

## Thermoelectric properties of $(R, \text{Sr})\text{CoO}_3$ ( $R=\text{La, Pr, Nd, Sm}$ )

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We studied the thermoelectric properties of  $R_{1-x}\text{Sr}_x\text{CoO}_3$  ( $R=\text{La, Pr, Nd, and Sm}$ ) polycrystalline samples. Resistivity ( $\rho$ ) decreased systematically with Sr content, and its temperature coefficient was positive over a wide temperature range for  $x \geq 0.2$  regardless of the  $R$  element. The Seebeck coefficient ( $S$ ) also decreased with Sr doping, but was less susceptible to the Sr content in the small  $x$  regime. Therefore, the power factors of slightly Sr-doped  $R=\text{La}$  and  $\text{Pr}$  samples were large, being comparable to that of polycrystalline  $\text{NaCo}_2\text{O}_4$ . The Sr content dependence of  $S$  at 300 K of  $(\text{La,Sr})\text{CoO}_3$  can be well accounted for by a theory proposed by Koshibae *et al.* when  $x$  is small with assuming intermediate spin (IS) states for both  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions. The dependence of  $S$  on  $x$  of  $R=\text{Pr, Nd, and Sm}$  samples, on the other hand, suggests that the stability of IS state of  $\text{Co}^{3+}$  increases with Sr doping while the end members have a low spin configuration. The Seebeck coefficient decreased faster than expected when Sr content was increased beyond  $x=0.05$ , probably because the transfer integral of the carriers increased.

Key words: thermoelectric materials, Co oxide, carrier concentration dependence, spin state

### 1. INTRODUCTION

Recently, cobalt oxides such as  $\text{NaCo}_2\text{O}_4$  [1],  $\text{Ca}_3\text{Co}_4\text{O}_9$  [2], and  $(\text{Bi,Pb})_2\text{Sr}_3\text{Co}_2\text{O}_9$  [3,4] have attracted much attention as potential thermoelectric materials. For example,  $\text{NaCo}_2\text{O}_4$  exhibits a large thermopower (100  $\mu\text{V/K}$ ) and a low resistivity (200  $\mu\Omega\text{cm}$ ) at 300 K [1], which are comparable to conventional thermoelectric materials. The thermoelectric properties depend strongly on the carrier density, and the thermoelectric materials currently used as devices are heavily doped semiconductors [5]. However, the carrier density of the cobalt oxides is  $\sim 10^{21} \text{ cm}^{-3}$  [1,2], two orders of magnitude higher than what has been considered to be the optimum for conventional thermoelectric materials.

Large thermopower and large carrier concentration are usually not compatible, and it is believed that strong electron correlation plays a key role for the high thermoelectric properties in cobalt oxides. Specific heat measurement on  $\text{NaCo}_2\text{O}_4$  revealed an order of magnitude larger electronic specific-heat coefficient than a simple metal, which is taken as evidence of strong correlation [6]. The electron correlation causes a narrow band with a strongly energy dependent density of states in the vicinity of Fermi energy ( $E_F$ ), according to a band structure calculation [7]. The estimated Seebeck coefficient ( $S$ ) of  $\text{NaCo}_2\text{O}_4$  at room temperature based on the band calculation is 110  $\mu\text{V/K}$ , which is very close to the measured value. A different approach to understand the large thermoelectric power of strongly correlated materials was reported by Koshibae *et al.* based on entropy consideration [8]. They pointed out that it is important to take into account the degeneracy of  $3d$  electrons since

the thermoelectric power is given by the entropy per carrier.

The properties of strongly correlated materials usually vary drastically with carrier density, as exemplified by high temperature superconductors. In fact, from both models mentioned above, a strong carrier concentration dependence for  $S$  is expected; a slight shift of  $E_F$  with doping will significantly change the magnitude of  $S$  in the framework of the band picture because the band is narrow due to strong correlation. It is also unclear whether or not the rigid band picture holds. On the other hand, the degeneracy that determines the thermopower in the theory of Koshibae *et al.* varies with carrier density, because the population ratio of  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions changes.

$\text{LaCoO}_3$  is an already well studied system with a rather simple crystal structure, and is considered to be a charge transfer insulator. Doping with Sr is easy, which alters the system to a metal, while the electronic specific heat coefficient is much larger than simple metals, about 45  $\text{mJ/molK}^2$  when 20% of La is substituted by Sr [9]. Hence, this material is a good example to study the carrier dependence of thermoelectric properties in a strongly interacting electron system. It is also possible to substitute La by another rare earth ( $R$ ) element, and we carried out a systematic study of the thermoelectric properties of  $R_{1-x}\text{Sr}_x\text{CoO}_3$  with  $R=\text{La, Pr, Nd, and Sm}$ . This was also motivated by an interesting prediction made by Koshibae *et al.* [8], namely the thermoelectric properties may depend on  $R$  because an NMR study had concluded that the spin state of Co at room temperature of the end member ( $x=0$ ) is different from that of  $R=\text{La}$  when  $R=\text{Pr, Nd, Sm, and Eu}$  [10].

## 2. EXPERIMENTAL PROCEDURE

Polycrystalline  $R_{1-x}Sr_xCoO_3$  ( $R=La, Pr, Nd, Sm$ ,  $0 \leq x \leq 0.35$ ) samples were prepared by solid state reaction. A stoichiometric mixture of  $R_2O_3$  ( $R=La, Nd, Sm$ ) or  $Pr_6O_{11}$ ,  $SrCO_3$  and  $Co_3O_4$  was ground and calcined several times at  $1070^\circ C$  for 24 h. The obtained powders were pressed into pellets, and sintered at  $1070^\circ C$  for 24 h. X-ray diffraction measurements were carried out with a Rigaku diffractometer using  $Cu K\alpha$  radiation to confirm the phase purity. The magnetization measurements were performed with a Quantum Design's SQUID magnetometer. Resistivity was measured using a four-probe method. The Seebeck coefficient was measured with Seebeck effect measurement system of MMR Technologies Inc.

## 3. RESULTS AND DISCUSSION

The x-ray diffraction measurements indicated that all samples studied in this work were in a single phase.  $LaCoO_3$  can be indexed by a rhombohedral or hexagonal unit cell [11],  $PrCoO_3$  and  $NdCoO_3$  have cubic symmetry [12], and  $SmCoO_3$  possesses an orthorhombic structure [12]. The crystal symmetries were unaltered with doping Sr up to  $x=0.35$ , while the lattice constants increased because the ionic size of  $Sr^{2+}$  is larger than  $R^{3+}$ .

Figure 1 shows the temperature ( $T$ ) dependence of resistivity ( $\rho$ ) of the  $R=La$  samples. It can be seen that  $\rho$  drastically decreased with a slight doping of Sr to the parent compound, and systematically decreased with further increasing  $x$ . The temperature coefficient of  $\rho$  was positive over a wide temperature range when  $x \geq 0.2$ . A similar metal-insulator transition was observed at around  $x=0.2$  regardless of the  $R$  element.

Figure 2 shows the temperature dependence of magnetic susceptibility ( $\chi$ ) of the Sr non-doped

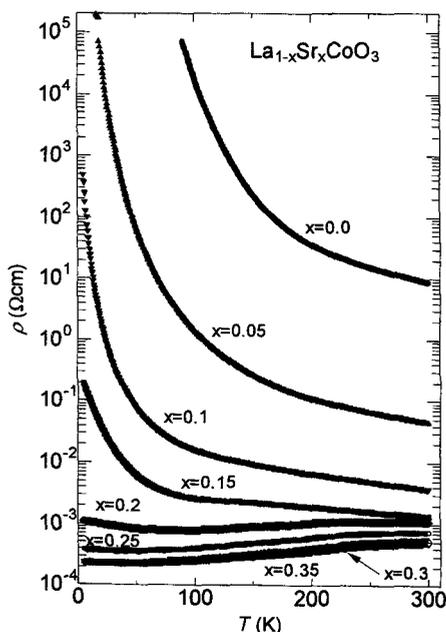


Fig. 1 Temperature dependence of resistivity of  $La_{1-x}Sr_xCoO_3$  ( $0 \leq x \leq 0.35$ ).

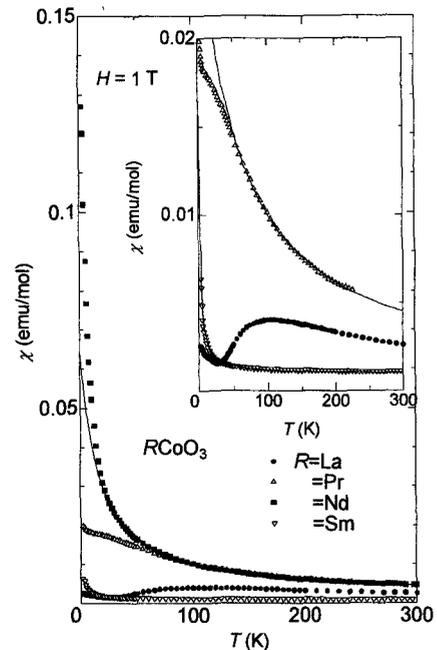


Fig. 2 Temperature dependence of magnetic susceptibility of the Sr-undoped  $RCoO_3$  ( $R=La, Pr, Nd, \text{ and } Sm$ ). The inset shows the same data of  $R=La, Pr$  and  $Sm$  with an expanded scale. The solid curves show the Curie-Weiss fitting.

$RCoO_3$  samples. For  $LaCoO_3$ , it has been established that  $Co^{3+}$  ions undergo a spin state transition from low-spin (LS) state to a higher spin state, the intermediate-spin (IS) state or the high-spin (HS) state [13]. Corresponding to the spin-state transition,  $\chi$  of  $LaCoO_3$  increased rapidly with temperature above 35 K, and showed a broad maximum at around 100 K. On the other hand,  $RCoO_3$  with  $R=Pr, Nd, \text{ and } Sm$  exhibited a Curie-Weiss behavior up to 300 K. We fitted the Curie-Weiss law

$$\chi = \frac{C}{T - \theta} + \chi_0 \quad (1)$$

to the susceptibility data. The calculated effective magnetic moments ( $\mu_{eff}$ ) were  $3.49\mu_B$ ,  $2.85\mu_B$ , and  $0.427\mu_B$  for  $R=Pr, Nd, \text{ and } Sm$ , respectively, where  $\mu_B$  is a Bohr magneton. These values are smaller than the effective moments of a free  $R^{3+}$  ( $R=Pr, Nd, Sm$ ) ion, suggesting that  $Co^{3+}$  ions remained in the nonmagnetic LS state up to 300 K, consistent with the conclusion of an NMR measurement [10].

Figure 3 shows the values of  $\rho$  and  $S$  at 300 K for all studied samples. In accordance with resistivity, the Seebeck coefficient was large in the parent compounds and decreased with increasing  $x$ . The thermopower was positive regardless of  $R$  indicating a  $p$ -type conduction, except at low temperature for  $x \geq 0.3$  when  $R=La$  and  $x=0.35$  when  $R=Pr$ . Interestingly,  $\rho$  dropped rapidly with a slight doping of Sr, while the decrease of  $S$  was rather moderate in the same composition range. Note here that both quantities of Fig. 3 are plotted on the same scale. The rapid increase of

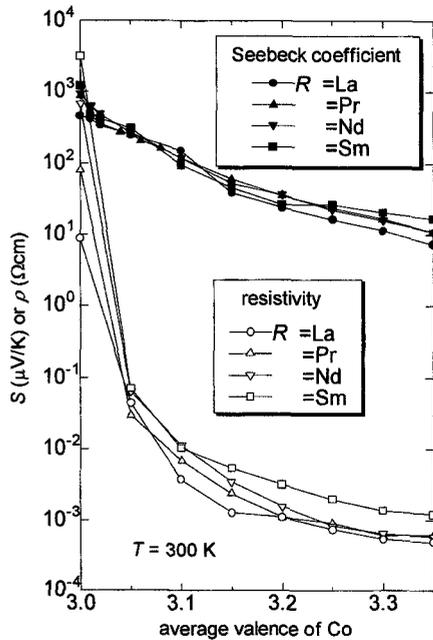


Fig.3 The Seebeck coefficient and resistivity at 300 K as a function of the average valence of Co. Note that  $S$  and  $\rho$  are plotted on the same scale.

electronic conductivity with doping a slight amount of carriers was similarly observed for high temperature superconducting materials, and seems to be characteristic of a Mott-Hubbard or a charge transfer insulator.

Figure 4 shows the power factor  $S^2/\rho$  at 300 K as a function of the average valence of Co. For the calculation of the average valence, we assumed a stoichiometric oxygen content because it was reported that the deviation in the oxygen content is negligible for  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  at least for  $x \leq 0.25$  [14]. The power factor shown in Fig. 4 takes a maximum at about  $x=0.05-0.1$ . Furthermore, the power factors of slightly Sr-doped  $R=\text{La}$  and  $\text{Pr}$  samples are comparable to that of polycrystalline  $\text{NaCo}_2\text{O}_4$  [15]. This can be attributed to the much faster decrease of resistivity than thermopower with increasing  $x$  in the slightly doped regime.

Now, it is interesting to compare our results with the theory of Koshibae *et al.* [8]. According

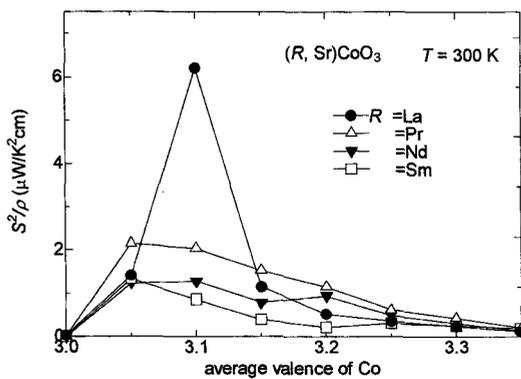


Fig. 4 The power factor at 300 K as a function of the average valence of Co.

to that theory,  $S$  in the high temperature limit is expressed as

$$S = -\frac{k_B}{e} \ln\left(\frac{g_3 x}{g_4 (1-x)}\right) \quad (2)$$

where  $x$  is the concentration of  $\text{Co}^{4+}$  ions (Sr content in our case),  $g_3$  and  $g_4$  are the degeneracy of  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$ ,  $e$  the absolute value of electron charge, and  $k_B$  the Boltzmann constant. This equation implies that  $S$  should depend on  $\ln(x^{-1}-1)$ , and we plotted the measured values of  $S$  at 300 K as a function of this quantity in Fig. 5. It should be kept in mind that the theory assumes the high temperature limit, while we plotted the room temperature data. This may cause a quantitative discrepancy between the theory and experiment, but Koshibae *et al.* pointed out that the thermopower at room temperature is close to that in the high-temperature limit for parameters that are appropriate for transition-metal oxides [8].

To compare our results with the theory, we need first discuss the spin state of Co of the present material. As already mentioned, Sr-undoped  $\text{LaCoO}_3$  undergoes a spin state transition at about 100 K. The spin state at high temperature has been a matter of argument for decades, although the IS state seems to be prevailing. For Sr-doped  $\text{LaCoO}_3$ , magnetic susceptibility measurements at high temperature suggest that  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions are both in the IS state at room temperature [16]. An x-ray absorption spectroscopy measurement combined with cluster calculation had also concluded that  $\text{Co}^{4+}$  of  $(\text{La},\text{Sr})\text{CoO}_3$  is in the IS state [17]. Therefore, the theoretical curve for the case of both ions being in the IS state is drawn as line (a) in Fig. 5. On the other hand,  $\text{Co}^{3+}$  is in the LS state in the Sr non-doped samples with  $R=\text{Pr}$ ,  $\text{Nd}$ , and  $\text{Sm}$  as already discussed. For LS  $\text{Co}^{3+}$  and IS  $\text{Co}^{4+}$ , the theory predicts line (b).

Roughly, the measured Seebeck coefficients are between lines (a) and (b) when  $x$  is small. The thermopower depended on  $R$  when  $x$  was small,

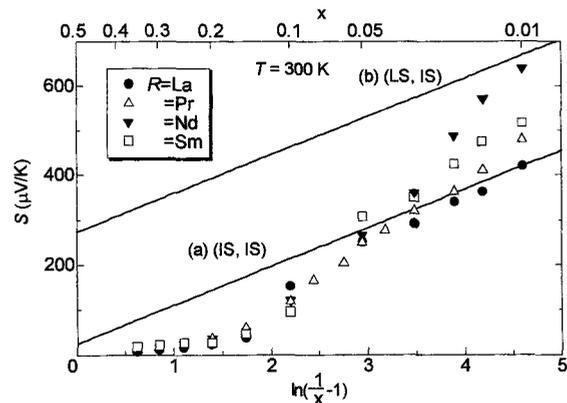


Fig. 5 The Seebeck coefficient at 300 K plotted as a function of  $\ln(x^{-1}-1)$  where  $x$  is the Sr content. The lines indicate the expectation of the theory by Koshibae *et al.* in the high temperature limit [8] if (a)  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions have both the IS configuration, and (b) for LS  $\text{Co}^{3+}$  and IS.

while this  $R$  dependence tended to diminish with Sr doping. In the case of  $R=La$ , the experimental results followed fairly well line (a) up to  $x=0.05$ . On the other hand, the Sr content dependence of  $S$  was quite different from the theoretical curves when  $R=Pr, Nd$ , and  $Sm$ . Note that the slope of the theoretical curve is the same whatever the spin configuration is, as is obvious from Eq. (2), if the spin states do not depend on  $x$ .

It has been suggested that Sr doping to  $LaCoO_3$  stabilizes the IS state of  $Co^{3+}$ . This is possibly caused by the expansion of the lattice volume with Sr doping, as an LDA+U calculation showed that the IS state is more stable for an increased lattice volume [18]. While it was reported that  $Co^{3+}$  ions of the parent materials ( $x=0$ ) were in the LS state for  $R=Pr, Nd$ , and  $Sm$ , Sr doping probably stabilizes the IS state similarly as for  $R=La$ . At least we can point out that the lattice constants increased with  $x$  for all compounds studied in this work, as already described. Therefore, the faster decrease of  $S$  with increasing  $x$  compared to the theoretical line (b) for  $R=Pr, Nd$ , and  $Sm$  may be attributed to the increased population of the IS state.

Figure 5 shows that the Seebeck coefficient of  $La_{1-x}Sr_xCoO_3$  deviated from line (a) when Sr content was increased beyond  $x=0.05$ . The  $R$  dependence of the Seebeck coefficient is small in this composition regime. These results may be taken as an indication of another change in the spin configuration. However, we rather think that the metal-insulator transition observed at around  $x=0.2$  is related to this result. The high temperature limit for which Eq. (2) was derived corresponds to  $t \ll k_B T$  where  $t$  denotes the transfer integral [8]. This condition is not fulfilled when  $t$  is large, and it is necessary to calculate  $S$  at finite temperature [19]. The deviation of the experimental data from curve (b) beyond  $x=0.05$  is probably because the transfer integral already started to increase, violating the assumption of the theory.

When the Fermi-liquid picture holds, the thermopower can be evaluated from the electronic structure using the Boltzmann's transport equation. For a system with itinerant carriers, such description would be suitable, and it is interesting to see how the thermopower of  $R_{1-x}Sr_xCoO_3$  with large  $x$  is correlated with the electronic structure.

#### 4. CONCLUSIONS

We have investigated thermoelectric properties of  $R_{1-x}Sr_xCoO_3$  ( $R=La, Pr, Nd$ , and  $Sm$ ) polycrystalline samples. The resistivity decreased with increasing Sr content, and the temperature coefficient was positive for a wide temperature range when  $x \geq 0.2$  regardless of the  $R$  element. The temperature dependence of magnetic susceptibility of Sr non-doped  $LaCoO_3$  resembled well the reported data in the literature, while those of  $RCoO_3$  ( $R=Pr, Nd$ , and  $Sm$ ) can be interpreted by assuming a LS state for  $Co^{3+}$  ions with no transition up to 300 K, consistent with the reported NMR data. Our results show that resistivity is

more susceptible when a small amount of carrier is doped to the parent compounds. As a consequence, we found a large power factor for slightly Sr-doped  $R=La$  and  $Pr$  samples, which is comparable to that of polycrystalline  $NaCo_2O_4$ . When compared with the theory by Koshibae *et al.*,  $S$  of  $(La,Sr)CoO_3$  follows well the prediction of the theory for small  $x$  if both  $Co^{3+}$  and  $Co^{4+}$  ions are in the IS state. The Seebeck coefficient showed a much stronger Sr content dependence for  $R=Pr, Nd$ , and  $Sm$ , which is probably caused by an increased stability of the IS state of  $Co^{3+}$  with Sr doping. The Seebeck coefficient deviated from the theoretical curve when Sr content was increased beyond  $x=0.05$ , probably because of the increase in the transfer integral of the carriers.

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