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Abstract
We report measurements and analyses of resistivity, thermopower and the Hall coefficient of single-crystalline samples of the layered Rh oxide $K_{0.49}RhO_2$. The resistivity is proportional to the square of the temperature up to 300 K, and the thermopower is proportional to the temperature up to 140 K. The Hall coefficient increases linearly with the temperature above 100 K, which is ascribed to the triangular network of Rh in this compound. The different transport properties between Na_xCoO_2 and $K_{0.49}RhO_2$ are discussed on the basis of the different bandwidth between Co and Rh evaluated from the magnetotransport.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the discovery of large thermopower with low resistivity in Na_xCoO_2 [1], Co oxides with the CdI_2-type CoO_2 layer such as Ca–Co–O and Bi–Sr–Co–O have been studied as thermoelectric materials [2–6]. These materials have large thermopower comparable to conventional thermoelectric materials, which is considered to be due to the degeneracy of spins and orbitals [7]. In addition to the large thermopower, these Co oxides show many interesting properties. For example, Na_xCoO_2 exhibits magnetic order ($x \sim 0.75$), charge order ($x \sim 0.5$) and even superconductivity ($x \sim 0.35$) in its hydrated form [8–10]. The Bi–Sr–Co–O compound shows pseudogap, ferromagnetism and negative magnetoresistance [5, 11].

The layered Rh oxides with the CdI_2-type RhO_2 layer are found to have good thermoelectric properties similar to Co oxides [12–18]. This indicates that Rh ions in these Rh oxides have similar electronic states to Co ions in the layered Co oxides [7]. In particular, the Bi–Ba–Rh–O compound which is isomorphic to the Bi–Sr–Co–O compound shows a pseudogap and negative magnetoresistance [13, 14]. We focus on K_xRhO_2 which can be a reference material for Na_xCoO_2. There are few reports on A_xRhO_2 (A: alkali metals) and its hydrated form [20–23] and no reports on their thermoelectric properties. Recently, we successfully prepared single-crystalline samples

of $K_{0.49}RhO_2$ [19]. Figure 1 shows the crystal structure of $K_{0.49}RhO_2$ and a photographic image of a sample [24]. The typical size of the sample is $0.5 \times 0.3 \times 0.05$ mm³. $K_{0.49}RhO_2$ crystallizes in the γ-Na_xCoO_2-type structure (space group $P6_3/mmc$) with the lattice parameters of $a = 3.0647(4)$ Å and $c = 13.600(2)$ Å [19]. The CdI_2-type RhO_2 layer and the K_x layer are alternately stacked along the c-axis direction. In this paper, we report the transport properties of single-crystalline samples of $K_{0.49}RhO_2$ and compare them with those of other layered Co/Rh oxides.

2. Experimental details

Single-crystalline samples of $K_{0.49}RhO_2$ were prepared by a flux-growth method. A mixture of K_2CO_3 and Rh_2O_3 with a molar ratio of 25:1 was kept at 1373 K for 1 h, slowly cooled down to 1023 K at a rate of 2 K h⁻¹ and then cooled down to room temperature. K_2CO_3 was used as a self-flux. As-grown crystals were removed from the products by washing with distilled water. The crystals were characterized by electron probe micro-analysis and x-ray diffraction, and were identified to be isomorphic to γ-Na_xCoO_2 [19].

Resistivity and thermopower were measured by a conventional dc four-probe method and a steady-state method, respectively. Hall coefficient was measured with a physical property measurement system (Quantum Design). Current
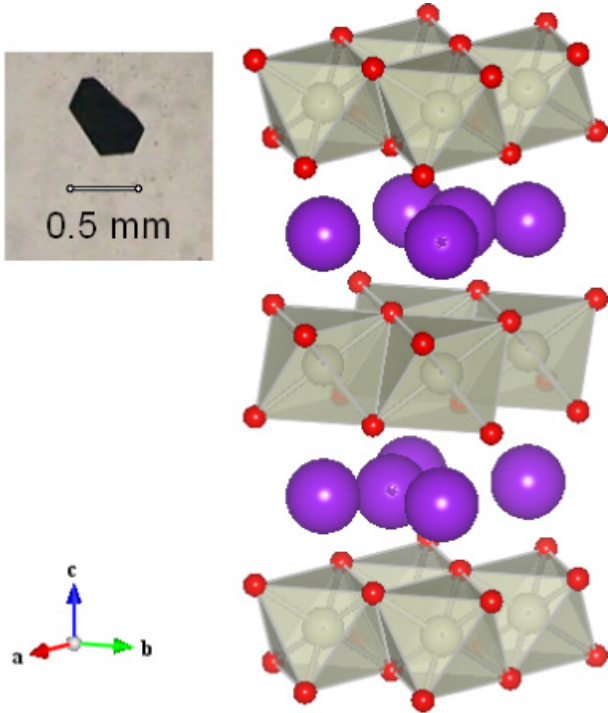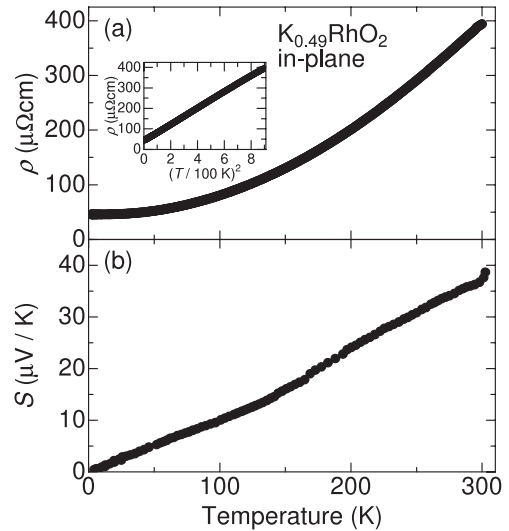
Figure 1. Crystal structure of $K_{0.49}RhO_2$. Purple (dark grey), grey (light grey) and red (dark grey) spheres represent K, Rh and O atoms, respectively. This material crystallizes in the γ-Na_xCoO_2-type structure. A photographic image of a sample of $K_{0.49}RhO_2$ is shown in the left upper corner.

Figure 2. (a) In-plane resistivity and (b) thermopower of $K_{0.49}RhO_2$. The inset shows the T^2 behaviour of the resistivity.

and temperature gradient were applied along the in-plane direction and a magnetic field was applied along the out-of-plane direction.

3. Results and discussion

Figure 2 shows the temperature dependence of the in-plane resistivity (ρ) and thermopower (S) of $K_{0.49}RhO_2$. ρ shows metallic behaviour with a magnitude of 400 $\mu\Omega$ cm at 300 K, which is twice as large as that of Na_xCoO_2 [1]. This fairly low resistivity suggests a high mobility of the CdI_2-type RhO_2 layer like an isomorphic CoO_2 layer [12–18]. ρ shows Fermi-liquid behaviour ($\rho = AT^2+B$, where T is temperature) up to 300 K, where A and B are 4.0×10^{-9} Ω cm K^{-2} and 4.2×10^{-5} Ω cm, respectively. Compared to the heavy-fermion systems, it is unusual that the T^2 power law is observed up to 300 K, but one can also see a T^2 power law up to high temperatures in doped $SrTiO_3$ [25] and doped $CuRhO_2$ [26]. This behaviour is completely different from that of Na_xCoO_2 whose resistivity is not proportional to T^2 [9, 27]. This suggests that the electronic correlation in $K_{0.49}RhO_2$ is weaker than that in Na_xCoO_2, although the T^2 law indicates significant correlation. Indeed, ρ of Na_xCoO_2 is proportional to T^2 under the magnetic field [28], and we expect that the spin fluctuations are weaker in $K_{0.49}RhO_2$ than in Na_xCoO_2, because the magnetic field suppresses the spin fluctuations.

As shown in figure 2(b), the magnitude of S is 40 μV K^{-1} at 300 K, which is half of that of Na_xCoO_2 [1]. S is almost

proportional to T up to 300 K with a kink at 140 K, while S for the $Na_{0.71}CoO_2$ sample increases with T at low temperature and is almost T-independent at around 300 K [27]. Kuroki and Arita suggest that a 'pudding-mould' band can explain the transport properties of Na_xCoO_2 [29]. Compared to the S of Na_xCoO_2, correlation in $K_{0.49}RhO_2$ is weaker because the S of $K_{0.49}RhO_2$ increases almost linearly with T (see (1)). We should note that the kink at around 140 K is not seen in the resistivity. In $SrRhO_3$ and $Sr_3Rh_2O_7$, the thermopower shows a similar kink near 140 K. Yamaura *et al* speculated that the kink in the thermopower may be structurally related [30]. This suggests that Rh oxides commonly show this thermopower anomaly. As for the thermoelectric materials, the largest power factor S^2/ρ of $K_{0.49}RhO_2$ is 4.0 μW cm^{-1} K^{-2} at 300 K. Although this value is 10 times smaller than that of Na_xCoO_2, it is the largest among the layered Rh oxides [12–18].

Let us discuss the transport properties of $K_{0.49}RhO_2$ quantitatively. We evaluate the Fermi energy of this compound from the slope in the thermopower below 140 K using the following equation [37]:
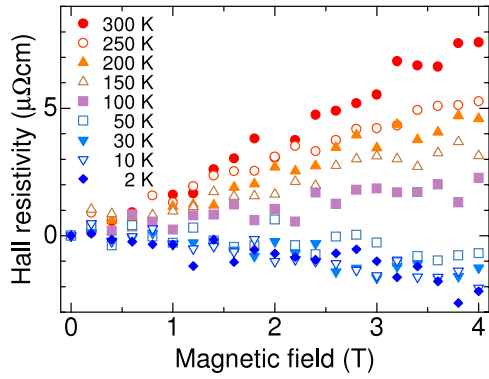
$$S = -\frac{\pi^2}{2e}\frac{k_B^2 T}{E_F},\qquad(1)$$

where e, k_B and E_F represent the elementary charge, the Boltzmann constant and the Fermi energy, respectively. The evaluated E_F is 4200 K, which is much higher than 140 K, and this is consistent with the T-linear behaviour of S.

From the crystal structure of $K_{0.49}RhO_2$, this material is regarded as a two-dimensional material. E_F for a two-dimensional system is written as [38]

$$E_F = \hbar^2\pi d_c \frac{n}{m^*},\qquad(2)$$

where $\hbar$, d_c, n and m^* represent the Planck constant, the interlayer distance, the carrier concentration and the effective mass, respectively. Here, we adopt $d_c = c/2 = 6.8$ Å from crystallographic analysis [19].

Figure 3. Magnetic field dependence of Hall resistivity of $K_{0.49}RhO_2$.

Figure 4. Hall coefficients of various kinds of layered (a) Rh and (b) Co oxides. The numbers indicate 1: $(Bi_{0.8}Pb_{0.2})_{1.8}Ba_2Rh_{1.9}O_y$ [13], 2: $Bi_{0.78}Sr_{0.4}RhO_{3+\delta}$ [18], 3: $K_{0.49}RhO_2$ (this work), 4: $Ca_{2.8}Nd_{0.2}Co_4O_9$ [36], 5: $Bi_{1.56}Pb_{0.44}Sr_2Co_{1.9}O_y$ [32], 6: $Ca_3Co_4O_9$ [34], 7: $[Sr_2O_{2-\delta}]_{0.53}CoO_2$ [35], 8: $Na_{0.68}CoO_2$ [31] and 9: $NaCo_{1.9}Pd_{0.1}O_4$ [33].

If we adopt n evaluated from the composition, we will estimate the effective mass from (2) to be 80 times larger than the bare mass of electrons at 300 K. Although this value seems too large, it mostly comes from the narrow t_{2g} bands. This is quantitatively explained by the band calculations of $NaCoO_2$ and $NaRhO_2$ [13]. These band calculations revealed that the difference between 3d and 4d orbitals is cancelled because the Rh–Rh distance in the RhO_2 layer is larger than the Co–Co distance in the CoO_2 layer, which gives a smaller overlap integral in the $NaRhO_2$ [13]. The calculated bandwidth is comparable to that from another Rh oxide [26]. Thus the actual bandwidths of Rh oxides may be comparable to those of Co oxides. The mobility is evaluated from ρ to be 3.4 cm^2 V^{-1} s^{-1} at 300 K, which is comparable to that of Na_xCoO_2 [1].
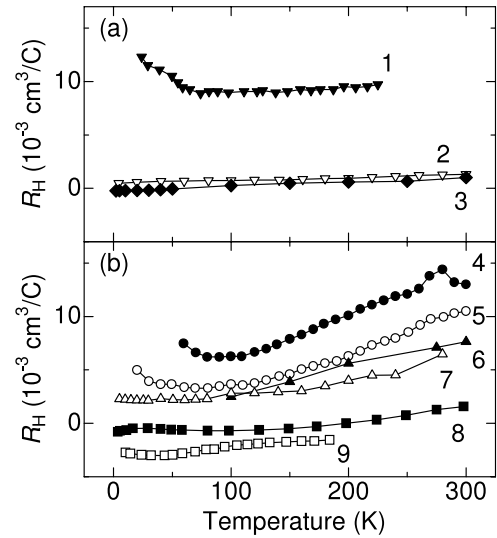
The thermopower and the electronic specific heat coefficient have the relation [39, 40]

$$\frac{S}{T}\frac{N_{AV}e}{\gamma} = \text{const.}, \qquad (3)$$

where N_{AV} represents the Avogadro number and the constant value is of the order of 1, and we adopt a constant value of 1. From this relation we can evaluate the magnitude of the electronic specific heat coefficient. The smaller temperature coefficient in the thermopower of $K_{0.49}RhO_2$ indicates that the electronic specific heat coefficient γ of $K_{0.49}RhO_2$ is smaller than that of Na_xCoO_2, which means that the correlation is weaker in Rh oxides. We can also estimate γ from the Kadowaki–Woods relation ($A/\gamma^2 = 1.0 \times 10^{-5}$ $\mu\Omega$ cm (mol K/mJ)^2) using the T^2 coefficient in ρ [41, 42]. The estimated values are of the order of 10^{-2} J mol^{-1} K^{-1}, and reasonably agree.

Figure 3 shows the magnetic field dependence of Hall resistivity of $K_{0.49}RhO_2$ at various temperatures. The Hall resistivity shows negative field dependence below 50 K while it shows positive dependence at 300 K. This indicates that the Hall coefficient of $K_{0.49}RhO_2$ changes its sign with temperature. Figure 4 shows the T dependence of the Hall coefficients (R_H) of various layered Co/Rh oxides. We can see the layered Co/Rh oxides commonly shows the T-dependent R_H.

Now we discuss the T-dependent R_H of $K_{0.49}RhO_2$. The first possibility is that the carrier concentration changes with

temperature. R_H of $K_{0.49}RhO_2$ increases with temperature and changes its sign around 50 K. In the Drude model (free carrier in one band), the change in the sign of R_H is unphysical. The second possibility is that there are two kinds of carriers. The sign of R_H is negative below 50 K, which means that electrons are the majority carrier as long as mobilities for electrons and holes are equal. Then the change in the sign of R_H around 50 K may indicate that holes are dominant at high temperature. This behaviour is observed in Sr_2RuO_4. Positive S with negative R_H in Sr_2RuO_4 is ascribed to the ratio of the densities between holes and electrons, and the dS/dT has an anomaly around 20 K where R_H changes its sign [43, 44]. In $K_{0.49}RhO_2$ no anomalies are detected even in the dS/dT around 50 K, which implies that the two-carrier model is unlikely. The third possibility is that the T-dependent R_H in $K_{0.49}RhO_2$ is caused by a special geometry of the crystal structure. In fact, T-dependent R_H of triangular- and Kagomé-lattice systems is theoretically suggested by means of high temperature expansion formulae [45–47] and consistent with experiments. Koshibae and Maekawa suggest that the electronic states in the triangular-lattice system of the Co oxides are effectively regarded as four interpenetrating Kagomé lattices [48]. From the structural similarities, the layered Rh oxides are expected to show such behaviour. The high temperature R_H of these systems depends on temperature as [47]

$$R_H(T) = -\frac{v}{4e}\frac{k_BT}{t}\frac{1+y}{y(1-y)}, \qquad (4)$$

where v, t and y are the unit cell volume, the transfer integral and the electron concentration, respectively. This indicates that R_H is linear in T.

In figure 4 we can see the T-linear R_H in all materials and find a clear difference in dR_H/dT between Rh (nos. 1–3

Table 1. Temperature coefficient of R_H of various layered Co/Rh oxides above 100 K. There is a clear difference in the slope of R_H between Co and Rh.

No.	Material	dR_H/dT (10^{-6} cm^3 C^{-1} K^{-1})	$S_{300 K}$ (μV K^{-1})	Crystal	Ref.
1	$(Bi_{0.8}Pb_{0.2})_{1.8}Ba_2Rh_{1.9}O_y$	4.4	95	Poly	[13]
2	$Bi_{0.78}Sr_{0.4}RhO_{3+\delta}$	2.7	65	Single	[18]
3	$K_{0.49}RhO_2$	2.7	40	Single	This work
4	$Ca_{2.8}Nd_{0.2}Co_4O_9$	44	147	Poly	[36]
5	$Bi_{1.56}Pb_{0.44}Sr_2Co_{1.9}O_y$	32	—	Single	[32]
6	$Ca_3Co_4O_9$	31	129	Single	[34]
7	$[Sr_2O_{2-\delta}]_{0.53}CoO_2$	14	70	Single	[35]
8	$Na_{0.68}CoO_2$	11	90	Single	[31]
9	$NaCo_{1.9}Pd_{0.1}O_4$	6[a]	35	Poly	[33]

[a] Data exist only below 200 K.

in figure 4) and Co oxides (nos. 4–9 in figure 4). In addition to these materials, TiS_2 with a triangular lattice also shows T-linear R_H [49], which seems qualitatively consistent with (4). Table 1 summarizes dR_H/dT of these layered Co/Rh oxides in units of 10^{-6} cm^3 C^{-1} K^{-1} from a T-linear fit above 100 K. Equation (4) indicates that dR_H/dT depends on t and the carrier concentration. In real materials such as Ca–Co–O and Bi–Sr–Co–O, the T-linear part of R_H has a weak relation with carrier concentration [36, 32].

To see the relation between the thermopower and R_H, we also put the thermopower data of the layered Co/Rh oxides at 300 K in table 1. The Rh oxides show smaller dR_H/dT and smaller thermopower than the Co oxides [50], which may be due to the difference between 3d and 4d orbitals. The misfit oxides (nos. 1, 4, 5, 6 and 7) have T-independent thermopower at 300 K, which has been explained by the Heikes formula. Since the Heikes formula is independent of the bandwidth t, dR_H/dT has little to do with the magnitude of S.

Equation (4) shows that the carrier concentration dependence of R_H is almost independent of y where the carrier concentration is nearly half ($y \sim 0.5$), and accordingly the four-times difference in dR_H/dT between $Na_{0.68}CoO_2$ and $K_{0.49}RhO_2$ is ascribed to the difference in t. In fact, the estimated t's from these dR_H/dT's in $Na_{0.68}CoO_2$ and $K_{0.49}RhO_2$ are ~ 25 K [31] and ~ 160 K, respectively. Kobayashi *et al* report $t \sim 200$ K in $Bi_{0.78}Sr_{0.4}RhO_{3+\delta}$ [18].

We should note that angle-resolved photoemission spectroscopy data of $Na_{0.7}CoO_2$ suggest $t \sim 120$ K [51] which is different from the evaluated $t \sim 25$ K for $Na_{0.68}CoO_2$ [31]. The discrepancy in the magnitude of t is a factor of 5 in Na_xCoO_2. In the case of Na_xCoO_2, the photoemission data successfully explains the magnitude of the thermopower [52], which indicates that the value of t is underestimated in R_H. One may notice that the evaluated E_F from (1) is also much larger than t (a factor of 26) in $K_{0.49}RhO_2$, but E_F/t would be of the same order if we did the same evaluation for Na_xCoO_2. This indicates that the value of t evaluated in (4) may be renormalized from the bare bandwidth of the material, because (4) is valid for infinitely large Coulomb repulsion, which is not realized in real materials. Furthermore, T-linear R_H is derived from the assumption that the material of $y \sim 0$ is a Mott insulator, but the real material (i.e. CoO_2) is a paramagnetic metal [53]. Further studies both experimental and theoretical are necessary.

4. Summary

We have measured the transport properties of single-crystalline samples of $K_{0.49}RhO_2$ which is isomorphic to γ-Na_xCoO_2. Resistivity and thermopower at 300 K are 400 $\mu\Omega$ cm and 40 μV K^{-1}, respectively. Resistivity shows a T^2 dependence up to 300 K and thermopower is proportional to the temperature up to 140 K. The temperature dependence of transport properties of $K_{0.49}RhO_2$ are different from those of Na_xCoO_2, which suggests that the correlation in Rh oxides is weaker than that in Na_xCoO_2. The estimated power factor at 300 K is 4.0 μW cm^{-1} K^{-2}, which is the largest among other layered Rh oxides. The Hall coefficient is almost proportional to the temperature above 100 K, which is similar to other layered Co/Rh oxides. Quantitative analysis of this T-linear term of the Hall coefficient indicates that the effective bandwidth related to the magnetotransport is much larger in Rh oxides. Further study is needed for the understanding of Co/Rh oxides.

Acknowledgments

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