Enhanced magnetocaloric effect in single crystalline Nd0.5Sr0.5MnO3

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Enhanced magnetocaloric effect in single crystalline Nd$_{0.5}$Sr$_{0.5}$MnO$_3$

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The magnetocaloric effect in single crystalline Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ (NSMO 0.5) is investigated by computing the field dependent entropy change (ΔS) and adiabatic temperature change (ΔT_{ad}). At the charge ordering temperature (T_{CO}), the value of ΔS_{max} is found to be much higher than ΔS_{max} reported in polycrystalline samples. This "giant" entropy change is attributed to interplay (stronger in single crystals) among spin, charge, lattice, and orbital degrees of freedom resulting in a field induced transition at T_{CO}. In contrast, the change in entropy associated with Curie temperature (T_C) is very low. The direct measurements of the field induced temperature change (ΔT) are in agreement with the computed value of ΔS. The presence of short-range correlations with charge/orbital order (COO) above and below T_C may be responsible for the suppression of the negative MCE at T_C. A critical exponent analysis of the paramagnetic (PM) to ferromagnetic (FM) transition using magnetization data yields mean-field-like values, which is likely to be operative in inhomogeneous systems such as NSMO 0.5 with correlated COO clusters larger than lattice parameter. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2710221]

I. INTRODUCTION

Doped manganites with the general formula $R_{1-x}A_x$MnO$_3$ (R=La,Nd,Pr etc.; A=Ca,Sr, etc.) exhibit a significant magnetocaloric effect (MCE)—external magnetic field induced temperature change—in addition to colossal magnetoresistance.[1] In this report, we present our MCE investigations in single crystalline Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ (NSMO 0.5) by computing the field induced entropy change (ΔS) using magnetization data and by directly measuring the field induced temperature change (ΔT). The mechanisms behind MCE is associated with the two transitions in NSMO 0.5; (a) the second order paramagnetic (PM) to ferromagnetic (FM) transition at T_C(=243 K) and (b) the first order transition from an orthorhombic ferromagnet to a monoclinic charge and orbital ordered antiferromagnet (AFM) at T_N=T_{CO} (=150 K) are discussed.

II. EXPERIMENTAL DETAILS

Single crystals of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ used in this work were grown in an infrared image furnace by the floating zone technique.[2] The x-ray diffraction, structural characterization, and preliminary magnetic and electrical transport measurements performed are reported in Ref. 3. The dc magnetization measurements used for critical exponent analysis were made using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer.

The expression for the change in entropy in the presence of magnetic field across a second order transition is obtained using Maxwell's thermodynamic relations,

$$\Delta S_H = \int_0^{H_{max}} \left(\frac{\partial S}{\partial H} \right)_T dH = \int_0^{H_{max}} \left(\frac{\partial M}{\partial T} \right)_H dH. \tag{1}$$

The entropy change was evaluated using the measurements of temperature dependence of magnetization in the presence of different magnetic fields up to 1.4 T using the discrete version of Eq. (1).[4]

For a first order transition, Maxwell's relation is not applicable since a discontinuous entropy change is involved. So the Clausius-Clapeyron equation is used to compute ΔS. The change in the transition temperatures ($\Delta \Theta$) for a field change of ΔH is given by

$$\left| \frac{\Delta \Theta}{\Delta H} \right| = \left| \frac{\Delta M}{\Delta S} \right| = \text{const}, \tag{2}$$

where ΔM is the difference between the magnetization values corresponding to ΔH. The temperature dependence of magnetization data was measured in a EG&G vibrating sample magnetometer from liquid nitrogen temperature to room temperature

To complete the magnetocaloric evaluation of a material, it is necessary to determine the field induced temperature change. The direct measurements of ΔT were performed as follows: The crystal was mounted in a Teflon holder with a platinum resistance thermometer mounted in direct contact with the sample. The temperature was monitored continuously using a Lakeshore temperature controller. The influence of the magnetic field on the sensor was tested in ad-

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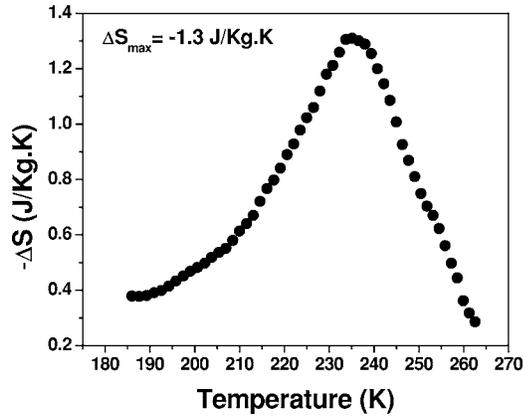
FIG. 1. Temperature dependence of ΔS of NSMO 0.5 around T_C.

vance and was found to be negligible. The sample holder was placed inside a liquid nitrogen cryostat between the poles of an electromagnet. Adiabatic conditions were ensured by evacuating the sample space. The sample was cooled to the lowest temperature, and readings were taken during a natural warming process at a slow rate of about 0.2 K/min. The difference between the temperatures recorded before and after applying the magnetic field is defined as ΔT.

III. RESULTS AND DISCUSSIONS

The changes in entropy across T_C for ($\Delta S_{max}=-1.32$ J/kg K) computed using Eq. (1) and across T_{CO} ($\Delta S_{max}=+10.45$ J kg^{-1} K^{-1}) computed using Eq. (2) are shown in Figs. 1 and 2 for $H=1.4$ T. The magnetization data used for the computation is shown in the inset of Fig. 2, which clearly shows the transitions at T_C and T_{CO}.

The direct measurement of the field induced temperature change for $H=1$ T gives $\Delta T_{max}=-1.39$ K across T_{CO} (Fig. 3) and $\Delta T_{max}=+0.3$ K across T_C (inset of Fig. 3), in agreement with the ΔS obtained by computation.

For an AFM material subjected to a magnetic field, the value of ΔS is positive.[5] The ΔS contribution due to the suppression of charge/orbital order (COO) is also positive.[6] Although the transition at T_{CO} (with/without an external magnetic field) is related to a complex interplay among spin,
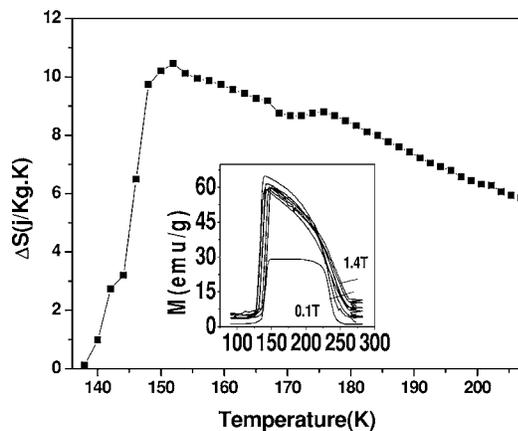
FIG. 2. ΔS vs T around T_{CO}. Inset shows M vs T in various applied fields.
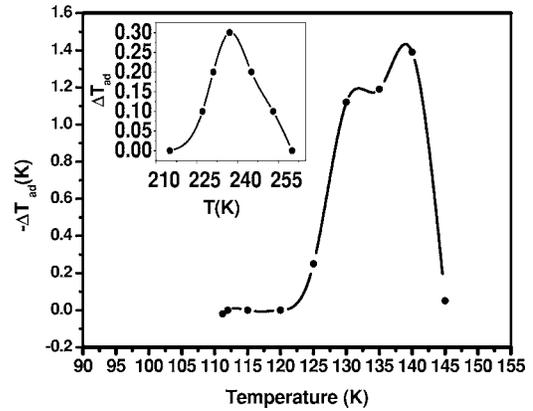
FIG. 3. Direct measurements of ΔT_{ad} vs T around T_{CO} with inset showing ΔT_{ad} vs T around T_C. $H=1$ T.

charge, lattice, and orbital degrees of freedom, the observed positive entropy change for NSMO 0.5 may be thought of arising from the sum of the $+\Delta S$ associated with the suppression of COO (Ref. 6) and the $+\Delta S$ associated with the field induced AFM to FM transition,[7] resulting in a "giant" MCE. A large $+\Delta S$ ($-\Delta T$ or negative MCE) is also observed in Mn$_3$GaC, which exhibits an AFM to FM transition at 165 K (without charge/orbital order).[8]

The superior MCE properties of single crystalline manganites compared to polycrystalline manganites may be attributed to the absence of grain boundaries, resulting in a stronger interplay among various degrees of freedom. Phan *et al.*[9] who obtained higher ΔS and ΔT values for crystals compared to polycrystalline samples, support our results. The maximum change in entropy and adiabatic temperature at T_C are found to be $\Delta S_{max}=-1.3$ J kg^{-1} K^{-1} ($H=1.4$ T) and $\Delta T_{max}=+0.3$ K (direct measurement). The obtained entropy change in our case is, in fact, a little lower than that for polycrystalline samples [-2.63 J kg^{-1} K^{-1} ($H=1$ T)].[10]

A plausible explanation is provided to account for this observation. In single crystals of NSMO 0.5, short-range correlations COO clusters have been observed by synchrotron x-ray measurements above and below T_C.[11] The ΔS contribution of spins across a PM to FM transition is negative while that associated with COO is positive.[6] This may result in a suppression of the net observed ΔS at T_C. Such an effect may not be operative in polycrystalline manganites, where COO correlations are expected to be weak due to granularity.

A critical exponent analysis was carried out in order to understand the nature of the transition at T_C. Modified Arrott plot technique is used for determining critical exponents, which has a scaling equation of state as $(H/M)^{1/\gamma}=at+bM^{1/\beta}$ that causes isothermal curves of $M(H)$ data to fall into a set of parallel straight lines in a plot of $M^{1/\beta}$ vs $(H/M)^{1/\gamma}$.[12] The isothermal line that passes through the origin is the critical isotherm at $T=T_C$. The modified Arrott plot is shown in Fig. 4. From the x,y intercepts in Fig. 4, the values of M_S, $1/\chi$, and T_C [241.5(1) K] were determined by iteration procedure, and insets of Fig. 4 show the ln-ln plot used to get the final values of $\beta=0.52(1)$ and $\gamma=1.08(2)$. The values are closer to those predicted by mean field approximation ($\beta=0.5$, $\gamma=1$) rather than three-dimensional
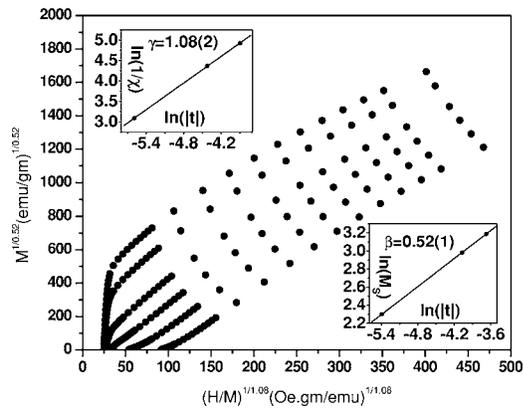
FIG. 4. Modified Arrott plot for NSMO 0.5 with inset showing (a) $\ln(M_S)$ vs $\ln(|t|)$ (slope gives β) (b) $\ln(1/\chi)$ vs $\ln(|t|)$ (slope gives γ).

(3D) Heisenberg model ($\beta=0.37$, $\gamma=1.39$) exhibited by other FM manganites with near-neighbor interactions.[13] A mean-field-like interaction is likely to be operative in inhomogeneous systems such as NSMO 0.5 with correlated COO clusters larger than the lattice parameter.

The ΔS_{max} observed for single crystal NSMO 0.5 around T_{CO} is about 2.5 times higher than for Gd,[14] a prototype MCE material. The direct measurement of the field induced temperature change gives $\Delta T_{max}=-1.39$ K ($\Delta H=1$ T) across T_{CO}, a little smaller than the ~ 2.7 K observed for Gd for the same ΔH.[15] This is attributed to the larger heat capacity of manganites that has a moderating effect on the field induced temperature change.[16] It has been suggested[17] that the MCE efficiency of manganites may be increased by adopting a refrigeration cycle that removes the lattice and electronic heat loads with a regenerator as proposed by Brown.[18] While this may, in principle, be possible for FM metallic manganites, its relevance to charge ordered manganites is an open question because of the strong interplay among various degrees of freedom. It must further be kept in mind that the charge ordering state "melts" under a strong magnetic field [

~ 7 T for NSMO 0.5 (Ref. 19)]. Thus, although single crystalline NSMO 0.5 is a reasonable choice of an active magnetic refrigerant around 150 K, maximum efficiency is achievable only at low magnetic fields.

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