Mechanism of the metal-insulator transition of hollandite vanadate $K_2V_8O_{16}$

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Abstract. We make the electronic structure calculations of hollandite vanadate $K_2V_8O_{16}$ using the generalized gradient approximation (GGA) in the density functional theory, where the Hubbard-type repulsive interaction $U$ is taken into account (GGA+$U$). We in particular calculate the electronic structure of the low-temperature phase of this material using the crystal structure reported by Komarek et al. We find that the electronic wave functions near the Fermi level are predominantly of the $d_{xy}$ character and form the quasi-one-dimensional energy bands. The energy bands are made of the single chains of the VO$_6$ octahedra rather than the double chains. The effects of strong electron correlations play an essential role here. Based on these results, we discuss possible mechanisms of the observed metal-insulator transition of this material.

1. Introduction
The metal-insulator phase transition (MIT) associated with charge and orbital ordering has been one of the central issues in physics of strongly correlated electron systems. An example is a hollandite vanadate $K_2V_8O_{16}$ studied in this paper: Isobe et al. [1, 2] reported that the MIT occurs at $\sim 160$ K, which is accompanied by a rapid reduction of the magnetic susceptibility. A characteristic superlattice of $\sqrt{2a} \times \sqrt{2a} \times 2c$ was observed below the transition temperature. A possible charge-ordering phase transition accompanied by the spin-singlet formation was thereby suggested [1, 2]. The phase diagram under high pressures was also obtained [3], where a variety of charge-ordered phases were suggested to appear. The MIT was also observed in Bi$_x$V$_8$O$_{16}$ [4, 5].

The crystal structure of $K_2V_8O_{16}$ belongs to a group of hollandite-type phases and has a V$_8$O$_{16}$ framework composed of double chains of edge-shared VO$_6$ octahedra. Here, V ions are in the mixed-valent state with the average valence of $V^{3.75+}$ ($d^{1.25}$), i.e., there are formally $V^{3+}$ ($d^2$) and $V^{4+}$ ($d^1$) ions in a 1 : 3 ratio. Thus, the central issue in the present system is the mechanism of the MIT concerning how the highly frustrated spin, charge and orbital degrees of freedom at high temperatures are relaxed by lowering temperatures and what type of orders is realized in the ground state.

This material was studied in the strong correlation limit [6], where a high-energy model Hamiltonian was set up and strong-coupling perturbation theory was applied to obtain the low-energy effective spin-orbit Hamiltonian. The obtained effective Hamiltonian was analyzed numerically and the possible orbital and spin structure of the ground state was proposed [6]. Komarek et al. [7, 8] studied the low-temperature crystal structure by means of the neutron and
X-ray diffraction experiments and identified a lattice dimerization as the main character of the MIT; i.e., a half of the V chains is dimerized perfectly, which explains the partial suppression of the magnetic susceptibility due to the formation of spin singlets. Ishige et al. [9] made X-ray photoemission spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) experiments and showed that the V$^{4+}$-V$^{4+}$ pair formation is essential for the MIT as well as for the drop of the magnetic susceptibility. They also argued that the existence of the V$^{3+}$ components gives additional orbital instability in the insulating phase to enhance the V$^{3+}$-V$^{4+}$ coupling in the ab plane and suppresses the V$^{4+}$-V$^{4+}$ pairing along the c axis. Shimizu et al. [10] made $^{51}$V NMR measurements at ambient and high pressures to give microscopic evidence for the spin-singlet formation at pressures up to 2 GPa. They also suggested that a pressure-induced switching of the spin-singlet texture occurs across the critical pressure. The measured anisotropic electric-field gradient supports the ordering of the $d_{xy}$ orbitals and formation of the spin singlets along the chain. The $d_{xy}$ orbital is magnetically most active in the metallic state, suggesting the strong electron correlation in the $d_{xy}$ bands.

Figure 1. (a) Schematic representation of the low-temperature crystal structure of K$_2$V$_8$O$_{16}$ obtained by Komarek et al. [7, 8]. The high-temperature tetragonal lattice are indicated by dashed lines. Gray circles represent K ions, blue octahedra contain non-dimerized V$^{4+}$ ions, red octahedra contain V$^{4+}$ ions and green octahedra contain V$^{3+}$ ions. (b) Brillouin zone of the low-temperature phase of K$_2$V$_8$O$_{16}$.

However, although experimental data have thus been accumulated, not much is known for the basic electronic structure of this material from the band-theoretical viewpoint. The purpose of this paper is therefore to present results of the density-functional-theory-based electronic structure calculations and to discuss possible mechanisms of the MIT of this material. Here, we use the generalized gradient approximation (GGA) for electron correlations, taking into account the Hubbard-type repulsive interaction (GGA+$U$) [12].

In this paper, we will show the following. The electronic structure near the Fermi level consists of the quasi-one-dimensional energy bands, coming predominantly from the $d_{xy}$ orbitals of V ions. In the low-temperature phase, the energy bands split into lower 8 bands and upper 8 bands due to the doubling of the unit cell along the c axis, resulting in a small gap between the two. The Fermi level is located in the upper bands, causing one extra d electron per 4 V ions. Thus, we point out that the system can be insulating if the extra (or doubly occupied) $d_{xy}$ electrons are removed from the upper bands due to the strong intra-orbital Coulomb repulsion and are put on the $d_{yz}$ and $d_{zx}$ orbitals and if these electrons on the $d_{yz}$ and $d_{zx}$ orbitals are moreover localized due to possible charge or orbital orderings. Because these two orbitals are exactly degenerate in the high-temperature phase, the occurrence of such charge or orbital orderings may well be expected, the mechanism of which needs to be explored in future.

2. Method and results of calculation
We employ the computer code WIEN2k [11] based on the full-potential linearized augmented-plane-wave method. The spin-orbit interaction is not taken into account. No spin-polarization is
Figure 2. Calculated band dispersion of $K_2V_8O_{16}$ near the Fermi level (horizontal line) calculated at $U = 6$ eV for the (a) high-temperature and (b) low-temperature phases.

Figure 3. Calculated DOS of $K_2V_8O_{16}$ near the Fermi level (vertical line) calculated at $U = 6$ eV. (a) partial DOS in the high-temperature phase, (b) Partial DOS of the dimerized V site in the low-temperature phase, and (c) partial DOS of the non-dimerized V site in the low-temperature phase.

assumed in the present calculation. We assume the crystal structure reported in Ref. [13] for the the high-temperature phase and that reported in Ref. [7, 8] for the low-temperature phase. We note that in the high-temperature phase there are 4 V ions (or 12 $t_{2g}$ bands) with 5 3$d$ electrons in the unit cell and in the low-temperature phase there are 16 V ions (or 48 $t_{2g}$ bands) with 20 3$d$ electrons in the unit cell. Preliminary results for the high-temperature phase obtained without $U$ were given in Ref. [14].

The calculated results are shown in Figs. 2 and 3. First, we note that the partial density of states (DOS) (see Fig. 3) indicate that the 3$d$ electrons almost solely occupy the $d_{xy}$ orbitals both in high- and low-temperature phases. The calculated band dispersion (see Fig. 2(a)) indicates that there are 4 bands coming from the V $3d_{xy}$ orbitals, which are nearly one-dimensional along the chain direction. Then, in the low-temperature phase, the partial DOS of the dimerized V ions shown in Fig. 3(b) indicates that there occurs the bonding-antibonding splitting due to
the bond alternation of V ions. On the other hand, those of the non-dimerized V ions do not show any splitting and have a peak in DOS at the Fermi level (see Fig. 3(c)). A band gap appears between the lower 8 bands filled with 16 electrons and upper 8 bands filled with extra 4 electrons where the Fermi level is located. The calculated numbers of d electrons inside the muffin-tin spheres are almost the same among 6 independent V sites and thus there is no charge and orbital orderings detected in the present GGA+U approximation. However, it seems quite natural to assume that the $d_{xy}$ orbital can accommodate at most only one electron due to the strong Coulomb repulsion, which results in a half-filled Mott-insulating chains of the $d_{xy}$ orbitals. This implies that the Fermi level shifts down into the gap, emptying the upper bands, and these extra d electrons are moved to the $d_{yz}$ and $d_{zx}$ orbitals. Because these two orbitals are exactly degenerate in the high-temperature phase, we may expect that there occurs a phase transition accompanying the charge and orbital orderings, which leads to the localization of the electrons in the low-temperature phase. Further studies need to be explored, which will be presented in our forthcoming paper [15].

3. Summary
We have made the electronic structure calculations of $K_2V_8O_{16}$ using GGA+U, where we have assumed the experimentally determined low-temperature crystal structure. We have found that the wave function near the Fermi level are predominantly of the $d_{xy}$ character and form the quasi-one-dimensional energy bands and that the energy bands are made of the single chains of the VO$_6$ octahedra rather than the double chains. We have suggested the mechanism of the metal-insulator transition of this system based on the idea of possible charge and orbital orderings.

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