

Transport properties of the delafossite Rh oxide $\text{Cu}_{1-x}\text{Ag}_x\text{Rh}_{1-y}\text{Mg}_y\text{O}_2$: Effect of Mg substitution on the resistivity and Hall coefficient

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Polycrystalline samples of the delafossite Rh oxide $\text{Cu}_{1-x}\text{Ag}_x\text{Rh}_{1-y}\text{Mg}_y\text{O}_2$ were investigated to clarify its transport properties. Mg substitution dramatically decreases the resistivity and the Hall coefficient, whereas it does not change the thermopower and the mobility. As an origin for this, we propose that the holes doped by the Mg ions are spatially segregated in the sample, and move away from the Mg ions to retain high mobility. In the parent oxide CuRhO_2 , the conductivity in the Cu layer is comparable with that in the RhO_2 layer at 300 K, which characterizes this material as a two-hole-band conductor.

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I. INTRODUCTION

Thermoelectric materials are functional materials that can convert heat into electrical energy and vice versa, whose performance is characterized by the dimensionless figure-of-merit $ZT = S^2 T / \rho \kappa$, where S , ρ , κ , and T represent the thermopower, electrical resistivity, thermal conductivity, and absolute temperature, respectively. Thermoelectric power generation from waste heat definitely favors oxides because of the chemical stability at high temperatures, but their ZT was too low for practical use. Such situations were changed after the discovery of good thermoelectric properties in the layered Co oxide Na_xCoO_2 ,¹ and material hunt for good thermoelectric oxides has been conducted by a number of researchers, from which the Ca-Co-O and Bi-Sr-Co-O systems were discovered.^{2,3} Like Na_xCoO_2 , these Co oxides commonly have the CdI_2 -type CoO_2 layer, which should be associated with the mechanism of their good thermoelectric properties. Although various models are proposed, it is still controversial at present.^{4,5}

Rh oxide is a key material to understand the thermoelectric Co oxides. First, Rh is located just below Co in the periodic table, and their chemical properties are expected to be similar. Second, Rh ions favor the low spin state, and a large thermopower is expected from an extended Heikes formula proposed by Koshibae *et al.*⁴ Third, similar layered Rh oxides were synthesized, whose properties are comparable to those of the Co oxides.⁶⁻⁸

The layered Rh oxide CuRhO_2 has the delafossite structure as shown in Fig. 1, where the Cu layer and the CdI_2 -type RhO_2 layer are alternately stacked along the c axis. Very recently, Kuriyama *et al.* have found that $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$ shows a metal-insulator transition near $y=0.05$, and that a sample of $y=0.1$ shows a low resistivity of 4 m Ω cm together with a large thermopower of 130 $\mu\text{V}/\text{K}$ at room temperature.⁹ Based on their findings, they have proposed that $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$ is a promising candidate for oxide thermoelectrics. However, they did not report on the Hall coefficient, which is essential to quantitative discussion on metal-insulator transition. Another controversial issue is that both the RhO_2 layer and the Cu layer can be conduction paths in CuRhO_2 . Thus it should be carefully discussed which layer is responsible for the metallic conduction in $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$. In

this paper, we clarify the conductivity in the two layers from the resistivity, thermopower, and Hall coefficient measured in a series of samples substituted for the Cu and the Rh sites.

II. EXPERIMENT

Polycrystalline samples of $\text{Cu}_{1-x}\text{Ag}_x\text{Rh}_{1-y}\text{Mg}_y\text{O}_2$ were prepared by a conventional solid-state reaction. Stoichiometric amounts of CuO, Ag_2O , Rh_2O_3 , and MgO of 99.9% purity were carefully mixed, calcined at 1203 K for 36 h in air.¹⁰ The calcined mixtures were finely ground, pressed into pellets, and sintered at 1203 K for 72 h in air. The samples were characterized by powder x-ray diffraction (XRD) analysis using Cu $K\alpha$ radiation with $2\theta=10$ to 100° . The resistivity and the thermopower were measured by a conventional dc four-probe method and a steady-state method, respectively. The Hall coefficient (R_H) was measured using physical property measurement system (Quantum Design). External magnetic field (B) was swept from -4 to 4 T at fixed temperatures to obtain the Hall resistance from the resistance component proportional to B .

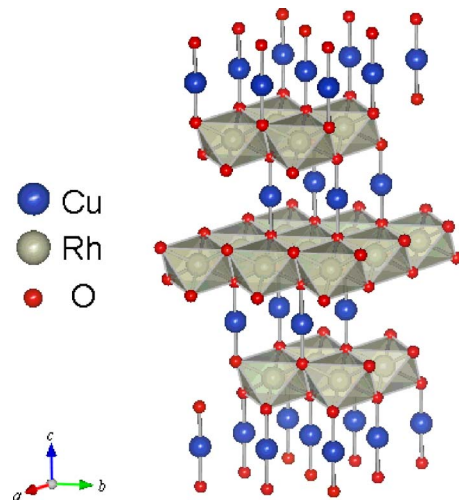


FIG. 1. (Color online) Crystal structure of CuRhO_2 . Blue (dark gray), gray (light gray), and red (dark gray) spheres represent Cu, Rh, and O atoms, respectively. This material has the CdI_2 -type RhO_2 layer like the layered Co oxides.

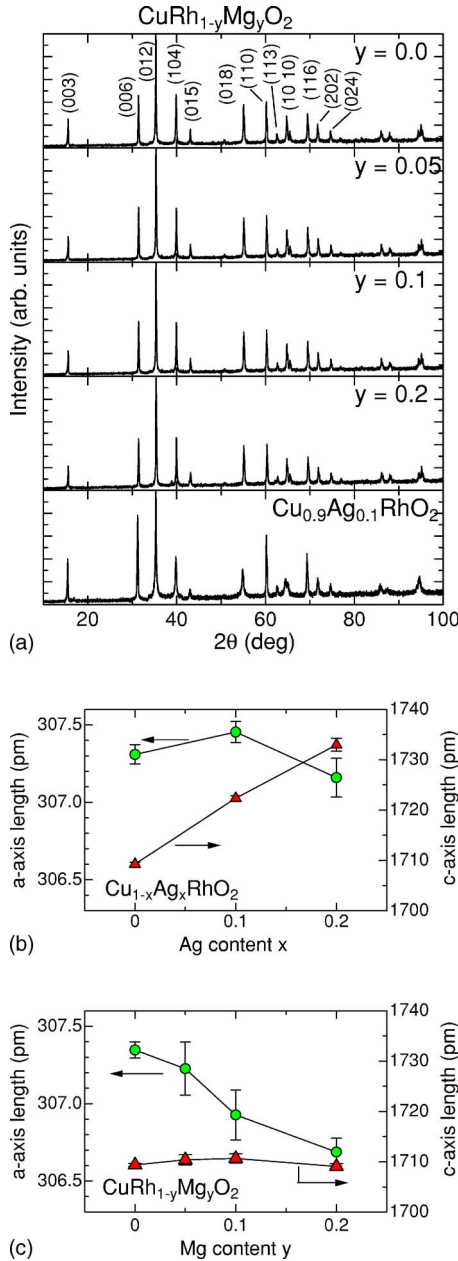


FIG. 2. (Color online) (a) XRD patterns of $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$ and $\text{Cu}_{0.9}\text{Ag}_{0.1}\text{RhO}_2$, and the lattice constants of (b) $\text{Cu}_{1-x}\text{Ag}_x\text{RhO}_2$ and (c) $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$.

III. RESULTS

Figure 2(a) shows the XRD patterns of $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$ and $\text{Cu}_{0.9}\text{Ag}_{0.1}\text{RhO}_2$, in which all the peaks are indexed as the delafossite structure without any other impurity peaks. Figure 2(b) shows the lattice constants of $\text{Cu}_{1-x}\text{Ag}_x\text{RhO}_2$, in which the c -axis length considerably increases with the Ag content x , whereas the a -axis length remains unchanged. The increase in the c -axis length is reasonable, since a large ion of Ag^+ (0.67 \AA) is partially substituted for a small ion of Cu^+ (0.46 \AA).¹¹ The x -independent a -axis length implies the chemically rigid RhO_2 block. A similar case is seen in the misfit layered Co oxides, where the size of the CdI_2 -type CoO_2 block is independent of that of the block layer.¹² In

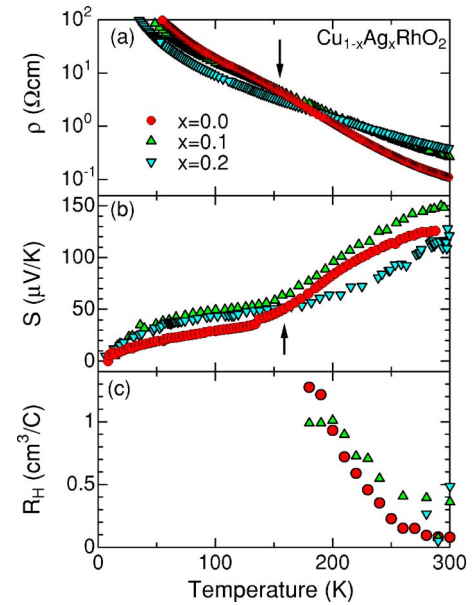


FIG. 3. (Color online) (a) Resistivity, (b) thermopower, and (c) Hall coefficient of $\text{Cu}_{1-x}\text{Ag}_x\text{RhO}_2$. An arrow indicates the kink in ρ and S (see text).

contrast, as shown in Fig. 2(c), the c -axis length of the Mg-substituted samples is almost independent of the Mg content y , while the a -axis length systematically decreases with y . This can be understood by assuming that the substitution of Mg^{2+} (0.72 \AA) for Rh^{3+} (0.67 \AA) creates Rh^{4+} (0.62 \AA).¹¹ The different trends against x and y deserve that the Ag and the Mg ions are substituted for the different sites in the host compound.

Figure 3(a) shows the resistivity of $\text{Cu}_{1-x}\text{Ag}_x\text{RhO}_2$. All the resistivities increase with decreasing temperature. As indicated by an arrow in Fig. 3(a), ρ of $x=0$ shows a kink near 150 K, above which it deviates downwards. This suggests that an additional conduction begins to contribute above 150 K. No kink in the Ag-substituted samples suggests that the additional conduction should be ascribed to the Cu layer. In Fig. 3(b), the thermopower of CuRhO_2 also shows an anomaly near 150 K (indicated by an arrow), above which S/T increases roughly by two times. Unlike ρ , each S for the Ag-substituted samples shows a similar kink, though it is somewhat smeared in the sample of $x=0.2$. This indicates that the carriers are thermally excited for all the samples, but cannot move in the Ag-substituted samples. This is consistent with the fact that the Cu layer is disordered by the substituted Ag ions, and we think that the low mobility suppresses the conduction in the Cu layer. The thermally excited carriers are actually detected in R_H as shown in Fig. 3(c), where R_H rapidly increases with decreasing temperature. The carrier density was too low to detect the Hall signal below 150 K, which consistently shows that the additional conduction is essentially terminated below 150 K. Note that each R_H for $x=0.1$ and 0.2 remains nearly the same value of $x=0.0$ at 300 K, indicating that the thermally excited carriers are still present for the Ag-substituted samples.

Figure 4(a) shows the resistivity of $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$. As Kuriyama *et al.*⁹ first found, it decreases with y . The nonme-

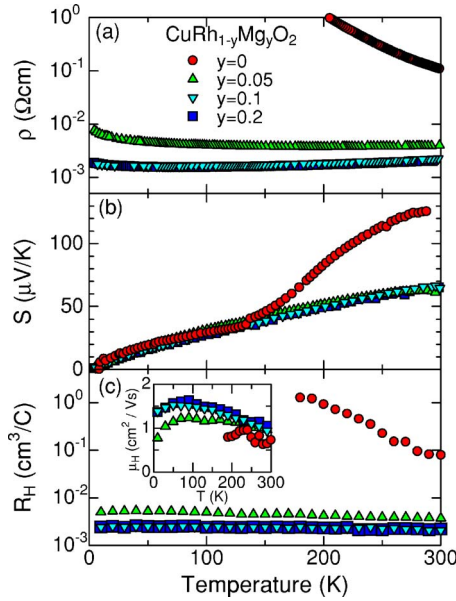


FIG. 4. (Color online) (a) Resistivity, (b) thermopower, and (c) Hall coefficient of $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$. Hall mobility (μ_H) of $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$ is shown in the inset.

tallic temperature dependence is rapidly weakened with y , and the metallic conduction $d\rho/dT > 0$ is realized at 300 K. ρ reaches a low value of 2 m Ω cm at room temperature for $y \geq 0.1$, showing that this material is as conductive as the high-temperature superconducting Cu oxides—one of the most conductive transition-metal oxides. Figure 4(b) shows the thermopower of $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$, in which the data for $y \geq 0.05$ fall into a single curve. In particular, all the data below 150 K are essentially the same. As discussed in Fig. 3, the RhO_2 layer is mainly responsible for the conduction below 150 K in CuRhO_2 . The temperature dependence of S for $y \geq 0.05$ is so smooth that the charge transport is likely to evolve smoothly from the low-temperature states. Thus we conclude that the substituted Mg ions supply holes in the RhO_2 layer, not in the Cu layer. In fact, S shares common features with S of other layered Rh oxides:^{6–8} it shows a fairly large value of 70 $\mu\text{V}/\text{K}$ at 300 K, and is roughly linear to T at low temperatures. However, the y -independent S is quite unconventional. In general, the thermopower decreases in magnitude with increasing carrier concentration, which is seriously incompatible with Fig. 4(b). A possible origin of this will be discussed in detail later. Contrary to S , R_H systematically decreases with y , as shown in Fig. 4(c). From $y=0$ –0.5, the magnitude decreases by two orders of magnitude, and R_H for $y \geq 0.05$ is nearly independent of temperature. Note that R_H of $y=0.05$ remains a finite value of 5×10^{-3} cm^3/C at 10 K, which clearly demonstrates the existence of finite density of states in the ground state. This is unambiguous evidence for the metal-insulator transition in this system.

Let us examine the Ag-substitution effects in the metallic samples made by the Mg substitution. As shown in Fig. 5(a), the resistivity of $\text{Cu}_{1-x}\text{Ag}_x\text{Rh}_{0.8}\text{Mg}_{0.2}\text{O}_2$ slightly increases with the Ag content x , but the increase ratio is at most 50% at room temperature of $x=0.2$. This indicates that the RhO_2

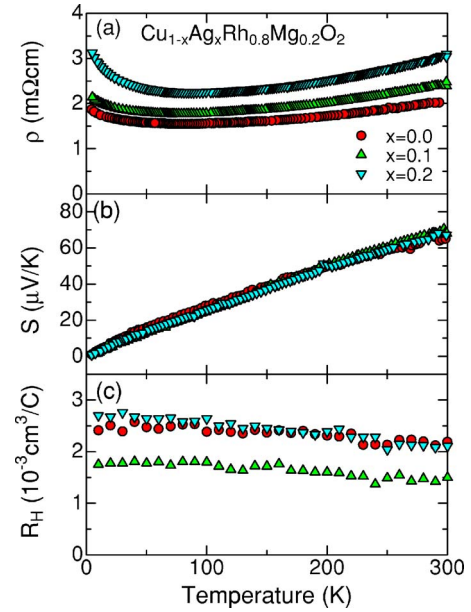


FIG. 5. (Color online) (a) Resistivity, (b) thermopower, and (c) Hall coefficient of $\text{Cu}_{1-x}\text{Ag}_x\text{Rh}_{0.8}\text{Mg}_{0.2}\text{O}_2$.

block is mainly responsible for the metallic conduction in the Mg-substituted samples. If the conduction path were on the Cu layer, the metallic conduction would be completely suppressed. In the high-temperature superconducting oxide $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, 4% substitution of Zn for Cu completely suppresses the metallic conduction.¹³ As shown in Figs. 5(b) and 5(c), S and R_H are nearly independent of x , which further consolidates our argument that the Cu layer does not affect the metallic conduction.

We should emphasize that CuRhO_2 is exceptional in the sense that the Cu layer is a predominant conducting path in the other Cu-based delafossite oxides.^{14–19} In such oxides, the resistivity is high and semiconductive, while the magnitude of S decreases with doping. These features are highly incompatible with ρ and S in Fig. 4. This strongly suggests that the RhO_2 layer is the predominant conduction path, which is consistent with the photoemission spectrum and the LDA calculation in which the electronic states near the Fermi energy are mainly composed of Rh $4d$.⁹ A preliminary study of the spinel oxide $\text{ZnRh}_{2-x}\text{Mg}_x\text{O}_4$ shows that S and ρ decreases with increasing Mg content,²⁰ indicating that Mg supplies carriers to the Rh-O network. We further note that the conduction in the Cu layer does exist in CuRhO_2 , but the contribution is limited at high temperatures (see the next section).

At the end of this section, we will summarize the characteristics of the charge transport of $\text{Cu}_{1-x}\text{Ag}_x\text{Rh}_{1-y}\text{Mg}_y\text{O}_2$ as follows. (i) In the parent compound CuRhO_2 , both the Cu layer and the RhO_2 layer can contribute to the conduction. The conductivity of the Cu layer rapidly decreases with decreasing temperature, and is negligibly small below 150 K. (ii) The Mg substitution for Rh supplies holes, and the 5% substitution causes a metal-insulator transition. (iii) The metallic state induced by Mg is insensitive to the Ag substitution for Cu, which suggests that the RhO_2 layer is responsible for the metallic conduction.

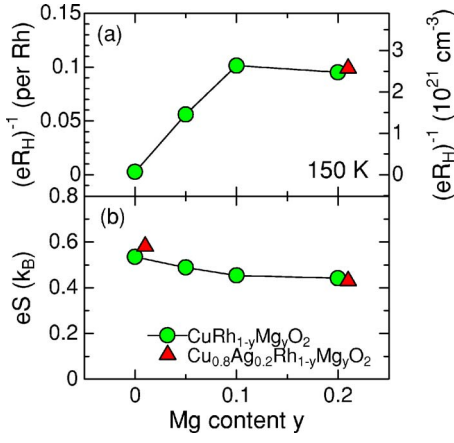


FIG. 6. (Color online) (a) The carrier concentration evaluated from the Hall coefficient and (b) the transport entropy evaluated from the thermopower. The data are taken at 150 K to pick up the RhO₂ contribution.

IV. DISCUSSION

In order to address the origin of the carrier-independent thermopower of CuRh_{1-y}Mg_yO₂, let us begin with the Boltzmann equation for conduction electrons in solids written as

$$\mathbf{j} = \sigma(-\nabla V) + \sigma S(-\nabla T), \quad (1)$$

$$\mathbf{q} = \sigma S T(-\nabla V) + \kappa'(-\nabla T), \quad (2)$$

where \mathbf{j} and \mathbf{q} are the electric current density and the thermal current density, respectively. κ' is the thermal conductivity in the absence of the electric field ($-\nabla V$), which is expressed by the experimentally measured thermal conductivity κ as $\kappa = \kappa' - T\sigma S^2$. In the absence of the temperature gradient $\nabla T = 0$, \mathbf{q} is written by \mathbf{j} as

$$\frac{\mathbf{q}}{T} = S\mathbf{j}. \quad (3)$$

The quantity in the left-hand side is equivalent to the entropy current density, and hence the thermopower S is reduced to the ratio of the entropy to the charge per carrier. Thanks to the thermodynamic identity, the entropy per carrier is equal to $-d\mu/dT$, where μ is the chemical potential. Thus we may write the thermopower as

$$eS \sim -\frac{\partial \mu}{\partial T}, \quad (4)$$

which clearly shows that the thermopower is a probe for the chemical potential, not for the carrier concentration. We therefore conclude that μ is nearly independent of the carrier concentration n in CuRh_{1-y}Mg_yO₂.

In order to see this, we plot $(eR_H)^{-1}$ in Fig. 6(a), which is a good measure for n through the relation of $R_H = (ne)^{-1}$. Note that $R_H = (ne)^{-1}$ is valid when carriers in a single band are responsible for the electric conduction. Thus we take the data at 150 K, because the RhO₂ layer dominates the electric conduction at this temperature. Figure 6(a) clearly shows that the carrier concentration $n = (eR_H)^{-1}$ per Rh is roughly equal to y for $y \leq 0.1$, that is, one Mg ion supplies one hole in the

RhO₂ layer. However, $(eR_H)^{-1}$ of $y=0.2$ is nearly the same as that of $y=0.1$, suggesting that more than 10% substituted Mg cannot supply holes to the system, although the XRD pattern deserves the single phase. Figure 6(b) shows eS at 150 K, which is a good measure for $-d\mu/dT$. Within experimental accuracies, eS is independent of y or n . $(eR_H)^{-1}$ and eS are essentially unchanged by the Ag substitution, which is consistent with our argument that the RhO₂ layer dominates the electric conduction below 150 K.

If the thermopower is weakly dependent on n ($\partial S/\partial n \sim 0$), we get

$$\frac{\partial S}{\partial n} \sim -\frac{1}{e} \frac{\partial^2 \mu}{\partial n \partial T} = -\frac{1}{e} \frac{\partial}{\partial T} \frac{\partial \mu}{\partial n} \sim 0. \quad (5)$$

Since $\partial n/\partial \mu$ is the compressibility, $\partial \mu/\partial n \sim 0$ means a divergently large compressibility—a sign for phase separation. In other words, the doped holes can be segregated in space and forms a percolation conducting network, where the substituted Mg ions can be away from the conduction paths. Actually, the Mg ions act as weak scatterers for the carriers. As shown in the inset of Fig. 4(c), the Hall mobility (μ_H) evaluated as R_H/ρ is weakly dependent on y , and shows a considerably large value of 1–1.5 cm²/Vs at 150 K. Thus, the weak dependence of S and μ_H on y are consistently explained by the phase-separation scenario mentioned above, although ρ shows the upturn at low temperatures, which indicates that the disorder begins to cause the weak localization.

Having clarified the conduction in the RhO₂ layer, next we will discuss the conduction in the Cu layer of CuRhO₂. Since the conduction in the Cu layer is suppressed in Cu_{0.8}Ag_{0.2}RhO₂, we may identify its conductivity to the conductivity of the RhO₂ layer in CuRhO₂ (σ_{RhO_2}). We can also evaluate the thermopower in the RhO₂ layer in CuRhO₂ (S_{RhO_2}) by assuming that it should be equal to the n -independent S of CuRh_{1-y}Mg_yO₂.

Now we can evaluate the conductivity and the thermopower in the Cu layer (σ_{Cu} and S_{Cu}) by utilizing a conventional two-carrier model given by

$$\sigma_0 = \sigma_{\text{Cu}} + \sigma_{\text{RhO}_2}, \quad (6)$$

$$\sigma_0 S_0 = \sigma_{\text{Cu}} S_{\text{Cu}} + \sigma_{\text{RhO}_2} S_{\text{RhO}_2}, \quad (7)$$

where σ_0 and S_0 are the conductivity and the thermopower of CuRhO₂, respectively.²¹ As the contribution of the RhO₂ layer, we employ σ of Cu_{0.8}Ag_{0.2}RhO₂ as σ_{RhO_2} and S of CuRh_{0.8}Mg_{0.2}O₂ as S_{RhO_2} . Then σ_{Cu} and S_{Cu} above 150 K can be numerically calculated from the measured data. Figure 7 thus shown obtained σ_{Cu} and S_{Cu} together with R_H of CuRhO₂ as a function of $1000/T$. σ_{Cu} and R_H obey an activation-type transport with the same activation energy of 0.16 eV, which is nearly the same value as that for other delafossite oxide CuAlO₂ (Refs. 16 and 22) and CuCrO₂.¹⁵ The value of 0.16 eV corresponds to a ten times larger value of the thermal energy at 150 K, below which the thermally excited carriers are negligibly small in number. S_{Cu} is evaluated as a temperature-independent value of 200 $\mu\text{V}/\text{K}$ near

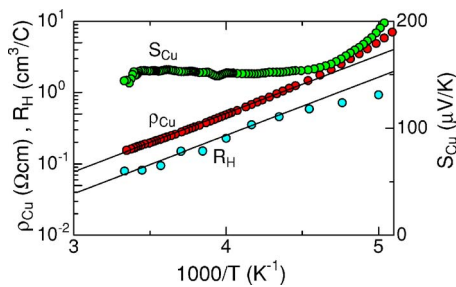


FIG. 7. (Color online) The resistivity (ρ_{Cu}) and thermopower (S_{Cu}) in the Cu layer of CuRhO_2 evaluated from the measured data (see text). The Hall coefficient of CuRhO_2 is also plotted for comparison.

300 K, which is qualitatively consistent with the thermopower of CuAlO_2 .¹⁶ In CuAlO_2 , the Cu layer is believed to be responsible for the electric conduction,^{17,23} which agrees well with our analysis.

A unique feature of CuRhO_2 is that it has two conduction channels of p type. In conventional semiconductors, thermally excited carriers are always the minority carriers having the opposite sign to the majority carriers, which decreases the magnitude of the thermopower in the intrinsic regime at high temperatures. In CuRhO_2 , however, thermally excited carriers are holes in the Cu layer, and the majority carriers are also holes self-doped in the RhO_2 layer. Thus, holes in the Cu layer decrease the resistivity, and *increase* the thermopower at the same time. In this context, we may call CuRhO_2 a two-hole-band conductor.

Finally we will briefly compare the transport parameters with those of the layered Co oxide Na_xCoO_2 ($x > 0.5$). First, a similar charge segregation occurs in polycrystalline samples of Na_xCoO_2 . The resistivity increases with the Na content x from 0.55 to 0.7, whereas the thermopower remains intact.²⁴ This is quite similar to what was observed in Fig. 4. Second, S of $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$ is very similar to that of

Na_xCoO_2 , which is consistent with the extended Heikes formula given by Koshibae *et al.*⁴ Third, R_H shows different temperature dependence. R_H of $\text{CuRh}_{1-y}\text{Mg}_y\text{O}_2$ is independent of temperature, and R_H of Na_xCoO_2 increases with increasing temperature.^{1,25} This may be associated with the susceptibility:²⁶ CuRhO_2 is a nonmagnetic insulator (susceptibility at 300 K is 5.7×10^{-7} emu/g), while Na_xCoO_2 is a Curie-Weiss metal.²⁷

V. SUMMARY

We have prepared a series of samples of Ag- and Mg-substituted CuRhO_2 , and clarified their conduction mechanism from the measured resistivity, thermopower, and Hall coefficient. One Mg ion substituted for Rh supplies one hole in the RhO_2 layer up to 10% substitution, which keeps the mobility and the thermopower essentially unchanged. We associate this with a kind of charge segregation in the RhO_2 layer, in which a percolation network of the metallic region dominates the conduction. Since the metallic region is away from the Mg ions, they do not scatter the carriers, working as an ideal dopant. On the other hand, the Cu layer is less important for the electric conduction, and the Ag substitution does not change the transport data of the Mg-substituted samples very much. The contribution of the Cu layer is most remarkably seen in the parent compound CuRhO_2 , which we have successfully evaluated using a two-carrier model. At 300 K, the RhO_2 and the Cu layers have comparable conductivity, which characterizes this material as a two-hole-band conductor.

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- ²¹Note that the contribution of the Cu layer could not be separated from that of the RhO₂ layer, even if single crystalline samples were used. They can give anisotropy in the transport parameters, in which the two contributions are always mixed.
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