Hollandite ruthenate $\text{K}_2\text{Ru}_8\text{O}_{16}$ as a new Tomonaga-Luttinger-liquid system

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Abstract. The electronic structure of hollandite ruthenate $\text{K}_2\text{Ru}_8\text{O}_{16}$ is calculated using the generalized gradient approximation in the density functional theory, where the Hubbard-type repulsive interaction is taken into account. We find that the band structure near the Fermi level consists only of a single band, which is highly quasi-one-dimensional, exactly at half filling, and has a pair of two nearly-parallel sheetlike Fermi surfaces separated by $\pi/c$. These results are consistent with observed quasi-one-dimensional transport properties of the material and thus establish that $\text{K}_2\text{Ru}_8\text{O}_{16}$ belongs to a class of Tomonaga-Luttinger-liquid systems.

1. Introduction

Transition-metal oxides (TMO) showing quasi-one-dimensional electron conduction are relatively rare in many metallic TMO systems. Among them is a ruthenate material with a hollandite-type crystal structure studied in this paper. The crystal structure (see Fig. 1) consists of double chains of the edge-shared $\text{MO}_6$ octahedra ($M=$transition element), which form a spatially sparse structure with large tunnels, wherein a variety of cations $A$ are introduced as in the chemical formula $A_xM_8\text{O}_{16}$ with $0 \leq x \leq 2$. It has been reported that the ruthenate ($M=$Ru) and rhodate ($M=$Rh) materials show interesting physical properties: a quasi-one-dimensional electron conduction has been reported in KRu$_4\text{O}_8$, RbRu$_4\text{O}_8$, and Cs$_{0.8}\text{Li}_{0.2}\text{Ru}_4\text{O}_8$ [1, 2], as well as in BaRu$_6\text{O}_{12}$ [3] with a similar crystal structure. In the Rh series, a quasi-one-dimensional electron conduction has also been reported [4, 5, 6, 7].

In this paper, we make the electronic structure calculations employing the WIEN2k code [8], where we use the generalized gradient approximation (GGA) in the density functional theory, taking into account the Hubbard-type repulsive interaction (GGA+$U$) [9]. We here focus in particular on $\text{K}_2\text{Ru}_8\text{O}_{16}$. This material has a body-centered tetragonal crystal structure and all the Ru sites are crystallographically equivalent [1, 2, 10]. 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 a 3 : 1 ratio. Quasi-one-dimensional electronic properties have recently been reported [1]: the temperature dependence of the electric resistivity along the chain direction always decreases with decreasing temperature, whereas that perpendicular to the chains increases with decreasing temperature down to $\sim$180 K, indicating the quasi-one-dimensionality of the electron conduction of the system. The anisotropy ratio of the resistivity has been reported to be $\sim$34 ($\sim$20) at 4.2 K (150 K).

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We will show from our calculations that, despite its structural complexity, the electronic state of $\text{K}_2\text{Ru}_8\text{O}_{16}$ 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 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. These results establish that $\text{K}_2\text{Ru}_8\text{O}_{16}$ belongs to a class of materials for further studies of Tomonaga-Luttinger liquids [11].

2. Results of calculation
We use the experimental crystal structure of $\text{K}_2\text{Ru}_8\text{O}_{16}$ observed at room temperature with the lattice constants $a = 9.866$ and $c = 3.131$ Å [10]. The symmetry of the lattice is body-centred-tetragonal ($I4/m$ space group, see Fig. 1). The primitive unit cell contains four Ru ions, one K ion, and eight O ions. All the Ru 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. In the self-consistent calculations, we use 1,060 $k$ points in the irreducible part of the Brillouin zone (see Fig. 1) with an anisotropic sampling to achieve better convergence. We use the plane-wave cutoff of $K_{\text{max}} = 3.65$ Bohr$^{-1}$. To improve the description for the electron correlations in the Ru 4$d$ orbitals, we use the rotationally invariant version of the GGA$+U$ method [9, 12] as well, assuming the value $U = 3.0$ eV for the Ru 4$d$ orbitals. We use the codes VESTA [13] and XCrySDen [14] for graphical purposes.

2.1. Band dispersion
The calculated band dispersion near the Fermi energy is shown in Fig. 2. We find that there are 12 bands coming mainly from the Ru 4$d$ $t_{2g}$ orbitals (which we call the $t_{2g}$ manifold) and the Fermi level crosses only the fourth band counted from the top and thus the fourth band is exactly at half filling. The fourth band is highly dispersive along the $\Gamma$-K$_1$, X-P, and M-K$_2$ lines and weakly dispersive along the $\Gamma$-X, P-K$_1$, and K$_1$-K$_2$ lines, reflecting the quasi-one-dimensionality of the electronic state of this material. This result is consistent with the observed large anisotropy of the electric resistivity of the single crystal of this material [1].

To describe the band structure more precisely, we note that the uppermost four bands in the $t_{2g}$ manifold come predominantly from the $d_{yz}$ and $d_{zx}$ orbitals of Ru hybridized strongly with the $p_z$ orbital of O(2) and that the first and fourth bands counted from the top are highly dispersive and the second and third bands are less dispersive. This characteristic band structure
Figure 2. Calculated band dispersion of $K_2Ru_8O_{16}$ near the Fermi level (horizontal line) where the labels of the $k$-points are shown in Fig. 1. The results at $U = 0$ eV (left panel) and $U = 3$ eV (right panel) are shown. There are 12 bands of the Ru 4$d t_{2g}$ orbitals, where the fourth band from the top is at half filling.

can roughly be understood by the tight-binding model consisting of the $d_{yz}, d_{zx}$, and $p_z$ orbitals of an isolated column made of four Ru-O(2) chains running along the c-axis, of which the column structure can be realized if each of the Ru-O double chains in hollandite is cut into two at O(1) and resulting four single Ru-O(2) chains are gathered to form the column structure of the four Ru-O(2) chains, as in the rutile structure. Thus, the coupling (or electron hopping) via the 2$p$ orbitals of O(1) is rather small in $K_2Ru_8O_{16}$. See Ref. [15] for further details.

We also find in Fig. 2 that the fifth to eighth bands counted from the top of the $t_{2g}$ manifold, which have the strong $d_{xy}$ character, shifts significantly to lower energies by increasing the value of $U$. Note that the fourth band then tends to be isolated in the energy bands and thus the one-dimensionality is enhanced by increasing the value of $U$.

Figure 3. Calculated Fermi surfaces of $K_2Ru_8O_{16}$ at (a) $U = 0$ eV and (b) $U = 3$ eV.

2.2. Fermi surface

The calculated results for the Fermi surface are shown in Fig. 3. We find that only the fourth band counted from the top of the $t_{2g}$ manifold crosses the Fermi level to form the Fermi surfaces.
If the system were strictly one-dimensional, a pair of the parallel Fermi surfaces should appear at $k_z = \pm k_F$ with $2k_F = \pi/c$. We actually find such a situation of the pair of the Fermi surfaces in Fig. 3, but the surfaces are considerably warped, indicating that the one-dimensionality is not perfect, which we call the quasi-one-dimensional Fermi surfaces. We find that the one-dimensionality is enhanced when the value of $U$ increases. This system in the presence of electron correlations is therefore a good candidate for further studies of the Tomonaga-Luttinger liquids [11]. We should point out that the nesting feature in the two nearly-parallel Fermi surfaces seen in Fig. 3 does not lead to any instabilities in the actual material because the nesting is not perfect: if the nesting were sufficiently strong, the $2k_F$ instability would result in, e.g., the opening of the band gap, as in $K_2Cr_8O_{16}$ [16, 17].

3. Summary
The electronic structure of hollandite ruthenate $K_2Ru_8O_{16}$ has been calculated using GGA in the density functional theory, where the Hubbard-type repulsive interaction is taken into account (GGA+$U$). We have found that the electronic structure near the Fermi level consists 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 ions connecting the double RuO chains. The band structure near the Fermi level is highly quasi-one-dimensional, exactly at half filling, and has a pair of two nearly-parallel sheetlike Fermi surfaces separated by $\pi/c$. The calculated results are consistent with observed quasi-one-dimensional transport properties of this material. These results establish that $K_2Ru_8O_{16}$ belongs to a class of the simplest possible Tomonaga-Luttinger-liquid materials.

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