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Magnetocaloric effect in Er- and Eu-substituted ferromagnetic La-Sr manganites

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Abstract

We have studied the magnetocaloric effect in $La_{0.7}Sr_{0.3}MnO_3$ colossal magnetoresistive manganites, where La is substituted by Er or Eu. The addition of these rare-earth ions allows a tunable decrease in the Curie temperature, T_C. For example, in the LaEuSrMnO3 system T_C drops from 360 to 308 K for 0.14% of Eu substitution. We find quite large values of magnetic entropy change. For an applied magnetic field of 1 T, the maximum values for both studied systems are close to that of the parent $La_{0.7}Sr_{0.3}MnO_3$, near their respective T_C's. Relative cooling power value increases notably for higher concentrations of Eu, in contrast to the Er-substituted samples. These results are discussed in terms of magnetoelastic and electron interaction contribution to the magnetic entropy.

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Keywords: Magnetic entropy change; Manganite; Magnetic cooling

The magnetocaloric effect (MCE) is intrinsic to magnetic materials, and is induced via coupling of the magnetic sublattice with the magnetic field, which alters the magnetic part of the total entropy due to a corresponding change of the magnetic field. The MCE can be estimated via the magnetic entropy change $\Delta S_M(T, \Delta H)$, and is a function of both temperature T and magnetic field change ΔH, being usually recorded as a function of temperature at a constant ΔH. In addition, the MCE has a significant technological importance, since magnetic materials with large values of $\Delta S_M(T, \Delta H)$ could be employed in various thermal devices [1].

The magnetic entropy is related to the magnetization M, magnetic field strength H and absolute temperature T through the Maxwell relation [2]:

$$\left(\frac{\partial S_M(T,H)}{\partial H}\right)_T = \left(\frac{\partial M(T,H)}{\partial T}\right)_H, \tag{1}$$

which after integration yields

$$\Delta S_M(T,\Delta H) = \int_{H_I}^{H_F} \mathrm{d}S_M(T,H)_T = \int_{H_I}^{H_F} \left(\frac{\partial M(T,H)}{\partial T}\right)_H \mathrm{d}H. \tag{2}$$

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Hence, $\Delta S_M(T, \Delta H)$ can be numerically calculated using Eq. 2 and the measured magnetization as a function of magnetic field and temperature. Generally, since temperature stabilization is the longest step in the process of collecting magnetization data, the measurements are usually carried out isothermally, by varying the magnetic field.

Several authors, through many decades, have studied the magnetocaloric effect in a large variety of magnetic materials. However, more recently, an enormous amount of work [3] and references therein was devoted to explore the MCE in the mixed-valency manganites $AMnO_3$, where A is a trivalent rare earth mixed with a divalent alkaline earth. Particularly interesting are the $La_{1-x}Sr_xMnO_3$ manganites, since their phase diagram exhibits a rich variety of magnetic and electric structures. In addition, for $x > 0.20$, the Curie temperature lies above room temperature, making these samples good candidates for technological applications. The well-known CMR manganite $La_{0.7}Sr_{0.3}MnO_3$ presents a remarkable magnetic entropy change, however, at ~80 K over room temperature [4]. Introducing a rare-earth ion such as Gd on the La site of the $La_{0.7}Sr_{0.3}MnO_3$ system is known to shift its T_c from ~370 to ~270 K [5]. In this direction, we aim to explore the magnetocaloric effect in the $La_{0.7-x}Er_xSr_{0.3}MnO_3$ and $La_{0.7-y}Eu_ySr_{0.3}MnO_3$ manganites, with $x,y = 0.035$ and 0.14.

The Er-substituted and $La_{0.7}Sr_{0.3}MnO_3$ samples were prepared by the ceramic route, starting from the stoichiometric amount of Er_2O_3, $SrCO_3$ and MnO_2, and heated in air with intermediate crushing/pressing steps. On the other hand, for Eu-substituted samples, we used the sol–gel method with urea, following the procedure described in Ref. [6]. The final crushed powders were compressed and sintered in air at 1300 °C during 60 h (for the ceramic route), and 1350 °C during 68 h (for the sol–gel technique), with a subsequent fast freezing of the samples. The magnetization curves were measured using a commercial VSM magnetometer.

The temperature and field dependence of the magnetization $M(T, H)$ was measured for all samples. The inset of Fig. 1 shows isothermal magnetization curves for the parent sample $La_{0.7}Sr_{0.3}MnO_3$. Also shown is the corresponding Arrott plot. Thus, using the measured magnetization and Eq. 2, we calculate the magnetic entropy change, presented in Fig. 2.

As expected, the Curie temperature decreases for both series with almost constant values of maximum magnetic entropy change ΔS_M^{max}. On the other hand, the relative cooling power [7]

$$RCP = -\Delta S_M^{max} \delta T_{fwhm} \quad (3)$$

has a remarkable change depending on the substituted ion. Above, T_{fwhm} means the full-width at the half-maximum of the magnetic entropy change curve, as indicated in Fig. 2. Since the RCP represents a good way for comparing magnetocaloric materials, the Eu-substituted sample with $y = 0.14$ is promising, due to the high RCP and T_C close to room temperature. In addition, a small amount of Er or Eu rare-earth included in $La_{0.7}Sr_{0.3}MnO_3$ manganite is not able to increase the RCP, independent of either element. However, a different scenario arises for higher concentrations, where the RCP strongly depends on the rare-earth ion. These features are shown in Fig. 3.

Recently, we have discussed in terms of the Landau theory for phase transitions the influence of the magnetoelastic coupling on the magnetic–entropy change and its temperature dependence [8–10]. Thus,

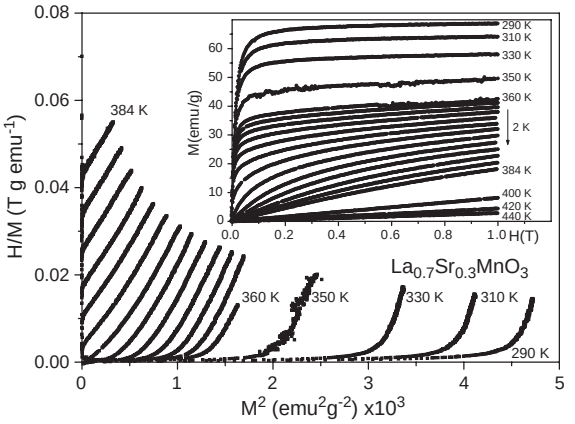

Fig. 1. Arrot plot obtained from measured M vs. H isotherms (inset), for the parent sample $La_{0.7}Sr_{0.3}MnO_3$.

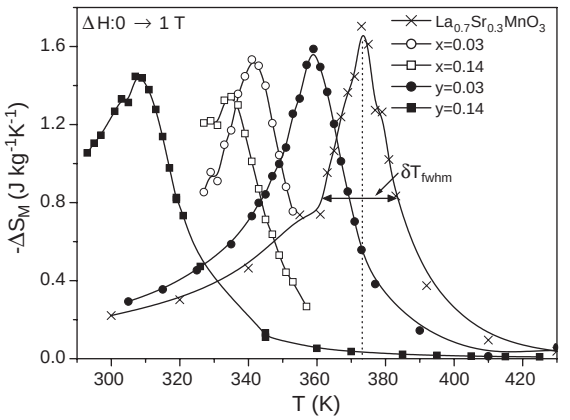

Fig. 2. Magnetic entropy change, for 1 T of magnetic field change, obtained for the series $La_{0.7-x}Er_xSr_{0.3}MnO_3$ and $La_{0.7-y}Eu_ySr_{0.3}MnO_3$.

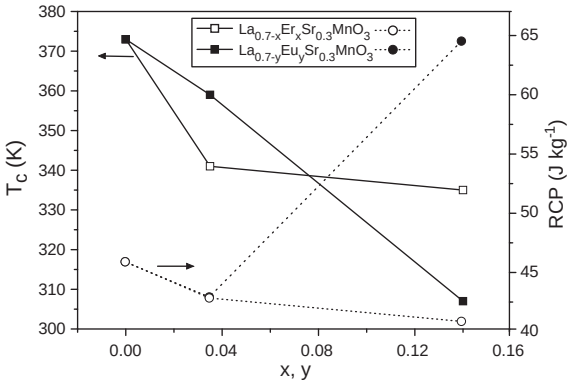

Fig. 3. Relative cooling power (Eq. (3)) and T_C as a function of Er(x) and Eu(y) concentrations.

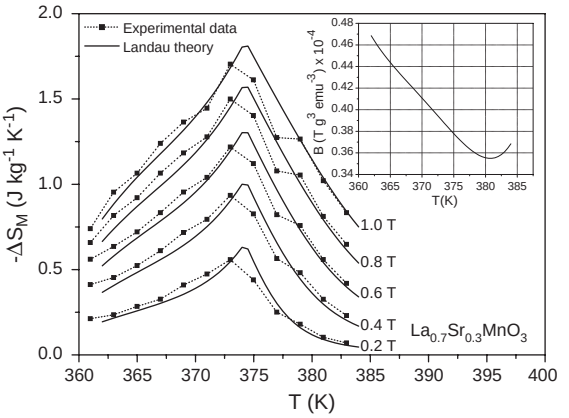

Fig. 4. Experimental and theoretical magnetic entropy change for the parent sample $La_{0.7}Sr_{0.3}MnO_3$. Inset: temperature dependence of the B parameter.

the Gibbs free energy can be written as:

$$G(T,M) = G_0 + \tfrac{1}{2}AM^2 + \tfrac{1}{4}BM^4 - M \cdot H, \quad (4)$$

where the B coefficient also includes the elastic and magnetoelastic terms, $\frac{1}{2}eQ^2$ and dQM^2, respectively, of the free energy (d and e are coefficients and Q represents mechanical stress), in accordance with Ref. [11]. From energy minimization, a magnetic equation of state can be derived

$$\frac{H}{M} = A + BM^2 \quad (5)$$

and the corresponding magnetic entropy is obtained from differentiation of the magnetic part of the Gibbs free energy with respect to temperature

$$S_M(T,H) = -\tfrac{1}{2}A'(T)M^2 - \tfrac{1}{4}B'(T)M^4, \quad (6)$$

where $A'(T)$ and $B'(T)$ are the temperature derivatives of the expansion coefficients. For a simple ferromagnet (B positive constant), $\Delta S_M(T,H)$ presents a narrow peak at T_C. On the other hand, the magnetoelastic coupling and electron interactions contribute directly to the magnetic entropy and its temperature dependence, defining the shape of the referred curve. This occurs when the parameter B is a function of temperature. This effect was already found in La-manganites [8].

Fig. 4 shows ΔS_M curves for various applied ΔH, up to 1 T. Dashed lines represent experimental data, while full lines show the results obtained by the Landau theory. The inset in Fig. 4 shows the dependence of the B coefficient on temperature.

In order to obtain results from the Landau theory that correctly represent experimental data for the samples in the study, the dependence of B on temperature cannot be disregarded. In other words, the magnetoelastic coupling and electron interaction influence is an important factor in the study of the magnetocaloric properties of these materials.

In summary, we analyzed the magnetocaloric properties of Eu and Er-substituted $La_{0.7}Sr_{0.3}MnO_3$ manganites. Compared to the parent sample, the Er and Eu-substituted manganites have lower Curie temperature and almost constant maximum magnetic entropy change. In addition, 14% of Eu is able to increase 30% of the RCP. We analyzed these samples using the Landau theory and concluded that magnetoelastic coupling and electronic interaction define the shape of the magnetic entropy change curves, directly affecting the ΔS_M^{max} and RCP values.

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