Evidence for Oxygen Holes due to $d$-$p$ Rehybridization in Thermoelectric $\text{Sr}_{1-x}\text{Rh}_2\text{O}_4$

Y. Ishida,¹ T. Baba,¹ R. Eguchi,¹ M. Matsunami,² M. Taguchi,¹ A. Chainani,¹ Y. Senba,² H. Ohashi,² Y. Okamoto,³ H. Takagi,⁴ and S. Shin¹,³

¹RIKEN SPring-8 Center, Sayo, Sayo, Hyogo 679-5148, Japan
²JASRI/SPring-8, Sayo, Sayo, Hyogo 679-5198, Japan
³ISSP, University of Tokyo, Kashiwa-no-ha, Kashiwa, Chiba 277-8561, Japan
⁴RIKEN, The Institute for Physical and Chemical Research, Wako, Suitama 351-0198, Japan

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Soft-x-ray photoemission and absorption spectroscopies are employed to investigate the electronic structures of $\text{Sr}_{1-x}\text{Rh}_2\text{O}_4$. Similarly to the layered cobaltates such as $\text{Na}_{1-x}\text{Co}_2\text{O}_4$, a valence-band satellite feature (VBS) occurs at higher binding energy to the O 2p band. We find that the VBS resonates at the O 1s edge. Additionally, core absorption shows clear $x$ dependence in the O 1s edge rather than in the Rh 3p edge. These results indicate that the holes in the initial state mainly have O 2p character presumably due to $d$-$p$ rehybridizations affected by $\text{Sr}^{2+}$ vacancy potentials. The resultant inhomogenous charge texture may have impact on the TE transport properties at low $x$.

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The search for efficient thermoelectric (TE) materials is extensively pursued with the aim at practical applications such as TE batteries and Peltier refrigerators. Since metallic materials had been considered to exhibit poor TE performance, it was a surprise that a low-resistive layered cobaltate $\text{Na}_{1-x}\text{Co}_2\text{O}_4$ ($x < 0.5$) exhibited large TE power ($Q$) at high temperatures. The covalent features such as electronic structure, the band-theoretical density of states (DOS), and TE power were reported by photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS) at the O 1s edge followed by $d$-$p$ rehybridizations that redistribute the holes from d states to p states beyond a rigid-band-shift picture.

From a band-theoretical viewpoint, the valence band of $\text{NaCoO}_2$ consists of a filled $t_{2g}$ band positioned just below the chemical potential ($\mu$) and an O 2p band at higher binding energy ($E_B$) as schematically shown in the upper panel of Fig. 1(a). With Na⁺ deintercalation, $\mu$ is shifted into the $t_{2g}$ band, and holes of mainly $t_{2g}$ character are introduced into the triangular lattice of $\text{Co}^{3+}$ ions. Valence-band spectra of $\text{Na}_{0.9}\text{Co}_2\text{O}_4$ recorded by photoemission spectroscopy (PES) indeed show the $t_{2g}$ and the O 2p bands, but in addition, there is a valence-band satellite feature (VBS) at $E_B \sim 11$ eV as schematically shown in the lower panel of Fig. 1(a). Similar VBSs occur in other layered cobaltates such as $\text{LiCoO}_2$ and $\text{Ca}_2\text{CuO}_3$ (VBSs in TE Bi-Sr-Co-O system are obscured by Bi 6s states at $E_B \sim 11$ eV). Thus, the VBS is a ubiquitous feature in the TE cobaltates, which is missing in the band-theoretical density of states (DOS).

Herein, we investigate element-specific electronic structures of $\text{Sr}_{1-x}\text{Rh}_2\text{O}_4$ using soft-x-ray absorption (XAS) and resonant PES. $\text{Sr}_{1-x}\text{Rh}_2\text{O}_4$ is structurally and electronically analogous to $\text{Na}_{1-x}\text{Co}_2\text{O}_4$: hole carriers are introduced into the layered triangular lattice of low-spin Rh ions (nominally $t_{2g}^6$) through $\text{Sr}^{2+}$ deintercalation [inset of Fig. 1(b)] to show insulator-to-metal transition at $x \sim 0.2$ [Fig. 1(b)], and the $x = 0.22$ sample shows $Q \sim 70 \mu$V/K at 300 K [Fig. 1(c)] similarly to the cobaltates. We find a VBS in $\text{Sr}_{1-x}\text{Rh}_2\text{O}_4$. Moreover, the VBS resonates at the O 1s edge followed by O 1s$2p$ Auger emissions, providing strong constraints on its origin. We also find clear $x$ dependence in the O 1s XAS rather than in the Rh 3p XAS. The results indicate that holes in $\text{Sr}_{1-x}\text{Rh}_2\text{O}_4$ have strong O 2p character presumably due to so-called $d$-$p$ rehybridizations that redistribute the holes from d states to p states beyond a rigid-band-shift picture.

Single-phase well-sintered $\text{Sr}_{1-x}\text{Rh}_2\text{O}_4$ ($x = 0.11$ and 0.22) were prepared by a conventional solid state reaction as described elsewhere. The resistivity ($\rho$) and $Q$ of the samples [Fig. 1(b)] and (c), respectively] nicely reproduced those reported previously. XAS and PES were performed at BL17SU of SPring-8 equipped with a VG Scienta SES2002 analyzer. Sample surfaces were obtained by fracturing the samples inside the spec-
tronometer under ultrahigh vacuum ($<5 \times 10^{-8}$ Pa). XAS spectra were recorded at 300 K in the total electron yield method. PES spectra were recorded at 50 K at $\sim 250$-meV energy resolution and $E_B$ was referenced to $\mu$ of Au in contact with the sample and the analyzer. PES spectra were normalized to the incident photon flux.

**FIG. 2:** Rh 3$p$-4$d$ resonant PES of Sr$_{1-x}$Rh$_2$O$_4$ ($x = 0.22$). (a) Valence-band spectra recorded across the Rh 3$p_{3/2}$ edge. (b) CIS spectra and Rh 3$p_{3/2}$ XAS. CIS spectra are normalized to the intensity at 486.4 eV and have arbitrary offsets. The labels (i-x) on the spectra in (b) correspond to the photon energies indicated by bars on the Rh 3$p_{3/2}$ XAS in (c).

Figure 2(a) shows valence-band spectra of Sr$_{1-x}$Rh$_2$O$_4$ ($x = 0.22$) recorded across the Rh 3$p_{3/2}$ edge. We find a VBS at $E_B \sim 11.7$ eV, a feature missing in the LDA DOS, as well as the Rh 4$d$ and the O 2$p$ bands centered at $E_B \sim 1.5$ and 6 eV, respectively. Figure 2(b) shows constant-initial-state (CIS) spectra at $E_B = 1.5, 4.5, 6.5,$ and 11.5 eV. One can see resonant enhancement of Rh 4$d$ states at the Rh 3$p_{3/2}$ edge [shaded area in Fig. 2(b)] in all features including the VBS (CIS at $E_B = 11.5$ eV). This indicates that the Rh 4$d$ weight is spread over a wide energy range and that the VBS has some Rh 4$d$ character. The presence of the Co 3$d$ character in the VBSs of the cobaltates was similarly confirmed through Co 3$d$ resonant PES [23, 24].

Next, we performed resonant PES at the O 1$s$ edge to obtain information about the O 2$p$ states. Figure 3(a) and (b) show, respectively, the valence-band spectra recorded in the vicinity of the O 1$s$ edge and the difference to the off-resonant spectra recorded at $h\nu = 527.5$ eV. One can see that the VBS resonates at $h\nu = 527.5$ eV, and subsequently, O 1$s$2p2p Auger peak emerges from the vicinity of the VBS. The results indicate that the final state of the 11.7-eV VBS is similar to that of the O 1$s$2p2p Auger emission, namely, the O 2$p$-two-hole final state [see schematic in Fig. 3(a)]. This interpretation is the same as that of the 6-eV satellite of Ni identified to a Ni 3$d$-two-hole final state [25]. To reach the O 2$p$ two-hole final state by photoemission, the initial state should contain an electronic configuration that has a single hole in the O 2$p$ state. We here-after denote the initial oxygen-hole configuration as $p^1_S$.

We note that the $p^1_S$ state is different from the ligand-hole states of the configuration-interaction CoO$_x$ cluster-model analyses [24, 35], since the $p^1_S$ state is considered to be affected by the cation vacancy potentials [36] (discussed later). At $h\nu \geq 528.7$ eV, the O 1$s$2p2p Auger peak position is shifted to higher $E_B$ since the kinetic energy of an O 1$s$2p2p Auger electron is independent of $h\nu$ [inset in Fig. 3(c)]. The resonant peak position at $h\nu = 527.5$ eV slightly deviates from the constant kinetic energy of the normal O 1$s$2p2p Auger, perhaps since the $p^1_S$ configuration is mixed to some $d$-hole configurations as inferred from the Rh 4$d$ resonant PES [Fig. 2].

**FIG. 3:** Valence-band spectra of Sr$_{1-x}$Rh$_2$O$_4$ ($x = 0.22$) recorded across the O 1$s$ edge. (a) Valence-band spectra recorded in the vicinity of the O 1$s$ edge. Inset shows a schematic of the final state of an O 1$s$2p2p Auger-electron emission. (b) Difference spectra to the 523.0-eV spectrum. The labels (A-H) on the spectra correspond to the photon energies indicated on the O 1$s$ XAS in the inset in (b). The dotted vertical lines indicate the 11.7-eV VBS, and the bars indicate the O 1$s$2p2p Auger peaks. The O 1$s$2p2p Auger peak positions are plotted in the inset in (b), in which the dotted line indicates the constant kinetic energy.

**FIG. 4:** Rh 3$p_{3/2}$ (a) and O 1$s$ (b) XAS. The arrows in (b) indicate the change with increasing $x$. 

*a*...
Evidence for oxygen holes in the initial state is also found in the XAS as shown in Fig. 4. With increasing $x$, the height of the prepeak feature in the O 1s XAS at $h\nu = 528.7$ eV becomes large and that of the main peak at $h\nu = 531.2$ eV becomes small (for each composition, the line shape at $h\nu < 533$ eV was reproducible for 3 fractures). On the other hand, the Rh 3p XAS is hardly changed with $x$. Since the O 1s prepeak intensity is almost in proportional to $x$, we assign it to Sr-vacancy induced states mainly having O $2p$ character, so that the prepeak is assigned to $(1s)^{2}(2p_{\nu}^{o}) \rightarrow (1s)^{2}(2p_{\nu}^{s})$. The spectral-weight transfer seen in O 1s XAS is often taken as a signature of strong electron correlation [34]. In the XAS studies of (Li/Na)$_{1-x}$CoO$_2$ [37, 38, 39], main changes with $x$ occurred in the O 1s XAS rather than in the Co 2p XAS. Thus, oxygen holes in the initial state are common features in the TE rhodates and cobaltates.

The oxygen holes in Sr$_{1-x}$Rh$_2$O$_4$ revealed by resonant PES and XAS at the O 1s edge indicate that the electronic-structure evolution with $x$ goes beyond a rigid-band-shift picture. Otherwise, $\mu$ would shift with increasing $x$ into the Rh 4d band resulting in holes that mainly have Rh 4d character. The spectral weight should therefore be redistributed with increasing $x$, most likely due to $d$-$p$ rehybridization [27, 28, 29, 30]: as evidenced from the charge densities calculated [40] for Li$_{1-x}$CoO$_2$ [27, 28] and Na$_{1-x}$CoO$_2$ [29], the holes introduced via Li/Na deintercalation are not homogeneously distributed in the Co layers but reside at oxygen sites neighboring the Li/Na vacancies, i.e., the cation vacancy potential binds the holes to form the $p_{\nu}^o$ state [28]. The charge density at a Co site was nearly unchanged with increasing $x$ [27, 28, 29], since the $t_{2g}$ holes were dressed by $e_g$ electrons transferred from the O 2p states through the $d$-$p$ rehybridization. The essence of the charge rearrangement with doping can be captured in a simple model, namely, transition-metal impurities in semiconductors [30, 31]. The rigidity of the Rh 3p XAS line shape with $x$ [Fig. 4(a)] is thus considered as a fingerprint that the $d$-$p$ rehybridization is self-regulating the local charge density about the Rh site to a nearly constant value.

A striking difference between the O 1s XAS of Sr$_{1-x}$Rh$_2$O$_4$ and those of (Na/Li)$_{1-x}$CoO$_2$ [34, 37, 38, 39] is that the $x$-dependent prepeak in the former is well separated from the main peak [Fig. 4(b)], whereas those in the latter are merging into the main peaks. This can be understood that the degree of localization of the $p_{\nu}^o$ state is affected by the strength of the cation vacancy potentials. Since the divalent Sr$_2^+$ vacancy potential is stronger than those of the monovalent Li$^+$/Na$^+$, the holes are more strongly bound around the vacancies in the former than in the latter [28]. Hence, the $p_{\nu}^o$ state appears to be more localized in Sr$_{1-x}$Rh$_2$O$_4$, so that the prepeak appears to be a sharp level. The localized character of the $p_{\nu}^o$ state is supported by an $^{17}$O NMR study of Na$_{1-x}$CoO$_2$ ($x=0.28$), revealing that $\sim 30\%$ of the oxygen sites carry local magnetic moments [42]. We naturally identify these magnetic oxygens to have the $p_{\nu}^o$ configuration.

It should be noted that a VBS was also observed in stoichiometric LiCoO$_2$ having no Li vacancies [24]. Through a configuration-interaction cluster-model analysis, the VBS of LiCoO$_2$ was attributed to large $d$-$p$ hybridization and orbital degeneracy of the $d$ states [24]. Thus, the $d$-$p$ rehybridization with doping effectively occurs when the parent compound has large $d$-$p$ hybridization and orbital degeneracy. Large $d$-$p$ hybridization generally occurs in $t_{2g}$ electron system having unoccupied $e_g$ orbitals (this includes $d^n$ insulators [43, 44]). In fact, $d$-$p$ rehybridization was reported to occur when carriers are doped into SrTiO$_3$, a nominally $d^0$ insulator [45]. It is also interesting that a layered Cu$_2$TiSe$_2$, which shows TE properties as good as the cobaltates [46], is also considered to exhibit $d$-$p$ rehybridization [47]. Here, the hybridization of the Se 4p states into the unoccupied Ti 3d states opens the channel of $d$-$p$ rehybridization, and Cu$^+$ act as a source of “occupancy” potential. Thus, the TE cobaltates, rhodates, and the intercalated Ti dichalcogenides can be categorized to those exhibiting $d$-$p$ rehybridization affected by the cation vacancy/occupancy potentials.

Since the holes in the initial state are not homogeneously distributed in the Rh layers as expected in a rigid-band-shift picture but are further redistributed due to the $d$-$p$ rehybridizations and the Sr vacancy potentials, the charge density is considered to be nonperiodic compared to the crystallographic periodicity of SrRh$_2$O$_4$ (please see the nonperiodic charge densities calculated for (Li/Na)$_{1-x}$CoO$_2$ [27, 28, 29]). Thus, it would be necessary to realize that the transport is occurring on such an inhomogenous charge texture with O 2p holes bound to cation vacancies. For example, as was pointed out in [32], the nonmetallic conduction at $x \lesssim 0.2$ of Sr$_{1-x}$Rh$_2$O$_4$ [26] can be viewed as a variable-range hopping, i.e., the low-energy excitations relevant to the transport show weak localizations as they are subject to randomness [48]. The mobility-edge crossing occurring at $x \approx 0.2$ in Sr$_{1-x}$Rh$_2$O$_4$ is reasonably larger than that of Na$_{1-x}$CoO$_2$ occurring at $x < 0.1$ [3], since the vacancy potential of Sr$_{2}^+$ is stronger than that of Na$^+$, although single crystal data will be helpful for further investigations [49]. Another point to be noted is, when a nonmetallic transport is realized by randomness in a spin-orbitally degenerate system such as in Fe$_2$O$_{1-x}$F$_x$ [50], a hump feature occurs at $T \sim 100$ K in a $Q$-$T$ curve [49, 50, 51]. This feature is very similar to the enhanced $Q$ at $\sim 100$ K in metallic Na$_{1-x}$CoO$_2$ at low $x$ [3], which is considered to be on the verge of the metal-nonmetal transition. Further studies are necessary to clarify the relationship between the randomness and the transport properties in the rhodates and the cobaltates particularly at low $x$.

In summary, we have performed resonant PES and XAS on Sr$_{1-x}$Rh$_2$O$_4$ and find that the holes have strong O 2p character. The VBS, which commonly occurs in the TE cobaltates, is proven from resonant PES at the O 1s edge to be a fingerprint of the O 2p holes in the
initial state. The results indicate a non-rigid-band evolution of the electronic structure with doping due to the \(d-p\) rehybridization affected by the cation vacancy potentials [27–29, 30], resulting in an inhomogenous charge texture that may affect the transport properties at low \(x\).

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