# Large magnetocaloric effect in manganites with charge order

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(Received 24 May 2001; accepted for publication 16 July 2001)

In this work, we report the magnetocaloric effect ($|\Delta S_M|$), around the charge/orbital ordering transition in the mixed valent manganite $Nd_{0.5}Sr_{0.5}MnO_3$. The magnitude of $|\Delta S_M|$ around this first-order transition is around three times larger than that obtained around the second-order transition (ferromagnetic-metallic-to-paramagnetic-insulator) in the same compound. Actually, the magnetocaloric response around the charge-order transition is comparable to pure Gd, the rare earth with the highest magnetocaloric effect. The possibility of an easy tuning of the charge-order transition temperatures in doped manganites opens a way of investigation materials usable in magnetic refrigerators. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1403317]

The conventional thermomechanical cooling techniques, through expansion and gas liquefaction, can be improved by magnetic techniques, which reduce the size of the refrigerators, making them more efficient and more ecologically clean. The magnetic refrigerators are based on the magnetocaloric effect (MCE),[1,2] i.e., the magnetic entropy change ($\Delta S_M$) produced by changes in the magnetic field applied to the system. If this change of magnetic entropy is made under adiabatic conditions it is compensated by an equal but opposite change in the entropy of the lattice, which produces a variation in the temperature of the material. The MCE has been used for many years to achieve low temperatures (of the order of milikelvins) through adiabatic demagnetization of paramagnetic salts.[3] However, above ~20 K, their magnetocaloric response is not large enough to provide efficient cooling, and it is necessary to find materials with higher working temperatures. In the last few years a large $|\Delta S_M|$ has been discovered in ceramic manganites ($A_{1-x}A'_xMnO_3$ with A=La and A′=Ca, Sr, Gd, etc.),[4–7] associated with the ferromagnetic-to-paramagnetic (FM-to-PM) transition at Curie temperature ($T_C$) (which usually coincides with a maximum in the colossal magnetoresistance associated with the metal-to-insulator transition). The possibility of fine tuning of their transition temperatures make manganites excellent candidates for working materials in magnetic refrigeration, covering a wide range of temperatures.[4]

Charge/orbital ordering (CO/OO) states, due to interatomic Coulomb and spin-lattice interactions, are common in perovskites. A typical example of a CO state is that stabilized below $T_{CO} \sim 155$ K in $Nd_{0.5}Sr_{0.5}MnO_3$.[8] At $T_{CO}$, a first-order transition occurs from a FM-metallic state towards a low-temperature antiferromagnetic (AF) insulator (CE-type) phase. In this low-temperature AF state, there is a real spatial order of $Mn^{3+}/Mn^{4+}$ ions on the (001) plane of the orthorrombic lattice, while the $3x^2-r^2/3y^2-r^2$-type orbitals lie along the $b$ axis of the plane.[9] In this situation only the superexchange interaction is active, leading to FM zig-zag chains in the (001) plane, this plane being AF coupled in the $c$ axis.[10] The transition temperature can be fine tuned through the control of the size of the $A$-site cation ($\langle r_A \rangle$) due to the wide range of $\langle r_A \rangle$ compatible with the perovskite structure. In this letter, we focus our attention on the MCE from 100 K to room temperature for $Nd_{0.5}Sr_{0.5}MnO_3$. The large value of magnetization in this compound, and its abrupt drop at the first-order transition at $T_{CO}$, makes $Nd_{0.5}Sr_{0.5}MnO_3$ an ideal candidate for showing a large MCE around this CO/OO transition.

The $|\Delta S_M|$ can be measured through either the adiabatic change of temperature ($\Delta T_{ad}$) by the application of a magnetic field, or through the measurement of classical $M(H)$ isotherms at different temperatures.[11] We employed the second method to avoid the difficulty of adiabatic measurements. The variation of magnetic entropy and $M(H)$ isotherms are related by the thermodynamic Maxwell relation[2]

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

From Eq. (1), the isothermal entropy change can be calculated by means of magnetic measurements:

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

For magnetization measurements made at discrete field and different temperatures, Eq. (2) can be approximated by[11]

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

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.

The sample used in our experiment was prepared by the ceramic method. Stoichiometric mixtures of $Nd_2O_3$, $SrCO_3$, MnO, and $MnO_2$ (at least 99.99% purity) were ground, pressed, and heated in air several times with intermediate grinding. The final sintering treatment was at 1300 °C for 100 h. It resulted in a polycrystalline sample of

 

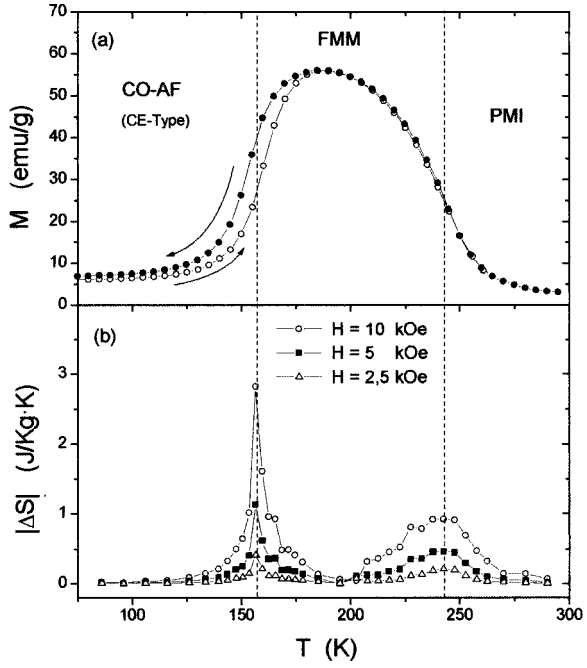


FIG. 1. (a) Temperature-dependent magnetization and (b) magnetic entropy variation with temperature for different applied fields, for $Nd_{0.5}Sr_{0.5}MnO_3$. The two maxima of $|\Delta S_M|$ coincide with $T_{CO}$ and $T_C$.

$Nd_{0.5}Sr_{0.5}MnO_{3+\delta}$. Oxygen content was determined by iodometric analysis, with a result of $\delta = 0.034$. Careful Rietveld analysis of the x-ray powder diffraction patterns confirm the formation of the perovskite phase without the presence of any other secondary phase within an accuracy of 99%. Lattice parameters coincide quite well with those available in the literature.[8] A vibrating-sample magnetometer (VSM) was used for magnetic measurements. The field change in the VSM was slow enough (~100 Oe/s) to consider all magnetization processes as isothermal.

Figure 1(a) shows the temperature dependence of magnetization of $Nd_{0.5}Sr_{0.5}MnO_3$. Two magnetic transitions are clear from this curve: the PM-to-FM transition at $T_C \sim 240$ K, and the FM-to-AF transition at $T_N \sim 155$ K. Associated with this last magnetic transition at $T_N$ was a jump in the resistivity (not shown), associated with the transition towards the low-temperature CO/OO state, in agreement with previous results of other groups.[8] Figure 2 shows the magnetization versus applied field obtained at different temperatures for $Nd_{0.5}Sr_{0.5}MnO_3$ and in Fig. 1(b) is shown the magnetic entropy change over the whole temperature interval $[|\Delta S_M(T)|]$, for different external fields, calculated from $M(H)$ isotherms [Eq. (3)]. There is a sharp peak in $|\Delta S_M(T)|$, with a maximum value of 2.8 J/kg K, at the charge-order temperature ($T_{CO}$) with an external field of only 10 kOe. This is the one of highest values of MCE in manganites reported to date for similar fields. It is very close to the value for pure Gd, and has a comparable value to garnets, which are commonly used as magnetic refrigerators[12] (see Table I). On the other hand, the value of $|\Delta S_M|$ around $T_C$ (~240 K) is of the same order as that for similar compounds studied by others, like $La_{0.67}Ca_{0.33}MnO_3$,[4] but much lower than $|\Delta S_M|$ near $T_{CO}$ in $Nd_{0.5}Sr_{0.5}MnO_3$. Szewczyk *et al.* have measured the MCE in a manganite with CO,[7] but they did not study the effect in $T_{CO}$ around $T_C$.

TABLE I. Maxima values of the entropy change at $H = 10$ kOe (*$H = 9$ kOe) for several materials considered for magnetic refrigeration.

| Material | $T_{max}$ (K) | $\lvert\Delta S_M\rvert$ (J/kg K) | Source of data |
|---|---|---|---|
| $Nd_{0.5}Sr_{0.5}MnO_3$ | 155 | 2.8 | This work |
| $La_{0.67}Ca_{0.33}MnO_3$ | 260 | ~1 | Ref. 4 |
| $La_{0.87}Sr_{0.13}MnO_3$ | 195 | ~2 | Ref. 7 |
| Gd | 293 | 3.25 | Ref. 10 |
| $*Gd_3Ga_{2.5}Fe_{2.5}O_{12}$ | ~10 | ~2 | Ref. 11 |

Figure 3 shows the behavior of the entropy change with applied field for several temperatures. It increases monotonically as the field increases, and it is expected to obtain higher values for the MCE for higher fields.

In summary, we have obtained a very large value of $|\Delta S_M|$ associated with the CO transition of a manganite ($Nd_{0.5}Sr_{0.5}MnO_3$), comparable to materials considered good for magnetic refrigerators (see Table I). A large MCE was measured at a charge-order transition, opening a way for the investigation of materials useful for magnetic refrigerators.

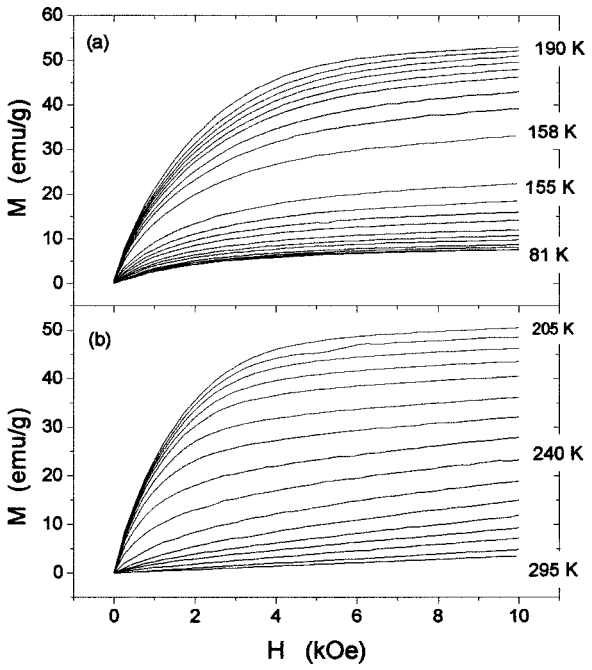


FIG. 2. $M(H)$ isotherms at different temperatures, for $Nd_{0.5}Sr_{0.5}MnO_3$. (a) Around the CO/OO transition and (b) around $T_C$.

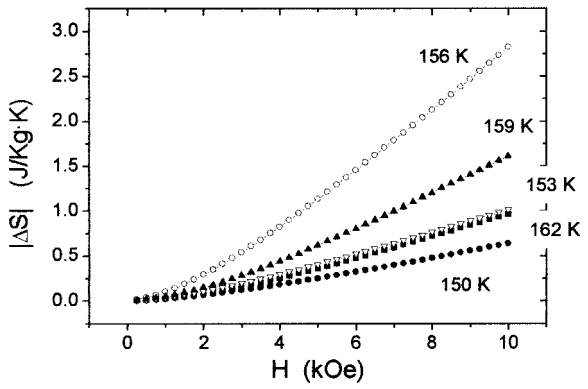


FIG. 3. Field dependence of $|\Delta S_M|$ at different temperatures around $T_{CO}$ for $Nd_{0.5}Sr_{0.5}MnO_3$.

This promises to be very rich due to the variety of $T_{CO}$ in different perovskites, their different temperatures of transition, chemical stability, and low cost.

The authors want to acknowledge the Spanish DGCYT for financial support through Project No. MAT98-0416. L. E. Hueso and P. Sande also acknowledge to MEC and Diputación da Coruña, respectively, for financial support.

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