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Spin-dependent and spin-independent channels of electrical transport in perovskite manganites

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A model with two channels of electrical transport (TCET) for perovskite manganites is proposed, and it is described by an equivalent device with two current-carrier channels. In one channel, there is a spin-independent resistor (R_3) with an equivalent resistivity of ρ_3 . In the other channel, there are two spin-dependent resistors in series (R_1 and R_2) with an equivalent resistivity of $\rho_1 + \rho_2$. The component ρ_1 includes residual resistivity and the resistivity contributed by crystal-lattice scattering. The other component of the equivalent resistivity, ρ_2 , originates from the spin orientations of the itinerant electrons and the local electrons of the outer O 2p and Mn 3d orbitals that deviate from the orientation of their ground states when the test temperature is close to the Curie temperature. Using this model, we fitted the experimental curves of the resistivity *versus* test temperature for single-crystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.00 \leq x \leq 0.40$) and polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($0.00 \leq x \leq 0.30$). In addition, we investigated the effects of the fraction of the antiferromagnetic phase, scattering at the crystallite interfaces, and the crystal-cell constants on the samples' resistivity. The physical mechanism of the TCET model was explained using an O 2p itinerant-electron model, which has been used in other studies to explain the magnetic ordering of several series of spinel ferrites and perovskite manganites.

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1. Introduction

There have been many investigations on the electronic transport and magnetic properties of perovskite oxides^{1–12} because of their potential application in both electronic and magnetic information-storage devices. There are several models for the electronic-transport properties of these materials, and spin-dependent transport has been taken into account by most researchers. One of the popular views is that there is polaron hopping below the Curie temperature (T_C) on the basis of the double-exchange interaction.^{3,3,13} In this view, the current carriers of perovskite manganites originate from the d electrons of manganese cations. Another view was proposed by Alexandrov *et al.*,^{13,14} who argued that the current carriers of perovskite manganites originate from the p holes of oxygen anions rather than the d electrons of manganese cations, based on the experimental results of electron-energy-loss spectroscopy^{15,16} and X-ray absorption spectroscopy.¹⁷ Alexandrov *et al.*^{13,14} therefore established a current-carrier-density collapse (CCDC) model for the electrical-transport mechanism, and many researchers followed with investigations on this CCDC model.^{18–21}

The presence of p holes of oxygen anions in an oxide can be easily understood as there are O^{1-} anions in addition to O^{2-}

anions. When compared with an O^{2-} anion ($2s^22p^6$) with a closed outer electron shell, it is clear that a p hole exists in the outer orbit of an O^{1-} anion ($2s^22p^5$). This fact was further confirmed by theoretical calculations^{22,23} and experiments.^{24–26}

Taking into account that there are both O^{1-} and O^{2-} anions in oxides,^{22–27} our group has proposed an O 2p itinerant-electron model for magnetic oxides (IEO model),^{28,29} which is similar to the O 2p hole model proposed by Alexandrov *et al.*^{13,14} Using the IEO model, our group studied the relationship between the magnetic moment and cation distribution of several series of Cr (Ti, Mn)-doped spinel ferrites.^{28–36} We also studied the magnetic ordering in perovskite manganites.^{37–40}

In this study, we used a model of two channels of electrical transport (TCET), which was derived from the IEO model, to fit the temperature dependence of the resistivity for two series of perovskite manganites: single crystallines $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.00 \leq x \leq 0.40$) reported by Urushibara *et al.*⁴¹ and polycrystallines $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($0.00 \leq x \leq 0.30$) prepared in this work. In addition, we will discuss the effects of the proportion of the antiferromagnetic phase, scattering at crystallite interfaces, and crystal-cell constants on the samples' resistivity.

2. Experiment and results

The polycrystalline perovskites examined in this study, $\text{La}_{0.60-x}\text{Sr}_{0.40}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0 \leq x \leq 0.3$), were prepared using the sol-gel method:^{42,43} (i) stoichiometric amounts of La_2O_3 (purity: 99.99%, fired in air at 1073 K for 3 h before it was used),

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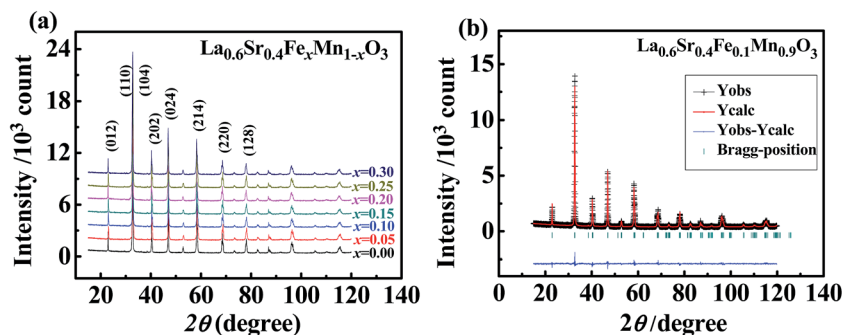


Fig. 1 (a) Powder XRD patterns of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$. (b) Fitted and observed XRD patterns for the sample $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.1}\text{Mn}_{0.9}\text{O}_3$, obtained using the Fullprof software. The crosses represent the observed data, and the curve represents the fitted results; the vertical bars represent the Bragg sites for the space group $R\bar{3}c$. The difference between the observed and fitted patterns is shown at the bottom.

$\text{Sr}(\text{NO}_3)_2$ (purity: 99.5%) powder, and a $\text{Mn}(\text{NO}_3)_2$ solution (purity: 50%) were dissolved in a dilute HNO_3 solution at 343 K. Citric acid and ethylene glycol were added to the mixed solution as complexing agents until a completely homogeneous transparent solution was obtained. The molar ratio of citric acid (or ethylene glycol) to the perovskite molecule was 6 : 1. (ii) The mixture was then evaporated at 363 K for 24 h in a water bath until a highly viscous residue was formed. Upon further heating at 373 K for 12 h and then at 473 K for 24 h, a gel developed. The gel was ground. (iii) All ground gel samples of different compositions were further heat treated. The temperature was increased from 473 to 573 K, in increments of 25 K, with 45 min spent at each step. Next, the temperature was increased from 573 to 673 K in increments of 20 K, with 50 min spent at each step. Finally, the temperature was increased from 673 to 773 K in increments of 10 K, with 1 h spent at each step. The samples were finely ground for 30 min to obtain a homogeneous mixture. After that, the samples were calcined at 873 K for 5 h to eliminate the organic material, ground, and calcined again at 1073 K for 10 h to eliminate any residual organic material. Each sample was then divided into two parts to measure their magnetic and electrical properties, and they were subjected to further heat treatment using slightly different methods.

To prepare the samples used to measure the magnetic properties, the powder obtained after grinding was pressed into pellets with a diameter of 13 mm and thickness of about 2 mm under a pressure of 11 ton per cm^2 . The pellets were calcined at

1273 K for 10 h, after which powder samples were obtained by grinding.

To prepare the samples used to measure the electrical-transport properties, the powder obtained after grinding was pressed into pellets under a pressure of 10 ton per cm^2 . The pellet samples were then sintered at 1573 K for 24 h.

Structural characterization was carried out by analyzing X-ray diffraction (XRD) patterns, which were measured using an X-ray diffractometer (X'Pert Pro, PANalytical, The Netherlands) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The data were collected in the 2θ range of 15° to 120° in increments of 0.0167° . The field and temperature dependence of the specific magnetization, $\sigma(H)$ and $\sigma(T)$, were measured using a physical-property measurement system (PPMS, Quantum Design, Inc., USA). Using electrical-transport characterization equipment (Versa Lab, Quantum Design, Inc., USA), the temperature dependence of the electrical resistivity $\rho(T)$ was measured by the conventional four-point probe technique at 50 K.

Fig. 1(a) shows the XRD patterns, which indicate that all the samples had only a single ABO_3 perovskite phase with the space group $R\bar{3}c$. The XRD patterns were fitted using the Fullprof software (Institut Laue-Langevin, France). The goodness-of-fit factor ($s \leq 1.37$) is listed for all samples in Table 1. As an example, the fitted result for the $\text{La}_{0.60}\text{Sr}_{0.40}\text{Fe}_{0.1}\text{Mn}_{0.9}\text{O}_3$ sample is shown in Fig. 1(b). The fitted result; the dependence on the Fe-doping level, x ; the lattice parameters, a and c ; the crystal-cell volume, v ; the Mn–O bond

Table 1 Crystal structural parameters of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ at room temperature: a and c are the cell constants, v is the cell volume, $d_{\text{B-O}}$ and Θ are the Mn–O distance and Mn–O–Mn bond angle, all which were obtained by fitting the XRD patterns; s is the goodness-of-fit factor. σ_s and μ_{obs} are the specific saturation magnetization and the average molecular magnetic moment at 10 K, respectively. T_C and T_N are the Curie temperature and the Néel temperature, respectively; T_{MI} is the temperature at which the resistivity has the maximum value

x	s	a (Å)	c (Å)	v (Å ³)	$d_{\text{B-O}}$ (Å)	Θ (°)	σ_s (A m ² kg ⁻¹)	μ_{obs} (μ_B)	T_C (K)	T_N (K)	T_{MI} (K)
0	1.34	5.4861	13.356	348.14	1.9357	172.05	80.55	3.194	364.5	—	292
0.05	1.32	5.4898	13.359	348.69	1.9367	171.66	78.53	3.114	321.8	—	231
0.1	1.30	5.4920	13.362	349.04	1.9374	171.22	78.46	3.112	267.9	—	192
0.15	1.30	5.4936	13.365	349.30	1.9379	170.86	72.77	2.887	187.3	—	133
0.2	1.37	5.4945	13.366	349.44	1.9381	170.67	1.72	0.068	68.9	40.5	—
0.25	1.27	5.4961	13.368	349.69	1.9386	170.35	1.64	0.065	51.3	37.6	—
0.3	1.26	5.4971	13.370	349.88	1.9390	170.16	0.91	0.036	45.5	32.9	—



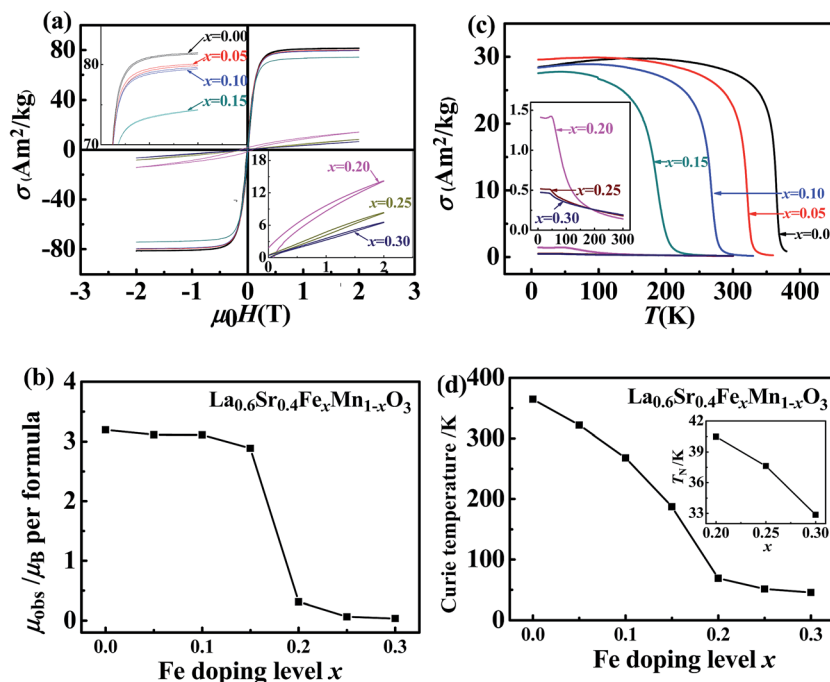


Fig. 2 Magnetic properties of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$: (a) magnetic hysteresis loops at 10 K; (b) magnetic moment, μ_{obs} , at 10 K as a function of Fe content, x ; (c) temperature dependence of the specific magnetization, σ , at an applied magnetic field of 0.05 T; (d) magnetic transition temperature as a function of Fe content, x . The insert of (c) enhanced the variations of the curves. The insert of (d) shows the Néel temperature, T_{N} , as a function of Fe content, x .

length, $d_{\text{B-O}}$; and the Mn–O–Mn bond angle, Θ , are listed in Table 1. It can be seen that the values of these parameters slightly varied: the values of a , c , v , and $d_{\text{B-O}}$ increased with increasing x ; and the value of Θ decreased with increasing x . The equivalent cubic cell constants (a_{e}) per formula, calculated using the crystal-cell volume, v , will be used to discuss the samples' resistivity in Section 4.4.

Fig. 2(a) shows the magnetic hysteresis loops of the samples measured at 10 K. Using the specific saturation magnetization, σ_{s} , at 10 K, the average values of the molecular magnetic moment, μ_{obs} , were obtained. Fig. 2(b) shows the curve of μ_{obs} versus x . Fig. 2(c) shows the curves of σ versus T under an applied magnetic field of 0.05 T. The values of the Curie temperature, T_{C} , defined as the temperature at which $d\sigma/dT$ reaches its minimum value, are shown in Fig. 2(d). In

addition, the inset in Fig. 2(c) shows that there was a different Néel temperature, T_{N} , for each sample with $x \geq 0.20$. Below T_{N} , the value of σ exhibited no significant change; above T_{N} , the value of σ decreased distinctly. The variation of T_{N} with x is shown in the inset in Fig. 2(d). The values of μ_{obs} , T_{C} , and T_{N} are listed in Table 1.

The data points in Fig. 3 show the temperature dependence of the electrical resistivity, ρ , of the samples, and it can be seen that ρ increased with increasing x . In addition, there was a resistivity peak at a characteristic temperature, T_{MI} , for each sample when $x \leq 0.15$, and these characteristic temperatures are listed in Table 1. The curves in Fig. 3 also show the fitted results, which will be discussed in the following sections.

The following trends can be observed in Fig. 2 and 3: (i) when $x \leq 0.15$, the samples were ferromagnetic conductors. The value of μ_{obs} decreased slowly from $3.194 \mu_{\text{B}}$ ($x = 0.00$) to $2.887 \mu_{\text{B}}$ ($x = 0.15$); the value of T_{C} decreased rapidly from 364.5 K ($x = 0.00$) to 187.3 K ($x = 0.15$); the maximum resistivity increased from $0.0222 \Omega \text{ cm}$ ($x = 0.00$) to $4.47 \Omega \text{ cm}$ ($x = 0.15$). (ii) When $x \geq 0.20$, the samples were semiconductors with both an antiferromagnetic phase and a ferromagnetic phase. The resistivity increased rapidly with decreasing temperature, exceeding $100 \Omega \text{ cm}$ when the test temperature was below 123.6, 140.2, and 159.3 K, when $x = 0.20$, 0.25, and 0.30, respectively. In addition, when $x = 0.20$, 0.25, and 0.30, respectively, the values of T_{N} of the antiferromagnetic phase were 40.5, 37.6, and 32.9 K; the Curie temperatures of the ferromagnetic phase were 68.9, 51.3, and 45.5 K; and the μ_{obs} values were 0.068, 0.065, and $0.036 \mu_{\text{B}}$.

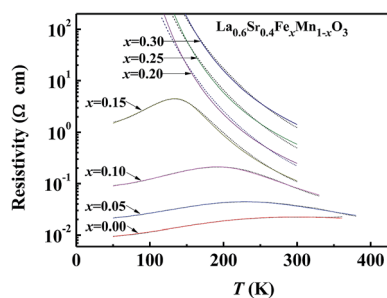


Fig. 3 Temperature dependence of electrical resistivity of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ samples. The data points represent the observed values, and the curves represent the fitted results.



3. Model with two channels of electrical-transport (TCET) for perovskite manganites

In order to explain the electrical-transport properties of perovskite manganites, we propose a model with two channels of electrical transport (TCET), which was derived from the IEO model.^{29,37} The IEO model is based on the following three postulates: (i) in a given sublattice, an O 2p electron with a constant spin direction can hop from an O²⁻ anion to an O 2p hole belonging to an adjacent O¹⁻ anion, with the metal cation acting as the intermediary. (ii) The two O 2p electrons in the outer orbit of an O²⁻ anion, which have opposite spin directions, become itinerant electrons of two different sublattices (such as the (A) and [B] sublattices of (A)[B]₂O₄ spinel ferrites, or the A and B sublattices of ABO₃ manganites). (iii) Since an itinerant electron has a constant spin direction in a given sublattice and owing to Hund's rules,⁴⁴ the directions of the magnetic moments of cations with $n_d \leq 4$ (where n_d is the number of 3d electrons in 3d transition metal cations), such as Mn³⁺ or divalent and trivalent Cr cations, will couple antiferromagnetically with those of magnetic moments of cations with $n_d \geq 5$, such as Mn²⁺ or divalent and trivalent Fe, Co, and Ni cations. This occurs because in the 3d orbits of transition elements, a maximum of five electrons can have their spins aligned in the same direction.

It is well known that there are two sublattices in ABO₃ perovskite manganites: the A–O sublattice and the B–O sublattice. According to the above IEO model, there are O–A–O–A–O and O–B–O–B–O ionic chains, which can be regarded as two current-carrier channels. In La_{1-x}Sr_xMnO₃, the movement of O 2p electrons along the first channel, *i.e.*, the O–A–O–A–O (where La and Sr occupy the A sites) ionic chain, is a spin-independent process because there is no magnetic ordering. The resistance of the first channel is labeled R_3 (with an equivalent resistivity of ρ_3). The movement of O 2p itinerant electrons along the second channel, *i.e.*, the O–Mn–O–Mn–O (where Mn occupies the B site in O–B–O–B–O) ionic chain, is a spin-dependent process below

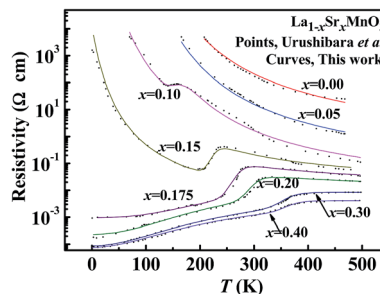


Fig. 5 Temperature dependence of electrical resistivity of the single-crystalline La_{1-x}Sr_xMnO₃ samples. The data points represent values observed by Urushibara *et al.*,⁴¹ and the curves represent the fitted values obtained in this work.

the Curie temperature because there is magnetic ordering. The resistance of the second channel is represented by two resistors in series, R_1 and R_2 (with an equivalent resistivity of $\rho_1 + \rho_2$), where ρ_1 includes the residual resistivity and the resistivity resulting from scattering by the crystal lattice, and ρ_2 originates from the spin orientations of the itinerant electrons and local electrons of the outer O 2p and Mn 3d orbits that deviate from the orientation of their ground states because of thermal fluctuation. Therefore, the TCET model for a perovskite manganite sample can be represented by the equivalent circuit shown in Fig. 4(a), with the resistance, R , and resistivity, ρ , defined as follows:

$$R = \frac{(R_1 + R_2)R_3}{R_1 + R_2 + R_3}, \quad \rho = \frac{(\rho_1 + \rho_2)\rho_3}{\rho_1 + \rho_2 + \rho_3} \quad (1)$$

A series of curves of ρ versus test temperature, T , for single-crystalline La_{1-x}Sr_xMnO₃ ($0.00 \leq x \leq 0.40$) were reported by Urushibara *et al.*,⁴¹ and they were fitted using the TCET model. As shown in Fig. 5, the fitted curves are very close to the observed results (data points).

When $0.175 \leq x \leq 0.40$, we found that the resistivities in eqn (1) can be expressed as follows:

$$\rho_1 = \rho_0 + a_1(T_1 + T)^3, \quad \rho_2 = a_2 \exp\left(-\frac{E_2}{k_B T}\right), \\ \rho_3 = a_3 \exp\left(\frac{E_3}{k_B T}\right) \quad (2)$$

where k_B is the Boltzmann constant. The parameters in eqn (2) were determined by fitting the experimental curves of ρ versus T , and the results are listed in Table 2. For example, the parameters for the sample with $x = 0.20$ were determined as follows: first, it can be seen that the curve of ρ versus $(T_1 + T)^3$ can be approximated as a straight line at lower temperatures by adjusting the parameter T_1 , as shown in Fig. 6(a). We then determined the residual resistivity, ρ_0 , and the parameter a_1 from the intercept and slope, respectively, of the straight line in Fig. 6(a). Second, an approximate straight line of $\ln \rho$ versus $1/k_B T$ can be seen at higher temperatures, as shown in Fig. 6(b). We obtained the approximate values of $\ln a_3$ and E_3 from the intercept and slope, respectively, of the straight line in Fig. 6(b).

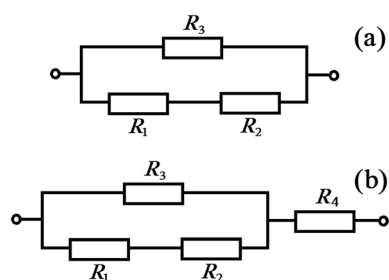


Fig. 4 The equivalent circuit of the TCET model of (a) single-crystalline and (b) polycrystalline perovskite manganites. R_1 includes the residual resistance and the resistance resulting from scattering by the crystal lattice. R_2 originates from the spin orientations of the itinerant electrons and local electrons of the outer O 2p and Mn 3d orbitals that deviate from the orientation of their ground states because of thermal fluctuation. R_3 is spin-independent resistance. R_4 originates from the scattering by the crystallite interfaces in the polycrystalline sample.



Table 2 Parameters of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ obtained by fitting the experimental curves of resistivity (ρ) versus test temperature (T) reported by Urushibara *et al.*⁴¹ The ρ_0 is the residual resistivity in ρ_1 ; The a_1 and T_1 are the parameters (in the ρ_1) which result from scattering by the crystal lattice; The a_{11} and E_1 are the parameters in the ρ_1 of the samples with $x = 0.10$ and 0.15 ; The a_2 and E_2 are the parameters (in the ρ_2) which originate from the spin orientations of the itinerant electrons and local electrons of the outer O 2p and Mn 3d orbitals that deviate from the orientation of their ground states because of thermal fluctuation. The a_3 and E_3 are the parameters (in the ρ_3) which originate from the spin-independent transition

Sr content x	ρ_0 (Ω cm)	a_1 (Ω cm K^{-3})	T_1 (K)	a_{11} (Ω cm)	E_1 (eV)	a_2 (Ω cm)	E_2 (eV)	a_3 (Ω cm)	E_3 (eV)
0.00	—	—	—	—	—	—	—	0.2440	0.175
0.05	—	—	—	—	—	—	—	0.0220	0.170
0.10	—	—	—	0.009	0.15	4×10^5	0.115	0.0050	0.150
0.15	—	—	—	0.0014	0.08	1×10^{11}	0.515	0.0115	0.075
0.175	9.5×10^{-4}	2.4×10^{10}	10	—	—	8×10^{10}	0.650	0.0112	0.0515
0.20	2.3×10^{-4}	1.5×10^{10}	20	—	—	4.5×10^{10}	0.730	0.0095	0.0354
0.30	8.5×10^{-5}	5.5×10^{-11}	30	—	—	9×10^9	0.860	0.0084	1×10^{-4}
0.40	7.5×10^{-5}	4.2×10^{-11}	35	—	—	7×10^9	0.880	0.0041	5×10^{-5}

Third, we determined the parameters a_2 and E_2 by fitting the curves of ρ versus T . In this fitting process, the parameters ρ_0 , a_1 , and T_1 remained constant, but a_3 and E_3 required slight adjustments. The curves of observed ρ , and fitted ρ_1 , ρ_2 and ρ_3 versus T are shown in Fig. 6(c). Finally, the dependence of the observed (data points) and fitted (curve) ρ of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ on the test temperature, T , is shown in Fig. 6(d). It can be seen that the fitted curve is very close to the observed results.

For the antiferromagnetic semiconductor samples with $x = 0.00$ and 0.05 , the curves of ρ versus T can only be fitted by the equation $\rho = a_3 \exp\left(\frac{E_3}{k_B T}\right)$. The values of the fitted parameters a_3 and E_3 are listed in Table 2.

For the samples with $x = 0.10$ and 0.15 , the curves of ρ versus T can be fitted using eqn (1) and (2), but the expression $\rho_1 = a_{11} \exp\left(\frac{E_1}{k_B T}\right)$ must substitute for ρ_1 in eqn (2). The values of the fitted parameters a_{11} , E_1 , a_2 , E_2 , a_3 , and E_3 are listed in Table 2.

For the polycrystalline samples of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0.00 \leq x \leq 0.30$) prepared in this work, scattering by the crystallite interfaces affected the sample resistivity, ρ , and the equivalent circuit is shown in Fig. 4(b). We first fitted the observed curves of ρ versus T using eqn (1) and (2), and the effect of scattering at the crystallite interfaces was then analyzed, as discussed in following Section 4.3. The fitted curves of ρ versus T for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0.00 \leq x \leq 0.30$) are shown in Fig. 3. It can be seen that the fitted curves are very close to the observed results. The values of the fitted parameters are listed in Table 3.

4. Discussion

4.1 Spin-dependent and spin-independent electrical transport in perovskite manganites, and their difference from free electron transport in magnetic metals

Fig. 6(c) shows that at lower temperatures, the spin-independent resistivity, ρ_3 , of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ prepared by Urushibara *et al.* was so high that the electrical transport occurred along the spin-dependent channel, and the value of ρ was close to ρ_1 , which increased with increases in the test temperature T owing to the thermal vibration of ions. When T was close to T_C , the transition probability of the itinerant electrons decreased rapidly and ρ_2 increased rapidly because the spin orientations of the itinerant electrons and the electrons in the outer O 2p and Mn 3d orbitals deviated from the direction of their ground states. When T was higher than T_C , the spin orientations of the itinerant electrons changed into disorder, and the electrical transport became spin-independent along both O–A–O–A–O and O–B–O–B–O ionic chains.

It should be noted that the resistivity of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, also prepared by Urushibara *et al.*, was $84 \mu\Omega$ cm at 2 K,⁴¹ which is far higher than the resistivities of the magnetic metals Fe ($8.6 \mu\Omega$ cm), Ni ($6.14 \mu\Omega$ cm), and Co ($5.57 \mu\Omega$ cm). Therefore, it can be

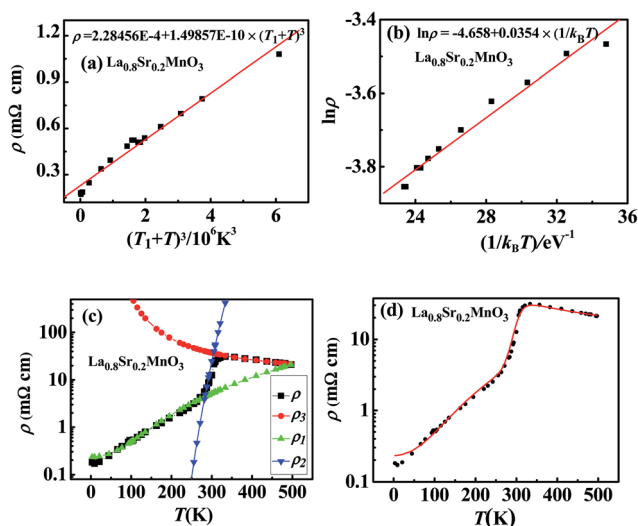


Fig. 6 Fitting process of the temperature (T) dependence of the resistivity (ρ) for single-crystalline $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$. The data points in (a, b and d) represent values observed by Urushibara *et al.*⁴¹ (a) Fitting results of the curve of ρ versus $(T_1 + T)^3$ at lower temperatures. (b) Fitting results of the curve of $\ln \rho$ versus $1/k_B T$ at higher temperatures. (c) Curves of observed ρ (squares),⁴¹ fitted ρ_1 (triangles), fitted ρ_2 (inverted triangles), and fitted ρ_3 (circles) versus T . (d) Dependence of observed (data points⁴¹) and fitted (curve) ρ on T .



Table 3 Parameters of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ obtained by fitting the experimental curves of ρ versus T from this work. The ρ_0 is the residual resistivity in ρ_1 ; The a_1 and T_1 are the parameters (in the ρ_1) which result from scattering by the crystal lattice; The a_2 and E_2 are the parameters (in the ρ_2) which originate from the spin orientations of the itinerant electrons and local electrons of the outer O 2p and Mn 3d orbitals that deviate from the orientation of their ground states because of thermal fluctuation. The a_3 and E_3 are the parameters (in the ρ_3) which originate from the spin-independent transition. All these parameters include the effect of the crystallite interfaces

Fe content x	ρ_0 (Ω cm)	a_1 (Ω cm K^{-3})	T_1 (K)	a_2 (Ω cm)	E_2 (eV)	a_3 (Ω cm)	E_3 (eV)
0	0.0072	2.794×10^{-10}	150	0.05	0.060	0.0044	0.0650
0.05	0.0172	1.050×10^{-9}	107	0.40	0.090	0.0020	0.0865
0.1	0.0737	1.116×10^{-8}	63	25	0.110	0.0019	0.0995
0.15	1.1000	1.159×10^{-6}	20	20 000	0.120	0.0018	0.1070
0.2	—	—	—	—	—	0.0030	0.1140
0.25	—	—	—	—	—	0.0056	0.1200
0.3	—	—	—	—	—	0.0114	0.1245

concluded that the spin-dependent transport of itinerant electrons in perovskite manganites below T_C is distinctly different from the spin-independent transport of free electrons in magnetic metals.

4.2 Effect of proportion of the antiferromagnetic phase on the resistivity of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0.00 \leq x \leq 0.30$)

Our previous investigation^{37–39} showed that all Mn and Fe ions are trivalent in $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$. According to the IEO model, an itinerant electron with up-spin in a sample with no Fe doping moves along the $\text{O}^{2-}\text{--Mn}^{3+}\text{--O}^{1-}\text{--Mn}^{3+}\text{--O}^{2-}$ ion chain, which always occupies the highest energy level whenever it reaches a Mn^{3+} or O^{2-} ion, as shown in Fig. 7(a). In this transition process, the itinerant electron consumes a small fraction of the energy of the system. When an itinerant electron with up-spin moves along the $\text{O}^{2-}\text{--Fe}^{3+}\text{--O}^{1-}\text{--Mn}^{3+}\text{--O}^{2-}$ ion chain, it always occupies the highest energy whenever it reaches a Mn^{3+} or O^{1-} ion, but the lowest energy level of an Fe^{3+} ion, as shown in Fig. 7(b), because the $\text{Fe}^{3+}(3d^5)$ cation couples antiferromagnetically with the $\text{Mn}^{3+}(3d^4)$ cation (see the IEO model). In this transition process, the itinerant electron must consume more energy of the system, resulting in lower transition probabilities for the itinerant electrons and increased resistivity. Therefore, the resistivity increases with increasing proportion of the antiferromagnetic phase. As shown in Fig. 7(a and b), the

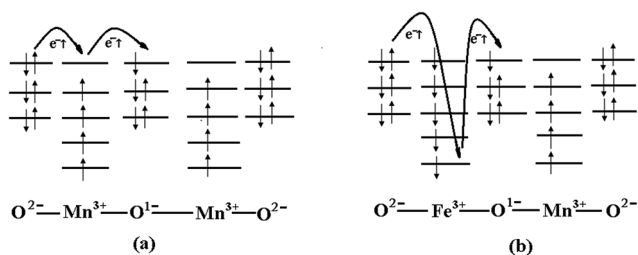


Fig. 7 Schematic diagrams of the transit of itinerant electrons in a spin-dependent process. (a) An itinerant electron with up-spin moves along the $\text{O}^{2-}\text{--Mn}^{3+}\text{--O}^{1-}\text{--Mn}^{3+}\text{--O}^{2-}$ ion chain. (b) An itinerant electron moves along the $\text{O}^{2-}\text{--Fe}^{3+}\text{--O}^{1-}\text{--Mn}^{3+}\text{--O}^{2-}$ ion chain. Here, the majority spin orientation of 3d electrons in Mn^{3+} cations is up; the majority spin orientation of 3d electrons in Fe^{3+} cations and O 2p electrons in O^{1-} anions is down.

spin orientation of the majority of 3d electrons in Mn^{3+} cations is up; the spin orientation of the majority of local 3d electrons in Fe^{3+} cations and local O 2p electrons in O^{1-} anions is down.

The difference between the energy consumed by the itinerant electrons in polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.1}\text{Mn}_{0.9}\text{O}_3$ was estimated from their Curie temperatures (364.5 and 267.9 K, respectively; see Table 1) to be 8.3 meV.

4.3 Resistivity (ρ_4) originating from scattering at the crystallite interfaces of polycrystalline samples

It is interesting to compare the resistivity of the polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ sample (ρ_P) prepared in this work to that of the single-crystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ sample (ρ_S) reported by Urushibara *et al.*,⁴¹ as shown in Fig. 8(a). We found that ρ_P is 97 times (at 50 K) and 9 times (at 360 K) the value of ρ_S , which suggests that the resistivity (ρ_4) originating from scattering at the crystallite interfaces of the polycrystalline sample was far higher than those originating from lattice thermal vibrating (ρ_1) and spin-dependent scattering (ρ_2). Therefore, for the polycrystalline manganites, the TCET model can be represented by the equivalent circuit shown in Fig. 4(b). Fig. 8(b) shows a comparison of ρ_4 with ρ_P , where ρ_4 was estimated using $\rho_4 = \rho_P - \rho_S$.

According to the report by Urushibara *et al.*,⁴¹ the temperature T_{MI} for maximum resistivity is very close to the value of T_C for single-crystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.175 \leq x \leq 0.40$). However, as shown in Table 2, the values of T_{MI} were distinctly lower than T_C for the polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0.00 \leq x \leq 0.15$) samples. This was simply due to ρ_4 of the polycrystalline samples. For the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ sample, the temperature at which ρ_4 reached a maximum was 287 K (see Fig. 8(b)), which is distinctly lower than its T_C (364.5 K).

4.4 Effect of crystal-cell constants on the samples' resistivity

For the antiferromagnetic semiconductor, polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.3}\text{Mn}_{0.7}\text{O}_3$, its resistivity was far lower than that of single-crystalline LaMnO_3 , with a ρ_P/ρ_S ratio of 0.51% at 270 K and 0.58% at 300 K, as shown in Fig. 8(c). A comparison of Fig. 8(a) and (c) shows an interesting phenomenon: the change in amplitude of the resistivity from that of the polycrystalline ferromagnetic conductor, $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, to that of the



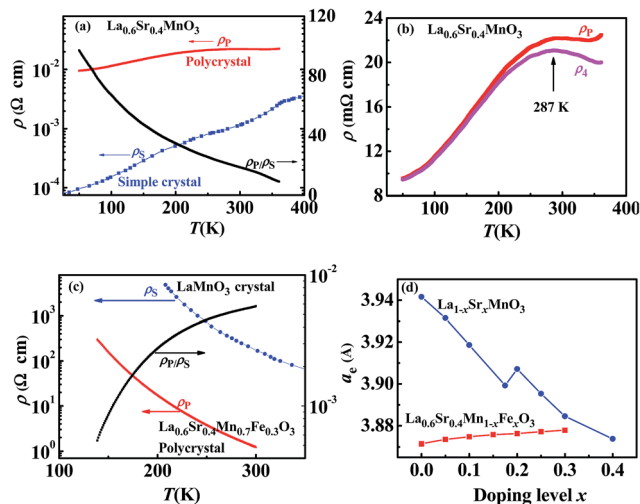


Fig. 8 (a) Temperature dependence of the resistivities, ρ_P and ρ_S ,⁴¹ of polycrystalline and single-crystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, and their ratio, ρ_P/ρ_S . (b) Temperature dependence of the observed resistivity, ρ_P , and the estimated resistivity resulting from crystallite interface scattering, ρ_4 , of polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. (c) Temperature dependence of ρ_P of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.3}\text{Mn}_{0.7}\text{O}_3$ and ρ_S of LaMnO_3 , and their ratio, ρ_P/ρ_S . (d) Dependence of the equivalent cubic cell constant, a_e , of the single-crystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ samples⁴¹ and the polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ samples on the doping level, x .

antiferromagnetic semiconductor, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.3}\text{Mn}_{0.7}\text{O}_3$, is far lower than the change in amplitude of the resistivity from that of the single-crystalline ferromagnetic conductor, $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, to that of the antiferromagnetic semiconductor, LaMnO_3 . The primary causes of this phenomenon may be the distinct difference in the crystal-cell constants of the two systems, and the proportion of the antiferromagnetic phase. The equivalent cubic cell constants (a_e) of single-crystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (ref. 41) and polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ are shown in Fig. 8(d), which were calculated using the average volume per formula of each sample. The samples of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0.0 \leq x \leq 0.3$) and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.175 \leq x \leq 0.40$) exhibited rhombohedral structures, while $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.00 \leq x \leq 0.15$) was reported to have an orthorhombic structure.⁴¹ The value of a_e of the polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ is very close to that of the single-crystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. However, the value of a_e of polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ prepared in our study increased from 3.872 Å ($x = 0.00$) to 3.878 Å ($x = 0.30$), while the value of a_e of single-crystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ was reported to increase from 3.874 Å ($x = 0.40$) to 3.942 Å ($x = 0.00$). According to previous investigations,^{37,38} there are only Mn^{3+} cations in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.15 \leq x \leq 0.40$). Therefore, the increase in resistivity from $x = 0.40$ to $x = 0.15$ occurred because of the increase in the crystal-cell constant, while the increase in resistivity from $x = 0.15$ to $x = 0.00$ occurred because of increases in both the crystal-cell constant and the proportion of the antiferromagnetic phase.

Obviously, an increase (in increments of 0.01 Å, for example) in a_e may rapidly reduce the transition probability of the itinerant electrons whenever spin-dependent or spin-independent transitions take place, resulting in an increase in the

resistivity. This may be the reason the samples of $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ and $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ exhibited high resistivity at low temperatures, as shown in Fig. 5. For the sample of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$, $\rho > 500 \Omega \text{ cm}$ when $T < 10 \text{ K}$ because of the large crystal lattice constant, a_e , which resulted in a lower spin-dependent transition probability of the itinerant electrons. The value of ρ decreased with increasing T below 202 K because of the thermal energy of the itinerant electrons, which resulted in an increase in their spin-dependent transition probability. In the temperature range of 202–234 K, ρ increased with increasing T because the spin orientation of the itinerant electrons and local electrons of the outer O 2p and Mn 3d orbits deviated from their ground state direction, resulting in a decrease in their spin-dependent transition probability.

4.5 Activation energy (E_3) of spin-independent electron transition

The values of the activation energy, E_3 , of the spin-independent electron transition in the polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0.00 \leq x \leq 0.30$) samples ranged from 65.0 to 124.5 meV (see Table 3), which are similar to the values (90.5 to 148.3 meV) of the polaron activation energy, E_p , obtained by Liu *et al.* with the CCDC model for $\text{La}_{0.7}\text{Ca}_{0.3}\text{Ti}_x\text{Mn}_{1-x}\text{O}_3$ ($0.00 \leq x \leq 0.07$).¹⁸ The comparable results indicate that the TCET model in this work is similar to the CCDC model.^{13,14,18–20} However, the physical mechanism of the TCEP model, which includes spin-dependent and spin-independent electron transitions, is easier to be understood than that of the CCDC model, which assumes that the current-carrier density changes sharply at the magnetic-transition temperature.

Tables 2 and 3 show that among the ferromagnetic samples, E_3 of polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (65.0 meV) is far higher than that of single-crystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (0.05 meV) owing to scattering at the crystallite interfaces in the polycrystalline sample. However, among the antiferromagnetic samples, E_3 of polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.3}\text{Mn}_{0.7}\text{O}_3$ (124.5 meV) is distinctly lower than that of antiferromagnetic LaMnO_3 (175 meV), which may have been caused by the different crystal-cell constants, as discussed in the previous section.

The value of the parameter a_3 (0.0044 Ω cm, see Table 3) of the polycrystalline conductor, $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, is very close to that of the single-crystalline conductor, $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (0.0041 Ω cm, see Table 2). However, the value of a_3 (0.0114 Ω cm) of the polycrystalline semiconductor, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.3}\text{Mn}_{0.7}\text{O}_3$, is far lower than that of the single-crystalline semiconductor, LaMnO_3 (0.2440 Ω cm). This may be attributed to the effect of the crystal-cell constant, as discussed in Section 4.4.

4.6 Regression coefficients of ρ_1 and ρ_2

As shown in eqn (2) and Tables 2 and 3, the spin-dependent resistivities, ρ_1 and ρ_2 , are represented by parameters (or regression coefficients) that play interesting roles:

(i) The resistivity ρ_1 in eqn (2) is determined by three parameters: the residual resistivity, ρ_0 ; the parameters a_1 and T_1 resulting from scattering by the crystal lattice. All three parameters of the polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$



samples— $\rho_0 = 0.0072$ to $1.100 \text{ } \Omega \text{ cm}$, $a_1 = 2.794 \times 10^{-10}$ to $1.159 \times 10^{-6} (\text{ } \Omega \text{ cm}) \text{ K}^{-3}$, $T_1 = 150$ to 20 K —are higher than those of the single-crystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ samples— $\rho_0 = 0.075$ to $0.95 \text{ m}\Omega \text{ cm}$, $a_1 = 4.2 \times 10^{-11}$ to $2.4 \times 10^{-10} (\text{ } \Omega \text{ cm}) \text{ K}^{-3}$, and $T_1 = 35$ to 10 K —because of the effect of crystallite interfaces in the polycrystalline samples.

(ii) The resistivity ρ_2 in eqn (2) is determined by two parameters: the amplitude a_2 ; the activation energy E_2 , which originated from spin-dependent scattering. The value of E_2 of the single-crystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ samples increased from 0.515 eV ($x = 0.15$) to 0.88 eV ($x = 0.40$), which was the result of competition between two factors. One factor was the increase in the cant angle between magnetic moments of Mn^{3+} cations from 0 ($x = 0.15$) to 34.9° ($x = 0.40$).³⁷ Another factor was the decrease in crystal cell volume with increasing x . The value of E_2 of the polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ samples increased from 0.06 eV ($x = 0.00$) to 0.12 eV ($x = 0.15$), which can be attributed to the increase in Fe-doping level because the magnetic moments of Fe^{3+} cations couple antiferromagnetically with those of Mn^{3+} cations.³⁹ The a_2 values of the polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ samples are far lower than those of the single-crystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ samples, possibly because of the intense scattering at the crystallite interfaces to reduce the effect of spin-dependent scattering.

5. Conclusion

In order to explain the dependence of the resistivity (ρ) of perovskite manganites on the test temperature (T), we propose a model with two channels of electrical transport (TCET): a spin-independent channel (with resistivity ρ_3) and a spin-dependent channel (with resistivity $\rho_1 + \rho_2$). At low temperature, ρ_3 is very high, and the electrical transport occurs along the spin-dependent channel. When T is far lower than the Curie temperature (T_C), ρ is very close to ρ_1 , which increases with increasing T owing to the thermal vibration of the crystal lattice. When T is close to T_C , ρ_2 increases rapidly owing to the spin orientations of the itinerant electrons, and the local electrons of the outer O 2p and Mn 3d orbits deviating from the orientation of their ground states. Therefore, the spin-dependent electrical transport in perovskite manganites at temperatures below T_C is distinctly different from the spin-independent electrical transport in metals. When T is higher than T_C , the spin orientations of the itinerant electrons change into disorder, and electrical transport occurs along both channels, with the spin-independent transition, ρ , being close to ρ_3 .

Several determining factors of the resistivity have been discussed: (i) the increase in the proportion of the antiferromagnetic phase may result in an increase in ρ . (ii) The resistivity ρ_4 originating from crystallite-interface scattering in the polycrystalline samples is far higher than ρ_1 and ρ_2 at temperatures below T_C . (iii) Increases in the crystal-cell constant, in increments as small as 0.01 \AA , may result in rapid increases in ρ , which may be the reason of the high resistivity of $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ and $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ at low temperatures.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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