



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Magnetism and Magnetic Materials 290–291 (2005) 694–696

www.elsevier.com/locate/jmmm

Magnetocaloric effect of the (Pr,Ca)MnO₃ manganite at low temperatures

A.M. Gomes^{a,*}, F. Garcia^b, A.P. Guimarães^b, M.S. Reis^c,
V.S. Amaral^c, P.B. Tavares^d

^a*Instituto de Física, Lab. Baixas Temperaturas, UFRJ, C.P. 68528, 21941-972 Rio de Janeiro, Brazil*

^b*Centro Brasileiro de Pesquisas Físicas, R. Dr. Xavier Sigaud 150, 22290-180 Rio de Janeiro, Brazil*

^c*Department de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal*

^d*Department de Química, Univ. de Trás-os-Montes e Alto Douro, 5001-911 Vila Real, Portugal*

Available online 14 December 2004

Abstract

We have studied the magnetocaloric effect of the Pr_{1-x}Ca_xMnO₃ manganite, with 0.30 ≤ x ≤ 0.45, from 2.5 upto 50 K. At this temperature range, the (Pr,Ca)MnO₃ system present ferro/antiferromagnetic phase mixture which is responsible for the colossal magnetoresistance. Magnetocaloric studies in manganites, up to now, have neglected this magnetic phase mixture, mainly due to the antiferromagnetic phase which is not so well explored in magnetic refrigeration studies as ferromagnetic systems is. In our study, we explain the origin of the negative and positive values of the magnetic entropy change, their temperature dependence as well as the high values. The study of systems with antiferromagnetic phase, as shown in this work, may open an important field in the search of new magnetic materials for magnetic refrigeration.

© 2004 Elsevier B.V. All rights reserved.

PACS: 75.30.Sg; 65.40.Ba; 65.40.Gr

Keywords: Manganites; Magnetocaloric effect; Metamagnetism

1. Introduction

Extensive research about the magnetocaloric effect (MCE) has been carried out over the last years [1,2], and nowadays the main goal of the MCE study is related to its potential for magnetic refrigeration [3]. Among the magnetic materials with potential for magnetic refrigeration, the manganites are reported in the literature as promising ones [4,5]. This is based on the high value of magnetic entropy change under magnetic field variation,

and also the well-established fabrication process which usually follows a ceramic route [4] and allows a fine control of their physical properties.

Despite the extensive literature, several aspects are still not fully understood in manganite systems, among these we can cite the huge MCE at the charge-ordering transition temperature [6–9], as well as the mixture of magnetic phases with different electrical behavior.

In addition, some manganites present a coexistence of ferromagnetic (FM) and antiferromagnetic (AFM) phases. In this sense, Pr_{1-x}Ca_xMnO₃ manganites are particularly interesting, presenting a strong phase coexistence around x = 0.30 and a charge-ordering phenomenon for 0.30 < x < 0.90. Hereafter, we focus

*Corresponding author. Tel.: +55 21 2562 7666;
fax: +55 21 2562 7368.

E-mail address: amgomes@if.ufrj.br (A.M. Gomes).

on the sample with $x = 0.32$ on which we have observed the largest MCE.

The magnetocaloric effect is responsible for the applicability of the magnetic materials in a refrigeration cycle. It is characterized by the increase of the temperature of the magnetic material when subjected to a positive change of the magnetic field and cooling when the process is reversed. This is due to the coupling of the lattice entropy with the magnetic entropy of the material. For ferromagnetic materials, a negative maximum is observed in the magnetic entropy change ΔS_{mag} and in the adiabatic temperature change ΔT_{adiab} near the Curie temperature T_c . Usually, the desired temperature for maximum magnetocaloric values are obtained by different stoichiometric sample composition or by sample doping, in order to shift the magnetic transition temperature. Up to now, the literature has not explored systems where antiferromagnetic [10] and ferromagnetic phases coexistence [11] are involved, as well as the behavior of MCE when metamagnetic transitions occurs. For this reason, there is no satisfactory explanation for the behavior observed for ΔS_{mag} , which turns to be positive or negative in a given temperature range [12].

In this letter, we present a model to explain the ΔS_{mag} due to first-order metamagnetic transition in AFM system. We investigated a class of manganites that present coexistence of FM/AFM phases. For this purpose, we have studied the $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ system, which is known to present a charge-ordered state for Ca concentration higher than 30 percent.

2. Experimental setup

The sample was prepared by the conventional ceramic route with the following pure stoichiometric quantities: Pr_2O_3 (99.99%) CaCO_3 (>99%) and MnO_2 (>99%). The stoichiometric mixture was heated in air, with five cycles of crushing and pressing. To complete the fabrication process, the powder was compressed and sintered in air at 1350 °C for 45 h. The lattice parameters obtained from Rietveld analysis are $a = 5.4379(5)$ Å, $b = 5.4607(6)$ Å, and $c = 5.4399(5)$ Å. This analysis confirmed the orthorhombic structure of Pbnm space group.

Fig. 1 shows the ZFC hysteresis curve for $T = 25$ K. From zero to 1 T the main contribution is due to the intrinsic FM multi-domains that tends to saturate in the applied field. Up to 2.5 T there is a coexistence of FM single-domain and AFM phases and the susceptibility of this last one is responsible for the slope of the magnetization curve observed in this magnetic field range. For higher values of magnetic field an irreversible metamagnetic transition occurs, which has the microscopic effect of decreasing (increasing) gradually the

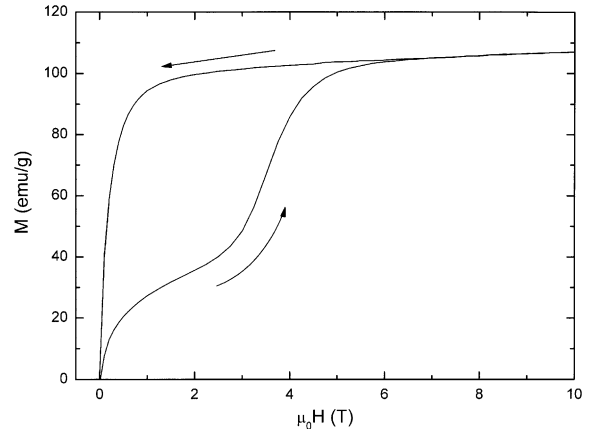


Fig. 1. Hysteresis curve of the $\text{Pr}_{0.68}\text{Ca}_{0.32}\text{MnO}_3$ at 25 K. The saturation value is estimated in 107 emu/g.

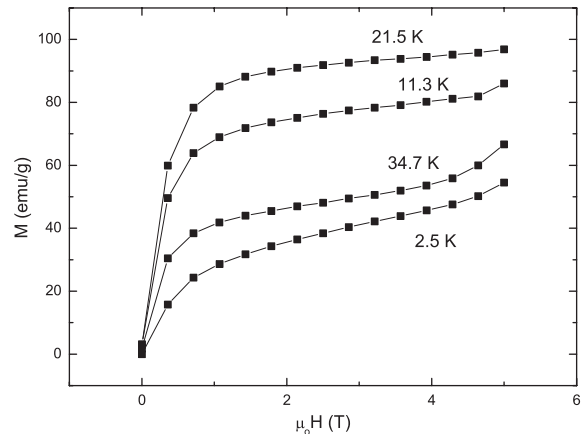


Fig. 2. Some isothermal magnetization curves. For the same value of magnetic field, the magnetization increases as temperature.

AFM (FM) phases, until a fully FM metallic phase is reached, with $M_{\text{sat}} = 107$ emu/g.

We measured successive hysteresis curves, from lower to higher temperatures and up to a certain value of magnetic field H_{max} .

Actually, we stopped the isothermal magnetization at the beginning of the metamagnetic transition; this procedure enabled us to access a new initial magnetic state for each subsequent isothermal curve as we increase the temperature. Some measurements performed in fields up to 5.0 T are shown in Fig. 2. Note the unusual behavior of magnetization, which increases for higher values of temperature. It is a consequence of the procedure related above, that gradually increases the proportion the FM phase. In other words, each isothermal magnetization curve transforms a small

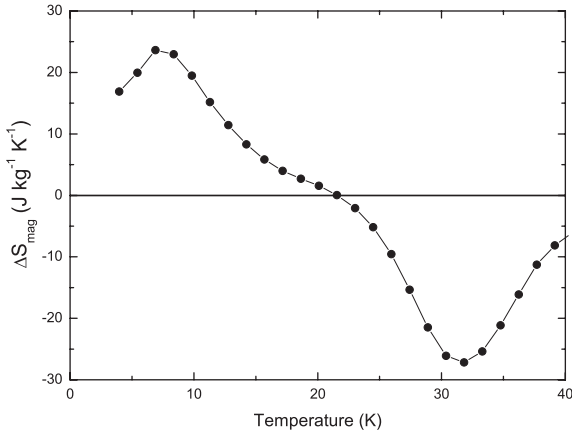


Fig. 3. Magnetic entropy change for the $\text{Pr}_{0.68}\text{Ca}_{0.32}\text{MnO}_3$ for a magnetic field change of 5 T (0–5 T).

amount of AFM phase into FM phase, increasing the FM fraction for the next M vs. H curve. This effect is cumulative up to a critical temperature T_0 , above which the isothermals are reversible. For $H_{\max} = 5.0$ T, $T_0 = 21.5$ K. At this temperature, the sample is almost completely saturated, as can be observed. For $T > T_0$, the thermal energy contribution starts to reduce the alignment induced by the magnetic field, and the system returns to the AFM phase.

The magnetic entropy change ΔS_{mag} can be derived from the Maxwell relations, and can be written as follows:

$$\Delta S_{\text{mag}} = \int_{H_0}^{H_F} \left(\frac{\partial M}{\partial T} \right) dH. \quad (1)$$

In the study of the magnetocaloric effect it is usual to deal with the total entropy of the system, which has three main contributions: S_{mag} , the magnetic contribution, S_{lat} , the lattice contribution and S_{el} , the electronic contribution. The magnetic entropy contribution can be obtained from Maxwell relations if we assume that S_{lat} and S_{el} are not field-dependent. We calculate the magnetic entropy by performing integration described by Eq. (1). The final result is obtained by numerical integration.

Fig. 3 presents the magnetic entropy change as a function of temperature for a $\Delta H = 5.0$ T. The position of the positive maximum is dependent on H_{\max} , whereas the negative minimum is not. These features can be analyzed in terms of the FM–AFM phase coexistence and the ratio between these phases when submitted to a different value of H_{\max} . On increasing the magnetic field, it tends to align the FM domains up to H_{\max} which is at the onset of the metamagnetic transition, as can be observed in Fig. 2 and at this value of the magnetic field

some AFM domains become FM, increasing the FM/AFM ratio. For higher temperatures, the magnetic field value required to start the metamagnetic transition should therefore be lower and consequently the entropy is positive as the most ordered state is at a higher temperature. This process continues up to 31 K, from this temperature and above we have the FM transformed by the temperature into a less ordered state and the magnetic entropy increases. The same behavior was found for the compounds with $0.30 \leq x \leq 0.40$ as expected due to the AFM/FM phase mixture at low temperatures.

The magnetocaloric effect in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ manganites reveals a rich means of understanding the magnetic phases at low temperatures. The same behavior of ΔS_{mag} is expected to be present in any system that shows a metamagnetic transition.

Acknowledgements

The authors would like to thank L. Ghivelder for the use of the magnetization system. We also acknowledge FCT/Portugal (POCTI/CTM/35462/00), ICCTI/CAPES in Brasil–Portugal bilateral collaboration, CT-Petro/CNPq and Faperj for financial support.

References

- [1] K.A. Gschneidner Jr., V.K. Pecharsky, *Annu. Rev. Mater. Sci.* 30 (2000) 287.
- [2] E. Bruck, O. Tegus, X.W. Li, F.R. de Boer, K.H.J. Buschow, *Phys. B* 327 (2003) 431.
- [3] B.F. Yu, Q. Gao, B. Zhang, X.Z. Meng, Z. Chen, *Int. J. Refrig.* 26 (2003) 622.
- [4] Y. Xu, M. Meier, P. Das, M.R. Koblichka, U. Hartmann, *Cryst. Eng.* 5 (2002) 383.
- [5] M.H. Phan, S.B. Tian, D.Q. Hoang, S.C. Yu, C. Nguyen, A.N. Ulyanov, *J. Magn. Magn. Mater.* 258–259 (2003) 309.
- [6] R. Mahendiran, B.G. Ueland, P. Schiffer, A. Maignan, C. Martin, M. Hervieu, B. Raveu, M.R. Ibarra, L. Morellon, *cond-mat/0306223*.
- [7] X.X. Zhang, J. Tajada, Y. Xin, G.F. Sun, K.W. Wong, X. Bohigas, *Appl. Phys. Lett.* 69 (1996) 3596.
- [8] A. Szewczyk, H. Szymczak, A. Wisniewski, K. Piotrowski, R. Kartaszynski, B. Dabrowski, S. Kolesnik, Z. Bukowski, *Appl. Phys. Lett.* 77 (2000) 1026.
- [9] Z.B. Guo, Y.W. Du, J.S. Zhu, H. Huang, W.P. Ding, D. Feng, *Phys. Rev. Lett.* 78 (1997) 1142.
- [10] R.J. Joenk, *Phys. Rev.* 128 (1962) 1634.
- [11] M.S. Reis, A.M. Gomes, J.P. Araújo, P.B. Tavares, I.S. Oliveira, V.A. Amaral, *J. Magn. Magn. Mater.* 272–276 (2004) 2393.
- [12] T. Tohei, H. Wada, T. Kanomata, *J. Appl. Phys.* 94 (2003) 1800.