The presence of short range ordered ferromagnetic correlations as a result of B-site substitution in the \( \text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.9} \) compound for a few of the selected samples is explored using SANS measurements, in the length scale of 10–1000 Å. The SANS intensity as a function of \( Q \), \( I(Q) \), in the \( \text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.9}\text{Fe}_{0.01}\text{O}_3 \) compound (1% Fe doping) at various temperatures is shown in figure 13. Two distinct regimes in \( Q \) are observed from this figure. In the \( Q < 0.03 \text{ Å}^{-1} \) range, the intensity does not exhibit any temperature dependence, while in the high \( Q \) regime significant change in intensity is observed. In the low \( Q \) regime, the intensity exhibits \( Q^{-4} \) dependence, obeying the classical Porod’s law [77]. This behavior is attributed to the clustered structure, where smooth sphere particles are embedded in a matrix background. On the other hand, in the high \( Q \) regime i.e. at smaller length scales, above the ordering temperature \( T_\text{C} \approx 230 \text{ K} \), the intensity has contributions from both disordered paramagnetic scattering and nuclear scattering. On lowering the temperature below the magnetic ordering, the paramagnetic disorder scattering is reduced and only the nuclear contribution persists as the antiferromagnetic phase does not contribute to the SANS intensity. The inset to figure 13 shows the temperature dependence of the scattered neutron intensity at \( Q = 0.224 \text{ Å}^{-1} \) in the \( \text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.9}\text{Fe}_{0.01}\text{O}_3 \) compound. For a length scale of about 118 Å and beyond, a maximum at 230 K is observed, which coincides with the weak hump in \( M(T) \) (figure 5(a)). In neutron diffraction measurements we do not observe any evidence of long range ferromagnetic ordering in this sample. The decrease in the maximum value of \( \rho(T) \) (figure 5(b)) in this sample together with these results suggests that the reduction in intensity below 230 K indicates the suppression of paramagnetic scattering with the onset of short range ferromagnetic ordering. However, no further evidence of ferromagnetic ordering is observed in the low \( Q \) regime as observed in other samples. Therefore, from both neutron diffraction and the SANS study no signature of ferromagnetic ordering behavior is observed in the zero field CE-type antiferromagnetic state for the 1% Fe doped sample. Figure 14 shows the SANS intensity in the \( \text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.9}\text{Fe}_{0.02}\text{O}_3 \) (2% Fe doping) compound at several temperatures between
In the Qgoverned by reduction in the lattice strains in the system [78].

Clusters within the antiferromagnetic insulating phase was magnetic properties, wherein the growth of ferromagnetic is evident. Meanwhile, in the high Q regime wherein the minimum in magnetization close to 100 K M the temperature derivative of ZFC magnetization, dM/ZFC/dT, shows the temperature dependence of the correlation length (ξ) in the 2% Fe doped sample. The continuous line is a guide for the eyes.

15 and 295 K. However, in contrast to the 1% Fe doped sample, enhancement in the intensity in the Q < 0.03 Å⁻¹ regime is observed on lowering the temperature below T_C = 100 K. The temperature dependence of the SANS intensity at Q = 0.00705 and 0.224 Å⁻¹ for the 2% Fe doped sample is shown in the inset to figure 14. This figure shows the rise in intensity at Q = 0.00705 Å⁻¹ below 100 K, indicating the ferromagnetic transition, in agreement with neutron diffraction and M(T) measurements. This behavior correlates well with the temperature derivative of ZFC magnetization, dM/ZFC/dT, wherein the minimum in magnetization close to 100 K is evident. Meanwhile, in the high Q range at Q = 0.224 Å⁻¹, behavior similar to the 1% Fe doped sample is observed, which is identified as reduction in paramagnetic disorder scattering accompanied by the onset of the short range ordered ferromagnetic state. The comparison between the SANS intensity and the temperature dependence of the strain parameters (O_2 and O_3) in the 2% Fe doped sample (inset to figure 4) shows that the favoring of ferromagnetic ordering is accompanied by a reduction in lattice strain. This behavior is in agreement with a previously reported SANS study on the Pr_{0.7}Ca_{0.3}MnO_3 compound exhibiting similar magnetic properties, wherein the growth of ferromagnetic clusters within the antiferromagnetic insulating phase was governed by reduction in the lattice strains in the system [78].

In the Q regime between 0.05 and 0.31 Å⁻¹, the Q dependence of the scattering intensity has been described by a combination of Porod’s law (Q⁻⁴ dependence) and a Lorentzian profile function (Q⁻² dependence) given as

\[ I = \frac{I_1}{Q^2} + \frac{I_2}{Q^2 + \kappa^2} \]  

where \( I_1 \) and \( I_2 \) are scattering amplitudes and \( \kappa = 1/\xi; \) \( \xi \) is the correlation length of magnetic clusters. The corresponding fits are shown in figure 14 by the continuous line at 15 K. Similar behavior has been reported previously, wherein the Q⁻⁴ dependence is ascribed to the scattering by the phase separation interface, while Q⁻² dependence arises from nanometric magnetic inhomogeneities [79]. However, according to Simon et al., in a Pr_{0.7}Ca_{0.3}MnO_3 single crystal sample, the Q⁻² dependence may be a characteristic of two-dimensional ferromagnetic stripes, suggesting a red cabbage structure [80]. The correlation length (ξ) as a function of temperature shown in inset (iii) to figure 14 exhibits a broad maximum between 150 and 250 K, which suggests the presence of short range ordered ferromagnetic clusters even above the ferromagnetic ordering temperature. In a previous study, we had observed the evidence of diffuse neutron scattering in the region T > T_C, in related La_{0.5}Ca_{0.5−x}Sr_xMnO_3 compounds, indicating the existence of short range ordered magnetic correlations in the paramagnetic regime greatly above the ordering temperatures [81]. The existence of a short range ordered ferromagnetic phase is also reported in many of the SANS measurements on other perovskite manganite systems [78–80] and is a signature of magnetic polarons. The scattering amplitude \( I_1 \) follows the temperature dependence of the intensity at Q = 0.00705 Å⁻¹, shown in the inset to figure 14, while no significant change in \( I_2 \) as a function of temperature is observed.

In figure 15, the temperature dependence of the SANS intensity at Q = 0.00705 and 0.224 Å⁻¹ for the La_{0.5}Ca_{0.5}Mn_{0.99}Ru_{0.01}O_3 (1% Ru doping) sample is shown. In this sample, the temperature dependence of the SANS intensity as a function of Q exhibits behavior similar to the 2% Fe doped compound (figure 14). In the low Q regime (0.00705 ≤ Q ≤ 0.033 Å⁻¹), the scattering intensity follows a Q⁻⁴ dependence, whereas at higher Q values the behavior is described by equation (1). The obtained correlation length...
as a function of temperature, shown in the inset to figure 15, exhibits a sharp maximum across the ferromagnetic ordering temperature. The temperature of such a feature correlates well with the one obtained from the magnetization measurement \((T_C \approx 200 \text{ K})\). At \(Q = 0.00705 \text{ Å}^{-1}\), the intensity as a function of temperature, shown in figure 15, displays an increase on cooling below 200 K, indicating the ferromagnetic nature of the sample. This behavior is followed by an increase in the SANS intensity on raising the temperature above 200 K, at smaller \(Q = 0.224 \text{ Å}^{-1}\), evident in figure 15. This behavior also correlates with the minimum observed in the \(dM_{ZFC}/dT\) plot. In this 1% Ru doped compound also, similarly to 2% Fe doping, evidence of ferromagnetic ordering on two different length scales is observed.

The variation of the SANS intensity as a function of \(Q\), at several temperatures between 18 and 300 K, for the \(\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.99}\text{Al}_{0.01}\text{O}_3\) (1% Al doping) sample is shown in figure 16. The neutron diffraction measurements on the 1% Al doped sample show two transitions at \(T_N \approx 150 \text{ K}\) and \(T_C \approx 100 \text{ K}\). In figure 16, for low \(Q\) values at low temperatures, the crossing over of SANS curves is found. However, the enhancement in intensity at low \(Q\) values below \(0.044 \text{ Å}^{-1}\) is considerably smaller, as compared to the 2% Fe and 1% Ru compounds. The temperature variation of the intensity at \(Q = 0.00705 \text{ Å}^{-1}\) exhibits almost linear increase upon cooling below 300 K (inset to figure 16). At a high \(Q\) value of 0.224 \text{ Å}^{-1}, the scattering intensity displays a sharp peak at 200 K, coinciding with the broad hump in the \(M(T)\) data. This indicates the existence of nanometric size ferromagnetic regions, which coexist with the long ranged antiferromagnetic phase below \(T_N \approx 150 \text{ K}\). SANS measurements have also been performed on a higher Al doped sample of \(\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.95}\text{Al}_{0.05}\text{O}_3\) (5% Al doping). In contrast, this sample exhibits the stabilization of the A-type antiferromagnetic state at low temperatures. The temperature variation of the SANS intensity \(I(Q)\) for the 5% Al doped sample displays characteristics similar to the 1% Fe doped compound (figure 13). At low \(Q\) (<0.055 \text{ Å}^{-1})\) values the scattering curves overlap, displaying no significant change with temperature. Meanwhile, in the high \(Q\) regime at \(Q = 0.224 \text{ Å}^{-1}\), the scattering intensity exhibits a decrease below 200 K, attributed to the reduction of paramagnetic disorder scattering accompanied by the growth of nanometric sized ferromagnetic regions.

The above results clearly demonstrate the contrasting natures of magnetic (Fe and Ru) and non-magnetic dopants (Al and Ga) in the half-doped \(\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\) compound. According to previous studies on B-site substituted charge ordered manganites, the contrasting nature of the stabilization of magnetic ground states has been ascribed to different mechanisms, such as the valence state of the dopants; the magnetic exchange interaction with Mn ions, and between dopants plays an essential role. These studies have shown that Fe ions couple antiferromagnetically with Mn ions [82–84], while Ru ions couple ferromagnetically with Mn ones [15, 85–87]. In addition, Ru doping enhances the local \(e_g\) electron density, therefore strongly favoring the ferromagnetic metallic phase [88]. These effects may together contribute toward the favoring of the insulator to metal transition in Ru doped samples [47, 48]. On the other hand, the non-magnetic dopants are considered as random impurities, not having any magnetic coupling with the Mn ions. The effect of random substitution at the B-site by magnetic and non-magnetic dopants has been investigated by Monte Carlo simulation studies in half-doped manganites [47, 48, 88]. The non-magnetic impurity doping at the B-site is introduced as lattice defects and may modify the \(e_g\) electron density, while in the case of magnetic doping, the magnetic exchange interactions are also taken into account. Our experimental studies are fairly consistent with these theoretical studies, wherein the long range ordered antiferromagnetic state collapses into a ferromagnetic phase and this behavior is ascribed to lattice defects introduced in the form of non-magnetic B-site dopants. However, our studies indicate the absence of the proposed C-type antiferromagnetic state [47], and instead the presence of an A-type antiferromagnetic state in the vicinity of the melting of the CE-type antiferromagnetic and ferromagnetic phases is observed. This behavior has been predicted theoretically by Pradhan et al for B-site dopants with \(3+\) valence, where the phase separation window lies between charge ordered CE-type and A-type antiferromagnetic phases [48].

Summarizing, our experimental studies show that the charge and orbitally ordered antiferromagnetic state can be significantly destabilized by the induced B-site disorder, leading to variation in favoring of magnetic ground states with different dopants. These include competing long range ordered ferromagnetic metallic or insulating states, a short range ordered ferromagnetic phase coexisting with or without the antiferromagnetic state, or a system may enter a magnetically frustrated, spin glass like state. In particular, the development of A-type antiferromagnetic tendencies observed here is driven by the non-magnetic substitution (Al or Ga) in the \(\text{La}_{0.4}\text{Ca}_{0.5}\text{MnO}_3\) compound. The growth of the ferromagnetic phase for a low concentration of B-site dopants

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**Figure 16.** The SANS intensity as a function of \(Q\) for the \(\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.99}\text{Al}_{0.01}\text{O}_3\) (Al 1%) sample at several temperatures. The inset shows the SANS intensity as a function of temperature at \(Q = 0.00705\) and 0.224 \text{ Å}^{-1} in the 1% Al doped sample. The continuous line is a guide for the eyes.
and its suppression at higher concentrations is understood to be a combined effect of defect induced and density driven phenomena.

4. Conclusions

The influence of B-site doping on the crystal and magnetic structure in La$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$B$_{x}$O$_3$ (B = Fe, Ru, Al and Ga) has been investigated using neutron diffusion, SANS, magnetization and resistivity techniques. The B-site doped samples are isostructural and crystallize in an orthorhombic structure in the Pnma space group at 300 K. On lowering the temperature, an orthorhombic to monoclinic structural transition is observed in compounds exhibiting CE-type antiferromagnetic ordering. This structural transition is absent in other compounds which exhibit A-type antiferromagnetic and ferromagnetic ordering. In the $\%$ Fe doped compound CE-type antiferromagnetic and ferromagnetic ordering is found similar to that of the $x = 0$ sample. However, the moments on both Mn$^{4+}$ and Mn$^{5+}$ are reduced. With higher Fe doping, the CE-type antiferromagnetic state is suppressed at the expense of the ferromagnetic insulating phase in $0.02 \leq x \leq 0.06$ compounds. At higher Fe doping of $x > 0.06$, the ferromagnetic state is also suppressed, and no evidence of long range magnetic ordering is found. In contrast, Ru doping as low as $x = 0.01$ favors the ferromagnetic metallic state at $T_C \approx 200$ K and $T_{MI} \approx 125$ K. With Al substitution of $0.01 \leq x \leq 0.03$, the charge ordered CE-type antiferromagnetic state is retained, coexisting with a ferromagnetic metallic phase. On increasing the Al doping ($x > 0.03$), both the CE-type antiferromagnetic and ferromagnetic phases are gradually suppressed and an A-type antiferromagnetic insulating state is stabilized in $0.05 \leq x \leq 0.07$, which is also suppressed eventually at higher doping. On doping with Al, the charge and orbitally ordered state is retained up to a much higher doping level with $x = 0.07$. Similarly, substitution with Ga is observed to induce similar effects to those described for Al doped samples. The contrasting behavior of magnetic Fe and Ru as against the non-magnetic dopants Al and Ga is evidenced from this study. Doping with Fe and Ru is found to result in either ferromagnetic or antiferromagnetic phases, while doping with Al and Ga results in coexisting ferromagnetic and antiferromagnetic phases.

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