## Observation of Metal–Insulator Transition in Hollandite Vanadate, K<sub>2</sub>V<sub>8</sub>O<sub>16</sub>

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We have synthesized hollandite vanadate,  $K_2V_8O_{16}$ , by a solid-state reaction under 4 GPa at 1473 K for one hour, and investigated its structural and electromagnetic properties. We found a metal-insulator transition with a two-step jump of resistivity of about three orders at around 170 K. The magnetic susceptibility is reduced to a small value at the transition, suggesting the formation of  $V^{4+}-V^{4+}$  singlet pairs and  $V^{3+}-V^{3+}$  pairs in the low-temperature insulator phase. The transition is of first order accompanied by a structural change from a tetragonal to a monoclinic structure. The low-temperature phase has a superlattice of  $\sqrt{2}a \times \sqrt{2}a \times 2c$ , where *a* and *c* denote the parameters of the primitive cell for the simple tetragonal hollandite structure, suggesting a charge ordering of  $V^{4+}$  and  $V^{3+}$ . We construct a possible charge order model from the obtained results, in which two kinds of double-chain formed by  $V^{3+}$  and  $V^{4+}$  chains and by single  $V^{4+}$  chains order in a manner that gives a superlattice of  $\sqrt{2} \times \sqrt{2}$  in the *a*-*b* plane. The  $V^{4+}-V^{4+}$  and  $V^{3+}-V^{3+}$  pairs are formed in each chain along the *c*-axis, resulting in a duplication of the *c*-axis.

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Since 1949 when a metal-insulator (MI) transition was first observed in V2O3 by Foëx,1) vanadium oxides have been a central material in the study of strongly correlated electrons. Many compounds exist in a binary V-O system, many of which show MI transitions as a function of temperature.<sup>2,3)</sup> The MI transitions in mixed-valent vanadium oxides such as V<sub>4</sub>O<sub>7</sub> are accompanied by charge separation and charge order.<sup>4,5)</sup> In their low-temperature insulator phases, spin singlet V<sup>4+</sup>–V<sup>4+</sup> pairs are formed, resulting in a large reduction in magnetic susceptibility at the MI transitions.<sup>4,5)</sup> In the extension of our study on vanadium oxides to ternary systems, two (MI and YU) of the authors reported ternary  $AV_2O_5$  (A = Li, Na, Cs, Mg, and Ca) which are insulators and quantum spin systems.<sup>6–8)</sup> The monovalent V<sup>4+</sup>-compounds, MgV<sub>2</sub>O<sub>5</sub> and CaV<sub>2</sub>O<sub>5</sub>, are spin singlets in the ground state, which originates from the geometry of the structure, that is, the trellis lattice with two leg ladders.<sup>9,10)</sup> On the other hand, mixed-valent compounds  $(A = \text{Li},^{7,11})$ Na,<sup>6)</sup> Cs<sup>7)</sup>) with  $V^{4+}/V^{5+} = 1$  are low-dimensional magnets. In particularly, the discovery<sup>6)</sup> of a spin-Peierls-like transition in NaV<sub>2</sub>O<sub>5</sub> triggered an explosion of worldwide research on  $NaV_2O_5$ . It is now established that the transition in NaV<sub>2</sub>O<sub>5</sub> is a charge-order transition accompanied by the formation of a spin gap.<sup>12,13</sup> The research on NaV<sub>2</sub>O<sub>5</sub> reached a peak at the discovery of the "devil's flower"-type pressure-temperature (P-T) phase diagram.<sup>15)</sup> Another series of ternary vanadium oxides is the  $\beta$ -vanadium bronzes  $A_xV_2O_5$  (A = Li, Na, Ag, Ca, Sr, Pb). We found MI transitions as a function of temperature in  $\beta$ -A<sub>0.33</sub>V<sub>2</sub>O<sub>5</sub> (A = Li, Na, Ag, Ca, Sr).<sup>16–18)</sup> Interestingly we discovered pressure-induced superconductivity in  $\beta$ - $A_{0.33}$ V<sub>2</sub>O<sub>5</sub> (A = Na, Ag).<sup>19,20)</sup> The charge-ordered insulator phases are suppressed under hydrostatic pressure, and the superconducting phases adjacent to the charge-ordered phases appear at around 9K and 8 GPa for A = Na and 8 K and 7 GPa for  $A = Ag.^{19,20)}$ The obtained P-T phase diagrams are similar to those of other superconducting systems,  $f^{-21,22}$  and  $\pi$ -electron<sup>23)</sup> systems, except for the magnetic ordered phases adjacent to the superconducting phases in the f- and  $\pi$ -electron systems.

We have been continuously engaged in the development of new vanadium oxides. Our next target is the development of hollandite vanadium oxides because a series of isostructural compounds will enable us to systematically investigate their structural and physical properties. "Hollandite" is one of the manganese minerals. Its structure was determined in 1950.<sup>24)</sup> Hollandite-type compounds have the general chemical formula  $A_x M_8 O_{16}$  ( $x \le 2$ ). Its structure consists of a tubular  $M_8 O_{16}$  network and A-cations at the tunnel sites of the  $M_8 O_{16}$  framework, as shown in Fig. 1. The  $M_8 O_{16}$ framework is constructed of double-chains, and each doublechain is formed by the sharing of the edges of the  $MO_6$ octahedra. The  $M_8 O_{16}$  network has rectangular tubes surrounded by four double-chains and A-cations occupy the sites within each rectangular tube.

Some hollandite vanadium oxides with  $A = K^{25,26}$  Ba,<sup>27)</sup> Bi,<sup>28-30)</sup> Pb<sup>31)</sup> and Tl<sup>26)</sup> have been reported. Among them, only the A = Bi compound, in which the MI transition was observed, has been studied in detail.<sup>28-30)</sup> The compounds with A = K and Tl were synthesized under the high pressure of about 3 GPa. The first report on K<sub>2</sub>V<sub>8</sub>O<sub>16</sub> was by Okada *et al.* in 1978.<sup>25)</sup> They reported a semiconductor–semiconductor–like transition and an anomaly in the magnetic susceptibility possibly caused by an antiferromagnetic transition.<sup>16)</sup> There has been no report on K<sub>2</sub>V<sub>8</sub>O<sub>16</sub> since then. We successfully obtained K<sub>2</sub>V<sub>8</sub>O<sub>16</sub> by high-pressure synthesis and observed an MI transition at 170 K. In this letter, we report the structural and electromagnetic properties of K<sub>2</sub>V<sub>8</sub>O<sub>16</sub>.

Powder samples of  $K_2V_8O_{16}$  were prepared by a solidstate reaction of  $KVO_3$ ,  $V_2O_3$  and  $V_2O_5$  under 4 GPa at



Fig. 1. (a) Schematic crystal structure of tetragonal  $K_2V_8O_6$  viewed from *c*-direction and (b) schematic illustration of double-chain made up of corner- and edge-sharing VO<sub>6</sub> octahedra (gray polyhedra). The  $V_8O_{16}$ framework is formed by the sharing of the edges of VO<sub>6</sub> octahedra with the double-chains, and K<sup>+</sup> ions (filled circles) occupy the tunnel sites surrounded by the double-chains.

1473 K for one hour. Starting reagents were ground thoroughly and the mixture was wrapped in platinum foil and put into a pressure cell. KVO<sub>3</sub> was obtained by a reaction of  $K_2CO_3$  and  $V_2O_5$ .  $V_2O_3$  was prepared by reducing of  $V_2O_5$ under a H<sub>2</sub> gas flow at 1173 K. A cubic-type apparatus was used for the high-pressure synthesis. Sample identification and the determination of the lattice parameters were performed using powder X-ray diffraction. Very small single crystals were found in the sintered sample. The typical size of a crystal was  $0.1 \times 0.1 \times 0.4 \text{ mm}^3$ . The structure analysis was performed by X-ray diffraction of the obtained single crystal using an imaging plate Weissenberg camera. The electrical resistivity was measured along the *c*-axis by a conventional four-probe method using a single crystal. The magnetic susceptibility of the powdered sample was measured using a superconducting quantum interference device (SQUID) magnetometer.

The powder X-ray diffraction pattern of the obtained K<sub>2</sub>V<sub>8</sub>O<sub>16</sub> shows a typical tetragonal hollandite structure at room temperature. The crystal symmetry determined by single-crystal X-ray diffraction is the space group of I4/m and the lattice parameters are a = 9.9455(1)Å and c =2.9116(1) Å at room temperature, in agreement with the previous report.26) The composition of K ions was determined from single-crystal X-ray diffraction to be almost stoichiometric. Temperature dependences of electrical resistivity and magnetic susceptibility are shown in Figs. 2(a) and 2(b), respectively. We first found a MI transition with a two-step jump of resistivity at about three orders at around 170 K ( $T_{\rm MI}$ ). The resistivity behavior above  $T_{\rm MI}$  is that of a typical metal, which is in disagreement with the previous report.<sup>25)</sup> Such a discrepancy might be ascribed to the quality of the crystals. The MI transition is accompanied by a gradual reduction in magnetic susceptibility from 175 to 150 K. The two-step transition observed in the electrical resistivity was not clearly seen in the magnetic susceptibility measured using the powdered sample. The magnetic susceptibility showed an increase at low temperatures, which obeys the Curie law. The obtained Curie constant corresponds to about 4.5% impurity with S = 1/2. After the



Fig. 2. (a) Temperature dependence of resistivity measured along *c*-axis in single crystal  $K_2V_8O_6$ . (b) Temperature dependence of magnetic susceptibility for powder  $K_2V_8O_6$ . The solid line shows the magnetic susceptibility derived by subtracting the Curie term in the low-temperature region from the raw data.

subtraction of the Curie tail from the raw data, the magnetic susceptibility is almost constant below 150 K, as shown in Fig. 2(b). Both curves of resistivity and magnetic susceptibility show significant hysteresis at the transition, which indicates a first-order transition. The X-ray diffraction pattern at 100 K below  $T_{\rm MI}$  can be indexed to a pseudoorthorhombic structure, or more precisely, a monoclinic structure with  $\beta \sim 90.07^{\circ}$ . It was difficult, however, to determine the crystal symmetry of the low-temperature phase because the diffraction spots were split into some spots across the MI transition, which may be due to the firstorder transition. The temperature dependences of the lattice constants obtained from powder X-ray diffraction are shown in Fig. 3. The X-ray diffraction pattern shows the coexistence of the two phases through the transition, indicating a first-order transition. Below  $T_{\rm MI}$ , the *a-b* plane in the tetragonal structure shrinks and the c-axis extends, resulting in an increase of volume of about 0.14%. Furthermore, from a single-crystal X-ray photograph using an imaging plate Weissenberg camera, we observed superreflections associated with a supercell of  $\sqrt{2}a \times \sqrt{2}a \times 2c$ , where a and c denote the primitive cell for the simple tetragonal hollandite structure. We also observed the splitting of diffraction spots through the transition in the X-ray diffraction pattern, which implied a two-step transition from tetragonal to monoclinic



Fig. 3. Temperature dependences of lattice constants for  $K_2V_8O_6$ . The crystal structure changes from a tetragonal structure in the high-temperature phase to a monoclinic structure in the low-temperature phase. The monoclinic *b*-axis corresponds to the tetragonal *c*-axis.

and then from monoclinic to monoclinic upon cooling. However, it was difficult to determine the precise structure of the intermediate- and low-temperature phases because the crystal was split into diffrent domains across the transition. The origin of the two-step transition is still unknown.

Many binary vanadium oxides show MI transitions accompanied by the reduction in magnetic susceptibility, as mentioned above. In some oxides, such as  $V_2O_3^{32,33}$  and V<sub>8</sub>O<sub>15</sub>,<sup>34)</sup> antiferromagnetic transitions occur simultaneously MI transitions, whereas in other oxides, such as  $V_n O_{2n-1}$ (n = 4, 5, 6),<sup>35,36)</sup> MI transitions are followed by antiferromagnetic transitions below  $T_{\rm MI}$ . Furthermore, the MI transitions in  $V_n O_{2n-1}$  are accompanied by the charge separation and charge ordering of  $V^{4+}$  and  $V^{3+}$ .<sup>4,5)</sup> The reduction in magnetic susceptibility at the MI transitions in  $V_n O_{2n-1}$ originates from the formation of  $V^{4+}-V^{4+}$  spin-singlet pairs and  $V^{3+}-V^{3+}$  pairs. We cannot confirm whether the reduction in magnetic susceptibility at the MI transition in  $K_2 V_8 O_{16}$  is due to an antiferromagnetic transition or to the formation of  $V^{4+}-V^{4+}$  spin-singlet pairs and  $V^{3+}-V^{3+}$  pairs; nevertheless, we consider the latter to be plausible because of the rather small magnetic susceptibility, about  $5 \times 10^{-4}$ (emu/V-mol), of the insulator phase. The superlattice of  $\sqrt{2}a \times \sqrt{2}a \times 2c$  observed in the low-temperature phase of  $K_2V_8O_{16}$  suggests charge ordering. Taking these results into consideration, we propose a possible charge-ordered model, as shown in Fig. 4. In this model, there are two kinds of double-chain: one (A) is formed by  $V^{3+}O_6$  and  $V^{4+}O_6$ chains and the other (B) is formed by only  $V^{4+}O_6$  chains. Four A and B double-chains form two kinds of rectangular tube, respectively. These tubes are ordered in the manner shown in Fig. 4. This model satisfies the ratio of  $V^{4+}/V^{3+} =$ 3/1 and forms the superlattice of  $\sqrt{2} \times \sqrt{2}$  in the *a*-*b* plane. Furthermore the  $V^{4+}-V^{4+}$  and  $V^{3+}-V^{3+}$  pairs are formed in



Fig. 4. Model of charge order in low-temperature phase of  $K_2V_8O_6$ . Where two kinds of rectangular tube formed by two kinds of doublechain, A and B, are ordered in a checkerboard pattern, giving a superlattice of  $\sqrt{2} \times \sqrt{2}$  in the *a*-*b* plane. The double-chains A and B are made up of V<sup>3+</sup>O<sub>6</sub> and V<sup>4+</sup>O<sub>6</sub> octahedral chains and by only V<sup>4+</sup>O<sub>6</sub> octahedral chains, respectively. In each chain, V<sup>4+</sup>-V<sup>4+</sup> and V<sup>3+</sup>-V<sup>3+</sup> pairs are formed along the *c*-axis, resulting in a duplication of the *c*-axis.

each chain along the *c*-axis, resulting in a duplication of the *c*-axis.

In summary, we have successfully synthesized hollandite vanadate,  $K_2V_8O_{16}$ , by a solid-state reaction under 4 GPa at 1473 K for 1 h, and measured its electrical resistivity, magnetic susceptibility and structure as functions of temperature. We found a MI transition with a two-step jump of resistivity of about three orders at around 170 K. The transition is accompanied by a reduction in magnetic susceptibility to a small value, suggesting the formation of  $V^{4+}-V^{4+}$ spin-singlet pairs and  $V^{3+}-V^{3+}$  pairs in the low-temperature insulator phase. The transition is of first order and accompanied by a structural change from a tetragonal to a monoclinic structure. The low-temperature phase has a superlattice of  $\sqrt{2a} \times \sqrt{2a} \times 2c$ , where a and c denote the parameters of the simple tetragonal cell, suggesting a charge ordering of  $V^{4+}$  and  $V^{3+}$ . We propose a possible chargeorder model, in which two kinds of rectangular tube are ordered in a checkerboard pattern, giving a superlattice of  $\sqrt{2} \times \sqrt{2}$  in the *a*-*b* plane. The two kinds of rectangular tube consist of two kinds of double-chain formed by V<sup>3+</sup> and  $V^{4+}$  chains and by only  $V^{4+}$  chains.  $V^{4+}-V^{4+}$  and  $V^{3+}-V^{3+}$ pairs are formed in each chain along the *c*-axis. resulting in a duplication of the *c*-axis.

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