Effect of suppression of local distortion on magnetic, electrical and thermal transport properties of Cr substituted bi-layer manganite LaSr$_2$Mn$_2$O$_7$

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We have investigated magnetic, electrical and thermal transport properties (Seebeck effect and thermal conductivity) of LaSr$_2$Mn$_{2-y}$Cr$_y$O$_7$ polycrystalline samples ($y=0.1, 0.2, 0.4$ and $0.6$). The Cr$^{3+}$ substitution for Mn$^{3+}$ sites causes a removal of $d_{x^2-y^2}$ orbital of $e_g$-electron resulting in a volume shrinkage of lattice. Magnetic measurements reveal the appearance of a glassy behavior for Cr-doped samples, accompanied by both a collapse of the A-type antiferromagnetic structure and the growth of ferromagnetic clusters. Cr-doping effect on electrical transport strongly enhances an insulating behavior over a wide range of temperature, while it suppresses a local minimum of thermoelectric power at lower temperatures. For all polycrystalline samples with Cr-substitution, the variable-range-hopping (VRH) conduction model gives a reasonable fit to both resistivities and Seebeck coefficients. The phonon thermal conduction gradually rises with increasing Cr content, which is in contrast to a typical impurity effect on thermal conductivity. We attribute this to a suppression of local lattice distortion through the introduction of Jahn-Teller inactive ions of Cr$^{3+}$.

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I. INTRODUCTION

The discovery of colossal magnetoresistance (CMR) effect in doped manganites with perovskite structure has stimulated considerable interest for the understanding of their physical properties. Though the insulator to metal (IM) transition and its associated CMR are well explained on the basis of the double exchange (DE) model, it is pointed out that the dynamic Jahn-Teller (JT) effect due to the strong electron-phonon interaction, plays a significant role in the appearance of CMR as well as the DE interaction. Furthermore, Dagotto et al propose a phase separation model where the ferromagnetic (FM) metallic and antiferromagnetic (AFM) insulating clusters coexist and their model strongly supports recent experimental studies on the physics of manganites.

In bilayer manganites La$_{2-x}$Sr$_1+x$Mn$_2$O$_7$, in which a MnO$_2$ bilayer is alternatively stacked with a (La, Sr)$_2$O$_2$ blocking layer along the c-axis, the physical properties strongly depend on hole doping level. In particular, neutron diffraction study on half doped LaSr$_2$Mn$_2$O$_7$($x=0.5$) has revealed the coexistence of the A-type antiferromagnetic (AFM) phase and CETYPE antiferromagnetic charge-ordered/orbital-ordered (CO/OO) phase. It is well known that the CE-type CO/OO state in cubic manganites is unstable against Cr-substitution for Mn-site and lightly Cr doping up to a few percents yields a drastic collapse of the CO/OO phase, resulting in a FM metallic phase even in the absence of any applied magnetic field. While several reports on the effect of Cr substitution on the physical properties of the cubic manganites have appeared, very few reports have appeared on such studies in the case of bilayer manganites. Here, we give some comments on pressure effect on a two-dimensional network of MnO$_6$ octahedra in bilayer manganites La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$. Argyriou et al., reported that the Mn-O(3)-Mn bond angle is almost unchanged by application of pressure, indicating no tilting of the MnO$_6$ octahedra in the ab plane. Thus, it is possible to examine the internal and external pressure effect in bilayered manganites, varying the bond length of the MnO$_6$ octahedra but keeping the bond angle almost $180^\circ$. In this paper, we report magnetic, electrical and thermal transport properties of single-phase LaSr$_2$Mn$_{2-y}$Cr$_y$O$_7$ polycrystalline samples ($y=0.1, 0.2, 0.4$ and $0.6$). The Cr-substitution for Mn sites causes a monotonic shrink of a(b)-axis in contrast with a gradual elongation of c-axis, accompanied by $d_{x^2-y^2}$ orbital deficiencies of $e_g$-electron as listed in Table. The 3d electronic state of Cr$^{3+}$ ion is taken as $t_{2g}^3e_g^0$ (spin quantum number $S=3/2$), resulting in undistorted CrO$_6$ octahedron sites free from local Jahn-Teller effect. This finding is quite reasonable with a volume shrinkage observed due to Cr-doping because a removal of $d_{x^2-y^2}$ orbital...
from Mn$^{3+}$ sites easily causes a suppression of local lattice distortion as discussed later. In the parent material LaSr$_2$Mn$_2$O$_7$, a majority phase of the A-type AFM state coexists with a minority phase of CE-type AFM charge-ordered/orbital-ordered state. We focus our attention on Cr-doping effect on the A-type AFM majority phase because it is expected that the CO/OO minority phase is strongly suppressed by Cr-doping.

II. EXPERIMENT

Polycrystalline samples of LaSr$_2$Mn$_{2-x}$Cr$_x$O$_7$ ($y=0.1, 0.2, 0.4$ and $0.6$) were synthesized by solid-state reaction of La$_2$O$_3$, SrCO$_3$, MnO$_2$ and Cr$_2$O$_3$ powders with high purity. The oxygen concentration of typical samples with $y=0.2$ and $0.6$ was determined using the infrared absorption method because the existence of the Cr ions may affect the valence estimation of Mn ion made by the chemical analysis. The composition of cations was examined by inductively coupled plasma analysis. For the $y=0.2$ and $0.6$ samples, we got La$_{1.02}$Sr$_{2.01}$Mn$_{1.83}$Cr$_{0.19}$O$_{6.99}$ at $y = 0.2$ and La$_{1.01}$Sr$_{1.95}$Mn$_{1.41}$Cr$_{0.59}$O$_{7.05}$ at $y = 0.6$. Thus, we conclude that our samples prepared by the solid state reaction technique are close to nominal compositions. Let us consider the difference in oxygen concentration (hole concentration). The values of $7-\delta=6.99$ at $y=0.2$ and $7-\delta=7.05$ at $y=0.6$ give hole contents of $x = 0.5$ and $x = 0.55$, respectively. Recent neutron powder diffraction studies on La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ revealed the magnetic and crystallographic phase diagram in the region $x > 0.33$. In particular, when $0.42 < x < 0.66$, appears the A-type AFI state with antiferromagnetic coupling along the $c$-axis between FM single layers within one bilayer. We believe that the excess oxygen content ($x=0.55$) gives little effect on the magnetic property because the AFM magnetic transition temperature is stable over the range of hole concentration up to $x = 0.6$.

The x-ray powder diffraction patterns were recorded for all samples on a RIGAKU diffractometer with CuK$\alpha$ radiation as depicted in Fig. 1. The x-ray data are indexed in terms of (La,Sr)$_3$Mn$_2$O$_7$ 327 phase except for a small amount of impurity phase. The lattice parameters calculated using the least squares fits as a function of Cr-content as listed in Table I.

![Fig. 1: (Color online) (a) The x-ray powder diffraction pattern on the $y=0.4$ sample. Dots and a solid line are the observed and calculated intensities. The x-ray data are indexed in terms of (La,Sr)$_3$Mn$_2$O$_7$ 327 phase except for a small amount of impurity phase. (b) The lattice parameters calculated using the least squares fits as a function of Cr-content as listed in Table I.](image)

| Sample | $y$ | $a$ (Å) | $c$ (Å) | $T_N$ (K) | $T_{SG}$ (K) |
|--------|----|---------|---------|--------|-----------|
| 0      | 0.1 | 3.8790  | 19.996  | 210   |           |
| 0.1    | 3.8716 | 20.020  | 175    |       |           |
| 0.2    | 3.8660 | 20.030  | 130    |       |           |
| 0.4    | 3.8571 | 20.062  | 38     |       |           |
| 0.6    | 3.8662 | 20.094  | 34.5   |       |           |

TABLE I: The lattice parameters, $a$ and $c$, A-type AFM transition temperature $T_N$, spin-glass like transition temperature $T_{SG}$. The $T_N$ is determined from a local maximum at higher $T$ in ZFC data while $T_{SG}$ is defined from the prominent peak located at low-$T$. The lattice parameters of singlecrystalline LaSr$_2$Mn$_2$O$_7$ are taken from ref. 13.

Magnetic measurements as a function of temperature were carried out using a SQUID magnetometer in both zero-field-cooled (ZFC) and field-cooled (FC) scans. The magnetic relaxation was measured as follows: First, the sample was cooled down to the respective temperatures in a zero field and then the applied field was held for 5 minutes. Finally, just after the field was switched off, remanent magnetization data were recorded as a function of time. Electrical resistivity was measured by a conventional four-probe technique. Magnetoresistance measurements were performed at National Institute for Materials Science. Here, an electric current supplied was parallel to the direction of the external field. The thermal conductivity was measured using a conventional heat-flow method. The thermoelectric power $S (=-dV/dT)$ was determined both from a temperature gradient and thermoelectric voltage, $dT$ and $dV$, which are generated from a thermal current in the longitudinal direction of samples.
III. RESULTS AND DISCUSSION

A. Magnetic property

First, let us show in Fig. 2 the ZFC and FC temperature dependences of the magnetization in polycrystalline \( \text{LaSr}_2\text{Mn}_{2-y}\text{Cr}_y\text{O}_7 \) \((y=0.1,0.2,0.4\) and \(0.6)\), measured at 10 mT. For comparison, the \(ab\)-plane magnetization data of parent crystal \(\text{LaSr}_2\text{Mn}_2\text{O}_7\) are presented in the inset of (a).

Fig. 2: ZFC and FC temperature dependences of the magnetization in polycrystalline \(\text{LaSr}_2\text{Mn}_{2-y}\text{Cr}_y\text{O}_7 \) \((y=0.1,0.2,0.4\) and \(0.6)\), measured at 10 mT. For comparison, the \(ab\)-plane magnetization data of parent crystal \(\text{LaSr}_2\text{Mn}_2\text{O}_7\) are presented in the inset of (a).

Upon cooling the Cr-free sample, a broad maximum in \(M_{ab}\) is observed near about 210K, associated with the A-type AFM transition.\(^\text{15,16}\) Cr-doping strongly suppresses Neel temperature \(T_N\), from 210 K at \(y=0\), through 175K at \(y=0.1\), down to 130K at \(y=0.2\) and such a magnetic anomaly finally disappears for the \(y=0.4\) and 0.6 samples. The \(T_N\) is determined from a local maximum at higher temperatures in ZFC data. In the A-type AFM structure, FM spins lying in \(ab\)-plane of respective \(\text{MnO}_2\) single layer are antiferromagnetically coupled along the \(c\)-axis within a \(\text{MnO}_2\) double layer. We expect that a partial substitution of \(\text{Cr}^{3+}\) for \(\text{Mn}^{3+}\) sites causes \(d_{x^2-y^2}\) orbital deficiencies of \(e_g\)-electron and weakens a AFM coupling working between respective single layers, resulting in an observed drop of \(T_N\). Instead, a low-\(T\) peak in ZFC scan rapidly grows with Cr-doping, accompanied by a hysteresis region surrounded between ZFC and FC curves. At further low temperatures, the ZFC magnetization of \(y=0.2-0.6\) shows a steep decrease, indicating the freezing of magnetic moments.\(^\text{17,18}\) These findings are reminiscent of magnetic behaviors of a standard spin-glass system due to a magnetic frustration between ferromagnetic and antiferromagnetic interactions.\(^\text{19}\) A characteristic temperature where the prominent peak in ZFC scan is located at low-\(T\) is defined as \(T_{SG}\) for the \(y=0.4\) and 0.6 samples at 10mT. In addition, the temperature variation of magnetization polycrystalline \(\text{LaSr}_2\text{Mn}_{2-y}\text{Cr}_y\text{O}_7 \) \((y=0.1,0.2\) and \(0.4)\) both in 0.1 T and 1T is shown in Fig. 3. At 0.1T, a history effect between ZFC and FC scans remains visible at lower-\(T\). However, at relatively high field of 1T, the irreversibility in magnetization curves is strongly suppressed and a ferromagnetic-like behavior appears at low temperatures. These tendencies depending on the applied fields are never observed in a conventional spin-glass system.

Fig. 3: (Color online) ZFC and FC temperature dependences of the magnetization in polycrystalline \(\text{LaSr}_2\text{Mn}_{2-y}\text{Cr}_y\text{O}_7 \) \((y=0.1,0.2\) and \(0.4)\), measured in a field of (a) 100mT and (b) 1 T.
The saturated magnetic moment plotted as a function of Cr-content. We notice that the initial M shows a steeper rise. Let us the development of ferromagnetic states. Upon increas-
tion of FM phase at 5T is almost insensitive of Cr con-
tent from the inset of Fig. 4 (b), but the volume frac-
tion of FM phase at 5T is almost insensitive of Cr con-
tent. The value of $M_{sat}(5T)$ is converged within 30 to
35 percents of full ferromagnetic moment. ($M_{full}$=3.4
$\mu_B$ at $y=0.2$ and $M_{full}$=3.2 $\mu_B$ at $y=0.6$.) We give
some comments on the apparent disagreement in Cr-
substitution effect between low and high field magnetic
properties. A partial substitution of Cr$^{3+}$ ion for Mn$^{3+}$
suppresses not only AFM coupling between single MnO$_2$
layers but also destroys FM double-exchange interaction
between Mn$^{3+}$ and Mn$^{4+}$ ions within the MnO$_2$ layer.
It is expected that the addition of Cr$^{3+}$ ions causes a
suppression of FM region mediated by DE interaction
through removing Mn$^{3+}$ ions. On the other hand, the
low field data support the occurrence of the ferromag-
netic moment induced by Cr substitution. Following the
Kanamori-Goodenough rules, the superexchange(SE) in-
teraction between Cr$^{3+}$ ($t^{2g}_{2e}e_{g}^0$) and Mn$^{3+}$ ($t^{2g}_{2e}e_{g}^1$) ions is ferromagnetic while the SE interaction between Cr$^{3+}$ and
Mn$^{4+}$ ($t^{3}_{2g}e_{g}^0$) becomes antiferromagnetic. The annihi-
lolation of the Mn$^{3+}$ - Mn$^{4+}$ FM pairs is compensated by
the creation of the Cr$^{3+}$ - Mn$^{3+}$ FM pairs accompanied by
the Cr$^{3+}$ - Mn$^{4+}$ AFM pairs. In other words, the DE driven FM regions are partially replaced by the SE
driven FM regions with increasing the Cr ions, keeping
the total FM fraction. The FM double-exchange interaction
between Mn$^{3+}$ and Cr$^{3+}$ is not possible in our samples because the occurrence of FM moment by Cr-
doping accompanies no metallic property as discussed
later in the Cr-doping effect on resistivity. At high fields,
the phase separation between the field-induced FM phase
and AFM second phase is probably realized at the level
of clusters on the basis of the competition between FM
and AFM interaction. Next, we carried out the mag-
netic relaxation of the $y=0.4$ sample in order to exam-
ine the glassy state below $T_{SG}$. In Fig. 5 we show the remanent magnetization data of the $y=0.4$ sample as a
function of time, just after holding an applied field for 5
minutes and then switching it off. At 10mT, the mag-
netization relaxes faster at lower-$T$, in contrast with the
$M(t)$ data at 100mT. However, at 1T no slow relaxation
in $M$ is observed, which is consistent with no history ef-
effect in ZFC and FC scans. The slow decay of remanent
magnetization curves indicates that a difference in free
energy between the present excited and ground states is
quite small in comparison with thermal energy and the
system remains stable in various excited states. Thus,
a relatively fast relaxation of remanent $M$ at 10K
in 10mT scan leads to a larger difference of energy bar-
er between the ground and excited states than in the
case of 100mT at the same temperature. The metastable
state excited by the lower field is probably related to the
degree of a magnetic frustration between AFM and FM
clusters and/or the spatial distribution of frustrated clus-
ters. Furthermore, the coexistence of frustrated clusters
and ferromagnetic clusters plays a crucial role in the mag-
netic relaxation in 100mT. FM spins and/or FM domain
walls are pinned on the lattice defect sites like oxygen
vacancy, giving a longer relaxation time.
Fig. 5: Remanent magnetization data of the y=0.4 sample as a function of time, just after holding an applied field $H_a$ for 5 minutes and then switching it off. (a) $H_a=10$ mT and (b) $H_a=100$ mT.

B. Electrical transport property

Figure 6 displays the temperature dependence of the electrical resistivity in polycrystalline LaSr$_2$Mn$_{2-y}$Cr$_y$O$_7$ ($y=0.1, 0.2, 0.4$ and $0.6$). For comparison, the resistivity data of parent crystal LaSr$_2$Mn$_2$O$_7$ are also presented. The value of $\rho$ at lower $T$ exhibits a rapid increase by about four orders of magnitude, from $\sim 10^2$ $\Omega$cm at $y=0.1$ up to $10^6$ $\Omega$cm at $y=0.4$. Cr-doping strongly enhances an insulating behavior over a wide range of temperature because conduction paths are partially destroyed by $d_{x^2-y^2}$ orbital deficiencies of $e_g$-electron. Our data exclude in this system a possibility of the global double-exchange interaction between Mn$^{3+}$ and Cr$^{3+}$ ions, giving a metallic property.\[4\]

In particular, for the $y=0.2$ sample, the rapid rise in $\rho(T)$ below 50K is close to carrier localization effect due to a suppression of carrier hopping between single layers because at lower-$T$ orbital fluctuation of $d_{x^2-y^2}$ is gradually suppressed and motion of carriers are confined within respective single layer.\[5\]

We try to analyze the $\rho(T)$ data of Cr-doped samples using the small-polaron hopping model and Mott’s variable-range-hopping (VRH) model, to examine the conduction mechanism of bilayered manganite.\[6\] According to Mott’s VRH model, the temperature dependence of resistivities is represented by $\rho(T)=\rho_0\exp\left(\frac{T}{T_0}\right)$, where $\rho_0$ is a constant and $p = 1/(d + 1)$ with $d$ being the dimensionality of the system. Mott’s activation energy $T_0$ is proportional to $1/[N(E)\xi^d]$, where $N(E)$ is the density of states at the Fermi level and $\xi$ is the localization length. On the other hand, the adiabatic small-polaron model is described by $\rho(T)=\rho_0\exp\left(E_p/kT\right)$, where $\rho_0$ is a constant and $E_p$ represents the activation energy of small-polaron. For all

| Sample VRH regime | 2D VRH | 3D VRH |
|-------------------|--------|--------|
| $y$ | $\rho_0$ | $T_0$ | $\rho_0$ | $T_0$ |
| 0.1 | $T > 187$ | $2.1 \times 10^{-6}$ | $1.0 \times 10^9$ | $8.7 \times 10^{-9}$ | $5.4 \times 10^7$ |
| 0.2 | $T > 161$ | $3.0 \times 10^{-6}$ | $1.2 \times 10^6$ | $8.1 \times 10^{-9}$ | $7.0 \times 10^7$ |
| 0.4 | $T > 155$ | $2.0 \times 10^{-6}$ | $1.5 \times 10^6$ | $3.7 \times 10^{-9}$ | $8.9 \times 10^7$ |
| 0.6 | $T > 113$ | $2.6 \times 10^{-6}$ | $1.8 \times 10^6$ | $2.7 \times 10^{-9}$ | $1.2 \times 10^8$ |
samples with Cr-substitution, it is found that the VRH model gives a more reasonable fit to the experimental data over a wide range of temperatures, in comparison with the small-polaron model. In Fig.7(a), we present our results as a semilog plot of \( \rho \) versus \( T^{-p} \) with \( p = 1/3 \) for 2D VRH, while the inset of Fig.7(a) shows a semilog plot of \( \rho \) versus \( T^{-p} \) with \( p = 1/4 \) for 3D VRH. Although it is hard to distinguish a \( T^{-1/3} \) or \( T^{-1/4} \) dependence of \( \ln \rho \), we obtain a much better fit to Mott’s VRH than to a VRH model with \( p = 1/2 \) in the presence of Coulomb gap. The fitting parameters, \( \rho_0 \) and \( T_0 \), for polycrystalline samples of \( \text{LaSr}_2\text{Mn}_2-y\text{Cr}_y\text{O}_7 \) (\( y=0.1, 0.2, 0.4 \) and \( 0.6 \)) are listed in Table 11. With increasing Cr-content, the value of \( T_0 \) shows a monotonous increase for both 2D and 3D cases, indicating the decrease of the localization length. The localization effect enhanced due to Cr-substitution is probably associated with orbital disorders in Mn-O-Mn networks introduced by the removal of \( e_g \)-electrons.

We give some comments on the doping effect of other trivalent metallic ions (\( \text{Co}^{3+} \) and \( \text{Al}^{3+} \)) on the Mn sites of \( \text{LaSr}_2\text{Mn}_2\text{O}_7 \). The 3d electronic configuration of \( \text{Co}^{3+} \) ion follows as: \( t_{2g}^{2}e_{g}^{0} \) (\( S=0 \), low-spin state), \( t_{2g}^{2}e_{g}^{1} \) (\( S=1 \), intermediate spin state) and \( t_{2g}^{2}e_{g}^{2} \) (\( S=2 \), high-spin state). The \( \text{Al}^{3+} \) ion is a non magnetic ion without \( d \)-electrons. With increasing \( \text{Co}^{3+} \) (or \( \text{Al}^{3+} \)) doping level, the A-type AFM temperature shifts to low temperatures and the magnitude of magnetization decreases over a wide range of temperatures. The decrease of \( M \) implies a reduction of the net magnetic moments, which is consistent with low-spin state (\( S=0 \)) of \( \text{Co}^{3+} \) or non magnetic ion of \( \text{Al}^{3+} \). The latter tendency is in strong contrast with the magnetic effect of Cr-\( t_{2g}^{2}e_{g}^{0},S=3/2 \) doping on \( \text{LaSr}_2\text{Mn}_2\text{O}_7 \) although a suppression of Atype-AFM temperature is commonly observed for \( \text{Cr} \), \( \text{Co} \) and \( \text{Al} \) doping. On the other hands, the doping effects on electrical transport for \( \text{Cr} \), \( \text{Co} \) and \( \text{Al} \) ions exhibit such common features as the enhanced insulating state due to orbital deficiencies following the VRH model. In particular, the Al substitution without \( d \)-electrons for Mn site products a more rapid increase in resistivities.

Magnetoresistance (MR) effect of the \( y=0.2 \) sample as a function of temperature is depicted in Fig.7(b), where the negative MR is defined as \(-100 \times [ \rho(\text{8T})-\rho(\text{0T})] / \rho(\text{0T}) \). The value of giant MR increases from \( 25 \) % at \( 150 \)K up to \( 80 \) % at \( 4.2 \) K with decreasing \( T \). The existence of the field-induced FM clusters is probably related to the enhanced MR at low temperatures as we see from MT data in Fig.8(b). In the inset of Fig. 8(b), the MR of \( y=0.1 \) and \( 0.2 \) samples at \( 4.2 \)K is plotted as a function of field up to \( 8 \)T. Cr-doping also increases a low-\( T \) MR from \( 45 \) % at \( y=0.2 \) up to \( 80 \) % at \( y=0.6 \) under a field of \( 8 \)T at \( 40 \)K. The Cr-doping induced orbital disorders assist charge transfer along the c-axis across respective single layer of MnO2, giving the enhanced MR effect.

C. Thermal transport properties (Seebeck effect and thermal conductivity)

Next, the temperature variation of Seebeck coefficient \( S \) for the \( y=0.1-0.6 \) samples is displayed in Fig.8(a). For comparison, the \( S(T) \) data of single crystalline \( \text{LaSr}_2\text{Mn}_2\text{O}_7 \) are cited. For \( y=0-0.2 \), with decreasing \( T \), the value of \( S(T) \) shows a local maximum near the A-type AFM transition temperature \( T_N \) and then a shallow minimum at lower \( T \) is observed. At lower \( T \), Cr-doping gradually suppresses a local minimum of \( S(T) \) from a negative value at \( y=0 \) down to a small one at \( y=0.2 \) and finally at \( y=0.4 \) the local minimum in \( S(T) \) disappears, giving a monotonous decrease over the observed temperature range. Now, let us try to analyze the \( S(T) \) data of Cr-doped samples using the extended Mott’s VRH model to Seebeck coefficients. For the 2D VRH case, the corresponding form is described by \( S(T) \propto T^p \) with \( p = 1/3 \) (\( p = 1/2 \) for the 3D VRH case). In Fig.8(b), we present our results as a linear plot.
In a doped bilayer manganite with hole content $x=0.4$, the high temperature behavior of $S(T)$ is well explained on the basis of a model of Zener polarons, where a Zener polaron formed in the high-$T$ region occupy two manganese sites. It is true that this model qualitatively reproduces a negative sign in high-$T$ behavior of single crystalline La$_1$Sr$_2$Mn$_2$O$_7$. However, for all polycrystalline samples with Cr-substitution it seems that the VRH conduction gives a reasonable fit to both resistivities and Seebeck coefficients.

First of all, thermal carries are phonons since the electron component is estimated to be negligible from the resistivity data using the Widemann-Franz law. The phonon thermal conduction gradually increases with Cr-doping, which seems to be an unusual behavior because the introduction of Cr-impurity ions would disturb phonon conduction. However, this anomalous finding is reasonably resolved through clarifying a close relationship between phonon conduction and local lattice distortion of MnO$_6$.
due to Jahn-Teller effect. In our previous work on thermal conductivity in bilayered manganite single crystals, it has been made clear that the phonon conduction in the insulating state is scattered by local lattice distortions of Mn$^{3+}\cdot$O$_6$ but the metallic state realized by lowering of $T$ or by the applied field yields a upturn in $\kappa$ below $T_C$ or giant magnetothermal effect$^{35}$. This enhanced phonon conduction arises from a suppression of Mn$^{3+}\cdot$O$_6$ local distortions due to a screening effect of itinarent carriers. Cr-substitution for Mn$^{3+}$ sites removes $d_{x^2-y^2}$ orbitals of $e_g$-electron, resulting in a Cr$^{3+}\cdot$O$_6$ octahedron without local JT effect. In other words, Cr-doping effect on lattices causes a suppression of local lattice distortion through the introduction of JT inactive ions, giving an increase in phonon conduction. Surely, the $\kappa(T)$ of polycrystalline Sr$_2$Mn$_2$O$_7$($x=1$) shows a typical phonon conduction, whose behavior is free from JT distortion of Mn$^{3+}\cdot$O$_6$. In addition, the Cr-doping dependence of $a-$ and $c-$ axis lattice parameters in Table I reveals the volume shrinkage of the unit cell with increasing Cr-content as shown in Fig.8 (b). We note that the lattice constant of $y=0.6$ is influenced by a small amount of the impurity phase. This volume effect is associated with a number of deficiencies of $d_{x^2-y^2}$ orbitals of $e_g$-electron, which is quite consistent with the preceding discussion on the close relationship between the lattice distortion and phonon conduction.

IV. SUMMARY

We have carried out magnetic, electrical, Seebeck effect and thermal conductivity measurements of LaSr$_2$Mn$_{2-y}$Cr$_y$O$_7$ polycrystalline samples ($y=0.1, 0.2, 0.4$ and $0.6$). The Cr$^{3+}$ substitution for Mn$^{3+}$ sites produces a monotonic shrink of $a(b)$-axis in contrast with a gradual elongation of $c$-axis in association with a removal of $d_{x^2-y^2}$ orbital of $e_g$-electron. For Cr-doped samples, a glassy behavior appears accompanied by both a collapse of the A-type antiferromagnetic property and the development of ferromagnetic clusters. At high fields, the irreversibility in magnetization curves disappears and the saturated magnetic moment induced by the applied field reaches 30 to 35 percent of full ferromagnetic moment at 5$T$ for all Cr doped samples. This finding strongly suggests the presence of a phase separation between FM and second phases at the level of clusters, which originates from the frustration between FM and AFM interactions. The electrical transport for Cr-doped samples strongly enhances an insulting property over the wide range of temperature because conduction paths are partially destroyed by $d_{x^2-y^2}$ orbital deficiencies of $e_g$-electron. At lower $T$, Cr-doping gradually suppresses a local minimum of $S(T)$ from a relatively large value at $y=0$ down to a positively small one at $y=0.4$ in striking contrast to the more enhanced low-$T$ resistivity data. For all polycrystalline samples with Cr-substitution it seems that the VRH conduction gives a reasonable fit to both resistivities and Seebeck coefficients. The phonon thermal conduction gradually increases with increasing Cr content, which is contrast to a typical impurity effect on thermal conductivity. We propose that the increase in the phonon thermal conduction results from a suppression of local lattice distortion through the introduction of Jahn-Teller inactive ion of Cr$^{3+}$.

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