

# Magnetoresistance and magnetothermoelectric power of $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$

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We report the results of thermoelectric power (TEP) of a Cr doped  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $x=0-0.45$ ) system measured both in the presence and the absence of magnetic field ( $B=1.5$  T). The small field dependence of the Seebeck coefficient is observed around the metal-semiconductor transition (MST) temperature ( $T_p$ ) of the samples. The field dependence of TEP is stronger in the undoped sample. It is noticed from the TEP data that the small polaron hopping conduction mechanism is valid for all these samples (for  $T>T_p$ ). The polaron radius  $r_p$  is found to decrease with increase of magnetic field. Low-temperature (below  $T_p$ ) field-dependent and field-independent TEP data can be fitted with  $S=S_0+S_{3/2}T^{3/2}+S_4T^4$  suggesting that the electron-magnon scattering strongly affects the low-temperature (ferromagnetic phase) TEP data of the manganites. Activation energy gradually increases with increasing Cr concentration both in the presence and the absence of magnetic field. Field-dependent thermopower also indicates the importance of spin fluctuations affecting the phonon scattering. Power factor ( $S^2/\rho$ ) estimated from the Seebeck coefficient ( $S$ ) and resistivity ( $\rho$ ) (at zero and 1.5 T field) showed a minimum around the MST temperature similar to the field-dependent thermal conductivity data.

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## I. INTRODUCTION

The antiferromagnetic (AFM) insulating (semiconducting) oxides such as  $\text{RMnO}_3$  ( $R$ =rare earth elements such as lanthanum) of current interest can be driven to ferromagnetic (FM) metallic state by partial substitution of the trivalent rare earth by divalent metal.<sup>1,2</sup> The basic structural, magnetic and transport properties of these oxides viz  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $A$ =Sr, Pb, Ca, etc.)<sup>3-5</sup> were widely studied in recent past. For a wide range of doping ( $0.2<x<0.5$ ), there is a semiconducting to metallic transition (MST) with the lowering of temperature. The high-temperature (above MST temperature  $T_p$ ) semiconducting phase showed paramagnetic (PM) behavior, while the low temperature (below  $T_p$ ) phase exhibited ferromagnetic and metallic character. The magnetic and other properties of these compounds have traditionally been explained in terms of the double exchange (DE) mechanism,<sup>6</sup> which considers the magnetic coupling between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions. Recently, thorough investigation has been made showing evidence in favor of strong electron-phonon coupling due to Jahn-Teller effect of the  $\text{Mn}^{3+}$  ions which has also been considered to play a key role in the transport mechanism of these manganites.<sup>7</sup> The great structural analogy between superconducting cuprates and the colossal magnetoresistive (CMR) behavior of manganites suggested that the magnetotransport properties of the later should be sensitive to the doping at the manganese sites. The study of the effects of Mn site doping with other elements is expected to provide important clues to the mechanism of CMR behavior. Among various aspects of transport studies in these materials showing MST, thermoelectric power (TEP) has also attracted much attention as it is sensitive to the nature of charge carriers, their interaction with spins, and also to the thermal conductivity of the material through the thermoelectric figure

of merit  $ZT=S^2T/(\rho\kappa)$ , where  $\kappa$  is the thermal conductivity,  $\rho$  is the electrical resistivity, and  $T$  is the absolute temperature. The Seebeck coefficient ( $S$ ) of the manganite system shows very complicated behavior indicating both positive and negative signs depending on the temperature as well as on the degree of substitution that determines the carrier density of the system. In the low-temperature metallic phase, TEP is related to the changes in electronic structure and scattering process. In the insulating phase ( $T<T_p$ ), the temperature-dependent TEP data can provide information on the energy dependence of the parameters governing the high-temperature charge transport through the small polaron hopping mechanism.

Recently the Pb doped La-Mn-O system has been elaborately studied by other research group<sup>4</sup> because of its high magnetic ordering temperature around room temperature. It was found that doping at the Mn sites with foreign elements generally decreases Curie temperature  $T_c$  and metal semiconductor transition temperature  $T_p$ . Both concentration and nature of the doping element are found to have large effects on  $T_p$  and other properties. The doping element can be bivalent such as Mg,<sup>8</sup> Cu,<sup>9</sup> Ni,<sup>10</sup> Zn,<sup>9</sup> trivalent such as Al,<sup>11</sup> Fe,<sup>12</sup> Co,<sup>9,10,12</sup> Cr,<sup>9,13,14</sup> and also tetravalent Ti (Ref. 15) etc., but TEP data (both in the presence and absence of magnetic field) of none of these doped samples were thoroughly analyzed. Again, among the various doping impurities, Cr doping has a spectacular effect on the transport properties, which stimulates more research on these Cr doped samples. Barnabe *et al.*<sup>16</sup> found that among the various doping elements, Cr is the most efficient one to induce MST in the charge ordering system. Raveau *et al.*<sup>17</sup> also observed that Cr substitution on such system such as  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  can induce MST without applied magnetic field. Since electronic configuration of  $\text{Cr}^{3+}$  and  $\text{Mn}^{4+}$  are identical, Cr can replace

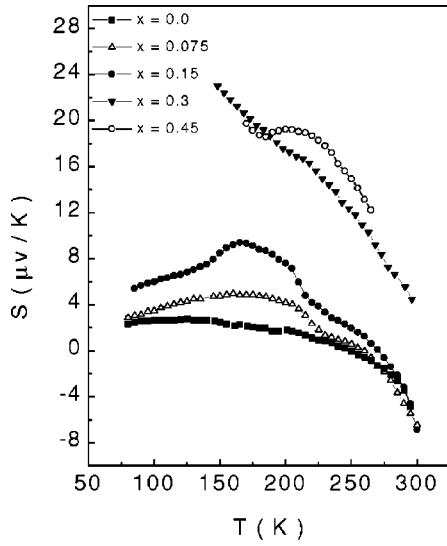


FIG. 1. Thermal variation of Seebeck coefficient ( $S$ ) of  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  with  $x=0.0, 0.075, 0.15, 0.3,$  and  $0.45$  (without showing MST).

Mn and affect the DE interaction between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ . As with conductivity and magnetic measurements, TEP is also expected to depend on magnetic field and can also provide interesting information about the mechanism of charge transport in the system.

In this paper, the effect of Cr substitution on the thermoelectric power and power factor of  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $0.0 < x < 0.45$ ) have been studied. The TEP data of the samples (measured both in presence and in absence of magnetic field) have been critically analyzed. Temperature-dependent Seebeck coefficients (both in presence and in absence of magnetic field) of different doped samples have been fitted with the theoretical model.

## II. EXPERIMENTAL

Polycrystalline  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $0.0 < x < 0.45$ ) samples of uniform grain size were synthesized by conventional solid state reaction method discussed earlier.<sup>14</sup> Appropriate amounts of  $\text{La}_2(\text{CO}_3)_3$ ,  $\text{PbO}$ ,  $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and  $\text{Cr}_2\text{O}_3$  (each of purity  $> 99.99\%$ ) were mixed and preheated at  $500^\circ\text{C}$  for 5 h. Then they were grounded and heated at  $900^\circ\text{C}$  for 70 h with intermediate grindings. The powder thus obtained was annealed at  $900^\circ\text{C}$  for 24 h and furnace cooled. The phase purity of the samples were checked by powder x-ray diffraction (XRD) using  $\text{CuK}\alpha$  radiation at room temperature. The XRD patterns proves that all the samples are in single phase.<sup>14</sup> Resistivity ( $\rho$ ) was measured by conventional four probe technique. Thermoelectric power was measured by standard differential technique in the 80–300 K temperature range.

## III. RESULTS

Figure 1 shows the thermal variation of thermoelectric power (TEP) of  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  with  $x=0.0, 0.075, 0.15, 0.3, 0.45$ . The TEP curve (Fig. 1) for the chromium free

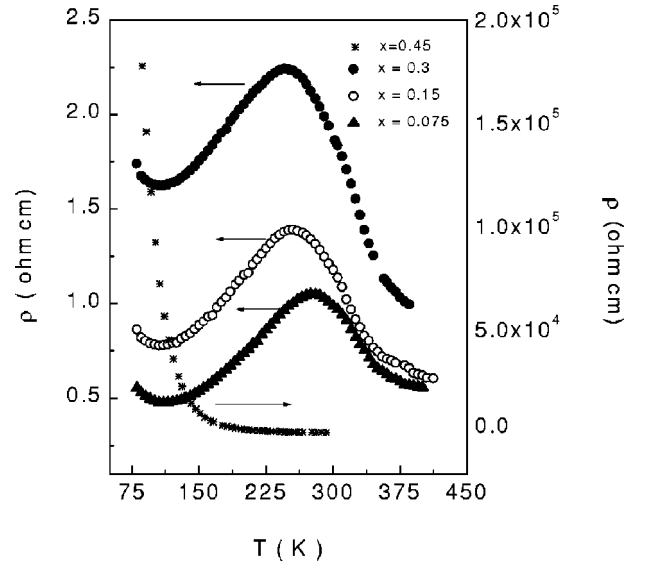


FIG. 2. Thermal variation of resistivity ( $\rho$ ) of  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  with  $x=0.075, 0.15, 0.3,$  and  $0.45$  (not showing MST).

sample, i.e.,  $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  agrees excellently with those obtained by Mandal<sup>18</sup> who studied TEP of this sample in absence of magnetic field. It is seen that for the Cr free sample, there is a change over in the sign of Seebeck coefficient ( $S$ ) with the change of temperature. This is a signature of the change in the nature of charge carrier. Interestingly, for the heavily Cr doped sample (with  $x > 0.3$ ),  $S$  is positive throughout the measured range of temperature. It is interesting to note that the magnitude of  $S$  increases with Cr doping similar to the increase of resistivity with increasing Cr content (Fig. 2) indicating the importance of impurity scattering with increasing Cr ion concentrations. Figure 2 shows the resistivity curve for some typical chromium doped samples, where the peak temperature  $T_p$  indicates metal-semiconductor transition. For  $T > T_p$ , the samples showed semiconducting nature, but for  $T < T_p$ , the samples indicated metallic character. For these samples, the ferromagnetic to paramagnetic phase transition temperature (Curie temperature  $T_c$ ) lies in the vicinity of  $T_p$ .<sup>4</sup> But the highly doped samples (for example, with  $x=0.45$ ) showed no such MST and it behaved as a semiconductor throughout the temperature range of our investigation (450–80 K). Figure 3 shows the temperature-dependent TEP both in the presence ( $B = 1.5$  T) and absence ( $B = 0.0$  T) of magnetic field for the three typical Cr doped samples. It is seen from this figures that application of a magnetic field ( $B = 1.5$  T, maximum range of our investigation) causes a decrease of Seebeck coefficient ( $S$ ) near  $T_p$ . Decrease in  $|S|$  near  $T_p$  is associated with the magnetoresistance (MR) effect. Thermal variation of magnetothermoelectric power (MTEP) ( $\Delta S/S_0 = |(S_0 - S_{1.5})/S_0 \times 100\%|$ ) plotted in Fig. 3 indicate a large anomaly around  $T_p$ . It is interesting to note that the field dependence of  $S(T)$  is limited around  $T_p$  or  $T_c$ . Analysis of the experimental results has been made in the following sections.

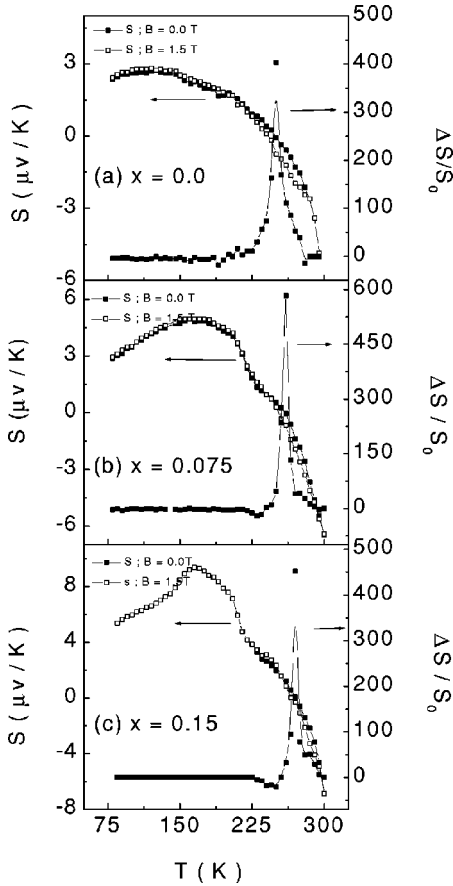


FIG. 3. Temperature dependent Seebeck coefficient ( $S$ ) and magnetothermoelectric power for  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  with  $x =$  (a) 0.0, (b) 0.075, and (c) 0.15 at  $B = 0.0$  and 1.5 T magnetic field.

#### IV. DISCUSSION

##### A. High-temperature ( $T > T_p$ ) TEP data

It is quite justified to assume that the electronic structure of the doping element plays a crucial role in explaining the TEP data of the La-Mn-O system. The dopant Cr is a neighbor of Mn in the periodic table and normally in the perovskite system Mn and Cr ions exist in the form of  $\text{Cr}^{3+}$  and  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  (Ref. 19). Their electronic structures are  $\text{Cr}^{3+}:t_g^{3/2}$  ( $S=3/2$ ),  $\text{Mn}^{4+}:t_g^{3/2}$  ( $S=3/2$ ), and  $\text{Mn}^{3+}:t_g^{3/2}e_g^1$  ( $S=2$ ), among which  $e_g^1$  electron of  $\text{Mn}^{3+}$  is the only electronically active electron. Due to nearly same ionic radii,<sup>20</sup> the doped Cr ions replace  $\text{Mn}^{3+}$  ions in the form of  $\text{Cr}^{3+}$ . Hence with Cr doping,  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio decreases and the presence of  $\text{Cr}^{3+}$  in the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  network structure disturbs the lattice. Again, as  $\text{Mn}^{4+}$  and  $\text{Cr}^{3+}$  are isoelectronic, there should be ferromagnetic double exchange (FMDE) interaction between  $\text{Mn}^{3+}$  and  $\text{Cr}^{3+}$ . But it is also known that the strength of  $\text{Mn}^{3+}\text{-O-Cr}^{3+}$ , double exchange (DE) interaction is smaller than that of  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  (Ref. 21). Hence with Cr doping, the effective DE interaction became weaker, resulting localization of only electronically active electron  $e_g^1$  of  $\text{Mn}^{3+}$ , which again causes the gradual shift of Seebeck coefficient  $S$  towards higher positive value with increasing Cr doping (Fig. 1). This explanation also

supports the gradual increase in the resistivity with doping of  $\text{Cr}^{3+}$  as doping of  $\text{Cr}^{3+}$  localizes more and more  $e_g^1$  electrons.<sup>14</sup>

It is known that very little attempt has so far been made to study and explain the field dependent TEP of the manganite samples.<sup>22</sup> The feature of temperature-dependent transport property of this system can be qualitatively understood in terms of Mott's formula for charge contribution to the Seebeck coefficient in metals<sup>23</sup> viz.

$$S = -(\pi^2 K_B T / 3e) \sigma'(\epsilon_F) / \sigma(\epsilon_F), \quad (1)$$

where  $e$  is the electronic charge,  $\sigma(\epsilon_F)$  is the conductivity at the Fermi level, and  $\sigma'(\epsilon_F)$  stands for  $(\partial/\partial\epsilon)\sigma(\epsilon)$ . The observed decrease in  $S$  around  $T_c/T_p$  in presence of magnetic field can be attributed to the increase in conductivity due to the phase transition to the metallic FM state (or due to the decrease of resistivity with the application of magnetic field), provided that the change of  $\sigma'(\epsilon_F)$  or the phonon-drag effect is regarded as a minor contribution. The large MTEP peak near  $T_c/T_p$  suggests its correlation with MR effect. It is interesting to note that the field dependence of  $S(T)$  is limited to a small temperature range near  $T_c/T_p$ , whereas  $\rho(T)$  retains its field dependency to a much lower temperature range.<sup>4</sup> Though several attempts<sup>24</sup> have been made to explain this behavior on the basis of individual grain contribution to thermopower and resistivity, but the total picture is still not clear. Thermoelectric power is usually less affected by the grains since heat flow from grain to grain is additive in nature.

In recent years, there has been extensive discussion on the polaronic transport in the high-temperature ( $T > T_p$ ) paramagnetic phase of this type of system.<sup>24,25</sup> We also noticed that the high-temperature TEP data fit very well with Mott's well known equation<sup>23</sup> of Seebeck coefficient which has the form

$$S = k_B / e [E_s / k_B T + \alpha'], \quad (2)$$

where  $E_s$  is the activation energy obtained from the TEP data and  $\alpha'$  is a constant, where  $\alpha' < 1$  suggests hopping due to small polaron and  $\alpha' > 2$  suggests the existence of large polaron.<sup>26</sup> Figure 4 shows the  $S$  vs  $1/T$  curve for some typical Cr doped sample with  $x = 0.075, 0.15, 0.3$  both in the absence and presence of magnetic field. The solid lines in Fig. 4 give the best fit curve to Eq. (2). From the slope of  $S$  vs  $1/T$  curves, we obtain the values of activation energy  $E_s$  for all the samples. The values of  $\alpha'$  obtained from fitting the curves (both at 0.0 and 1.5 T magnetic field) are shown in Table I. The values of activation energy ( $E_p$ ) obtained from the fitting of high-temperature resistivity data with Mott's<sup>23</sup> Eq. (3) viz.,

$$\rho = \rho_0 T \exp(E_p / k_B T) \quad (3)$$

are also displayed in Table I (at zero and 1.5 T field) for comparison. It is clearly seen from Table I that activation energies ( $E_s$  and  $E_p$ ) gradually increase with Cr doping both in absence and presence of field. Interestingly,  $E_s$  obtained from thermopower measurement is nearly one order of magnitude smaller than that ( $E_p$ ) estimated from the resistivity

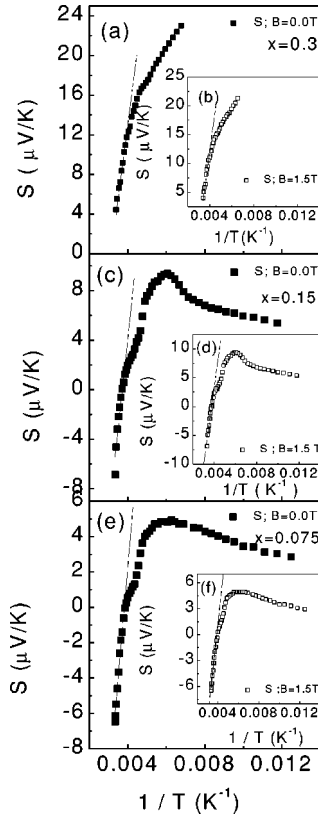


FIG. 4. Variation of thermopower  $S$  as a function of inverse temperature  $1/T$  for  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  with  $x=0.3$  (a) and (b),  $x=0.15$  (c) and (d),  $x=0.075$  (e) and (f) above the metal-semiconductor transition (MST) temperatures. The inset curves (b), (d), (f) represent the data taken in presence of magnetic field  $B=1.5$  T. Solid lines are the best fit to the Mott's SPH model [Eq. (2)].

data. The reason for this discrepancy as originally pointed out by Mott and Davis<sup>23</sup> is the thermal activation nature of the hopping transport at high temperature. The difference between the experimentally determined activation energy for the resistivity and thermopower is then the polaronic hopping energy  $W_H = E_p - E_s$ . The estimated values of  $W_H$  at 0.0 and 1.5 T magnetic field are shown in Table I. It is observed that all the parameters  $E_p$ ,  $E_s$ , and  $W_H$  increase with increasing Cr doping which can be explained on the

basis of localization of charge carrier ( $e_g^1$  electron of  $\text{Mn}^{3+}$  ion) as discussed above. For a fixed Cr content ( $x$ ), magnetic field decreases the activation energy. This may be due to delocalization of  $e_g^1$  electron, which decreases the activation energy. Unlike  $E_p$ ,  $E_s$  varies slightly with Cr content. Similar result was also reported by others.<sup>27</sup> Change of  $W_H$  with field, implies an increase of the radius of the polaron with field,<sup>25</sup> which is also supported from the relation due to Mott<sup>23</sup>

$$W_H = e^2/4\epsilon(1/r_p - 1/R), \quad (4)$$

where  $r_p$  is the polaronic radius and it is found that  $W_H$  varies inversely with  $r_p$ , which also supports that polaronic radius increase with field. From the calculated values of  $\alpha'$  from Eq. (2) for both 0.0 T field and 1.5 T field, we find  $\alpha' < 1$ . This supports small polaron hopping conduction valid for the present system.<sup>26</sup> Moreover, increase of  $\alpha'$  with field, is a strong evidence in support of our claim that  $r_p$  increases with magnetic field.

### B. Low-temperature ( $T < T_p$ ) TEP data

It is to be noted that strong temperature dependence of  $S$  and the appearance of broad maxima in FM phase have not been analyzed in detail to date.<sup>18</sup> Unlike the high-temperature ( $T > T_p$ ) paramagnetic phase, there is no standard theoretical relation to explain the TEP data corresponding to the FM phase. Similar to electrical conduction, several factors viz. impurity, complicated band structure, electron-electron, electron-magnon scattering, etc., affect thermoelectric power data. Though the picture is still not very clear, it is quite justified to assume that the electrical conduction and thermoelectric power data are closely related to the similar mechanism. According to the analysis of Snyders *et al.*<sup>28</sup> and Urushibara *et al.*,<sup>29</sup> the low-temperature ( $T < T_p$ , FM phase) conductivity data is dominated by electron-electron scattering term ( $T^2$  dependency). An additional  $T^{4.5}$  contribution was also included by Snyders *et al.*<sup>28</sup> and the authors demand that this additional contribution was due to electron-magnon scattering process. On the other hand, Urushibara *et al.*<sup>29</sup> showed that this contribution is actually due to spin wave scattering and the electron-magnon scattering process is better expressed by the  $T^{2.5}$  dependency.<sup>30</sup> We have observed from the present experimental data that in the low temperature FM phase, a  $T^{2.5}$  dependence (electron-magnon

TABLE I. The values of activation energies estimated from conductivity ( $E_p$ ) and thermoelectric power ( $E_s$ ) of  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  in the presence and absence of magnetic field. The estimated values of hopping energy ( $W_H$ ) and the constant term ( $\alpha'$ ) are also given for different samples both in 0.0 and 1.5 T field.

$x$	$E_p$ (meV)		$E_s$ (meV)		$W_H$ (meV)		$\alpha'$	
	0.0 T	1.5 T	0 T	1.5 T	0 T	1.5 T	0 T	1.5 T
0.0	107.3	101.3	8.54	6.62	98.76	94.68	-0.38	-0.31
0.075	111.56	102.98	12.65	11.09	98.91	91.89	-0.56	-0.49
0.15	117.47	108.73	14.45	13.51	102.99	95.22	-0.62	-0.59
0.3	123.00	115.64	14.98	14.28	108.02	101.36	-0.54	-0.52
0.45	172.00	169.97	15.06	14.43	156.94	155.54	-0.53	-0.51

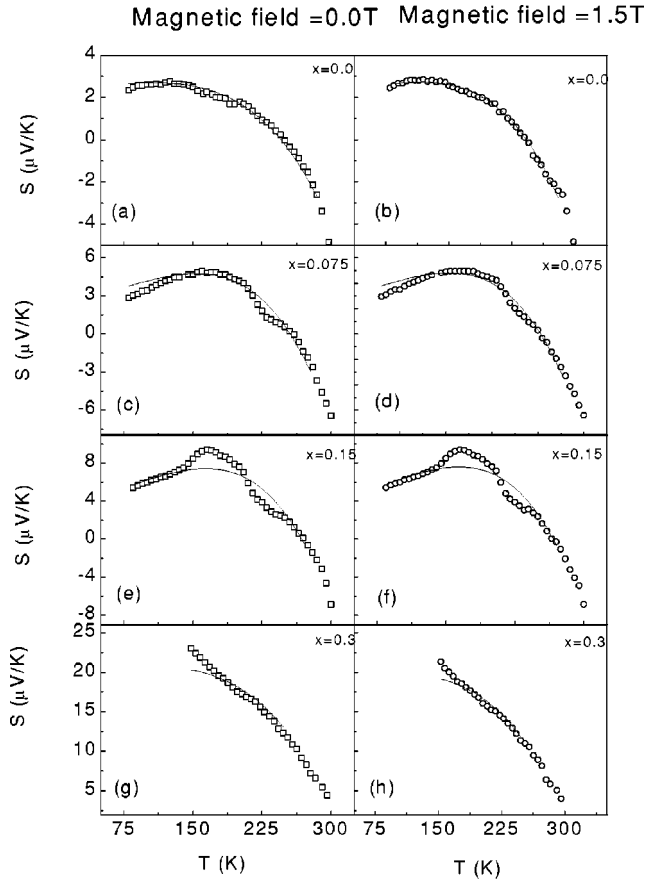


FIG. 5. Plot of  $S$  vs  $T$  for  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  with  $x=0.0$  (a) and (b),  $x=0.075$  (c) and (d),  $x=0.15$  (e) and (f),  $x=0.3$  (g) and (h). Curve (a), (c), (e), and (g) are TEP data obtained in absence of magnetic field, whereas curves (b), (d), (f), and (h) are those obtained in presence of magnetic field ( $B=1.5$  T). The solid lines represent the fitting curves with Eq. (5) as discussed in the text.

scattering) term dominates the conduction phenomenon.<sup>14</sup> The importance of magnon scattering has also been reported earlier<sup>31</sup> in the same La-Pb-Mn-O system. We, therefore, attempted<sup>3</sup> to analyze the thermoelectric power data in the FM phase using an expression<sup>18</sup> of the form

$$S = S_0 + S_{3/2}T^{3/2} + S_4T^4, \quad (5)$$

where the  $S_0$  term ( $S$  at  $T=0$  K) has no physical origin. The  $T^{3/2}$  behavior suggests that electron-magnon scattering strongly affects the low temperature (FM phase) TEP of this

type of manganites as in the case of electrical conduction. The origin of the  $S_4T^4$  term is still not clear. It may be due to spin wave fluctuation in the FM phase, as discussed by Urushibara *et al.*<sup>29</sup> to explain their low-temperature conductivity data. Though several authors<sup>28,29</sup> obtain an additional  $T^{4.5}$  (spin wave scattering) contribution to explain conductivity data, we observed no such additional temperature dependency while explaining the corresponding low-temperature data in the FM phase of the  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  system.<sup>14</sup> Figure 5 shows the best fit curve (solid line) in the metallic FM phase of the Cr doped samples showing MST. As the sample with maximum  $x$  ( $=0.45$ ) showed no MST, and had no FM phase at low temperature, TEP data of this sample has not been fitted with Eq. (5). Equation (5) is also used to analyze the TEP data obtained in presence of magnetic field. Similar equation was also used<sup>18</sup> earlier to fit the zero field TEP data of the FM phase of  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $A=\text{Pb, Sr, Ca, Ba}$ ). Experimental TEP data of the Cr free sample, i.e.,  $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  also shows excellent agreement with Eq. (5). The corresponding fitting parameters are given in Table II. Though we made a successful attempt to fit the TEP data of all Cr doped samples showing MST, it is also noticed from Fig. 5 that with increasing Cr content, fitting curve (solid line in Fig. 5) gradually deviates from the experimental data particularly for the samples with higher concentrations of Cr content. It may be due to the fact that presence of  $\text{Cr}^{3+}$  in the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  network disturbs the lattice and hence the heat flow as discussed above. From Table II one also finds a systematic variation of the fitting parameters  $S_0$ ,  $S_{3/2}$ ,  $S_4$  for the Cr doped La-Pb-Mn-O samples. Thus Eq. (5) fits the TEP data both in presence and in absence of magnetic field with reasonable values of the model parameter. Very little is, however, known about the interdependency of the individual term in Eq. (5). Such findings would be more interesting. It is further asserted that both thermopower ( $S$ ) and resistivity ( $\rho$ ) are determined only by the electronic properties of the material and thus often combined to a form  $S^2/\rho$ , the “power factor” which is related to the thermal conductivity of the sample. In contrast, the thermal conductivity  $\kappa = \kappa_l + \kappa_e$  is composed of a lattice contribution ( $\kappa_l$ ) and an electronic contribution ( $\kappa_e$ ). The power factor estimated from the TEP and resistivity data are shown in Fig. 6, both in presence and in absence of magnetic field. Similar to thermal conductivity,<sup>5</sup> the  $S^2/\rho$  term first decreases with lowering of temperature for all the samples showing MST and it shows a minimum around  $T_p$ . With further lowering of temperature

TABLE II. The values of the parameters  $S_0$ ,  $S_{3/2}$ , and  $S_4$  obtained from fitting the low temperature (ferromagnetic phase) thermoelectric power data with Eq. (5) both in presence and in absence of magnetic field.

$x$	$S_0$ ( $\mu\text{V/K}$ )		$S_{3/2}$ ( $\mu\text{V/K}^{5/2}$ )		$S_4$ ( $\mu\text{V/K}^5$ )	
	0.0 T	1.5 T	0 T	1.5 T	0 T	1.5 T
0.0	2.479	2.365	$3.1 \times 10^{-4}$	$4.5 \times 10^{-4}$	$-1.01 \times 10^{-9}$	$-1.18 \times 10^{-9}$
0.075	2.574	2.499	$1.8 \times 10^{-3}$	$1.9 \times 10^{-3}$	$-2.36 \times 10^{-9}$	$-2.54 \times 10^{-9}$
0.15	3.593	3.483	$2.9 \times 10^{-3}$	$3.1 \times 10^{-3}$	$-3.16 \times 10^{-9}$	$-3.37 \times 10^{-9}$
0.3	20.559	19.527	$5.3 \times 10^{-3}$	$5.5 \times 10^{-3}$	$-2.51 \times 10^{-9}$	$-2.61 \times 10^{-9}$

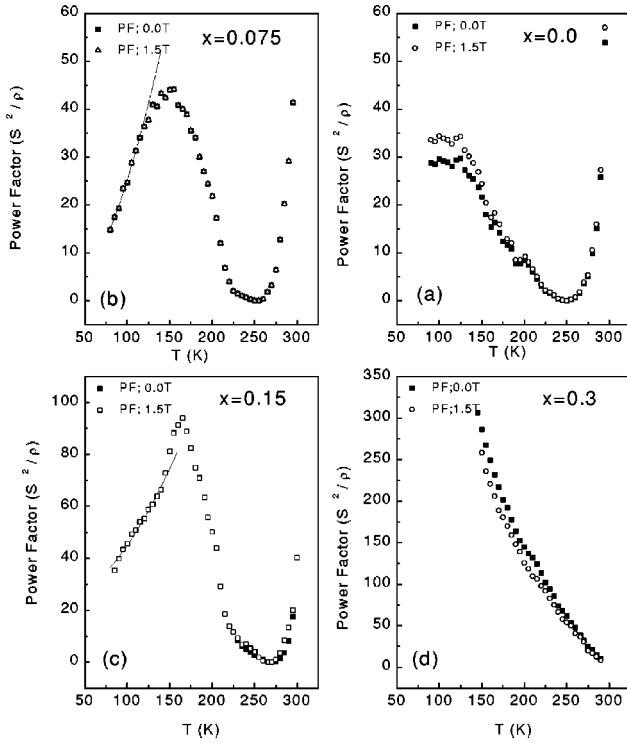


FIG. 6. Temperature dependent power factor ( $S^2/\rho$ ) for  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  with  $x =$  (a) 0.0, (b) 0.075, (c) 0.15, and (d) 0.3 at  $B = 0.0$  and 1.5 T magnetic field.

below  $T_p$ , power factor increases and shows a peak around 150 K and then again decreases. The  $S^2/\rho$  vs  $T$  curve below the peak temperature (150 K) approaches  $T^2$  variation as shown by the solid lines in Figs. 6(a), 6(b). On the high-temperature side of the peak, the power factor and hence conductivity decreases presumably as a result of phonon-phonon umklapp scattering as suggested by Chen *et al.*<sup>5</sup> The power factor showed a minimum value around the metal-semiconductor transition temperature ( $T_p$ ). A similar minimum (dip) around  $T_p$  was also observed in the thermal conductivity vs temperature curve of other sample viz. La-Ca-Mn-O,<sup>5</sup>  $\text{CoF}_2$ ,<sup>32</sup>  $\text{MnO}$ .<sup>33</sup> For the present samples with  $x > 0.3$ , the power factor, however, did not show peak in the low-temperature region up to 150 K [Fig. 6(d)]. The said peak might, however, exist at much lower temperature (below 100 K). However, because of the high value of the  $S$  and thermal fluctuation, we could not measure  $S$  of these samples below 150 K. In the present system, magnetic field dependence of thermoelectric power and resistivity indicate that

phonons experience scattering proportional to the deviation of magnetization  $\delta M$  from its saturation value.<sup>5</sup> Referring to the temperature dependence, a peak in  $\delta M$  at the critical temperature will cause a minimum in the thermal conductivity and power factor as observed from the experimental results. Actually, due to the spin fluctuation, the phonon mean free path ( $\lambda_p$ ) splits into two parts ( $1/\lambda_p = 1/\lambda_{nm} + 1/\lambda_{mag}$ ) viz. nonmagnetic and magnetic parts.<sup>34</sup> The magnetic part  $1/\lambda_{mag}$  is proportional to the deviation of the magnetization from the saturated value viz.  $\delta M$ . At finite temperature  $T$ , a magnetic field will cause a smaller spin fluctuation and hence smaller  $\delta M$  and larger  $1/\lambda_p$ . This is indicated by the little smaller values of the thermopower and hence the power factor in presence of magnetic field, particularly around  $T_p$ . Similarly field-dependent thermal conductivity also show a lower value<sup>5</sup> than that of the corresponding zero field value.

## V. CONCLUSIONS

In conclusion, the magnetic-field-dependent transport property of the Cr doped  $\text{La}_{0.5}\text{Pb}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  ( $x = 0-0.45$ ) system has been investigated. Compared to the undoped system, the conductivity and thermoelectric power of the Cr doped system showed smaller field dependence observed around the metal-semiconductor transition temperature ( $T_p$ ) of the samples. Both conductivity and thermoelectric power data support small polaron hopping conduction mechanism in these oxides above the metal-semiconductor transition temperature. Low-temperature (below  $T_p$ ) field-dependent TEP data can be fitted with  $S = S_0 + S_{3/2}T^{3/2} + S_4T^4$ . The second term suggests the importance of electron-magnon scattering strongly affecting the low temperature (ferromagnetic phase) TEP data. However, the  $T^4$  term is not well understood and not very important for the present samples of our investigation. Spin fluctuations, which are smaller in presence of magnetic field, are effective in scattering the phonons. Field-dependent transport studies on well characterized single crystal would be more interesting. However, since the overall character of thermoelectric power of the bulk sample is similar to that of single crystal, present experimental results would also be important to analyze the corresponding single crystal values in presence of magnetic field when available.

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<sup>1</sup>R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).

<sup>2</sup>S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, and L.H. Chen, Science **264**, 413 (1994).

<sup>3</sup>S. Uhlenbruck, B. Buchner, R. Gross, A. Freimuth, A.M. deLeon Guevara, and A. Revcolevschi, Phys. Rev. B **57**, R5571 (1998).

<sup>4</sup>R. Mahendiran, R. Mahesh, A.K. RayChaudhuri, and C.N.R. Rao, J. Phys. D **28**, 1743 (1995).

<sup>5</sup>B. Chen, A.G. Rojo, C. Uher, H.L. Ju, and R.L. Greene, Phys. Rev. B **55**, 15 471 (1997).

<sup>6</sup>C. Zener, Phys. Rev. **82**, 403 (1951).

<sup>7</sup>A.J. Millis, P.B. Littlewood, and B.I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).

<sup>8</sup>A. Maignan, C. Martin, and B. Raveau, Z. Phys. B: Condens. Matter **102**, 19 (1997).

<sup>9</sup>K. Ghosh, S.B. Ogale, R. Ramesh, R.L. Greene, T. Venkatesan, K.M. Gapchup, R. Bathe, and S.I. Patil, Phys. Rev. B **59**, 533

- (1999).
- <sup>10</sup>M. Rubinstein, D.J. Gillespie, J.E. Snyder, and T.M. Tritt, Phys. Rev. B **56**, 5412 (1997).
- <sup>11</sup>J. Blasco, J. Garcia, J.M. deTeresa, M.R. Ibarra, J. Perez, P.A. Algarabel, C. Marquina, and C. Ritter, Phys. Rev. B **55**, 8905 (1997).
- <sup>12</sup>J. Gutierrez, A. Pena, J.M. barendiaran, J.L. Pizarro, L. Iezama, M. Insanti, and T. Rojo, J. Phys.: Condens. Matter **12**, 10 523 (2000).
- <sup>13</sup>O. Cabeza, M. Long, C. Severae, M.A. Bari, C.M. Muirhead, M.G. Fransisconi, and G. Greaves, J. Phys.: Condens. Matter **11**, 2569 (1999).
- <sup>14</sup>Aritra Banerjee, S. Pal, and B.K. Chaudhuri, J. Chem. Phys. **115**, 1550 (2001).
- <sup>15</sup>X. Liu, X. Xu, and Y. Zhang, Phys. Rev. B **62**, 15 112 (2000).
- <sup>16</sup>A. Barnabe, A. Maignan, M. Hervieu, F. Damay, C. Martin, and B. Raveau, Appl. Phys. Lett. **71**, 3907 (1997).
- <sup>17</sup>B. Raveau, A. Maignan, and C. Martin, J. Solid State Chem. **130**, 162 (1997).
- <sup>18</sup>P. Mandal, Phys. Rev. B **61**, 14 675 (2000).
- <sup>19</sup>J. Zhang, Q. Yan, F. Wang, P. Yuan, and P.Z. Hang, J. Phys.: Condens. Matter **12**, 1981 (2000).
- <sup>20</sup>P.V. Vanitha, R.S. Singh, S. Natarajan, and C.N.R. Rao, J. Solid State Chem. **137**, 365 (1998).
- <sup>21</sup>A. Maignan, C. Martin, F. Damay, M. Hervieu, and B. Raveau, J. Magn. Magn. Mater. **188**, 185 (1998).
- <sup>22</sup>A. Asamitsu, Y. Moritomo, and Y. Tokura, Phys. Rev. B **53**, R2952 (1996).
- <sup>23</sup>N.F. Mott and E.A. Davis, in *Electronics Process in Non Crystalline Materials* (Clarendon, Oxford, 1971).
- <sup>24</sup>M. Jaime, M.B. Salamon, K. Pettit, M. Rubenstein, R.E. Treece, J.S. Horwitz, and D.B. Chrisey, Appl. Phys. Lett. **68**, 1576 (1996); S. Chatterjee, P.H. Chou, C.F. Chang, I.P. Hong, and H.D. Yang, Phys. Rev. B **61**, 6106 (2000).
- <sup>25</sup>M. Jaime, M.B. Salamon, M. Rubinstein, R.E. Treece, J.S. Horwitz, and D.B. Chrisey, Phys. Rev. B **54**, 11 914 (1996).
- <sup>26</sup>K. Segal, Y. Kuroda, and H. Sakata, J. Mater. Sci. **33**, 1303 (1998).
- <sup>27</sup>Y. Sun, X. Xu, and Y. Zhang, Phys. Rev. B **63**, 054404 (2000).
- <sup>28</sup>G.J. Snyder, R. Hiskes, S. DiCarolis, M.R. Beasley, and T.H. Geballe, Phys. Rev. B **53**, 14 434 (1996).
- <sup>29</sup>A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, Phys. Rev. B **51**, 14 103 (1995).
- <sup>30</sup>J.M. De Teresa, M.R. Ibarra, J. Blasco, J. García, C. Marquina, P.A. Algarabel, Z. Arnold, K. Kamenev, C. Ritter, and R. von Helmolt, Phys. Rev. B **54**, 1187 (1996).
- <sup>31</sup>Sudipta Pal, Aritra Banerjee, E. Rozenberg, and B.K. Chaudhuri, J. Appl. Phys. **89**, 4955 (2001).
- <sup>32</sup>G.A. Slack, Phys. Rev. **122**, 1451 (1961).
- <sup>33</sup>G.A. Slack and R. Newman, Phys. Rev. Lett. **1**, 359 (1958).
- <sup>34</sup>C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).