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# Hydrostatic pressure effect on the spin reorientation transition of ferromagnetic $Sm_{0.7-x}La_xSr_{0.3}MnO_3$ (x = 0, 0.1) polycrystals [HPSTAR]

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The hydrostatic pressure effect on the resistivity and magnetization of the narrow band gap manganite  $Sm_{0.7-x}La_xSr_{0.3}MnO_3$  (x = 0, 0.1) systems has been investigated. At ambient pressure measurements, the parent compound Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> showed a ferromagnetic-insulating nature, whereas the 10% La-doped compound Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> showed a ferromagnetic-metallic nature. Furthermore, both samples showed a spin-reorientation transition  $(T_{SR})$  below Curie temperature, which originated from the Mn sublattice and was supported by an antiferromagnetic Sm(4f)-Mn(3d) interaction. Both samples exhibited a normal and inverse magnetocaloric effect as a result of these two different magnetic transitions. Magnetization measurements on Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> under pressure did not show an appreciable change in the Curie temperature, but enhanced  $T_{SR}$ , whereas an insulator-metallic transition was observed during resistivity measurements under pressure. On the other hand, for  $Sm_{0.6}La_{0.1}Sr_{0.3}MnO_3$ ,  $T_C$  increased and  $T_{SR}$  reduced upon the application of pressure. The metallic nature which is observed at ambient pressure resistivity measurement was further enhanced with 97% of piezoresistance. The pressure did not change the normal magnetocaloric effect of Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>, but increased it in Sm<sub>0.6</sub>La<sub>0.1</sub>  $Sr_{0.3}MnO_3$ . However, there was not much change in the inverse magnetocaloric effect of both compounds. These studies were analyzed based on the pressure effect on the activation energy and scattering interaction factors. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4984204]

## INTRODUCTION

Mixed valent manganites, with a formula of  $R_{1-x}A_xMnO_3$ (R: Rare-earth elements; A-Alkaline metals), exhibit a broad range of functional properties through the coupling between their structural, transport, and magnetic properties,<sup>1</sup> such as colossal magnetoresistance (CMR), charge-orbital ordering (COO), magnetocaloric effect (MCE), paramagnetic (PM)-ferromagnetic (FM) transition, insulator-metal (IM) transition, and so on. Out of these, the interplay between the transport and magnetic properties is one of the most salient phenomena in the manganites, where the IM transition is simultaneously accompanied by a PM-FM transition.<sup>2-4</sup> In the spin disordered paramagnetic state, Jahn-Teller distortion causes the selflocalization of charge carriers in the form of polarons, which leads to the insulating behavior of resistivity  $(\rho)$ .<sup>5,6</sup> Below  $T_C$ , FM alignment of the  $t_{2g}$  spins (where spin is conserved during electron hopping) lowers  $\rho$  by a reduction in the scattering rate and leads to a metallic nature.<sup>5,6</sup> In the case of  $T_N$ , the AFM alignment of the  $t_{2g}$  spins increases resistivity and leads to an insulating nature. This is a common phenomenon in wide bandwidth manganites. In narrow bandwidth manganites,<sup>7,8</sup> the insulating state persists even below  $T_C$  due to several competitive interactions with comparable strength, but there are only very few works on the origin of effect.<sup>2,9,10</sup> So far, two possible mechanisms have been proposed for the coexistence of a FM with an insulating nature: (i) in the majority of the samples, the FM phase has no percolation paths for the minority conducting phase<sup>11</sup> and (ii)  $e_g$  orbital ordering occurs through the FM super-exchange interaction above  $T_C$ .<sup>12,13</sup>

One of the prototypical narrowband manganites,  $Sm_{0.7}Sr_{0.3}MnO_3$ , exhibits a first-order FM under ambient conditions and insulating behavior below  $T_C$  due to the competition between the AFM super-exchange interaction of the  $t_{2g}$  spins and the FM double exchange interaction of the  $e_g$  holes.<sup>14–16</sup> The doping of 10% La at the Sm site ( $Sm_{0.6}La_{0.1}$   $Sr_{0.3}MnO_3$ ) increases the  $e_g$  electron bandwidth and decreases the electron-phonon coupling, inducing a second-order FM with metallic nature. The low temperature ground state of  $Sm_{0.7-x}La_xSr_{0.3}MnO_3$  (x = 0, 0.1) polycrystals is that of a metallic ferromagnet. Thus, a compositionally driven IM transition has been attained by La doping in these  $Sm_{0.7-x}La_xSr_{0.3}MnO_3$  (x = 0, 0.1) samples is the appearance of a cusp in the temperature dependent of magnetization

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[M(T)] much below the FM transition, which is termed a spin-reorientation transition (SRT). A similar kind of cusplike transition in M(T) below  $T_C$  was observed earlier in the  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  series for x = 0.3-0.5.<sup>17,18,22,23</sup> Aparnadevi et al., detected SRT through ac electrical transport measurements and suggested that the competition between the magnetocrystalline anisotropy of the Mn lattice, single ion anisotropy of the Sm<sup>3+</sup> ion, and the Sm-4*f*-Mn-3*d* ferromagnetic interaction caused a change in the direction of the easy Mn sublattice axis.<sup>24,25</sup> Hence, the spin-flop transition was observed in the magnetization curves, which indicates the reorientation of the Mn<sup>3+</sup> moments along with the ferromagnetic ordering of these samples. The hydrostatic pressure (P)effect on Sm<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>-doped systems had been previously reported.<sup>26–31</sup> Generally in these systems,  $T_C$  increases and width of the thermal hysteresis in magnetization decreases rapidly with increasing pressure. Above a critical value of P, the hysteresis disappeared completely and the transition becomes second-order.

By experiencing two magnetic transitions such as FM and SRT, Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> and Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> samples have both a normal and inverse MCE.<sup>25</sup> Generally, cooling by an adiabatic demagnetization cycle is termed a normal MCE, while cooling with adiabatic magnetization is termed an inverse MCE.<sup>32</sup> Thus, both processes can obtain cooling in these systems and these materials are considered to have potential for magnetic refrigeration.<sup>20,21,33–35</sup> In the same paper, it was reported that the value of the MCE around the FM transition was increased by La doping, whereas there was no change in the SRT.<sup>25</sup> P is also a fundamental thermodynamic variable, which can influence the electrical conducting properties as well as the interaction responsible for FM.<sup>36–40</sup> Here, we carried out magnetization and resistivity measurements on  $Sm_{0.7-x}La_xSr_{0.3}MnO_3$  (x = 0, 0.1) samples under different hydrostatic pressures. Although it changed the properties of both samples systematically, they were unusual and different by some nature. We observed that P enhanced the SRT transitions in pure  $Sm_0 _7Sr_0 _3MnO_3$ but suppressed them in the La-doped compound; thus, the MCE was also affected simultaneously. The pure Sm<sub>0.7-x</sub>La<sub>x</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> experienced an IM transition, whereas the metallic nature of the La-doped compound was further enhanced. This result is discussed by studying the activation energy and piezoresistance under pressure.

#### **EXPERIMENTAL DETAILS**

Polycrystalline samples of  $Sm_{0.3}Sr_{0.7}MnO_3$  and  $Sm_{0.6}La_{0.1}Sr_{0.3}MnO_3$  were prepared by a standard solid-state reaction method. For details of the sample preparation and characterization, see Aparnadevi *et al.*<sup>24,25</sup> Magnetization measurements under ambient and pressure conditions were performed using a PPMS-VSM (Quantum Design, USA). A clamp-type miniature hydrostatic pressure cell (MCell-10, EasyLab, UK) made of a nonmagnetic Cu-Be alloy was used for the high-pressure magnetization measurements. A mixture of flourinert #70 and flourinert #77 was used as a pressure-transmitting medium. The value of pressure was estimated from the shift of the superconducting transition

temperature of pure Sn with applied pressure.<sup>41</sup> The M(T)was recorded for cooling and warming cycles with an applied field  $(\mu_0.H)$  of 0.1 T in the temperature range of 300–2 K under various P up to  $\sim$ 1 GPa. Magnetization as a function of the magnetic field [M(H)] was recorded up to a field of 5 T for various P. The  $T_C$  was determined from the inflection point of the derivative (dM/dT) plot. Since the low-temperature cusp was broad,  $T_{SR}$  was taken when magnetization reached the maximum value. The temperature dependence of electrical resistivity  $[\rho(T)]$  at ambient and high pressure was measured by a conventional four-probe method using a closed cycle refrigerator variable temperature insert (CCR-VTI) set-up and a self-clamp type hybrid hydrostatic pressure cell. The pressure was calibrated using the resistive transitions of Bi I-II (2.55 GPa) and Bi II-III (2.7 GPa)<sup>42</sup> The IM transition temperature  $(T_{IM})$  of the samples was estimated from the peak point of the  $\rho(T)$  plots.

# RESULTS

# $Sm_{0.7}Sr_{0.3}MnO_3$

Figure 1 shows the  $\rho(T)$  of Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> under various pressures up to 2.63 GPa. At ambient P, the resistivity sharply increased below 80 K, indicating its insulating nature. At 0.79 GPa, there is a small hump at 69 K with a slight reduction in the magnitude, i.e., the sample tends towards a metallic nature. However, resistivity increased sharply again. Upon further application of P, the resistivity began to drop down at 53 K for 1.90 GPa. Thus, an IM transition in this system was identified by the negative of slope of  $d\rho/dT$  (< 0) under P. The slope of  $\rho(T)$  fell more with the application of P, showing an IM transition at 70 K for 2.63 GPa. Generally, high-temperature region resistivity arises from polaronic interactions. To understand the role of pressure in the polarons in the high-temperature regime, the polaronic activation energy  $(E_a)$  was calculated for various pressures using the small polaronic hopping model equation<sup>43</sup>

$$\rho(T) = AT \exp(E_g/k_B T). \tag{1}$$



FIG. 1. Temperature dependence of resistivity of  $Sm_{0.7}Sr_{0.3}MnO_3$  under various hydrostatic pressures up to 2.63 GPa [inset: Estimated activation energy ( $E_a$ ) as a function of pressure].

TABLE I. Values of the coefficients obtained by fitting of  $\rho(T)$  data in the power function [Eq. (2)] below the transition for Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>.

P (GPa)	$\rho_2 (\Omega. \text{ Cm. } \text{K}^2)$	$\rho_{\beta}$ ( $\Omega$ . Cm. K <sup>3</sup> )	$ ρ_{4.5} $ (Ω. Cm. K <sup>4.5</sup> )	$\rho_5 (\Omega. \text{ Cm. } \text{K}^5)$
1.90	11265	200	0.37903	0.02721
2.63	20	0.33258	$5.35e^{-4}$	$3.60e^{-5}$

The pressure reduced  $E_g$  in the high-temperature regime [inset of Fig. 1], suggesting the enhancement of a metallic nature in the Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> system.

As Fig. 1 shows, the  $\rho(T)$  of Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> exhibited an IM transition at a pressure of 1.9 and 2.63 GPa. In the low-temperature region, the resistivity of the metallic phase was approximated by an expression that includes some scattering mechanisms:

$$\rho(T) = \rho_0 + \rho_2 T^2 + \rho_3 T^3 + \rho_{4.5} T^{4.5} + \rho_5 T^5, \qquad (2)$$

where  $\rho_0$  is the temperature-independent residual resistivity,  $\rho_2 T^2$  is the resistivity associated with electron–electron scattering,  $\rho_3 T^3$  is the other scattering mechanisms caused by one-magnon,  $\rho_{4.5} T^{4.5}$  is associated with the electron–magnon scattering processes due to spin waves, and  $\rho_5 T^5$  describes the electron-phonon interaction scatterings.<sup>44,45</sup> Since this equation is only valid for the metallic ground state, it is not possible to estimate the coefficients for the set data 0 and 0.79 GPa. Hence, the  $\rho(T)$  of the 1.9 and 2.63 GPa pressure data was fitted with the above power function and the values of their scattering factors are given in Table I. Here, the magnitude of all coefficients decreased with increasing pressure from 1.9 to 2.63 GPa. We infer from the table that the values of all the coefficients decreased upon the application of *P*.

As the IM transition in the manganites was accompanied by a FM-to-PM phase transition, we investigated the temperature dependence of magnetization. Figure 2(a) shows the M(T) of Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> under a magnetic field ( $\mu_0$ .H) of 0.1 T for various P up to 0.75 GPa. At ambient pressure, the sample showed a cusp at 29 K ( $T_{SR}$ ) by the SRT and a PM-FM transition ( $T_C$ ) at 79 K. Both the transitions well agreed with reported data.<sup>24,25</sup> However, there was no anomaly in the dc-resistivity measurements corresponding to the spin-reorientation transition. The application of pressure reduced the magnitude of magnetization around the SRT transition [inset of Fig. 2(a)] but only broadened the PM-FM transition. The estimated values of  $T_{SR}$  and  $T_C$  are shown in Fig. 2(b) as a function of *P*.  $T_{SR}$  increased at a rate of 3.94 K/GPa without an appreciable change in the  $T_C$ .

Isothermal magnetizations [M(H)] of Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> were measured under various pressures in both the increasing (0-5 T) and decreasing (5-0 T) field modes from 2 K to 200 K at a temperature interval of 6 K. For clarity, the M(H)curves of selected temperatures are shown in Figs. 3(a)-3(d)under P of 0, 0.20, 0.54, and 0.75 GPa, respectively. Above  $T_C$  (~80 K), the M(H) curves showed straight lines, which indicated PM transition behavior. Below  $T_C$  (~80 K), the FM curves showed a FM nature (as expected). Further, the M(H) plots shifted upwards as temperature decreased from 192 K to 24 K, due to the increased magnitude of magnetization with the temperature decrement. However, a peculiar behavior was observed in the M(H) in all pressure ranges below 24 K, i.e., the M(H) of 2 K fall below the M(H) of 24 K and this behavior continued for all pressures, it is attributed to the spin reorientation transition. However, the application of external field maintains the FM nature below  $T_C$ , and does not affect the spin reorientation phase transition. This was due to the reduced magnitude of the magnetization in the M(T) measurements [Fig. 1(a)] below  $T_{SR}$  due to the SRT in the low-temperature region. Further, hysteresis was found in the M(H) of the low-temperature regions, suggesting the presence of a first-order transition. There was no indication of S-type behavior in any M(H) under either temperature or pressure points, suggesting the absence of a fieldinduced metamagnetic transition. Commonly, S-type Field induced Meta magnetic transition (FIMMT) might be raised by an antiferromagnetic ground state at low temperature. Hence, we confirmed that the reduction of magnetization below the cusp did not consist of an AFM nature and was only due to the SRT. On the other hand, the application of P increased the hysteresis width up to 0.75 GPa; hence, it stabilized the first-order transition. Since first-order transitions are associated with structural phase transitions, it is expected that pressure may also increase the magnetocaloric effect in  $Sm_{0.7}Sr_{0.3}MnO_3$ .

Materials exhibiting a first-order transition may show a large MCE, which is the measured value of magnetic refrigeration technology. Thus, the magnetic entropy change  $(\Delta S_m)$  as a function of temperature, using the M(H) data set under all the pressures, is evaluated using the Maxwell relation,



FIG. 2. (a) Temperature dependence of magnetization for  $\text{Sm}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  under a magnetic field of 0.1 T for various pressures up to 0.75 GPa [Inset: Enlarged view of the spin-reorientation transition in the low-temperature region for various hydrostatic pressures]; (b) Pressure dependence of  $T_{SR}$  (left axis) and  $T_C$  (right axis) of Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>.



FIG. 3. Magnetic field dependence of magnetization for  $Sm_{0.7}Sr_{0.3}MnO_3$  under various pressures; (a) 0 GPa, (b) 0.2 GPa, (c) 0.54 GPa, and (d) 0.75 GPa.

$$\Delta S_m = \int_0^H \left(\frac{\partial M}{\partial H}\right) dH.$$
 (3)

Figure 4(a) shows the  $-\Delta S_m(T)$  for various pressures for the magnetic field difference  $(\Delta \mu_0 H)$  of 1 and 5 T. The sign in  $\Delta S_m$  is determined from  $\partial M/\partial H$ ; hence, the negative and positive signs in the  $\Delta S_m$  are an indication of a normal MCE and an inverse MCE, respectively. As expected,  $-\Delta S_m$ increased with lowering temperature in the PM state and reached a maximum value around  $T_C$ , before it decreased below  $T_C$ . The pressure dependence of the maximum value of the normal MCE for  $\Delta \mu_0 H$  of 1 and 5 T is shown on the left axis of Fig. 4(b). The magnitude of  $-\Delta S_m(T)$  at the peak of  $T_C$  is almost equal (-0.9 J kg<sup>-1</sup> K<sup>-1</sup> for  $\Delta \mu_0 H$  of 1 T and  $-3.35 \text{ J kg}^{-1} \text{ K}^{-1}$  for 5 T) even with the application of P, i.e., there was no appreciable change in it under P, as magnetization at the FM transition does not change with P. Much below the FM transition, the sign of  $-\Delta S_m(T)$  changed from negative to positive at  $T_{SR}$ , which shows an inverse magnetocaloric effect. A horizontal dashed line at  $\Delta S_m = 0$  in Fig.



4(a) separates the normal MCE and the inverse MCE. The application of *P* increased the  $\Delta S_m$  very slightly below  $T_{SR}$ , since magnetization decreased under *P*.

Further, wide temperature transition materials might have high relative cooling power (RCP), which is also highly preferable for practical applications. RCP is nothing but a measure of the heat transfer amount between the hot and cold sinks during one ideal refrigeration cycle. We estimated it under various pressures for  $\Delta \mu_0$ .*H* of 1 and 5 T using the equation

$$RCP = \Delta S_{max}^m X \, \delta T_{FWHM}. \tag{4}$$

The right axis of Fig. 4(b) shows the pressure dependence of the RCP for  $\Delta\mu_0.H$  of 1 and 5 T. The RCP for  $\Delta\mu_0.H$  of 5 T increased with pressure, due to the FM transition temperature range (simultaneously  $\delta T_{FWHM}$ ) widening under pressure. There was no change in the inverse MCE of this compound, since the low-temperature shape of the cusp was retained under pressure.

FIG. 4. (a) Temperature dependence of  $-\Delta S_m$  of Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> for various pressures up to 0.75 GPa for  $\Delta \mu_0.H$  of 1 T (closed symbols) and 5 T (open symbols). The horizontal line separates the normal and inverse MCE below and above  $T_{SR}$ , respectively. (b) Pressure dependence of the normal MCE (left axis – black closed symbols) and RCP (right axis – blue open symbols) of Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> for  $\Delta \mu_0.H$  of 1 and 5 T.

## Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>

As discussed, 10% La-doping at the Sm site of Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> exhibits a paramagnetic insulator-to-ferromagnetic metallic transition even at ambient pressure, with a transition temperature of 95 K.<sup>24,25</sup> Here, we carried out resistivity and magnetization measurements under P on Sm<sub>0.6</sub>La<sub>0.01</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>. The main panel of Fig. 5(a) shows the  $\rho(T)$  of Sm<sub>0.67</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> under various P up to 2.63 GPa. At ambient P, the  $\rho(T)$  showed a peak at 90 K, corresponding to the IM transition, which is almost nearer to  $T_C$ of this sample. The application of pressure increased  $T_{IM}$  at a rate  $(dT_{IM}/dP)$  of 9.34 K/GPa [Fig. 5(a) inset, left axis] with a drastic reduction in resistivity [Fig. 5(a) inset, right axis]. The reduction in the magnitude of the resistivity by the pressure resistivity was analyzed through the estimation of Piezoresistance (PR) using the following relation:  $-PR = \{ [\rho(P) - \rho(0)] / \rho(0) \} * 100\%$ . This is plotted with the pressure in Fig. 5(b-left axis). The negative sign in this equation suggested a reduction of resistivity with pressure. The maximum -PR (~97%) was observed at  $T_{IM}$  for P = 2.63 GPa. Similar to the Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>, the La-doped compound also showed a reduction in the slopes of resistivity below and above transition region. Hence, it was necessary to study the effect of pressure on the high-temperature activation energy  $(E_{g})$  through a small polaronic hopping model and low-temperature scattering factors through the scattering mechanism expression. The estimated values of  $E_{a}$ in the high-temperature region under pressure are plotted as the right axis of Fig. 5(b). At ambient P, the value of  $E_{g}$  is 80 meV, which is approximately closer to the values reported for the  $\text{Sm}_{0.52}\text{Sr}_{0.48}\text{MnO}_3$  system (100 meV).<sup>28</sup> The  $E_g$ decreased monotonically as P increased and reduced to almost zero at P = 2.63 GPa. This implies that the applied P suppressed the formation of the Jahn-Teller polarons in the high-temperature regime and enhanced the metallic nature of the Sm<sub>0.67</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> system. For the low-temperature region, scattering factors such  $\rho_2$ ,  $\rho_3$ ,  $\rho_{4.5}$ , and  $\rho_5$  were estimated from each pressure data using the equation, and the results are given in Table II. All the factors were reduced by pressure, suggesting that the scattering by various interactions was reduced and thus, the resistivity decreased appreciably to induce a negative piezoresistance of 97%.

TABLE II. Values of the coefficients obtained by fitting of  $\rho(T)$  data in the power function [Eq. (2)] below the transition for Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>.

P (GPa)	$\rho_2$ ( $\Omega$ . Cm. K <sup>2</sup> )	$\rho_3$ ( $\Omega$ . Cm. K <sup>3</sup> )	$ \rho_{4.5} \times 10^{-5} $ ( $\Omega$ . Cm. K <sup>4.5</sup> )	$\rho_5 \times 10^{-6}$ ( $\Omega$ . Cm. K <sup>5</sup> )
0	263.2	3.225	340.0	199.0
0.79	108.7	3.120	85.9	42.0
1.9	53.4	3.465	4.35	2.53
2.43	44.1	0.633	2.54	1.27
2.63	38.6	0.387	2.27	1.07

The M(T) for Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> at a  $\mu_0.H$  of 0.1 T for various P up to 0.95 GPa is shown in Fig. 6. At ambient pressure, this sample showed a PM-FM transition  $(T_C)$  at 96 K, which is analogous to the  $T_{IM}$  during the resistivity measurement. Moreover, this sample also exhibited a low-temperature cusp around 48 K which is but the SRT  $(T_{SR})$ , similar to the parent compound. The application of P shifted the M(T)towards high temperature, which, in turn, increased the  $T_C$  at a rate of 6.24 K/GPa in Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>. Obviously, this value is high compared to the parent compound (3.94 K/GPa). The P broadened the low-temperature SRT transition and flattened it, i.e., the SRT transition may have been completely suppressed by higher P. Hence, this flatness made the FM transition sharpen slightly and reduced the transition temperature width. The M(H) for Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> was also measured under various pressures in both the increasing (0-5T) and decreasing (5-0T) field modes at a temperature interval of 6 K. For clarity, the M(H) curves of selected temperatures are shown in Figs. 7(a)-7(d) under pressures of 0, 0.40, 0.57, and 0.95 GPa, respectively. As expected, M(H) shows PM nature above  $T_C$ , and FM nature below  $T_C$ . The La-doped compound also did not show an S-type FIMMT anywhere either, which confirms the presence of a SRT only (if it was present, the presence of an antiferromagnetic interaction could be suggested). The nature of the M(H) curves at various pressures was similar to the parent compound Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>, except for the absence of a hysteresis effect in the low temperature region, i.e., a pure second-order ferromagnetic transition (without structural phase transition) occurred in this sample. The



FIG. 5. Temperature dependence of resistivity  $\text{Sm}_{0.6}\text{La}_{0.01}\text{Sr}_{0.3}\text{MnO}_3$  under various pressures up to 2.63 GPa; (Inset): Pressure dependence of  $T_{IM}$  (left axis) and  $\rho_{peak}$  (right axis) of  $\text{Sm}_{0.67}\text{La}_{0.1}\text{Sr}_{0.3}\text{MnO}_3$ . (b) Pressure dependence of Piezoresistance (left axis) and activation energy (right axis) of  $\text{Sm}_{0.67}\text{La}_{0.1}\text{Sr}_{0.3}\text{MnO}_3$ .



FIG. 6. Temperature dependence of magnetization for  $Sm_{0.6}La_{0.1}Sr_{0.3}MnO_3$ under various pressures at  $\mu_0.H$  of 0.1 T. Inset: pressure dependence of  $T_C$ .



FIG. 7. Magnetic field dependence of magnetization for  $Sm_{0.6}La_{0.1}Sr_{0.3}MnO_3$  at hydrostatic pressures of (a) 0 GPa, (b) 0.40 GPa, (c) 0.57 GPa, and (d) 0.95 GPa.

critical behavior analysis suggested the presence of long-range ferromagnetism in this compound.<sup>25</sup> As the La-doped compound exhibited ferromagnetic metallic nature in ground state, the saturation magnetization for the La-doped sample (~90  $\text{Am}^2\text{kg}^{-1}$ ) is much higher than that of the parent compound (~60  $\text{Am}^2\text{kg}^{-1}$ ). Moreover, the absence of magnetic hysteresis in the La-doped sample suggests the second order transition. At ambient pressure, M(H) of 2 K up to 2 T falls below M(H)of 24 K. This is due to the SRT below  $T_{SR}$ . Above 2 T, M(H)of 2 K an 24 K merged. Higher magnetic fields (> 2 T) suppress spin-reorientation transition in the Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> sample. During the application of *P*, magnetization in the low temperature region below  $T_{SR}$  does not affect. Hence, the same trend of merging in M(H) for 2 and 24 K above 2 T is continued under all pressures [Fig. 7(b)–7(d)].

The magnetic entropy change  $(-\Delta S_m)$  for  $Sm_{0.67}La_{0.1}Sr_{0.3}MnO_3$ also is estimated using the Maxwell relation [Eq. (3)]. Figure 8(a) shows  $-\Delta S_m$  for various pressures under  $\Delta \mu_0.H$  of 1 and 5 T. As expected, the trend of  $-\Delta S_m$  vs. T for all pressures is the same by having both normal and inverse MCE also around  $T_C$  and  $T_{SR}$ , respectively, as such in a parent compound.

It is clear from the left axis of Fig. 8(b) that *P* increases  $-\Delta S_m^{max}$  for  $\mu_0.\Delta H$  of 1 and 5 T, and this is due to the fact that both pressure and field enhance magnetization, in turn, increase MCE around  $T_C$  in the Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>. But, pressures do not change the magnetization of Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> in *M*(*T*) measurements below  $T_{SR}$ ; hence, no change is observed in the inverse MCE values. While calculating RCP using Eq. (4), RCP decreases slightly by the pressure for 1 and 5 T [Fig. 8(b) right axis]. As discussed above, *P* reduces the temperature width, although it increases the  $\Delta S_m^{max}$ ; hence, RCP is reduced by *P*.

# DISCUSSION

The pressure of 1.90 GPa during resistivity measurements in the parent compound reduced the scattering factors of various interactions and decreased the Mn-O bond length and increased the Mn-O-Mn bond angle. As a result, there was an increase in the Mn-O-Mn orbital overlapping, which leads to a broader bandwidth for the itinerant  $e_g$  electrons. Therefore, the electron transfer integral between  $3d_{x-y}^{2}^{2}$  and  $3d_z^2$  orbital was enhanced through the double exchange (DE) phenomenon in the low-temperature region. In addition, as  $E_{a}$  reduced with pressure, polaron formation was also suppressed in the high-temperature region. Thus, the Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> system exhibited a metallic nature under pressure.<sup>44,45</sup> However, there was no anomaly for the lowtemperature SRT in our resistivity measurements even under ambient conditions and we could not analyze the effect of pressure on it for the parent compound during resistivity measurements. The application of pressure during the magnetization measurements up to 0.75 GPa in Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> did not change any of its properties such as the ferromagnetic transition, spin-reorientation transition and/or first-order nature. As the ionic radius of Sm and Sr differs significantly, the value of quenched disorder is quite large in the Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> system.<sup>2,9,30,48–51</sup> Hence, it will preserve its properties until a large local disorder is introduced, i.e., the pressure of 0.75 GPa during magnetization measurements was not enough to suppress the formation of polarons. Hence, there was no appreciable change in the  $T_C$  and/or its first-order hysteresis nature in the low temperature region. However, the pressure slightly widened the temperature range of M(T) around the FM transition, and the spinreorientation transition appeared to increase slightly [shown by arrow in the Fig. 2(a) inset]. In earlier results,  $T_C$  linearly varied with pressure in similar compounds such as  $Sm_{0.52}Sr_{0.48}MnO_3^{28}$  and  $Sm_{0.55}(Sr_{0.5}Ca_{0.5})_{0.45}MnO_3^{33}$  and this nature suggests that lying of spin in the easy axis of magnetization.<sup>52</sup> However, in the parent compound, there was strong deviation from the linear increase of  $T_C$  with pressure [Fig. 2(b)-left axis], and there was no change in the cusp-shape of the spin-reorientation transition either. These phenomena suggest that a change happened in the spin configuration from the magnetization easy axis and it was retained as such up to  $0.75 \text{ GPa.}^{53}$  As  $T_C$  did not change much in the parent compound, there was also no appreciable change in MCE. Conversely, RCP increased due to the widening of the ferromagnetic transition. The presence of a firstorder nature in the low-temperature cusp suggested by the hysteresis leads to an inverse MCE with appreciable values around the spin-reorientation transition.

The substitution of the larger ionic radius  $La^{3+}$  (1.21 Å) at the smaller  $\text{Sm}^{3+}$  (1.09 Å) increased the bandwidth of Sm<sub>0.7-x</sub>La<sub>x</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>; hence, the DE mechanism enhanced more and highly increased the electron transfer integral between  $3d_{x-y}^{2}$  and  $3d_{z}^{2}$  orbital.<sup>46,47</sup> Thus, the La-doped compound exhibited ferromagnetic metallic nature in ground state. However, the low-temperature spin-reorientation transition was retained in this system. During the application of pressure, the Mn-O bond length increased monotonically and the direction of the easy axis for M changed from within the ab plane to along the easy c-axis.<sup>54,55</sup> Hence, the occupation number of the  $3d_z^2$  further increased easily, while that of the  $3d_{x-v}^{2}$ decreased comparatively. This was also



FIG. 8. (a) Temperature dependence of  $-\Delta S_m$  for Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> for various pressures up to 0.95 GPa for  $\Delta \mu_0.H$  of 1 T (closed symbols) and 5 T (open symbols). The horizontal line separates the normal and inverse MCE below and above  $T_{SR}$ , respectively. (b) Pressure dependence of the  $-\Delta S_m^{max}$  (left axis – black closed symbols) and RCP (right axis – blue open symbols) of Sm<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> for  $\Delta \mu_0.H$  of 1 and 5 T.

experimentally proven by Hao and Wang.<sup>56</sup> Therefore, pressure has the stronger effect and favors the easy c- axis in this sample for magnetization and the change that occurred during the spin-reorientation transition returns it to its easy axis, thus suppressing the spin-reorientation transition in the lowtemperature region. Since  $T_C$  only increased with pressure without a change in the width of the transition, the MCE increased. Conversely, no change in the RCP was observed in the La-doped compound. As discussed, the La-doped compound showed a second-order transition in the low temperature region, and the value of the inverse MCE became lower than that of the parent compound. During resistivity measurements under pressure, the formation of polarons was suppressed in the high-temperature region (T > $T_{IM}$ ) and  $E_g$  was reduced with pressure. In the low-temperature region, the pressure reduced the various interactions in the scattering coefficients. The metallic nature of the La-doped compound was further enhanced with the negative piezoresistance of 97% at 2.63 GPa. The La-doped compound showed a second-order transition in the low-temperature region, and the value of the inverse MCE of this compound became lower than that of the parent compound.

### CONCLUSION

The change in the easy axis of Sm<sub>0.7-x</sub>La<sub>x</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (x = 0, 0.1) showed a spin-reorientation transition below  $T_C$ , which occurred due to the ferrimagnetic interaction between the Sm(4f) and Mn(3d) sublattices. Hence, the spin-flop transition observed in the magnetization curves, which indicates the reorientation of the Mn<sup>3+</sup> moments along with the ferromagnetic ordering of these samples. Hence, both samples contained a normal and inverse magnetocaloric effect by having two different transitions. With the application of pressure, the spin-reorientation transition of the La-doped compound was well influenced by external pressure, whereas there was no change in the parent compound. The pressure favored the easy c- axis of Sm<sub>0.6</sub>La<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> for easy magnetization compared to the parent compound, due to the large difference of the ionic radius. Moreover, pressure induced the IM transition in the parent compound, whereas the metallic nature was more enhanced in the La-doped compound. Hence, this shows a negative piezoresistance of 97% at 2.63 GPa. Pressure did not change the MCE (RCP) of the parent compound (La-doped compound) but increased the MCE (RCP) of La-doped compound (parent compound).The inverse MCE of the parent compound was slightly high by having a first-order nature, whereas it was less for the second-order La-doped compound.

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