Tricritical point and critical exponents of La_{0.7}Ca_{0.3−x}Sr_xMnO_3 (x = 0, 0.05, 0.1, 0.2, 0.25) single crystals

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ABSTRACT

The nature of ferromagnetic phase transition and its critical properties in La_{0.7}Ca_{0.3−x}Sr_xMnO_3 (x = 0, 0.05, 0.1, 0.2 and 0.25) single crystals have been studied systematically. Based on magnetic measurements and critical behavior analysis using Banerjee criterion and Kouvel–Fisher method, we demonstrate the existence of a tri-critical point, with critical exponents (β = 0.26 ± 0.01, γ = 1.06 ± 0.02) at x ~ 0.1, that separates “discontinuous” first-order magnetic transition (FOMT) for x < 0.1 compositions from “continuous” second-order magnetic transition (SOMT) for x > 0.1 compositions. Above the tricritical point, the system (e.g. x = 0.2) shows a SOMT with the critical exponents (β = 0.36 ± 0.01, γ = 1.22 ± 0.01) belonging to the Heisenberg universality class (β = 0.365 ± 0.003, γ = 1.336 ± 0.004). This suggests that the magnetic interaction in these manganites is of short-range type. Our systematic studies show that chemical (internal) pressure induced by substituting larger Sr ions for smaller Ca ions, cooperative Jahn–Teller distortions, antiferromagnetic coupling, and formation of ferromagnetic clusters all have significant impact on the nature of the ferromagnetic phase transition, the conduction mechanism and colossal magnetoresistance (CMR) in the doped manganites.

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1. Introduction

The discovery of colossal magnetoresistance (CMR) in doped manganites with the general formula R_1−xM_xMnO_3 (R = La, Pr, Nd, Sm, and M = Sr, Ca, Ba, and Pb) has stimulated intense research into their physical properties [1]. The relationship between the ferromagnetism and conductivity (e.g. the relationship between the metal–insulator (MI) transition and the paramagnetic–ferromagnetic (PM–FM) transition) in several CMR materials has continued to generate interest and reveal new insights, primarily due to the complexity of the systems [2–7]. It has been experimentally shown that while the parent compound RMnO_3 is an insulating antiferromagnet, substitution of the trivalent R^3+ ion by a divalent M^2+ ion leads to coexistence of Mn^3+ and Mn^4+ ions and, at sufficiently high doping levels (x), the material becomes a conductive ferromagnet [1]. The A-site (A = R, M) doping has been shown to control an effective one-electron bandwidth (W) which primarily governs the magnetic and magnetotransport properties of the materials [1–7]. The metallic ferromagnetic state in doped manganites was widely interpreted using the double-exchange (DE) mechanism [8,9]. According to this model, the transfer of an itinerant e_g electron between the neighboring Mn sites (local t_2g spins) through the O^2− ion results in a ferromagnetic interaction due to the on-site Hund’s rule coupling. The strength of the DE interaction is evaluated by the transfer integral, t_{DE} = t_0 cos(θ/2) (θ is a relative angle between the local spins). As a magnetic field is applied to the material, it will force the local t_{2g} spins to align thus reducing spin scattering (i.e. resistivity decreases) and enhancing the ferromagnetic phase. The DE theory has been shown to describe quite well the properties of the metallic ferromagnetic state in doped manganites with relatively large W, such as La_{0.7}Sr_{0.3}MnO_3 [10]. However, it alone cannot explain the features of the MI transition and CMR observed in manganites with narrow W such as La_{0.7}Ca_{0.3}MnO_3 [3], where other effects such as collective Jahn–Teller (JT) distortions and antiferromagnetic (AFM) interactions coexist and strongly compete with the ferromagnetic phase. Indeed, experimental studies have revealed that the occurrence of the MI transition and CMR in La_{0.7}Ca_{0.3}MnO_3 results mainly from the combination of the DE interaction between Mn^3+ and Mn^4+ ions and a strong JT effect [3,11]. This system has been found to undergo a discontinuous FOMT at the Curie temperature (T_C) [12,13], and the nature of FOMT is associated with a strong electron–phonon coupling and/or an intrinsic inhomogeneity in the material.
that gives rise to competing coexisting ground states [14,15]. Meanwhile, the La$_{0.7}$Sr$_{0.3}$MnO$_3$ system (which is free from JT lattice distortions) has been found to undergo a continuous SOMT and exhibit a canonical magnetoresistance (MR) behavior [3,16]. From a crystal structure standpoint, we note that La$_{0.7}$Ca$_{0.3}$MnO$_3$ crystallizes in an orthorhombic (Pbnm) structure, whereas La$_{0.7}$Sr$_{0.3}$MnO$_3$ possesses a rhombohedral ($R\bar{3}c$) structure [17–19].

One way to stabilize intermediate phases bridging the two systems is co-substitution of both Sr and Ca in the lattice. The substitution of large Sr$^2+$ ions for smaller Ca$^{2+}$ ions in La$_{0.7}$Sr$_{0.3}$MnO$_3$ ($0 \leq x \leq 0.3$) manganites leads to a structural change from the orthorhombic to rhombohedral structure which consequently results in the different properties of the materials [3,17,19]. Notably, Tomioka et al. [3] reported that with increasing Sr-doped content, the sharp MI transition and “colossal” MR behavior for La$_{0.7}$Ca$_{0.3}$MnO$_3$ ($x=0$) were transformed to the metallic state and “canonical” MR behavior for La$_{0.7}$Sr$_{0.3}$MnO$_3$ ($x=0.3$). However, the physical origin of the observed phenomena is still not fully understood. Particularly, the mechanism of a metal-like conductivity in the paramagnetic region in La$_{0.7}$Sr$_{0.3}$MnO$_3$ compounds with $x>0.1$ remains an open question [3]. In addition, it is unclear how the magnetic interactions are renormalized near the PM–FM transition range and what universality class governs the PM–FM transitions in these systems.

To address these important and as yet unresolved issues, we have conducted a comprehensive study of the ferromagnetic phase transitions and critical exponent trends near these transitions in La$_{0.7}$Ca$_{0.3}$MnO$_3$ ($x=0, 0.05, 0.1, 0.2$ and $0.25$) single crystals. Based on the $H/M$ vs. $M^2$ analyses and using Banerjee criterion, we demonstrate a transition from the discontinuous FOMT to the continuous SOMT at $x \sim 0.1$. The critical analyses, based on the magnetic data using the Kouvel–Fisher method, affirm that $x \sim 0.1$ is a tri-critical point that separates FOMT for $x<0.1$ from SOMT for $x>0.1$. Above the tri-critical point ($x=0.2$, $0.25$), the system exhibits a SOMT with the critical exponents ($\beta=0.36 \pm 0.01, \gamma=1.22 \pm 0.01$) belonging to the Heisenberg universality class ($\beta=0.365 \pm 0.003, \gamma=1.336 \pm 0.004$) with short-range exchange interactions. This indicates that the magnetic interactions in these manganites is of short-range type. Our results and analyses reveal that while the DE mechanism and metal-like conducting behavior in La$_{0.7}$Ca$_{0.3}$MnO$_3$ with $x=0.2$ and $0.25$, other effects such as cooperative Jahn–Teller distortions and antiferromagnetic coupling are important additions for understanding the nature of the ferromagnetic transition, the MI transition and CMR in La$_{0.7}$Ca$_{0.3}$MnO$_3$ with $x=0, 0.05$ and $0.1$. Our studies provide physical insights into the relationship between the ferromagnetism and conductivity in doped manganites.

2. Experimental

Single crystals of La$_{0.7}$Ca$_{0.3}$MnO$_3$ ($x=0, 0.05, 0.1, 0.2, 0.25$) were prepared by the floating-zone method using an infrared radiation convergence-type image furnace that consist of four mirrors and halogen lamps; details of the growth conditions can be found elsewhere [20]. The starting ceramic rods were obtained from the solid-state reaction of a stoichiometric mixture of La$_2$O$_3$, CaCO$_3$, SrCO$_3$ and MnCO$_3$. X-ray diffraction (XRD) data and electron-probe microanalysis confirmed the quality of the crystals. The XRD analyses indicated that the crystal structure is orthorhombic for $x=0$, $0.05$ and $0.1$ compositions and is rhombohedral for $x=0.2$ and $0.25$ compositions. These results are fully consistent with those reported in previous works [17–19]. Magnetic measurements were performed using a commercial Physical Property Measurement System (PPMS) from Quantum Design in the temperature range of 2–350 K at applied fields up to 7 T. To extract the critical exponents of the samples accurately, the magnetic isotherms for all samples were measured in the range of 0–2 T and with a temperature interval of 1 K in the vicinity of their Curie temperatures ($T_C$).

3. Results and discussion

Fig. 1 shows the temperature dependence of magnetization taken at an applied field of 5 kOe for La$_{0.7}$Ca$_{0.3}$MnO$_3$ ($x=0, 0.05, 0.1$ and $0.25$) samples. It is observed in Fig. 1 that all the samples undergo a PM–FM transition and this transition broadens gradually with increasing Sr doping. The Curie temperatures ($T_C$) of the samples, which are defined by the minimum in $dM/dT$, are plotted as a function of Sr-doping, as shown in the inset of Fig. 1. In connection with the crystal structure of the samples, one can see clearly in the inset of Fig. 1 that with increasing Sr doping ($x=0, 0.05$ and $0.1$) than in the rhombohedral phase ($x=0.2$ and $0.25$). The boundary line between these two crystalline phases is taken at $x=0.15$, which corresponds to a tolerance factor $t=0.92$ determined from previous studies [3,19,21]. It has been noted in doped manganites that cooperative JT distortions are present in the orthorhombic phase but are not allowed due to the higher symmetry of the MnO$_6$ octahedra in the rhombohedral phase [22–24].

This also explains the increase of $T_C$ with Sr addition in the orthorhombic phase than in the rhombohedral phase (see Fig. 1). This also explains a faster increasing rate of $T_C$ with Sr addition in the orthorhombic phase than in the rhombohedral phase (see the inset of Fig. 1). To determine the type of magnetic phase transition in La$_{0.7}$Ca$_{0.3}$MnO$_3$ ($x=0, 0.05, 0.1, 0.2$ and $0.25$) samples, we have analyzed $H/M$ vs. $M^2$ curves (which were converted from the isothermal $H$–$M$ data) using Banerjee criterion [25] and the results of which are presented in Fig. 2. According to this criterion, the magnetic transition is of second order if all the $H/M$ vs. $M^2$ curves have a positive slope [26]. On the other hand, if some of the $H/M$ vs. $M^2$ curves show a negative slope at some point, the transition is of first order [26,27]. It can be observed in Fig. 2 that the $H/M$ vs. $M^2$ curves of the $x=0$ and $0.05$ samples show a negative slope at $T>T_C$, indicating that the magnetic transition is of FOMT type for these samples. However, the $H/M$ vs. $M^2$ curves of the $x=0.1, 0.2$ and $0.25$ samples have positive slopes, implying that these samples belong
to the class of SOMT materials. Nevertheless, a closer examination of the $H/M$ vs. $M^2$ curves at low magnetic fields for $x = 0.1$ reveals that this sample is not a purely SOMT material and some degree of FOMT may be still present in the material. It has been noted that a precise determination of the type of magnetic transition using Banerjee criterion becomes difficult when the magnetic transition is a mixture of FOMT and SOMT [28]. Our study shows that the Sr doping in La$_{0.7}$Ca$_{0.3}$,…

Since the La$_{0.7}$Ca$_{0.3}$… samples exhibit SOMT, we have used the Kouvel–Fisher (K–F) method [29] to determine precisely the critical exponents of these samples. This method consists of an iterative procedure which starts by constructing the Arrott–Noakes (A–N) plot (i.e. the plot of $M^2$ vs. $(H/M)^{1/2}$). From it, the values for $M_0(T)$ are computed from the intercepts of various isothermal magnetization vs. field curves on the ordinate of the plot (for temperatures below $T_C$). The intercept on the abscissa (for temperatures above $T_C$) allows calculating $\chi_0(T)$. Once the $M_0(T)$ and $\chi_0(T)$ curves have been constructed, two additional parameter data sets, $X(T)$ and $Y(T)$, may be determined:

$$X(T) = \chi_0^{-1} \left( \frac{d\chi_0^{-1}}{dT} \right)^{-1} = \frac{T - T_C}{\gamma} \tag{1}$$

$$Y(T) = M_0 \left( \frac{dM_0}{dT} \right)^{-1} = \frac{T - T_C}{\beta} \tag{2}$$

In the critical region, both $X(T)$ and $Y(T)$ should be linear, with slopes which give the values of the critical exponents, and intercepts of the temperature axis which correspond to the Curie temperature. The values of the critical exponents are refined by using an iterative method: once Eqs. (1) and (2) produce the values of the critical exponents, a generalized Arrott–Noakes plot ($M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$) is constructed and used to calculate new $M_0(T)$ and $\chi_0(T)$ curves, which are subsequently input into Eqs. (1) and (2), resulting in newer values for $\beta$ and $\gamma$. The procedure terminates when the desired convergence of the parameters is achieved. $T_C$ is obtained as the intercept on the abscissa of both $X$ and $Y$ lines.

Fig. 3 shows the A–N plots of the La$_{0.7}$Ca$_{0.3}$… samples with optimized critical exponents ($\beta$ and $\gamma$) obtained from the K–F method. Fig. 4 shows the K–F plot for one representative sample ($x = 0.2$). The best fits yield the values of $T_C = 289\,K$, $\beta = 0.26 \pm 0.01$ and $\gamma = 2.23 \pm 0.02$ for the $x = 0.1$ sample; $T_C = 326\,K$, $\beta = 0.36 \pm 0.01$ and $\gamma = 2.22 \pm 0.01$ for the $x = 0.2$ sample; $T_C = 344\,K$, $\beta = 0.42 \pm 0.02$ and $\gamma = 1.14 \pm 0.05$ for the $x = 0.25$ sample. Using the Widom scaling relationship [30], $\beta + \gamma = \beta_0$, the critical exponent ($\delta$) is determined to be $5.1 \pm 0.2$, $4.4 \pm 0.2$ and $3.7 \pm 0.2$ for $x = 0.1, 0.2$ and 0.25 compositions, respectively. This relationship has been tested by plotting $M(T - T_C)$ versus $H^{\beta(\beta + \gamma)} = H^{1/\delta}$ and checking the linearity of the curve as shown in Fig. 5.

The reliability of the obtained exponents and Curie temperatures can also be ascertained by checking the scaling of the magnetization curves. Two different constructions have been used in this work, both based on the scaling equation of state. For magnetic systems, the scaling equation of state takes the form [31]

$$\frac{H}{M^{\frac{1}{\beta}}} = h \left( \frac{\varepsilon}{M^{1/\beta}} \right), \tag{3}$$

where $\varepsilon = (T - T_C)/T_C$ is the reduced temperature, $T_C$ is the Curie temperature, $h(x)$ is a scaling function and $\beta$ and $\delta$ are critical exponents which characterize the magnetization behavior along the coexistence ($H = 0$, $\varepsilon < 0$) and the critical isotherm ($\varepsilon = 0$), respectively. Eq. (3) may be formally inverted as:

$$\frac{M}{|\varepsilon|^{\beta}} = m_{\pm} \left( \frac{H}{|\varepsilon|^{1/\delta}} \right), \tag{4}$$
Fig. 3. Modified Arrott plot isotherms with 1K temperature interval for the La$_{0.7}$Ca$_{0.3-x}$Sr$_x$MnO$_3$ ($x=0.1, 0.2$ and $0.25$) samples.

Fig. 4. Temperature dependence of spontaneous $M_s$ (square) and inverse initial susceptibility $1/\chi$ (circles) for the $x=0.2$ sample; solid lines are fitting curves to Eqs. (1) and (2), respectively.

Fig. 5. The linearity of the $M(T=T_c)$ versus $H^{1/\delta}$ curves validates the value of $\delta$ calculated using the Widom relationship with the experimental data.

where $\Delta = \beta \delta$ is the gap exponent, and the plus (minus) sign corresponds to $\varepsilon > 0$ ($\varepsilon < 0$), respectively. Therefore, according to Eq. (3), if the appropriate values for the critical exponents and for the Curie temperature are used, the plot of $M/H^{1/\delta}$ versus $\varepsilon H^{1/\Delta}$ should correspond to a universal curve onto which all experimental data points collapse. Alternatively, Eq. (4) indicates that $M/|\varepsilon|^{\beta}$ versus $H/|\varepsilon|^{\gamma}$ should result in two universal curves, one for $\varepsilon > 0$ and the other for $\varepsilon < 0$. For a more convenient visualization of the results, this plot is usually represented in logarithmic scale. However, this second representation tends to cover the small deviations of the experimental data with respect to the universal curves caused by an inappropriate choice of the parameters. Using the values of $\beta$, $\gamma$ and $T_C$ obtained from the K–F method, the scaled data are plotted in Fig. 6 for the $x=0.1$ and $0.2$ samples, respectively. In the case of scaling using Eq. (4), it can be observed that all the experimental points fall on two curves, one for $T<T_C$ and the other for $T>T_C$. This clearly indicates that the obtained values of $\beta$, $\gamma$ and $T_C$ for these samples are reliable and in agreement with the scaling hypothesis. A less perfect overlap of the data points has been observed for the $x=0.1$ sample in comparison with the $x=0.2$ sample (see Fig. 6a and b). This agrees with our previous observation (Fig. 2c) and argument that this sample is not a purely SOMT material and some degree of FOMT is still present in it.

To put our obtained results in the context of previous works, we summarize in Table 1 the values of the critical exponents of La$_{0.7}$Ca$_{0.3-x}$Sr$_x$MnO$_3$ ($x=0.1, 0.2$ and $0.25$) samples, of different theoretical models [32,33] and of other manganites in the literature [34–60]. It has been argued that in homogeneously magnetic systems the universality class of the magnetic phase transition should depend on the range of the exchange interaction, $J(r)$ [61]. If $J(r)$ decays with distance ($r$) at a rate faster than $r^{-5}$ then the Heisenberg exponents ($\beta = 0.365 \pm 0.003$, $\gamma = 1.336 \pm 0.004$) are valid for a 3D isotropic ferromagnet [32]. However, if $J(r)$ decays at a rate slower than $r^{-4.5}$ then the mean-field exponents ($\beta = 0.5$, $\gamma = 1$) are valid. According to the DE theory, the effective ferromagnetic interaction is driven by the kinetics of the electrons which favor extended states. Therefore, one could expect the critical exponents in the DE model to be described within the framework of the mean-field theory [35,62]. However, computational studies have demonstrated that the critical exponents in the DE model are con-
Fig. 6. Normalized isotherms of La\(_{0.7}\)Ca\(_{0.3-x}\)Sr\(_{x}\)MnO\(_3\) (x = 0.1 and 0.2) samples below and above Curie temperature (\(T_C\)) using the values of \(\hat{\beta}\) and \(\gamma\) determined using from the K–F method.

Table 1
Comparison of the values of the critical exponents of La\(_{0.7}\)Ca\(_{0.3-x}\)Sr\(_{x}\)MnO\(_3\) (x = 0.1, 0.2 and 0.25) single crystals with those of theoretical models and of other manganites in the literature. Bulk magnetization technique was used for studying the critical properties of all samples compared. SC: single crystal; PC: polycrystal; TF: thin film.

<table>
<thead>
<tr>
<th>Material Structure</th>
<th>(T_C) (K)</th>
<th>(\hat{\beta})</th>
<th>(\gamma)</th>
<th>(\delta)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(<em>{0.7})Ca(</em>{0.2})Sr(_{0.1})MnO(_3) (SC) Orthorhombic</td>
<td>289</td>
<td>(0.26\pm0.01)</td>
<td>(1.06\pm0.02)</td>
<td>(5.1\pm0.2)</td>
<td>This work</td>
</tr>
<tr>
<td>La(<em>{0.7})Ca(</em>{0.1})Sr(_{0.2})MnO(_3) (SC) Rhombohedral</td>
<td>326</td>
<td>(0.36\pm0.01)</td>
<td>(1.22\pm0.01)</td>
<td>(4.4\pm0.2)</td>
<td>This work</td>
</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})MnO(_3) (SC) Rhombohedral</td>
<td>344</td>
<td>(0.42\pm0.02)</td>
<td>(1.14\pm0.05)</td>
<td>(3.7\pm0.2)</td>
<td>This work</td>
</tr>
<tr>
<td>Mean-field model</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
<td>3.0</td>
<td>[32]</td>
</tr>
<tr>
<td>3D Heisenberg model</td>
<td>0.365 ± 0.003</td>
<td>1.336 ± 0.004</td>
<td></td>
<td>4.80 ± 0.04</td>
<td>[32]</td>
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<td>3D Ising model</td>
<td>0.325 ± 0.002</td>
<td>1.241 ± 0.002</td>
<td></td>
<td>4.82 ± 0.02</td>
<td>[32]</td>
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<tr>
<td>Tricritical mean-field model</td>
<td>0.25</td>
<td>1</td>
<td></td>
<td>5</td>
<td>[33]</td>
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<td>La(<em>{0.7})Ca(</em>{0.3})MnO(_3) (SC) Orthorhombic</td>
<td>229</td>
<td>0.14 ± 0.02</td>
<td>0.81 ± 0.03</td>
<td>1.22 ± 0.04</td>
<td>[39]</td>
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<tr>
<td>La(<em>{0.7})Ca(</em>{0.3})MnO(_3) (PC)</td>
<td>265</td>
<td>0.25 ± 0.03</td>
<td>1.03 ± 0.05</td>
<td>5.0 ± 0.8</td>
<td>[33]</td>
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<tr>
<td>La(<em>{0.67})Sr(</em>{0.33})Mn(<em>{0.9})Ga(</em>{0.1})O(_3) (PC)</td>
<td>116</td>
<td>0.387 ± 0.006</td>
<td>1.36 ± 0.002</td>
<td>4.6 ± 0.03</td>
<td>[46]</td>
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<tr>
<td>La(<em>{0.67})Sr(</em>{0.33})MnO(_3) (TF)</td>
<td>261</td>
<td>0.368 ± 0.003</td>
<td>1.384 ± 0.001</td>
<td>4.76 ± 0.32</td>
<td>[41]</td>
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<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Ga(</em>{0.1})O(_3) (SC)</td>
<td>346</td>
<td>0.40 ± 0.02</td>
<td>1.27 ± 0.06</td>
<td>4.12 ± 0.33</td>
<td>[40]</td>
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<td>La(<em>{0.7})Sr(</em>{0.3})MnO(_3) (SC)</td>
<td>354</td>
<td>0.37 ± 0.04</td>
<td>1.22 ± 0.03</td>
<td>4.25 ± 0.2</td>
<td>[44]</td>
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<td>La(<em>{0.7})Ba(</em>{0.3})MnO(_3) (PC)</td>
<td>306</td>
<td>0.356 ± 0.004</td>
<td>1.120 ± 0.003</td>
<td>4.15 ± 0.05</td>
<td>[36]</td>
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<td>La(<em>{0.7})Ba(</em>{0.3})MnO(_3) (PC)</td>
<td>162</td>
<td>0.498</td>
<td>1.456</td>
<td>3.92</td>
<td>[50]</td>
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<td>Nd(<em>{0.85})Pb(</em>{0.15})MnO(_3) (SC) Tetragonal</td>
<td>109</td>
<td>0.372 ± 0.004</td>
<td>1.347 ± 0.001</td>
<td>4.67 ± 0.03</td>
<td>[49]</td>
</tr>
<tr>
<td>Nd(<em>{0.6})Pb(</em>{0.4})MnO(_3) (SC) Tetragonal</td>
<td>148</td>
<td>0.361 ± 0.013</td>
<td>1.325 ± 0.001</td>
<td>4.62 ± 0.04</td>
<td>[49]</td>
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<tr>
<td>Nd(<em>{0.8})Pb(</em>{0.2})MnO(_3) (SC) Tetragonal</td>
<td>156</td>
<td>0.374 ± 0.006</td>
<td>1.329 ± 0.003</td>
<td>4.54 ± 0.10</td>
<td>[43]</td>
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<tr>
<td>Pr(<em>{0.7})Pb(</em>{0.3})MnO(_3) (SC) Pseudocubic</td>
<td>167</td>
<td>0.344 ± 0.001</td>
<td>1.352 ± 0.006</td>
<td>4.69 ± 0.02</td>
<td>[55]</td>
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<tr>
<td>Pr(<em>{0.5})Pb(</em>{0.5})MnO(_3) (SC) Pseudocubic</td>
<td>197</td>
<td>0.404 ± 0.001</td>
<td>1.357 ± 0.006</td>
<td>4.37 ± 0.09</td>
<td>[55]</td>
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<td>LaMn(<em>{0.9})Te(</em>{0.1})MnO(_3) (PC)</td>
<td>172</td>
<td>0.378 ± 0.007</td>
<td>1.29 ± 0.02</td>
<td>4.19 ± 0.03</td>
<td>[54]</td>
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<td>LaMn(<em>{0.9})Te(</em>{0.1})MnO(_3) (PC)</td>
<td>145</td>
<td>0.375 ± 0.005</td>
<td>1.25 ± 0.02</td>
<td>4.11 ± 0.04</td>
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<td>LaMn(<em>{0.9})Te(</em>{0.1})MnO(_3) (PC)</td>
<td>121</td>
<td>0.376 ± 0.003</td>
<td>1.24 ± 0.01</td>
<td>4.16 ± 0.03</td>
<td>[54]</td>
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<tr>
<td>LaMn(<em>{0.9})Te(</em>{0.1})MnO(_3) (PC)</td>
<td>95</td>
<td>0.359 ± 0.004</td>
<td>1.28 ± 0.01</td>
<td>4.21 ± 0.05</td>
<td>[54]</td>
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<td>La(<em>{0.7})Te(</em>{0.1})MnO(_3) (PC)</td>
<td>239</td>
<td>0.201 ± 0.003</td>
<td>1.27 ± 0.04</td>
<td>7.14 ± 0.04</td>
<td>[53]</td>
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<tr>
<td>Pr(<em>{0.5})Sr(</em>{0.5})MnO(_3) (SC) Orthorhombic</td>
<td>261</td>
<td>0.443 ± 0.002</td>
<td>1.339 ± 0.006</td>
<td>4 ± 0.03</td>
<td>[57]</td>
</tr>
<tr>
<td>Nd(<em>{0.5})Sr(</em>{0.5})MnO(_3) (PC)</td>
<td>239</td>
<td>0.5 ± 0.001</td>
<td>1.02 ± 0.02</td>
<td>4.02 ± 0.02</td>
<td>[51]</td>
</tr>
<tr>
<td>LaMnO(_{3.14}) (PC)</td>
<td>141</td>
<td>0.415</td>
<td>1.470</td>
<td>4.542</td>
<td>[37]</td>
</tr>
</tbody>
</table>
sistent with those expected for the 3D Heisenberg model [63]. It has also been theoretically shown that PM–FM transitions may become discontinuous, depending on doping level and competition with superexchange AFM interactions [64].

The values of the critical exponents of La0.7Ca0.3−xSrxMnO3 (x = 0.1, 0.2 and 0.25) samples are in agreement with those predicted by the latter models [63,64]. It is clear in Table 1 that the critical exponents of the x = 0.1 sample (β = 0.26 ± 0.01, γ = 1.06 ± 0.02) match well with those derived from the tricritical mean-field model (β = 0.25, γ = 1). The existence of this tricritical point (x = 0.1) clearly sets a boundary between FOMT (x < 0.1) and SOMT (x = 0.1) with the ferromagnetic range (0 ≤ x ≤ 0.25). A similar case has also been reported on La1−xCaxMnO3 (0.2 ≤ x ≤ 0.5) polycrystalline manganites, where the tricritical point is found at x = 0.4 [33]. To further confirm that the PM–FM transition becomes a conventional SOMT above the tricritical point, the critical exponents of the samples with x > 0.1 are expected to match those predicted for the 3D Heisenberg model [53]. As one can see clearly in Table 1, the values of the critical exponents of the x = 0.2 sample (β = 0.36 ± 0.01, γ = 1.22 ± 0.01) are close to those expected for the 3D Heisenberg model (β = 0.365 ± 0.003, γ = 1.336 ± 0.004). For the x = 0.25 sample, the value of β = 0.42 ± 0.02 is relatively larger than that expected for the 3D Heisenberg model (β = 0.365 ± 0.003) but is consistent with that of La0.7Sr0.3MnO3 (β = 0.45 ± 0.02) reported previously by Ziese [38] and Taran et al. [47] using the A–N method and by Lofland et al. [16] using microwave absorption methods. The critical exponent of the x = 0.25 sample (γ = 1.14 ± 0.05) is smaller than that of the x = 0.2 sample (γ = 1.22 ± 0.01). A gradual decrease of γ with Sr addition is clearly seen in Table 1 for La0.7Ca0.3−xSrMnO3 (x = 0.2 and 0.25) reported by us and for La0.7Sr0.3MnO3 (x = 0.3) reported by Ziese [38]. It has been argued that for a true SOMT the critical exponents are independent of the microscopic details of a system due to the divergence of correlation length and correlation time close to a transition point and hence their values are almost the same for a transition that may occur in different physical systems [31]. This hypothesis has been experimentally validated for the case of Nd1−xPrxMnO3 (x = 0.15, 0.3 and 0.4) [43,49] and LaMn1−xTixO3 (x = 0.05, 0.1 and 0.15) [54], where the critical exponents (both β and γ) are almost Pr- or Ti doping independent and are consistent with those expected for the 3D Heisenberg model. However, one must note secondary effects on the PM–FM transition (hence on the critical exponents) of a system due to magnetic anisotropies or dipolar long-range couplings of ferromagnetic clusters [42,48,50,65]. It has been pointed out that a Mn-ion triplets containing a Mn3+/Mn4+−Mn3+−Mn4+−Mn3+ clusts have significant binding energy of about half the binding energy of the bulk [66]. The large spin moments of these ferromagnetic clusters are expected to enhance the dipole–dipole interaction in the case of the 3D Heisenberg model thus resulting in larger values of the critical exponents than those predicted by this model [47,66]. Recently, magnetization and electron paramagnetic resonance (EPR) studies have revealed that ferromagnetic clusters persisting even in the paramagnetic region have significant influence on the magnetic order parameters (i.e. the critical exponents) in doped manganites, such as La0.95Pr0.05MnO3 (β = 0.498, γ = 1.456) [50] and Pr0.5Sr0.5MnO3 (β = 0.443 ± 0.002, γ = 1.339 ± 0.006) [57,67].

In the case of La0.7Ca0.3−xSrMnO3 (x = 0.1, 0.2 and 0.25) samples, the x = 0.1 composition is on the crossover region of FOMT → SOMT. This composition has also been noted to be on the crossover region of a MI transition (for x < 0.1 compositions the MI transition is well defined, but this transition is largely suppressed and instead a metal–like conducting behavior is observed in the paramagnetic region for x > 0.1 compositions) [3]. This coincidence clearly demonstrates a coherent relation between the magnetism and conductivity in the doped manganites. Furthermore, we note the nonlinearity of the modified Arrott plots (Fig. 3), signifying the nature of ferromagnetic clusters in the La0.7Ca0.3−xSrMnO3 samples [43,49,55]. The formation of ferromagnetic clusters in these samples has been evidenced from EPR spectra [68]. Therefore, it can be proposed that it is the formation of ferromagnetic clusters that leads to a percolation mechanism for conduction and metallic behaviors observed at T = Tc in the paramagnetic region for the x = 0.2 and 0.25 samples [55,69]. A recent study has shown that the PM–FM transition of a (Sm0.7Nd0.3)0.52Sr0.48MnO3 manganite transforms from a FOMT to a SOMT when subjected to an external pressure [58]. The critical exponents of this sample (β = 0.358, γ = 1.297) under external pressure are close to those expected for the 3D Heisenberg model (β = 0.365, γ = 1.336). It has been argued that the presence of external pressure at a certain level can suppress the polaronic state, increase the bandwidth (W) of the system, and as a result the FOMT converts to SOMT [58]. In the case of La0.7Ca0.3−xSrMnO3 (x = 0, 0.05, 0.1, 0.2 and 0.25) manganites, we argue that the substitution of large Sr2+ ions ([Ir] ~ 1.31 Å) for smaller Ca2+ ions ([Ir] ~ 1.18 Å) introduces chemical (internal) pressure without affecting the valency of the Mn ions (the ratio of Mn3+/Mn4+ is unchanged or no change of electronic density) [18,19]. It has been shown that the chemical pressure modifies local structural parameters such as the Mn–O bond distance and Mn–O–Mn bond angle, which directly influence the case of electron hopping between Mn ions (i.e. the electronic bandwidth − W) [13,18,19]. Therefore, the change of internal pressure with Sr addition is expected to increase W which consequently increases the Tc and converts the FOMT into SOMT at a threshold pressure (which corresponds to a Sr-doping level, x = 0.1). Above the critical point (x > 0.1), the system shows a SOMT with the critical exponents belonging to the Heisenberg universality class. The change in nature of the PM–FM transition with chemical (internal) pressure (Sr doping) clearly points to a strong coupling between the magnetic order parameter and lattice strain in these doped manganites [58].

Furthermore, the theory predicts that the PM–FM transition of La1−xMgMnO3 (M = Ca, Sr) becomes continuous or discontinuous, depending upon the change in the relative strength of the DE interaction (i.e. the FM interaction) and AFM coupling [64]. In the present study, we note that the ground state of La0.7Ca1−xMnO3 (x = 0) is ferromagnetic, but the AFM phase is also present and competing with the FM phase [14,15]. The substitution of Sr for Ca in La0.7Ca0.3−xSrMnO3 (x = 0.05, 0.1, 0.2 and 0.25) suppresses the AFM phase while it enhances the FM phase. As a result, the PM–FM transition changes from discontinuous to continuous at x ~ 0.1. In addition, we recall that strong JT lattice distortions are possible in the x = 0.05 and 0.1 samples that crystallize in an orthorhombic structure, whereas this effect is negligible in the x = 0.2 and 0.25 samples possessing a rhombohedral structure. These important observations, coupled with the magnetic, magnetotransport and critical exponent analyses, clearly suggest that in addition to the DE interaction, cooperative JT effects and AFM coupling are important for the exchange of the magnetic interaction and the MI transition including CMR in La0.7Ca0.3−xSrMnO3 (x = 0.05 and 0.1) manganites. While the DE model is sufficient to explain the canonical MR behavior in La0.7Ca0.3−xSrO3 (x = 0.2 and 0.25) samples where AFM interactions are weak and JT lattice distortions are negligible, the formation of ferromagnetic clusters likely leads to a percolation mechanism for the conduction and metallic behavior observed in the paramagnetic region for these samples.

4. Conclusions

The ferromagnetic phase transitions and critical behavior of La0.7Ca0.3−xSrMnO3 (x = 0, 0.05, 0.1, 0.2 and 0.25) single crystals
have been studied systematically. Using Banerjee criterion and Kouvel–Fisher method, we show that $x \sim 0.1$ is a tricritical point that separates FOMT for $x < 0.1$ from SOMT for $x > 0.1$. Above the tricritical point, the system exhibits a SOMT with the critical exponents belonging to the Heisenberg universality class with short-range exchange interactions. This indicates that the magnetic interaction in these systems is of short-range type. We show that while the DE mechanism and formation of ferromagnetic clusters can account for the canonical MR and metal-like conducting behavior in La$_{0.7}$Ca$_{0.3}$MnO$_3$ with $x = 0.2$ and 0.25, other effects such as cooperative Jahn–Teller distortions and antiferromagnetic coupling are important additions for understanding the relationship between the PM–FM transition and MI transition, including CMR in La$_{0.7}$Ca$_{0.3}$MnO$_3$ with $x = 0.05$ and 0.1. The change of the PM–FM transition with chemical (internal) pressure introduced by substitution of larger Sr ions for smaller Ca ions points to the strong coupling between the magnetic order and structural parameters in these doped manganites.

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References