Electron-Hole Asymmetry in $GdBaCo_2O_{5+x}$: Evidence for Spin Blockade of Electron Transport in a Correlated Electron System

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In $R\mathrm{BaCo_2O_{5+x}}$ compounds (R is rare earth), the variability of the oxygen content allows precise doping of CoO_2 planes with both types of charge carriers. We study transport properties of doped $GdBaCo_2O_{5+x}$ single crystals and find a remarkable asymmetry in the behavior of holes and electrons doped into a parent insulator $GdBaCo_2O_{5.5}$. The doping dependencies of resistivity, Hall response, and thermoelectric power reveal that the doped holes greatly improve the conductivity, while the electron-doped samples always remain poorly conducting. This doping asymmetry provides strong evidence for a spin blockade of the electron transport in $R\mathrm{BaCo_2O_{5+x}}$.

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In condensed matter physics, the concept of electron-hole symmetry, which states that electrons and holes basically can be regarded as equivalent quasiparticles, is one of the fundamental paradigms which dramatically simplifies the description of charge transport. However, in systems with strongly correlated electrons, a coupling of spin and charge degrees of freedom can drastically change this simple picture. One of the most prominent examples of how spins can affect charge motion is the ‘‘spin blockade’’ phenomenon observed in quantum dot systems [1].

Recently, existence of a spin blockade for electron transport in cobaltites has been suggested in Ref. [2] to explain the temperature dependence of the thermoelectric power in $HoBaCo_2O_{5.5}$. In $R\mathrm{BaCo_2O_{5.5}}$ compounds (where R is a rare earth), the crystal lattice is composed of equal numbers of CoO_6 octahedra and CoO_5 square pyramids [2–9] as schematically shown in Fig. 1(a), and the valence of all the Co ions is $3+$. At low temperature, the Co^{3+} ions adopt the low-spin (LS) state in octahedral positions and the intermediate-spin (IS) state in pyramidal positions [2,3,6–9]. Generation of electron-hole pairs, or Co^{2+}-Co^{4+} states in a localized picture, determines the transport behavior of $R\mathrm{BaCo_2O_{5.5}}$ [2–9]. Since electron and hole carry not only a charge, but also a spin, their motion through a Co^{3+} background can be rather different. In particular, it was argued that hopping of a high-spin (HS) Co^{2+} electron through a LS Co^{3+} host should be suppressed because of a spin blockade mechanism [2], effectively excluding electrons from the overall charge transport. A large and positive Seebeck coefficient in $HoBaCo_2O_{5.5}$ observed at low temperatures has been suggested in Ref. [2] to be possible evidence of the spin blockade for electron transport.

However, the Seebeck coefficient S in oxygen-variable $R\mathrm{BaCo_2O_{5+x}}$ is very sensitive to oxygen content; it diverges at $x = 0.5$, changing sign from negative for $x < 0.5$ to positive for $x > 0.5$ [9,10]. In fact, at the exact $x = 0.5$ composition, the low-temperature Seebeck coefficient turns out to be negative [9]. Even a small excess of oxygen content over $x = 0.5$ can provide holes into the system and makes S positive (it is possible that this was the case with $HoBaCo_2O_{5.5}$ studied in Ref. [2]). Therefore, to establish the existence of the spin blockade of electron transport, one needs to make a direct comparison of electron and hole behavior in CoO_2 planes.

In this Letter, we present a detailed study of doping dependences of resistivity, Hall coefficient, and thermoelectric power in $GdBaCo_2O_{5+x}$ single crystals. This study reveals a remarkable asymmetry in the behavior of holes and electrons: For hole doping, concomitant decrease of the absolute values of resistivity ρ, Hall coefficient R_H, and Seebeck coefficient S with increasing carrier concentration

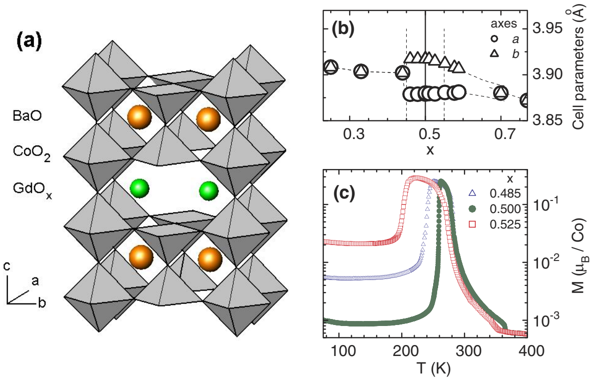

FIG. 1 (color online). (a) A sketch of the crystal structure of $GdBaCo_2O_{5.5}$. Owing to the ordering of oxygen into alternating empty and filled chains, Co^{3+} ions become nonequivalent and exhibit either LS state in octahedral positions or IS state in pyramidal positions. (b) The evolution of room-temperature in-plane lattice parameters in $GdBaCo_2O_{5+x}$ under variation of oxygen content x, demonstrating that the orthorhombic crystal structure survives only in the narrow range around $x = 0.5$. (c) The magnetization behavior in $GdBaCo_2O_{5+x}$ with oxygen content close to $x = 0.5$ in a magnetic field of 0.1 T applied along the ab plane.

indicates an eventual establishment of a metallic state. On the other hand, for electron doping, the temperature dependences of resistivity and Hall coefficient do not show any appreciable change, indicating that electrons introduced into the system are effectively immobile. This doping asymmetry strongly supports the idea that the spin blockade of electron transport takes place in RBaCo$_2$O$_{5+x}$, making a solid case that the spin blockade phenomena occurs not only in quantum dot systems but also in transition-metal oxides.

High-quality GdBaCo$_2$O$_{5+x}$ single crystals are grown using a floating-zone technique [9]. Carrier doping to single crystal samples is performed by precisely changing the oxygen content Δx with an accuracy better than 0.001 using an elaborate set of high-temperature annealing and quenching procedures [9,11]. To avoid complications due to a modification of the crystal structure upon changing the oxygen concentration [4,9], the change of oxygen content in the present study is restricted to the range of $0.45 < x < 0.55$, where GdBaCo$_2$O$_{5+x}$ keeps an orhorhombic crystal structure originating from anion ordering as evidenced by the doping dependence of the in-plane lattice parameters shown in Fig. 1(b). In addition, in this narrow doping range the dc magnetization in GdBaCo$_2$O$_{5+x}$ [see Fig. 1(c)] shows qualitatively the same type of successive paramagnetic to ferromagnetic (FM), and then to antiferromagnetic (AF), phase transitions upon cooling in both parent and doped crystals, implying basically the same underlying microscopic spin structure [12]. Since oxygen vacancies created in the GdO$_x$ plane upon doping do not change the in-plane Co-O framework [see Fig. 1(a)], all transport measurements have been performed along the ab plane.

The resistivity is measured using a standard ac four-probe method. Both current and voltage contacts are made with gold paint before all the heat treatment procedures that are used to vary the oxygen content. The Hall resistivity is measured using a standard six-probe technique by sweeping the magnetic field $\mathbf{H} \parallel c$ to both plus and minus polarities at fixed temperatures; the electric current is always along the ab plane. The thermoelectric power is measured in a slowly oscillating thermal gradient of $\sim$1 K along the ab plane. The contribution from the gold wires ($\sim$2 μV/K) used as output leads is subtracted.

Figure 2(a) shows temperature dependences of the in-plane resistivity ρ of GdBaCo$_2$O$_{5+x}$ crystals for $0.45 < x < 0.55$. At high temperatures, all curves show an almost temperature-independent "metallic" behavior. Upon cooling below $\approx$ 360 K, GdBaCo$_2$O$_{5+x}$ crystals undergo a metal-insulator transition (MIT). As has been established for RBaCo$_2$O$_{5.5}$ [3–7], the MIT coincides with a spin-state transition of Co^{3+} ions: On the metallic side, half of the cobalt ions (in octahedral positions) adopt the HS state and another half (in pyramidal positions) adopt the IS state. On the insulator side, HS-Co^{3+} ions change their spin state into the LS state [2,3,7–9,12]. This spin-state transition is manifested in the change of the magnetization behavior [6,9,12] at $\approx$360 K [see Fig. 1(c)].

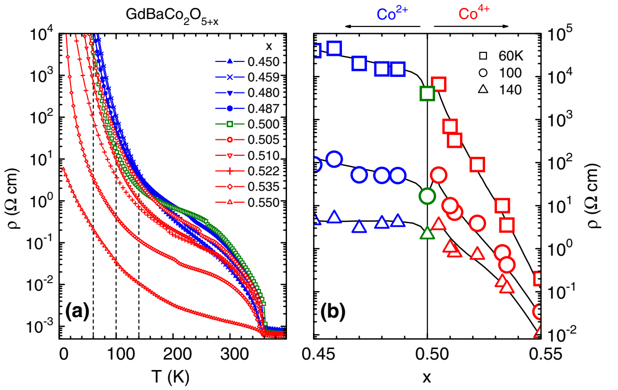

FIG. 2 (color online). (a) Temperature dependences of the in-plane resistivity $\rho(T)$ of GdBaCo$_2$O$_{5+x}$ crystals with oxygen content close to $x = 0.5$. (b) Doping dependences of the in-plane resistivity $\rho(x)$ of GdBaCo$_2$O$_{5+x}$ crystals at several temperatures (shown by dashed lines in the left panel).

Since we are interested in how doping changes the ground state of a parent insulator, the focus of our study is on the doping dependence of transport properties at low temperatures. For both electron-doped and hole-doped crystals, the $\rho(T)$ curves show clear kinks at T_N, where the FM ordering abruptly changes into an AF one [see Fig. 1(c)]. In the AF state, the resistivity of GdBaCo$_2$O$_{5+x}$ grows rapidly with decreasing temperature. Although all $\rho(T)$ curves demonstrate essentially insulating behavior in the $0.45 < x < 0.55$ concentration range, an introduction of carriers into the system changes the absolute value of resistivity, and this change is very different for electrons and holes. The difference in the doping response is most clearly illustrated in Fig. 2(b), which shows the doping dependence of resistivity in the AF phase at several temperatures [shown by dashed lines in Fig. 2(a)]. The most striking feature here is an asymmetry for electron and hole doping: While the hole doping leads to a steady decrease in resistivity (for example, ρ changes by almost 5 orders of magnitude at 60 K as x increases from 0.50 to 0.55), the electron doping causes little change in resistivity.

The same asymmetry in the doping dependence is observed in the Hall data as well. Figure 3(a) shows temperature dependences of the Hall coefficient $R_H(T)$ in GdBaCo$_2$O$_{5+x}$ with oxygen concentrations in the same range as for the resistivity data. All measurements are done below T_N in the AF phase, where the anomalous Hall effect is expected to be negligible and the Hall coefficient has a simple physical meaning. Indeed, as shown in the insets in Fig. 3(a), the Hall resistivity is almost perfectly linear in magnetic field. Also, as expected for positive and negative charge carriers, the sign of the Hall coefficient in GdBaCo$_2$O$_{5+x}$ is positive for hole-doped crystals ($x > 0.5$) and negative for electron-doped crystals ($x < 0.5$). Figure 3(b) shows the doping dependence of the

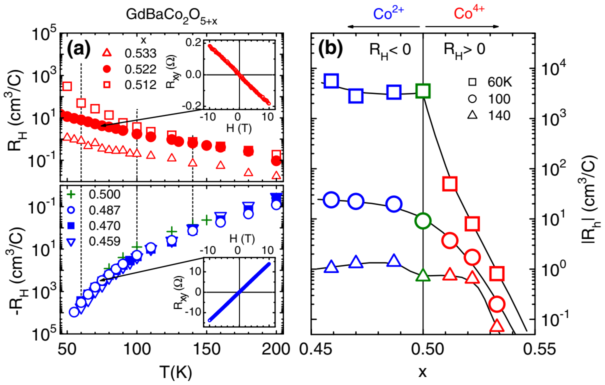

FIG. 3 (color online). (a) Temperature dependences of the Hall coefficient $R_H(T)$ of $GdBaCo_2O_{5+x}$ crystals with oxygen content close to $x = 0.5$. Asymmetric in magnetic field parts of the $R_{xy}(H)$, which directly determine a sign and a value of the Hall coefficient, are presented in the upper and the lower insets. (b) Doping dependences of the absolute value of the Hall coefficient $|R_H(x)|$ of $GdBaCo_2O_{5+x}$ crystals at several temperatures (shown by dashed lines in the left panel).

absolute value of the Hall coefficient $|R_H(x)|$ at the same temperatures as for the resistivity data. An asymmetry in the Hall response for hole-doped and electron-doped crystals correlates well with the asymmetry in the doping dependence of the resistivity: While the Hall coefficient decreases by several orders of magnitude upon doping by holes, meeting the expectation for a doping procedure, the electron doping causes almost no change in the Hall response at any temperature below T_N, as if electrons introduced into a crystal are immobile.

The thermoelectric power is another transport property that can distinguish between electrons and holes. Figure 4(a) shows temperature dependences of the Seebeck coefficients in $GdBaCo_2O_{5+x}$. At high temperatures, S is very small and negative for both electron-doped and hole-doped crystals, suggesting that the doping little affects the metallic state. On the other hand, at low temperatures the thermoelectric power is very sensitive to the type of carriers: $S > 0$ for hole-doped crystals, and $S < 0$ for electron-doped counterparts, similar to the Hall coefficient behavior. Note that the temperature dependences of the Seebeck coefficient $S(T)$ do not follow a simple law related to an insulating behavior either for hole-doped or for electron-doped crystals.

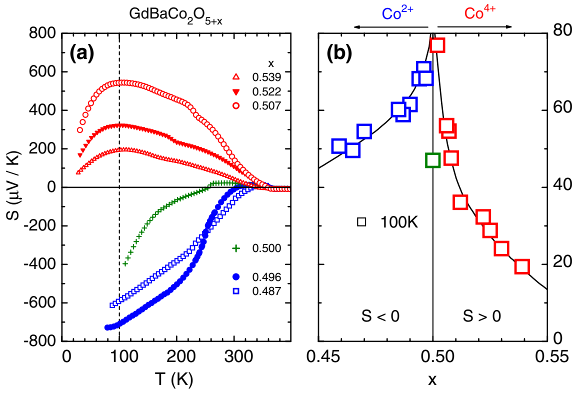

FIG. 4 (color online). (a) Temperature dependences of the Seebeck coefficient $S(T)$ of $GdBaCo_2O_{5+x}$ crystals with oxygen content close to $x = 0.5$. (b) The doping dependence of the absolute value of the Seebeck coefficient $|S(x)|$ in $GdBaCo_2O_{5+x}$ at $T = 100$ K.

The most prominent feature of the doping dependence of the Seebeck coefficient, shown in Fig. 4(b) for $T = 100$ K, is a sharp divergence at $x = 0.5$. Its absolute value $|S|$ is extremely large in the immediate proximity to $x = 0.5$, reaching $\sim 800\ \mu\mathrm{V/K}$, and decreases rapidly as x deviates from 0.5, albeit in a different way for electrons and holes. Such $S(x)$ behavior has been attributed to the hopping transport of charge carriers in $GdBaCo_2O_{5+x}$ [10].

Thus, as evidenced by the resistivity, Hall effect, and thermoelectric power measurements, both electrons and holes can be introduced into the parent $GdBaCo_2O_{5.5}$ by changing its oxygen content, but their transport is very different.

In order to understand the origin of the electron-hole asymmetry in this material, one needs to understand the mechanism of charge transport in $GdBaCo_2O_{5+x}$ at low temperature. The parent $GdBaCo_2O_{5.5}$ is a gapped insulator as evidenced by an activation behavior of conductivity [Fig. 5(a)]. Excitations of electron-hole pairs across the energy gap ≈ 140 meV determine the temperature dependences of conductivity, Hall coefficient, and thermoelectric power [9]. The low-temperature transport in the parent

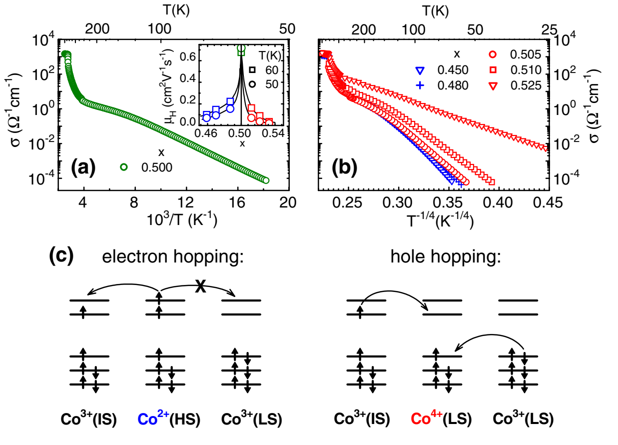

FIG. 5 (color online). (a) The low-temperature conductivity $\sigma(T)$ in the parent $GdBaCo_2O_{5.5}$ compound ($x = 0.5$) shows an activation behavior. The inset demonstrates a diminishing Hall mobility $\mu_H = \sigma R_H$ caused by a doping-induced disorder. (b) The low-temperature conductivity $\sigma(T)$ in $GdBaCo_2O_{5+x}$ shows 3D variable-range hopping for crystals doped by both electrons and holes. (c) The scheme of electron Co^{2+} and hole Co^{4+} hopping through the IS and LS states of Co^{3+} ions, illustrating the phenomenon of the spin blockade for electron hopping.

material is dominated by electrons, which are thermally created in relatively wider energy bands than holes; the higher mobility of electrons determines the negative sign of the Hall coefficient and the Seebeck coefficient [13]. The concentration of electrons (and holes) in $GdBaCo_2O_{5.5}$ decreases exponentially with decreasing temperature [down to $\sim 10^{15}$ cm^{-3} at 60 K as estimated from the Hall data (Fig. 3)]. The "effective" mobility $\mu_H = \sigma R_H$, which would be the Hall mobility if only one type of charge carriers were present, is around ~ 1 $cm^2\,V^{-1}\,s^{-1}$, being already somewhat close to a borderline for a "band" transport.

A change of oxygen content by only $\Delta x = \pm 0.001$ provides a large number of extra carriers $\sim 10^{19}$ cm^{-3}, implying a great increase in conductivity. On the other hand, doping of both electrons and holes leads to a diminishing mobility [see inset in Fig. 5(a)], suggesting an effective carrier localization, which is probably caused by disorders in the oxygen sublattice. The conductivity data, shown in Fig. 5(b), reveal a 3D variable-range hopping behavior of charge carriers in $GdBaCo_2O_{5+x}$ crystals for both electrons and holes. This type of behavior is well known in systems where the low-temperature transport is governed by phonon-assisted tunneling of carriers between localized states randomly distributed in energy and position [14]. The increase in the density of states upon doping in such systems naturally leads to an increasing conductivity, as is observed in hole-doped $GdBaCo_2O_{5+x}$ crystals for $x > 0.5$. What is peculiar here is that electron doping little changes the conductivity of $GdBaCo_2O_{5+x}$ for $x < 0.5$.

Keeping in mind the hopping character of the low-temperature charge transport in $GdBaCo_2O_{5+x}$, the difference in the behavior of electrons (Co^{2+} ions, moving in the background of Co^{3+} ions) and holes (Co^{4+} ions) can be understood as a difference in their hopping probability. The motion of an extra carrier through a crystal can be considered as a hopping process, which leads to an interchange of the spatial positions of a Co^{2+} (or Co^{4+}) ion with a neighboring Co^{3+} ion. Indeed, if one of the seven $3d$ electrons of a Co^{2+} ion moves to a neighboring Co^{3+} ion, which has six $3d$ electrons, as shown in the left panel of Fig. 5(c), the ions interchange their valence states, i.e., the Co^{2+} ion moves to the neighboring position. The same is true for hopping of a Co^{4+} ion, with the only difference that an electron moves from a Co^{3+} ion to a Co^{4+} ion, which has five $3d$ electrons, as shown in the right panel of Fig. 5(c). As can be inferred from our discussion for the parent material, in $GdBaCo_2O_{5+x}$ at low temperatures, nearly half of the Co^{3+} ions are in a LS state and the rest are in an IS state. On the other hand, Co^{2+} ions are always in a HS state owing to a weaker crystal field than for Co^{3+} ions, and Co^{4+} ions are always in a LS state owing to a stronger crystal field [15]. Figure 5(c) shows the scheme of hopping of HS-Co^{2+} and LS-Co^{4+} ions onto IS-Co^{3+} and LS-Co^{3+} ions: As one can see, a LS-Co^{4+} ion can always interchange its position with an IS-Co^{3+} ion or a LS-Co^{3+} ion, keeping the same spin states before and after the hopping event [as shown in the right panel of Fig. 5(c)]. On the contrary, a HS-Co^{2+} ion can interchange its position only with a IS-Co^{3+} ion because moving one $3d$ electron to a LS-Co^{3+} ion creates a non-HS-Co^{2+} ion which is energetically unfavorable. This means that hopping through a LS-Co^{3+} ion [marked by a cross in the left panel in Fig. 5(c)] hardly occurs. This phenomenon, which has been called the spin blockade [2], can effectively suppress electron transport in $GdBaCo_2O_{5+x}$ compounds. Hence, the concept of the spin blockade provides a simple explanation for the observed electron-hole asymmetry in $GdBaCo_2O_{5+x}$, although the rigorous quantitative understanding of the doping dependences of the transport properties in $GdBaCo_2O_{5+x}$ is a challenging issue.

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