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Charge-ordering contribution to the magnetic entropy change of (Pr, Ca)MnO_3 manganites

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Abstract

In the present work, we analyze the influence of the charge-ordering on the magnetic entropy change of $Pr_{1-x}Ca_xMnO_3$ manganites ($0.20<x<0.95$). The samples with $x<0.30$ and $x>0.90$ present the usual ferromagnetic and antiferromagnetic behavior, peaking at the Curie and Néel temperature, respectively. In contrast, for the samples with charge-ordering ($0.30<x<0.90$), a much smaller positive peak on the magnetic entropy change was observed around the charge-ordering temperature T_{CO}. This effect is associated to a negative contribution from the spin ordering ΔS_{spin}, which is superimposed to a positive contribution due the charge-ordering ΔS_{CO}. We could also appraise ΔS_{CO}^{max} as a function of Ca content ($0.30<x<0.90$), under 4 T of magnetic field change. ΔS_{CO}^{max} vanishes for the limits $x \sim 0.30$ and ~ 0.90, and presents a deep minimum around $x \sim 0.50$, with two maxima at $x \sim 0.35$ and 0.65.

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Keywords: Magnetic entropy change; Manganite; Charge-ordering

Particularly interesting as candidates to technological applications are the $Pr_{1-x}Ca_xMnO_3$ manganites, since their phase diagram exhibits a rich variety of magnetic, electric and crystallographic structures. In this direction, we aim to explore the magnetocaloric effect through a wide range of Ca concentrations ($0.20<x<0.95$).

For $0.15<x<0.30$ a ferromagnetic-insulator (FMI) phase arises, with Curie temperature around 120 K [1]. For $0.30<x<0.90$, an antiferromagnetic-insulator (AFMI) phase arises for temperatures typically below 170 K [1–3], coexisting with a charge-ordered (CO) state with onset temperature T_{CO} between 210 K, for $x = 0.30$, and 110 K, for $x = 0.85$ [1]. Additionally, it is well established [2] that the clusters embedded in the antiferromagnetic matrix achieve the ferromagnetic order around 110 K, for $x = 0.30$, and 42 K, for $x = 0.40$ [3]. For the Ca-rich samples $x>0.90$, another strong phase coexistence arises, with ferromagnetic domains embedded in a non-charge-ordered antiferromagnetic (NCO AFMI) matrix. For $x = 0.90$ the ferromagnetic phase is stable, decreasing its volume fraction as the Ca content x increasing towards unity, reaching the well-known *G*-type antiferromagnetic $CaMnO_3$ [4]. Ref. [5]

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provides more details concerning the Pr–Ca series and the preparation procedure of the present samples.

The temperature and field dependence of the magnetization $M(T,H)$ were measured for all samples available ($x = 0.20$, 0.25, 0.30, 0.32, 0.35, 0.40, 0.45, 0.50, 0.55, 0.65, 0.70, 0.75 and 0.95). From the data analysis of several M vs. H isotherms, we could build the curves for the thermal dependence of the magnetization, at a fixed magnetic field. Thus, the magnetic entropy change

$$\Delta S_M(T,\Delta H) = \int_{H_I}^{H_F} \left(\frac{\partial M(T,H)}{\partial T}\right)_H \mathrm{d}H \qquad (1)$$

were evaluated and are shown in Fig. 1, for all samples available. For $x = 0.25$ and 0.30, concentrations completely embedded within the ferromagnetic region, an usual behavior for ΔS_M are found for both, as presented in Fig. 1(a). On the other hand, for samples with $0.30<x<0.90$, the CO arrangement plays a decisive role. When the temperature is further decreased, the magnetic entropy change ΔS_M follows the usual shape until the CO temperature T_{CO}, below which such behavior is completely broken, as can be observed in Fig. 1(b)(c). Finally, for $x = 0.95$, with a NCO AFMI phase, the magnetic entropy change recovers the usual shape, as sketched in Fig. 1(d).

To analyze this intriguing and anomalous feature that arises for $0.30<x<0.90$, some aspects should be taken into account. First of all, we consider two different contributions to the total magnetic entropy change ΔS_M: one refers to the spin rearrangement ΔS_{spin}, and the other concerning the CO rearrangement ΔS_{CO}, as follow: $\Delta S_M = \Delta S_{spin} + \Delta S_{CO}$.

For $T_N<T<T_{CO}$, i.e., in the paramagnetic phase, an applied magnetic field forces a rude alignment of the spins, increasing the $Mn^{3+}-Mn^{4+}$ electron hopping and decreasing the concentration of $Mn^{3+}-Mn^{4+}$ CO when compared with the zero-field case. Consequently, the entropy due to the CO increases under an external applied magnetic field, allowing a positive CO entropy change. On the other hand, for $T>T_{CO}$, there is no CO, implying, of course, a null CO entropy change. In addition, the paramagnetic phase of these samples have ferromagnetic fluctuations [5] ($\theta_p>0$), even they being antiferromagnetic. Thus, we considered, as a first approximation, that ΔS_{spin} arises from a simple ferromagnetic mean-field interaction, at least around $T_{CO}(>T_N)$, i.e., in the paramagnetic phase. In this direction, the effective field can be written as

$$H_{eff} = H_{ext} + \lambda g J \mu_B B_J(x), \qquad (2)$$

where H_{ext} stands for the external magnetic field, λ the mean-field parameter, $B_J(x)$ the Brillouin function and

$$x = \frac{gJ\mu_B H_{eff}}{k_B T}. \qquad (3)$$

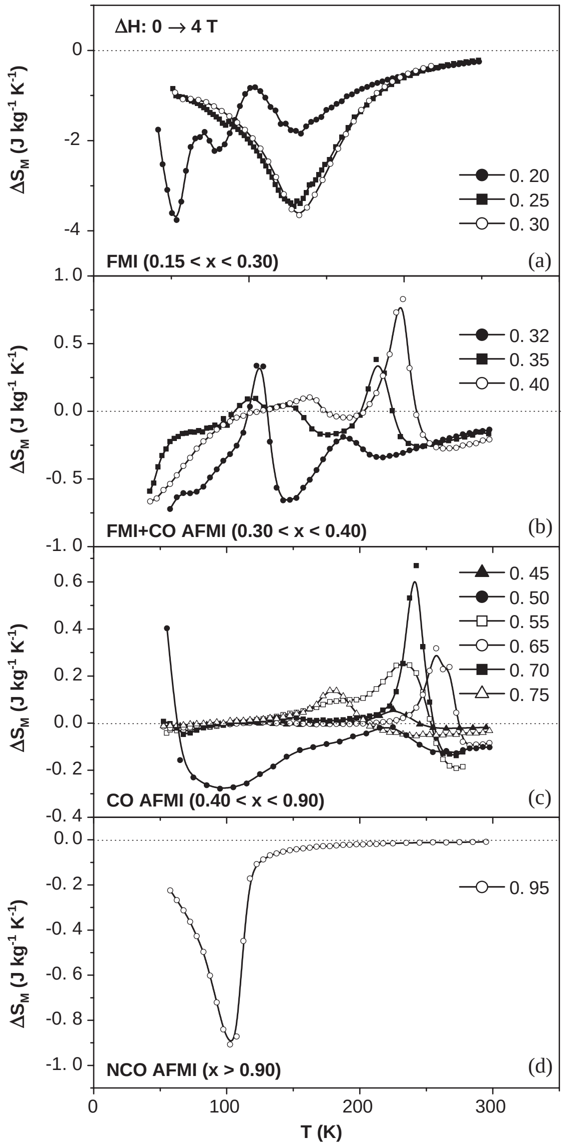

Fig. 1. Temperature dependence of the magnetic entropy change, under 4 T of magnetic field change, for all samples available, covering all different magnetic phases of the $Pr_{1-x}Ca_xMnO_3$ series. FMI—ferromagnetic insulator; CO AFMI—charge-ordered antiferromagnetic insulator; NCO AFMI—non-charge-ordered antiferromagnetic insulator.

Thus, from the Gibbs-Von Neumann entropy

$$S = -k_B \mathrm{Tr}\{\hat{\rho} \ln \hat{\rho}\} \qquad (4)$$

is possible to obtain the magnetic entropy due to the spin ordering, in k_B units:

$$S_{spin}(T,H_{ext}) = \ln\left[\frac{\sinh[x(1+1/2J)]}{\sinh[x/2J]}\right] - xB_J(x), \qquad (5)$$

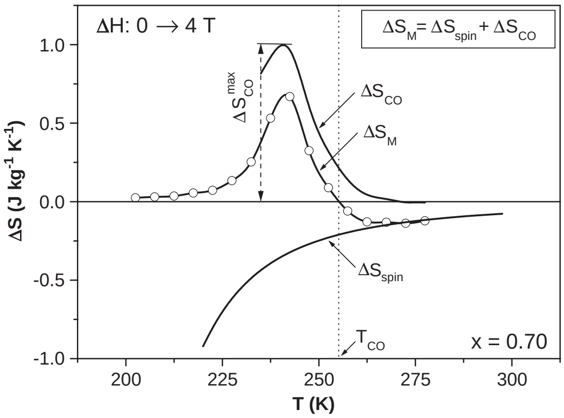

Fig. 2. Estimative of the CO contribution ΔS_{CO} to the total magnetic entropy change ΔS_M. See text for details concerning the spin contribution ΔS_{spin} (Eq. (6)).

where $\hat{\rho}$ is the density operator corresponding to a Hamiltonian $\mathscr{H} = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{H}$. Finally, the magnetic entropy change due to the spin ordering can be written as

$$\Delta S_{spin}(T, \Delta H) = S_{spin}(T, H_{ext}) - S_{spin}(T, 0). \tag{6}$$

However, from high-temperature magnetic measurements [5], it is possible to obtain the paramagnetic Curie temperature θ_p and the paramagnetic effective moment p_{eff}, and, from the well-known relationships

$$p_{eff} = g\sqrt{J(J+1)} \quad \text{and} \quad \lambda = \frac{3k_B\theta_p}{p_{eff}^2}, \tag{7}$$

estimate the mean-field parameter λ and the total angular moment J, considering $g = 2$, since this value was already found for several manganites [6,7]. Thus, using the measured λ and J, we estimated ΔS_{spin} (Eq. (6)), that exactly match ΔS_M at high values of temperature. Consequently, we could appraise ΔS_{CO}^{max}, the value of CO contribution slightly below T_{CO}, i.e., around the maximum of ΔS_M, as drawn in Fig. 2, for $x = 0.70$.

Following the procedure described above, the concentration dependence of ΔS_{CO}^{max} could be built, vanishing for the limits $x \sim 0.30$ and 0.90, and presenting a deep minimum for $x \sim 0.50$, with two maxima around $x \sim 0.35$ and 0.65, as shown in Fig. 3.

For $Pr_{1-x}Ca_xMnO_3$ manganites the CO entropy arises from the excess of Mn^{3+} or Mn^{4+}, depending if $x<0.50$ or $x>0.50$, respectively. Since there are 1–2x Mn^{3+} unpaired (for $x<0.50$, for example), and such excess vanish at $x = 0.50$, it is expected that ΔS_{CO}^{max} have a deep minimum around $x = 0.50$.

Summarizing, in the present work we analyzed the magnetic entropy change ΔS_M for a wide range of Ca concentrations ($0.20<x<0.95$), covering several kinds of magnetic order. For $x<0.30$ and $x>0.90$ we found the usual behavior for ΔS_M, since these samples are ferromagnetic and NCO AFMI, respectively. On the contrary, we found an anomalous magnetic entropy change for $0.30<x<0.90$ (concentrations exhibiting charge-ordering phenomenon), and the results could be explained considering a spin and CO contributions. In addition, taking some considerations into account, we could evaluate ΔS_{CO}^{max} as a function of Ca content, x.

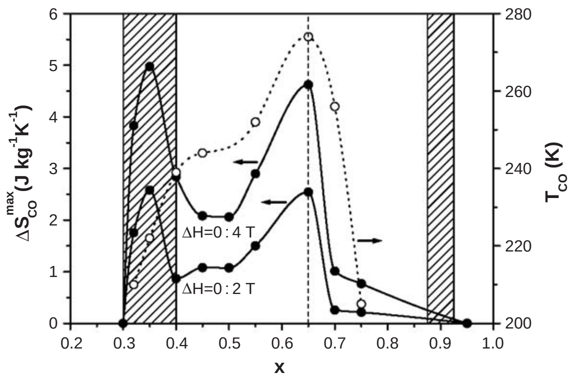

Fig. 3. Left axes: ΔS_{CO}^{max} as a function of Ca content, x, for $\Delta H = 2$ and 4 T. Right axes: CO temperature as a function of Ca content, x. See text for the meaning of ΔS_{CO}^{max}.

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