Transport properties of the layered Rh oxide K$_{0.49}$RhO$_2$

S Shibasaki$^1$, T Nakano$^1$, I Terasaki$^1$, K Yubuta$^2$ and T Kajitani$^3$

$^1$ Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan
$^2$ Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
$^3$ Department of Applied Physics, Graduate School of Engineering, Tohoku University, Sendai 980-5777, Japan

E-mail: g01k0374@suou.waseda.jp (S Shibasaki)

Received 28 December 2009, in final form 6 February 2010
Published 5 March 2010
Online at stacks.iop.org/JPhysCM/22/115603

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$_x$CoO$_2$ 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$_x$CoO$_2$ [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 thermoelectric properties 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$_x$CoO$_2$ 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$_x$RhO$_2$ which can be a reference material for Na$_x$CoO$_2$. There are few reports on A$_x$RhO$_2$ (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 $0.5 \times 0.3 \times 0.05$ mm$^3$. K$_{0.49}$RhO$_2$ crystallizes in the $\gamma$-Na$_x$CoO$_2$-type structure (space group $P6_3/mmc$) with the lattice parameters of $a = 3.0647(4)$ $\text{Å}$ and $c = 13.600(2)$ $\text{Å}$ [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$_2$CO$_3$ and Rh$_2$O$_3$ 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$_2$CO$_3$ 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 $\gamma$-Na$_x$CoO$_2$ [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
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 ($\rho$) and thermopower ($S$) of $K_{0.49}RhO_2$. $\rho$ shows metallic behaviour with a magnitude of 400 $\mu$\Omega cm at 300 K, which is twice as large as that of Na$_4$CoO$_2$ [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]. $\rho$ shows Fermi-liquid behaviour ($\rho = AT^2 + B$, where $T$ is temperature) up to 300 K, where $A$ and $B$ are $4.0 \times 10^{-9}$ $\Omega$ cm K$^{-2}$ and $4.2 \times 10^{-3}$ $\Omega$ 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$_4$CoO$_2$ whose resistivity is not proportional to $T^3$ [9, 27]. This suggests that the electronic correlation in $K_{0.49}RhO_2$ is weaker than that in Na$_4$CoO$_2$, although the $T^3$ law indicates significant correlation. Indeed, $\rho$ of Na$_4$CoO$_2$ 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$_4$CoO$_2$, because the magnetic field suppresses the spin fluctuations.

As shown in figure 2(b), the magnitude of $S$ is 40 $\mu$V K$^{-1}$ at 300 K, which is half of that of Na$_4$CoO$_2$ [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$_4$CoO$_2$ [29]. Compared to the $S$ of Na$_4$CoO$_2$, 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$_3$Rh$_2$O$_7$, 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 $S^2/\rho$ of $K_{0.49}RhO_2$ is 4.0 $\mu$W cm$^{-1}$ K$^{-2}$ at 300 K. Although this value is 10 times smaller than that of Na$_4$CoO$_2$, 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]:

$$S = -\frac{\pi^2 k_B^2 T}{2e E_F},$$

(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]

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

(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].
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 those of Co oxides. The mobility is evaluated from $\rho$ to be $3.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300 K, which is comparable to that of Na$_2$CoO$_2$ [1].

The thermopower and the electronic specific heat coefficient have the relation [39, 40]

$$\frac{S}{T} = \frac{N_A e}{\gamma} \text{ const.},$$

(3)

where $N_A$ 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 $\gamma$ of K$_{0.49}$RhO$_2$ is smaller than that of Na$_2$CoO$_2$, which means that the correlation is weaker in Rh oxides. We can also estimate $\gamma$ from the Kadowaki–Woods relation ($A/\gamma^2 = 1.0 \times 10^{-5} \mu \Omega \text{ cm} (\text{mol K/mJ})^2$) using the $T^2$ coefficient in $\rho$ [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 temperature dependence of the Hall coefficients of various layered Co/Rh oxides. We can see the layered Co/Rh oxides commonly show 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$_2$RuO$_4$. Positive $S$ with negative $R_H$ in Sr$_2$RuO$_4$ 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, a $T$-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. Koshiba 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]

$$R_H(T) = -\frac{1}{4\pi} \frac{k_B T}{t} \frac{1 + y}{y(1 - y)},$$

(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

---

**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$_{2/3}$Pb$_{1/3}$Ba$_2$Rh$_{1.9}$O$_y$ [13], 2: Bi$_{2/3}$Sr$_{1/3}$RhO$_{4+d}$ [18], 3: K$_{0.49}$RhO$_2$ (this work), 4: Ca$_2$Nd$_2$Co$_3$O$_8$ [36], 5: Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Co$_{1.9}$O$_y$ [32], 6: Ca$_2$Co$_3$O$_8$ [34], 7: Sr$_2$Ru$_{1.8}$O$_4$ [33], 8: Na$_{0.46}$Co$_2$O$_2$ [31] and 9: NaCo$_{1.9}$Pd$_0.1$O$_4$ [33].
in figure 4) and Co oxides (nos. 4–9 in figure 4). In addition to these materials, TiS₂ 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 \( 10^{-6} \) cm³ 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 \( \text{Na}_{0.69}\text{CoO}_2 \) and \( \text{K}_0.49\text{RhO}_2 \) is ascribed to the difference in \( t \). In fact, the estimated \( t \)'s from these \( dR_H/dT \)'s in \( \text{Na}_{0.69}\text{CoO}_2 \) and \( \text{K}_0.49\text{RhO}_2 \) are \( \sim 25 \) K [31] and \( \sim 160 \) K, respectively. Kobayashi et al report \( t \sim 200 \) K in \( \text{Bi}_{0.78}\text{Sr}_{0.2}\text{Rh}_{3} \) [18].

We should note that angle-resolved photoemission spectroscopy data of \( \text{Na}_{0.17}\text{CoO}_2 \) suggest \( t \sim 120 \) K [51] which is different from the evaluated \( t \sim 25 \) K for \( \text{Na}_{0.69}\text{CoO}_2 \) [31]. The discrepancy in the magnitude of \( t \) is a factor of 5 in \( \text{Na}_x\text{CoO}_2 \). In the case of \( \text{Na}_x\text{CoO}_2 \), 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 \( \text{K}_0.49\text{RhO}_2 \), but \( E_F/t \) would be of the same order if we did the same evaluation for \( \text{Na}_x\text{CoO}_2 \). 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. \( \text{CoO}_2 \)) 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 \( \text{K}_0.49\text{RhO}_2 \) which is isomorphic to \( \gamma\text{-Na}_x\text{CoO}_2 \). Resistivity and thermopower at 300 K are 400 \( \mu \Omega \cdot \text{cm} \) and 40 \( \mu \text{V} \cdot \text{K}^{-1} \), 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 \( \text{K}_0.49\text{RhO}_2 \) are different from those of \( \text{Na}_{0.69}\text{CoO}_2 \), which suggests that the correlation in Rh oxides is weaker than that in \( \text{Na}_x\text{CoO}_2 \). The estimated power factor at 300 K is 4.0 \( \mu \text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-2} \), 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

We thank W Kobayashi, Y Klein, M Abdel-Jawad, K Kuroki, T Katsufuji and D J Singh for fruitful discussions. This work was partially supported by a Grant-in-Aid for JSPS Fellows.

### References

[1] Terasaki I, Sasago Y and Uchinokura K 1997 Phys. Rev. B 56 R12685
[2] Miyazaki Y, Kudo K, Akoshima M, Ono Y, Koike Y and Kajitani T 2000 Japan. J. Appl. Phys. 39 L531
[3] Maset A C, Michel C, Maignon A, Hervieu M, Toulemonde O, Studer F, Raveau B and Hejtmanek J 2000 Phys. Rev. B 62 166
[4] Funahashi R, Matsubara I and Sodeoka S 2000 Appl. Phys. Lett. 76 2385
[5] Itoh T and Terasaki I 2000 Japan. J. Appl. Phys. 39 6658
[6] Funahashi R and Matsubara I 2001 Appl. Phys. Lett. 79 362
[7] Kishibai W, Tsutsui K and Maekawa S 2000 Phys. Rev. B 62 6869
[8] Mototani T, Ueda R, Nauljus E, Tojo T, Terasaki I, Atake T, Karpiphen M and Yamauchi H 2003 Phys. Rev. B 67 064406
[9] Foo M L, Wang Y, Watauchi S, Zandbergen H W, He T, Cava R J and Ong N P 2004 Phys. Rev. Lett. 92 247001

### 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 | \( dR_H/dT \) (\( 10^{-6} \) cm³ C⁻¹ K⁻¹) | \( S_{300\,\text{K}} \) (\( \mu \text{V} \cdot \text{K}^{-1} \)) | Crystal | Ref. |
|----|----------|-----------------------------------|-----------------|--------|-----|
| 1  | \( \text{Bi}_{0.3}\text{Sr}_{0.7}\text{RhO}_3 \) | 2.7                              | 65              | Single | [18]|
| 2  | \( \text{K}_0.49\text{RhO}_2 \) | 4.4                              | 95              | Poly   | [13]|
| 3  | \( \text{Ca}_3\text{Nd}_2\text{CoO}_6 \) | 11                               | 70              | Single | [35]|
| 4  | \( \text{Na}_1\text{CoO}_2 \) | 31                               | 129             | Single | [34]|
| 5  | \( \text{Na}_{0.69}\text{CoO}_2 \) | 11                               | 90              | Single | [31]|
| 6  | \( \text{NaCoO}_2\text{Pd}_0\text{O}_4 \) | 600                             | 35              | Poly   | [33]|

\( ^{\text{a}} \) Data exist only below 200 K.
