

Drop of magnetocaloric effect related to the change from first- to second-order magnetic phase transition in $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$

J. Mira,^{a)} J. Rivas, and L. E. Hueso

Departamento de Física Aplicada, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain

F. Rivadulla and M. A. López Quintela

Departamento de Química-Física, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain

From data of initial magnetization isotherms, the magnetic entropy change ΔS_M of the series of ferromagnetic perovskites $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$, with $x=0, 0.05, 0.15, 0.25, 0.50, 0.75$ and 1 , has been measured near their Curie temperatures. The results go from $3.7 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ to $1.5 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$. Nevertheless, the evolution of ΔS_M with x is not monotonic, it shows a steep decrease between $x=0.05$ and $x=0.15$. This point corresponds to a tolerance factor $t=0.92$, at which the system changes from orthorhombic ($Pbnm$) to rhombohedral ($R\bar{3}c$) structure, and the magnetic phase transition from first to second order. Provided that rhombohedral symmetry forbids static long-range cooperative Jahn–Teller distortions, present in orthorhombic samples, we interpret our results as the strong increase of lattice effects in them. The anomalous thermal expansion at the Curie temperature, due to these lattice effects, is thought to underlie the jump in ΔS_M with x . © 2002 American Institute of Physics.

[DOI: 10.1063/1.1451892]

I. INTRODUCTION

Ferromagnetic-to-paramagnetic (FM–PM) phase transitions are usually taken in textbooks as paradigmatic second-order ones. This implies that the considered order parameter, i.e., magnetization, is destroyed by thermal randomization until it disappears at the Curie temperature T_C in a continuous way. From a thermodynamic point of view, it means that the entropy, monotonically and continuously related to the magnetization, suffers no discontinuous change. Of course, the change of phase is reflected by a discontinuity in the specific heat at T_C , but there is not latent heat at the critical point.

Materials of formula $\text{R}_{2/3}\text{A}_{1/3}\text{MnO}_3$ (R =lanthanide, A =divalent alkali) that crystallize in the perovskite structure are known to be ferromagnetic from decades ago.^{1–3} In those years the double-exchange mechanism was also described as the source of their magnetic coupling.^{4–6} In principle this means that these systems behave as standard ferromagnets, with a second-order FM–PM transition at their particular T_C s. Nevertheless, in the last years, several features have been found in them near the critical point that are not common in conventional ferromagnets. Among them are colossal magnetoresistance,^{7–9} anomalous thermal lattice expansions,¹⁰ and a large magnetic entropy change ΔS_M at T_C .^{11,12} In this context, Mira *et al.*¹³ have evidenced a crossover in the nature of the magnetic transition in a series of ferromagnetic manganites of formula $\text{La}_{2/3}(\text{Ca},\text{Sr})_{1/3}\text{MnO}_3$. In order to test if this crossover has something to do with the

entropy change of these manganites, we have studied it in this series of samples.

II. EXPERIMENTAL DETAILS

Samples $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$, with $x=0, 0.05, 0.15, 0.25, 0.50, 0.75$, and 1 , were prepared by solid state reaction of La_2O_3 , CaO , SrCO_3 , MnO_2 , and MnO (at least 99.995% in purity), which were heated in air in two steps (1100°C 70 h and 1200°C 27 h) and pressed into disks. The temperature was slowly ramped at $5^\circ\text{C}/\text{min}$, and cooled down to room temperature at $2^\circ\text{C}/\text{min}$. Intermediate grindings were made. Pellets were finally annealed at 1300°C for 100 h, with an intermediate grinding at 30 h. The nominal oxygen content was near the stoichiometric value as determined by iodometric analysis (for example $3 \pm \delta = 2.965(3)$ and $2.98(2)$ for LaSrMnO and LaCaMnO , respectively). X-ray powder patterns were collected at room temperature using a Philips PW1710 diffractometer, working with $\text{Cu } K\alpha$ radiation. The lattice parameters for the end members of the series, derived by Rietveld analysis, are in agreement with those reported in the literature. Electron spin resonance spectra of the samples were taken at 9.5 GHz (X band) between 110 and 700 K with a Bruker ESP-300 and an X-band Bruker EMX spectrometer. The small linewidth observed in our samples is a significant of the good quality and homogeneity of the material.¹⁴ For the calculation of the ΔS_M , magnetization versus field isotherms were measured with a DMS-1660 vibrating sample magnetometer, in fields up to 10 kOe.

III. RESULTS AND DISCUSSION

The magnetocaloric effect can be measured either by the adiabatic change of temperature under the application of a

^{a)} Author to whom correspondence should be addressed; electronic mail: fajmirap@usc.es

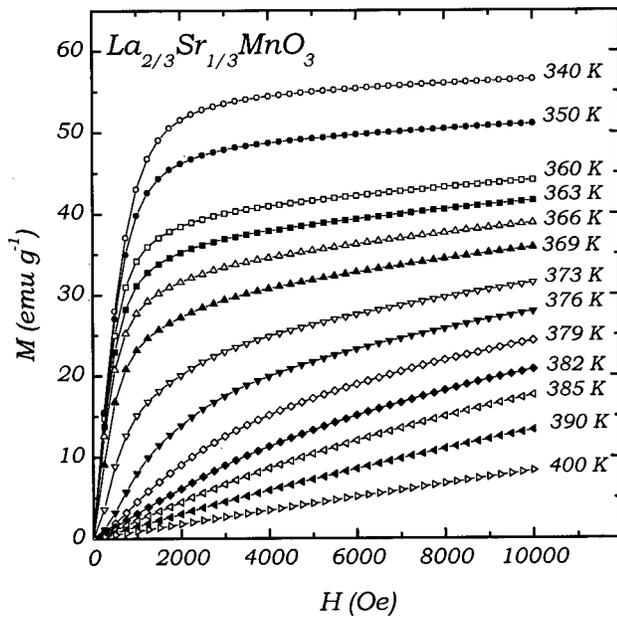


FIG. 1. Initial magnetization isotherms for $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$, around its Curie temperature (≈ 370 K).

magnetic field or through the measurement of initial isothermal magnetization versus field at different temperatures.¹⁵ We have used the second method to avoid the difficulties of adiabatic measurements. For this purpose, isothermal initial magnetization versus field curves were obtained around the T_C s, that range from ≈ 260 K for LaCaMnO to ≈ 370 K for LaSrMnO . Figure 1 shows an example of such curves for one of the members of the series. Before each run, the temperature was raised well beyond T_C , in order to ensure a perfect demagnetization. In this way, the magnetocaloric effect can be related to the magnetic measurements by the Maxwell relation¹⁵

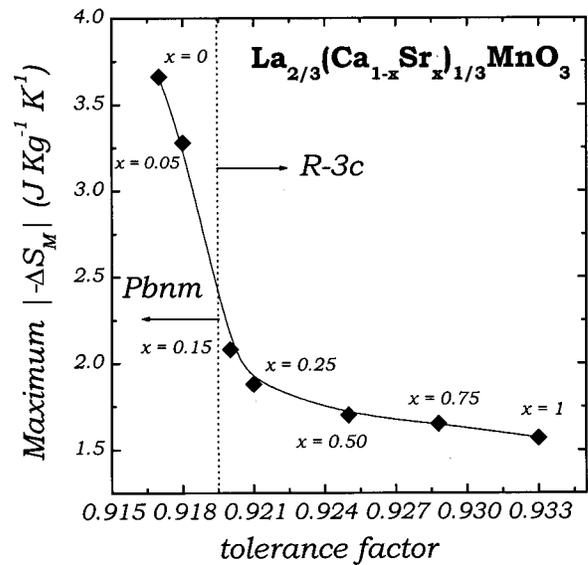


FIG. 3. Dependence of the maximum absolute value of ΔS_M with x . The dashed line separates samples with first-order magnetic transitions at T_C from those with second-order ones.

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \quad (1)$$

From this relation, the isothermal entropy change can be calculated from

$$\Delta S_M(T, H) = S_M(T, H) - S_M(T, 0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_{H'} dH' \quad (2)$$

that can be approximated by

$$|\Delta S| = \sum \frac{(M_n - M_{n+1})H}{T_{n+1} - T_n} \Delta H_n, \quad (3)$$

where M_n and M_{n+1} are the magnetization values measured in a field H at temperatures T_n and T_{n+1} , respectively.

In this way we obtained the ΔS_M in the different samples at different temperatures, which are plotted in Fig. 2. The first that attracts our attention is the step decrease in the maxima, by about a factor of 2, between $x=0.05$ and 0.15 , the same samples for which Mira *et al.* found a crossover in the nature of the magnetic transition, from first to second order.¹³ The difference between them is that the former crystallizes in an orthorhombic structure ($Pbnm$) and the latter in a rhombohedral one ($R\bar{3}c$).¹⁶ The boundary line between both crystalline phases is at a tolerance factor $t=0.92$, as already described by Radaelli *et al.*¹⁷ The point is that in the orthorhombic phase cooperative-long-range Jahn–Teller (JT) distortions are possible^{18,19} (and in fact, experimental data have demonstrated its presence^{20,21}), whereas the higher symmetry of the MnO_6 octahedra in the ($R\bar{3}c$) phase does not allow them (the JT distortion modes are tetragonal or orthorhombic, rhombohedral symmetry does not split the e_g orbital).

A change in the nature of the magnetic transition suggests a variation in the nature of the magnetic coupling.

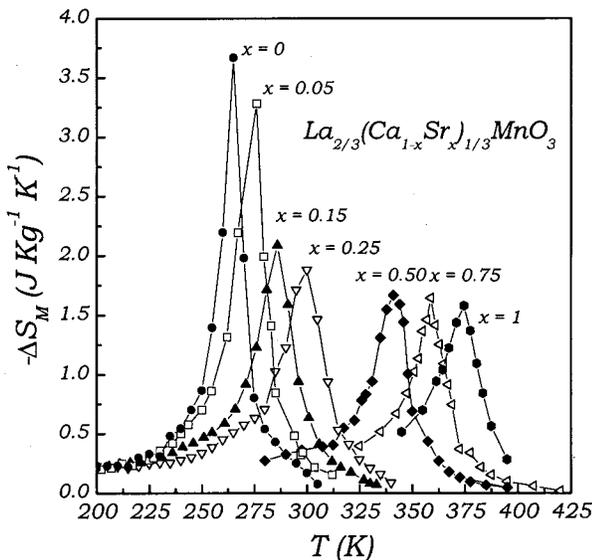


FIG. 2. Magnetic entropy change ΔS_M vs temperature, for a field of 10 kOe for the $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$ series. Note the variation between the $x=0.05$ and the 0.15 samples.

Goodenough has suggested that in manganites the static-cooperative JT distortions are replaced in the ferromagnetic phase by dynamic JT distortions that introduce vibrational modes into the spin–spin interaction, giving rise to an extra superexchange term.^{22,23} That is, in our case there is a higher influence of lattice effects in samples with $x < 0.15$, which is reflected in strong variations in several physical properties.¹⁶ Among them is an anomalous volume change at T_C in $Pbnm$ samples that is not seen in $(R\bar{3}c)$ ones,²⁴ supporting the first-order character of the transition in the former and the second-order character in the latter. An abrupt variation of magnetization and a sharp volume change at T_C (two signatures of first-order transitions, present here in samples with $x < 0.15$) are two of the key conditions to have a large ΔS_M . For samples with $t > 0.92$ the transition is of second order, the abovementioned conditions are not present, and therefore ΔS_M falls considerably, as seen in Fig. 3.

ACKNOWLEDGMENT

Spanish DGICYT Grant No. MAT98-0416, is acknowledged for financial support.

¹G. H. Jonker and J. H. van Santen, *Physica (Amsterdam)* **19**, 120 (1953).

²E. O. Wollan and W. C. Koehler, *Phys. Rev.* **100**, 545 (1955).

³J. B. Goodenough, *J. Phys. Chem. Solids* **6**, 287 (1958).

⁴C. Zener, *Phys. Rev.* **82**, 403 (1951).

⁵P. W. Anderson and H. Hasegawa, *Phys. Rev.* **100**, 675 (1955).

⁶P. G. de Gennes, *Phys. Rev.* **118**, 141 (1960).

⁷C. W. Searle and S. T. Wang, *Can. J. Phys.* **47**, 2703 (1969).

⁸R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, *Phys. Rev. Lett.* **71**, 2331 (1993).

⁹S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, *Science* **264**, 413 (1994).

¹⁰M. R. Ibarra, P. A. Algarabel, C. Marquina, J. Blasco, and J. García, *Phys. Rev. Lett.* **75**, 3541 (1995).

¹¹Z. B. Guo, J. R. Zhang, H. Huang, W. P. Ding, and Y. W. Du, *Appl. Phys. Lett.* **70**, 904 (1997).

¹²Z. B. Guo, Y. W. Du, J. S. Zhu, H. Huang, W. P. Ding, and D. Feng, *Phys. Rev. Lett.* **78**, 1142 (1997).

¹³J. Mira, J. Rivas, F. Rivadulla, C. Vázquez Vázquez, and M. A. López Quintela, *Phys. Rev. B* **60**, 2998 (1999).

¹⁴M. T. Causa *et al.*, *Phys. Rev. B* **58**, 3233 (1998).

¹⁵See for example, A. H. Morrish, *The Physical Principles of Magnetism* (IEEE, New York, 2001).

¹⁶J. Mira, J. Rivas, L. E. Hueso, F. Rivadulla, M. A. López Quintela, M. A. Señaris Rodríguez, and C. Ramos, *Phys. Rev. B* **65**, 024418 (2001).

¹⁷P. G. Radaelli, G. Iannone, M. Marezio, H. Y. Hwang, S-W. Cheong, J. D. Jorgensen, and D. N. Argyriou, *Phys. Rev. B* **56**, 8265 (1997).

¹⁸J. B. Goodenough, *J. Appl. Phys.* **81**, 5330 (1997).

¹⁹J. B. Goodenough and J. M. Longo, *Landolt-Börnstein Tabellen* (Springer, Berlin, 1970), Vol. III/4.

²⁰C. H. Booth, F. Bridges, G. H. Kwei, J. M. Lawrence, A. L. Cornelius, and J. J. Neumeier, *Phys. Rev. Lett.* **80**, 853 (1998).

²¹A. J. Millis, *Nature (London)* **392**, 147 (1998).

²²J.-S. Zhou and J. B. Goodenough, *Phys. Rev. Lett.* **80**, 2665 (1998).

²³J. B. Goodenough, *Aust. J. Phys.* **52**, 155 (1999).

²⁴C. A. Ramos *et al.*, *J. Magn. Magn. Mater.* **226-230**, 582 (2001).