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Positive and 'colossal' magnetocaloric effect due to charge ordering in CMR manganites

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Abstract

The magnetocaloric effect (ΔS_M) is studied across the ferromagnetic to charge ordered composition range in $Pr_{1-x}Ca_xMnO_3$ manganites ($0.25 \leqslant x \leqslant 0.40$). The ferromagnetic phase transition leads to usual entropy decrease on the application of a magnetic field. The charge order transition ($T_{CO} \sim 220-250$ K) leads to an uncommon entropy increase, of comparable magnitude ($4\,J\,kg^{-1}\,K^{-1}$ for 40 kOe). At lower temperatures ($T < 50$ K), close to the field-induced mixed phase, extremely large values of ΔS_M are found (for $x = 0.32$, $-20.8\,J\,kg^{-1}\,K^{-1}$ for 40 kOe at 26 K).

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Keywords: Magnetocaloric effect; Manganite; Charge order; $Pr_{1-x}Ca_xMnO_3$

The $Pr_{1-x}Ca_xMnO_3$ system shows a rich electric and magnetic phase diagram [1]. At high temperatures, the system is paramagnetic and insulator (PMI). For $0.15 < x < 0.30$ a ferromagnetic insulator (FMI) phase is established. A more complex electric–magnetic phase diagram is found for $0.30 < x < 0.85$, where the charge-ordering effect (CO) coexists with an antiferromagnetic insulator (AFMI). In addition, this insulating state can be driven metallic by an applied magnetic field. $Pr_{1-x}Ca_xMnO_3$ ($x = 0.25$, 0.30, 0.32, 0.35 and 0.40) samples were prepared by the ceramic route, starting from stoichiometric amounts of Pr_2O_3, $CaCO_3$ and MnO_2 and heating in air, with 5 intermediate crushing/pressing steps and final sintering in air at 1350°C for 45 h, with a subsequent fast freezing. From X-ray diffraction we find that all the samples are pure phase, orthorhombic, with the space group Pbnm. The magnetic entropy variation $\Delta S_M(T, \Delta H)$ under a magnetic field change $\Delta H = H_F - H_I$ at temperature T is

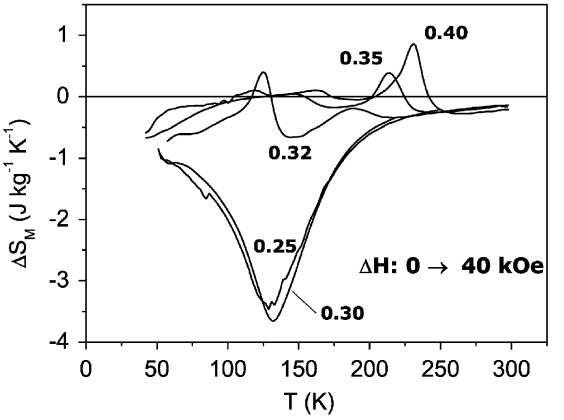

Fig. 1. Magnetic entropy change under 40 kOe field change for ferromagnetic ($x \leqslant 0.30$) and charge ordered samples ($x > 0.30$).

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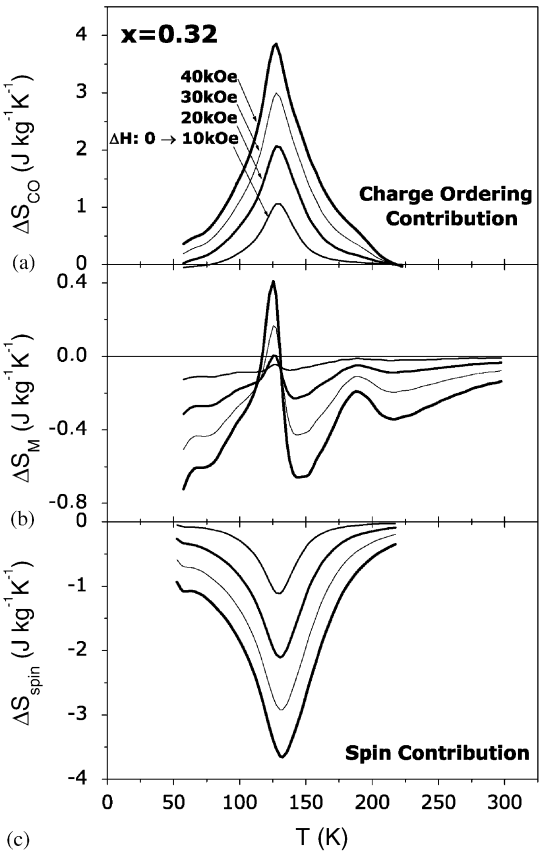

Fig. 2. Temperature dependence of the (a) charge-ordering ΔS_{CO} and (c) spin contributions ΔS_{spin} (b) total magnetic entropy change ΔS_M under several values of field for sample $x = 0.32$.

determined from isothermal magnetization $M(T, H)$ data and usual thermodynamic relations [2]. The magnetic measurements are performed using a commercial *quantum design* SQUID magnetometer.

The magnetic entropy change ΔS_M under the application of a magnetic field of 40 kOe in the temperature range 50–300 K is presented in Fig. 1. The results for $x \leqslant 0.30$ show a regular ferromagnetic phase transition effect with a negative peak at $T_c \sim 130$ K. However, for the samples above the onset concentration for the charge ordering (~ 0.30) an anomalous magnetic entropy change is observed just below the charge ordering temperature ($T_{co} > 220$ K). A positive ΔS_M peak develops, increasing in amplitude with Ca content (higher T_{co}). This uncommon effect is associated to the supression of charge-ordering, with an increase of accessible states due to the enhancement of electron mobility, under an applied magnetic field. Interestingly, this effect appears superimposed to the negative contribution ΔS_{spin} due to spin-ordering: $\Delta S_M = \Delta S_{CO} + \Delta S_{spin}$. Above T_{co}, ΔS_M is very similar for all the samples. In Fig. 2 the separation of both

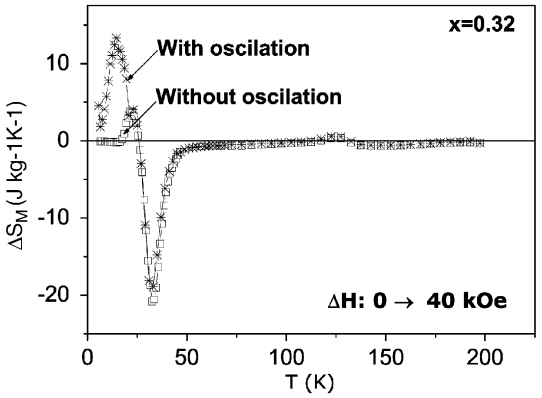

Fig. 3. ΔS_M at $H = 40$ kOe for $x = 0.32$, reaching very high values below 50 K. At lower temperatures, ($T < 26$ K) strong irreversibility effects are observed.

contributions is shown for sample $x = 0.32$, taking the spin contribution from the $x = 0.30$ sample. In the entire field range the CO positive contribution onsets at T_{CO}.

If the magnetic field is sufficiently high, the charge-ordered state is melted and an insulator–metal transition is induced. However, there is a broad mixed phase magnetic field interval (with coexistence of CO and metallic regions) separating the two phases [1,3]. For $x \leqslant 0.4$, the mixed phase exists even at $H = 0$ and strong irreversibility effects arise. The presence of ferromagnetic regions dispersed in the antiferromagnetic matrix leads to a magnetization increase on cooling just below about 50 K, peaking at a lower temperature [4]. In this temperature range, we find extremely large values of ΔS_M, establishing a 'colossal' magnetocaloric effect in manganites. This is shown in Fig. 3 for the sample $x = 0.32$, for which ΔS_M at $T = 26$ K and 40 kOe reaches $-20.8\,\mathrm{J\,kg^{-1}\,K^{-1}}$. At still lower temperatures, ΔS_M becomes positive and strongly depends on the previous magnetic history of the sample, i.e., on the fact that the applied magnetic field was cycled through zero to demagnetize the coil (and the sample) before a subsequent temperature for magnetization measurement was established.

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