Critical behavior of La₀.7Ca₀.3Mn₁₋ₓNiₓO₃ manganites exhibiting the crossover of first- and second-order phase transitions


Abstract

We used Banerjee’s criteria, modified Arrott plots, and the scaling hypothesis to analyze magnetic-field dependences of magnetization near the ferromagnetic-paramagnetic (FM-PM) phase-transition temperature (T_C) of perovskite-type manganites La₀.7Ca₀.3Mn₁₋ₓNiₓO₃ (x = 0.09, 0.12 and 0.15). In the FM region, experimental results for the critical exponent β (0.171 and 0.262 for x = 0.09 and 0.12, respectively) reveals two first samples exhibiting tricriticality associated with the crossover of first- and second-order phase transitions. Increasing Ni-doping content leads to the shift of the β value (0.320 for x = 0.15) towards that expected for the 3D Ising model (β = 0.325). This is due to the fact that the substitution of Ni ions into the Mn site changes structural parameters and dilutes the FM phase, which act as fluctuations and influence the FM-interaction strength of double-exchange Mn⁺⁺₃+-Mn⁺⁺₄+ pairs, and the phase-transition type. For the critical exponent γ (0.976–0.990), the stability in its value demonstrates the PM behavior above T_C of the samples. Particularly, around T_C of La₀.7Ca₀.3Mn₁₋ₓNiₓO₃ compounds, magnetic-field dependences of the maximum magnetic-entropy change can be described by a power law of (ΔS_magnetic × H^n), where values n = 0.55–0.77 are quite far from those (n = 0.33–0.48) calculated from the theoretical relation n = (β−1)/(β+γ). This difference is related to the use of the mean-field theory for the samples exhibiting the magnetic inhomogeneity.

1. Introduction

It is known that hole-doped lanthanum manganites of La₁₋ₓ(Ca, Sr, Ba)₂MnO₃ with x = 0.3 (corresponding to Mn³⁺/Mn⁴⁺ = 7/3) usually exhibit colossal magnetoresistance (MR) and magnetocaloric (MC) effects around their ferromagnetic-paramagnetic (FM-PM) phase-transition temperature (the Curie temperature, T_C) [1]. With this doping content, double-exchange (DE) FM interactions between Mn³⁺ and Mn⁴⁺ are dominant as comparing with super-exchange anti-FM interactions of Mn³⁺–Mn³⁺ and Mn⁴⁺–Mn⁴⁺ pairs. The strength of magnetic interactions thus depends on the average bond length (Mn–O), and bond angle (Mn–O–Mn) of the perovskite structure. Different compounds have different bond parameters, which are related to Jahn–Teller lattice distortions due to strong electron-phonon coupling [2]. In reference to the symmetry of MnO₆ octahedra, it has been noted that cooperative Jahn–Teller distortions are present in an orthorhombic structure rather than in the rhombohedral one [3].

Among hole-doped manganites, orthorhombic La₀.7Ca₀.3–
MnO₃ is known as a typical material exhibiting MR and MC effects much greater than those obtained from the other compounds. Particularly, depending on bulk or nanostructured sample types, its T_C in the range of 222–265 K [3–9] can be tuned towards room temperature by doping Sr, Ba or Pb [10–14]. Meanwhile, the transition-metal doping (such as Co, Fe, Ni and so forth) lowers T_C [15–17]. Additionally, its discontinuous FM–PM transition at T_C is followed up with structural changes, and is known as a first-order magnetic phase transition (FOMT) [8,9,12]. This discontinuous phase transition can be rounded to a continuous one of a second-order magnetic phase transition (SOMT) upon the doping, and reduced dimensionality (i.e., finite-size effects), and external fields [5,7,11,12,16,18,19]. The assessment of a continuous SOMT can base on the success in determining the critical exponents β, γ, and δ associated with temperature dependences of the spontaneous magnetization.
$M_i(T)$, inverse initial susceptibility, $\chi_i^{-1}(T)$, and critical isotherm at $T_c$, respectively [20,21]. Distinguishing the FOMT from the SOMT can be based on the criteria proposed by Banerjee [22], who performed $H/M$ versus $M^2$ curves (where $H$ is the field, and $M$ is the magnetization) in the vicinity of $T_c$, and then suggested that their positive or negative slopes are indication of a second- or first-order phase transition, respectively.

Reviewing previous studies, one can see that many works focused on $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_1\text{O}_3$-based materials showing the FOMT and/or SOMT. However, the crossover region from first-order to second-order phase transitions, and some related physical properties, such as the magnetic entropy change versus $T$ and $H$, $\Delta S_m(T, H)$, have not been widely studied. Furthermore, there is no much attention given to the assessment of a magnetic ordering parameter ($n$) determined from the relations $n=1+\beta/\gamma$ [23], and from a power law $\Delta S_{\text{max}}(H) \propto H^n$ [24] (where $\Delta S_{\text{max}}$ is the maximum magnetic entropy change around $T_c$). To get more insight into the above problems, we prepared $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ compounds, and have studied their critical behaviors upon Banerjee’s criteria [22], modified Arrott plots and the scaling hypothesis [20,21]. The determined critical values are then discussed together with the magnetic ordering parameter $n$.

2. Experimental details

Three polycrystalline perovskite-type manganites $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_1\text{O}_3$ with $x=0.09, 0.12$ and $0.15$ were prepared by solid-state reaction as using purity commercial powders $\text{La}_2\text{O}_3$, $\text{CaO}$, $\text{NiO}$, and $\text{MnCO}_3$ ($99.9\%$) as precursors. These powders combined with stoichiometrical quantities were well mixed and ground, and then pre-annealed at 900 $^\circ$C for 24 h. After pre-annealing, three mixtures were re-ground and pressed into pellets, and annealed at 1300 $^\circ$C for 72 h in air. For reference, the parent compound $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_3\text{O}_3$ was also prepared with the same conditions as described. X-ray diffraction (XRD) patterns of the final products checked by an X-ray diffractometer (Bruker AXS, D8 Discover) revealed the single phase in an orthorhombic structure (the space group $\text{Pbnm}$) of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ samples, see Fig. 1(a). Basing on the XRD data, we calculated the lattice parameters ($a$, $b$, and $c$) and unit cell ($V$), as shown in Table 1. The variation of these parameters indicates the substitution of Ni ions (could be Ni$^{2+}$, Ni$^{3+}$, and/or Ni$^{4+}$) for Mn in the perovskite structure. Magnetic measurements were performed on a superconducting quantum interference device magnetometer (SQUID). The $T_c$ values obtained from the flexion points in temperature dependences of magnetization, $M(T)$, with the applied field $H=100$ Oe, Fig. 1(b) are about 200, 185 and 170 K for $x=0.09, 0.12$ and 0.15, respectively, which are lower than the value $T_c \approx 260$ K of the parent compound.

3. Results and discussion

Fig. 2 shows $M$–$H$ data and inverse Arrott plots ($H/M$ versus $M^2$) at different temperatures in the FM–PM phase transition of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$. It appears from the $M$–$H$ data that there is no saturation magnetization value in spite of the $H$ variation up to 40 kOe. This is assigned to the existence of the magnetic inhomogeneity or short-range FM order. At a given temperature, higher Ni-doping content reduces the magnetization. With increasing temperature, nonlinear $M$–$H$ curves in the FM region become linear because the samples enter the PM state. Different from the parent compound [5,7–9,12], there is no S-like shape in the $M$–$H$ curves, and negative slopes in the $H/M$ versus $M^2$ curves, see Fig. 2. These tokens demonstrate our Ni-doped samples undergoing the FOMT [22,25].

According to the mean-field theory (MFT), proposed for a ferromagnet exhibiting the SOMT and long-range FM interactions [26], the free energy $G_t$ is expanded in even powers of $M$: $G_t=aM^2+bM^4+\cdots=HM$, where $a$ and $b$ are temperature-dependent parameters. Minimizing $G_t$ as $\partial G_t/\partial M=0$ results in the relation $H/M=2a+4bM^2$. It means that if magnetic interactions of the FM system exactly obey the MFT, $M^2$ versus $H/M$ curves in the vicinity of $T_c$ are parallel straight lines. At $T_c$, the $M^2$ and $H/M$ line passes through the origin [27,28]. However, these features are absent from the Arrott performance shown in Fig. 2(b, d, and e). It means that magnetic interactions in the samples could not be the long-range type. The critical exponents $\beta=0.5$ and $\gamma=1.0$ (in the normal Arrott plots [20,27]) based on the MFT are thus not suitable to describe magnetic interactions taking place in our samples. Within the framework...

Table 1 Values of the lattice parameters and unit cell calculated from XRD analyses of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ with $x=0.09, 0.12$ and 0.15.

<table>
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<th>Sample, $x$</th>
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<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
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<td>7.711</td>
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<td>5.474</td>
<td>5.450</td>
<td>7.713</td>
<td>230.10</td>
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</table>

Fig. 1. (Color online) (a) Room-temperature XRD patterns, and (b) normalized $M(T)$ curves with the applied field of $H=100$ Oe for $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ ($x=0$, 0.09, 0.12, and 0.15).
of the MFT, we need to find other sets of the critical-exponent values reflecting more frankly the magnetic properties of the samples. This work is based on the modified Arrott plot (MAP) method [20], which is generalized by the scaling equation of state, $(H/M)^{1/β} = c_1 ε + c_2 M^{1/γ}$, where $c_1$ and $c_2$ are temperature-dependent parameters, and $ε = (T - T_c)/T_c$ is the reduced temperature. $β$ and $γ$ values can be obtained from the asymptotic relations [18,20]

$$M_s(T) = M_0(-ε)^β, \quad β < 0,$$

$$\chi^{-1}_0(T) = (h_0/M_0)\epsilon^γ, \quad ε > 0,$$

$$M = DH^{1/δ}, \quad ε = 0,$$

where $M_0$, $h_0$, and $D$ are the critical amplitudes. Additionally, according to the static-scaling hypothesis [21], $M$ is a function of $ε$ and $H$, $M(H, ε) = |ε|^β f_1(H/|ε|^{1-γ})$. This equation reflects that, with determined $β$ and $γ$ values, plotting $M/|ε|^β$ versus $H/|ε|^{1-γ}$ makes all data points falling on the $f_1$ and $f_2$ branches for $T < T_c$ and $T > T_c$, respectively. Here, determining the critical parameters is based on the MAP method, and started from the scaling equation of state. Correct $β$ and $γ$ values make $M–H$ data points falling on a set of parallel straight lines in the performance of $M^{1/β}$ versus $(H/M)^{1/γ}$. Moreover, the $M^{1/β}$ versus $(H/M)^{1/γ}$ line passes through the origin at $T_c$. Similar to the MFT case, our analyses indicated that the exponent values $β = 0.365$ and $γ = 1.336$ expected for the 3D Heisenberg model [21] do not match with the descriptions of the MAP method. Only $β = 0.25$ and $γ = 1.0$ expected for the tricritical MFT model (T-MFT), and $β = 0.325$ and $γ = 1.241$ expected for the 3D Ising model [12,29] can be used as initially trial values to find optimal exponent values for the samples with $x = 0.09$ and 0.12, and for $x = 0.15$, respectively. With these trial values, $M_s(T)$ and $\chi_0(T)$ data would be obtained from the linear extrapolation in the high-field region for the isotherms to the co-ordinate axes of $M_s$ and $\chi_0$ data. More importantly, the $T_c$ values of the samples obtained from the linear extrapolation are then fitted to Eqs. (1) and (2), respectively, to achieve better $β$, $γ$, and $T_c$ values, as can be seen from Fig. 3. These new values of $β$, $γ$, and $T_c$ are continuously used for next MAP processes until their optimal values are achieved. Notably, the $T_c$ values of the samples obtained from $M–T$ measurements were also used as reference in the fitting. With such the careful comparison, only the sets of critical parameters with $T_c ≈ 199.4 \text{ K}$, $β = 0.171 ± 0.006$ and $γ = 0.976 ± 0.012$ for $x = 0.09$; $T_c ≈ 184.4 \text{ K}$, $β = 0.262 ± 0.005$ and $γ = 0.979 ± 0.012$ for $x = 0.12$; and $T_c ≈ 170 \text{ K}$, $β = 0.320 ± 0.009$...
and $\gamma = 0.990 \pm 0.082$ for $x = 0.15$ are in good agreement with the MAP descriptions, see Fig. 4. With the obtained critical exponents, the scaling performance of $M/(\varepsilon^\beta)$ versus $H/(\varepsilon^\gamma)$ curves, see Fig. 5 and their inset, reveals the $M-H$ data points at high-magnetic fields falling into two $f_-$ and $f_+$ universal branches for $T < T_C$ and $T > T_C$, respectively. These results prove the reliability in value of the critical values obtained from our work. It should be noticed that the MAP method only works well for the fields $(H_H)$ higher than 28, 24 and 12 kOe for $x = 0.09$, 0.12 and 0.15, respectively. At the fields lower than $H_H$, there may be rearrangement of magnetic domains, the effect due to the uncertainty in the calculation of demagnetization factor, and/or the persistence of the FOMT (particularly for the samples with $x = 0.09$ and 0.12) [12,30]. Unexpected errors for critical values can thus be occurred, leading to the scattering of the $M-H$ data points (at the fields lower than $H_H$) from the universal curves [5,12], as can be seen in Fig. 5. For the exponent $\delta$, its value can be obtained from fitting the isotherms at $T = T_C$ to Eq. (3). Basically, the $\delta$ values determined from Eq. (3) would be equal to those calculated from the Widom relation $\delta = 1 + \gamma/\beta$ [21]. In our work, $\delta$ values are about 6.7, 4.7, and 4.1 for $x = 0.09$, 0.12 and 0.15, respectively. Clearly, with increasing Ni concentration in La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$Ni$_x$O$_3$, there is a shifting tendency of the exponent values ($\beta$, $\gamma$, and $\delta$) towards those of the MFT (with $\beta = 0.5$, $\gamma = 1$ and $\delta = 3$). This is tightly related to the FOMT–SOMT transformation. The better applicability of the MAP method has been found for the samples with high-enough Ni concentrations as $x > 0.12$. We believe that the substitution of Ni ions into the Mn site not only changes structural parameters of $\langle$Mn–O$\rangle$ and $\langle$Mn–O–Mn$\rangle$, but also leads to the additional presence of anti-FM interactions related to Ni ions (for example, super-exchange pairs of Ni$^{2+}$–Ni$^{2+}$, Ni$^{3+}$–Ni$^{3+}$, Ni$^{4+}$–Ni$^{4+}$, and/or Ni$^{2+}$–Ni$^{4+}$–Mn$^{3+}$–Mn$^{4+}$) besides pre-existing anti-FM interaction pairs of Mn$^{3+}$–Mn$^{3+}$ and Mn$^{4+}$–Mn$^{4+}$. These factors act as fluctuations, reduce the strength of Mn$^{3+}$–Mn$^{4+}$ FM interactions (which thus reduce the magnetization and $T_C$ values), and influence the phase transition as well.

Comparing with the theoretical models [21,29], one can see that the values of $\gamma$ (=0.976–0.990) are quite stable, demonstrating the complete PM state in the samples at temperatures above $T_C$. For the FM region, however, $\beta = 0.262$ for $x = 0.12$ is close to that expected for the T-MFT ($\beta = 0.25$). This sample thus exhibits tricriticality associated with the crossover of first- and second-order phase transitions. Similar results were also found in some manganites [9,12,29]. A smaller value of $\beta = 0.171$ for $x = 0.09$ reveals this sample lying in the region close to the crossover, where the FOMT is still persistent. It is also known that the MAP application for the materials with the presence
of the FOMT makes of their exponent values different from those expected for the theoretical models, such as the cases of La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.5}$Te$_{0.1}$MnO$_3$ [5,31]. With a higher Ni-doping content of $x=0.15$, one can see that its $\beta$ value ($=0.320$) is close to that expected for the 3D Ising model ($\beta=0.325$), indicating the existence of short-range FM order associated with the magnetic inhomogeneity, and FM/anti-FM mixed phase. It comes to our attention that the $\beta$ value tends to shift towards the values of the Heisenberg model and MFT if Ni content ($x$) in La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$Ni$_x$O$_3$ is higher than 0.15. For inhomogeneous ferromagnets, the critical values usually depend on the magnetic field ranges employed for MAP analyses because of a significant field-induced change in the nature and range of the FM interaction [9,32]. Performing a renormalization group analysis of exchange-interaction systems, Fisher et al. found the exponent values depending on the range of exchange interaction characterized by $J(r)=1/[d^{d-\sigma}]$ (where $d$ and $\sigma$ are the dimension of the system, and the interaction range, respectively) [33]. The MFT exponents are valid for $\sigma<1/2$ while the Heisenberg ones are valid for $\sigma>2$. The exponents belong to other universality classes (such as the T-MFT and 3D Ising models) if $1/2<\sigma<2$, which can be the case taking place in our samples.

Together with assessing the critical behaviors of La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$Ni$_x$O$_3$ samples, we have also considered the magnetic-entropy change ($\Delta S_m$) and its field dependence, as shown in Fig. 6. At a given temperature for each sample, $-\Delta S_m$ increases with increasing $H$. Around $T_C$, $-\Delta S_m(T)$ curves reach the maxima, $|\Delta S_{\text{max}}|$. The $|\Delta S_{\text{max}}|$ values determined for $x=0.10$, 0.12, and 0.15 in the field $H=40$ Koe are about 7.1, 5.2, and 3.4 $\text{J}^{-1} \text{K}^{-1}$, respectively, which are smaller than those obtained from the parent compound [7]. Though the Ni doping reduces the $|\Delta S_{\text{max}}|$ value, the linewidth of the $-\Delta S_m(T)$ curves become broadened due to the FOMT–SOMT transformation, enhancing the refrigerant capacity (RC). Particularly, at $T_C$ the $H$ dependences of $|\Delta S_{\text{max}}|$ can be well described by a power law of $|\Delta S_{\text{max}}| \propto H^n$ [24], where values $n=0.55$, 0.68, and 0.77 for $x=0.09, 0.12$, and 0.15, respectively. These values are different from those ($n=0.33, 0.41, and 0.48$ for $x=0.09, 0.12, and 0.15$, respectively) calculated from the relation $n=1+(\beta-1)/(\beta+\gamma)$ [23]. As shown in Ref. [34], $n$ is known as a function of $T, H$ and $|\Delta S_m|$, which can also be obtained from the relation $n=d\ln(\Delta S_m)/d\ln H$. Depending on the variation of these parameters, $n$ would be different. It reaches the minimum at temperatures in the vicinity of $T_C$ [23]. We believe that a large deviation of the $n$ values obtained from two routes is because the exponent values $\beta$ and $\gamma$ determined from the MAP method are much different from those expected for the MFT. In other words, La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$Ni$_x$O$_3$ samples are not conventional ferromagnets. There are the magnetic inhomogeneity, and the existence of FOMT and/or SOMT properties (particularly for two samples with $x=0.09$ and 0.12 lying in the crossover region). For conventional ferromagnets obeyed the MFT, $n$ is equal to 2/3. However, experimental results based on the framework of the SOMT (MFT) theory for inhomogeneous ferromagnets, like the present cases, introduce the values $n$ different from $2/3$ [23,24].

4. Conclusions

We studied the critical behavior and related physical properties of manganites La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$Ni$_x$O$_3$ ($x=0.09, 0.12$ and $0.15$) around their $T_C$ values. Detailed analyses of the $M$–$H$–$T$ data based on the MAP method revealed the stability in value of $\gamma \approx 1$, demonstrating the real PM behavior above $T_C$ in the samples. However, in the FM region, experimental results revealed the sample $x=0.15$ undergoing the SOMT. Its $\beta$ exponent is close to that expected for the 3D Ising model. For the samples with lower Ni-doping contents, their exponents $\beta$ ($=0.171$ and 0.262 for $x=0.09$ and 0.12, respectively) indicate the samples exhibiting tricriticality associated with the FOMT–SOMT transformation; in which, the FOMT is dominant at the fields lower than $H_C$. Short–range FM interactions are thus found in all the samples. Interestingly, around $T_C$, field dependences of $|\Delta S_{\text{max}}|$ can be described by a power law $|\Delta S_{\text{max}}| \propto H^n$. The $n$ values ($=0.55-0.77$) obtained from the power-law fitting are higher than those ($n=0.33-0.48$) calculated from the relation $n=1+(\beta-1)/(\beta+\gamma)$. We believe that the deviation of the $n$ values obtained from two ways is related to the using of the approximate MFT (the MAP method) for unconventional ferromagnets (with the existence of the magnetic inhomogeneity, and FOMT and/or SOMT properties), where the exponent values $\beta$ and $\gamma$ determined are much different from those expected for the MFT.
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References


Fig. 6. (Color online) $\Delta S_m(T)$ curves with the fields $H=10, 20, 30$ and $40$ kOe, and field dependences of $\Delta S_{max}$ at $T_C$ fitted to a power law $\Delta S_{max} \propto H^n$ for La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$Ni$_x$O$_3$ with (a, b) $x=0.09$, (c, d) $x=0.12$ and (e, f) $x=0.15$. 