

# Effects of Cr doping in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ : Magnetization, resistivity, and thermopower

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The effects of Cr substitution on Mn sites in the colossal magnetoresistance (CMR) compound  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  have been studied by preparing the series  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \leq 0.3$ ). A careful study in the magnetic and electrical transport properties has been carried out by the measurements of magnetization, resistivity, magnetoresistance, and thermopower. It was found that Cr is impotent in lowering  $T_C$  when  $x \leq 0.2$ . An extraordinary magnetotransport behavior, characterized by double bumps, was observed around  $x = 0.1$ . As a result, the temperature range of CMR is greatly broadened. The analysis of resistivity and thermopower data in the paramagnetic state enable us to identify the polaronic transport mechanism. Moreover, it is found that the polaron activation energy as well as polaron binding energy are almost constant within a broad Cr content. We suggest these peculiar effects of Cr doping could be the consequence of the possible double exchange interaction between  $\text{Mn}^{3+}$  and  $\text{Cr}^{3+}$ .

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## I. INTRODUCTION

Mixed-valence manganites with the perovskite structure have been studied for a long time. Early research was motivated by a need to develop insulating ferromagnets with a large magnetization for high-frequency applications. Recent renewed interest has focused on the negative colossal magnetoresistance (CMR) effect observed near the Curie temperature.<sup>1-3</sup> The basic structural, magnetic, and transport properties of  $R_{1-x}A_x\text{MnO}_3$  ( $R$ =rare earth,  $A$ =Ca, Sr, Ba) were widely studied in the past years. For a broad doping range,  $0.2 \leq x \leq 0.5$ , there is an insulating-metallic (IM) transition associated with a paramagnetic-ferromagnetic transition. The ferromagnetism and the magnetic correlation of transport property in these compounds has been traditionally explained in terms of the double exchange (DE) mechanism<sup>4</sup> which considers the magnetic coupling between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  that results from the motion of an electron across the two partially filled  $d$  shells with strong on-site Hund's coupling. Recent detailed research has, however, shown that DE alone is insufficient to account for the rich variety of phenomena found in these compounds. Instead, a strong electron-phonon coupling due to the Jahn-Teller effect of  $\text{Mn}^{3+}$  ion was proposed to play a key role in these manganites.<sup>5-7</sup> It has been becoming generally recognized that the system involves complex interplays among charge, lattice, and spin. In this kind of situation, localization of the charge carriers as magnetic polaron in the high-temperature paramagnetic state is believed to be a key factor to give rise of the observed colossal magnetoresistance.<sup>8,9</sup>

The great analogy between superconducting cuprates and CMR manganites suggests that the magnetotransport properties of the latter should be sensitive to the doping of the manganese sites. The study of the effects of Mn-site doping with other elements is expected to provide important clues concerning the mechanism of CMR as well as the exploring of novel CMR materials. During the past two years, there have been increasing reports on the effects of Mn-site element substitution. It was found that doping Mn sites with foreign elements generally decreases Curie temperature  $T_C$

and the IM transition temperature  $T_p$ . However, the exact effect depends on the nature of the doping element. The doping element can be divalent [such as Mg,<sup>13</sup> Cu,<sup>14</sup> Ni,<sup>15-18</sup> and Zn (Ref. 14)], trivalent [such as Al,<sup>19</sup> Fe,<sup>16,20-22</sup> Ga,<sup>16,23</sup> Co,<sup>14,15,24</sup> Cr (Refs. 14, 16, 25 and 26)], and tetravalent [Ti and Sn (Ref. 16)]. Among these doping elements, Cr has a spectacular effect and attracts more attention. Maignan *et al.* reported the rather constant  $T_C$  values in  $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  system.<sup>16</sup> Raveau *et al.*<sup>26</sup> and Barnabé *et al.*<sup>27</sup> found that Cr substitution on the charge ordered insulator  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  can induce an IM transition without applied magnetic field. In this paper, we will discuss our investigation concerning the effect of Cr substitution on the prototype CMR material  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  by magnetization, electrical transport, magnetoresistance, and thermopower measurements within a broad doping level  $0.05 \leq x \leq 0.3$ . The experimental results prove Cr doping could be a potent way in tuning CMR response, and implies the possibility of DE between  $\text{Mn}^{3+}$  and  $\text{Cr}^{3+}$ .

## II. EXPERIMENT

Polycrystalline samples of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $0.0 < x \leq 0.3$ ) were synthesized by conventional solid-state reaction method. Appropriate amounts of  $\text{La}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{MnO}_2$ , and  $\text{Cr}_2\text{O}_3$  were mixed and heated in air at 900 °C for 12 h, 1000 °C for 12 h, and 1150 °C for 24 h with intermediate grinding. After pressed into pellets, a final sintering was carried out at 1400 °C for 24 h. The structure and phase purity of as-prepared samples were checked by powder x-ray diffraction (XRD) using  $\text{Cu } K_\alpha$  radiation at room temperature. The XRD patterns prove that all samples are single-phase with orthorhombic perovskite structure. Magnetization measurements were performed using a vibrating sample magnetometer (VSM). After zero-field cooling down to 5 K, the magnetization data were collected in 50 Gauss field during the warming process. Resistivity  $\rho$  under zero and 6-T magnetic field was measured by standard four-probe method. Thermopower  $S$  was measured by conventional differential method in the 80–300-K temperature range.

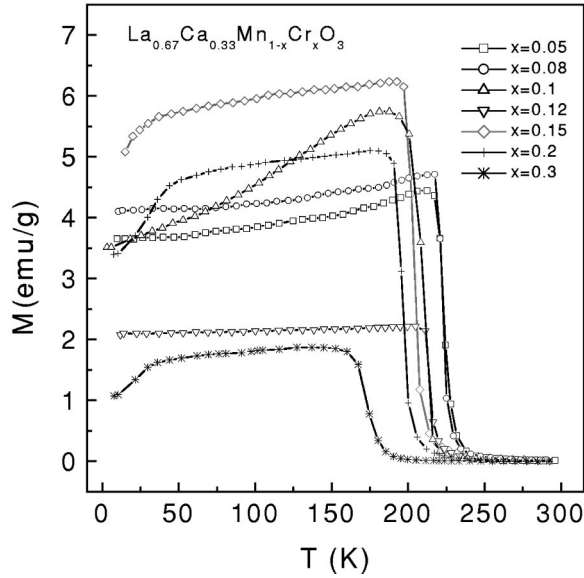


FIG. 1. Temperature dependence of magnetization in a 50-G magnetic field for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \leq 0.3$ ).

### III. RESULTS AND DISCUSSION

#### A. Magnetic properties

The temperature dependence of magnetization of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  system ( $x \leq 0.3$ ) is shown in Fig. 1. All samples, even for the doping level  $x=0.3$ , exhibit a steep ferromagnetic-paramagnetic transition. The Curie temperature  $T_C$ , which is defined as the inflection point of  $M \sim T$  curve, are summarized in Table I for all samples. From it one can see that  $T_C$  decreases rather slowly with increasing Cr content for  $x \leq 0.2$ , and a little more rapidly for  $x=0.3$ . In contrast, it was reported that Fe, Ni, Co, Ga, Al, etc., are all potent in lowering  $T_C$ . The inefficiency in driving  $T_C$  suggests that Cr doping does not destroy double exchange ferromagnetism remarkably as some other elements. This feature of Cr substitution was found previously. But there seems no consistent interpretation reached yet. Maignan *et al.* reported the rather constant  $T_C$  values in  $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \leq 0.2$ ),<sup>16</sup> and ascribed it to the  $\text{Mn}^{3+}\text{-O-Cr}^{3+}$  ferromagnetic interaction which may be also double exchange type in terms of the identical electronic configuration ( $t_{2g}^3 e_g^0$ ) between  $\text{Mn}^{4+}$  and  $\text{Cr}^{3+}$ . On the other hand, some authors argued that Cr ions are unable to take

TABLE I. Parameters on magnetic and transport properties for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ .

Sample	$T_C$ (K)	$T_p$ (K)	$E_p$ (meV)	$E_s$ (meV)	$E_b$ (meV)
$x=0.05$	224	225	138	7	262
$x=0.08$	221	216	146		
$x=0.1$	208	208	133	12	242
$x=0.12$	216	212	142		
$x=0.15$	202	205	139	14	250
$x=0.2$	195		163		
$x=0.3$	175			11	

part in DE and explained the rather weak dependence of  $T_C$  on Cr content as that DE between Mn ions is not strongly affected until a given Mn ion has Cr ions as a significant fraction of its nearest neighbors.<sup>25</sup> We are inclined to the former view. If the role of Cr doping is merely to dilute DE between Mn ions, like that of Fe, Co, Ni, there should no big difference of the effect on  $T_C$  for them, opposing the experimental results. Although there is no definite evidence proving DE between  $\text{Mn}^{3+}$  and  $\text{Cr}^{3+}$  at present, the possibility of it keeps alive considering the peculiar magnetic and magnetotransport behaviors induced by Cr doping. In the Sec. III B, we will discuss it in details with the transport and CMR data.

The maximum of magnetization in a 50-G field keeps increasing from  $x=0.05$  to  $x=0.15$ . Then it goes down with further Cr content. We note that the case of  $x=0.12$  sample stands out for its obviously low value of magnetization. Correspondingly, the resistivity of  $x=0.12$  sample also exhibits abnormally large result, which will be demonstrated in the subsequent section. Both magnetization and resistivity are remeasured for this sample, but the results retains. We are not sure if this abnormalcy is intrinsic and originates from the certain fraction of Cr content. However, since our samples are polycrystalline, some extrinsic factors such as grain size and boundary can not be excluded to be responsible for it.

For all samples, the magnetization below  $T_C$  shows a slight drop with cooling. Especially, for highly doped samples ( $x=0.15, 0.2$ , and  $0.3$ ), there is a fast drop of magnetization at the lowest temperatures. The peculiar shape of  $M-T$  curves suggests a complex magnetic structure below  $T_C$ . Although the ferromagnetic interaction dominates after the magnetic transition, there also exists antiferromagnetic interaction between  $\text{Cr}^{3+}$  ions. The coexistence of, and competition between, ferromagnetic and antiferromagnetic interaction could lead to the formation of cluster-glass state. The steep drop of magnetization at low temperature may signify the freezing of such cluster-glass state. In fact, previous extensive studies have disclosed that a cluster (spin) glass behavior is usually observed in Mn-site doped manganites.<sup>18,21</sup>

#### B. Transport properties

Figure 2 depicts the temperature dependence of resistivity of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  system under zero and 6 T magnetic field. It is well known that  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  shows a metallic-insulating (MI) transition near Curie temperature  $T_C \sim 265$  K. When Mn is partly substituted by Cr, the system displays a more complicated and interesting transport behavior. With increasing Cr content, the MI transition shifts to lower temperature, and an additional bump grows up after it. As a result, the  $R(T)$  curves of  $x=0.08$  and  $0.1$  samples display double-bumps feature (as seen clearly in the inset of Fig. 2). For the  $x=0.12$  sample, the original peak is weak enough to merge into the greatly enhanced additional bump. When  $x$  reaches  $0.15$ , no insulating-metallic transition occurs though the double-bending feature of the  $R(T)$  curve is still clear. When  $x$  exceeds  $0.15$ , the resistivity exhibits insulating behavior in all temperatures studied. We note that the

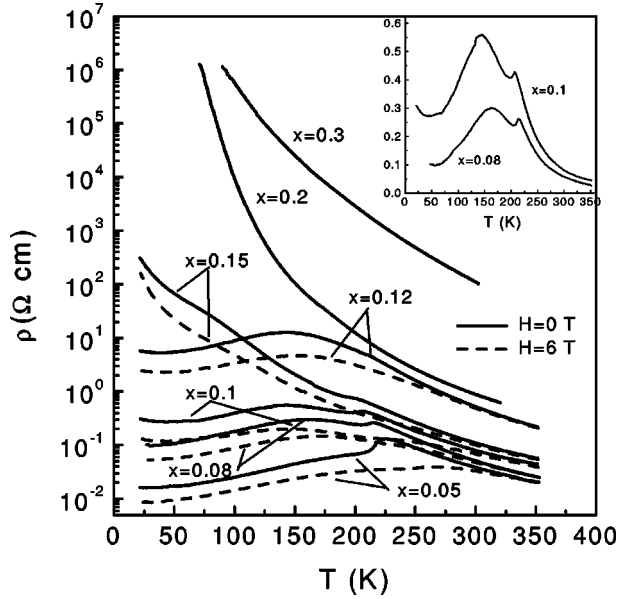


FIG. 2. Temperature dependence of resistivity under zero and 6-T magnetic field for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \leq 0.3$ ).

double-bump feature of  $R(T)$  curve was also observed in  $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{Mn}_{1-y}\text{Cr}_y\text{O}_3$  ( $y = 0.07$  and  $0.10$ ) (Ref. 16) and  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-y}\text{Cr}_y\text{O}_3$  ( $y = 0.10$ ).<sup>16,26</sup> From these consistent results we can conclude that this double-bumps feature of resistivity is intrinsic and originates from the crucial role of Cr element. Under an applied magnetic field, both bumps of resistivity are deeply compressed. This peculiar feature of resistivity with and without magnetic field leads to the extraordinary CMR effect in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ .

In Fig. 3, we demonstrate the temperature dependence of CMR response for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  system ( $x \leq 0.15$ ), where MR is defined as  $\text{MR} = [\rho(0) - \rho(6T)]/\rho(6T)$ . In contrast to the case in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  that CMR occurs merely near  $T_C$ , the temperature range of CMR response is enormously broadened by Cr doping. Corresponding to the double bumps in zero-field resistivity, CMR also exhibits two peaks. With increasing Cr content, the original peak of CMR decays while the additional peak of CMR rises. The coexistence of two peaks of MR results in CMR remains in a broad temperature range from the lowest to near room temperature, especially for doping level  $x$  around 0.1. This extraordinary CMR behavior is beneficial and informative to practical application in terms of the very broad temperature range of CMR response. Therefore it proves that Cr substitution on Mn site could be a potent way in tuning CMR.

The first peak of CMR lies very near  $T_C$ , which suggests that it originates from the same mechanism based on the DE between Mn ions as in undoped  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ . The second peak of MR grows with increasing Cr content. Therefore it should be ascribed to the crucial role of Cr. As we mentioned above, there is a possibility of the occurrence of DE through  $\text{Mn}^{3+}\text{-O-Cr}^{3+}$  due to the identical electronic configuration between  $\text{Cr}^{3+}$  and  $\text{Mn}^{4+}$ . The present results of CMR behavior in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  could be supporting evidence to this view. It is well known that DE correlates

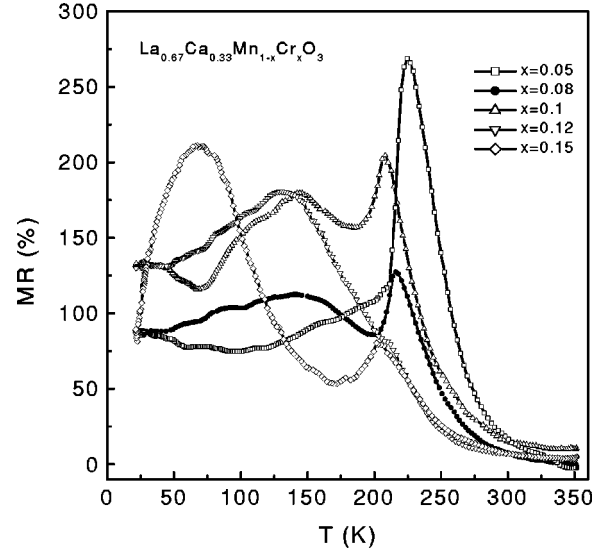


FIG. 3. Magnetoresistance versus temperature of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \leq 0.15$ ).

the electrical transport to magnetic configuration, i.e., a magnetic order favors the motion of carrier. Therefore an applied magnetic field promotes the conductivity and leads to CMR. The appearance of an additional peak of CMR in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  implies that the interaction through  $\text{Mn}^{3+}\text{-O-Cr}^{3+}$  could be of the nature of DE rather than superexchange because superexchange generally does not give rise to the CMR. Due to the different coupling constant between  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  and  $\text{Mn}^{3+}\text{-O-Cr}^{3+}$ , the delocalization of carriers by applied magnetic field happens at two separated regions, consequently resulting in two CMR peaks.

### C. Polaronic transport and thermopower

There have been extensive discussion on the polaronic transport behavior in the paramagnetic phase of  $R_{1-y}A_y\text{MnO}_3$ .<sup>10-12</sup> As shown in Fig. 4, we found that the high-temperature resistivity of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \leq 0.2$ ) can be fitted by the adiabatic small polaron hopping model,

$$\rho = BT \exp(E_p/k_B T), \quad (1)$$

where  $B$  is a constant,  $E_p$  is the resistivity activation energy, and  $k_B$  is Boltzmann constant. For  $x = 0.3$ , the resistivity data do not fit small polaron model well. But the low temperature resistivity of it can be fitted by the variable range hopping model,<sup>28</sup>  $\rho \sim \exp(T_0/T)^{1/4}$ , as shown in the inset of Fig. 4. From these fits, we obtain the resistivity activation energy  $E_p$ , which are listed in Table I. It can be seen the polaron activation energy is changed very little by the substitution of Cr. For  $x \leq 0.15$ ,  $E_p$  keeps nearly constant ( $\sim 140$  meV).

In order to obtain insight into the nature of polaron in paramagnetic state, we also performed measurements of thermopower  $S$  as a function of temperature for some typical samples. As shown in Fig. 5(a),  $S$  increases with cooling and a prominent peak develops at temperatures  $T_s$  with increasing  $x$ . At  $T < T_s$ , the thermopower drops suddenly and keeps nearly zero at low temperature when  $x \leq 0.15$ . For  $x = 0.3$

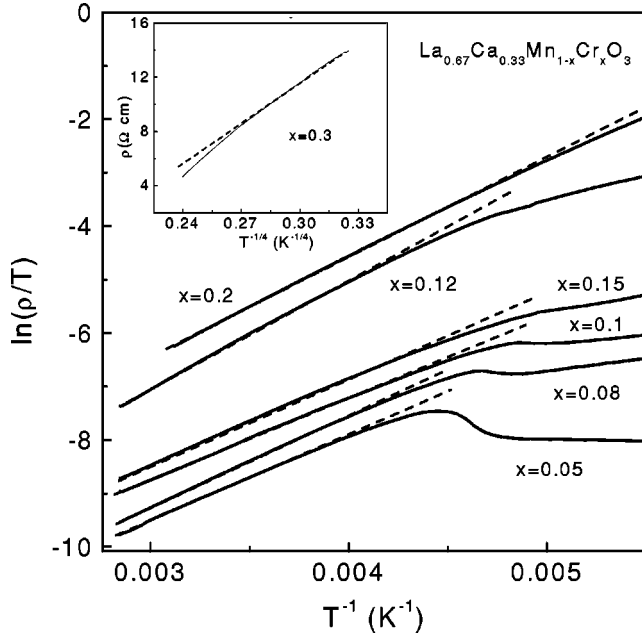


FIG. 4.  $\ln(\rho/T)$  versus  $1/T$  for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \leq 0.2$ ). The dashed lines are fits to small polaron model. The inset shows  $\ln(\rho)$  versus  $1/T^{1/4}$  for the  $x=0.3$  sample.

sample,  $S$  remains a high value after  $T_s$ . We found that  $T_s$  is near  $T_C$ , which suggests the prominent peak of  $S$  is related to the onset of long-range magnetic order. By fitting the thermopower data to the classical expression of the Seebeck coefficient for a thermally activated case,

$$S = \frac{k_B}{e} \left( \frac{E_s}{k_B T} \right) + S_\infty, \quad (2)$$

where  $E_s$  is the thermopower activation energy, and  $S_\infty$  is the Seebeck coefficient at high-temperature limit, as depicted in Fig. 5(b), we can draw out the thermopower activation energy  $E_s$  which are also summarized in Table I. There is a large discrepancy between  $E_\rho$  and  $E_s$ , which is a hallmark of polaronic transport.<sup>28</sup> With these  $E_\rho$  and  $E_s$  from above models we can calculate the polaron binding energy  $E_b = 2(E_\rho - E_s)$  for some typical samples, as listed in Table I. Within experimental resolution,  $E_b$  virtually varies slightly with Cr content, a surprising result. The nearly constant polaron activation energy  $E_a$  and binding energy  $E_b$  in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  suggest that the basic nature of the magnetic polaron does not remarkably changed by Cr doping. This dramatic feature, though not well understood, may further indicate the equality of  $\text{Cr}^{3+}$  with  $\text{Mn}^{4+}$ , and consequently add the support to DE between  $\text{Cr}^{3+}$  and  $\text{Mn}^{3+}$ . The possible occurrence of DE between  $\text{Mn}^{3+}$  and  $\text{Cr}^{3+}$  is an interesting and attractive subject. To clarify the answer, we

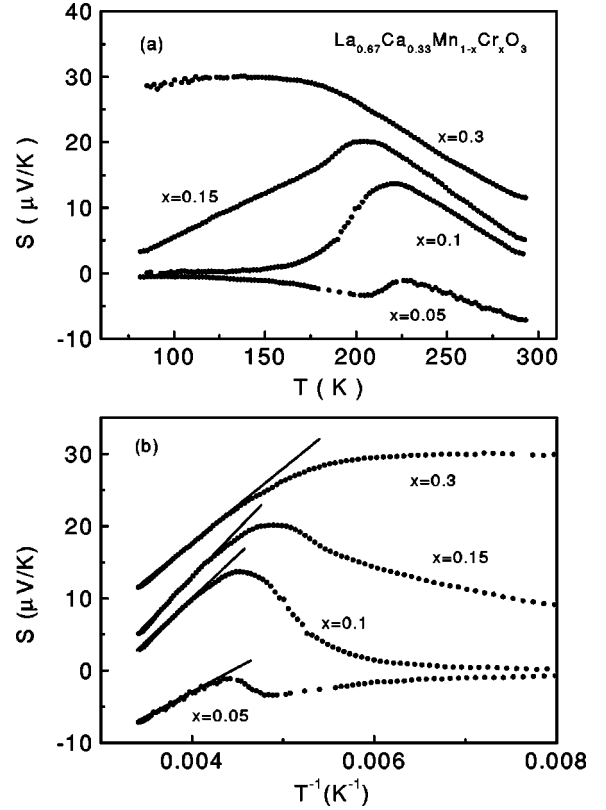


FIG. 5. (a) Temperature dependence of thermopower, and (b) thermopower  $S$  versus  $1/T$ , for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \leq 0.3$ ).

are undertaking a careful study on the  $\text{LaMn}_{1-x}\text{Cr}_x\text{O}_3$  system. The experimental results and discussion will come out in the future.

#### IV. CONCLUSIONS

We have investigated the effects of Cr doping in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  by magnetic, electrical transport, magnetoresistance, and thermopower measurements. The magnetic transition temperature decreases slowly with increasing Cr content. An extraordinary magnetotransport behavior, characterized by double bumps, was observed for  $x$  around 0.1. As a result, the temperature range of CMR response is greatly broadened by Cr substitution, beneficial to practical application. Besides, the large difference between  $E_\rho$  and  $E_s$  provides evidence of small polaron transport mechanism in the high-temperature paramagnetic state. The peculiar effects of Cr doping, especially the inefficiency in both magnetic order temperature  $T_C$  and polaron binding energy  $E_b$ , suggests the possibility of DE between  $\text{Mn}^{3+}$  and  $\text{Cr}^{3+}$ .

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