

Effects of Ru substitution for Mn on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ perovskites

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We report the investigations of crystal structure, electrical resistivity (ρ), magnetization (M), x-ray photoelectron spectroscopy (XPS), specific heat (C_p), thermal conductivity (κ), and thermoelectric power (TEP) on $\text{La}_{0.7}\text{Sr}_{0.3}(\text{Mn}_{1-x}\text{Ru}_x)\text{O}_3$ (LSMRO) compounds with $x=0$ to 0.90. From the analyzes of crystal structure and magnetization measurements, it is inferred that Ru should have a mixed valence of Ru^{3+} and Ru^{4+} for LSMRO with low level of Ru substitution, and an additional mixed valence of Ru^{4+} and Ru^{5+} with higher Ru substitution. Such a finding is further confirmed by the XPS measurements. Besides, it is found that all measured physical properties undergo pronounced anomalies due to the ferromagnetic-paramagnetic phase transition, and the observed transport properties of LSMRO can be reasonably understood from the viewpoint of polaronic transport. The Curie temperatures T_C determined from the magnetization measurements are consistently higher than those of the metal-insulator transitions T_{MI} determined from the transport measurements. By replacing Mn with Ru, both T_C and T_{MI} decrease concurrently and the studied materials are driven toward the insulating phase with larger value of x . It is also found that the entropy change during the phase transition is reduced with more Ru substitution. These observations indicate that the existence of Ru has the effect of weakening the ferromagnetism and metallicity of the LSMRO perovskites. © 2007 American Institute of Physics. [DOI: 10.1063/1.2761690]

I. INTRODUCTION

The hole-doped mixed-valence perovskite manganites of type $R_{1-x}A_x\text{Mn}_{1-y}B_y\text{O}_3$ (where R is a trivalent rare earth and A is a divalent alkali earth, and B denotes the transition metals) have attracted considerable attention during the past decade. In these perovskite compounds, the interplay between magnetism, charge ordering, and electronic transport have been studied in detail.¹⁻⁴ In particular, the metal-insulator transition near the Curie temperature in this class of materials have been interpreted in terms of the double exchange (DE) model, in which a strong exchange interaction occurs between Mn^{3+} and Mn^{4+} ions through intervening filled oxygen $2p$ states.^{5,6} In addition, there are some other mechanisms that have provided valuable insight into the colossal magnetoresistance (CMR) phenomenon in the manganites, such as the antiferromagnetic superexchange, Jahn-Teller effects, orbital and charge ordering.⁷⁻⁹ The knowledge of the crystal structure and the chemical bonding of these compounds is of capital importance to the understanding of the peculiar magnetotransport properties in these perovskites. It is known that the A -site substitution changes primarily the carrier density and affects strongly the Mn^{3+} -O- Mn^{4+} angle (lattice distortion), thus transforming the parent compound RMnO_3 from an insulating antiferromagnet into a metallic ferromagnet.⁴ On the other hand, the B -site substitution is a direct way of modifying the crucial Mn^{3+} -O- Mn^{4+} network.

The effect of substitution of Mn^{3+} ions in the B site by trivalent ions such as Fe, Ti, and Sc on ferromagnetism and CMR of these manganites has been studied.¹⁰⁻¹² It was experimentally found that any modification on the exchange interaction causes the pair-breaking effect associated with a drastic reduction in Curie temperature T_C . For example, T_C reduced by about 22 K for only 1 at. % Fe substitution for Mn in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$.¹⁰ Other $3d$ transition metals such as Ti, Co, and Ni have similar substitution effect as Fe.¹¹ However, it was reported that as high as 30 at. % of Ru can be substituted into the Mn sites in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ with no change in the crystal structure and has a weak effect on the reduction in T_C .¹³ It is argued that Ru has a more delocalized $4f$ orbital with itinerant t_{2g} electrons that facilitates the exchange coupling interaction. That is, Ru could make a magnetic pair with Mn to form the Mn-O-Ru network, thus favoring the DE-mediated transport mechanism. Enhanced magnetic and metal-insulator transition temperature in Ru-doped layered manganites $\text{La}_{1.2}\text{Ca}_{1.8}\text{Mn}_{2-x}\text{Ru}_x\text{O}_7$ has been reported.¹⁴ Even though a large number of studies on the Ru-doped manganites have been done, the valence state of Ru, which governs the relationships between the magnetism and transport properties of these compounds, is still a subject of debate. Krishnan and Ju reported the x-ray photoelectron spectroscopy (XPS) of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Ru}_{0.1}\text{O}_3$ in which the $\text{Ru}^{3+}/\text{Ru}^{4+}$ mixed state was suggested.¹⁵ On the other hand, Sahu and Manoharan presented the x-ray absorption spectra of the Ru $L_{2,3}$ edge in $\text{La}_{0.6}\text{Pb}_{0.4}\text{Mn}_{1-x}\text{Ru}_x\text{O}_3$ and showed a clear signature of the existence of Ru^{5+} up to $x=0.2$.¹⁶ Recent XPS

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spectra in Ru $3d_{5/2}$ region on $\text{La}_{0.45}\text{Sr}_{0.55}\text{Mn}_{0.6}\text{Ru}_{0.4}\text{O}_3$ also shows the existence of both Ru^{4+} and Ru^{5+} for the Ru ion.¹⁷ However, a x-ray absorption spectroscopy measurement has given a clear proof that Ru^{5+} is absent in the Na-doped $\text{La}_{1-x}\text{Na}_x\text{Mn}_{1-y}\text{Ru}_y\text{O}_{3+\delta}$ manganites.¹⁸ According to these XPS results the valence state of Ru in manganites has not yet reached a consensus, and thus the source of ferromagnetic interaction between Ru and Mn ions still remains an open question. Therefore, it is worthwhile examining this important issue with further consideration. Up to now, although a large number of investigations focused on the electronic and magnetic properties of the LSMRO compounds,^{13,15–22} only a few studies regarding thermal properties or higher level of Ru substitution ($x \geq 0.4$) were reported in the literature. In this article, we report a throughout investigation of crystal structure, resistivity, magnetization, x-ray photoelectron spectroscopy, specific heat, thermal conductivity, and thermoelectric power of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ru}_x\text{O}_3$ with $x=0$ to 0.90. A discussion of the valence state of Ru based on the results of crystal structure, saturation magnetization and XPS is given. The observed transport properties of LSMRO can be reasonably understood from the viewpoint of polaronic transport. Information of such a study makes it possible to determine a full range of physical properties in these Ru-doped manganites.

II. EXPERIMENTAL METHOD

Polycrystalline samples of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ru}_x\text{O}_3$ (LSMRO) were synthesized by a conventional solid-state reaction method, using the starting materials of La_2O_3 , SrCO_3 , MnCO_3 , and RuO_2 powders. Stoichiometric mixture of powders were ground and reacted at 1100 °C for 24 h in air. The samples were reground, pressed into pellets, and heated again at 1500 °C for 24 h. This procedure was repeated and the samples were finally cooled to room temperature at the rate of 5 °C/min in the last step. The syntheses were kept at the same conditions to prevent the composition variation among the samples. The x-ray powder diffraction (XRD) data were collected at room temperature from 20° to 80° with a 2θ step of 0.01° using a diffractometer (Shimadzu XRD6000, Japan) with Cu $K\alpha$ radiation. The resistivities and magnetizations of samples were obtained by a standard dc four-terminal method, and by a superconducting quantum interference device (SQUID) magnetometer, respectively. For analyzing the valence state of Ru, XPS (VG Scientific ESCALAB 250) with an experimental resolution of 0.02 eV was carried out, using photons of energy of 1253.6 eV from a Mg $K\alpha$ radiation source. Relative specific heats (C_p) were measured with a high-resolution ac calorimeter, using chopped light as a heat source. Thermal conductivity (κ) and thermoelectric power (TEP) measurements were carried out simultaneously in a close-cycle refrigerator by using a direct heat-pulse technique. The details of the measurement techniques can be found elsewhere.²³

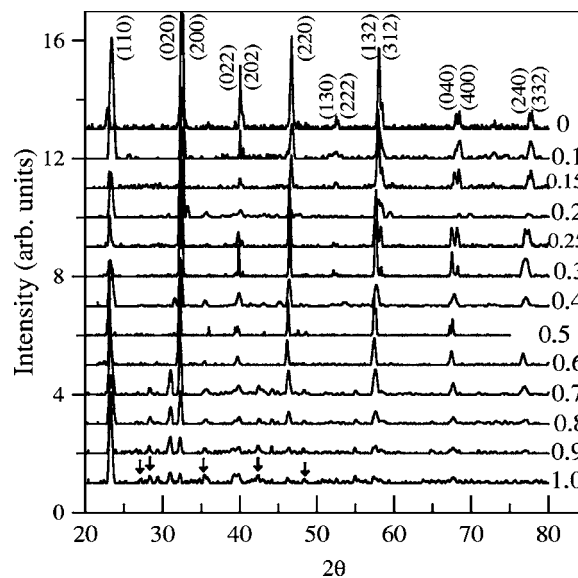


FIG. 1. Typical θ - 2θ x-ray diffraction spectra of LSMRO with $x=0$ -1.0. The arrows indicate the impurity phases of SrO_2 and La_2O_3 .

III. RESULTS AND DISCUSSION

A. Crystal structure

Figure 1 shows the typical θ - 2θ x-ray diffraction spectra of LSMRO with $x=0$ -1.0. As can be seen, the obtained diffraction spectra are consistent with the expected perovskite structure and can be indexed in an orthorhombically distorted structure of space group $P2_1/c$. It is noted that for LSMRO with $x > 0.7$, impurity phases such as SrO_2 and La_2O_3 were detected. The intensity of the strongest impurity peaks is around 5% of the main phase. For $\text{La}_{0.7}\text{Sr}_{0.3}\text{RuO}_3$ ($x=1$), some diffraction peaks remained unindexed, owing to unidentified impurity phases. Unknown impurity phases have also been observed in $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ polycrystalline samples.⁹ The influence of little impurity phases on the transport properties is thought to be ignorable for LSMRO with $x > 0.7$ due to the insulating impurities of SrO_2 and La_2O_3 . However, the magnetization contributed from the impurity is subtracted. Figures 2(a) and 2(b) show the lattice parameters and the unit cell volume V_{cell} as a function of Ru concentration (x) of LSMRO compounds, respectively. It is clearly seen that the lattice parameters a and b increase monotonously with Ru concentration, while the lattice parameter c increases initially for LSMRO for $x < 0.6$ and then decreases and saturates with higher level of substitution ($x \geq 0.6$). The variation of V_{cell} shows similar behavior to that of c -axis lattice parameter. The increase of lattice parameters at low levels of Ru substitution has also been observed in Ru-doped $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ samples.²⁴ The variation of lattice parameters provides us valuable information to the valence state of Ru in these compounds. Since Ru^{3+} (0.68 Å) and Ru^{4+} (0.62 Å) have larger ionic radii compared with that of the Mn^{3+} (0.65 Å)- Mn^{4+} (0.52 Å) pair, it is inferred that Ru should have a mixed valence of Ru^{3+} and Ru^{4+} , which could account for the observed increase in the lattice parameters for LSMRO with low level of Ru substitution ($x < 0.6$). In view of the fact that lattice parameters decrease with further

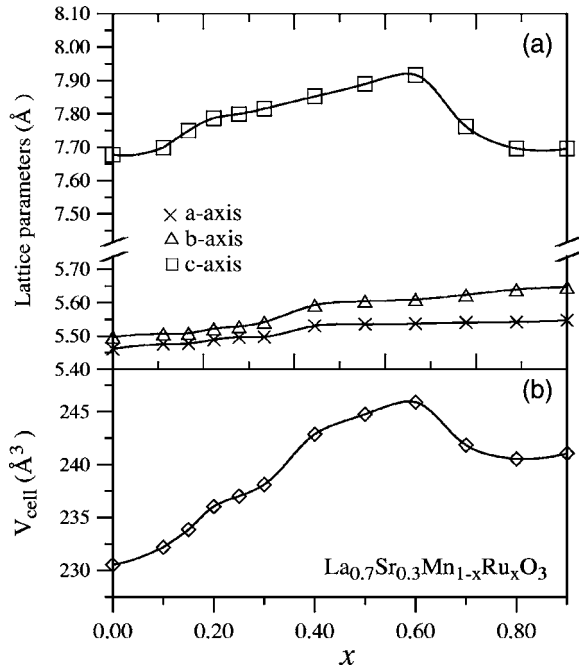


FIG. 2. (a) Lattice parameters and (b) unit cell volume V_{cell} as a function of Ru concentration (x) of LSMRO compounds.

Ru substitution ($x \geq 0.6$), it is expected that an additional valence of Ru^{5+} (0.56 \AA) might exist in the highly substituted compounds. As previously mentioned, the valence state of Ru in manganites is still under debate, we will further examine this issue in the following sections with further consideration.

B. Magnetization

Figure 3 shows the temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization for LSMRO. As can be seen, all the LSMRO samples undergo a paramagnetic to ferromagnetic phase transition. It is found that the Curie temperature T_C , determined by extrapolating linearly the temperature dependence of magnetic susceptibility $1/\chi$ in the paramagnetic state, decreases with increasing x . The variance of Curie temperature T_C versus Ru concentration for $x \leq 0.25$ is tabulated in Table I. The observed decrease of T_C is in good agreement with that reported in Ref. 15. This magnetic-transition behavior reveals the long-range ferromagnetic ordering up to $x=0.9$, indicating strong ferromagnetic exchange coupling between Mn and Ru centers. Interestingly, the difference between the ZFC and FC magnetization results is more pronounced with larger Ru substitution level, and the ZFC magnetization shows a sharp de-

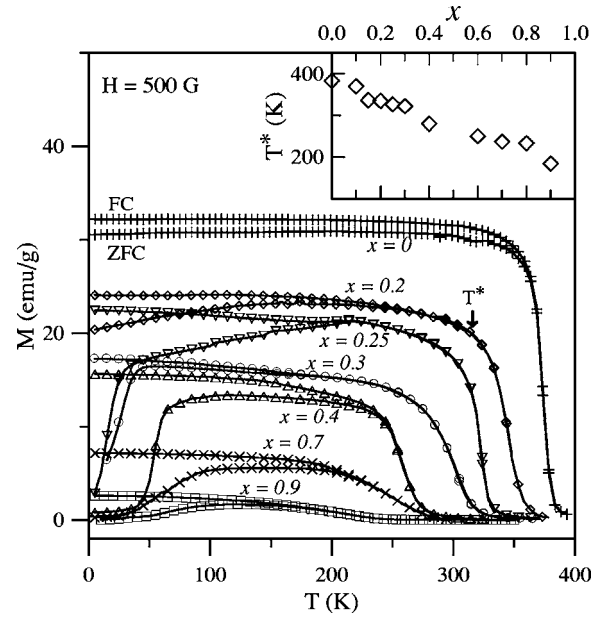


FIG. 3. Temperature dependences of the zero-field-cooled and field-cooled magnetization for LSMRO. The inset shows the irreversibility temperature T^* as a function of Ru concentration.

crease at low temperatures. This large thermomagnetic irreversibility has also been observed by others and interpreted as a cluster glass behavior.^{12,24} Such a feature is attributed to a spin freezing below the irreversibility temperature T^* , being often observed in inhomogeneous magnetic systems with ferromagnetic grains embedded in a nonferromagnetic background. On the contrary, the difference between FC and ZFC curves observed in the LSMRO samples becomes less obvious with lower Ru substitution ($x < 0.2$), reflecting the domain-motion character and larger ferromagnetic grains in the samples. For $x > 0.25$, strong irreversibility of the ZFC and FC magnetization is observed around the irreversibility temperature T^* , where the ZFC magnetization shows a peak, and below the peak, the magnetization decreases sharply with decrease of temperature, suggesting a spin-freezing behavior.²⁴ This indicates that the spin glass or cluster glass state appears for higher Ru doped samples. The irreversibility temperature T^* decreases with an increase in Ru substitution, as seen in the inset of Fig. 3. These $M(T)$ behaviors are similar to those observed in Ru-doped $\text{La}_{0.6}\text{Pb}_{0.4}\text{Mn}_{1-x}\text{Ru}_x\text{O}_3$ samples.¹⁶

Figure 4 shows typical hysteresis loops of the LSMRO compounds measured at 5 K. As can be seen, there is an increase in the coercive field with increasing Ru substitution, implying that the domain wall pinning increases with increasing x . Furthermore, the value of saturation magnetiza-

TABLE I. Parameters on transport and thermodynamic properties for LSMRO.

Sample	T_C (K)	T_{MI} (K)	$T_{c,\text{CP}}$ (K)	$\Delta S(\text{R})$	$T_{c,k}$ (K)	$T_{c,\text{TEP}}$ (K)	E_S (meV)
$x=0.00$	377	362.6	360.5	0.3376	367.1	367.1	33
$x=0.10$	369	362.7	358.5	0.3153	363.4	363.4	28
$x=0.15$	365	344.3	340.7	0.2993	349.0	349.0	8.1
$x=0.20$	359	337.4	330.4	0.2503	337.4	337.4	6.7
$x=0.25$	328	317.7	309.7	0.1870	314.3	314.3	0.83

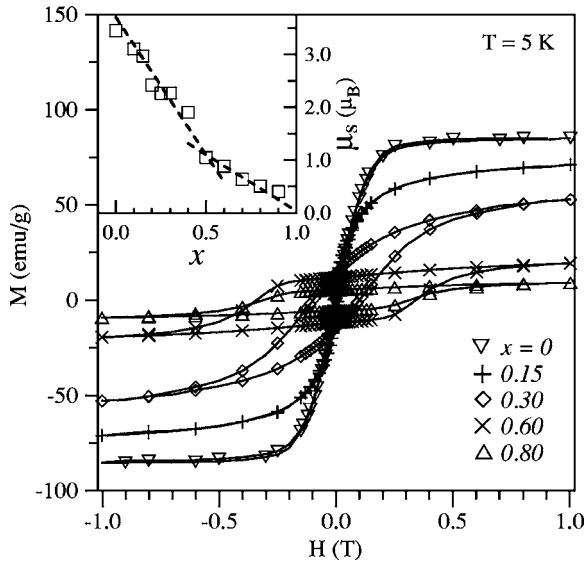


FIG. 4. Hysteresis loops of the LSMRO measured at 5 K. The inset shows the magnetic moment μ_s for Mn/Ru site as a function of Ru concentration. The dashed lines indicate the μ_s calculated by Eqs. (1) and (2) for both $x \leq 0.5$ and $x > 0.5$ as a function of x .

tion M_S can be approximately obtained from the high-field magnetization. The inset of Fig. 4 shows the magnetic moment μ_s for the Mn/Ru site estimated from the experimental M_S value as a function of Ru concentration. The obtained μ_s for the $x=0$ compound is $3.45 \mu_B$, close to the theoretical value of $3.67 \mu_B$. As seen in the inset of Fig. 4, it is noted that μ_s decreases quasilinearly with increase in x , but a noticeable slope change is observed at $x=0.5$. Recall that similar variations of V_{cell} and c -axis lattice parameter compounds were observed in these LSMRO. We connect these features to the appearance of different valence states of Ru ions in the low-doping (Ru^{3+}) and high-doping regions (Ru^{5+}). It has been proposed that Ru^{3+} , with a half-filled shell electronic configuration, will result in a local antiferromagnetic coupling with neighboring Mn ions.¹⁸ On the contrary, the introduction of Ru^{3+} will lead to ferromagnetic coupling with Mn spins, which has been proposed for $\text{Sm}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{Ru}_y\text{O}_3$ series.²⁵ A detailed discussion of the valence states of Ru is given in next section.

C. Valence state of Ru

With the assumption that a mixed valence of $\text{Ru}^{3+}/\text{Ru}^{4+}$ in the lower-doping region ($x \leq 0.5$) while an additional mixed valence of $\text{Ru}^{4+}/\text{Ru}^{5+}$ appears in the high-doping region ($x > 0.5$), we can make a rough estimation for the magnetic moment of these LSMRO samples. The compounds with a chemical formula $\text{La}_{0.7}\text{Sr}_{0.3}(\text{Mn}_{1-x}\text{Ru}_x)_{0.7}^{3+}(\text{Mn}_{1-x}\text{Ru}_x)_{0.3}^{4+}\text{O}_3$ (for $x \leq 0.5$) lead to a ferromagnetic moment of

$$\mu_S(x \leq 0.5) = [4(0.7 - 0.7x) - 3(0.7x) + 3(0.3 - 0.3x) + 2(0.3x)]\mu_B = (3.7 - 5.2x)\mu_B, \quad (1)$$

where $\mu_{\text{Mn}^{3+}} = 4 \mu_B$ ($t_{2g}^3 e_g^1$ state), $\mu_{\text{Mn}^{4+}} = 3 \mu_B$ ($t_{2g}^3 e_g^0$ state), $\mu_{\text{Ru}^{3+}} = 3 \mu_B$ (t_{2g}^5 state), and $\mu_{\text{Ru}^{4+}} = 2 \mu_B$ (low-spin t_{2g}^3 state) are used. For the higher-doping LSMRO with $x > 0.5$, it can

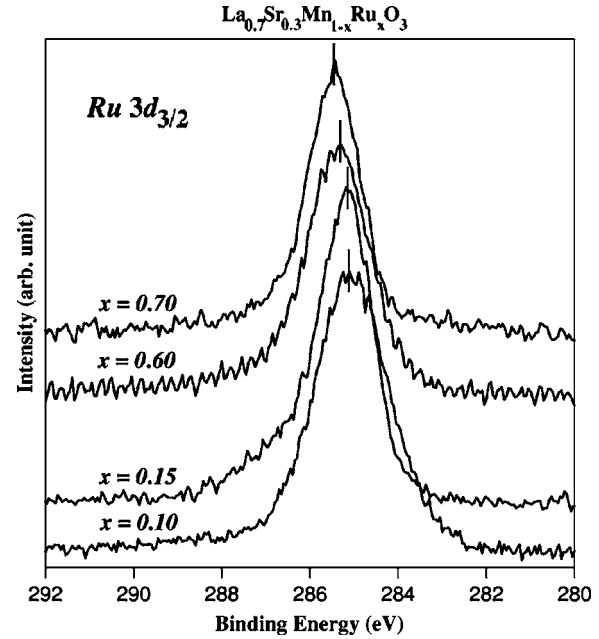


FIG. 5. X-ray photoelectron spectra of $\text{La}_{0.7}\text{Sr}_{0.3}(\text{Mn}_{1-x}\text{Ru}_x)\text{O}_3$. It is clearly seen that the $\text{Ru } 3d_{3/2}$ peak shifts to higher energy for the high-doping ($x > 0.5$) samples.

be simply assumed that the increasing Ru concentration has the valence of Ru^{5+} . As a result, the chemical formula for the high Ru substituted compounds can be represented by $\text{La}_{0.7}\text{Sr}_{0.3}(\text{Mn}_{1-x+3/7y}\text{Ru}_{0.5})_{0.7}^{3+}(\text{Mn}_{1-x-y}\text{Ru}_{0.5})_{0.3}^{4+}\text{Ru}_{x-0.5}^{5+}\text{O}_3$, where y is the reduced component of Mn^{4+} due to the presence of Ru^{5+} . According to the conservation of total valence, it can be obtained that $y = \frac{17}{9}(x - 0.5)$, and the ferromagnetic moment for $x > 0.5$ is

$$\mu_S(x > 0.5) = \left(\frac{13}{6} - \frac{6.4}{3}x \right) \mu_B, \quad (2)$$

where $\mu_{\text{Ru}^{5+}} = 1 \mu_B$ (low-spin t_{2g}^3 state) parallel to the Mn and Ru^{4+} moments is used. Equations (1) and (2) satisfy the situation that (1)=(2)=1.1 μ_B with $x=0.5$. The calculated μ_S as a function of x is also shown in the inset of Fig. 4 by dotted lines using Eqs. (1) and (2). As can be seen, the calculated μ_S is in excellent agreement with the experimental μ_S .

In order to confirm the validity of our proposed assumption on the variation of valence states of Ru ion in these $\text{La}_{0.7}\text{Sr}_{0.3}(\text{Mn}_{1-x}\text{Ru}_x)\text{O}_3$ compounds, XPS spectra were carried out to directly examine the evolution of the valence of Ru with respect to x . Figure 5 shows the Ru XPS spectra for samples with different Ru concentrations. It is found that the $\text{Ru } 3d_{3/2}$ peak positions at the binding energy of 285.1 eV, which is in agreement with the reported results.²⁶ The binding energy shifts systematically to the higher energy side with increasing x , which indicates that the Ru valence increases with the doping, and such a variation of binding energy was also observed in Ru-doped $\text{La}_{0.45}\text{Sr}_{0.55}\text{MnRuO}_3$.¹⁷ It was argued that the variation of Ru valence in these manganites is presumably due to the comparable reduction oxidation potential $\text{Ru}^{4+}/\text{Ru}^{5+}$ (1.07 eV) and $\text{Mn}^{3+}/\text{Mn}^{4+}$ (1.02 eV). As a result, Mn^{4+} gets reduced to the Mn^{3+} state while

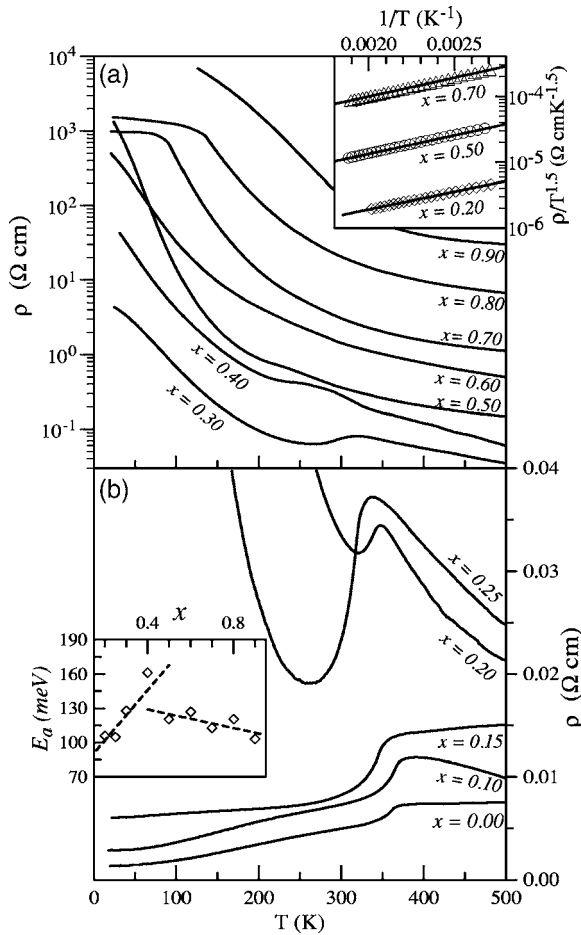


FIG. 6. Temperature-dependent resistivities between 20 to 500 K of LSMRO with (a) $x \geq 0.3$ and (b) $x \leq 0.25$. Inset of (a): the $\rho/T^{1.5}$ versus $1/T$ plots for LSMRO with $x=0.2, 0.5$, and 0.7 . The solid lines are the fitting of Eq. (3). Inset of (b): resistivity activation energy E_a as a function of x . The dashed lines are for guiding the eyes.

Ru^{4+} gets oxidized to the Ru^{5+} state.²⁷ Such a phenomenon is unambiguously revealed by our present crystal structure, saturation magnetization, and x-ray photoelectron spectroscopy measurements.

D. Resistivity

The temperature-dependent resistivities (ρ versus T) between 20 to 500 K of LSMRO are shown in Figs. 6(a) and 6(b) for $x \geq 0.3$ and $x \leq 0.25$, respectively. In general, we found that an increase in Ru substitution for Mn causes a substantial growth on the electrical resistivity of LSMRO. It is seen that the system exhibits metallic behavior (positive temperature coefficient) for low Ru substitution samples ($x \leq 0.15$), but shows semiconducting characteristics (negative temperature coefficient) for high Ru substitution samples ($x \geq 0.25$). With decreasing temperature, noticeable decrease in ρ marks the occurrence of metal-insulator transitions in the low Ru substitution samples. The metal-insulator transition temperature T_{MI} , determined from the maximum of $d\rho/dT$, increases initially on Ru substitution ($x=0.10$), then decreases upon further substitution of Ru ions, and finally disappears with $x \geq 0.50$ in this series of materials, as the resistivity shows no sign of anomaly but exhibits insulating

behavior for $x=0.5$. In Table I, we list the metal-insulator transition temperature T_{MI} with respect to respective compositions for this series of compounds with $0 \leq x \leq 0.25$. It is clearly seen from Table I that the Curie temperatures T_{C} determined from the magnetization measurements are consistently higher than those of the metal-insulator transitions T_{MI} determined from the electrical resistivity measurements, i.e., the metal-insulator transitions take place in the ferromagnetic phase. Such a behavior was also observed in the $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Ru}_x\text{O}_3$ system, and the discrepancies between different transition temperatures were ascribed to the coexistence and competition between $\text{Mn}^{3+}\text{-Mn}^{4+}$ double exchange and $\text{Mn}^{3+}\text{-Ru}^{4+}$ (Ru^{5+}) ferromagnetic superexchange interaction.¹⁷

A semiconductinglike characteristics for $0.25 \leq x \leq 0.40$ samples below T_{MI} 's is observed, and it can be explained by the charge carrier localization due to doping-induced random magnetic potential. On the other hand, an insulating behavior above T_{MI} for $x \geq 0.2$ is observed, leading to a temperature dependence of ρ which can be described by two approaches. One is the variable-range hopping of electrons in a band of localized states,²⁸ and the other is the polaron formation due to lattice distortion (polaron hopping model).²⁹ It is found that the data can be fitted into the variable-range-hopping equation,²⁸ $\rho = \rho_{\infty} \exp[(T_0/T)^{1/4}]$, to a reasonably good degree with $T_0 \approx (1.4\text{--}18) \times 10^6$ K and $\rho_{\infty} \approx (4\text{--}370) \mu\Omega \text{ cm}$. Even though these fitting parameters are comparable with those obtained in Sc substituting $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$,¹² the obtained prefactor ρ_{∞} is unphysical as discussed by Gayathri *et al.* for Co substituting $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$.³⁰ Typical ρ_{∞} should be of the order of ρ_{Mott} , the maximum metallic resistivity, which is seldom below 1–10 m $\Omega \text{ cm}$ for these oxides.³¹ This makes the variable-range hopping an unreasonable proposition for the electrical transport mechanism of LSMRO.

Alternatively, as shown in the inset of Fig. 6(a), we found that the high-temperature resistivity of LSMRO ($x \geq 0.2$) can be fitted by the nonadiabatic small polaron hopping model

$$\rho = RT^{3/2} \exp\left(\frac{E_a}{k_B T}\right), \quad (3)$$

where R is a constant, E_a is the resistivity activation energy (the potential barrier for polaron hopping), and k_B is the Boltzmann constant. The resistivity activation energy E_a as a function of Ru substitution is shown in the inset of Fig. 6(b). As can be seen, E_a increases rapidly with increase in x for $x \leq 0.4$, but decreases in the higher Ru-doping region ($x \geq 0.5$). The obtained E_a values of 103–161 meV are comparable with those of 135–160 meV for Co substituting $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$.²⁹ It is known that the small polarons can arise from the strong lattice-electron interaction originating from the Jahn–Teller distortion.²⁹ This makes a strong correlation between the lattice constant and E_a . As mentioned above, the V_{cell} increases initially with x for lower-doped LSMRO, and then decreases with higher level of Ru substitution, as seen in Fig. 2(b). It is reasonably believed that E_a increases with the lattice distortion, and the strong Jahn–Teller electron-phonon coupling will increase the tendency

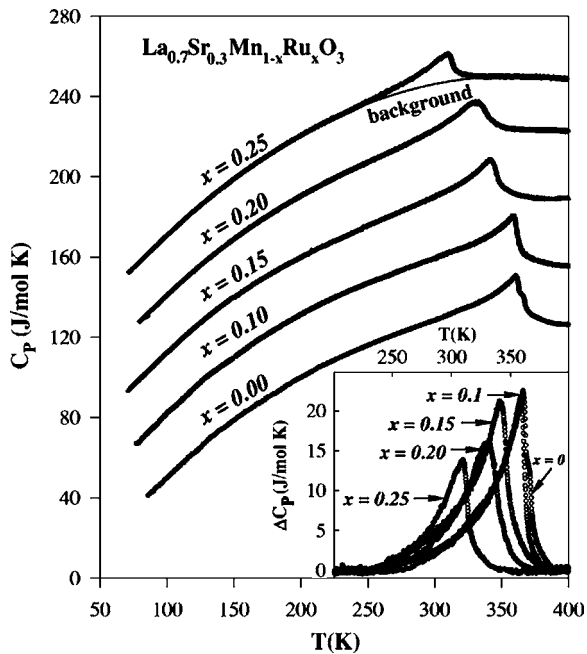


FIG. 7. Temperature dependence of specific heats for LSMRO with $0 \leq x \leq 0.25$. Each curve is offset by 30 J/mol K for clarity. The inset shows the specific-heat jumps with backgrounds subtracted.

of the electrons to become localized. It is apparent that both E_a and lattice constant exhibit similar variation with respect to Ru concentration, suggesting that the polaronic mechanism should be appropriate for the understanding of electrical transport in these LSMRO compounds, and a transport crossover occurring at Ru concentrations around $x=0.5$ can be observed.

E. Heat capacity

The T -dependent specific heat (C_p versus T) of LSMRO with x between 0 and 0.25 is illustrated in Fig. 7. Each curve is offset by 30 (J/mol K) for clarity. Note that ac technique does not give the absolute value of specific heat without detailed knowledge of the power absorbed from the light pulse. The absolute value of the specific heat above 130 K is determined by measuring a powder sample (~ 200 mg) using a differential scanning calorimetry (DSC). The ac results were corrected for their addendum heat capacities (GE varnish and thermocouple wire) and normalized to the DSC data at 200 K. The overall temperature-dependent specific heat of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ($x=0$) is consistent with that reported by Khlopkov *et al.*³² It is found that the specific heat undergoes pronounced peaks due to the ferromagnetic-paramagnetic phase transition in these compounds. The transition temperature T_{c,C_p} , taken as the temperature of peak position, decreases with increasing Ru substitution level and is found to be consistently lower than T_{MI} and T_C , as shown in Table I. Several other reports also suggested that the transition temperature determined from different physical properties may not be the same in these manganites.³³

The specific-heat jumps ΔC_p and entropy change ΔS near the transitions in LSMRO can be estimated by subtracting a smooth lattice background fitted far away from the transition, drawn as a solid curve in Fig. 7. The estimated

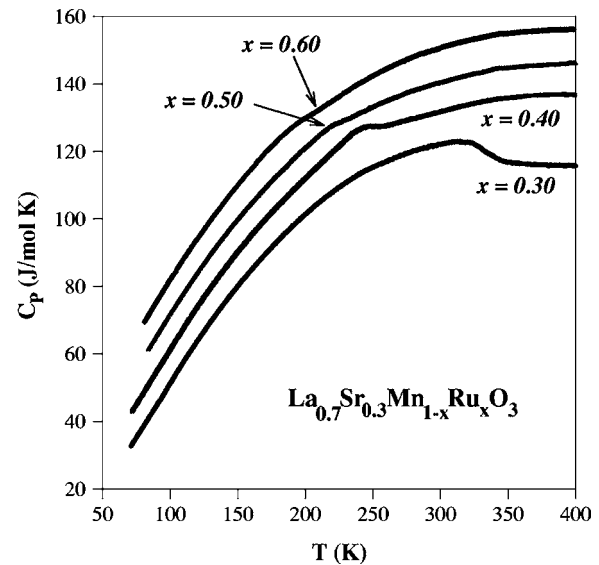


FIG. 8. Temperature dependence of specific heats for LSMRO with $0.30 \leq x \leq 0.60$. Each curve is offset by 10 J/mol K for clarity.

ΔC_p decreases with increasing x , as shown in the inset of Fig. 7. The corresponding entropy changes ΔS , evaluated by integrating the area under $\Delta C_p/T$ versus T curves, are also found to decrease with increasing x . A summary regarding the characteristics of the specific heat anomalies on LSMRO with $0 \leq x \leq 0.25$ is tabulated in Table I. Note that the entropy change ($\Delta S=0.34 R$) for the unsubstituted sample $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is about half that of the theoretical value $R \ln 2$ for a ferromagnetic-paramagnetic phase transition (R is the ideal gas constant). This discrepancy is ascribed to the inhomogeneity of the sample, or partially canted spins in the ferromagnetic state. A small shoulder is noticed around 365 K in the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ($x=0$) sample with our high-resolution ac calorimeter, again presumably owing to the sample inhomogeneity. Such a feature is commonly seen in LSMO polycrystalline samples, however, it becomes essentially invisible for the Ru substituted samples.

The T -dependent specific heat for high level of Ru substituted samples ($x=0.3$ to $x=0.6$) is shown in Fig. 8. In this figure each curve is offset by 10 (J/mol K) for clarity. It is clearly seen that the transition temperature continuously decreases with increasing Ru substitution and the pronounced peak in C_p gradually evolves into a broad hump for $x=0.40$, then a slope change for $x=0.50$. For the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.4}\text{Ru}_{0.6}\text{O}_3$ ($x=0.6$) sample, the anomalous feature is essentially undetectable in C_p , being consistent with the observations by electrical resistivity measurement.

F. Thermal conductivity

Figure 9 shows the observed thermal conductivity (κ) for LSMRO with $0 \leq x \leq 0.25$. As can be seen, the T -dependent thermal conductivities are rather similar for various values of x , except for the anomalous feature near phase transitions. The magnitude of κ is found to be between 10 to 40 mW/cm K in the temperature range we investigated, consistent with the values seen by others.^{34,35} At low temperatures, κ increases with temperature and a maximum ap-

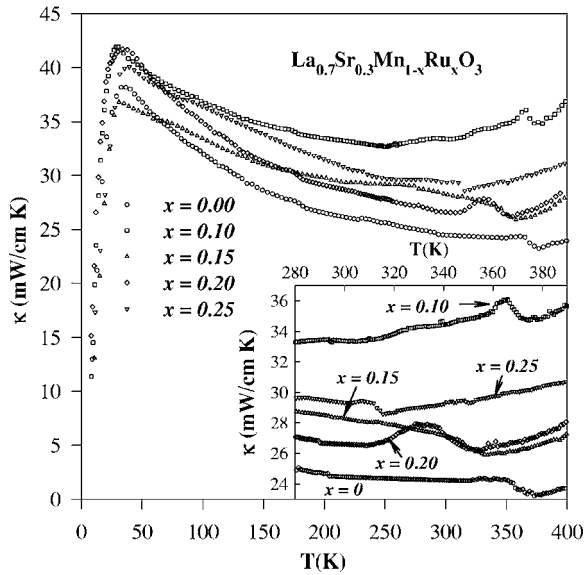


FIG. 9. Temperature-dependent thermal conductivities for LSMRO with $0 \leq x \leq 0.25$. The inset shows the blow-up plot near phase transitions.

pears around 40 K for all studied samples. This is a typical feature for the reduction of thermal scattering in solids at low temperatures. With further increase in temperature, κ decreases with temperature due to the enhanced phonon-phonon scattering (umklapp processes), then gradually saturate at high temperatures. Generally, the total thermal conductivity for ordinary metals and semimetals is a sum of electronic and lattice terms. The electronic thermal conductivity κ_e can be evaluated using the Wiedemann–Franz law $\kappa_e \rho / T = L_0$. Here ρ is the dc electric resistivity and the Lorentz number $L_0 = 2.45 \times 10^{-8} \text{ W}\Omega \text{ K}^{-2}$. From this estimation, it is found that the total thermal conductivity is mainly associated with the lattice phonons rather than the charge carriers, due to the high electric resistivity of these perovskites.

As seen from Fig. 9, all samples show distinct anomalous feature due to the occurrence of the metal-insulator transition. The transition temperatures $T_{c,\kappa}$, determined from the maximum of $d\kappa/dT$, are also listed in Table I for comparison. The inset of Fig. 9 shows a blow-up plot near the phase transitions. Since the thermal conductivity measurements provide valuable information about the various scattering processes of thermal carriers, the present data allows us to probe into the interplay between the lattice, charge, and spin degrees of freedom in these manganites. A common feature for the anomaly at $T_{c,\kappa}$ is that a sharp rise in κ is observed when the samples enter the ferromagnetic state. The anomalous part of thermal conductivity can be expressed as a combination of electronic, phonon, and magnetic contributions, i.e., $\Delta\kappa = \Delta\kappa_e + \Delta\kappa_{\text{ph}} + \Delta\kappa_{\text{mag}}$. The electronic term $\Delta\kappa_e$ could be safely excluded from the expression, since the contribution from charge carriers is insignificant as mentioned before. The anomalous enhancement of thermal conductivity at transition could be attributed to the reduction of phonon-phonon scattering due to the Jahn–Teller distortions, which become delocalized along with the charge carriers.³⁶ However, Ikebe *et al.* have claimed that the phonon alone is far too small to explain the observed enhancement in κ at ferro-

magnetic transitions.³⁴ Therefore, the magnetic contribution $\Delta\kappa_{\text{mag}}$ must be taken into account. It is argued that a suppression of spin-phonon scattering may result from the strong coupling between the lattice and the spin system through the double exchange interaction.³⁷ Another peculiar feature of the observed T -dependent thermal conductivity is that κ increases monotonically with temperature in the paramagnetic state ($T > T_{c,\kappa}$). Such kind of behavior is very unusual, since the high-temperature thermal conductivity of crystalline solids is expected to decrease with temperature according to the well-known formula $\kappa \propto aMC\theta_D/\gamma^2T$, where a is the lattice constant, M is the mass per atom, C is the specific heat, θ_D is the Debye temperature, and γ is the Gruneisen constant with a value ranging from 2 to 3 for solids. These parameters are considered to be a weak function of temperature at high temperatures. As a result, κ decreases with temperature through a reciprocal function of T . However, neutron scattering measurements in these manganites showed that the Gruneisen constant γ is not only much larger (~ 180) than usual, but also decreases markedly with temperature.³⁸ Thus, the increase in κ in the paramagnetic state could be understood with the scenario of local anharmonic lattice distortions.³⁹

G. Thermoelectric power

The temperature-dependent thermoelectric power (TEP) data for LSMRO with $0 \leq x \leq 0.25$ are shown in Fig. 10(a). The behavior of the TEP in these samples shows small and positive values at low temperatures, a signature of p -type conduction and metallic in nature. For all samples, it is seen that the measured TEP increases initially with T , develops into a broad maximum, then changes sign at higher temperatures. This sign change in TEP implies that the electronic state of these samples has been thermally altered from hole-like to electronlike. It is noted that additional maximums were observed around 30 K for $x=0.0$ and 0.15, ascribed to the phonon-drag effect. The phonon-drag peak is commonly seen in metals and is generally active at low temperatures. With further increase in temperature, noticeable anomalous feature, which marks the occurrence of phase transition, is clearly observed. The transition temperatures $T_{c,\text{TEP}}$ determined from the TEP data are tabulated in Table I. In addition to the systematic decrease in $T_{c,\text{TEP}}$ with respect to increasing x value, the temperatures with the sign change in TEP are found to decrease concurrently with $T_{c,\text{TEP}}$. Such an observation implies that the sign change in TEP is closely related to the magnetic property in these manganites, and can be attributed to the polaron transport, as discussed previously in resistivity. The spin polarization changes the electronic nature of charge carriers, and thus the thermoelectric transport.³⁷ Moreover, it is conventionally known that poor conductors usually have a larger TEP than that of good conductors and vice versa. Near $T_{c,\text{TEP}}$, a rapid increase in the absolute value of TEP was observed, corresponding well to the metal-insulator phase transition. For $x=0.10$, a spike-shaped feature at the transition in TEP was observed in this particular composition. Notice that the anomalous feature in κ was also more pronounced for the $x=0.10$ sample (see inset of Fig. 9). Such a finding suggests a possible enhancement of double

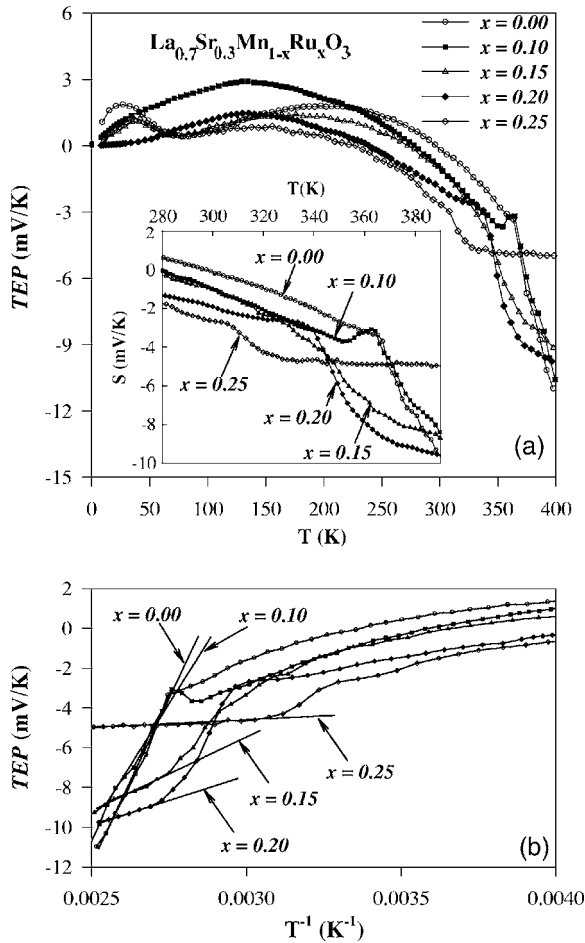


FIG. 10. (a) Thermoelectric power as a function of temperature for LSMRO with $0 \leq x \leq 0.25$. The inset shows the corresponding data at temperatures around the transition temperature. (b) Thermoelectric power TEP versus $1/T$ at high temperatures. The solid lines represent the fits to Eq. (5) in the paramagnetic state.

exchange interaction or/and improvement of the sample homogeneity at the low level of Ru substitution for Mn in these manganites. In view of the fact that both T_C and μ_S appears to be lower in the $x=0.10$ sample as compared with the unsubstituted sample, indicating that the latter scenario is favorable in explaining our experimental observations. It should be noted that similar behavior has been also observed in the specific heat measurements, as we discussed in the previous section. Nevertheless, with further Ru substitution the disorder effect takes over and smears out the peaks in these transport properties.

In the metallic region, the linear variation of TEP is often discussed using the well-known Mott formula

$$S_e = \frac{\pi^2 k_B^2}{3e} T \left(\frac{1}{\sigma(E)} \frac{\partial \sigma(E)}{\partial E} \right)_{E=E_F}, \quad (4)$$

by assuming a one-band model with an energy-independent relaxation time, where e is the elementary charge with a negative sign, and $\sigma(E)$ is the electrical conductivity. Generally a linear dependence of TEP in temperature (diffusive-like) is expected if the simple Mott's expression is obeyed, which is obvious not the case for the presently investigated LSMRO compounds. The deviation of Mott form and small

value of the measured thermoelectric power in the metallic state suggests that both hole and electron contribute to the thermoelectric transport. In the insulating region, the TEP is given by the classical expression

$$S = \pm \frac{k_B}{e} \left(\frac{E_S}{k_B T} + A \right), \quad (5)$$

where E_S is the activation energy for the thermoelectric power, and A is a constant of order unity. In Fig. 10(b), we show a plot of TEP versus $1/T$ of these manganites and the solid lines represent the fits of measured data to Eq. (5) in the insulating phase. It is seen that the high-temperature TEP data can be satisfactorily described using such a thermal-activated model, and the extracted activation energy E_S decreases with increasing x (see Table I). Such kind of E_S dependence on x has also been found in the partially Cr substitution for the Mn sites in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$.³⁹ It is worth mentioning that the activation energy E_a in the paramagnetic state is previously estimated to be of the order of 0.1 eV from electrical resistivity data. If Eq. (5) is valid, the TEP for these samples should be of the order of 1000 $\mu\text{V/K}$, which is two orders of magnitude larger than what we observed. With the fact that the thermoelectric power of this class of materials in the insulating phase is unexpectedly small, suggesting a comparable size of electron pockets and hole pockets in their energy band and these manganites are nearly compensated. Furthermore, the formation of polarons may also be essential to the thermoelectric transport in these materials.⁴⁰

IV. CONCLUSIONS

In conclusion, we have reported detailed investigations of crystal structure, x-ray photoelectron spectroscopy, transport (electrical resistivity, thermal conductivity, and thermoelectric power), and thermodynamic (magnetization and specific heat) properties on $\text{La}_{0.7}\text{Sr}_{0.3}(\text{Mn}_{1-x}\text{Ru}_x)\text{O}_3$ with a full range of x from 0 to 1. Based on the crystalline analyses, the magnetic moment and XPS measurements, it is inferred that Ru should have a mixed valence of Ru^{3+} and Ru^{4+} with lower level of Ru substitution ($x < 0.5$), and an additional mixed valence of Ru^{4+} and Ru^{5+} appears in LSMRO with higher level of Ru substitution ($x \geq 0.5$). It is found that all measured physical properties undergo pronounced anomalous features due to the ferromagnetic-paramagnetic phase transition in these compounds. However, the Curie temperatures T_C determined from the magnetization measurement are consistently higher than that of the metal-insulator transitions T_{MI} determined from the transport measurements. By replacing Mn with Ru, both T_C and T_{MI} decrease concurrently and the studied materials are driven toward the insulating phase with larger x . The transport properties of LSMRO can be reasonably understood in the viewpoint of polaronic transport. It is also found that the entropy change during the phase transition is reduced with increase in Ru substitution. These observations indicate that the existence of Ru has the effect of weakening the ferromagnetism and metallicity on the LSMRO perovskite. The present study constitutes, by far, the most throughout physical measurements

on full range of $\text{La}_{0.7}\text{Sr}_{0.3}(\text{Mn}_{1-x}\text{Ru}_x)\text{O}_3$ manganites, and provides a significant understanding to the valence state of Ru ions and transport mechanism for these compounds.

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