Structural, magneto transport and magnetic properties of Ruddlesden–Popper $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_{2}\text{O}_7$ $(0.42 \leq x \leq 0.52)$ layered manganites

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Structural, magneto transport and magnetic properties of Ruddlesden–Popper La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ (0.42 ≤ x ≤ 0.52) layered manganites

Abstract
The magneto transport of Ruddlesden–Popper, La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ (0.42 ≤ x ≤ 0.52), 2-dimensional bilayered manganites have been investigated in a broad temperature range. The samples have been synthesized using the solid-state reaction method. Rietveld refinement of the X-ray diffraction data indicates the tetragonal structure formation with I4/mmm space group. The resistivity curves of the samples present a general characteristic of metal-insulator (MI) transition at certain temperature (TMI). Besides, for samples with x = 0.48, 0.50, and 0.52, at a certain temperature (TCO) well below TMI the charge ordering is also evident. Furthermore, the samples display a shallow upturn in resistivity below Tmin due to the Kondo like spin scattering effect, weak localization and electron-phonon interaction. The high temperature semiconducting (T > TMI) region, the resistivity curve follows the 3D Mott's variable hopping transport mechanism. The overall suppression of resistivity accounts for a substantial magnetoresistance by applying a magnetic field and the characteristic change in TMI, TCO, and Tmin are discussed. Temperature-dependent magnetization demonstrates the suppression of ferromagnetism and evident of antiferromagnetic nature with an apparent charge ordering with increasing concentration of Sr$^{2+}$.

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I. INTRODUCTION

Ruddlesden–Popper compounds having general formula \((A)_{n+1}B_nO_{3n+1}\) \([\text{AO(ABO}_3]_n\) are a kind of perovskite structure consisting of a two-dimensional (2D) layered structure interspersed with cations (\(A = \text{La, Sr, and } B = \text{Mn}\)) and anions (Oxygen) and \(n\) represents the number of layers in perovskite-like array, stacked between rock-salt AO layers along the crystallographic c-axis. In this array, the perovskite structure corresponds to \(n = \infty\) and the \(K_2\text{NiF}_4\) structure to \(n = 1\). The 2-dimensional character in the compounds can be introduced by switching from the perovskite \((n = \infty)\) to the bilayer \((n = 2)\) array. Subsequently, due to the reduction in number of nearest neighbour B cations around each metal transition from 6 to 5 causing anisotropic reduction in the bandwidth of one electron, which in turn substantially alters the electronic and transport properties. The La-based Ruddlesden–Popper double layered manganite \(\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7\) have gained importance due to colossal magnetoresistance (CMR) analogous to 3D perovskite manganite \((\text{La}_{1-x}\text{Sr}_x\text{MnO}_3)\). However, in congruity with the three-dimensional (3D) half doped perovskite manganite, which shows charge exchange (CE) spin/charge ordering (CO), the A-type of antiferromagnetic (AFM) state is dominant in Ruddlesden–Popper half substituted layered manganite. Mitchell et al. studied the magnetic phase diagram of \(\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7\) studied using neutron diffraction for a series substitution of Sr in La site (x). Besides, the double exchange mechanism,
which basically accounts for intrinsic MR in 3D perovskite man-
ganite.\textsuperscript{10} Due to the high spin polarization of the conduction electron, the MR found in the 2D layered system is much larger than found in 3D.\textsuperscript{3,11,12} Further, the electrical transport mechanism in these 3D and 2D manganite has been reported on the accounts of various transport mechanism,\textsuperscript{13–18} such as; low temperature upturn due to Kondo effect, weak localization effect, electron-electron, electron phonon scattering and High temperature semiconducting region on account of 2D Mott’s variable range hopping model (2D M-VRH), 3D M-VRH, spin polarized conduction (SPC) etc.

In this study a comprehensive study of low temperature transport and high temperature semiconducting behavior in La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ (0.42 $\leq$ $x$ $\leq$ 0.52) are investigated. It is observed that the resistivity below $T_{\text{min}}$, shows $T^{1/2}$ dependence suggesting the incidence of weak localization. In the region $T$>$T_{M}$, electrical is expressed by Mott’s variable hopping model. In addition, samples with $x$ = 0.46, 0.48, and 0.50 shows significant $\sim$58$\%$ MR at 8T, measured at 5 K.

II. EXPERIMENTAL

The polycrystalline samples of Sr$^{2+}$ substituted La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ (0.42 $\leq$ $x$ $\leq$ 0.52) were synthesized adopting a conventional high temperature solid state reaction method. The La$_2$O$_3$, SrCo$_3$, and Mn$_2$O$_3$ powders of 99.9$\%$ purity procured from sigma Aldrich were weighed stoichiometric ratio and grounded several times until the homogeneous distribution was achieved. The homogenous powders thus, obtained were sintered at 1000 $^\circ$C for 48 hr with

![Image](https://via.placeholder.com/150)

FIG. 1. (a) X-ray diffraction profile (b-f) Resistivity as a function of temperature at different magnetic fields and inset (e) MR% vs. T at 5T (f) MR% vs. T at 5 K (0-8 T).
intermediate grindings. The obtained powder was pressed into pellets and at last sintered at 1350 °C for 30 hr, followed by furnace cooling in the air. Room temperature powder X-ray diffraction technique was carried out for the study of structural characterization and phase formation. A standard four probe set up equipped with 8T Oxford superconducting magnet (at UGC-DAE-CSIR, Indore Centre) was used for the measurement of temperature dependent DC electrical resistivity under different magnetic field.

### III. RESULTS AND DISCUSSION

The X-ray diffraction profile of La$_{2-2x}$Sr$_{1+2x}$Mn$_{2}$O$_7$ (0.42 ≤ x ≤ 0.52) shown in Fig. 1 (a), indicates that samples are formed in the single phase. The structure of the samples refined considering tetragonal unit cell, I4/mmm space group, shows excellent agreement between the experimental and the theoretical intensities. The refinement was carried out using Rietveld refinement technique with lattice parameters taken for the refinement are tabulated in Table I. The decrease in c/a ratio observed, the lower temperature side with the increasing substitution of Sr.

| Samples(x)-parameters | x = 0.42 | x = 0.46 | x = 0.48 | x = 0.5 | x = 0.52 |
|------------------------|-----------|-----------|-----------|-----------|-----------|
| a (Å)                  | 3.858(5)  | 3.867(2)  | 3.869(3)  | 3.8673(3) | 3.866(6)  |
| b (Å)                  | 3.858(5)  | 3.867(2)  | 3.869(3)  | 3.8673(3) | 3.866(6)  |
| c (Å)                  | 19.366(9) | 19.977(1) | 19.9444   | 19.927(7) | 19.917(1) |
| V (Å³)                 | 288.333   | 298.761   | 298.597   | 298.044   | 297.773   |
| c/a                    | 5.0199    | 5.164     | 5.155     | 5.152     | 5.151     |
| χ²                     | 2.59      | 2.07      | 1.28      | 1.16      | 1.362     |
| -MR% at 8T             | 43.3      | 57.9      | 58.3      | 58.3      | 50.5      |
| Best fit para. 0T      |           |           |           |           |           |
| ρ₀ (Ω-cm)              | 0.07      | 0.04      | 0.22      | 0.11      | 10.63     | 5.03      | 4.53      | 1.68      | 4.96      | 2.74      |
| ρ₁ (Ω-cm K)            | 0.003     | 0.002     | 0.024     | 0.008     | 2.04      | 0.69      | 0.82      | 0.23      | 0.78      | 0.35      |
| ρ₄ × 10^{8.3} (Ω-cm K^{0.5}) | -9.25 | 11.02    | 18.77     | 9.19      | 4113      | 271       | 988       | -1.61     | 1070      | -786      |
| ρ₉ × 10^{-13} (Ω-cm K^{2}) | 4.50 | -1.01    | 16.67     | 2.53      | 726.6     | 505.3     | 533.0     | 265.9     | 1146.8    | 650.3     |
| ρ₄ × 10^{-7} (Ω-cm K^{2.2}) | 1.40 | 0.47     | 3.46      | 1.29      | 90.39     | 107.5     | 58.05     | 41.48     | 142.4     | 78.42     |
| ρ₀ × 10^{-13} (Ω-cm K^{2.5}) | -87.94 | 7.245    | -294.1    | -53.1     | -12935.8  | -9425.5   | -9017.0   | -4651.5   | -18949.7  | -10643.3  |
| T₀ (K)                 | 1135.8    | 743.7     | 2019.9    | 1645.3    | 3487.5    | 3307.2    | 3614.4    | 3211.5    | 4036.7    | 3691.3    |
| Eₚ × 10^{-21} (eV^{-1} cm^{-3}) | 7.13 | 10.89     | 4.01      | 4.92      | 2.32      | 2.45      | 2.24      | 2.52      | 2.01      | 2.19      |

The temperature (T) dependent electrical resistivity (ρ) curve for the series of La$_{2-2x}$Sr$_{1+2x}$Mn$_{2}$O$_7$ (0.42 ≤ x ≤ 0.52) measured in the absence (0T) and in the presence of the applied field (H) is shown in Fig 2 (a–c). It can be observed from these figs that the samples demonstrate the generic metal-insulator transition at a certain temperature (TMI), which for x = 0.42, 0.46, 0.48, 0.50, and 0.52 is approximately 172, 182, 192, 203, and 199 K respectively. TMI is determined by the minimum in the dρ/dT curve. The shift of TMI first to the higher temperature side up to x = 0.48 and later shift to the lower temperature side with the increasing substitution of Sr$^{2+}$ at La$^{3+}$, suggesting the first incitement of the double exchange (DE) mechanism and later the inference of charge-ordering (marked as TCO in the fig) suppress the DE interaction in the samples with x = 0.50 and 0.52. Besides, for the samples, on the whole the resistivity decreases substantially and TMI falls to the high temperature region by applying a magnetic field. This proposes once more the eminence of DE due to the magnetic field, which leads to enhanced ferromagnetism and substantial magnetoresistance (MR) (shown in the inset of Fig. 1f) in the samples. The magnetoresistance ratio (MR %) was determined from the equation, MR % = (ρ_0 − ρ_H)/ρ_0 × 100, where, ρ_0 and ρ_H are the resistivity without and with field respectively. The (-) MR% isotherms at 5 K shown in the inset of Fig 1(f), indicates that MR increases with the field and at 8T, it’s comparable in the samples with x = 0.46, 0.48, and 0.50 (~58%). Besides, the x = 0.46 sample shows a significant low field MR (~18%, at 1T) compared to the other samples. It can also be observed from Fig 1 (b–f), that with the decreasing temperature, at a certain temperature (T_{min}), resistivity curve shows a shallow upturn and shifts to the higher temperature side with the increasing Sr$^{2+}$. For sample with comparatively high Sr$^{2+}$, T_{min} gets suppressed with charge ordering in the samples and shifts to the high temperature side. Besides, the application of magnetic field, T_{min} gets suppressed and also shifts to the lower temperature side. Therefore, it is understood that the spin-dependent scattering must be coupled with the resistivity minimum which is eventually reduced by the applied magnetic field. The perovskite manganite shows strongly correlated electronic behavior and to understand the transport behavior we have adopted the model considering the suitable interactions. The resistivity behavior in the region T<T_{min} could be well fitted using equation using equation,$^{27}$ ρ(T) = ρ₀ − ρ₁ . ln(T) + ρ₂ . T^{α} + ρ₄ . T^{β}. and the region T_{min}<T<T_{MI}, followed, ρ(T) = ρ₀ + ρ₅ . T^{a} + ρ₆ . T^{b}. Hence, the overall resistivity data for the temperature T<T_{MI} has been fitted

TABLE I. Lattice parameter, unit cell volume, MR% at 5K, best fit parameter to the resistivity curve using Eq. (1) and (2).

- MR% at 8T
- Best fit para. 0T
- ρ₀ (Ω-cm)
- ρ₁ (Ω-cm K)
- ρ₄ × 10^{8.3} (Ω-cm K^{0.5})
- ρ₉ × 10^{-13} (Ω-cm K^{2})
- ρ₄ × 10^{-7} (Ω-cm K^{2.2})
- ρ₀ × 10^{-13} (Ω-cm K^{2.5})
- T₀ (K)
- Eₚ × 10^{-21} (eV^{-1} cm^{-3})

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Here $\rho$ in a 3D system, $\rho_0$ is the “pre-exponential factor” and $T_B$ is the “Mott characteristic temperature” related to the density of state in near Fermi energy $N(E_F)$.

$$K_B T_B = 24/\pi \cdot N(E_F) \cdot \xi^2.$$

Here $\xi$ is the localization length. The density of state $N(E_F)$ can be determined from $T_B$ by the estimating value of $\xi$=0.45 nm$^{-1}$. Besides the resistivity behavior in the mid temperature region near $T_{MI}$ is identified to be percolative in nature and can be explained using two phase model (Ref. 24 and references therein); not a scope of present study.

Fig. 2 shows the temperature dependent magnetization plot of samples with $x = 0.42, 0.46, 0.48, 0.52$ measured at 1000 Oe and $x = 0.50$ at 100 Oe. In the inset dM/dT vs. T curves are plotted to estimate paramagnetic (PM) to ferromagnetic (FM) temperature, defined as Curie temperature $T_C$, transition and the charge ordering (CO) temperature ($T_{CO}$). The estimated $T_C$ is 332, 316, 294, 276, 262 K for $x = 0.42, 0.46, 0.48, 0.50, 0.52$ respectively and $T_{CO}$ is evident at 218, 232, 232, 236 K for $x = 0.46, 0.48, 0.50, 0.52$ respectively. Dediu et al.\textsuperscript{23} proposed that while the materials preserve the paramagnetic (PM) nature both above and below $T_{CO}$, the magnetic interaction at $T_{CO}$ may change from ferromagnetic (FM) ($T > T_{CO}$) to antiferromagnetic (AFM) ($T < T_{CO}$) evident as a peak-like feature, making up a sample anisotropic antiferromagnetic, which is a characteristic feature of 2D layered manganites.\textsuperscript{21} It is evident that $x = 0.42$, shows PM to FM transition with no evidence of charge ordering. Besides, with the increase of the concentration of Sr\textsuperscript{2+} at La-site, the CO (growth in peak-like feature) is apparent by suppressing the FM behavior and progression of AFM nature. As discussed previously, the aforementioned behaviors of the samples are in resemblance with the $\rho(T)$ characteristics. The reduction in $T_C$ and the enhancement of $T_{CO}$ could be understood due to the weakening of DE interaction with the increase of $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio. The disparity between $T_{MI}$ and $T_C$ can be interpreted as a consequence of non-magnetic randomness and active hopping disorder in the DE mechanism, that have a vital role in the evaluation of anomalous transport characteristics and magnetism in manganites.\textsuperscript{22}

### IV. CONCLUSION

In conclusion, we have presented the electrical transport behavior of La$_{2-x}$Sr$_{x}$Mn$_2$O$_7$ ($0.42 \leq x \leq 0.52$) in the absence and presence of a magnetic field. The common metal insulator transition at certain temperature ($T_{MI}$), which falls to higher temperature side on applying the field, is profound and understood owing to double exchange (DE) interactions. The low temperature resistivity upturn behavior
has been studied taking into account the various scattering processes, though the weak-localization effect is found to be dominant. Besides, the resistivity coefficients acquired considering numerous scattering processes are strongly dependent on the applied magnetic field. The metallic nature follows $T^{2.5}$ and $T^{4.5}$, suggesting the contribution of both single magnon and two magnon scattering processes. The high temperature semiconducting nature satisfies the Mott’s-variable range hopping mechanism in the wide temperature range. The temperature dependent magnetization behavior is in close agreement with the temperature dependent resistivity data. Besides, the difference between $T_{MI}$ and $T_C$ may be due to non-magnetic randomness and active hopping disorder in the DE mechanism.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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