Enhanced Seebeck coefficient by a filling-induced Lifshitz transition in $\text{K}_x\text{RhO}_2$

Naoko Ito, Mayu Ishii, and Ryuji Okazaki

Department of Physics, Faculty of Science and Technology, Tokyo University of Science, Noda 278-8510, Japan

We have systematically measured the transport properties in the layered rhodium oxide $\text{K}_x\text{RhO}_2$ single crystals ($0.5 \leq x \leq 0.67$), which is isostructural to the thermoelectric oxide $\text{Na}_x\text{CoO}_2$. We find that below $x = 0.64$ the Seebeck coefficient is anomalously enhanced at low temperatures with increasing $x$, while it is proportional to the temperature like a conventional metal above $x = 0.65$, suggesting an existence of a critical content $x^* \approx 0.65$. For the origin of this anomalous behavior, we discuss a filling-induced Lifshitz transition, which is characterized by a sudden topological change in the cylindrical hole Fermi surfaces at the critical content $x^*$.

The layered cobalt oxide $\text{Na}_x\text{CoO}_2$ has attracted a great deal of attention for its rich physical properties since the discovery of the large Seebeck coefficient [1]. This compound consists of alternately-stacked $\text{CoO}_2$ and $\text{Na}$ layers, and the conductive $\text{CoO}_2$ layer is formed by edge-shared $\text{CoO}_6$ octahedra, resulting in a two-dimensional (2D) triangular lattice of $\text{Co}$ ions. The uniqueness of this compound is the complex electronic properties drastically changing with Na content $x$ [2]. For rich Na content region, the large Seebeck coefficient is observed with metallic resistivity [3–5]. The magnetic property varies from Pauli-paramagnetic to Curie-Weiss (CW) behavior across a critical Na content $x^*_{\text{Na}} \approx 0.62$ [5–8]. A spin-density-wave and a charge-ordered insulating state have also been suggested for $0.75 \leq x$ and at $x \sim 0.5$, respectively [9–13]. Moreover, hydration induces unconventional superconductivity at around $x = 0.3$ [14–18].

The crucial points for understanding various emergent phenomena in $\text{Na}_x\text{CoO}_2$ are the characteristic electronic band structure and the topology of the Fermi surface. In this compound, the $t_{2g}$ bands from $\text{Co} 3d$ orbitals are composed of an $a_{1g}$ band and doubly degenerate $e_g$ bands, and the Fermi level lies across the $a_{1g}$ band to form a cylindrical Fermi surface reflecting the quasi-2D crystal structure [19–27]. Now the shape of the $a_{1g}$ band is peculiar, including a somewhat flat portion around a local minimum at the Γ point, which is called pudding-mold band shape [28]. With increasing Na content, the Fermi level rises and then touches the local minimum to create a small electron pocket as is resolved by the angle resolved photoemission spectroscopy (ARPES) [27]. Detailed thermodynamic study has revealed that this topological change in the Fermi surface, known as the Lifshitz transition [29], occurs at the critical content $x^*_{\text{Na}} \approx 0.62$ [8]. The Fermi level then locates around the flat region for $x > x^*_{\text{Na}}$, resulting in the large Seebeck coefficient due to a significant difference in the velocities of electrons and holes [28]. The flat band with large density of states may also contribute to the CW-like magnetic behavior observed above $x^*_{\text{Na}}$.

The issue to be addressed is whether the richness of these intriguing properties universally emerges in the related systems. $\text{K}_x\text{CoO}_2$ ($x \sim 0.5$) shows two phase transitions at low temperatures [30, 31], reminiscent of $\text{Na}_{0.5}\text{CoO}_2$, and similar electronic structures in these materials are suggested both experimentally and theoretically [22, 32]. The $4d$ system $\text{Na}_x\text{RhO}_2$ is also isostructural to $\text{Na}_x\text{CoO}_2$ [33, 34] and exhibits a metal-insulator transition which is explained by an Ioffe-Regel criterion [35], but the detailed electronic properties are still unexplored.

The isostructural $\text{K}_x\text{RhO}_2$ shows moderately large Seebeck coefficient with half the magnitude of $\text{Na}_x\text{CoO}_2$ [36–38]. The optical study suggests that the bandwidth of $\text{K}_x\text{RhO}_2$ is twice broader compared with $\text{Na}_x\text{CoO}_2$ owing to a difference of the orbital sizes between $\text{Co} 3d$ and $\text{Rh} 4d$ electrons [39]. Recent ARPES measurement has clarified that the band shape of $\text{K}_x\text{RhO}_2$ is closely similar to that of $\text{Na}_x\text{CoO}_2$ [40], indicating a possible emergence of rich electronic phase diagram. Furthermore, interesting phenomena, including a significant enhancement of thermoelectric efficiency by hydration [41] and a realization of topological quantum Hall effect [42], have been theoretically predicted in $\text{K}_x\text{RhO}_2$. However, the physical properties of $\text{K}_x\text{RhO}_2$ have been little known due to the difficulty of the synthesis of well controlled K content, single-phase samples [43, 44].

In this paper, we present the potassium composition dependence of the transport properties in $\text{K}_x\text{RhO}_2$ for $0.5 \leq x \leq 0.67$ using pure single-crystalline samples, which are systematically prepared by a self-flux method and a K de-intercalation process. We find that the Seebeck coefficient is highly sensitive to the K content $x$ and enhanced only below a critical content $x^* \approx 0.65$. This result is attributed to a filling-induced Lifshitz transition at $x^*$, at which the topology of the cylindrical hole surface dramatically changes. Moreover, near $x = 0.5$, distinct anomaly is observed at $T \approx 75$ K, implying that this rhodate also offers a fascinating platform for various electronic phases to be investigated.

Single-crystalline samples of $\text{K}_x\text{RhO}_2$ were grown by a self-flux method [36, 37]. A mixture of $\text{K}_2\text{CO}_3$ (99.999%) and $\text{Rh}_2\text{O}_3$ (99.9%) with a molar ratio of 50 : 1 was put in an alumina crucible and kept at 1373 K for 1 h, and then cooled down to 1123 K with a rate of 5 K/h. After washing with distilled water, we obtained thin hexagonal crystals as shown in the inset of Fig. 1(a). X-ray diffraction (XRD) measurements were performed by an X-ray diffractometer (Rigaku UltimaIV) with Cu Kα radiation in a 0-2θ scan mode. In the case of the single crystalline samples, the scattering vector was normal to the surface of the sample. The K content of as-grown samples is $x = 0.67$. To get the lower potassium content samples, we dipped the samples in I$_2$-acetonitrile solutions [44]. The potassium content was controlled by both the concentra-
We measured the K content in the inset of (a) shows the SEM image of as-grown K$_x$RhO$_2$ crystal. (d) The powder XRD pattern. Bars indicate the expected Bragg peaks for γ-type structure K$_x$RhO$_2$. The inset shows the relation between the K content $x$ and $c$-axis lattice parameter $c$. The dashed line represents a linear fitting result.

The powder XRD pattern refers to the hydrated phase, as is also pointed out by means of the optimization of the lattice constants [41]. On the other hand, the space group is preserved among the hydrated and non-hydrate samples, similar to the case of Na$_x$CoO$_2$ [14].

![Diagram](image)

**FIG. 1.** (Color online). (a-c) The XRD pattern of the single crystal: (a) as grown, (b) after de-intercalation, and (c) after annealing. The inset of (a) shows the SEM image of as-grown K$_x$RhO$_2$ crystal. (d) The powder XRD pattern. Bars indicate the expected Bragg peak positions for γ-type structure K$_x$RhO$_2$. The inset shows the relation between the K content $x$ and $c$-axis lattice parameter $c$. The dashed line represents a linear fitting result.

We first show the XRD patterns of a single crystal in each process of the K de-intercalation. The XRD patterns of as-grown and after-de-intercalation crystals are depicted in Figs. 1(a) and 1(b), respectively. As reported by Zhang et al [43, 44], several sets of the peaks are observed in after-de-intercalation crystals. On the other hand, after annealing, we find that a single-phase pattern is recovered as shown in Fig. 1(c). In the isostructural Na$_x$CoO$_2$, it is well known that the low Na-content sample is easily hydrated and a heating process removes H$_2$O molecules from the hydrated sample [45]. Thus the present result indicates that a hydrated phase is also formed in K$_x$RhO$_2$ after de-intercalation but can be recovered to the non-hydrate phase by the successive annealing. The existence of the hydrated K$_x$RhO$_2$ is also suggested by an ion exchange experiment [46]. Note that no superconductivity is observed in the hydrated K$_x$RhO$_2$ at present.

The powder XRD pattern of non-hydrate sample for $x = 0.651$ is represented in Fig. 1(d). Note that the measured powder is not ground and just collected as small single crystals with the size of ~50 μm, because the grinding induces the hydration significantly. As seen in Fig. 1(d), all the peaks are indexed using the γ-Na$_x$CoO$_2$-type structure (space group P6$_3$/mmc) with the lattice parameters of $a = 3.076(2)$ Å and $c = 12.233(5)$ Å. In the earlier reports, the $c$-axis lattice parameter is found to be 13.6 Å [36, 38], much larger than the present result. This discrepancy indicates that the powder XRD patterns in the earlier reports refer to the hydrated phase, as is also pointed out by means of the optimization of the lattice constants [41]. On the other hand, the space group is preserved among the hydrated and non-hydrate samples, similar to the case of Na$_x$CoO$_2$ [14].

We examine the relation between the $c$-axis lattice parameter and the K content $x$ using non-hydrate crystals as shown in the inset of Fig. 1(d). The $c$-axis lattice parameter decreases almost linearly with increasing K content $x$. In this system, when the K content increases, the Coulomb force holding the RhO$_2$ layers is enhanced to decrease the $c$-axis lattice parameter, which is also seen in Na$_x$CoO$_2$ [2]. The present data are fitted using a linear function $c = c_0 + c_1x$ with $c_0 = 13.13(4)$ Å and $c_1 = -1.37(7)$ Å as shown by the dashed line. The K content of crystals for the transport measurements is calculated from the $c$-axis lattice parameter using this relation in a similar manner to that of Na$_x$CoO$_2$ [5]. The $x$ values have a common error which is estimated at up to 0.04 due to the large error of $c_0$ and $c_1$. However, we can obtain relative amount of K content accurately by the comparison of the $c$-axis lattice parameter. From the K content, the hole concentration is approximately determined as $1 - x$ holes/Rh [40].

We then discuss the transport properties of K$_x$RhO$_2$. Figure 2 shows the temperature dependence of the Seebeck coefficient (left axis) and the resistivity normalized by the room-temperature resistivity $\rho_{RT}$ (right axis) of K$_x$RhO$_2$ for $x = 0.50$ and 0.51. The dashed line represents the temperature at which the distinct anomaly is observed.

![Graph](image)

**FIG. 2.** (Color online). Temperature dependence of the Seebeck coefficient (left axis) and the resistivity normalized by the room-temperature resistivity $\rho_{RT}$ (right axis) of K$_x$RhO$_2$ for $x = 0.50$ and 0.51. The dashed line represents the temperature at which the distinct anomaly is observed.
The temperature dependence of \( S/T \) for K\(_2\)RhO\(_2\) at \( T = 10 \) K (blue) and \( 295 \) K (red). The dashed lines are guides for eyes. (b) Contour plot of \( S/T \).

The anomaly is clearly demonstrated in the Seebeck coefficient divided by temperature, \( S/T \), shown in Figs. 3(c) and (d). For \( 0.57 \leq x \leq 0.64 \), \( S/T \) gradually increases with lowering temperature. It also increases with increasing \( x \) but the behavior drastically changes in the narrow range of \( 0.64 < x < 0.65 \) into almost no temperature dependence, as expected in a conventional metal, suggesting that there is a critical content \( x^* \) in this narrow range. Figure 4(a) represents \( S/T \) as a function of \( x \) at constant temperatures and the contour plot is depicted in Fig. 4(b). At low temperature, \( S/T \) shows a divergent behavior at \( x^* \) only from the lower \( x \) side. This is distinct from the divergence of \( S/T \) from both sides of the critical point of the Landau-type phase transition associated with broken symmetry [47]. Also, no structural transition is observed at \( x^* \). It is a key point that the enhancement is observed for only low temperature, while \( S/T \) continuously increases with \( x \) near room temperature, which is readily explained by the change in the carrier concentration.

Now we discuss the origin of the enhancement of the Seebeck coefficient. According to the observed band structure of K\(_{0.62}\)RhO\(_2\), the Fermi level lies across the \( a_{1g} \) band [40]. The Fermi level is elevated as \( x \) increases, and as is the case in Na\(_2\)CoO\(_2\), the topological change in the Fermi surface would also occur at a certain content in K\(_2\)RhO\(_2\). Note that the present critical content \( x^* \) is close to \( x_{\gamma} \approx 0.62 \), at which the Lifshitz transition occurs in Na\(_2\)CoO\(_2\) [3]. Moreover, near the Lifshitz transition, the low-temperature Seebeck coefficient is predicted to increase steeply when the Fermi level approaches a critical point from only one side, the one for which the number of Fermi surfaces is larger, owing to the divergence in the energy derivative of the density of states [48, 49], as is also explored in several alloys experimentally [50, 51]. Thus the observed enhancement indicates the existence of a Lifshitz transition in K\(_2\)RhO\(_2\). We also note that the resistivity has no singularity around the Lifshitz transition [49]. In the insets of Figs. 3(a) and (b), we show the temperature dependence of the normalized resistivity, which exhibits no significant change across \( x^* \), consistent with above picture.

We examine the detailed mechanism of the Lifshitz transition. In Fig. 5, we show the schematic band structure and the Fermi surface of Na\(_2\)CoO\(_2\) and K\(_2\)RhO\(_2\). Since the \( \gamma \)-type
structure has two Co/Rh ions in the unit cell, we consider two \( d_{1g} \) bands labelled as higher and lower bands in Figs. 5(a) and 5(e) [19], although these are almost degenerate and difficult to be resolved separately by ARPES measurements. In \( \text{Na}_x\text{CoO}_2 \), there are two hole cylinders for \( x < x_{\text{Na}}^* \) as shown in Fig. 5(b), and with increasing \( x \), the Fermi level rises and then touches the local minimum of the lower band at \( x = x_{\text{Na}}^* \) [Fig. 5(c)] to create a small electron pocket at the \( \Gamma \) point for \( x > x_{\text{Na}}^* \) [Fig. 5(d)]. In this case, the low-temperature Seebeck coefficient would be critically enhanced owing to the disappearance of the electron pocket only when \( x \) approaches \( x_{\text{Na}}^* \) from the high \( x \) side. Indeed, negatively enhanced Seebeck coefficient is seen for \( x > x_{\text{Na}}^* \) although the experiments have been done in polycrystalline samples [8].

On the other hand, the enhancement of the Seebeck coefficient is observed for \( x < x^* \) in \( \text{K}_x\text{RhO}_2 \), indicating that the topological change in the Fermi surfaces differs from that of \( \text{Na}_x\text{CoO}_2 \). According to recent ARPES measurement [40], the band structure of \( \text{K}_x\text{RhO}_2 \) is closely similar to that of \( \text{Na}_x\text{CoO}_2 \), and thus we consider a local minimum structure at the \( \Gamma \) point as well. In \( \text{Na}_x\text{CoO}_2 \), this minimum structure is induced by a third nearest hopping \( t_3 \), and the local minimum sinks more deeply as the ratio \( |t_3/t_1| \) becomes larger (\( t_1 \) being the first nearest hopping) [28]. Now, the \( 4d \) orbital is broader than \( 3d \) one, but the ionic radius of Rh is also larger than Co, resulting in an accidental cancelation of the effect of the broader \( 4d \) orbital in some materials [52]. In \( \text{K}_x\text{RhO}_2 \), the broader bandwidth is indeed observed [39] [40], but \( |t_3/t_1| \) may be smaller than that of \( \text{Na}_x\text{CoO}_2 \) because oxygen \( 2p \) contribution in \( t_3 \) would be small due to the larger Rh-Rh distance. In such a case, the local minimum structure of the band top would be shallow in \( \text{K}_x\text{RhO}_2 \) as illustrated in Fig. 5(e), also implied by the DFT calculations [40].

This scenario is schematically depicted in Figs. 5(e-h). In \( \text{K}_x\text{RhO}_2 \), the shallow local minimum structure may be undetectable because of thermal fluctuations even at low temperatures. For increasing \( x \), the Fermi level is elevated and then the lower \( d_{1g} \) band is fully occupied at \( x^* \). In this case, the inner hole cylinder gradually diminishes and then completely disappears for \( x > x^* \), which is also supported by a highly 2D character of the Fermi surface [40]. Thus, in \( \text{K}_x\text{RhO}_2 \), the low-temperature enhancement of \( S/T \) occurs only for \( x < x^* \), where the number of hole cylinders is larger than that for \( x > x^* \). It should be noted that the disappearance of the electron pocket in \( \text{Na}_x\text{CoO}_2 \) contributes to the Seebeck coefficient negatively but the disappearance of the hole cylinder in \( \text{K}_x\text{RhO}_2 \) contributes positively, enhancing the total Seebeck coefficient that also includes the contribution from the outer hole cylinder. Therefore, our results suggest the Lifshitz transition as a fundamental means to increase the Seebeck coefficient at low temperatures in this system, in addition to the previously reported pudding-mold band structure [28] and the large entropy flow of the \( d \) electrons [53].

To summarize, we have synthesized single crystal \( \text{K}_x\text{RhO}_2 \) for \( 0.50 \leq x \leq 0.67 \) and find that, while the Seebeck coefficient monotonically increases with increasing \( x \) near room temperature, it exhibits an enhancement at low temperatures only below \( x^* \approx 0.65 \). As an origin, we propose a Lifshitz transition associated with disappearance of the inner hole cylinder due to the flat band structure around the \( \Gamma \) point. Moreover, we have discovered a distinct phase transition for \( x \approx 0.5 \), suggesting that \( \text{K}_x\text{RhO}_2 \) also offers a fascinating platform for various electronic phases, similar to \( \text{Na}_x\text{CoO}_2 \).

We thank K. Fujimoto, H. Yaguchi, T. Yamanaka for discussion and D. Kabasawa, W. Takagi for experimental supports. This work was supported by JSPS KAKENHI Grants No. JP17H06136, No. JP18K03503, and No. JP18K13504.

---

[1] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B 56, R12685 (1997).
[2] M. L. Foo, Y. Wang, S. Watauchi, H. W. Zandbergen, T. He, R. J. Cava, and N. P. Ong, Phys. Rev. Lett. 92, 247001 (2004).
[3] T. Motohashi, E. Naujalis, R. Ueda, K. Isawa, M. Karppinen, and H. Yamauchi, Appl. Phys. Lett. 79, 1480 (2001).
[4] M. Lee, L. Viciu, L. Li, Y. Wang, M. L. Foo, S. Watauchi, R. A. Pascual, R. J. Cava, and N. P. Ong, Nat. Mater. 5, 537 (2006).
[5] M. Yokoi, T. Miyoshi, Y. Kobayashi, M. Soda, Y. Yasui, M. Sato, and K. Kakurai, J. Phys. Soc. Jpn. 74, 3046 (2005).
[6] D. Yoshizumi, Y. Muraoka, Y. Okamoto, Y. Kiuchi, J. Yamamura, M. Mochizuki, M. Ogata, and Z. Hiroi, J. Phys. Soc. Jpn. 76, 063705 (2007).
[7] G. Lang, J. Bobroff, H. Alloul, G. Collin, and N. Blanchard, Phys. Rev. B 78, 155116 (2008).
[8] Y. Okamoto, A. Nishio, and Z. Hiroi, Phys. Rev. B 81, 0217603@ed.tus.ac.jp
okazaki@rs.tus.ac.jp
[9] No. JP18K03503, and No. JP18K13504.
