

Dedicated to Academician Professor Dr. Emil Burzo on His 80th Anniversary

MAGNETIC PHASE TRANSITION AND MAGNETOCALORIC EFFECT IN THE PEROVSKITE $\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$

I.G. DEAC^{1*}, A. VLADESCU^{1,2}, R. TETEAN¹

ABSTRACT. We report results of magnetic and magnetocaloric investigations of the perovskite manganite $\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$. The sample shows ferromagnetic behavior at low temperatures. Magnetocaloric effect was estimated from the magnetic entropy change ΔS_M obtained from isothermal magnetization data. We have found large values for $|\Delta S_M|$ around T_C 's, of about 4.58 J/kg·K for $\mu_0\Delta H = 4$ T, with reasonable large relative cooling power (~ 233 J/kg). Critical exponents associated with the ferromagnetic phase transition were analyzed and found to be close to those expected for the three-dimensional Heisenberg model. This model was also verified by using the field dependence of magnetic entropy change method.

Keywords: Perovskite ceramics, Magnetic phase transition, Magnetic measurements, Magnetocaloric effect.

INTRODUCTION

In recent times, there has been a significant increase in research on the magnetocaloric effect (MCE) [1]. The magnetic refrigeration, using the magnetocaloric effect, seems to be more effective and environmentally friendly than the vapor compression refrigeration. Earlier works indicated that gadolinium (Gd) has been considered as the most active magnetic refrigerant in room-temperature magnetic refrigerators [2]. A much larger MCE, twice larger as in Gd, was found in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ [3]. In the last few years, some other alternative materials were considered to be of practical importance, such as $\text{Gd}_5(\text{Si}_{1-x}\text{Ge}_x)_4$ [3], $\text{MnAs}_{1-x}\text{Sb}_x$ [4], $\text{MnFeP}_{1-x}\text{As}_x$ [5], $\text{Tb}_{1-x}\text{Gd}_x\text{Al}_2$ [6]

¹ Faculty of Physics, Babes-Bolyai University, Str.M. Kogalniceanu 1, Cluj-Napoca, Romania

² Emerson Process Management – Roxar Division Cluj-Napoca, Romania

* Corresponding author e-mail: iosif.deac@phys.ubbcluj.ro

and the hole-doped manganites with the general formula $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (Ln = trivalent rare earth, A = divalent alkaline earth) [2, 7-10]. Since the Gd-based alloys have expensive cost prices, the research has been focused on materials that are cheaper but displaying larger MCEs [1, 2, 7, 9, 10]. A very important quality of these refrigerant materials is to show a large magnetic entropy change $|\Delta S_M(T; H)|$, under an external magnetic field variation. The mixed-valence manganites $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ which are known for their colossal magnetoresistance (CMR) effect are promising materials since their Curie temperature T_C and saturation magnetization are strongly composition dependent and the magnetic refrigeration can be realized at various temperature ranges.

The perovskite $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is an important member in manganite family with intermediate bandwidth [11]. The La-based manganites show a very rich magnetic phase diagram including the charge/orbital ordering (CO/OO) state, FM and antiferromagnetic (AFM) states (and coexistence) [12, 13]. For $x < 0.5$, they possess a strong FM-PM phase transition and a large magnetoresistance effect. When $x > 0.5$, it shows a CO-antiferromagnetic (AF) state. The compound $\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$, lies very close to the boundary of FM and CO-AF phase, being still ferromagnetic, having a high Curie temperature and a narrow FM - PM transition. These facts suggest the possibility of a large MCE in this compound that can be potentially used in magnetic refrigerators. Usually, MCE at T_C is higher for a first order magnetic transition, but because the transition takes place in a narrow temperature range, the resulting *cooling power* is lower [1, 2]. The materials that show second order phase transitions, have a smaller magnitude of entropy change $|\Delta S_M|$, but it is extended on a broader temperature range, resulting in a larger *cooling power*.

The present work is a study of the critical magnetic behavior and of the magnetocaloric effect in $\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$ manganite. We have found quite large values of magnetic entropy change and high relative cooling power in this compound, making it interesting for magnetic refrigeration over a wide temperature range. The magnetic phase transition and the magnetic entropy change in the region of the transition temperature can be described in the frame of the short-range 3 D Heisenberg model.

EXPERIMENTAL

The sample $\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$ was synthesized using the conventional solid state reaction method, and it was the same which was studied in a previous experiment [14].

A commercial cryogen-free VSM magnetometer (Cryogenic Ltd.) was used for magnetic measurements in the temperature range 5 - 300 K and in magnetic fields up to 12 T. Zero field-cooled (ZFC) and field-cooled magnetizations, as a function of temperature, were measured in 0.1 T.

As known, the MCE can be estimated calculating the magnetic entropy change $\Delta S_M(T; H_0)$, associate with a change in magnetic field. For a second order phase transitions we can use the approximation [1]:

$$\Delta S_M(T, H_0) = \frac{\mu_0}{\Delta T} \int_0^{H_0} [M(T + \Delta T, H) - M(T, H)] dH \quad (1)$$

In consequence, we measured the isothermal $M(H)$ curves at a temperature interval of $\Delta T = 5$ K around the magnetic transition to calculate the magnetic entropy change.

The cooling power per unit volume - the relative cooling power (*RCP*) - is a very important parameter for selecting magnetic refrigerants:

$$RCP(S) = -\Delta S_M(\text{max}) \times \delta T_{\text{FWHM}} \quad (2)$$

here $\Delta S_M(\text{max})$ is the maximum value of change in the magnetic entropy and δT_{FWHM} is the full width at half maximum (FWHM) of ΔS_M vs. T curve. A good magnetocaloric material needs to have both a large magnitude of ΔS_M and a broad width of the $\Delta S_M(T)$ curve.

RESULTS AND DISCUSSIONS

The diffraction pattern showed a pure LCMO sample having an orthorhombic unit cell with lattice parameters: $a = 5.428 \text{ \AA}$; $b = 7.663 \text{ \AA}$; $c = 5.443 \text{ \AA}$ [14].

Figure 1 illustrates the temperature dependence of FC and ZFC magnetization taken in 0.1 T. The Curie temperature $T_C = 251$ K was determined as the point where dM/dT has a minimum, as shown in the inset of Fig.1. The magnetization has a low history dependence with a bifurcation between ZFC and FC $M(T)$ curves.

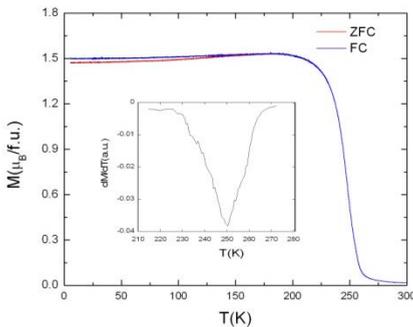


Fig. 1. FC and ZFC magnetization as a function of temperature, measured in 0.1 T. Inset: $dM(T)/dT$.

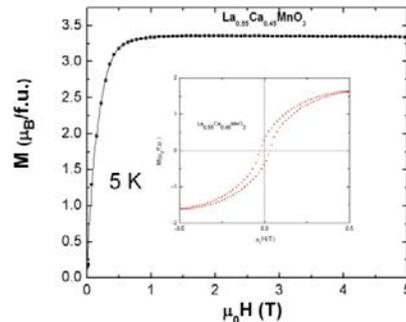


Fig. 2. $M(\mu_0 H)$ curve taken at 5 K up to 5 T. Inset: $M(\mu_0 H)$ hysteresis loop at 5 K.

At low temperatures the magnetization M_s (5 K) $\approx 3.4 \mu_B$ was close to the theoretical saturation value ($3.55 \mu_B$) in fields higher than 1 T. The inset of Fig. 2 indicate a very weak magnetic hysteresis with $H_c = 0.033$ T at 5 K. The magnetic behaviour described in Figs. 1 and 2 indicates a FM behavior of this compound below T_C . Since we are faced with a sharp magnetic phase transition, we expect a large MCE, around T_C .

In Fig. 3 we show the $M(H)$ curves for temperatures taken from 190 K to 285 K. As can be seen, below T_C the $M(H)$ increases rapidly at low fields. It is important to note that the main changes of the magnetization occurred in a relative low-field range (below 1 T), which is very important for the household applications. The order of the phase transition was established analyzing the Arrot plot (M^2 versus H/M) [15] on the Banerjee criterion [16] basis.

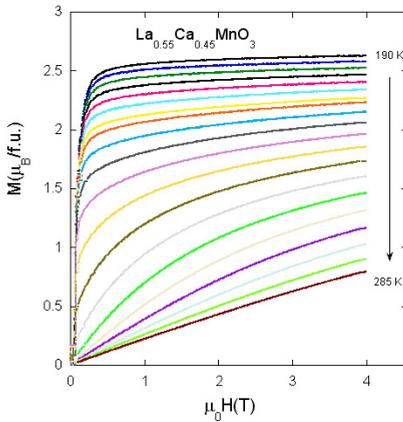


Fig. 3. Isothermal magnetization curves $M(\mu_0 H)$ taken at fixed temperature interval of 5 K, from 190 to 285 K.

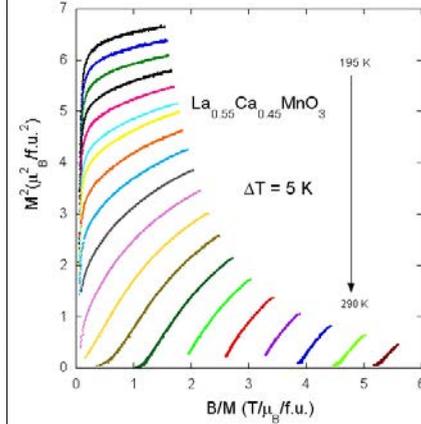


Fig. 4. Arrot plots obtained from measured M vs. H isotherms.

According to this, if the H/M versus M^2 curves has positive slopes, close to T_C , we are faced with a second order phase transition. If negative slope curves are presents, the transition is first order. The Arrot plot for our system can be seen in Fig.4. The curves have positive slopes in all the M^2 range indicating a second order magnetic phase transition [16]. In the case of a second order magnetic phase transition, the entropy change ΔS_M can be readily calculated from $M(H)$ isotherm data, by using the approximation given in eq. (1).

We estimated the MCE, from the magnitude of the magnetic entropy change, which was calculated from the isothermal magnetization curves. These curves were measured in the range 0 – 4 T around T_C with a temperature interval of 5 K and a field step of 1 T.

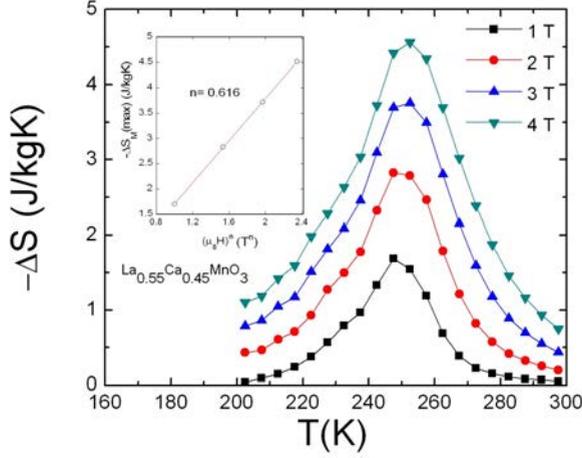


Fig. 5. The magnetic entropy change $-\Delta S_M$ as a function of temperature in various fields for $\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$. In the inset: the maximal entropy change vs. applied magnetic field; the solid line is the fitting curve.

To analyze the magnetocaloric effect, $-\Delta S_M$ is plotted in Fig. 5, as a function of temperature for different values of $\mu_0 H$, from 1 to 4 T.

As expected, the magnetic entropy change curves present peaks located very close to the Curie temperature T_C , at about 252 K. The maximum value, $-\Delta S_M$ (max), was about 4.58 J/kg K in 4 T and it still has a large value of 1.70 J/kg K when the change of the field was 1 T, which is high enough for magnetic refrigeration.

The transition range becomes broader in higher applied magnetic fields, and δT_{FWHM} changes from about 24 K in 1 T, to 45 K in 4 T. These lead to a large RCP indicating a material with a high cooling capacity. It can be seen in Fig. 5, that the ΔS_M distribution is rather uniform, which is also a very important aspect for a magnetic cooler. The RCP for this compound reaches 233 J/kg for $\mu_0 \Delta H = 4$ T. Some quantitative parameters related to magnetocaloric effect in $\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$ are given in Table 1.

The magnitudes of the MCE obtained for our sample at T_C are higher or comparable to those measured in the case of other manganites [1, 2, 7-10] indicating that this material could be used in magnetic cooling.

A large entropy change was expected in this compound where the magnetization has a sharp variation around T_C . A larger MCE is expected in a system that shows a stronger spin–lattice coupling, as usually happens in manganese perovskites [17].

Table 1. Maximum entropy changes, $-\Delta S_M^{\max}$, full width at half maximum of the $\Delta S_M(T)$ curve δT_{FWHM} and relative cooling powers (RCP) when $\mu_0\Delta H = 1 - 4$ T, temperature of the maximum entropy change $T(\text{max}) = 252$ K for the sample $\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$.

$\mu_0\Delta H$ (T)	$-\Delta S_M^{\max}$ ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$)	δT_{FWHM} (K)	RCP ($\text{J}\cdot\text{kg}^{-1}$)
1	1.68	31	52
2	2.87	40	114
3	3.80	48	182
4	4.58	51	233

We can also use the Arrot plot to analyze the critical behavior of this compound near the phase transition. The M^2 vs. H/M curves, in Fig. 4, are not straight, mainly at low magnetic fields, indicating that the mean field model is not valid to describe this phase transition. To calculate the critical exponents we have used the modified Arrot plot (MAP) method [18]. The critical exponents β , γ and δ are defined as [19, 20]:

$$M_s(T) = M_0(-\varepsilon)^\beta \quad T < T_c \quad (3)$$

$$\chi_0^{-1}(T) = \left(\frac{h_0}{M_0} \right) \varepsilon^\gamma \quad T > T_c \quad (4)$$

$$M = DH^{1/\delta} \quad T = T_c \quad (5)$$

where ε is the reduced temperature $\varepsilon = (T-T_c)/T_c$ and M_0 , h_0/M_0 and D are critical amplitudes; β , γ and δ also satisfy the Widom scaling relation: $\beta + \gamma = \beta \delta$.

The MAP method is an iterative procedure presumes the use of the Arrott–Noakes (A–N) [18] plot (i.e. the plot of $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$). The spontaneous magnetization value $M_s(T,0)$ is obtained from the intercepts of isothermal $M(H)$ curves on the ordinate of the plot (for temperatures below T_c). In a similar way, the reciprocal susceptibility $\chi_0^{-1}(T)$ is obtained from the intercepts on abscissa.

Thermal variation of the spontaneous magnetization $M_s(T)$ and the inverse susceptibility $\chi_0^{-1}(T)$ obtained from the modified Arrot plot are displayed in Fig. 6.

The values of the critical exponents can be derived by fitting these values to eq. (3), (4) and (5). By successive iterations, the best fits we got: $T_c = 252$ K, $\beta = 0.385$, $\gamma = 1.350$ and $\delta = 4.506$. These values are closer to that predicted by the 3D-Heisenberg ferromagnets ($\beta = 0.36$; $\gamma = 1.39$; $\delta = 4.8$) [19].

Such a behavior was also demonstrated by using numerical calculations [21, 22]. These showed that in frame of the double-exchange model, the critical exponents can be consistent with those expected for the isotropic short range 3D Heisenberg model. Also, the phase separation scenario in manganites, agrees with the short range magnetic interaction in these compounds. The presence of the ferromagnetic clusters in manganites was often found in simple magnetic measurements [23].

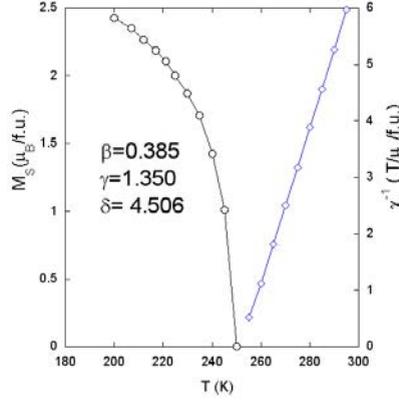


Fig. 6. The spontaneous magnetization $M_S(T)$ and the inverse initial susceptibility $X_0^{-1}(T)$ along with the fitting curves for $\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$.

A magnetic field dependence of magnetic entropy change, a universal relation $|\Delta S_M| \propto H^n$, is expected [24] in a magnetic system with a second-order phase transition. The local exponent n can be calculated as [25]:

$$n = 1 + \frac{\beta - 1}{\beta + \gamma} \quad (6)$$

The field dependence of maximum magnetic entropy change is described in the inset of Fig. 5. It can be seen, that the dependency $|\Delta S_M| \propto H^n$, is linear when $n = 0.616$. If we combine eq. (4) with Widom scaling relation, the values of the critical exponents can be readily obtained as: $\beta = 0.366$ and $\gamma = 1.283$ presuming $\delta = 4.506$ (using: $M = DH^{1/\delta}$ at $T = T_C$). The values of the critical exponents found in this way are in very good agreement to the values obtained by using MAP method, confirming the suitability of the short-range order 3 D- Heisenberg model to describe the critical magnetic behavior of this compound.

CONCLUSIONS

Magnetic critical phase transition and magnetocaloric material potential of $\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$ were studied. We obtained a large magnetic entropy change $|\Delta S_M| \sim 4.58$ J/kg K for $\mu_0 \Delta H = 4$ T at the FM - PM phase transition temperature, and a high relative cooling power $RCP \sim 233$ J/kg. The critical phase transition was investigated by using the modified Arrot plot (MAP) method. The phase transition

was found to be second order having critical exponents corresponding to those predicted for the short-range 3 D-Heisenberg model. This result was also confirmed analyzing the field dependence of the magnetic entropy change.

ACKNOWLEDGEMENTS

This work was supported by the grant IDEI code PN-II-ID-PCE-2011-3-0583 of CNCS, Romania.

REFERENCES

- [1] A.M. Tishin, Y.I. Spichkin, *The Magnetocaloric Effect and Its Applications*, Institute of Physics, Bristol 2003.
- [2] K.A. Gschneidner Jr., V.K. Pecharsky, A.O. Tsokol, *Rep. Prog. Phys.* 68 (2005) 1479–1539.
- [3] V.K. Pecharsky, K.A. Gschneidner, Jr., *Phys. Rev. Lett.* 78 (1997) 4494 - 4497.
- [4] S. Gama, A. Coelho, de Campos, et al., *Phys. Rev. Lett.* 93 (2004) 237202.
- [5] O. Tegus, E. Brück, K.H.J. Buschow, and F.R. de Boer, *Nature* (London) **415**, 150 (2002).
- [6] W. Wang, X.X. Zhang, F.X. Hu, *Appl. Phys. Lett.* 77 (2000) 1360-1368.
- [7] M.-H. Phan, S.-C. Yu, *J. Magn. Magn. Mater.* 308 (2007) 325–340.
- [8] V.B. Naik, S.K. Barik, R. Mahendiran, B. Raveau, *Appl. Phys. Lett.*, 98 (2011) 112506 (1-3).
- [9] M.-H. Phan, S.-C. Yu, *J. Magn. Magn. Mater.* 308 (2007) 325–340.
- [10] W. Zhong, C-T Au, Y-W Du, *Chin. Phys. B* 22 (2013) 057501 (1-11).
- [11] A. Ramirez, *J. Phys.: Condens. Matter* 9 (1997) 8171–8199.
- [12] P. Schiffer, A.P. Ramirez, W. Bao, and S.-W. Cheong, *Phys. Rev. Lett.* **75**, (1995) 3336-3339.
- [13] Y. Tokura, Y. Tomioka, *J. Magn. Magn. Mater.* 200 (1999) 1-23.
- [14] I.G. Deac, I. Balasz, *Mater. Chem. Phys.* 136 (2012) 850-857.
- [15] A. Arrott, *Phys. Rev.* 108 (1957) 1394-1396.
- [16] S.K. Banerjee, *Phys. Lett.* 12, (1964) 16-17.
- [17] A. Asamitsu, Y. Moritomo, Y Tomioko, T. Amira and Y. Tokura, *Nature* 373 (1995) 407-409.
- [18] A. Arrott, J.E. Noakes, *Phys. Rev. Lett.* 19 (1967) 786-789.
- [19] H. Eugene Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Clarendon Press, Oxford (1971)
- [20] M.E. Fisher, *Reports on Progress in Physics* 30 (1967) 615-730.
- [21] J.L. Alonso, L.A. Fernandez, F. Guinea, V. Laliena, V. Martin-Mayor, *Nucl. Phys. B* 596, (2001) 587-610.
- [22] Y. Motome and N. Furukawa, *J. Phys. Soc. Jpn.* 70, (2001) 1487-1490.
- [23] S. Hcini, S. Zemni, A. Triki, H. Rahmouni, M. Boudard, *J. Alloys Compd.* 509 (2011) 1394–1400.
- [24] H. Oesterreicher and F.T. Parker, *J. Appl. Phys.* 55, (1984) 4334-4338.
- [25] V. Franco, A. Conde, J.M. Romero-Enrique, and J.S. Blazquez, *J. Phys.: Condens. Matter* 20, (2008) 285207(1-5).