Prominent electron-hole asymmetry in thermoelectric transport of LaCoO$_3$

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We have measured the electrical resistivity and thermopower of electron-doped perovskite cobaltites LaCo$_{1-y}$Te$_y$O$_3$. In contrast to hole-doped systems such as metallic ferromagnets La$_{1-x}$M$_x$CoO$_3$ (M = Ca, Sr, Ba), the electron-doped samples show an insulating behavior even in a heavily doped range due to a spin-state blockade mechanism that an electron hopping from a high-spin Co^{2+} to low-spin Co^{3+} site is energetically suppressed. We find that, despite electron doping, the thermopower shows relatively large positive values above $y = 0.05$, strikingly distinct from the hole-doped case where it comes close to zero with doping. This prominent electron-hole asymmetry seen in the thermopower originates from a bipolar conduction which consists of a slight number of mobile holes and the main immobile electrons, demonstrating the impact of a spin-state blockade on thermoelectric transport.

I. INTRODUCTION

An electron-hole symmetry, which treats an electron hole as a positively charged quasiparticle on essential equality with the electron itself, is a fundamental concept to construct the theory of solids [1], as is widely seen in various systems of contemporary condensed matter physics [2–4]. Such an equivalence between electrons and holes approximately holds in metals owing to a small energy dependence of the density of states near the Fermi level. On the other hand, electron-hole symmetry is generally absent in semiconductors, mainly due to the difference in the *orbital* characters of conduction and valence bands.

An exotic origin to induce electron-hole asymmetry comes from the *spin* sector of the internal degrees of freedom of electrons, and a peculiar class of Co oxides offers an intriguing playground to examine such spin-driven asymmetry [5]. In a CoO$_6$ octahedron, fivefold degenerate Co 3d orbitals split into twofold e_g and threefold t_{2g} levels, and the spin state can be sensitively varied due to a delicate energy balance between the crystal-field splitting and the Hund coupling; for instance, in a Co^{3+} ion, t_{2g} orbitals are fully occupied by six d electrons to form a low-spin (LS) configuration ($e_g^0 t_{2g}^6$, $S = 0$) when the crystal-field splitting is larger than the Hund coupling. For the opposite situation, Co^{3+} ions take a high-spin (HS) state ($e_g^2 t_{2g}^4$, $S = 2$). Most interestingly, such spin configurations significantly affect the hopping probability of correlated carriers. As schematically shown in Fig. 1(a), a LS Co^{3+} ion cannot accept electron hopping from a HS Co^{2+} ion owing to a highly unstable resulting LS Co^{2+} state, which can be referred to as a spin-state blockade. On the other hand, hole hopping from a LS Co^{4+} ion is acceptable, as shown in Fig. 1(b), leading to an electron-hole asymmetry in the conduction process.

The material realization of such spin-state-induced asymmetry has been discussed in several Co oxides [5–10]. Among them, a perovskite cobaltite LaCoO$_3$ may serve as an ideal case for the investigation of asymmetric transport in the background of LS Co^{3+}, as was first claimed by Maignan *et al.* [5]. Indeed, the crystal structure of LaCoO$_3$ consists of a simple three-dimensional network of corner-shared CoO$_6$ octahedra, in contrast to rather complicated structures of the other cobaltites reported in earlier studies such as oxygen-deficient perovskites [5–8] and charge-ordered double-perovskite oxides [9]. On the doping effect, although hole doping has been intensively investigated in La$_{1-x}$A$_x$CoO$_3$ (A = Ca, Sr, Ba) [11–21], the electron doping effect, which could be achieved by substituting tetravalent ions (A = Ce, Th, Te), is less studied mainly due to difficulties in the sample preparations; a single-phase bulk of Ce-substituted compounds is difficult to obtain [22–24] and Th is radioactive [25]. The structural and magnetic properties of La$_{1-x}$Te$_x$CoO$_3$ are available [26,27], yet the microscopic valence state of Co ions is unclear. The electron doping effect is mostly demonstrated in LaCo$_{1-y}$Ti$_y$O$_3$ [28–32], and a detailed transport measurement has been performed while the systematic results are limited at a high-temperature regime with a small population of LS Co^{3+} ions [33], which are essential for the spin-state blockade. Thus, the underlying transport mechanism that shows how the spin-state blockade works in electron-doped LaCoO$_3$ is still missing.

To examine the suggested electron-hole asymmetry in LaCoO$_3$, we here report a systematic evolution of the thermopower in electron-doped LaCo$_{1-y}$Te$_y$O$_3$. In this compound, the valence state of Te ions is confirmed as nonmagnetic Te^{6+} by microscopic experiments of x-ray absorption spectra (XAS) and electron spin resonance [34] as well as macroscopic magnetization measurements [35], providing a suitable platform to study asymmetric electron transport. Also, the thermopower is a sensitive probe to detect
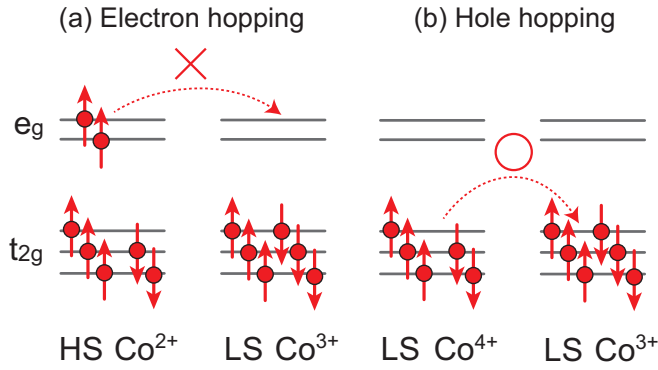
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FIG. 1. Schematic figures of (a) an electron hopping from a high-spin (HS) Co^{2+} to low-spin (LS) Co^{3+} site and (b) a hole hopping from a LS Co^{4+} to LS Co^{3+} site. Electron hopping into a LS Co^{3+} site is not allowed because the resultant LS Co^{2+} is highly unstable.

electron-hole asymmetry [36]. We find that electron-doped samples show an insulating resistivity even in a heavily doped range due to a spin-state blockade mechanism for electrons. Remarkably, the thermopower of $LaCo_{1-y}Te_yO_3$ shows relatively large positive values above $y = 0.05$ in spite of the electron doping. This is in sharp contrast to the hole-doped case where it comes close to zero in a usual manner for carrier doping. We suggest a bipolar conduction composed of mobile holes and immobile electrons, giving a clear picture for observed electron-hole asymmetry in the thermopower.

II. EXPERIMENTS

Polycrystalline samples of $LaCo_{1-y}Te_yO_3$ ($y = 0$, 0.01, 0.03, 0.05, 0.10, 0.15) were synthesized by a conventional solid-state reaction [34,35]. The starting materials, La_2O_3 (99.99% purity), Co_3O_4 (99.9%), and TeO_2 (99.9%) powders, were mixed in the stoichiometric ratio, ground thoroughly, pelletized, and heated twice on ZrO_2 plates at 1473 K in air for 12 h each time (24 h in total). No impurity phases were detected in the x-ray diffraction measurements.

The resistivity was measured using a standard four-probe method. The excitation current of $I = 10$ μA was provided by a Keithley 6221 current source and the voltage was measured with a synchronized Keithley 2182A nanovoltmeter using a built-in delta mode to cancel the thermoelectric voltage. The thermopower was measured using a steady-state technique with a typical temperature gradient of 0.5 K/mm made by a resistive heater. The thermoelectric voltage of the sample was measured with a Keithley 2182A nanovoltmeter. The temperature gradient was measured with a differential thermo-couple made of copper and constantan in a liquid N_2 cryostat below 300 K and with two platinum temperature sensors in high-temperature equipment from 300 to 700 K [37,38]. In both measuring apparatuses, the thermoelectric voltage from the wire leads was subtracted. A part of the data is lacking near room temperature, which is just the gap between the low- and high-temperature apparatuses.
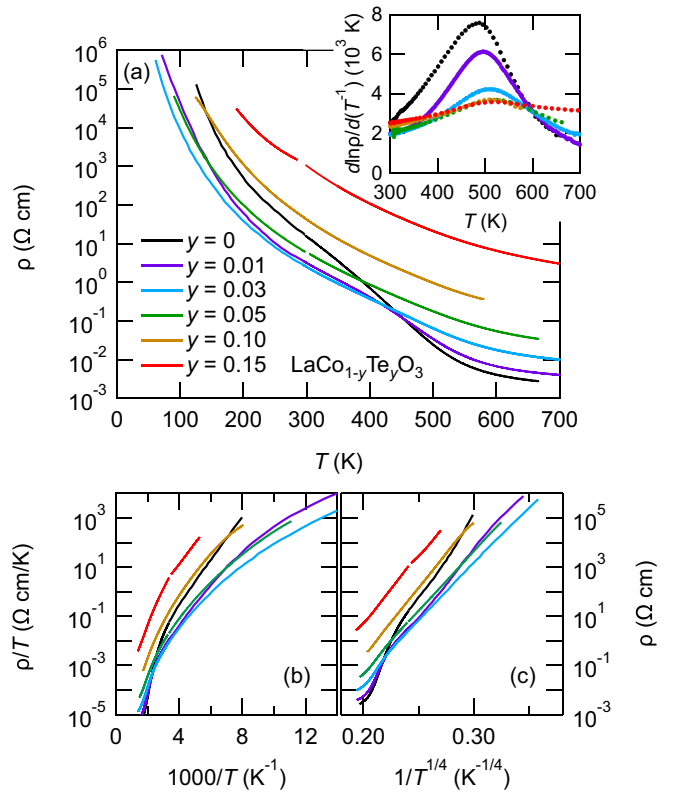

FIG. 2. (a) Temperature variations of the resistivity ρ of poly-crystalline $LaCo_{1-y}Te_yO_3$ ($y = 0$, 0.01, 0.03, 0.05, 0.10, 0.15). The inset depicts the temperature dependence of $d \ln \rho/d(T^{-1})$ above room temperature. (b) T^{-1} dependence of ρ/T and (c) $T^{-1/4}$ dependence of ρ.

III. RESULTS AND DISCUSSION

Figure 2(a) represents the temperature variations of the electrical resistivity in polycrystalline $LaCo_{1-y}Te_yO_3$. In an earlier report [34], the resistivity was measured only below room temperature and the Te content y was limited to $0 \leqslant y \leqslant$ 0.05. Here, we find that the temperature dependence of the resistivity is insulating for all the Te-substituted samples up to $y = 0.15$ in spite of electron doping by Te^{6+} substitutions. It should noted that the present results are clearly distinct from the hole doping effect in $La_{1-x}A_xCoO_3$ ($A =$ Ca, Sr, Ba), in which the metallic temperature dependence of the resistivity is observed for heavily doped samples [17]. Therefore, the insulating behavior in the present electron-doped $LaCoO_3$ indicates that the electron mobility is significantly low, as is expected in the spin-blockade scheme shown in Fig. 1 [5]. Together with the thermopower results, a detailed comparison between the electron and hole doping effects on the transport properties will be discussed later.

In $LaCoO_3$, the resistivity significantly decreases with heating across a crossover temperature $T_{MI} \approx 530$ K from low-temperature insulating to high-temperature metallic states, at which the specific heat exhibits a broad peak [39]. This crossover is seen in temperature variations of $d \ln \rho/d(T^{-1})$, which would be equivalent to an activation energy Δ/k_B for the activation-type resistivity of $\rho(T) = \rho_0 \exp(\Delta/k_B T)$ if the activation energy is temperature

independent (where ρ_0 and k_B is a high-temperature extrapolation and the Boltzmann constant, respectively) [40]. The inset of Fig. 2(a) represents the temperature variations of $d \ln \rho / d(T^{-1})$ in LaCo$_{1-y}$Te$_y$O$_3$. A pronounced peak corresponding to the crossover is clearly seen in the parent compound, and although the peak is smeared, it seems to shift slightly to higher temperatures with Te substitutions. This tendency is similar to that in electron-doped LaCo$_{1-y}$Ti$_y$O$_3$ [30], and may be consistent with a picture where doped electrons are immobile due to the blockade to enhance the insulating nature.

Below room temperature, the resistivity of LaCoO$_3$ has been analyzed in terms of a small polaron hopping model [41], in which the resistivity is given as $\rho(T) \propto T \exp[(W_H + E_g/2)/k_B T]$, where W_H and E_g are the hopping energy of a polaron and the band gap, respectively. In Fig. 2(b), we show a T^{-1} dependence of ρ/T for LaCo$_{1-y}$Te$_y$O$_3$. Although ρ/T in pure LaCoO$_3$ behaves as a linear variation in the log plot as expected in the small polaron model, the ρ/T data in Te-substituted LaCoO$_3$ are convex upward, indicating a considerable disorder effect. Indeed, in an earlier study [34], $\rho(T)$ in LaCo$_{1-y}$Te$_y$O$_3$ ($0 < y \leqslant 0.05$) is fitted by a power-law relation of $\rho(T) \propto 1/T^\nu$ ($\nu = 8$-10), which is expected in a situation where carriers hop over barriers of variable heights [42], in a similar manner to the case of LaCo$_{1-y}$Ti$_y$O$_3$ [30]. On the other hand, the resistivity in such a disordered system is often analyzed by adopting a variable-range-hopping (VRH) formula of $\rho(T) \propto \exp(1/T)^{1/(1+d)}$, where d denotes the dimensionality [43,44]. Figure 2(c) represents the $T^{-1/4}$ dependence of ρ for LaCo$_{1-y}$Te$_y$O$_3$, in which one can see linear variations for Te-substituted samples, implying a validity of VRH conduction in three-dimensional systems. In general, however, it is difficult to uniquely determine the conduction mechanism from the resistivity; both the power-law and VRH formulas seem to be applicable for the present Te-substituted case, and the disorder effect due to Te substitutions is essential for both conduction processes.

Figure 3 displays the temperature variations of the thermopower in LaCo$_{1-y}$Te$_y$O$_3$ and the inset shows the sample dependence for the parent compound LaCoO$_3$. In the low-temperature insulating state of LaCoO$_3$, the sign of the thermopower has been reported to be either positive or negative [14,45], which originates from a tiny amount of impurity. This uncontrolled sample dependence is also seen in the present study as shown in the inset. Here, the temperature dependence of the thermopower and the electrical resistivity in LaCoO$_3$ is analyzed with a semiempirical bipolar model [14]. This model takes account of thermally excited p- and n-type small polarons, which respectively correspond to Co^{4+} and Co^{2+}, with an activation energy incorporating the Coulomb screening interaction. Then, the conductivity σ and the thermopower Q are obtained using a bipolar model as $\sigma = \sigma_p + \sigma_n$ and $Q = (\sigma_p Q_p + \sigma_n Q_n)/\sigma$, where σ_i (Q_i) ($i = p, n$) is the conductivity (the thermopower) of the i-type carrier, by adopting a mobility ratio among the p- and n-type polarons. Note that, although the thermopower Q_i was calculated using the Heikes formula [46], which is particularly essential for Co oxides [47–49], spin and orbital degeneracies were not involved in Ref. [14]. Even by employing degeneracies, however, the observed thermopower may be reproduced by a
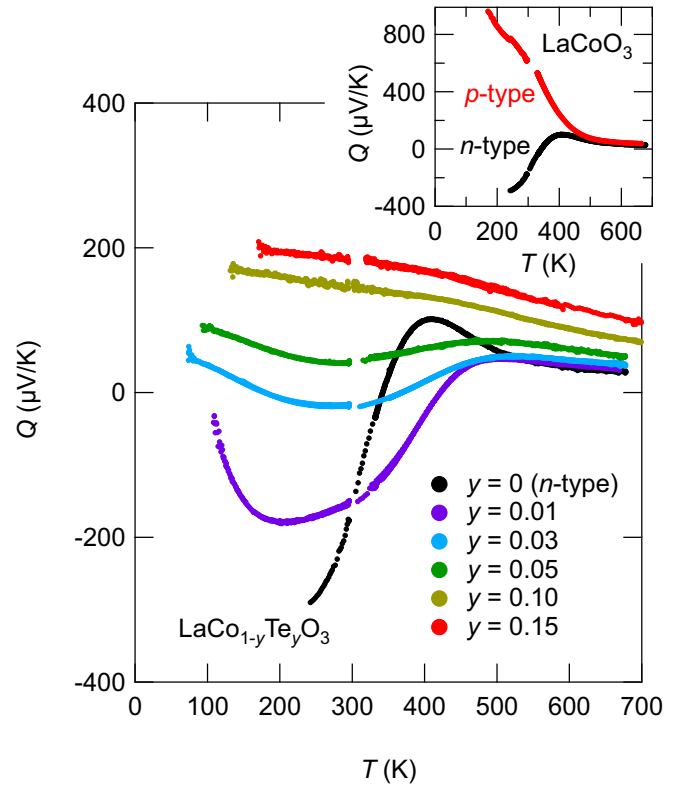

FIG. 3. Temperature variations of thermopower Q in polycrystalline LaCo$_{1-y}$Te$_y$O$_3$. The inset shows the sample dependence of the thermopower in LaCoO$_3$.

slight modification in the mobility ratio, because it is given by an exponential form [14] while the degeneracy is taken in the Heikes formula logarithmically.

We then focus on the electron doping effect on thermopower. As seen in Fig. 3, the thermopower dramatically changes with Te substitution, and most interestingly, the sign becomes positive for $y \geqslant 0.05$ in spite of the electron doping. The present result is then distinct from the hole doping effect observed in La$_{1-x}$A$_x$CoO$_3$ ($A =$ Ca, Sr, Ba). To compare these doping effects, we plot the resistivity and the thermopower measured at a constant temperature of $T = 200$ K as a function of the Co valence ν in Figs. 4(a) and 4(b), respectively. Here, we use the 200-K data at which a considerable number of LS Co^{3+} ions exist to discuss the spin-state blockade as is also mentioned later. Note that ν in LaCo$_{1-y}$Te$_y$O$_3$ is estimated as $\nu = (3 - 6y)/(1 - y)$, since the valence state of Te^{6+} is confirmed by XAS [34]. For the hole doping regime, the data of La$_{1-x}$Sr$_x$CoO$_3$ are taken from Refs. [18,19] and ν is estimated as $\nu = 3 + x$.

Now we discuss the prominent asymmetry between the electron and hole doping effects in LaCoO$_3$ as seen in Figs. 4(a) and 4(b). In contrast to a conventional carrier doping effect in a hole-doped system, the resistivity initially decreases with Te substitutions ($y \leqslant 0.03$), but then increases above $y = 0.05$, indicating that electrons are doped but the electron mobility is too low due to the aforementioned spin-state blockade. We emphasize that the affinity of the HS Co ions favors the surrounding LS Co^{3+} nearest neighbors [50,51], corroborating the spin-state blockade picture for the
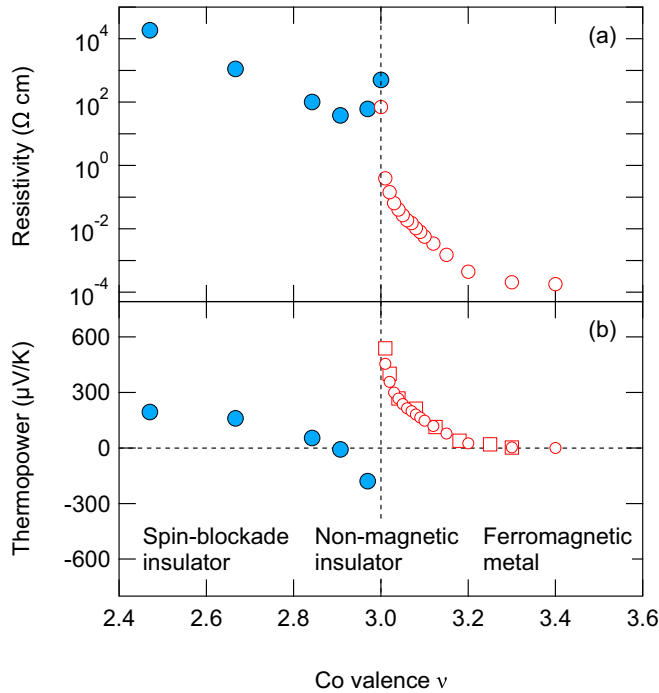
We also discuss an entropy backflow mechanism [65] for the observed positive thermopower in the electron-doped region. In a simple nondegenerate case, an entropy of $k_B \ln 2$ (only spin degeneracy) is carried by a charge [36]. On the other hand, if the degeneracy of the destination site (g_d) is larger than that of the initial site (g_i) in a local hopping picture, the entropy flows back against the charge hopping [$k_B \ln(g_i/g_d) < 0$]. As a result, the sign of the thermopower becomes opposite to the sign of the charge of the carriers, as reported in the Mn oxides [65]. In electron-doped $LaCoO_3$, we consider the electron hopping from HS Co^{2+} to low-lying LS Co^{3+} or thermally excited HS Co^{3+} (or IS Co^{3+}) at $T = 200$ K. Here, the degeneracy of the initial site of HS Co^{2+} is $g_{HS,Co^{2+}} = 12$. Then, the degeneracy of the destination site is given as follows: For the LS Co^{3+} case, the degeneracy of LS Co^{3+} is unity ($g_{LS,Co^{3+}} = 1$), and thereby the entropy flow is forward while the hopping probability is low due to the spin-state blockade. On the other hand, the degeneracy of HS (IS) Co^{3+} is $g_{HS,Co^{3+}} = 15$ ($g_{IS,Co^{3+}} = 18$), which is larger than the degeneracy of HS Co^{2+} ($g_{HS,Co^{2+}} = 12$), indicating an entropy backflow. However, for the HS (IS) Co^{3+} case, the absolute value of backflow thermopower is estimated as $|(k_B/e) \ln(g_i/g_d)| \simeq 19$ μV/K (35 μV/K) for $\nu = 2.5$, at which Co^{2+} and Co^{3+} exist in equal amounts. This estimated value is much smaller than the observed thermopower of $Q \simeq 200$ μV/K at $\nu = 2.5$. Hence, the backflow mechanism is not solely responsible. Here, we carry on a qualitative discussion since the temperature dependence of the thermopower is also complicated; a detailed consideration based on theoretical calculations, along with further transport investigations such as the Hall effect, should be a future study.

Let us compare with earlier results on the Co oxides. While attempts have been made to investigate the electron doping effect on thermopower in $La_{1-x}Ce_xCoO_3$ [23], owing to the difficulty of the sample synthesis, the number of data points is too small to discuss the overall doping dependence. Interestingly, the thermopower of $LaCoO_3$ is drastically changed by Ti^{4+} substitution [30], while the doping dependence is limited. The detailed carrier doping effect has been explored in oxygen-deficient perovskites $RBaCo_2O_{5+\delta}$ ($R = $ Gd, Nd) [6–8]. Indeed, the resistivity of electron-doped $RBaCo_2O_{5+\delta}$ is too high, similar to the present study, indicating a universal electron blockade transport in the Co oxides consisting of LS Co^{3+}. However, let us emphasize that the thermopower behavior in $RBaCo_2O_{5+\delta}$ is in total contrast to the present results; the thermopower in $RBaCo_2O_{5+\delta}$ remains a negative value against electron doping, and a large absolute value is discussed in terms of the extended Heikes formula rather than electron-hole asymmetry in the thermopower. These results highlight that the present Te-substituted $LaCoO_3$ is a minimal model to demonstrate electron-hole asymmetry caused by a spin-state blockade for thermoelectric transport.

IV. SUMMARY

To summarize, systematic measurements of the resistivity and thermopower on the electron-doped $LaCo_{1-y}Te_yO_3$ have

FIG. 4. (a) The resistivity and (b) the thermopower measured at $T = 200$ K as a function of Co valence ν. The present data of $LaCo_{1-y}Te_yO_3$ are plotted in the electron-doped regime as solid circles. In the hole-doped regime, the resistivity and the thermopower data of $La_{1-x}Sr_xCoO_3$ taken from Ref. [19] are shown by open circles. The thermopower data depicted by the open squares are taken from Ref. [18].

doped electrons [Fig. 1(a)]. Note that the spin-state nature of $LaCoO_3$ in this temperature range near 200 K is a controversial issue; the excited spin state is either an intermediate spin (IS) [52–56] or HS state [57–63]. It has been suggested that a collective heptamer picture involving an IS and HS dual nature, which may also give a reasonable explanation to the polaron conduction, is essential [64]. On the other hand, even at 200 K, a considerable number of LS states, which are essential for the spin-state blockade, are remaining [63], and this situation is the same for both doping cases. It should also be noted that, although the impurity effect is certainly seen in the resistivity, the concentration of scattering centers in Te-substituted compounds is much less than that in the hole-doped system, because a substituted Te ion is hexavalent to act as an effective electron donor.

The spin-state blockade for electrons may give a comprehensible explanation for the observed sign change in thermopower above $y = 0.05$. Based on the bipolar conduction in the parent compound [14], thermopower is weighted by the conductivity of each carrier as $Q = (\sigma_p Q_p + \sigma_n Q_n)/\sigma$. In the present electron-doped case, the electron mobility is significantly low and then the Peltier conductivity of holes may become relatively larger than that of electrons ($|\sigma_n Q_n| \ll |\sigma_p Q_p|$), resulting in a positive thermopower possibly due to remnant minority holes, while the underlying nature of the minority holes is unclear at present.

been carried out. In sharp contrast to the hole-doped case, the resistivity is significantly increased by electron doping. Furthermore, the thermopower exhibits a prominent feature characterized by a sign change against electron doping. These transport results underlie electron-hole asymmetry due to the spin-state blockade.

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