Anomalous electronic structures of transition-metal oxides with hollandite-type crystal structure

T Toriyama¹, T Konishi² and Y Ohta¹

¹ Department of Physics, Chiba University, Chiba 263-8522, Japan
² Graduate School of Advanced Integration Science, Chiba University, Chiba 263-8522, Japan
E-mail: ohta@faculty.chiba-u.jp

Abstract. We make the electronic structure calculations of transition-metal oxides with a hollandite-type crystal structure \( \text{A}_2\text{M}_8\text{O}_{16} \) using the generalized gradient approximation (GGA) in the density functional theory, where the Hubbard-type repulsive interaction is taken into account (GGA+\( U \)). We first examine the electronic structure of the 3\( d \) series (\( M = \text{Ti, V, Cr, Mn} \)) as well as the 4\( d \) series (\( M = \text{Mo, Ru, Rh} \)) to discuss their generic features. We then discuss in particular the origins of the metal-insulator transition observed in \( \text{K}_2\text{Cr}_8\text{O}_{16} \) and quasi-one-dimensional electron conduction observed in \( \text{K}_2\text{Ru}_8\text{O}_{16} \). We also consider the observed metal-insulator transition in \( \text{K}_2\text{V}_8\text{O}_{16} \) where the effect of electron correlations may play an essential role.

1. Introduction
Hollandite materials have attracted considerable attention in recent years in the field of physics of strong electron correlations. The crystal structure of hollandites resembles that of the rutile structure but the single chains of \( \text{MO}_6 \) octahedra (\( M = \text{transition element} \)) in rutiles are replaced by the double chains of the edge-shared \( \text{MO}_6 \) octahedra in hollandites, resulting in a sparse structure with large tunnels, wherein a variety of cations \( \text{A} \) can be introduced as in the chemical formula \( \text{A}_x\text{M}_8\text{O}_{16} \) with \( 0 \leq x \leq 2 \).

We may point out that the material series with the 3\( d \) transition-metal elements \( M = \text{Ti, V, Cr, and Mn} \), which are in a mixed valent state, show a variety of unusual electronic and magnetic properties: In Ti series, \( \text{K}_x\text{Ti}_8\text{O}_{16} \) has been reported to be either a dilute ferromagnetic semiconductor [1] or a paramagnetic metal [2], depending on the carrier concentration. In V series, \( \text{K}_2\text{V}_8\text{O}_{16} \) shows a variety of physical properties associated with the metal-insulator transition [2, 3, 4, 5, 6, 7, 8, 9, 10]. In Cr series, \( \text{K}_2\text{Cr}_8\text{O}_{16} \) has been reported to exhibit phase transitions from metallic paramagnet to ferromagnet and then to insulating ferromagnet by lowering temperatures [11, 12]. In Mn series, a variety of structural, electronic, and magnetic phase transitions have been reported as well [13, 14].

We may also point out that the material series with the 4\( d \) transition-metal elements \( M = \text{Mo, Ru, and Rh} \) show interesting physical properties: In Mo series, an \( \text{Mo}_4 \) clustering has been reported to occur in \( \text{Rb}_{1.5}\text{Mo}_8\text{O}_{16} \) [15]. In Ru series, a quasi-one-dimensional electron conduction has been reported in \( \text{KRu}_4\text{O}_8 \), \( \text{RbRu}_4\text{O}_8 \), and \( \text{Cs}_{0.8}\text{Li}_{0.2}\text{Ru}_4\text{O}_8 \) [16, 17, 18], as well as in \( \text{BaRu}_6\text{O}_{12} \) [19] with a similar crystal structure. In Rh series, a quasi-one-dimensional electron conduction has also been reported [20, 21, 22, 23].
In this paper, motivated by such materials development, we make the electronic structure calculations of the series of hollandite-type transition-metal oxides to clarify their basic electronic structures. We use the generalized gradient approximation (GGA) in the density functional theory, where the Hubbard-type repulsive interaction $U$ is taken into account (GGA+$U$). We thereby examine the 3$d$ series ($M$=Ti, V, Cr, Mn) as well as the 4$d$ series ($M$=Mo, Ru, Rh) to discuss generic features in the electronic structure of hollandites first. Then, we in particular study the quasi-one-dimensional electron conduction observed in K$_2$Ru$_8$O$_{16}$ and K$_2$Rh$_8$O$_{16}$ by focusing on singularities in their calculated band structures and Fermi surfaces. The origins of the metal-insulator transition observed in K$_2$Cr$_8$O$_{16}$ is discussed in this respect. We also study the electronic structure of K$_2$V$_8$O$_{16}$ to consider the origins of the observed anomalous electronic states and metal-insulator transition and find that the effect of electron correlations plays an essential role in the metal-insulator transition of this material.

2. Method of calculation
We employ the computer code WIEN2k [24] based on the full-potential linearized augmented-plane-wave (FLAPW) method. We use the experimental crystal structure of each material observed at room temperatures. The symmetry of the lattice at high-temperature phase is body-centred-tetragonal ($I4/m$ space group). The primitive unit cell contains four $M$ ions, one K ion, and eight O ions. All the $M$ ions are crystallographically equivalent but there are two inequivalent O ions, i.e., O(1) inside the double chains and O(2) connecting the double chains. To improve the description for the electron correlations in the $d$ orbitals, we use the rotationally invariant version of the GGA+$U$ method [25, 28] as well. We use the codes VESTA [29] and XCrySDen [30] for graphical purposes.

3. Results of calculation
3.1. Generic features
Let us discuss some common features in hollandites first. The calculated densities of states show that there appear the $t_{2g}$ and $e_g$ bands separated by $10D_q$ of $\sim 2$ eV for the 3$d$ series and $\sim 3$ eV for the 4$d$ series and O 2$p$ states well below the $d$ bands. The hybridization between the $d$ and 2$p$ states are considerably strong. The Fermi level is located somewhere in the $t_{2g}$ manifold, depending on the number of $d$ electrons. The rigid-band approximation works well in the series considered at least in the high-energy scale of a few eV.

More precisely, there are 12 bands in the $t_{2g}$ manifold, the character of which differs strongly between the topmost 4, the lowermost 4, and the middle 4 bands. The Fermi level is located in the topmost 4 bands in the Ru, Rh, and ferromagnetic Cr systems, in the lowermost 4 bands in the Ti, V, and Mo systems, and in the middle 4 bands in the Mn systems. Thus, the number of valence $d$ electrons or the location of the Fermi level determines the basic electronic properties of hollandite-type transition-metal oxides.

3.2. K$_2$Ru$_8$O$_{16}$
The Ru ions are in the mixed valent state with the average valence of Ru$^{3.75+}$ ($d^{4.25}$), i.e., there are formally Ru$^{4+}$ ($d^1$) and Ru$^{3+}$ ($d^5$) in the 3 : 1 ratio. We find from the GGA+$U$ calculations that, despite its structural complexity, the electronic state of K$_2$Ru$_8$O$_{16}$ near the Fermi level is surprisingly simple, consisting only of a single band coming predominantly from the 4$d_{yz}$ and 4$d_{zx}$ orbitals of Ru ions with strong admixture of the 2$p_z$ orbitals of corner-shared O ions connecting the double RuO chains. The electronic band structure near the Fermi level is highly quasi-one-dimensional, exactly at half filling, and has a pair of nearly parallel sheetlike Fermi surfaces separated by $\pi/c$. The calculated results are consistent with observed quasi-one-dimensional electron conduction of this material [16]. These results establish that K$_2$Ru$_8$O$_{16}$...
belong to a class of materials for further studies of Tomonaga-Luttinger liquids [27]. See Ref. [18] for details.

3.3. $K_2Rh_8O_{16}$

There are some experimental reports on the hollandite rhodates: $Ba_{1.2}Rh_8O_{16}$ [20, 21], $(Ba,Bi)_{1.54}Rh_8O_{16}$ [22], and $Sr_{1.5}Rh_8O_{16}$ [23]. The formal oxidation state of Rh in these materials ranges between $Rh^{3.37+} (d^6.43^3$ and $Rh^{3.7+} (d^5.3^3$. The number of $d$ electrons thus indicates that the second band counted from the top in the $t_{2g}$ manifold crosses the Fermi level with the filling of electrons roughly between a half to three quarters if the second band is isolated (although of course more than one band can cross the Fermi level). Our preliminary electronic structure calculations indicate that the band structure is not very simple but there is in fact a highly quasi-one-dimensional band, as expected from our results for $K_2Ru_8O_{16}$, which is consistent with the quasi-one-dimensional transport properties reported in $Ba_{1.2}Rh_8O_{16}$ [20, 21].

3.4. $K_2Cr_8O_{16}$

We point out that the above two materials have an interesting similarity with the ferromagnetic hollandite $K_2Cr_8O_{16}$ [11], where Cr ions are in the oxidation state $Cr^{3.75+} (d^{2.25})$. The electronic structure calculations [12] have shown that the system is a fully spin-polarized half metal and that the Fermi level is located between the third and fourth bands counted from the top of the $t_{2g}$ manifold for majority-spin electrons, or that both of the third and fourth bands cross the Fermi level to form a semimetallic (or compensated metallic) band structure. In fact, it has been found [12] that the Fermi surface of the fourth band is highly quasi-one-dimensional, as in the present $K_2Ru_8O_{16}$. The observed metal-insulator transition of the Cr system is therefore related to the nesting feature of the quasi-one-dimensional Fermi surfaces, details of which will be discussed elsewhere [31].

3.5. $K_2V_8O_{16}$

Such situations as above are in strong contrast to the hollandite vanadate $K_2V_8O_{16}$. The average valence of V ions is $V^{3.75+} (d^{1.25})$, i.e., in the mixed valent state of $V^{3+} : V^{4+} = 3d^2 : 3d^1 = 1 : 3$, and therefore the Fermi level is located in the third band counted from the lowest in the $t_{2g}$ manifold in the paramagnetic state. Our GGA+$U$ calculations have shown [32] that the lowest four bands are predominantly of the $d_{xy}$ character and show the nearly one-dimensional dispersion. The nesting of the Fermi surfaces may play some role in the observed metal-insulator transition but the effects of electron correlations, i.e., the charge and orbital ordering as well as the Mott localization, should rather be more important in $K_2V_8O_{16}$ than in other systems. In fact, depending on the values of $U$ used, the calculated band structure and Fermi surfaces change largely, and the spin and orbital structure obtained in the low-temperature phase displays a variety of patterns, which are not expected from the $2k_F$ singularity in the high-temperature phase [32].

3.6. Other materials

Besides the materials discussed above, we have also made the electronic structure calculations of other hollandite-type transition-metal oxides. We find that the calculated electronic structure of $K_2Ti_8O_{16}$ is consistent with the observed paramagnetic metallic state. We also find that the band structure of $K_2Mn_8O_{16}$ is complicated, i.e., the Fermi level is located somewhere in the middle 4 bands of the $t_{2g}$ manifold.

4. Summary

We have made the electronic structure calculations of transition-metal oxides with the hollandite-type crystal structure using GGA and GGA+$U$ in the density functional theory. We have
examined the 3d series ($M$=Ti, V, Cr, Mn) as well as the 4d series ($M$=Mo, Ru, Rh) to discuss generic aspects in the electronic structure of hollandites first. Then, we in particular study the origins of the metal-insulator transition observed in $K_2CrO_3$ and quasi-one-dimensional electron conduction observed in $K_2RuO_3$ by focusing on singularities in their calculated band structures and Fermi surfaces. We also study the electronic structure of $K_2V_3O_6$ to consider the origins of the observed anomalous electronic states and metal-insulator transition.

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