Anomalous band renormalization due to a high-energy kink in K$_{0.65}$RhO$_2$ with colossal thermoelectric power factor

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We identify highly correlated hole pocket on the Fermi surface of colossal thermoelectric material K$_{0.65}$RhO$_2$, studied using high-resolution angle-resolved photoemission spectroscopy (ARPES) and density-functional theory (DFT) calculations. Most importantly, two kinks at binding energies of 75 and 195 meV have been observed below the Fermi level. While the low-energy kink at 75 meV can be understood as a result of the electron-phonon interaction, the high-energy kink at 195 meV is a discovery of this system, leading to anomalous band renormalization, possibly originated from the bosonic excitations at higher frequencies. We further notice that the high-energy anomaly has important implications on the colossal thermoelectric power of K$_{0.65}$RhO$_2$.

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I. INTRODUCTION

Strong electronic correlations are vital in yielding various exotic systems such as high-$T_c$ superconductors [1], heavy fermionic materials [2], quantum anomalous Hall insulators (QAHIs) [3], half metals [4], Mott insulators [5], itinerant magnets [6], and high-thermopower materials [7]. Electron-electron ($e-e$) correlations turn the materials to heavy fermionic systems, QAHIs, half metals and Mott insulators, while the electron-magnon interactions are expected to cause the itinerant ferromagnetism [8,9]. On the other hand, the electron-phonon ($e$-ph) interactions are thought to play a major role in the high-$T_c$ superconductivity [10] and high thermoelectricity [11].

For a quite some time, the compounds of the type $A$_x$B$_2$O$_5$ ($A$ = Li, Na, and K, $B$ = Co and Rh) have been the scientific topic of much interest due to their diverse physical properties [12–15]. Interestingly, depending on the amount of Na present in Na$_x$CoO$_2$, it exhibits superconductivity in the hydrated state for $x ≈ 0.35$ [16], shows giant Seebeck coefficient for $0.7 < x < 1$ [17], possesses magnetic ordering for $x ≈ 0.75$ [18,19] and charge ordering for $x ≈ 0.5$ [20]. Crystal-field splitting [21], strong spin-orbit interactions [22], electron-electron [23], and electron-phonon interactions [24] are suggested for the cause of unusual physical properties. On the other hand, K$_x$RhO$_2$ a similar layered compound does not seem to be showing the physical properties as diverse as Na$_x$CoO$_2$. It was reported to show a large thermoelectric power [15,25,26], but still is half to that of Na$_x$CoO$_2$ [13], despite both showing $e$-ph interactions at a Debye frequency of 70-75 meV [27–29]. Earlier ARPES report on K$_x$RhO$_2$ hinted at the importance of electron-boson scattering for the recorded high thermopowers [29]. In this contribution, we study the effect of electronic correlation on the low-energy electronic structure of the layered K$_{0.65}$RhO$_2$ single crystal using ultrahigh energy resolution ARPES technique and DFT calculations [30].

II. EXPERIMENTAL DETAILS

Single-crystal growth. Single crystals of K$_x$RhO$_2$ were grown from the mixtures of K$_2$CO$_3$ and Rh$_2$O$_3$. The total charge mixture of 4.5 grams was placed in an alumina crucible and heated to the 1200 $^\circ$C in a box furnace, after a dwelling time of 2 hours, the furnace is slowly cooled to 950 $^\circ$C and later fast-cooled to room temperature. Plate-like hexagonal-shaped single crystals were grown at the bottom of the crucible. Crystals were grown in layered morphology in hexagonal structure up to few mm$^2$ in size. Compositional analysis from EDX gives the phase with the stoichiometry K$_{0.65}$RhO$_2$. As-grown single crystals were crushed and measured with powder x-ray diffraction (XRD).

ARPES measurements. ARPES measurements were performed in Swiss Light Source (SLS) at the SIS beamline using a VG-Scienta R4000 electron analyzer. The photon energy was varied between 20 and 140 eV. Overall energy resolution was set between 15 and 25 meV depending on the photon energy. The angular resolution was fixed at 0.2$^\circ$. Samples were cleaved in situ at a sample temperature of 15 K and the chamber vacuum was better than $5 \times 10^{-11}$ mbar during the measurements.

III. RESULTS AND DISCUSSION

ARPES data of K$_{0.65}$RhO$_2$ are shown in Fig. 1. From the Fermi-surface map shown in Fig. 1(a), we observe one nearly
circular-shaped Fermi pocket centered at $\Gamma$ with a Fermi vector of $k = 0.51 \pm 0.02 \, \text{Å}^{-1}$. From the constant energy contour taken at a binding energy of 0.25 eV, shown in Fig. 1(b), we observe six tiny spectral sheets near six $K$ points. Moreover, at this binding energy, size of the Fermi pocket centered at $\Gamma$ has increased and the circular shape is turned into a hexagonal shape. Energy distribution maps (EDMs) taken along the $\Gamma-K$, $\Gamma-M$, and $M-K$ high-symmetry directions further confirm this. From the EDMs taken along the $\Gamma-K$ and $K-M$ directions, we realize that the tiny spectral sheet near the $K$ point originates from another hole-like band dispersion with a band-top at 0.25 eV below $E_F$. This is further confirmed from the second derivative intensity $(I)$ of the EDMs ($\frac{d^2I}{dk^2}$) as shown in the bottom panels of Fig. 1(c). Arrow on the second derivative EDM in the $\Gamma-K$ direction indicates an antiband crossing between the two hole-like band dispersions at $\approx 0.4 \, \text{eV}$ below $E_F$. Above this binding energy, the two hole-like bands are well separated in the momentum space. Importantly, no antiband crossing is found from the second derivative EDM in the $\Gamma-M$ direction, down to 0.8 eV of the binding energy. Next, comparing our experimental band structure with the available ARPES data on these type of $\text{K}_0\text{.}_5\text{RhO}_2$ from the Fermi surface map. Most importantly, in agreement with the previous report on $\text{K}_0\text{.}_5\text{RhO}_2$ [29], we identified an antiband crossing at $\approx 0.4 \, \text{eV}$ below $E_F$ in the $\Gamma-K$ direction. Furthermore, the top of hole-like band at the $K$ point is found nearly at the same binding energy of 0.25 eV. Additional comparison between our ARPES data and DFT calculations can be found in the the Supplemental Material [30].

![Image](59x540 to 295x642)

![Image](60x662 to 142x731)

**FIG. 1.** ARPES measurements of $\text{K}_0\text{.}_5\text{RhO}_2$. The data are measured using $p$-polarized light with a photon energy of 140 eV. (a) Fermi-surface map. (b) Constant energy map taken at a binding energy of 0.25 eV below $E_F$. (c) Energy distribution maps (EDMs) showing the band dispersions along the $\Gamma-K$, $\Gamma-M$, and $M-K$ high-symmetry directions.

Having thoroughly established the low-energy electronic structure of $\text{K}_0\text{.}_5\text{RhO}_2$, experimentally, we then move on to the spectral function analysis of our experimental data. The band dispersion shown in Fig. 2(b) is extracted from the EDM of Fig. 2(a) by fitting the momentum distribution curves (MDCs) with a Lorentzian function, analogous to the spectral function

$$A(E, k) = \frac{-1}{\pi} \frac{\Sigma''}{(E_k - E_0 - \Sigma')^2 + (\Sigma'')^2}.$$  

Here, $\Sigma(E)$ and $\Sigma''(E)$ are the real and imaginary parts of the complex self-energy function defined as $\Sigma(E) = \Sigma' + i\Sigma''$. $E_k$ is the renormalized band dispersion which is generally obtained from the ARPES measurements [see Fig. 2(b)] and $E_0$ is the bare band dispersion which is generally obtained by fitting the tight-binding parameters to the experimental data. Nevertheless, the bare band dispersion can also be obtained reasonably by fitting experimental data at higher binding energies where the electronic correlations are negligible. The black-dashed curve in Fig. 2(b) is one such fitting at higher binding energies. Then, the difference between $E_k$ [orange data in Fig. 2(b)] and $E_0$ [solid black line in Fig. 2(b), momentum offset to the dashed black line] provides the real part of the self-energy $\Sigma(E) = E_k - E_0$, as shown in Fig. 2(c). On the other hand, the imaginary part of the self-energy shown in Fig. 2(d) is calculated from the energy-dependent spectral width $\Delta k(E)$, derived from the MDC fitting, multiplied by the renormalized Fermi velocity $(v_F = 0.6 \, \text{eV Å})$, $\Sigma'' = \Delta k(E) v_F$.  

![Image](334x658 to 414x725)

**FIG. 2.** (a) Energy distribution map taken along the $\Gamma-M$ orientation as shown in the inset. (b) Band dispersion extracted by fitting the momentum distribution curves of the EDM shown in panel (a) using a Lorentzian function. Black dashed line in panel (b) is a linear fit to band dispersion at the higher binding energy within the window of ($-0.2 \, \text{eV}$, $-0.09 \, \text{eV}$). The arrows in panel (b) show the energy positions of the kinks. (c) Real part of the self-energy $(\Sigma')$ extracted from the EDM shown in panel (a). In panel (c), the black line is linear fit to the data performed to extract the coupling constant $\lambda = 2.7 \pm 0.3$. (d) Imaginary part of the self-energy $(\Sigma'')$ extracted from the EDM shown in panel (a). In panel (d), the black curve represents fitting with combined functions of Fermi-liquid theory type and Eliashberg spectral functions (see text).
Most interestingly, we observe two \textit{kinks} from the band dispersion shown in Fig. 2(b). These \textit{kinks} have direct implications on the real and imaginary parts of the self-energy as shown in Figs. 2(c) and 2(d), respectively. The means that $\Sigma''$ possesses two humps corresponding to these two \textit{kinks}. To understand the origin of the hump, we performed a fitting to $\Sigma''$ using multiple Eliashberg spectral functions [green dashed curves in Fig. 2(d)] following the Debye model \cite{33}. The fitting resulted in two Debye frequencies $75 \pm 6$ and $195 \pm 10$ meV, which are very much in agreement with the energy positions of the \textit{kinks} found from the band dispersion [Fig. 2(b)]. In addition to multiple Eliashberg spectral functions, we needed to add a Fermi liquid-type spectral function [red dashed curve in Fig. 2(d)], following the Debye model.

Using the fitting to $\Sigma''$ linearly with momentum $\mathbf{k}$, we extracted a total coupling constant $\lambda = 2.7 \pm 0.3$ by fitting $\Sigma''(E)$ linearly with the formula of $\lambda = \frac{2\hbar^2}{m_e}\frac{1}{\Omega_{\mathbf{k}}}$. To understand the origin of the hump, we performed a fitting to $\Sigma''$ linearly with momentum $\mathbf{k}$, we extracted a total coupling constant $\lambda = 2.7 \pm 0.3$ by fitting $\Sigma''(E)$ linearly with the formula of $\lambda = \frac{2\hbar^2}{m_e}\frac{1}{\Omega_{\mathbf{k}}}$. To understand the origin of the hump, we performed a fitting to $\Sigma''$ linearly with momentum $\mathbf{k}$, we extracted a total coupling constant $\lambda = 2.7 \pm 0.3$ by fitting $\Sigma''(E)$ linearly with the formula of $\lambda = \frac{2\hbar^2}{m_e}\frac{1}{\Omega_{\mathbf{k}}}$.

Next, electronic correlations have been evaluated for the out-of-plane momentum $k_z$ direction, as shown in Fig. 4. Figure 4(a) depicts the Fermi surface (FS) map taken in the $k_z$,-$k_{\parallel}$ plane by varying the photon energy $h\nu$ between 40 and 100 eV in steps of 4 eV. As can be seen from the $k_z$, FS map, no change in the Fermi vector is noticed along the $k_z$ direction, suggesting a nearly two-dimensional hole pocket without electron hopping in the $k_z$ direction. In Fig. 4(b) we show representative imaginary part of the self-energy extracted from the EDMs measured with varying photon energies ($k_z$ dependent). From each photon energy data, we consistently observe two humps in $\Sigma''(E)$, within the error-bars almost at the same binding energies of 75 and 195 meV. This is in very good agreement with \textit{kinks} observed from the band dispersions extracted from corresponding photon energies [see Fig. 4(c)]. As discussed earlier, we could reasonably fit $\Sigma''$ at every photon energy using combined double-Eliashberg and Fermi-liquid-type spectral functions as shown in Fig. 4(b). We estimated $\beta$ from the fittings and is plotted as a function of $k_z$ ($h\nu$) as shown in Fig. 4(d). From Fig. 4(d), we notice that the e-e correlations hardly change along $k_z$ (within the error bars). The estimated Fermi and group velocities are plotted in Fig. 4(e) as a function of $k_z$. From Fig. 4(e), we notice that all the velocities vary sinusoidally with $k_z$ having minima at 60 and 92 eV and maxima at 43 and 75 eV photon energies. By considering the inner potential $V_0 = 12 \pm 2$ eV and using the formula $k_z = \left[ \frac{\pi}{\hbar}\left(V_0 + E_k\right)\right]^{1/2}$, we identify that the photon energies
60 and 92 eV extract the bands from the AHL plane and the photon energies 45 and 75 eV extract the bands from the ΓMK plane. Thus, from Fig. 4(e), we can find that the Fermi velocity is minimum at the A point \( (v_F = 0.6 \pm 0.04 \text{ eV Å}) \) and is maximum at the Γ point \( (v_F = 0.76 \pm 0.06 \text{ eV Å}) \). Similarly, the group velocities \( v_m \) and \( v_b \) are minimum at \( A(2.3 \pm 0.3, 4.76 \pm 0.5) \text{ eV Å} \) and are maximum at \( Γ(3.53 \pm 0.5, 6.06 \pm 0.8) \text{ eV Å} \). With the help of Fermi velocity and Fermi momentum, we estimated the effective mass of the hole pocket and plotted them as a function of \( k_z \) as shown in Fig. 4(f). A maximum effective mass is realized \( (m^∗ = 6.51 m_e) \) at \( A \), while a minimum effective mass is realized \( (m^∗ = 5.06 m_e) \) at \( Γ \). Furthermore, the \( k_z \)-dependent total coupling constants are plotted in Fig. 4(f). Note here that the maximum \( (\lambda = 3.37) \) and minimum \( (\lambda = 2.38) \) coupling constants are shifted by \( hv = 5 \text{ eV} \) from the photon energy positions of the high-symmetry points, while still the photon energy difference between the two extrema is invariant \((≈15 \text{ eV})\).

Since we completely extracted the in-plane and the out-of-plane Fermi sheets using ARPES, with the help of Luttinger’s theorem [37], we are able to estimate the hole carrier density \( n_h = 0.33 \pm 0.03 \) per unit cell. This value is in very good agreement with the \( K \) deficiency percentage of the measured sample \( \text{K}_0.65\text{RhO}_2 (1 - x = 0.35 \pm 0.02) \) from the stoichiometric \( \text{KRhO}_2 \). Thus, the ARPES data confirm EDAX estimate of the chemical composition. As clearly demonstrated from our ARPES data, \( \text{K}_0.65\text{RhO}_2 \) possess two \textit{kinks}. While the \textit{kink} at 75 meV is consistent with the previous studies of Raman spectroscopy showing active \( E_{1g} + E_{2g} + A_{1g} \) Raman modes at around 500 cm\(^{-1}\) from \( \text{K}_0.63\text{RhO}_2 \) [38], the high-energy \textit{kink} at 195 meV is a finding of this study. Although the origin of low energy \textit{kink} is reasonably understood, the origin of the HE \textit{kink} is yet to be established. So far existing ARPES studies on these systems did not concentrate on the electronic correlations beyond 0.2 eV binding energy. Therefore, we are unable to compare the HE \textit{kink} directly with previous ARPES studies of these systems. Nevertheless, as can be seen from Figs. 2 and 4, we can reasonably fit \( \Sigma''(E) \) with multiple Debye frequencies at 75 and 195 meV. This suggests a plausible phononic origin for the HE \textit{kink}. In fact, such an observation of bosonic scattering at higher energies has been noticed from Fe (100) at \( ≈160 \text{ meV} \) [39], graphene

at \( ≈200 \text{ meV} \) [40], and cuprates at \( ≈350–400 \text{ meV} \) below \( E_F \) [41,42]. The other existing mechanisms for the HE anomaly are the matrix element effects [43,44] and spin-fluctuations [45]. As observed in this study and reported in the literature, near the Fermi level only one band disperses from \( E_F \) down to a binding energy of 0.4 eV [29,46]. The same has been confirmed from the DFT calculations as well, especially in \( \text{AHL} \) plane [47]. Since the observed HE \textit{kink} is at around 195 meV and only one band dispersion present within this energy range, it is highly unlikely that the HE \textit{kink} originates from the matrix elements. Furthermore, the spin-fluctuations origin can be negated as the transport properties of \( \text{K}_0.63\text{RhO}_2 \) are nearly insensitive to the applied magnetic fields down to the lowest possible temperature [48]. Finally, as demonstrated in Fig. 1, the antiband crossing occur at \( ≈0.4 \text{ eV} \) below \( E_F \) which shows no effect on the \textit{kink} at 195 meV, ruling out the band-structure origin as well. Hence, the only convincing mechanism for the HE \textit{kink} must be the electron-boson scattering at higher frequencies. But the present available literature on these systems is insufficient to confirm the same.

Our estimate of average Fermi velocity over the entire Brillouin zone \( v_F = 0.62 \pm 0.04 \text{ eV Å} \) is far less than the Fermi velocity \( (v_F = 0.96 \pm 0.02 \text{ eV Å}) \) reported earlier on \( \text{K}_0.62\text{RhO}_2 \) [29]. On the other hand, the average carrier effective mass estimated from this study, \( m^∗ = 6.44 m_e \) is a factor of 4.7 less than the effective mass reported for \( \text{Na}_3\text{CoO}_2 \) [27]. From this, we can conclude that \( \text{K}_0.63\text{RhO}_2 \) is relatively less correlated compared with \( \text{Na}_3\text{CoO}_2 \), but more correlated than what was thought earlier [29]. With the help of the average Fermi vector \( (k_F = 0.51 \pm 0.02 \text{ Å}^{-1}) \) and Fermi velocity, we estimated the Seebeck coefficient using the Boltzmann theory [7,47], \( S = \frac{2\pi^2 k_B^2 T}{3e m^* v_F} \), of 46 ± 5 \( \mu \text{V/K} \) at \( T = 300 \text{ K} \). This value is in excellent agreement with the Seebeck coefficient \( S_{300K} = 46.3 \mu \text{V/K} \) derived from the transport measurements on \( \text{K}_0.63\text{RhO}_2 \) [25]. We further verified the validity of Boltzmann theory in the present context by evaluating the Seebeck coefficient for \( \text{Na}_0.67\text{CoO}_2 \). Considering \( k_F = 0.6 \text{ Å}^{-1} \) and averaged \( v_F = 2.75 \text{ eV Å} \) from Ref. [31], we estimated the coefficient \( S_{300K} = 89 \mu \text{V/K} \) which is in very good agreement with the value of \( ≈90 \mu \text{V/K} \) obtained from the transport measurements on \( \text{Na}_0.67\text{CoO}_2 \) [49] and with the value of
≈85 μV/K obtained from DFT calculations on Na_{0.65}CoO_2 [50]. Thus, the Boltzmann theory is sufficient to understand the enhanced thermoelectric power in these systems.

IV. CONCLUSIONS

In conclusion, we systematically studied the low-energy electronic structure of K_{0.65}RhO_2 using ARPES technique and DFT calculations. Two kinks at the binding energies of 75 and 195 meV have been observed below E_F. As demonstrated above the strength of e-ph scattering, represented by the coupling constant λ, strongly depends on the in-plane and out-of-plane momenta. Most importantly, from this study we discover that the high-energy kink at 195 meV, leading to anomalous band renormalization near the Fermi level, plays a crucial role in obtaining the colossal thermoelectric power in these systems.

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[1] D. J. Scalapino, The electron-phonon interaction and strong-coupling superconductors, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, NY, 1969), Chap. 10, pp. 449–560.
[2] G. R. Stewart, Heavy-fermion systems, *Rev. Mod. Phys.* **56**, 755 (1984).
[3] C.-X. Liu, S.-C. Zhang, and X.-L. Qi, The quantum anomalous Hall effect: Theory and experiment, *Annu. Rev. Condens. Matter Phys.* **7**, 301 (2016).
[4] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, New Class of Materials: Half-Metallic Ferromagnets, *Phys. Rev. Lett.* **50**, 2024 (1983).
[5] N. F. Mott, The basis of the electron theory of metals, with special reference to the transition metals, *Proc. Phys. Soc., London, Sect. A* **62**, 416 (1949).
[6] T. Moriya and Y. Takahashi, Itinerant electron magnetism, *Annu. Rev. Mater. Sci.* **14**, 1 (1984).
[7] D. K. C. MacDonald, *Thermoelectricity: An Introduction to the Principles* (Dover Publications, Mineola, New York, 2006), pp. 1–65.
[8] J. A. Hertz and D. M. Edwards, Electron-magnon interactions in itinerant ferromagnetism. i. formal theory, *J. Phys. F: Met. Phys.* **3**, 2174 (1973).
[9] D. M. Edwards and J. A. Hertz, Electron-magnon interactions in itinerant ferromagnetism. ii. strong ferromagnetism, *J. Phys. F: Met. Phys.* **3**, 2191 (1973).
[10] A. Lanzara, P. V. Bogdanov, X. J. Zhou, S. A. Kellar, D. L. Feng, E. D. Lu, T. Yoshida, H. Eisaki, A. Fujimori, K. Kishio, J.-I. Shimoyama, T. Noda, S. Uchida, Z. Hussain, and Z.-X. Shen, Evidence for ubiquitous strong electron–phonon coupling in high-temperature superconductors, *Nature (London)* **412**, 510 (2001).
[11] H. Wang, Y. Pei, A. D. LaLonde, and G. J. Snyder, Weak electron-phonon coupling contributing to high thermoelectric performance in N-type PbSe, *Proc. Natl. Acad. Sci. USA* **109**, 9705 (2012).
[12] J. van Elp, J. L. Wieland, H. Eskes, P. Kuiper, G. A. Sawatzky, F. M. F. de Groot, and T. S. Turner, Electronic structure of CoO, Li-doped CoO, and LiCoO_2, *Phys. Rev. B* **44**, 6090 (1991).
[13] I. Terasaki, Y. Sasago, and K. Uchinokura, Large thermoelectric power in NaCoO_2 single crystals, *Phys. Rev. B* **56**, R12685(R) (1997).
[14] J. Sugiyama, H. Nozaki, Y. Ikedo, K. Mukai, J. H. Brewer, E. J. Ansaldo, G. D. Morris, D. Andreica, A. Amato, T. Fujii, and A. Asamitsu, Static Magnetic Order in Metallic K_{0.40}CoO_2, *Phys. Rev. Lett.* **96**, 037206 (2006).
[15] S. Shibasaka, T. Nakano, I. Terasaki, K. Yubuta, and T. Kajitani, Transport properties of the layered Rh oxide K_{0.40}RhO_2, *J. Phys.: Condens. Matter* **22**, 115603 (2010).
[16] R. Schaak, T. Klimczuk, M. Foo, and R. Cava, Superconductivity Phase Diagram of Na_{x}CoO_2 · 1.3H_2O, *Nature (London)* **424**, 527 (2003).
[17] M. Lee, L. Viciu, L. Li, Y. Wang, M. Foo, S. Watauchi, R. Pascal, R. Cava, and N. Ong, Large enhancement of the thermopower in Na_{x}CoO_2 at high Na doping, *Nat. Mater.* **5**, 537 (2006).
[18] L. M. Helme, A. T. Boothroyd, R. Coldea, D. Prabhakaran, D. A. Tennant, A. Hiess, and J. Kulda, Three-Dimensional Spin Fluctuations in Na_{0.75}CoO_2, *Phys. Rev. Lett.* **94**, 157206 (2005).
[19] S. P. Bayrakci, I. Mirebeau, P. Bourges, Y. Sidis, M. Enderle, J. Pascal, R. Cava, and N. Ong, Large enhancement of the thermopower in Na_{x}CoO_2 at high Na doping, *Nat. Mater.* **5**, 537 (2006).
[20] S. Shibasaka, T. Nakano, I. Terasaki, K. Yubuta, and T. Kajitani, Transport properties of the layered Rh oxide K_{0.40}RhO_2, *J. Phys.: Condens. Matter* **22**, 115603 (2010).
[21] L. M. Helme, A. T. Boothroyd, R. Coldea, D. Prabhakaran, D. A. Tennant, A. Hiess, and J. Kulda, Three-Dimensional Spin Fluctuations in Na_{0.75}CoO_2, *Phys. Rev. Lett.* **94**, 157206 (2005).
[22] S. P. Bayrakci, I. Mirebeau, P. Bourges, Y. Sidis, M. Enderle, J. Pascal, R. Cava, and N. Ong, Large enhancement of the thermopower in Na_{x}CoO_2 at high Na doping, *Nat. Mater.* **5**, 537 (2006).
[23] L. M. Helme, A. T. Boothroyd, R. Coldea, D. Prabhakaran, D. A. Tennant, A. Hiess, and J. Kulda, Three-Dimensional Spin Fluctuations in Na_{0.75}CoO_2, *Phys. Rev. Lett.* **94**, 157206 (2005).
[24] S. P. Bayrakci, I. Mirebeau, P. Bourges, Y. Sidis, M. Enderle, J. Pascal, R. Cava, and N. Ong, Large enhancement of the thermopower in Na_{x}CoO_2 at high Na doping, *Nat. Mater.* **5**, 537 (2006).
[25] L. M. Helme, A. T. Boothroyd, R. Coldea, D. Prabhakaran, D. A. Tennant, A. Hiess, and J. Kulda, Three-Dimensional Spin Fluctuations in Na_{0.75}CoO_2, *Phys. Rev. Lett.* **94**, 157206 (2005).
[26] S. P. Bayrakci, I. Mirebeau, P. Bourges, Y. Sidis, M. Enderle, J. Pascal, R. Cava, and N. Ong, Large enhancement of the thermopower in Na_{x}CoO_2 at high Na doping, *Nat. Mater.* **5**, 537 (2006).
[27] L. M. Helme, A. T. Boothroyd, R. Coldea, D. Prabhakaran, D. A. Tennant, A. Hiess, and J. Kulda, Three-Dimensional Spin Fluctuations in Na_{0.75}CoO_2, *Phys. Rev. Lett.* **94**, 157206 (2005).
[28] S. P. Bayrakci, I. Mirebeau, P. Bourges, Y. Sidis, M. Enderle, J. Pascal, R. Cava, and N. Ong, Large enhancement of the thermopower in Na_{x}CoO_2 at high Na doping, *Nat. Mater.* **5**, 537 (2006).
[29] L. M. Helme, A. T. Boothroyd, R. Coldea, D. Prabhakaran, D. A. Tennant, A. Hiess, and J. Kulda, Three-Dimensional Spin Fluctuations in Na_{0.75}CoO_2, *Phys. Rev. Lett.* **94**, 157206 (2005).
[30] S. P. Bayrakci, I. Mirebeau, P. Bourges, Y. Sidis, M. Enderle, J. Pascal, R. Cava, and N. Ong, Large enhancement of the thermopower in Na_{x}CoO_2 at high Na doping, *Nat. Mater.* **5**, 537 (2006).
Y. Wang, N. Rogado, R. Cava, and N. Ong, Spin entropy as the likely source of enhanced thermopower in Na$_x$CoO$_2$, Nature (London) 423, 425 (2003).

A. Donkov, M. M. Korshunov, I. Eremin, P. Lemmens, V. Gnezdilov, F. C. Chou, and C. T. Lin, Electron-phonon interaction in the lamellar cobaltate Na$_x$CoO$_2$, Phys. Rev. B 77, 100504(R) (2008).

S. H. Yao, B. B. Zhang, J. Zhou, Y. B. Chen, S. T. Zhang, Z. B. Gu, S. T. Dong, and Y. F. Chen, Structure and physical properties of K$_{0.63}$RhO$_2$ single crystals, AIP Adv. 2, 042140 (2012).

Y. Saeed, N. Singh, and U. Schwingenschlögl, Colossal thermoelectric power factor in K$_{7/8}$RhO$_2$, Adv. Funct. Mater. 22, 2792 (2012).

M. Z. Hasan, Y.-D. Chuang, D. Qian, Y. W. Li, Y. Kong, A. P. Kuprin, A. V. Fedorov, R. Kimerling, E. Rotenberg, K. Rossnagel, Z. Hussain, K. Ko, N. S. Rogado, M. L. Foo, and R. J. Cava, Fermi Surface and Quasiparticle Dynamics of Na$_x$CoO$_2$ Investigated by Angle-Resolved Photoemission Spectroscopy, Phys. Rev. Lett. 92, 246402 (2004).

H.-B. Yang, Z.-H. Pan, A. K. P. Sekharan, T. Sato, S. Souma, T. Takahashi, R. Jin, B. C. Sales, D. Manandur, A. V. Fedorov, Z. Wang, and H. Ding, Fermi Surface Evolution and Luttinger Theorem in Na$_x$CoO$_2$: A Systematic Photoemission Study, Phys. Rev. Lett. 95, 146401 (2005).

S.-D. Chen, Y. He, A. Zong, Y. Zhang, M. Hashimoto, B.-B. Zhang, S.-H. Yao, Y.-B. Chen, J. Zhou, Y.-F. Chen, S.-K. Mo, Z. Hussain, D. Lu, and Z.-X. Shen, Large thermopower from dressed quasiparticles in the layered cobaltates and rhodates, Phys. Rev. B 96, 081109(R) (2017).

See supplemental material at http://link.aps.org/supplemental/10.1103/PhysRevMaterials.5.055402 for experimental methods, additional ARPES data, DFT calculations, EDAX and XRD data.

T. Arakane, T. Sato, T. Takahashi, T. Fujii, and A. Asamitsu, Angle-resolved photoemission study of the doping evolution of a three-dimensional Fermi surface in Na$_x$CoO$_2$, New J. Phys. 13, 043021 (2011).

Y. Okamoto, R. Matsumoto, T. Yagihara, C. Iwai, K. Miyoshi, J. Takeuchi, K. Horiba, M. Kobayashi, K. Ono, H. Kumigashira, N. L. Saini, and T. Mizokawa, Electronic structure and polar catastrophe at the surface of Li$_x$CoO$_2$ studied by angle-resolved photoemission spectroscopy, Phys. Rev. B 96, 125147 (2017).

F. Reinert and S. Hüfner, Photoemission Spectroscopy with Very High Energy Resolution: Studying the Influence of Electronic Correlations on the Millielectronvolt Scale, in Very High Resolution Photoelectron Spectroscopy (Springer, Berlin, Heidelberg, 2007), pp. 13–53.

A. Nicolaou, V. Brouet, M. Zacchigna, I. Vobornik, A. Tejeda, A. Taleb-Ibrahimi, P. Le Fèvre, F. Bertran, S. Hébert, H. Muguerra, and D. Grebille, Experimental Study of the Incoherent Spectral Weight in the Photoemission Spectra of the Misfit Cobaltate [Bi$_2$Ba$_2$O$_4$][(CoO$_2$)$_2$, Phys. Rev. Lett. 104, 056403 (2010).

J. Fink, S. Borisenko, A. Kordyuk, A. Koitzsch, J. Geck, V. Zabolotnyy, M. Knupfer, B. Büchner, and H. Berger, Dressing of the Charge Carriers in High-$T_c$ Superconduc-
tors, in Very High Resolution Photoelectron Spectroscopy, edited by S. Hüfner (Springer, Berlin, Heidelberg, 2007), pp. 295–325.

J. Geck, S. V. Borisenko, H. Berger, H. Eschrig, J. Fink, M. Knupfer, K. Koepenik, A. Koitzsch, A. A. Kordyuk, V. B. Zabolotnyy, and B. Büchner, Anomalous Quasiparticle Renormalization in Na$_{0.7}$CoO$_2$: Role of Interorbital Interactions and Magnetic Correlations, Phys. Rev. Lett. 99, 046403 (2007).

J. M. Luttinger, Fermi surface and some simple equilibrium properties of a system of interacting fermions, Phys. Rev. 119, 1153 (1960).

B.-B. Zhang, N. Zhang, S.-T. Dong, Y. Lv, Y. B. Chen, S. Yao, S.-T. Zhang, Z.-B. Gu, J. Zhou, I. Guedes, D. Yu, and Y.-F. Chen, Lattice dynamics of K$_x$RhO$_2$ single crystals, AIP Adv. 5, 087111 (2015).

J. Schäfer, D. Schrupp, E. Rotenberg, K. Rossnagel, H. Koh, P. Blaha, and R. Claessen, Electronic Quasiparticle Renormalization on the Spin Wave Energy Scale, Phys. Rev. Lett. 92, 097205 (2004).

F. Mazzola, J. W. Wells, R. Yakimova, S. Ulstrup, J. A. Miwa, R. Bolog, M. Bianchi, M. Leandersson, J. Adell, P. Hofmann, and T. Balasubramanian, Kinks in the $\sigma$ Band of Graphene Induced by Electron-Phonon Coupling, Phys. Rev. Lett. 111, 216806 (2013).

T. Valla, T. E. Kidd, W.-G. Yin, G. D. Gu, P. D. Johnson, Z.-H. Pan, and A. V. Fedorov, High-Energy Kink Observed in the Electron Dispersion of High-Temperature Cuprate Superconductors, Phys. Rev. Lett. 98, 167003 (2007).

D. S. Inosov, J. Fink, A. A. Kordyuk, S. V. Borisenko, V. B. Zabolotnyy, R. Schuster, M. Knupfer, B. Büchner, R. Follath, H. A. Dürr, W. Eberhardt, V. Hinkov, B. Keimer, and H. Berger, Momentum and Energy Dependence of the Anomalous High-Energy Dispersion in the Electronic Structure of High Temperature Superconductors, Phys. Rev. Lett. 99, 237002 (2007).

S. Basak, T. Das, H. Lin, J. Nieminen, M. Lindroos, R. S. Markiewicz, and A. Bansil, Origin of the high-energy kink in the photoemission spectrum of the high-temperature superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, Phys. Rev. B 80, 214520 (2009).

E. D. L. Rienks, M. Årrälä, M. Lindroos, F. Roth, W. Tabis, G. Yu, M. Greven, and J. Fink, High-Energy Anomaly in the Angle-Resolved Photoemission Spectra of Nd$_{2-x}$CeCu$_2$O$_4$: Evidence for a Matrix Element Effect, Phys. Rev. Lett. 113, 137001 (2014).

I. Graf, G.-H. Gweon, K. McElroy, S. Y. Zhou, C. Jozwiak, E. Rotenberg, A. Bill, T. Sasagawa, H. Eisaki, S. Uchida, H. Takagi, D.-H. Lee, and A. Lanzara, Universal High Energy Anomaly in the Angle-Resolved Photoemission Spectra of High Temperature Superconductors: Possible Evidence of Spinon and Holon Branches, Phys. Rev. Lett. 98, 067004 (2007).

H. W. Ou, J. F. Zhao, Y. Zhang, B. P. Xie, D. W. Shen, Y. Zhu, Z. Q. Yang, J. G. Che, X. G. Luo, X. H. Chen, M. Arita, K. Shimada, H. Namatame, M. Taniguchi, C. M. Cheng, K. D. Tsuei, and D. L. Feng, Novel Electronic Structure Induced by a Highly Strained Oxide Interface with Incommensurate Crystal Fields, Phys. Rev. Lett. 102, 026806 (2009).

D. J. Singh, Electronic structure of NaCoO$_2$, Phys. Rev. B 61, 13397 (2000).
[48] B.-B. Zhang, S.-T. Dong, S.-H. Yao, Y. B. Chen, S.-T. Zhang, Z.-B. Gu, J. Zhou, M.-H. Lu, Y.-F. Chen, and Y. G. Shi, Electrical, magnetic, and magneto-electrical properties in quasi-two-dimensional $K_{0.5}\text{RhO}_2$ single crystals doped with rare-earth elements, Appl. Phys. Lett. 105, 062408 (2014).

[49] M. S. Pandiyan, Ph.D. thesis, University of London, 2013 (unpublished).

[50] D. J. Singh and D. Kasinathan, Thermoelectric properties of Na$_x$CoO$_2$ and prospects for other oxide thermoelectrics, J. Electron. Mater. 36, 736 (2007).