Anomalous electronic states of hollandite-type transition-metal oxides

Y Ohta\textsuperscript{1}, T Toriyama\textsuperscript{1}, M Sakamaki\textsuperscript{2} and T Konishi\textsuperscript{3}

\textsuperscript{1} Department of Physics, Chiba University, Chiba 263-8522, Japan
\textsuperscript{2} Photon Factory, IMSS, KEK, Tsukuba 305-0801, Japan
\textsuperscript{3} 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 the hollandite-type crystal structure $A_2M_8O_{16}$ 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 discuss generic electronic structures of the 3\textit{d} ($M$=Ti, V, Cr, Mn) and 4\textit{d} ($M$=Mo, Ru, Rh) series of the materials and then consider the origins of the metal-insulator transition observed in $K_2Cr_8O_{16}$ and quasi-one-dimensional electron conduction observed in $K_2Ru_8O_{16}$. We also consider in particular the observed metal-insulator transition in $K_2V_8O_{16}$.

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 $MO_6$ octahedra ($M$=transition element) in rutiles are replaced by the double chains of the edge-shared $MO_6$ octahedra in hollandites, resulting in a sparse structure with large tunnels, wherein a variety of cations $A$ can be introduced as in the chemical formula $A_xM_8O_{16}$ with $0 \leq x \leq 2$. We point out that the material series with the 3\textit{d} transition-metal elements $M$ = Ti, V, Cr, and Mn, which are in a mixed valent state, show a variety of unusual electronic and magnetic properties, including the metal-insulator transition, spin-singlet formation, as well as ferromagnetism and antiferromagnetism. The material series with the 4\textit{d} transition-metal elements $M$ = Mo, Ru, and Rh also show interesting physical properties, including the quasi-one-dimensional electron conduction [1].

In this paper, motivated by such materials development, we make the electronic structure calculations on 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\textit{d} series ($M$=Ti, V, Cr, Mn) as well as the 4\textit{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 $K_2Ru_8O_{16}$ and $K_2Rh_8O_{16}$ [1] by focusing on singularities in their calculated band structures and Fermi surfaces. The origins of the metal-insulator transition observed in $K_2Cr_8O_{16}$ [2, 3] is discussed in this respect. We also study the electronic structure of $K_2V_8O_{16}$ to consider the origins of the observed anomalous electronic states and metal-insulator transition [4].
2. Method of calculation
We employ the computer code WIEN2k [5] 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-centered-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 as well.

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 $10D_g$ of $\sim 2$ eV for the 3$d$ series and $\sim 3$ eV for the 4$d$ series and O 2p states well below the $d$ bands. The hybridization between the $d$ and O 2p states are considerably strong. The Fermi level is located somewhere in the $t_{2g}$ manifold of the $d$ bands, 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. $K_2Ru_8O_{16}$
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 $Ru^{4+} (d^4)$ 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 $K_2Ru_8O_{16}$ near the Fermi level is surprisingly simple, consisting only of a single band coming predominantly from the $4d_{yz}$ and $4d_{zx}$ orbitals of Ru ions with strong admixture of the $2p_z$ orbitals of corner-shared O(2) 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 [1]. These results establish that $K_2Ru_8O_{16}$ belongs to a class of possible Tomonaga-Luttinger-liquid materials. See Ref. [1] for details.

3.3. $K_2Rh_8O_{16}$
There are some experimental reports on the hollandite rhodates [1]: $Ba_{1.2}Rh_8O_{16}$, (Ba,Bi)$_{1.54}Rh_8O_{16}$ and Sr$_{1.5}Rh_8O_{16}$. The formal oxidation state of Rh in these materials ranges between $Rh^{3.57+} (d^{5.43})$ and $Rh^{3.7+} (d^{5.3})$. 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 $Ba_{1.2}Rh_8O_{16}$ [1].
3.4. $K_2Cr_8O_{16}$

We point out that the above two materials have an interesting similarity with the ferromagnetic hollandite $K_2Cr_8O_{16}$ [2], where Cr ions are in the oxidation state $Cr^{3.75+} (d^{2.25})$. The electronic structure calculations [3] 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.

To clarify further the mechanism of the metal-insulator transition of this material, we seek for any instability in the ferromagnetic metallic phase. We calculate the band structure and Fermi surfaces in the ferromagnetic metallic phase, assuming the values $U = 2.5 - 4$ eV. We find that there are four bands near the Fermi level; three of them are mostly above the Fermi level and one of them is mostly below the Fermi level, which are almost separated, forming a “pseudogap” (which becomes a real gap in the ferromagnetic insulating phase). These states come predominantly from the Cr 3$d$ $d_{yz}$ and $d_{zx}$ orbitals with strong admixture of the O(2) 2$p_z$ orbitals between the double chains. The negative charge-transfer-gap situation [3] plays an essential role here. The calculated Fermi surfaces are shown in Fig. 1, where a very good one-dimensionality is immediately noticed; there are two pairs of the Fermi surfaces with a very good nesting feature of a nesting vector $(0, 0, 2\pi/c)$, where the pair consists of two closely adjacent Fermi surfaces, inside of which we have a small number of holes, which are compensated by a small number of electrons in small pocket-like Fermi surfaces. Thus, the system has a Peierls instability with the momentum $(0, 0, 2\pi/c)$. This result is in agreement with experiment [2], where there occurs no doubling of the unit cell along the $c$ axis in the low-temperature ferromagnetic insulating phase. Further details will be presented elsewhere.

![Figure 1. Calculated Fermi surfaces of the majority-spin band in the ferromagnetic metallic phase of $K_2Cr_8O_{16}$. The value $U = 4$ eV is assumed.](image_url)

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 of the $t_{2g}$ manifold in the paramagnetic state. Our GGA+$U$ calculations have shown that the lowest four bands are predominantly of the $d_{xy}$ character and have a nearly one-dimensional dispersion. The nesting of the Fermi surfaces may play an important 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 the materials discussed above. In fact, depending on the values of $U$ used, the calculated band structure and Fermi surfaces change largely with opening of a band gap in some cases, 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. Also noted is that the direct $d_{xy}-d_{xy}$ hopping of electrons predominantly governs the electronic structure near the Fermi level, which is in contrast to the case of $K_2Ru_8O_{16}$ and $K_2Cr_8O_{16}$. Further studies are in progress to identify the mechanism of the metal-insulator transition of this material.

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. The results for these materials will be presented in subsequent publications.

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 3$d$ series ($M$=Ti, V, Cr, Mn) as well as the 4$d$ 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 $K_2Cr_8O_{16}$ and quasi-one-dimensional electron conduction observed in $K_2Ru_8O_{16}$ by focusing on singularities in their calculated band structures and Fermi surfaces. We also study the electronic structure of $K_2V_8O_{16}$ to consider the origins of the observed anomalous electronic states and metal-insulator transition and find that the effect of electron correlations seems to play an essential role in the metal-insulator transition of this material.

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