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Anomalous magnetic field dependence of magnetocaloric effect at low temperature in $Pr_{0.52}Sr_{0.48}MnO_3$ single crystal

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We report the magnetocaloric effect (MCE) in a $Pr_{0.52}Sr_{0.48}MnO_3$ single crystal. A peak in the temperature dependence of magnetic entropy change (ΔS_M) with a fairly large negative value ($\approx$3.8 J/kg K) is observed at 275 K close to Curie temperature. MCE is spread over a wide temperature range resulting in a considerable refrigerant capacity ($\approx$293 J/kg). At low temperature the sign of ΔS_M changes, below which anomalous field dependence of ΔS_M is observed indicating the coexistence of ferromagnetic and antiferromagnetic interactions. Interplay between the interactions is strongly influenced by direction and magnitude of applied magnetic field in the ordered state. © *2010 American Institute of Physics*. [doi:10.1063/1.3340524]

Magnetic refrigeration based on the magnetocaloric effect (MCE) attracts considerable attention due to its potential advantage of environmental friendliness over gas refrigeration. MCE is a magnetothermodynamic phenomenon, in which a reversible change in temperature of a suitable material is caused by exposing the material to a change in magnetic field. The magnetic refrigeration technique based on large MCE has been recognized as a promising alternative to the conventional gas refrigeration.[1,2] Mostly, rare earth materials and their alloys show excellent magnetocaloric properties because of their strong magnetic anisotropy and large magnetic moment.[3] However, MCE has also been extensively investigated in manganites with the perovskite structure reviewed by Phan and Yu.[4] The low cost of preparation, higher chemical stability, high electrical resistivity with low eddy current, and large magnetic anisotropy of manganites are promising for the applications.

In addition to the technological applications, investigations on the MCE are fascinating for probing different issues of magnetism in varieties of systems including manganites with the perovskite structure.[5–10] A signature of nanoscale phase separation associated with large MCE was suggested in $Sm_{1-x}Sr_xMnO_3$.[5] The comparative studies of the influence of first and second order transitions on the MCE have been demonstrated in charge ordered $Pr_{0.5}Sr_{0.5}MnO_3$.[6,7] Anomalous thermal expansion at the Curie temperature was involved with the large MCE in $La_{1-x}Ca_xMnO_3$.[8] Whereas the effect of self-doping in $La_{0.87}MnO_3$ was attributed to the large MCE.[9] The MCE has been shown to be a useful tool for understanding the thermal evolution of spin and lattice degrees of freedom and the coupling between them in $Nd_{0.7}Sr_{0.3}MnO_3$.[10] In this communication, we demonstrate that field dependence of magnetic entropy change can be used as a probe for investigating competing magnetic interactions in the ordered state. Although macroscopic observations by magnetization curves as well as temperature dependence of resistivity exhibit the typical manifestation of a ferromagnetic (FM) metallic ground state, magnetic entropy changes as a function of temperature and magnetic field, applied along parallel ($\parallel$) and perpendicular ($\perp$) directions to the (110) plane of *Pbnm* symmetry in $Pr_{0.48}Sr_{0.52}MnO_3$, display the coexisting FM and anti-FM (AFM) interactions in the ordered state. The interplay between these interactions is found to be strongly dependent on the temperature as well as direction and magnitude of the applied magnetic field.

A single crystal of $Pr_{0.48}Sr_{0.52}MnO_3$ was fabricated using the floating zone technique. Composition of the single crystal was confirmed with energy dispersive spectroscopy analysis by a field emission scanning electron microscope (model: JSM-6700F) where the average Pr:Sr concentration ratio was found to be 51.9:48.1. A crystal structure of composition, $Pr_{0.48}Sr_{0.52}MnO_3$ with *Pbnm* space group is confirmed by Rietveld analysis of the diffraction pattern at room temperature. Magnetoresistance (MR) is defined as $[\rho(H)-\rho(0)]/\rho(0)$, where $\rho(H)$ and $\rho(0)$ are the resistivity (ρ) in a static field (H) and zero field, respectively. MR was measured in a commercial cryogen-free high-field system (Cryogenic Ltd., U.K.). Magnetization was measured in a commercial SQUID magnetometer (Quantum Design).

Temperature (T) dependence of magnetization measured at 100 Oe is shown in Fig. 1(a) where magnetic field was applied $\parallel$ and $\perp$ to (110) plane of the *Pbnm* symmetry. A considerable deviation between $\parallel$ and $\perp$ components of magnetization is observed below $\sim$295 K. The temperature derivative of $\parallel$ and $\perp$ components of magnetization typically provides the Curie temperature (T_C) which is $\sim$277 K in the present observation. Temperature dependence of ρ exhibits an anomaly around T_C where maximum MR is observed in the temperature dependence. Resistivity measured in field does not change with different directions of the applied magnetic field. The MR-H curves at 280 and 300 K are shown in the inset of Fig. 1(b) where 33% of MR at 50 kOe is noticed at 280 K close to T_C. Magnetization and MR results as a

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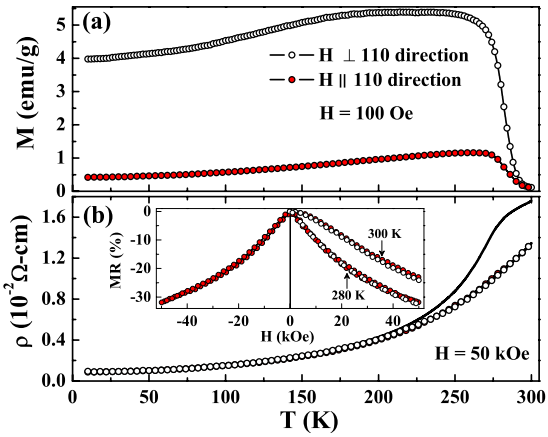

FIG. 1. (Color online) (a) Temperature (T) dependence of magnetization in field, $H=100$ Oe applied ∥ and ⊥ to (110) plane. (b) T dependence of ρ measured in zero field and field. Inset shows the MR curve at 280 and 300 K measured in field along ∥ and ⊥ directions.

function of temperature and magnetic field are in accordance with the results reported in the single crystal with composition $Pr_{0.52}Sr_{0.48}MnO_3$.[11,12]

In order to investigate MCE, magnetization (M-H) curves in the range 0–50 kOe were recorded in between 10 to 320 K. Figures 2(a) and 2(b) exhibit the M-H plots at selective temperatures. We note the drastic change in the initial magnetization curve close to T_C which indicates the large change in magnetic entropy (ΔS_M) around this temperature range. ΔS_M at a particular temperature can be estimated unambiguously using Maxwell relation given by

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \quad (1)$$

Representatives of $-\Delta S_M$ for a change in field (ΔH) from 0 to 10 kOe and 50 kOe are shown as a function of T in Fig. 2(c) where a peak in $-\Delta S_M$ is observed at 275 K close to T_C. We note symmetric distribution of ΔS_M with temperature around the peak which is typically observed for the single crystal. This is promising for an Ericsson-cycle magnetic refrigerator. The value of $-\Delta S_M$ is ≈3.8 J/kg K at 275 K with $\Delta H=50$ kOe. We further note that the magnitude of refrigerant capacity is 293 J/kg which is significantly large compared to other manganites.[4] The values of MCE are nearly the same in the range 250 K$\leq T \leq$320 K for the measurement at 50 kOe applied ∥ and ⊥ to (110) plane of the *Pbnm* symmetry. The value of the ∥ component is less than the ⊥ component below 250 K. A change in sign of ΔS_M or inverse MCE (IMCE) is noticed in the ∥ component around ~140 K with a minimum ($\Delta S_M \approx 0.3$ J/kg K) at 80 K which is also observed in the ⊥ component, although IMCE for the ⊥ component is much smaller than the ∥ component. At low field ($\Delta H=10$ kOe), MCE deviates from each other below T_C. The IMCE of the ∥ component is observed below ~200 K for $\Delta H=10$ kOe. Thus, the temperature at which the sign of MCE changes, can be tuned by controlling the magnitude as well as directions of the applied magnetic field which are highlighted in the inset of Fig. 2(c). The coexistence of MCE and IMCE was reported in varieties of materials where different origins have been proposed to interpret IMCE.[13–15] The giant IMCE was reported in FM Ni–Mn–Sn alloys which was involved with the martensitic phase transformation.[13] The change in sign of MCE was associated with the first-order field-induced metamagnetic transition from AFM to FM states at/below the Néel temperature.[14] Particle size dependent control of FM/AFM phase fraction and degrees of MCE/IMCE has been reported in nanocrystalline, $La_{0.125}Ca_{0.875}MnO_3$.[15] The MCE and IMCE associated with the coexistence of FM/AFM phases was reported in hole doped $Pr_{1-x}Ca_xMnO_3$.[16,17]

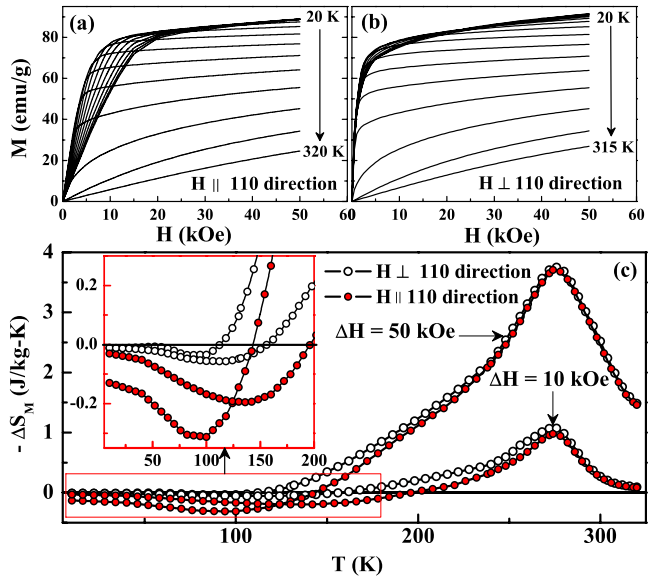

FIG. 2. (Color online) Magnetization curves at selective temperatures when field was applied (a) ∥ and (b) ⊥ to (110) plane of *Pbnm* symmetry. (c) Magnetic entropy change ($-\Delta S_M$) with temperature due to the change in field with $\Delta H=10$ and 50 kOe. Inset highlights the temperature region showing IMCE.

The study on the field dependence of $-\Delta S_M$ has been investigated either experimentally,[18–20] or theoretically using a mean-field approach.[21] According to mean-field approximation ΔS_M can be expressed as $\Delta S_M \propto H^n$, where the exponent, $n=2/3$ at T_C. Magnetic field dependences of $-\Delta S_M$ estimated at selective temperatures are shown in Figs. 3(a)–3(d), displaying varieties of features. At 275 K field dependence of $-\Delta S_M$ satisfactorily fits the above relation with $n=0.81$ and 0.76 for the ∥ and ⊥ components, respectively. The values of n are close to the value considering mean-field approximation where minor deviation from the mean-field value suggests that the measured temperature at 275 K slightly differs from the actual T_C. Magnetic field dependence of $-\Delta S_M$ exhibits anomalous field dependence both for the ∥ and ⊥ components at 140 K [Fig. 3(b)], around which the sign of $-\Delta S_M$∥ changes in the temperature dependence for $\Delta H=50$ kOe. Both the components show positive ΔS_M in the low-field region which increases in magnitude with field. The field dependence of $-\Delta S_M$ exhibits a dip at a certain field, above which the magnitude of ΔS_M decreases. A change of sign in $-\Delta S_M$ is noticed above a certain field for the ⊥ component while for the ∥ component it follows the similar trend. Magnetic field dependence of $-\Delta S_M$ at 100 K is displayed in Fig. 3(c) where a dip in $-\Delta S_M$ is observed in the T dependence for the ∥ component at $\Delta H=50$ kOe. The

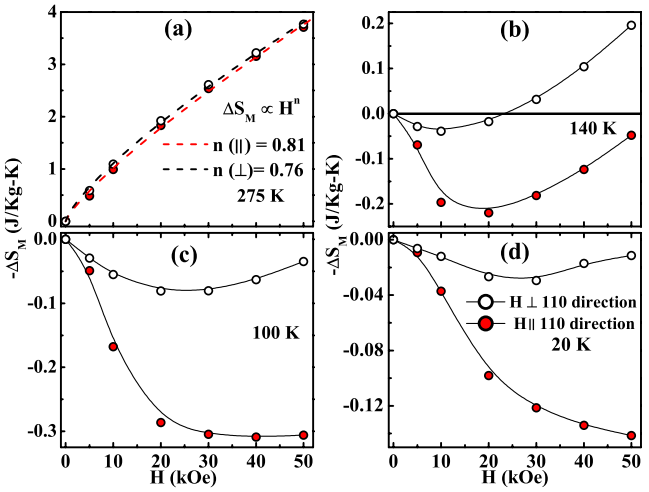

FIG. 3. (Color online) Field dependence of magnetic entropy change ($-\Delta S_M$) at (a) 275 K, (b) 140 K, (c) 100 K, and (d) 20 K. Continuous curves serve to guide the eye. The broken curves in (a) show the fits using equation, $\Delta S_M \propto H^n$.

$\perp$ component of $-\Delta S_M$ exhibits similar field dependence at 140 K, displaying a dip in the field dependence. Whereas the magnitude of the $\parallel$ component increases and shows a saturating trend for $H \geq 30$ kOe. Field dependent results at 20 K are displayed in Fig. 3(d) where the $\perp$ component shows similar field dependence at 100 and 140 K. The magnitude of the $\parallel$ component increases with field and it does not show any saturating trend even at 50 kOe. The T and H dependences of $-\Delta S_M$ reveal consistent behavior for both the $\parallel$ and $\perp$ components where MCE is strongly influenced by the magnetocrystalline anisotropy. In accordance with the previous reports in manganites,[15–17] the positive value of ΔS_M is involved with the AFM interaction and negative ΔS_M is attributed to the FM interaction.[20] Just below T_C strong FM interaction is dominant whereas low temperature behavior is governed by the interplay between FM and AFM interactions. We note that appearance of AFM interaction in the ordered state depends on the magnitude and direction of H which is observed here below the temperature range 140–200 K, around which the FM to AFM transition was reported in the single crystal with a slightly different composition, $Pr_{0.5}Sr_{0.5}MnO_3$.[12,22,23]

The single crystals of $Pr_{1-x}Sr_xMnO_3$ in a narrow compositional range $0.48 \leq x \leq 0.57$ exist close to the boundary between *Pbnm* and *I*4/*mcm* type perovskite structures at room temperature. The macroscopic cooperative distortions associated with tilting as well as local deformations of the MnO_6 octahedra and the Mn^{4+} content in between 48%–57% for $0.48 \leq x \leq 0.57$ lead to the considerable variation in magnetic ground states and transport mechanism.[12] The end compound with composition $x=0.48$ undergoes a paramagnetic to FM transition associated with the structural change around T_C from *Pbnm* to *I*4/*mcm*. The tetragonal *I*4/*mcm* symmetry of the FM ground state in $x=0.48$ exhibits a different distribution of Mn–O–Mn bonds unlike more common orthoperovskites, $R_{1-x}Ca_xMnO_3$ (R=rare earths) (Ref. 24) where one Mn–O–Mn bond angle is 180° and two others are close to 165°.[12] In the present observation $\rho(T)$ and *M*-*H* at low temperature typically exhibit the FM metallic ground state in accordance with the proposed *I*4/*mcm* ferromagnet.[12] It is important to note that the FM ground state with *I*4/*mcm* symmetry proposed in $Pr_{0.52}Sr_{0.48}MnO_3$ is quite unstable which can be transformed to the A-type AFM ground state with orthorhombic *Fmmm* symmetry either by minor chemical[12,25] or external pressures.[26] The characteristic feature of this magnetic state is an apical contraction of MnO_6 octahedra along the orthorhombic a axis due to the $d[y^2-z^2]$ e_g orbital polarization in *Fmmm* axes notation which results in the dominant FM double exchange interaction in the bc planes and AFM superexchange interactions along the a axis. Here, we further note the coexistence of FM and AFM interactions through the field dependence of the MCE where degrees of both the interactions are strongly influenced by the direction and magnitude of applied magnetic field at low temperature. The coexisting interactions are clearly evident from the magnetic field dependence of $-\Delta S_M$ in the ordered state.

In conclusion, a significant negative entropy change ($\approx$3.8 J/kg K) associated with the considerably large refrigerant capacity (293 J/kg) is observed close to T_C. In the ordered state signature of coexisting FM and AFM interactions is evidenced through the anomalous field dependence of ΔS_M where interplay between the interactions is strongly influenced by the direction and magnitude of the applied magnetic field. In this communication, we display that field dependence of magnetic entropy can be a useful probe for investigating competing FM and AFM interactions.

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