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# Lifshitz transition driven metal-insulator transition in moderately spin-orbit coupled $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$

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Motivated by the novel insulating state of  $\text{Sr}_2\text{IrO}_4$  from strong spin-orbit coupling (SOC), we investigate, by means of angle resolved photoemission (ARPES), the metal-insulator transition (MIT) mechanism in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  whose mother compound is isovalent and isostructural but has smaller SOC strength compared to  $\text{Sr}_2\text{IrO}_4$ . Transport and ARPES results from single crystalline  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  revealed that the MIT occurs coincidentally with a multi- to single-band transition (Lifshitz transition) at  $x = 0.4$ . Starting from  $x = 0.4$ , there is a gradual but anomalous enhancement in the band gap size with additional electron doping, suggesting that the insulating phase in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  is a new type which has been rarely investigated. These results suggest that the insulating phase in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  is likely induced by the moderate SOC strength and electron doping effect from the La. Our findings not only elucidate the MIT mechanism in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ , but may also open new avenues for novel MITs research in moderate SOC regimes.

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Mott physics has been one of the most intensively studied subjects in condensed matter physics. In early studies, the main focus was on materials with large on-site Coulomb repulsion ( $U$ ) in localized orbitals such as  $3d$  transition metal oxides (TMOs). However, discovery of the relativistic Mott insulating state in  $\text{Sr}_2\text{IrO}_4$ [1] has led to extensive studies on  $5d$  TMOs with an expectation that exotic phenomena due to strong spin-orbit coupling (SOC) may exist. In  $\text{Sr}_2\text{IrO}_4$ , the large SOC transforms the usual crystal field split eigenstates into  $J_{eff}$  states, and then the narrow bandwidth ( $W$ ) of the  $J_{eff} = 1/2$  states which is comparable to  $U$  results in a relativistic Mott state, forming upper and lower Hubbard bands. The insulating state is found to be easily broken with small amount of charge carrier doping [2] as observed in  $\text{Sr}_{2-x}\text{La}_x\text{IrO}_4$ , which indicates the fragile nature of the Mott state against carrier doping.

On the other hand, SOC in the  $4d$  TMO is smaller and is thus expected to play, in comparison to  $\text{Sr}_2\text{IrO}_4$ , a lesser role in the determination of the physical properties. A recent electronic structure study on  $\text{Sr}_2\text{Rh}_x\text{Ir}_{1-x}\text{O}_4$  revealed that Rh ( $4d$ ) substitution considerably reduces the SOC strength and leads to collapse of the relativistic Mott state in  $\text{Sr}_2\text{IrO}_4$ [3]. However, a theoretical study suggests that the electronic structure of  $\text{Sr}_2\text{RhO}_4$  still can be understood within the  $J_{eff}$  scheme even though the SOC strength in  $\text{Sr}_2\text{RhO}_4$  is much smaller than the case of  $\text{Sr}_2\text{IrO}_4$ [4]. This indicates that the moderate SOC in  $4d$  TMOs may still significantly affect the physical properties and that investigation of the role of SOC in  $4d$  TMOs may lead us to new exotic phases as in the case of  $\text{Sr}_2\text{IrO}_4$ .

In that regard, we pay our attention to the anoma-

lous metal-insulator transition (MIT) in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ . The resistivity of  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  gradually increases with the La ( $5d6s^2$ ) substitution for Sr ( $5s^2$ ) [5], turning the system from a metal into an insulating phase. This result is opposite to what is theoretically predicted in which itinerant metallic Stoner-type ferromagnetism is induced upon La doping to  $\text{Sr}_2\text{RhO}_4$ [6], thus the MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  has been understood within the Anderson localization picture from the disorder effect of La dopants [5, 7]. However, our experimental results are not consistent with such interpretation and thus the MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  is yet to be fully understood.

In this Letter, we report our electronic structure data regarding the exotic MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ . Our result shows clear emergence of band gap through the MIT, which is found to be inconsistent with previous assertions of MIT through the Anderson localization[5, 7]. In addition, the gradual increase of the band gap in the non-integer electron filling region starting from  $x = 0.4$  suggests the insulating state in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  is totally different from what have been investigated so far. We find that the exotic MIT may be attributed to the interplay between moderate SOC and  $U$  with a help of electron doping effect from La substitution. Our result not only is a discovery of a new-type of insulating state in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  but also introduces a new mechanism for novel MIT in which moderate SOC plays a significant role.

The  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  single crystals were grown from off-stoichiometric quantities of  $\text{SrCO}_3$ ,  $\text{Rh}_2\text{O}_3$ , and  $\text{La}_2\text{O}_3$  in order to compensate volatility of  $\text{Rh}_2\text{O}_3$  during the growth using the floating zone method. The powder was thoroughly ground and calcined in flowing  $\text{O}_2$ . Cal-

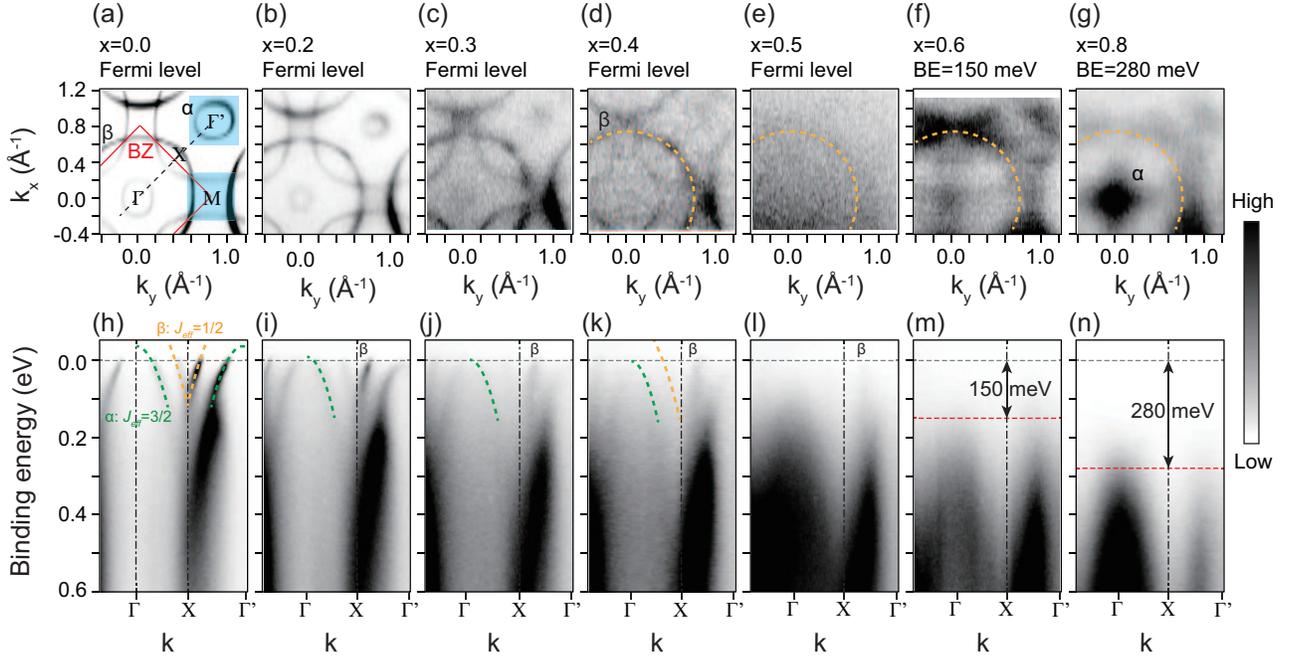


FIG. 1: (Color online) ARPES data from  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ . (a)-(g) Constant binding energy  $k_x$ - $k_y$  maps at the binding energies of 0 meV ( $x = 0.0, 0.2, 0.3, 0.4$  and  $0.5$ ), 150 meV ( $x = 0.6$ ) and 280 meV ( $x = 0.8$ ). The squares shaded in blue in panel (a) are integration regions for  $\alpha$  and  $\beta$  band spectra in Figs. 2(a) and (b). (h)-(n) ARPES data along the  $\Gamma$ -X line. The band gap size for  $x = 0.6$  (m) and  $x = 0.8$  (n) is also shown.

cined poly crystalline powder was then pressed into rods and sintered at  $1300^\circ\text{C}$  in flowing  $\text{O}_2$  gas for 4 hours. The crystal growth was performed in an image furnace with 10 atm  $\text{O}_2$  pressure. The growth speed was 10 mm/h. To compensate oxygen deficiencies due to the multi valence nature of Rh, all samples were annealed at  $1100^\circ\text{C}$  in flowing  $\text{O}_2$  gas after the growth. Resistivity measurement was done with Quantum Design physical property measurement system with the 4-probe method. ARPES measurements were performed at the beamline 4.0.3 of the Advanced Light Source, Lawrence Berkeley National Laboratory. Samples were cleaved *in situ* and measurements were performed with  $h\nu = 70$  eV at 30 K in an ultra-high vacuum better than  $5 \times 10^{-11}$  Torr.

Doping dependent electronic structure results are shown in Fig. 1. Two original as well as folded Fermi surface pockets of  $\text{Sr}_2\text{RhO}_4$  are seen in Fig. 1(a), which is consistent with previous ARPES studies [8]. The larger Fermi surface is usually labelled as  $\beta$  while the smaller pocket as  $\alpha$ . The energy dispersion in Fig. 1(h) indicates that the hole-like  $\alpha$  band (green dashed line) is occupied more than the  $\beta$  band (yellow dashed line). According to a theoretical study [4], the  $\alpha$  and  $\beta$  bands approximately correspond to  $J_{eff} = 3/2$  with  $|m_{J_{eff}}| = 3/2$  and  $J_{eff} = 1/2$  bands, respectively. Over the entire range of La content,  $\alpha$  band shows a rigid-band-like shift due to the electron doping from La. The  $\alpha$  pocket size decreases until  $x = 0.4$  (Figs. 1(a)-(d) and 1(h)-(k)). Then the

top of  $\alpha$  band gradually sinks below the Fermi level for  $x > 0.4$  (Figs. 1(e)-(g) and (l)-(n)). On the other hand, the Fermi surface size of the  $\beta$  band increases with the La content until  $x = 0.4$  (Figs. 1(a)-(d),(h)-(k)), and then it fades out from the Fermi level with a gradually increasing band gap (Figs. 1(e)-(g),(l)-(n)). These observations indicate that the critical doping level for the MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  is  $x = 0.4$ . This value for the critical doping is also consistent with that obtained from the result of resistivity measurements on single crystalline  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  (Supplementary Fig. S1 [9]).

The band gap evolution as a function of the La content is easily seen in symmetrized energy distribution curves (EDCs) plotted in Figs. 2(a) and (b). The plotted EDCs are obtained by averaging the EDCs from the regions near  $\alpha$  and  $\beta$  bands, respectively (shaded in blue in Fig. 1(a)). In order to investigate the evolution of the band gap systematically, we plot the band top energy as a function of La concentration in Fig. 2(c). The band top energy is defined as the  $x$ -axis intercept value of the linear fit of the leading edge ( $T_\alpha$  and  $T_\beta$  for  $\alpha$  and  $\beta$  bands, respectively). The resulting doping dependent  $T_\alpha$  and  $T_\beta$  are plotted in Fig. 2(c). As can be seen in Fig. 2(c), both  $T_\alpha$  and  $T_\beta$  are zero for  $x < 0.4$ , which indicates  $\alpha$  and  $\beta$  bands cross the Fermi level, and then monotonically increase from  $x = 0.4$ . It is worth noting that  $T_\alpha$  and  $T_\beta$  show almost identical behaviors over the entire doping levels. Such synchronized behavior is unexpected

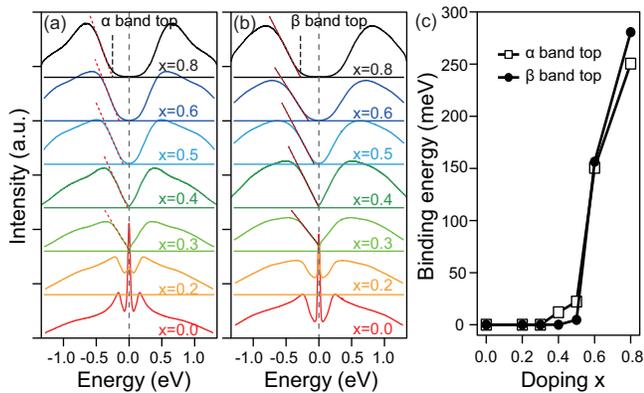


FIG. 2: (Color online) (a-b) Momentum averaged energy distribution curves (EDCs) from the regions of (a)  $\alpha$  and (b)  $\beta$  bands (blue shaded squares in Fig. 1(a)). (c) Doping dependent band top energies for  $\alpha$  ( $T_\alpha$ ) and  $\beta$  ( $T_\beta$ ) bands.  $T_\alpha$  and  $T_\beta$  are defined as the  $x$ -axis intercept value of a linear fit to the leading edge.

since the two bands are independent and well separated in the energy-momentum space as shown in Fig. 1(h).

Before we proceed to the details of the doping dependent electronic structure, we briefly discuss possible scenarios for the MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ . Our results clearly show that the MIT appears at  $x = 0.4$ , which means that the total number of electrons in the Rh  $4d$  orbitals is about 5.4 considering each La substitution provides an extra electron. Therefore, standard theories for band and Mott insulators cannot account for the MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  as the electron filling is a non-integer. An electronic or magnetic order might trigger a transition to an insulating phase. However, our (Supplementary Fig. S1 [9]) as well as previously reported [5, 7] measurements show that there is no signature for such ordered phases in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ . Another candidate we can consider is a structural transition from tetragonal to orthorhombic which originates from emergence of out-of-plane octahedral tilting distortion along the [110] direction [5, 7]. This transition can also be counted out as the cause of the MIT since the octahedral out-of-plane distortion along the [110] axis does not reduce the crystal symmetry that is needed to generate a hybridization gap [5, 15]. All of these point to a situation that the MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  is an unexpected phenomenon which cannot be easily explained. For such reason, the MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  has been attributed to a disorder effect driven phenomenon (Anderson localization) in previous reports [5, 7]. However, our ARPES result clearly contradicts such interpretation as it shows a fairly well-defined hard gap in the electronic structure that is unexpected for Anderson localization insulators [16, 17]. In addition, our temperature dependent resistivity measurements also suggest that Anderson localization is not an appropriate model to explain the MIT (Supplementary Fig. S1 [9]).

The proceeding discussion suggests that we need a different mechanism to explain the MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ . To unravel the MIT mechanism in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ , we may need further information from the measured electronic structure of  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ . Since La substitutes Sr (not Rh which determines the near Fermi energy electronic structure), we can assume that the  $4d$  orbital character remains intact upon the La substitution. Indeed, as mentioned above (Figs. 1(a)-(c) and (h)-(j)), there is only an approximate downward rigid-band-like shift upon La substitution without noticeable electronic structure change, up to  $x = 0.4$ . It is thus reasonable to assume that the main effect of La substitution is simple electron doping. It is interesting to note that, as La content increases, the insulating phase appears exactly when the  $\alpha$  band becomes fully occupied at  $x = 0.4$ . This observation makes us suspect that full occupation of the  $\alpha$  band may trigger the MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ . That is, the multi- to single-band transition (or Lifshitz transition) coming from the full occupation of the  $\alpha$  band might be the key factor in the MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ .

The first step is to see if localized character of electrons, an essential ingredient of correlated insulators, is enhanced across  $x = 0.4$ . In that respect, the single-band nature of the band should be more advantageous than the multi-band state. The statement can be intuitively understood in terms of conduction band width as schematically illustrated in Fig. 3. In the multi-band regime ( $x < 0.4$ ), partially filled  $\alpha$  and  $\beta$  bands are involved in the electron transport, and both bands should be considered for the bandwidth  $W$  of the conduction electrons (see the left two panels in Fig. 3). On the other hand, only the electrons in the  $\beta$  band can move in the single-band regime ( $x > 0.4$ ), and the effective bandwidth thus becomes significantly reduced compared to the multi-band regime (see right two panels in Fig. 3). In addition, electron doping is found to further reduce the bandwidth of  $\beta$  band. In a previous study on  $\text{Sr}_2\text{RhO}_4$ , the concept of 'effective SOC strength' has been proposed to explain experimentally observed large SOC effect compared to what is expected from the atomic SOC strength of Rh [18]. Our theoretical study (Supplementary section V [9]) reveals that electron doping in  $\text{Sr}_2\text{RhO}_4$  leads to a smaller effective SOC strength which in turn results in reduction of  $\beta$  bandwidth by mixing constituent  $J_{eff}$  states. In brief, Lifshitz transition should be the main culprit for the enhanced electron localization in the  $\beta$  band while the reduced bandwidth from decrease in the effective SOC upon electron doping is an additory factor.

The synchronized behavior between  $T_\alpha$  and  $T_\beta$  in Fig. 2(c) can be well understood within the picture depicted in Fig. 3. As the electron doping increases, the Fermi energy  $E_F$  eventually rises above the top of the  $\alpha$  band, with the  $T_\alpha$  being the difference between  $E_F$  and  $\alpha$  band top. Then, the system is in the single band regime with the  $\beta$  band and a correlation gap  $T_\beta$  develops. However,

such single band regime is limited to the energy region between  $E_F$  and  $\alpha$  band top. Therefore, the gap in the  $\beta$  band ( $T_\beta$ ) cannot exceed  $T_\alpha$  (Fig. 3) because  $\alpha$  and  $\beta$  bands energetically overlap below the  $\alpha$  band top, allowing interband interactions which are detrimental to electron localization. These observations lead to the synchronized behavior of  $T_\alpha$  and  $T_\beta$ . It is worth to note that, contrary to the fragile nature of the usual Mott insulating state against charge carrier doping, the insulating state of  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  shows a gradual enhancement of band gap size with electron doping (Figs. 2(a-b)). This, in combination with its a non-integer electron filling, strongly implies a new-type of insulating state which has not been studied yet.

We attribute emergence of a gradually increasing band gap in the insulating state to the moderate SOC in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ . Here, we briefly discuss the role of SOC in the formation of such insulating state. Strong SOC is an essential ingredient of the Mott state in  $5d$   $\text{Sr}_2\text{IrO}_4$  ( $\sim 0.4$  eV) since it splits  $t_{2g}$  bands into narrower  $J_{eff}$  states,  $J_{eff} = 3/2$  and  $J_{eff} = 1/2$ . Meanwhile, the SOC in  $\text{Sr}_2\text{RhO}_4$  ( $\sim 0.15$  eV) is not strong enough to induce fully occupied  $J_{eff} = 3/2$  and half-filled  $J_{eff} = 1/2$ , and this is the reason why  $\text{Sr}_2\text{RhO}_4$  is a metal (supplementary Fig. S3 and S4 [9]). However, we believe the moderate SOC in  $\text{Sr}_2\text{RhO}_4$  plays the key role in the novel insulating behavior. First of all, the SOC in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  can still lead to narrow and parallel bands required for a relativistic Mott insulating state. In addition, a moderate SOC is an essential condition to have the unique insulating state in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  — the gradually increasing band gap with the La concentration. As we explained above,  $T_\alpha$  is the key parameter that determines  $T_\beta$ . Therefore, a necessary condition for the band gap variation is that the  $\alpha$  band should be located near the Fermi level. Noting that the SOC strength is the key parameter to determine splitting size between  $\alpha$  and  $\beta$  bands (supplementary Fig. S4 [9]), a moderate SOC is indeed an essential ingredient of the novel insulating phase. In brief, moderate SOC is the only a way we could find to generate a gradually increasing band gap behavior since it provides SOC strong enough to induce the eventual correlated insulating gap but weak enough to have incomplete splitting between  $J_{eff}$  states.

A remaining question is if there is an effective model that can describe the insulating state of  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ . As already mentioned before, the Mott-Hubbard model (Mott insulator) cannot account for the insulating state in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  which has a non-integer electron filling. Furthermore, the observed hard band gap in the electronic structure (Fig. 2) suggests that disorder driven electron localization scenario (*i.e.*, Anderson localization) is not the one either [16, 17]. Instead, a possible candidate may be the Anderson-Hubbard (AH) model [19] which covers strong electron correlation as well as disorder. The AH Hamiltonian is given as [19]

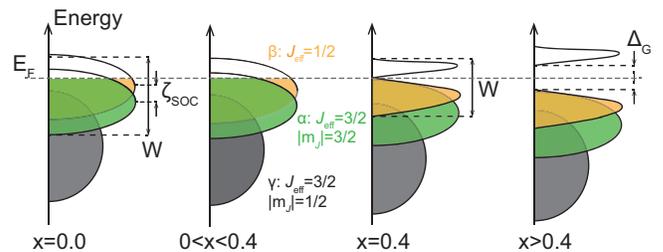


FIG. 3: Schematic illustration of the evolution of the electronic density of states with La substitution. Multi- ( $x < 0.4$ ) to single- ( $x > 0.4$ ) band transition by electron (La) doping reduces the band width  $W$ . In the single-band region ( $x > 0.4$ ), a band gap ( $\Delta_G$ ) develops.

$$H = -t \sum_{\langle i,j \rangle \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{i\sigma} W_i n_{i\sigma} \quad (1)$$

where  $c_{i\sigma}^\dagger$  ( $c_{i\sigma}$ ) is the creation (annihilation) operator for electron at site  $i$ ,  $\sigma$  the spin,  $t$  the hopping between the nearest-neighbor sites,  $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$  a local electron number operator at site  $i$ ,  $U$  the on-site Coulomb repulsion energy and  $W_i$  a random potential energy at each site. The first two terms are from the Mott-Hubbard Hamiltonian and the last term accounts for the disorder contribution. One of the most important aspects of the AH Hamiltonian is its capability to describe non-integer filling Mott insulating states by considering disorder effect (third term in equation (2)). Several studies show that impurities in the system make the Mott state robust against charge carrier doping [20–23]. In this respect, AH is a model that may provide a theoretical starting point to account for the non-integer filling insulating states in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ . Therefore, we expect that the AH hamiltonian can be a possible candidate to fully account for MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  if the role of moderate SOC effect can be additionally considered.

Our studies on MIT in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  have important implications. The first is on the discovery of exotic insulating state. While ordinary insulating states are quite fragile against charge carrier doping, the insulating state in  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  ( $x > 0.4$ ) is robust and has a gap size that is approximately proportional to the electron doping. This type of insulators have not been investigated and it certainly defies conventional knowledge on Mott insulators. Therefore, our study can be further expanded to explore new types of insulators like  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$ .

While there are recent discoveries of exotic phenomena, such as superconductivity, magnetism and MIT in  $4d$  TMOs [24–27], the detailed role of SOC in these compounds has not been clearly understood so far. Our study on  $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$  reveals how SOC can generate unexpected phenomena by modifying  $t_{2g}$  bands, and testifies the important role of SOC even in  $4d$  TMOs. Along

with the recent attempts to understand the intermediate eigenstates in  $4d$  TMOs such as Van-Vleck magnetism in  $\text{Ca}_2\text{RuO}_4$  [28], we believe our study should initiate further studies that will elucidate various exotic phenomena in systems with moderate SOC.

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- [1] B. J. Kim, *et al.* Phys. Rev. Lett. **101**, 076402 (2008).
- [2] A. de la Torre, *et al.* Phys. Rev. Lett. **115**, 176402 (2015).
- [3] T. F. Qi, O. B. Korneta, L. Li, K. Butrouna, V. S. Cao, X. Wan, P. Schlottmann, R. K. Kaul & G. Cao, Phys. Rev. B **86**, 125105 (2012).
- [4] Cyril Martins, *et al.* Phys. Rev. Lett. **107**, 266404 (2011).
- [5] Tetsuo Shimura, *et al.* Phys. Rev. B **49**, 8 (1994).
- [6] Kyo-Hoon Ahn, *et al.* J. Phys.: Condens. Matter **27**, 085602 (2015).
- [7] Z. W. Li, *et al.* Phys. Rev. Materials **1**, 044005 (2017).
- [8] R. S. Perry, *et al.* New J. Phys. **8**, 175 (2006).
- [9] See Supplemental Material at [url] for details of our resistivity, additional ARPES data, and tight-binding calculations, which includes Refs. [10-14].
- [10] Jean-Michel Delisle Carter, Doctor of philosophy, Univ. of Toronto (2013).
- [11] B. J. Kim, Jaejun Yu, H. Koh, I. Nagai, S. I. Ikeda, S.-J. Oh & C. Kim, Phys. Rev. Lett. **97**, 106401 (2006).
- [12] P. Zhang *et al.*, Rev. Sci. Instrum. **82**, 043712 (2011).
- [13] F. Baumberger *et al.*, Phys. Rev. Lett. **96**, 246402 (2006).
- [14] J. C. Slater & G. F. Koster, Phys. Rev. **94** 1498 (1954).
- [15] Y. F. Nie, *et al.* Phys. Rev. Lett. **114**, 016401 (2015).
- [16] Aaron Bostwick, *et al.* Phys. Rev. Lett. **103**, 056404 (2009).
- [17] Tianpin Ying, *et al.* Sci. Adv. **2**, e15012830 (2016).
- [18] Guo-Qiang Liu *et al.*, Phys. Rev. Lett. **101**, 026408 (2008).
- [19] M. Ma, Phys. Rev. B **26**, 5097 (1982).
- [20] Krzysztof Byczuk, *et al.* Phys. Rev. Lett. **90**, 196403 (2003).
- [21] Krzysztof Byczuk, *et al.* Phys. Rev. B **69**, 045112 (2004).
- [22] K. W. Kim, J. S. Lee, T. W. Noh, S. R. Lee & K. Char, Phys. Rev. B **71**, 125104 (2005).
- [23] T. Wu, *et al.* Solid State Commun. **145**, 293 (2008).
- [24] Y. Maeno, *et al.* Nature **372**, 532 (1994).
- [25] Clifford W. Hicks, *et al.* Science **344**, 283 (2014).
- [26] Satoru Nakatsuji, *et al.* J. Phys. Soc. Jpn. **66**, 1868 (1997).
- [27] J. P. Carlo, *et al.* Nat. Mater. **11**, 323 (2012).
- [28] Giniyat Khaliullin, Phys. Rev. Lett. **111**, 197201 (2013).