

Spin state, charge carrier and thermal transport in cobalt perovskites

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Abstract In continuation with both the thermoelectric evaluation and exciting physics of cobalt based perovskites we studied the interplay of thermal and electric transport, the spin state and the local symmetry of the coordination of Co ions. The comprehensive experimental examination of systems covering a wide range of $\text{Co}^{2+}/\text{Co}^{3+}/\text{Co}^{4+}$ ratio involving the cubic $Pm\bar{3}m$ and rhombohedral $R\bar{3}c$ phases, with straighten Co-O-Co bond, orthorhombically distorted $Pbmm$ perovskites and 2D perovskites $I4/mmm$ of $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ type, was performed in a wide temperature domain up to 1000 K. The observed results, referring namely the thermoelectric power and thermal conductivity, are discussed with respect to possible spin states and orbital degeneracy of $\text{Co}^{2+}/\text{Co}^{3+}/\text{Co}^{4+}$ species.

1. Introduction

Cobalt perovskites have been recently revised with respect to their promising thermoelectric potential- see.g.[1]. Furthermore, in spite of already 50 years research of the spin state of cobalt ions and the nature of the broad magnetic-electronic transitions in $\text{Ln}_{1-x}\text{A}_x\text{CoO}_3$ perovskites, the unequivocal physical background is still lacking [2]. In the ground state of prototype LaCoO_3 there is no magnetic moment on Co ions, which implies that all trivalent cobalt are in the diamagnetic, low-spin state (LS, $t_{2g}^6e_g^0$, $S = 0$)-see Fig.1. With increasing temperature the system becomes paramagnetic, the susceptibility increases rapidly and shows a broad maximum around 100 K. Another pronounced anomaly in the susceptibility accompanied with a significant decrease of the resistivity is observed at 500 K. The 100 K transition was first interpreted by Goodenough as a change of 50% of cobalt ions from the low-spin ground state to high-spin state (HS, $t_{2g}^4e_g^2$, $S = 2$) -see Table 1. Simultaneously, the 500 K transition was assigned to an order-disorder transition, where the e_g electrons become itinerant and destroy the LS-HS superstructure. The latter was, however, never observed experimentally when a dynamic resonance of LS and HS Co^{3+} states was proposed subsequently [3]. More recent experiments of photoelectron emission and X-ray absorption spectroscopy, supported by band structure calculations led to an alternative interpretation of the 100 K transition as a stabilisation of an intermediate spin state (IS, $t_{2g}^5e_g^1$, $S = 1$). This is an orbitally degenerate (Jahn-Teller active) state in which both the e_g electron and t_{2g} hole may be coupled with the same distortion mode of the CoO_6 octahedron of the E_g symmetry. Using the results of LDA+U, Korotin et al. [4] explained stabilization of Intermediate Spin state over High Spin state due to the large hybridization between Co-3d (e_g) and O-2p orbitals. The physical reason for this transition is a competition between crystal-field energy Δ_{cf} and intra-atomic (Hund) exchange energy Δ_{ex} (Fig. 1). In the ground state Δ_{cf} is only slightly larger than Δ_{ex} so the energy of the excited magnetic state of Co ion is relatively small and with increased temperature its population increases resulting in an increase of magnetic susceptibility. To demonstrate the complexity of the possible ground states (spin and orbital) the total degeneracy for Co^{2+} , Co^{3+} and Co^{4+} species is shown in Table 1.

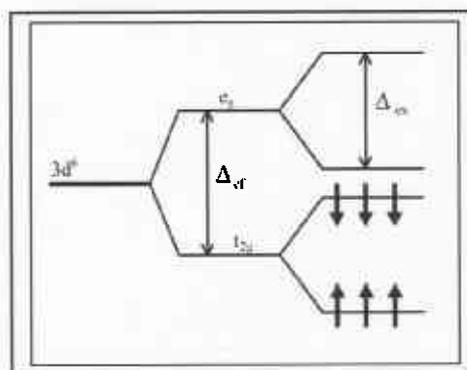


Fig 1. Scheme of energy levels for Low Spin state of Co^{3+} ions in LaCoO_3

When La ions are substituted in perovskite cobaltites by smaller rare earth and alkaline earths elements (inducing Co^{4+} formation), magnetic properties show significant changes as demonstrated in Fig.2 using our data.

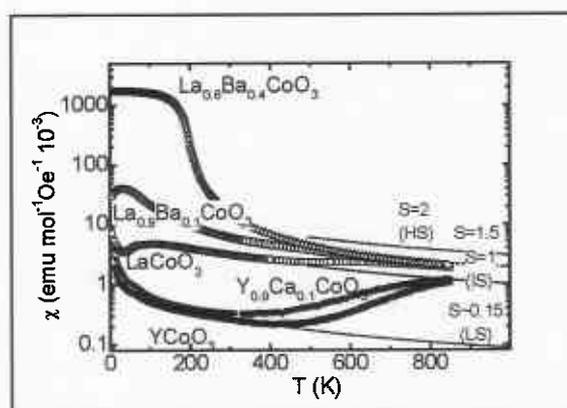


Fig2. The temperature dependence of the DC magnetic susceptibility for $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ and $\text{Y}_{1-x}\text{Ca}_x\text{CoO}_3$. In the LaCoO_3 the dominating interactions are antiferromagnetic while the $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$ is ferromagnetic due to introduction of Co^{4+} species.

Coherently the ^{59}Co Knight shift measurements showed that Co ions remain to be in the Low Spin state up

We suppose that, contrary to LS Na_xCoO_2 cobaltites, where the possible impact of spin and orbital degeneracy on the thermoelectric power was emphasized, the high value of thermoelectric power up to 700 K is dominantly influenced by a low concentration of charge carries.

3.2 $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$ system

We show in Fig. 4 the temperature dependence of the magnetic susceptibility for small Sr doping up to 0.1. We see that the incorporation of even very small concentration of formally Co^{4+} species via A^{2+} substitution leads to the appearance of FM interactions. and the ferromagnetism, competing with antiferromagnetic interactions in LaCoO_3 , leads to spin glass behaviour.

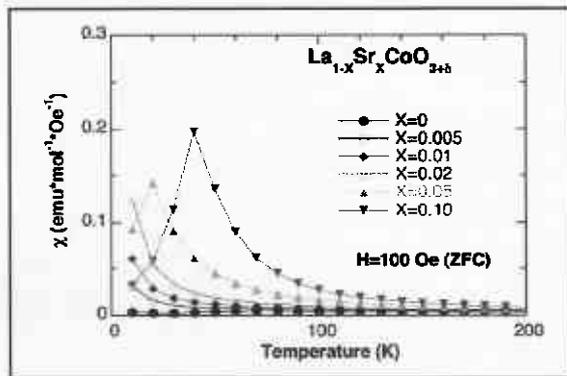


Fig4. The temperature dependence of the DC magnetic susceptibility for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$.

The magnetic fluctuations depress simultaneously the thermal conductivity, as evidenced in the Fig 5. Nonetheless the strongly depressed thermal conductivity below 300 K is observed also for pure LaCoO_3 . The low temperature phononic peak of λ_{ph} is, however, completely wiped out for $x > 0.02$.

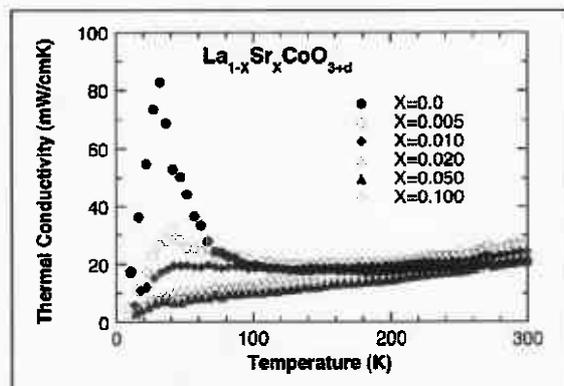


Fig5. The temperature dependence of the thermal conductivity for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$.

The origin of this behaviour resides as in the Jahn-Teller active IS Co^{3+} ($t_{2g}^5e_g^1$) dynamic modes (intermediate temperatures) as in a strong scattering due to fast hopping electrons between IS Co^{4+} ($t_{2g}^4e_g^1$) or LS Co^{4+} ($t_{2g}^5e_g^0$) and IS Co^{3+} ($t_{2g}^5e_g^1$) species (low temperatures). The association of the strongly depressed thermal conductivity with IS Co^{3+} is supported by comparison with the thermal conductivity for the LS $\text{Y}_{1-x}\text{Ca}_x\text{CoO}_3$ presented in Fig 6. Despite of a high disorder due to Ca for Y substitution (both size and mass mismatch) and high porosity of the sample the broad low temperature λ_{ph} peak is still present for $x=0.1$ sample.

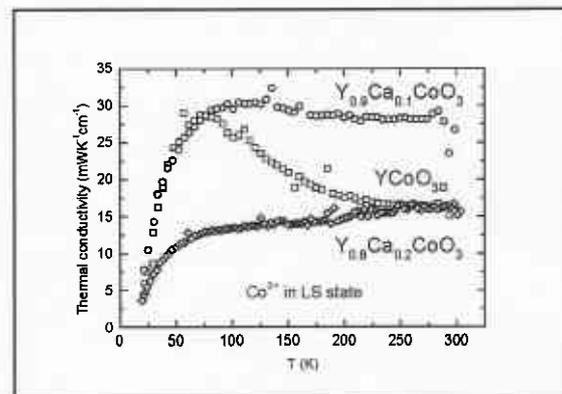


Fig6. The temperature dependence of the thermal conductivity for $\text{Y}_{1-x}\text{Ca}_x\text{CoO}_3$.

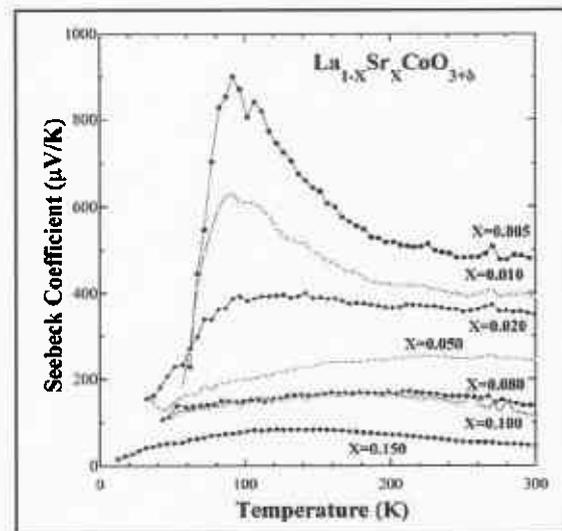


Fig7. The temperature dependence of the thermoelectric power for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$.

Finally we demonstrate in the Fig. 7 the temperature dependence of the thermoelectric power S for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$. For the lowest Sr concentrations the electrical resistivity exceeds the minimum metallic conductivity (the Ioffe-Regel "metallic" limit $\rho \sim 1-2 \text{ m}\Omega\text{cm}$)

and is strongly temperature dependent pointing to the hopping mechanism of the charge carrier transport. In coherence the thermoelectric power is temperature weakly dependent and its the absolute value at room temperature corresponds to that deduced from a simple Heiks configurational entropy approximation;

$$S_{\text{Heiks}} = \frac{k_B}{e} \ln \left[\frac{1-x}{x} \right] \quad [1]$$

Applying this formula e.g for $x=0.005$ we observe $S_{\text{Heiks}} = 455 \mu\text{VK}^{-1}$ which compares with $S_{\text{exp}} \sim 500 \mu\text{VK}^{-1}$, similarly for $x=0.05$ $S_{\text{exp}} \sim 250 \mu\text{VK}^{-1}$ matches with $S_{\text{Heiks}} \sim 257 \mu\text{VK}^{-1}$.

For the higher x the thermopower is reduced below the Heiks approximation and the behaviour approaches to that typical for the metals with a high carrier concentration. This corroborates with a strongly enhanced electrical conductivity approaching at 300 K to the Ioffe-Regel "metallic" limit .

3.3 N-type doping

We have attempted to introduce the n-type carriers in both LS (DyCoO_3) and IS (LaCoO_3) parent systems substitution of Co^{3+} by Ti^{4+} ($3d^0$) was found successful with respect to sample purity. As evidenced in Fig. 8 for $\text{DyCo}_{1-x}\text{Ti}_x\text{O}_3$ the thermopower is negative below ~ 400 K confirming thus the formation of n-type charge carriers at low temperatures.

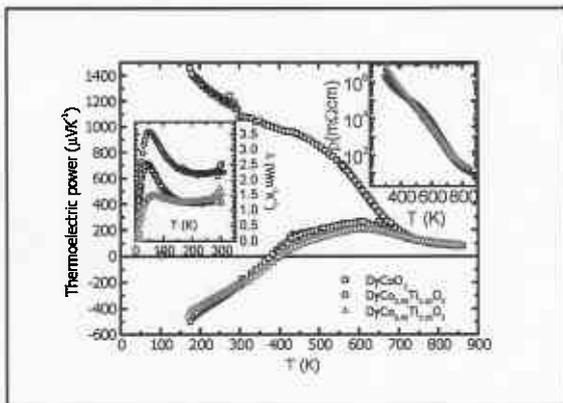


Fig8. The temperature dependence of the thermoelectric power for the Ti doped LS $\text{DyCo}_{1-x}\text{Ti}_x\text{O}_3$ up to 900 K ($x=0.02, 0.05$). In the insets the thermal evolution of the electrical resistivity and thermal conductivity is shown.

The creation of n-type carriers conductivity is not, however, accompanied by commonly observed decrease of electrical resistivity – see the inset. This indicates that the N-type charge carriers possess a very low mobility which corroborates with their limited impact on phonon scattering –see the inset. Above 400 K the thermopower switches to positive values indicating the dominance of P-type carriers and when the temperature is further increased above the ~ 700 K the broad metal-insulator transition is observed and accompanied by a

significant decrease of thermopower below $\sim 100 \mu\text{VK}^{-1}$. As a possible explanation of temperature limited N-type conductivity we propose the electron hopping between the Co^{2+} (stabilized eventually in LS state via LS Co^{3+} and/or JT distorted IS Co^{3+} environment) and nonmagnetic LS Co^{3+} . On the other hand the hopping between magnetic HS Co^{2+} and IS or HS Co^{3+} is strongly limited due to dominating antiferromagnetic interactions between these species. This picture is further supported on the study of 2D perovskites $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ as shown in following section.

3.4 2D perovskites $\text{La}_{2-x}\text{Sr}_x\text{CoO}_3$ system

In order to check the possibility of both N- and P-type conduction in a wide range using single prototype system we have performed the investigation of $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ layered perovskites where, in principle, the Co formal valence can be varied from $\text{Co}^{2.5+}$ up to $\text{Co}^{3.5+}$. The magnetic interactions are revealed in Fig.9 where the magnetic susceptibility of Co^{4+} rich side is presented. With the increasing Co^{4+} concentration, similarly as in case of 3D analogue, the Weiss constant increases and culminates at $\Theta \sim 170$ K for $x=1.4-1.5$ indicating, together with the high value of the susceptibility and spontaneous moment, the long range ferromagnetic order. Simultaneously with increasing Θ , the spin only number S increases from minimum for $x=1.0$ ($S \sim 0.9$) to $S \sim 1.2$ for $x=1.5$. The Co^{2+} rich side is characterized by negative Weiss constant decreasing down to $\Theta \sim -200$ K for $x=0.5$ ($\text{Co}^{2+}/\text{Co}^{3+}=1$) while the spin number increases up to $S \sim 1.8$.

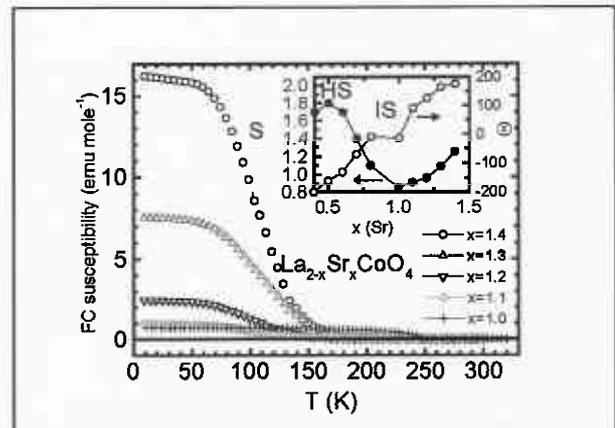


Fig9. The temperature dependence of the magnetic susceptibility for $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ ($1 < x < 1.5$). In the inset the composition dependence of the spin number S and Weiss constant Θ is shown (data for $0.4 < x < 1.0$ taken from Ref 6).

The increasing strength of antiferromagnetic interactions with decreasing cobalt valency is understandable presuming that the HS Co^{2+} species interact antiferromagnetically with surrounding IS or HS Co^{3+} network. The $\text{Co}^{2+}/\text{Co}^{3+}$ system is electrically insulating and contrary to 3D cobalt perovskites, even all ferromagnetic samples remain insulating down to low temperatures.

The interesting insight in the carries subsystem offers the complex Figure 9 where the temperature dependence of the thermopower is presented. The most important feature is that for any studied composition and for any temperature region the negative thermoelectric power is not achieved. At first glance this is very surprising, as intuitively one should presume, as a consequence of electron addition, the N-type conduction when lowering the valence below Co^{3+} . We speculate that this behaviour likely originates from the "immobility" of additional electrons associated with HS Co^{2+} species. On the other hand the introduction of Co^{4+} leads to substantial decrease of electrical resistivity accompanied simultaneously by decreased thermoelectric power, e.g. from $\sim 175 \mu\text{VK}^{-1}$ ($x=1.1$) down to $\sim 25 \mu\text{VK}^{-1}$ ($x=1.5$) at 300 K.

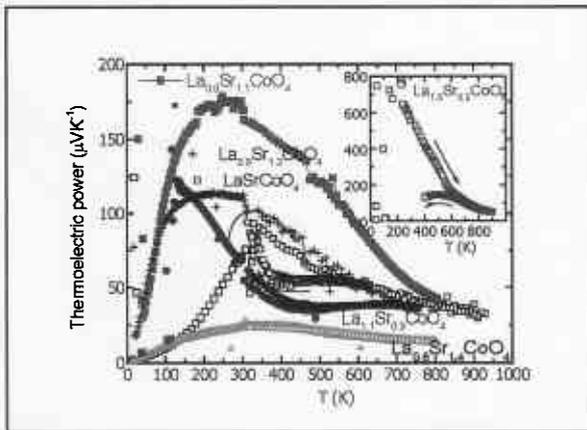


Fig10. The temperature dependence of the thermoelectric power for $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ ($1 < x < 1.5$) up to 900 K.

3.5 $\text{Co}^{3+}:\text{Co}^{4+}=1:1$

The role of mismatch was finally studied on 3D systems where the cobalt valence was fixed as $\text{Co}^{4+}/\text{Co}^{3+}=1/1$, i.e. where, supposing the hopping conduction, the simple Heikes configurational contribution is missing. In the Fig 11 we show the temperature dependence of thermopower for three cobalites which differ significantly with respect to structural matching of La(Sr,Ca,Y)-O and Co-O bonds – starting from relaxed $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ ($t=0.975$), via $\text{La}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$ ($t=0.95$) and ending by highly distorted $\text{La}_{0.3}\text{Y}_{0.2}\text{Ca}_{0.5}\text{CoO}_3$ ($t=0.94$). The most conducting cubic La-Sr system posses at room temperature resistivity of $\sim 0.3 \text{ m}\Omega\text{cm}$ and is ferromagnetic below $\sim 250 \text{ K}$, for the highly distorted La-Y-Ca system the resistivity increases up to $\sim 4.5 \text{ m}\Omega\text{cm}$ and T_c is lowered below 100 K. At 900 K the difference in electrical resistivity is decreased to $\sim 0.7 \text{ m}\Omega\text{cm}$ (La-Sr) and $\sim 2.7 \text{ m}\Omega\text{cm}$ (La-Y-Ca), respectively. In order to explain the temperature weakly dependent and relatively high value of the thermopower for La-Y-Ca system we employ the generalised Heikes formula

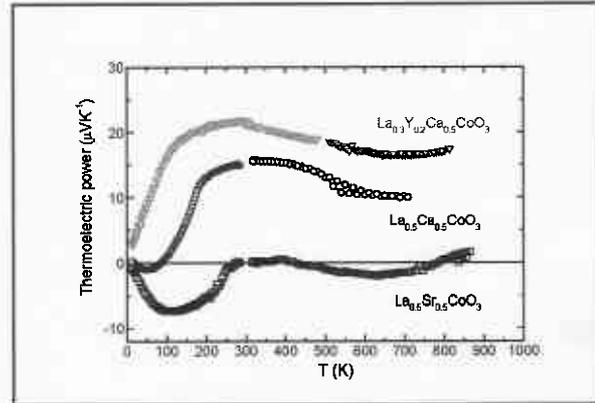


Fig. 11. The temperature dependence of the thermoelectric power for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, $\text{La}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$ and $\text{La}_{0.3}\text{Y}_{0.2}\text{Ca}_{0.5}\text{CoO}_3$ up to 900 K.

$$S = -\frac{k_B}{e} \ln \left[\beta_S \beta_O \frac{x}{1-x} \right] \quad [2]$$

supposing that dominating contribution to the thermopower is the configurational entropy of quasi-degenerate charge carriers. The additional $\beta_S \beta_O$ terms reflect the spin and orbital degeneracy (see Table 1) and $x = \text{Co}^{4+}/\text{Co}$, the fraction of Co^{4+} holes sitting on the Co sites, respectively.

This allows express $\beta_S \beta_O$ as the ratio $\frac{g_3}{g_4}$, where g_3 and g_4 stand for the degeneracy of configurations for trivalent and tetravalent cobalt in the octahedral coordination, respectively.

Using this picture the hopping conductivity of the Co^{4+} rich perovskites can be interpreted supposing the IS spin state of both Co^{3+} and Co^{4+} . In that case the holes of the t_{2g} character are involved and for identical Co^{3+} and Co^{4+} concentration, independently on the eventual Jahn-Teller distortion, the ratio between g_3 and $g_4 = 3/4$ leads to $\beta_S \beta_O = 3/4$ in the formula [2]. This leads to $S \sim 24 \mu\text{VK}^{-1}$ what is indeed very close to the value experimentally observed in highly mismatched 3D and 2D cobalites, containing 50% Co^{4+} , at high temperatures when hopping conductivity dominates - see Fig.10, 11. Nonetheless, when the structural distortion in 3D perovskite is decreased, the Co-O-Co bond is straightened and diffusive conduction of the itinerant or quasi-itinerant charge carriers e_g electrons start to dominate ($\rho \ll 1 \text{ m}\Omega\text{cm}$). This situation corroborates with the ferromagnetic coupling, observed for the high enough Co^{4+} concentration favouring the kinetic energy gain of the e_g electron linking the neighbouring Co ions. This makes the states before and after the electron transfer degenerate and corresponds to the $t_{2g}^5 \sigma^{*0.5}$ electronic configuration (by other words to 50% IS Co^{3+} and 50% LS Co^{4+}). This leads to similar magnetic exchange mechanism as known for ferromagnetic manganites- so called DoubleExchange. In the ferromagnetic state the corresponding thermoelectric power should be negative due to the electron diffusion in a quarter filled band. Indeed, as shown in Fig 11 for

ferromagnetic metallic La-Sr and La-Ca systems, this situation is experimentally observed.

4. Conclusions

The physical properties of various cobalt 3D and 2D perovskite cobaltites have been measured and analyzed. We summarize the complex experimental observation:

(i) independently on the cobalt valency the low spin ground-state of Co ions in $\text{Ln}_{1-x}\text{A}_x\text{CoO}_3$ is favoured by a small size of the interpolated cation. The LS state can be extended well above 300 K, promoting consequently the absolute value of thermoelectric power, (ii) the large depression of the thermal conductivity in LnCoO_3 is directly connected with the gradual stabilization of IS Co^{3+} species, the depressed thermal conductivity in $\text{Ln}_{1-x}\text{A}_x\text{CoO}_3$ is due to fast electron fluctuations between $\text{LS}(\text{IS})\text{Co}^{4+}$ and IS Co^{3+} species, (iii) the absence of negative thermoelectric power in 2D $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ and in 3D perovskites (at high temperatures only) is likely linked with the "immobility" of electrons associated with antiferromagnetically coupled HS Co^{2+} species surrounded by magnetic Co^{3+} species, (iv) the generalised

Heikes formula is applicable in interpretation of the hopping conductivity in perovskite cobaltites.

Acknowledgments

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