



Magnetocaloric-Transport Properties Correlation in La_{0.8}Ca_{0.2}MnO₃-Doped Manganites

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Abstract This investigation is interested in studying the relation between magnetocaloric effect and transport properties in La_{0.8}Ca_{0.2}MnO₃ manganite compound. The value of the magnetocaloric effect has been determined from the calculation of magnetization as a function of temperature under different external magnetic fields. This study also provides an alternative method to determine the magnetocaloric properties such as magnetic entropy change and heat capacity change on the basis of $M(T, H)$ measurements. On the other hand, based on magnetic and resistivity measurements, the magnetocaloric properties of this compound were investigated using an equation of the form $\Delta S = -\alpha \int_0^H \left[\frac{\delta \ln(\rho)}{\delta T} \right]_H dH$, which relates magnetic order to transport behavior of the compounds. As an important result, the values of MCE and the results of calculation are in good agreement with the experimental ones, which indicates the strong correlation between the electric and magnetic properties in manganites.

Keywords Magnetocaloric properties · Heat capacity change · Relative cooling power

1 Introduction

The theoretical and experimental studies of the magnetic materials with large magnetocaloric effect (MCE) have been the interest of many researchers thanks to their great potential applications in energy-efficient magnetic refrigeration (MR) technology [1–3]. Concerning the first reason, it pertains to the fact that magnetic cooling offers a competitive alternative to conventional gas compression-expansion refrigeration systems since it is highly energy-efficient and environment friendly. Actually, the need is neither for ozone-depleting nor global warming volatile refrigerants. As for the second one, it relates to the fact that magnetic refrigeration close to room temperature is only possible with materials that undergo a phase transition close to the working temperature of a refrigerator. Hence, the characterization of magnetocaloric materials commonly tends to become linked to a comprehensive study of their phase transition, which is also important from a fundamental standpoint. Many magnetocaloric materials have been thoroughly investigated over the past years due to their possible application in magnetic refrigeration near room temperature region, e.g., Gd₅Si₂Ge₂ alloy [4], NiMnGa [5], MnFeP_{1-x}As_x [6], LaFe_{13-x}Si_x [7], and ferromagnetic perovskite manganites [8–10]. Perovskite-like manganites La_{1-x}Ca_xMnO₃ exhibit a variety of physical properties depending on the Ca concentration x . The strong correlation among magnetic, electronic, orbital, and transport properties of manganites makes these systems principally sensitive to external perturbations, such as temperature variation, magnetic field application, or high pressure [11, 12].

The present research is a theoretical work that undertakes the study of the effect of quenching on the correlation between the electrical and magnetic properties of the La_{0.8}Ca_{0.2}MnO₃ polycrystalline.

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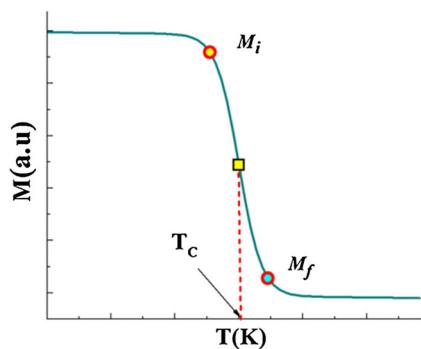


Fig. 1 Temperature dependence of magnetization in constant applied magnetic field

2 Theoretical Considerations

Using the phenomenological model, described in [13, 14], the variation of the magnetization with temperature is simulated by:

$$M(T, H = H_{\max}) = \left(\frac{M_i - M_f}{2} \right) \times [\tanh(A(T_C - T))] + BT + C \quad (1)$$

where M_i is an initial value of magnetization at ferromagnetic-paramagnetic transition and is the point of magnetization just after the linear line of magnetization (FM) and before the curvature (PM), while M_f is a final value of magnetization at paramagnetic-ferromagnetic transition exactly the point just after the curvature and before the linear line of magnetization (Fig. 1); $A = \frac{2(B - S_C)}{M_i - M_f}$; B is the magnetization sensitivity $\frac{dM}{dT}$ at ferromagnetic state before transition; S_C is the magnetization sensitivity $\frac{dM}{dT}$ at Curie temperature T_C ; and $C = \left(\frac{M_i - M_f}{2} \right) - BT_C$.

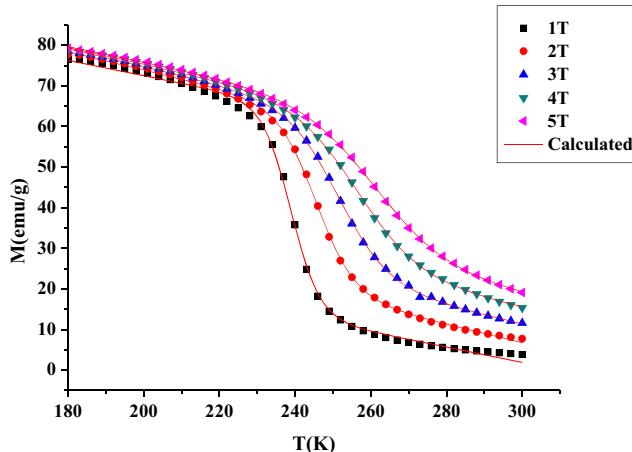


Fig. 2 Magnetization in different applied magnetic fields for the $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ sample versus temperature. Symbols are the experimental results and solid lines are the graphs fitted by (1)

Table 1 Model parameters for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ in different applied magnetic fields

$H(T)$	M_i (emu g $^{-1}$)	M_f (emu g $^{-1}$)	T_C (K)	B (emu g $^{-1}$ K $^{-1}$)	S_C (emu g $^{-1}$ K $^{-1}$)
1	61.77	9.98	238.88	-0.187	-3.79
2	62.90	18.43	245.56	-0.22	-2.56
3	62.99	21.76	251.41	-0.22	-1.89
4	61.47	22.07	256.47	-0.20	-0.17
5	63.16	25.10	261.04	-0.19	-0.17

The magnetic entropy change of a magnetic system under adiabatic magnetic field variation from 0 to final value H_{\max} is available by:

$$\Delta S_M = \left(-A \left(\frac{M_i - M_f}{2} \right) \operatorname{sech}^2 (A(T_C - T)) + B \right) H_{\max} \quad (2)$$

where $\operatorname{sech}(x) = 1 / \cosh(x)$.

The foundation of large magnetic entropy change is attributed to high magnetic moment and rapid change of magnetization at T_C . A result of (2) is a maximum magnetic entropy change ΔS_{\max} (where $T = T_C$), which can be evaluated as the following equation:

$$\Delta S_{\max} = \left(-A \left(\frac{M_i - M_f}{2} \right) + B \right) H_{\max} \quad (3)$$

Equation 3 is important for taking into consideration the value of the magnetic entropy change to evaluate magnetic cooling efficiency with its full-width at half-maximum.

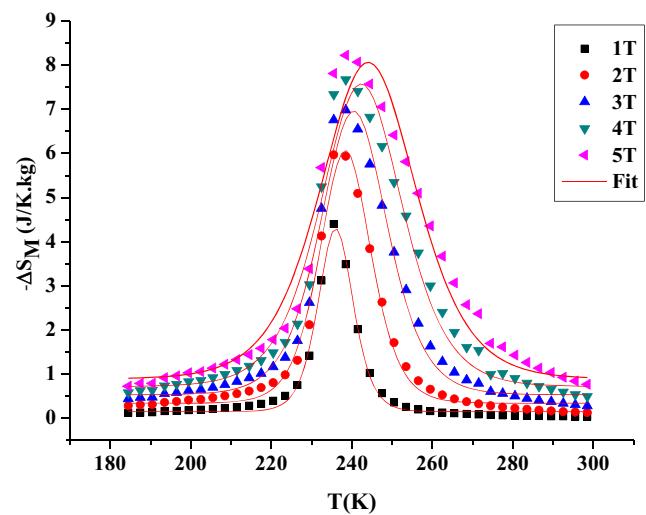


Fig. 3 Magnetic entropy change as a function of temperature for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ in different applied magnetic field variations. Symbols are the experimental results and solid lines are the graphs fitted by (2)

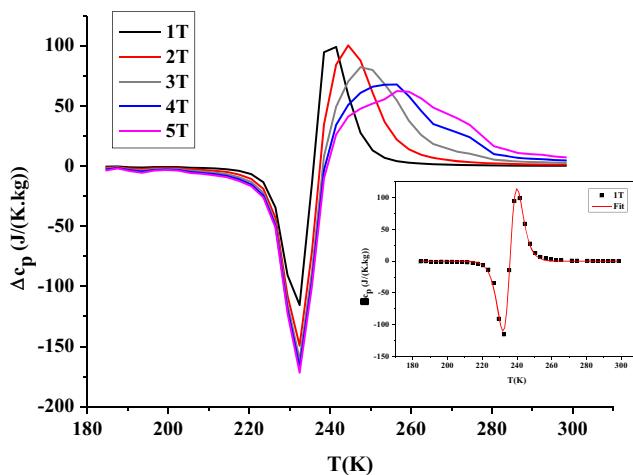


Fig. 4 Heat capacity changes as function of temperature for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ in different applied magnetic field variations. The inset shows the experimental and simulated results fitted by (7) to a field of 1 T

The determination of full-width at half-maximum δT_{FWHM} can be carried out as follows:

$$\delta_{\text{FWHM}} = \frac{2}{A} \operatorname{sech} \left[\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}} \right] \quad (4)$$

The magnetic cooling efficiency is estimated by considering the magnitude of magnetic entropy change ΔS_M , and its full-width at half-maximum δT_{FWHM} [15]. The product of $-\Delta S_M$ and δT_{FWHM} is called relative cooling power (RCP) based on magnetic entropy change:

$$\begin{aligned} \text{RCP} &= -\Delta S_M(T, H_{\max}) \times \delta_{\text{FWHM}} \\ &= \left(M_i - M_f - 2 \frac{B}{A} \right) H_{\max} \\ &\quad \times \operatorname{sech} \left[\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}} \right] \end{aligned} \quad (5)$$

The magnetization-related change of the specific heat is given by [16]:

$$\Delta C_{\text{P},\text{H}} = T \frac{\delta \Delta S_M}{\delta T} \quad (6)$$

Table 2 The predicted values of specific heat change in different applied magnetic fields

$H(T)$	$\Delta C_{\text{P},\text{H(max)}} (\text{J kg}^{-1} \text{K}^{-1})$	$\Delta C_{\text{P},\text{H(min)}} (\text{J kg}^{-1} \text{K}^{-1})$
1	99.15	-115.53
2	100.44	-149.27
3	82.18	-160.47
4	67.88	-167.02
5	62.43	-171.71

According to this model, $\Delta C_{\text{P},\text{H}}$ can be rewritten as:

$$\begin{aligned} \Delta C_{\text{P},\text{H}} &= -TA^2(M_i - M_f) \sec h^2 [A(T_C - T)] \\ &\quad \times \tanh [A(T_C - T)] H_{\max} \end{aligned} \quad (7)$$

On the other hand, the magnetic entropy change (ΔS_M) can be estimated using the following equation [17]:

$$\Delta S = -\alpha \int_0^H \left[\frac{\delta \ln(\rho)}{\delta T} \right]_H dH \quad (8)$$

where the parameter α determines the magnetic properties of the sample. Different functional dependences between M and ρ have been used to estimate α directly where $\rho = \rho_0 \exp \left(\frac{-M}{\alpha} \right)$ [17]. O'Donnell et al. [18] pointed out that the exact equation should be $\rho = \rho_0 \exp \left(\frac{-M^2}{\alpha} \right)$, while Chen et al. [19] proposed the equation $\rho = \rho_0 \exp \left(\frac{-M^2}{\alpha T} \right)$ for small and intermediate magnetization near and above the Curie temperature.

3 Model Application and Discussion

In order to apply the phenomenological model, Fig. 2 presents the magnetization versus temperature in different applied magnetic fields. This figure displays the simulated (solid line) and experimental results for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ sample. It can be seen that the computational results are in a good agreement with the experimental results.

The best-fit parameters are given in Table 1.

What is worthy to note is that the Curie temperature T_C increases significantly with the increase in magnetic field and the magnetization exhibits a continuous change around T_C in different magnetic fields.

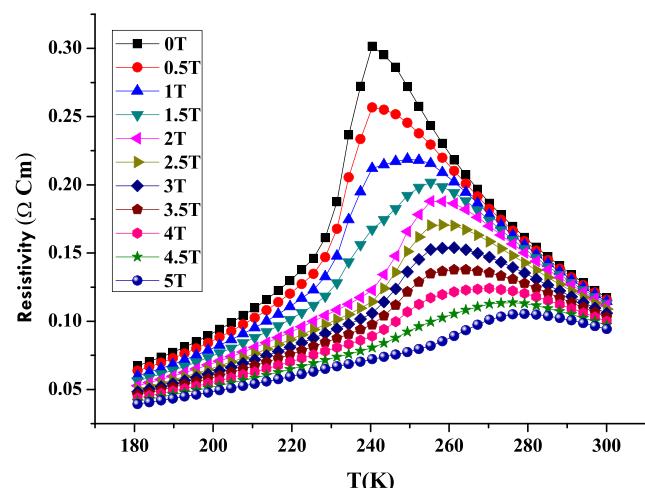


Fig. 5 Temperature dependence of the resistivity under different applied magnetic fields rising from 0 to 5 T for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ compound

We have recently studied the magnetocaloric effect of $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ sample [9] using the measured magnetization versus the applied magnetic field $M(H, T)$ at different temperatures (T) around T_C . In order to check the validity of this model, the experimental results from the magnetic entropy change have been fitted by (3) (Fig. 3). It is seen that the calculation results are in accordance with the experimental ones. Although the magnetocaloric effect increases with the increase of the applied magnetic fields, the maxima observed in the ΔS_M curves are related to a spin reorientation that occurs continuously. This can be explained by the fact that the effect reaches its maximum in the vicinity of magnetic phase transition points.

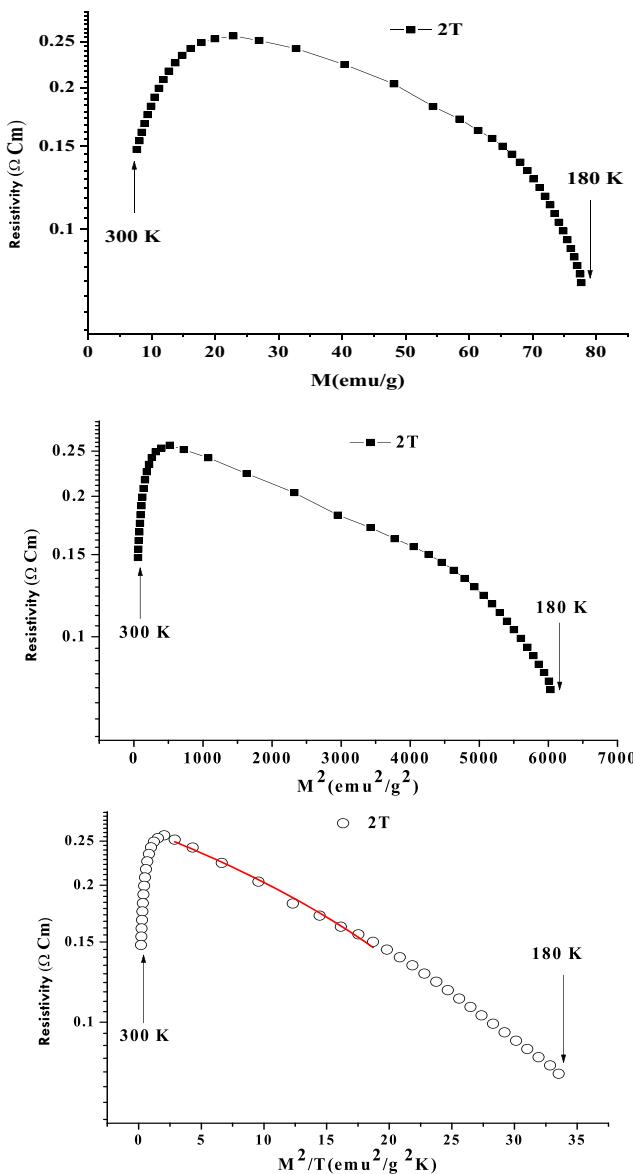


Fig. 6 ρ versus M , M^2 , and M^2/T under the field of 2 T. Solid line is a fit to the formula $\rho = \rho_0 \exp\left(\frac{-M^2}{\alpha T}\right)$

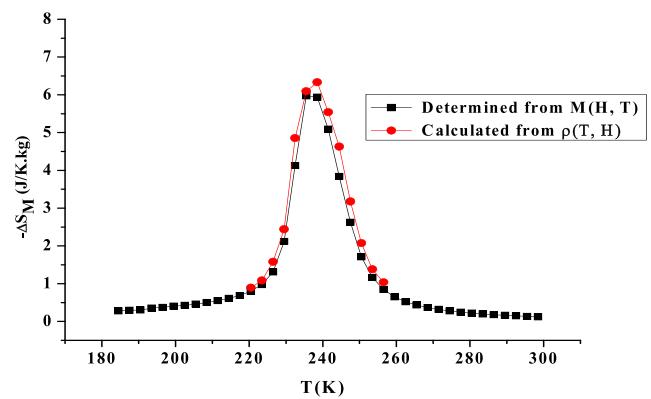


Fig. 7 Temperature dependence of the magnetic-entropy change measured and calculated using (8) an applied magnetic field of 2 T for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ sample

Figure 4 shows the modeled results of specific heat versus temperature for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ sample. The maximum and minimum values of specific heat change at different applied magnetic fields were calculated using (7) and listed in Table 2.

From the $\rho(H, T)$ curves plotted in Fig. 5, the magnetic entropy change (ΔS_M) has been estimated using (8), for an applied magnetic field of 2 T. For this aim, and as shown in Fig. 6, the variation ρ versus M , M^2 and M^2/T was studied. This research work has proven that the resistivity strongly depends on M^2/T . The results on the calculation of the change in magnetic entropy by (8) and the Maxwell relation, described in our previous research work [9], are shown in Fig. 7, where the value of the parameter α for our system is equal to 153.60 (emu) $^2 \text{ g}^{-2} \text{ K}$. This is determined from the fitting of ρ versus M^2/T curve around the transition temperature T_C with the equation $\rho = \rho_0 \exp\left(\frac{-M^2}{\alpha T}\right)$ (Fig. 5).

Eventually, the comparison in Fig. 8 shows the magnetic entropy changes determined according to Eqs. 3 and 8 by the experimental values determined from the $M(H, T)$.

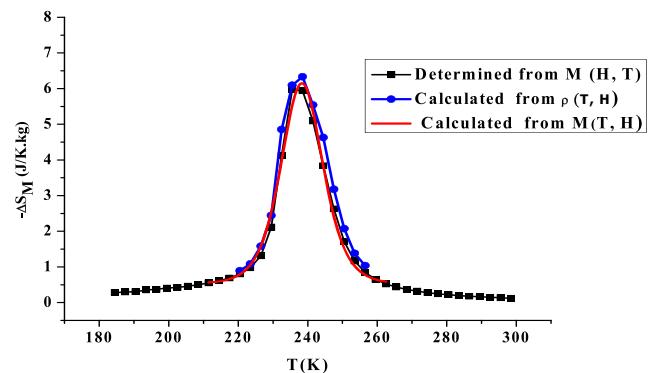


Fig. 8 Temperature dependence of the magnetic-entropy change measured and calculated using Eqs. 3 and 8 an applied magnetic field of 2 T for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ sample

From this figure, we note that the good quantitative agreement between calculated and experimental data from such analysis would be quite unexpected, but the fact of observing qualitative agreement between them reveals a strong correlation of electrical and magnetic properties in the manganites of $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ type near the phase transition temperature.

4 Conclusions

The phenomenological model can be considered as another indirect method that determines the change in magnetic entropy from the data of $M(T, H)$ measurements in manganites. Moreover, from the temperature dependence of the resistivity measured at several applied magnetic field $\rho(H, T)$, we have calculated the magnetic entropy change

based on the following equation: $\Delta S = -\alpha \int_0^H \left[\frac{\delta \ln(\rho)}{\delta T} \right]_H dH$.

An agreement between the experimental and calculated magnetic entropy change has been found. Finally, it is important to note that all equations derived for the magnetic entropy calculation are valid for other doping concentration such as $0.00 \leq x \leq 0.20$.

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