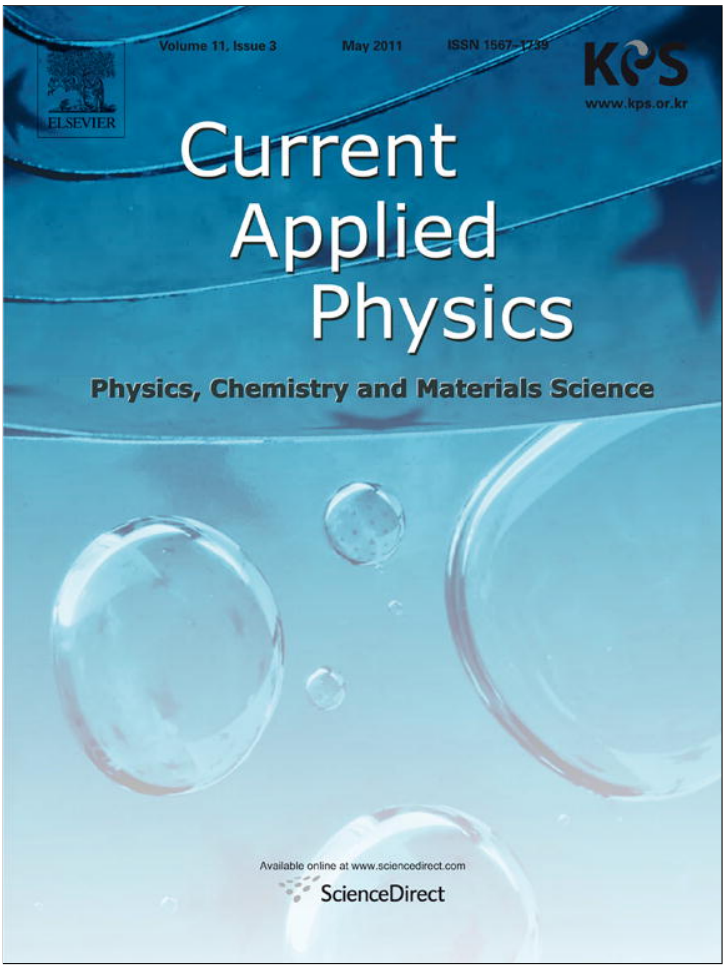

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# Critical behavior and magnetic entropy change in $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ perovskite manganite

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ABSTRACT

We studied the critical behavior and magnetic entropy change in a perovskite-manganite compound of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ around its Curie temperature of $T_C = 206.75$ K. Experimental results revealed that the sample exhibited the second-order magnetic phase transition with the exponents $\beta = 0.474$ and $\gamma = 1.152$ close to those expected from the mean-field theory ($\beta = 0.5$ and $\gamma = 1.0$). In the vicinity of $T_C$, the magnetic entropy change $\Delta S_M$ reached maximum values of 1.1, 1.7, and 2.7 J/kg K under magnetic-field variations of 10, 20, and 35 kOe, respectively. These $\Delta S_M$ values are much lower than those reported previously on the parent compound of $La_{0.7}Ca_{0.3}MnO_3$. The nature of this phenomenon is discussed by means of the characteristics of the magnetic phase transition, and critical exponents.



## 1. Introduction

$LaMnO_3$ is known as an anti-ferromagnetic insulator [1]. Recent discoveries of colossal magnetoresistance (CMR) around the ferromagnetic-to-paramagnetic phase transition in $LaMnO_3$-based materials have attracted intensive interest of research groups [2]. The magnetic and magneto-transport properties of this material system can be controlled simply by changing concentration of dopants. Depending on dopant types, one can fabricate hole-doped manganites ($La_{1-x}A_xMnO_3$, $A$ = Ca, Sr, Ba, Pb) or electron-doped manganites ($La_{1-x}B_xMnO_3$, $B$ = Ce, Te, Sb) [2,3]. Basically, the presence of dopants creates $Mn^{4+}$ and leads to the ferromagnetic double-exchange interaction between $Mn^{3+}$ and $Mn^{4+}$ ions, which completes with the anti-ferromagnetic interaction $Mn^{3+}$–$Mn^{3+}$ pre-existed in the parent compound $LaMnO_3$. A $LaMnO_3$-based compound usually exhibits CMR when the $Mn^{4+}$ concentration is high enough, where the ferromagnetic interaction is dominant.

Among perovskite manganites, $La_{1-x}Ca_xMnO_3$ is considered as one of the promising candidates for application of magnetic techniques because of showing CMR and a large magnetic entropy change (the magnetocaloric effect, MCE [4]) near room temperature. Earlier studies [5–8] revealed that the ferromagnetic interaction in $La_{1-x}Ca_xMnO_3$ became dominant as $x = 0.3$, corresponding to the ratio $Mn^{3+}/Mn^{4+} = 7/3$. With this discovery, many works on $La_{1-x}Ca_xMnO_3$ have been made. To explain a physical picture of CMR and MCE in $La_{1-x}Ca_xMnO_3$, it is based on the double-exchange model in addition to the Jahn-Teller polaron [2]. Experimentally, Booth and Shengelaya et al. [9,10] observed in the region of ferromagnetic–paramagnetic phase that there was a strong change in structural parameters of the <Mn–O> bond length and the <Mn–O–Mn> bond angle. They influenced directly on electronic-exchange processes between $Mn^{3+}$ and $Mn^{4+}$ ions. This phenomenon is also known as the first-order magnetic transition. The study of critical behaviour around the Curie temperature ($T_C$) would introduce the exponents ($\beta$, $\gamma$, and $\delta$) far from those obtained by conventional theoretical models of the mean-field theory, Ising model, and 3D Heisenberg model [6–8]. While $La_{0.7}Ca_{0.3}MnO_3$ exhibits the first-order magnetic transition, the doping of a small amount of Sr leads to the second-order magnetic transition [7]. To gain more insight into this aspect, we prepared a perovskite manganite sample of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$, in which $Zn^{2+}$ was expected to be in the Mn site [11]. Having compared to $La_{0.7}Ca_{0.3}MnO_3$, our work reveals that the presence of nonmagnetic Zn dopants in $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ reduces the $T_C$ value and magnetic entropy. Concurrently, the sample undergoes the second-order magnetic phase transition with the critical exponents $\beta$, $\gamma$, and $\delta$ fairly close to those expected from the mean-field theory.

## 2. Experiment

A polycrystalline sample of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ was prepared by conventional solid-state reaction, used commercial powders (>99.9% purity) of $MnCO_3$, $CaCO_3$, $La_2O_3$ and ZnO as precursors.

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These powders combined with appropriate masses were well-mixed, pressed into a pellet, and then pre-sintered at 900 °C for 2 h. After several times of the intermediate grinding and sintering, the pellet was annealed at 1050 °C for 24 h in air. The single phase of the final product in an orthorhombic structure (belonging to the space group *Pnma*) was confirmed by an X-ray diffractometer (Brucker D5005). Its lattice parameters *a*, *b*, and *c* determined are 5.441, 7.697, and 5.434 Å, respectively. For magnetic measurements, the dependences of magnetization on the magnetic field and temperature around $T_C$ were performed on a superconducting quantum interference device (SQUID).

## 3. Results and discussion

Magnetic measurements of magnetization versus temperature $M(T)$ for $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ around its Curie temperature $T_C$ reveal that with increasing temperature, magnetization slightly decreases, see Fig. 1(a). This is assigned to the collapse of the ferromagnetic order caused by thermal energy. At temperatures above 240 K, magnetization approaches to zero. The external-field change from 50 to 1000 Oe enhances magnetization values, but does not make modified the shape of $M(T)$ curves. Based on these $M(T)$ data, the performance of $dM/dT|_H$ introduces minima at the same temperature of about 210 K, which is close to $T_C$ of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$, as can be seen in Fig. 1(b).

The exact determination of $T_C$ and critical exponents $\beta$, $\gamma$, and $\delta$ for $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ can be based on magnetization versus the applied field $M(H)$ measured at various temperatures, known as magnetic isotherms. Here, $\beta$, $\gamma$, and $\delta$ are associated with the spontaneous magnetization $M_s(H = 0)$, initial magnetic susceptibility $\chi_0 = \partial M/\partial H|_{H=0}$, and critical isotherm $M(T_C,H)$, respectively [12]. Fig. 2 shows the isotherms recorded at temperatures 160–228 K (with a temperature increment of $\Delta T = 2$ K) and in the applied field range of 0–40 kOe. It is similar to other manganite compounds [6,12], the $M(H)$ curves do not reach saturation values

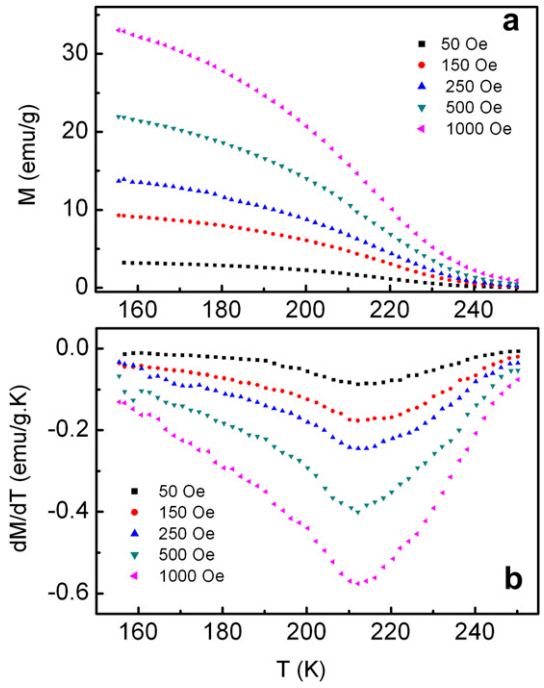


**Fig. 1.** (a) Temperature dependences of magnetization around $T_C$ under various applied fields of 50–1000 Oe. (b) The variations of $dM/dT$ curves versus temperature, which show minima at about 210 K close to the phase transition of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$.

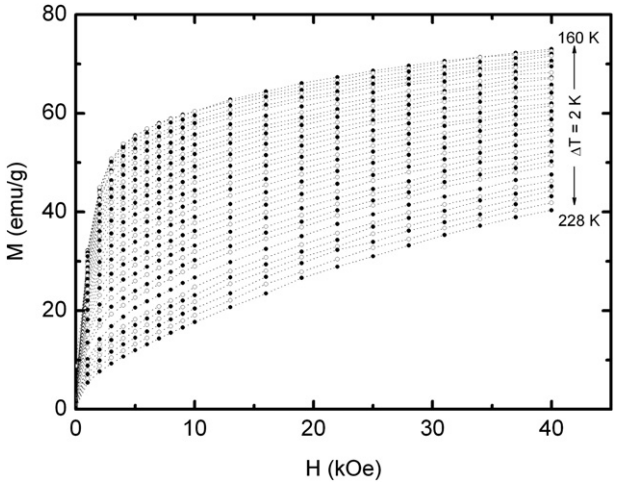


**Fig. 2.** Field dependences of magnetization $M(H)$ for $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ at various temperatures.

at high magnetic fields, as a consequence of the presence of the ferromagnetic short-range order. To further support this conclusion, we have based on the values of the critical exponents, which are obtained by the modified Arrott plot [13], because the normal Arrott plot [14] of $M^2$ versus $H/M$ was not successful in our case. The content of the method can be briefed as follows: start from trial exponents (for example, $\beta = 0.365$ and $\gamma = 1.336$ expected from the exponents of the Heisenberg model [15]), it is plotted the $M(T)$ data to $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$. The spontaneous magnetization versus temperature, $M_s(T)$, is then determined from the intersections of the linear extrapolation line (for high-magnetic field parts) with the $M^{1/\beta}$ axis. Similarly, the inversely initial magnetic susceptibility versus temperature, $\chi_0^{-1}(T)$, is also obtained from the intersections with the $(H/M)^{1/\gamma}$ axis. According to the approximate equation of state in the phase-transition region with $H \to 0$ and $T \to T_C$, there are asymptotic relations [15].

$$M_s(T,0) = M_0(-\varepsilon)^{\beta}, \varepsilon < 0; \quad (1)$$

$$\chi_0^{-1}(T) = (h_0/M_0)\varepsilon^{\gamma}, \ \varepsilon > 0; \quad (2)$$

$$M = DH^{1/\delta}, \quad \varepsilon = 0; \quad (3)$$

where $M_0$, $h_0$ and $D$ are constants, and $\varepsilon = (T-T_C)/T_C$ is the reduced temperature. By fitting the $M_s(T)$ and $\chi_0^{-1}(T)$ data to Eqs. (1) and (2),

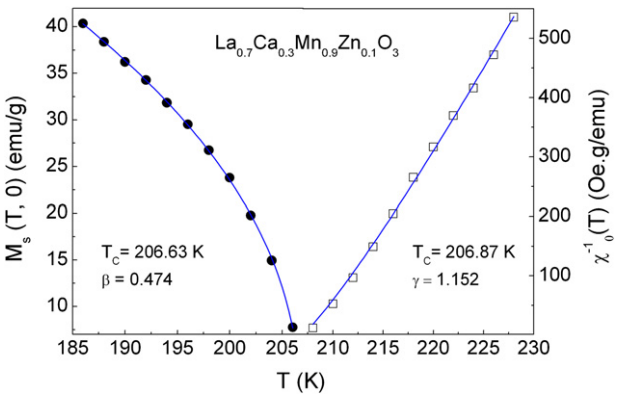


**Fig. 3.** Temperature dependences of the spontaneous magnetization $M_s$ (solid circles) and inverse initial susceptibility $\chi_0^{-1}$ (open squares) were fitted to Eqs. (1 and 2), respectively.

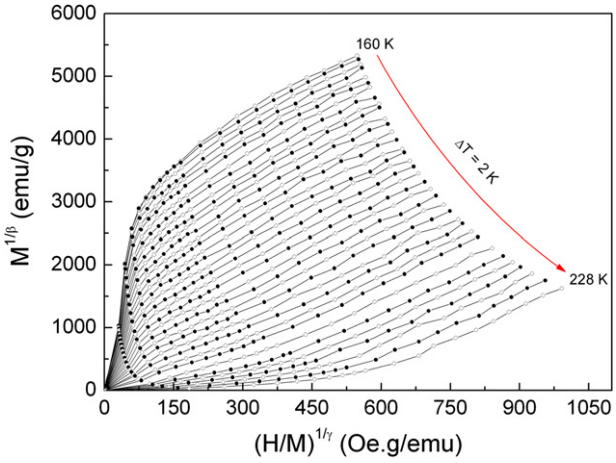


**Fig. 4.** The modified Arrott plot of $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$, with $\beta = 0.474$ and $\gamma = 1.152$.

respectively, new values of $\beta$ and $\gamma$ will be obtained. These values are then re-introduced to the scaling of the modified Arrott plot. After several times of such the scaling, $\beta$ and $\gamma$ converge to their optimal values. Concurrently, the Curie temperatures associated with the fitting of the $M_s(T)$ and $\chi_0^{-1}(T)$ data to Eqs. (1) and (2), respectively, are also determined.

Having relied upon the above described processes, the fitting $M_s(T)$ to Eq. (1) introduces $\beta = 0.474$ and $T_C = 206.63$ K, and $\chi_0^{-1}(T)$ to Eq. (3) introduces $\gamma = 1.152$ and $T_C = 206.87$ K. These data are graphed in Fig. 3. For calculations and discussions afterwards, we use an average value of $T_C = 206.75$ K. With the exponents determined, the plot of $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$ results in straight lines at sufficiently high fields, see Fig. 4. At a temperature $T = 206$ K, very close to $T_C$, the straight line passes through the origin.

Concerning the value of $\delta$, it can be determined directly from the critical isotherm $M(T_C, H)$. Fig. 5 performs $M(H)$ measured at some temperatures around $T_C$ on the log–log scale. The fitting of the data near $T_C$, with $T = 206$ K, to Eq. (3) introduces $\delta = 3.425$. This value is very close to $\delta = 3.430$ determined from the Widom scaling relation [16]

$$\delta = 1 + \gamma/\beta \tag{4}$$

According to the critical region theory [15], the magnetic isotherms can be described by the magnetic equation of state

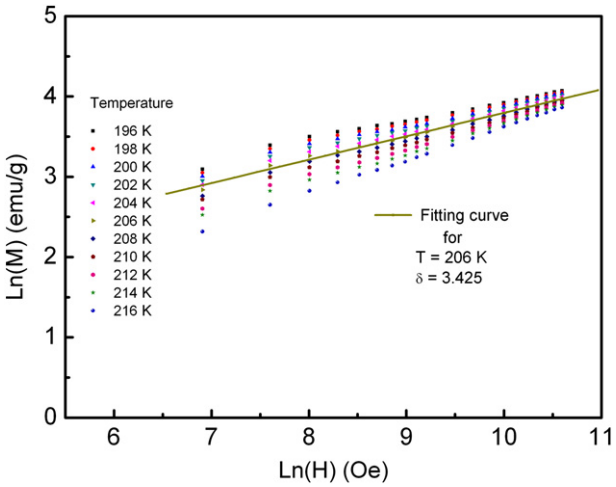


**Fig. 5.** The plot of $\ln(M)$ versus $\ln(H)$ at temperatures around $T_C$. The solid line is the fitting curve to Eq. (3) for $M(H)$ at $T = 206$ K, close to $T_C$.

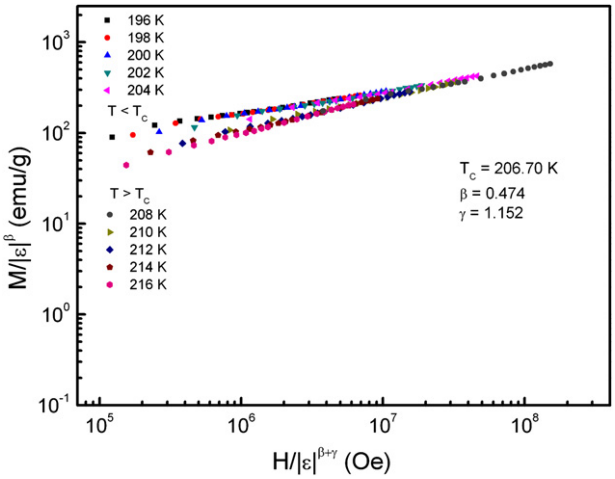


**Fig. 6.** Scaling plot of $M/|\varepsilon|^{1/\beta}$ versus $H/|\varepsilon|^{\beta+\gamma}$ on the log–log scale.

$$M(H,\varepsilon) = |\varepsilon|^{\beta} f \pm \left(H/|\varepsilon|^{\beta+\gamma}\right) \tag{5}$$

where $f_+$ for $T > T_C$ and $f_-$ for $T < T_C$ are scaling functions. In our case, the performance of $M/\varepsilon^{\beta}$ versus $H/\varepsilon^{\beta+\gamma}$ reveals that the magnetic isotherms in the vicinity of $T_C$ fall on two individual branches, one for $T < T_C$ and the other for $T > T_C$, see Fig. 6. This proves that the critical parameters determined are in good accordance with the scaling hypothesis. In other words, the $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ sample undergoes the second-order magnetic phase transition. If comparing to the critical exponents expected from the mean-field theory, Ising model, 3D Heisenberg model and tricritical mean-field theory [15], as shown in Table 1, our exponents ($\beta = 0.474$, $\gamma = 1.152$, and $\delta = 3.430$) are fairly close to mean-field theory with $\beta = 0.5$, $\gamma = 1.0$, and $\delta = 3.0$. A small difference in the exponents is assigned to an existence of the short-range ferromagnetic interaction in the sample, as mentioned above. It means that the material is not completely paramagnetic at temperatures $T > T_C$. Having paid attention to earlier studies on $La_{1-x}Ca_xMnO_3$, it was indicated that their critical exponents did not vary according to a given rule as changing the $x$ value, see Table 1. For the parent compound of $La_{0.7}Ca_{0.3}MnO_3$ exhibiting the first-order magnetic phase transition [5–7], its exponents $\beta = 0.14$ and $\gamma = 0.81$ [8] are far from those obtained in our work. Clearly, the presence of nonmagnetic Zn dopants influences remarkably the ferromagnetic $Mn^{3+}$–$Mn^{4+}$ interaction and the critical behavior of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$. This affects directly the magnetocaloric and magnetoresistance effects.

As an example, we consider the magnetocaloric effect in $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ through the magnetic entropy change ($\Delta S_M$) calculated by means of the following equation [4]

**Table 1**
Critical parameters of our sample $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ compared to those determined from theoretical models and $La_{1-x}Ca_xMnO_3$ materials.

| Material | $\beta$ | $\gamma$ | $\delta$ | $T_C$ (K) | Ref. |
|---|---|---|---|---|---|
| $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ | 0.474 | 1.152 | 3.430 | 206.75 | This work |
| Mean-field theory | 0.5 | 1.0 | 3.0 | – | [15] |
| Ising model | 0.325 | 1.241 | 4.82 | – | [15] |
| 3D Heisenberg model | 0.365 | 1.336 | 4.80 | – | [15] |
| Tricritical mean-field theory | 0.25 | 1 | 5 | – | [6] |
| $La_{0.6}Ca_{0.4}MnO_3$ | 0.25 | 1.03 | 5.0 | 265.5 | [6] |
| $La_{0.7}Ca_{0.3}MnO_3$ | 0.14 | 0.81 | 1.22 | 222.0 | [8] |
| $La_{0.8}Ca_{0.2}MnO_3$ | 0.36 | 1.45 | 5.03 | 174 | [5] |

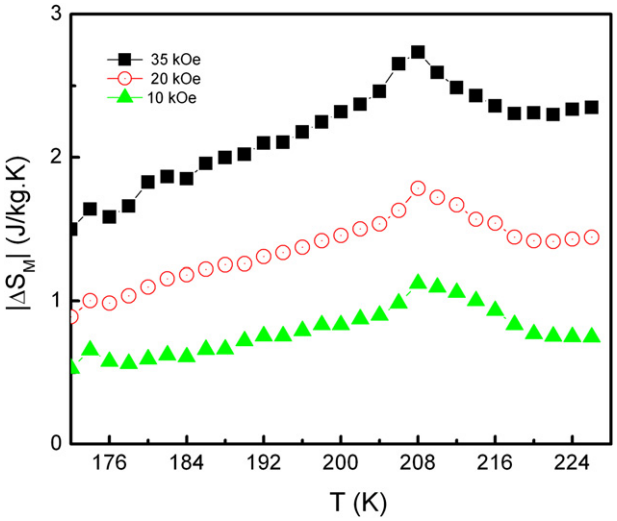


**Fig. 7.** Temperature dependences of the magnetic-entropy change for $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ under various applied-field variations of 10, 20, and 35 kOe.

$$\Delta S_M(T,H) = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T}\right)_H dH \tag{6}$$

It is integrated numerically in the desired range of magnetic fields on the basis of the set of magnetic isotherms $M(H)$ measured at different temperatures. Fig. 7 shows the temperature dependences of $\Delta S_M$. It is similar to other perovskite manganites [3,4], $\Delta S_M$ also reaches a maximum value in the vicinity of $T_C$. Under the applied-field variations of 10, 20, and 35 kOe, maximum $\Delta S_M$ values are 1.1, 1.7, and 2.7 J/kg K, respectively. Below and above $T_C$, $\Delta S_M$ gradually decreases. Comparing to $La_{0.7}Ca_{0.3}MnO_3$ ($\Delta S_M \approx 6.0$ J/kg K under a magnetic-field variation of ~10 kOe [17,18]), the $\Delta S_M$ values obtained from our sample is much lower. Recall that $La_{0.7}Ca_{0.3}MnO_3$ exhibits the first-order magnetic phase transition with the critical exponents ($\beta = 0.14$ and $\gamma = 0.81$ [8]) unclose to any theoretical model. In contrast, $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ exhibits the second-order magnetic phase transition with the exponents ($\beta = 0.474$ and $\gamma = 1.152$) fairly close to the mean-field theory ($\beta = 0.5$ and $\gamma = 1.0$). This difference is due to the Zn doping, which affects the ferromagnetic interaction between $Mn^{3+}$ and $Mn^{4+}$ ions (because $Zn^{2+}$ is a nonmagnetic ion [11,19]). Thus, it reduces the maximum $\Delta S_M$ value. With the results obtained, one can say that the first-order magnetic phase transition in perovskite manganites is a key point to gain a large value of $\Delta S_M$.

## 4. Conclusion

We prepared a perovskite manganite sample of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$, and then studied the critical behavior and magnetic entropy change around its $T_C$. By means of the modified Arrott plot, we have determined the critical parameters $T_C = 206.75$ K, $\beta = 0.474$, $\gamma = 1.152$, and $\delta = 3.430$, which are in good agreement with the magnetic equation of state. While the parent compound $La_{0.7}Ca_{0.3}MnO_3$ exhibits the first-order magnetic phase transition with the exponents unclose to any standard model, our sample $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ exhibits the second-order magnetic phase transition where the exponents are close to those expected from the mean-field theory. This difference is assigned to the presence of nonmagnetic Zn dopants, which influence the ferromagnetic interaction between $Mn^{3+}$ and $Mn^{4+}$ ions, and thus influence directly the magnetic entropy $\Delta S_M$.

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