Discovery of Ferromagnetic-Half-Metal-to-Insulator Transition in K₂Cr₈O₁₆

Kunihiro Hasegawa,¹ Masahiko Isobe,¹ Touru Yamauchi,¹ Hiroaki Ueda,¹ Jun-Ichi Yamaura,¹ Hirotada Gotou,²

Takehiko Yagi,² Hirohiko Sato,³ and Yutaka Ueda^{1,*}

¹Materials Design and Characterization Laboratory, Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan

²Division of New Materials Science, Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan

³Department of Physics, Chuo University, Tokyo 112-8551, Japan

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The hollandite chromium oxide $K_2Cr_8O_{16}$ has been synthesized in both powder and single-crystal form under high pressure. Combining electrical resistivity, magnetic susceptibility, and x-ray diffraction, we found that $K_2Cr_8O_{16}$ is a ferromagnetic metal (or half-metal) with $T_C = 180$ K and shows a transition to an insulator at 95 K without any apparent structural change but retaining ferromagnetism. $K_2Cr_8O_{16}$ is quite unique in three aspects: It has a rare mixed valence of Cr^{3+} and Cr^{4+} ; it has a metal (or half-metal)to-insulator transition in a ferromagnetic state; and the resulting low-temperature phase is a rare case of a ferromagnetic insulator. This discovery could open a new frontier on the relation of magnetism and conducting properties in strongly correlated electron systems.

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The metal-insulator (M-I) transition has been a central issue in strongly correlated electron systems [1]. There are two types of M-I transitions. One is the M-I transition as a function of the doping level, which is generally controlled by chemical substitution. The best example is hightemperature superconductivity in cuprates, which is brought by carrier doping into an antiferromagnetic insulator (AFI). In perovskite manganites, hole doping to an AFI drives into the ferromagnetic metal (FM) generated by the double exchange interaction [2]. In general, this type of M-I transition is observed as a crossover. The other is the M-I transition as a function of temperature, as is the present case. This type of M-I transition occurs drastically as it is often accompanied by structural change, charge order, orbital order, and/or magnetic order. Vanadium oxides are prominent compounds with this type of M-I transition. The typical examples are a paramagnetic-metal (PM)-to-AFI transition in V₂O₃ and a PM to spin-singlet insulator transition in VO₂ [1]. The intermediate compounds $V_n O_{2n-1}$ (n = 4, 5, 6, 8) with mixed valences of V³⁺ and V⁴⁺ also show first order M-I transitions, accompanied by the charge order and the formation of spin-singlet V^{4+} – V^{4+} pairs [3–5]. The M-I transitions with a charge ordering nature have also been found in ternary vanadium oxides: β -vanadium bronzes $\beta - A_{0.33}V_2O_5$ (A = Li, Na, Ag, Ca, Sr) [6,7]. The first superconductivity in vanadium oxides was discovered as the superconducting state next to the charge ordered AFI in the pressure-temperature phase diagrams of $\beta - A_{0.33}V_2O_5$ (A = Li, Na, Ag) [8– 10]. Recently, we found a similar M-I transition in the hollandite vanadium oxide $K_2V_8O_{16}$ with the isostructure of the titled compound [11]. Viewing these M-I transitions, we find that the insulator phases have antiferromagnetic orders or spin-gapped states and there is no FM-to--ferromagnetic-insulator (FI) transition. Strongly correlated electron systems including the wide class of transition-

metal oxides exhibit a quite general relation between magnetic order and electrical conductivity [12]: Ferromagnetism typically coexists with metallic conductivity, whereas insulators usually exhibit antiferromagnetism. It is always a challenge to understand exceptions from this rule. The close relation of the ferromagnetism metal and antiferromagnetism insulator is also seen in chromium oxides $Cr_2^{3+}O_3$ (AFI), $Cr^{4+}O_2$ (FM), and $Ba_3Cr_2^{5+}O_8$ (spingapped insulator with antiferromagnetic correlation) [13]. Very recently, the exception of an antiferromagnetic metal was found in CaCr⁴⁺O₃ [14].

In this Letter, we report the discovery of a rare mixedvalent chromium oxide with metallic conductivity, ferromagnetic order at 180 K, and a M-I transition at 95 K: the hollandite K₂Cr₈O₁₆. K₂Cr₈O₁₆ is quite unique in the aspect that it has a metal (or half-metal)-to-insulator transition in a ferromagnetic state, and the resulting lowtemperature phase is a rare case of a ferromagnetic insulator. K₂Cr₈O₁₆ is also unique in the formal valence of $2Cr^{3+} + 6Cr^{4+}$. Cr^{3+} and Cr^{4+} are very different in the stable atmosphere: Cr^{3+} is stable in the wide range from a reducing to ordinary oxidizing atmosphere, while Cr^{4+} is produced only in the extreme atmosphere with high oxygen pressure ~0.1 GPa. Therefore Cr^{4+} hardly coexists with Cr^{3+} , in general.

The first report on hollandite $K_2Cr_8O_{16}$ was done by Endo *et al.* in 1976 [15]. They reported high-pressure synthesis, a monoclinic structure, and a ferromagnetic order at 225 K. After a long time, Tamada *et al.* settled the crystal structure of a tetragonal I4/m symmetry [16]. There has been no report on $K_2Cr_8O_{16}$ except these two reports; particularly, there has been no information on transport properties.

The hollandite-type compounds have a general chemical formula $A_x M_8 O_{16}$ ($x \le 2$). The crystal structure consists of the $M_8 O_{16}$ framework and A cations, as shown in the inset

in Fig. 1. The M_8O_{16} framework is constructed from the double chains formed by sharing the edges of MO_6 octahedra. The M_8O_{16} framework has rectangular tubes surrounded by four double chains running along the *c* axis, and *A* cations occupy the sites within each rectangular tube and act as an electron donor. The most popular crystal symmetry is a tetragonal I4/m in which the crystallographically independent *M* site is unique.

Polycrystalline $K_2 Cr_8 O_{16}$ samples were prepared by a solid state reaction of a mixture with the ratio of $K_2Cr_2O_7:Cr_2O_3 = 1:3$ under 6.7 GPa at 1273 K for 1 h. Our original sample assembly with the mixture sandwiched by excess $K_2Cr_2O_7$ successfully gave single crystals of K₂Cr₈O₁₆, where K₂Cr₂O₇ worked as a self-flux. Under such high-pressure synthesis, the sample obtained at one time was limited to a small amount (less than 100 mg). The obtained powder samples always include a varying amount of the impurity $CrO_2(\sim 5\%)$. Close inspection showed that single-crystalline grains of up to 1 mm in length (along the c axis) and 50 μ m in diameter were obtained by this procedure. The sample characterizations at room temperature and temperature dependence of lattice parameters between 10 and 300 K have been carried out by powder x-ray diffraction. X-ray single-crystal structure analysis confirmed the close to perfect stoichiometry of our samples and a tetragonal I4/m crystal structure with a = 9.7792(7) Å and c = 2.9379(3) Å at room temperature, agreeing with the previous report [16]. The magnetic susceptibility and magnetization were measured by a SQUID magnetometer. The electric resistivity was measured by a dc four-point method on a single-crystal along the c axis.



FIG. 1 (color online). Temperature dependence of magnetization (*M*) measured by using a powder sample at H = 0.1 T in the zero-field cooling process. The inverse of magnetic susceptibility $[1/(\chi - \chi_0)]$ and the magnetization (*M*) of single crystals at H = 0.05 T are also plotted as a function of temperature. The inset shows an illustration of a crystal structure for the hollandite $A_x M_8 O_{16}$ ($x \le 2$) viewed along the *c* axis in a tetragonal I4/m structure.

The temperature dependence of magnetization M(T)measured by using powder samples of K₂Cr₈O₁₆ under a magnetic field (H) of 0.1 T is shown in Fig. 1. The M(T) sharply increases with decreasing temperature below 180 K and tends to saturate below 130 K, signifying a ferromagnetic transition around $T_C = 180$ K. The $T_C = 180$ K is somewhat lower than the reported $T_C = 225$ K [15]. In the previous report [15], the $T_C =$ 225 K was deduced from the M(T) curve measured at a rather high field of H = 1 T. This is probably a reason for their overestimation of $T_C = 225$ K. Actually, almost the same M(T) curve at H = 1 T was obtained in the present study. The field dependence of magnetization M(H) at 5 K is shown in Fig. 2. The M(H) draws a hysteresis curve little, indicating a soft magnet. The net magnetization of K2Cr8O16 was obtained by subtracting the contribution of impurity CrO₂ which was estimated from the M(H) curve at 300 K (Fig. 2). The thus obtained value of $17.7 \mu_B/8$ Cr is very close to a full moment of $18\mu_B/8$ Cr, $\{2$ Cr³⁺ $(d^3) + 6$ Cr⁴⁺ $(d^2)\}$, agreeing with the previous report [15]. Because of the coexistence of ferromagnetic impurity CrO₂, it was difficult to fit the magnetic susceptibility $\chi(T)$ to a Curie-Weiss (CW) law in the paramagnetic state. Then we tried to measure $\chi(T)$ by using single crystals. The thus obtained $\chi(T)$ and M(T) at H = 0.05 T are shown in Fig. 1. Here the sample molar was estimated from the saturated value of magnetization at 5 K in the ferromagnetic state, because the sample weight was inaccurate due to the limitation of rather small amounts (~ 0.4 mg) of small single crystals. The $\chi(T)$ can be fitted to a CW law: $\chi(T) = C/(T - \theta) + C$ χ_0 above 200 K, as represented by a linear relation of $1/(\chi - \chi_0)$ vs T plot in Fig. 1. The Weiss temperature $\theta =$ 175 K is consistent with $T_C = 180$ K. On the other hand, the Curie constant $C = 8.1 [\text{emu}/(\text{Cr mol})] \text{ K}(\sim 7\mu_B/\text{Cr})$



FIG. 2 (color online). Magnetic field dependences of magnetization (*M*) of a powder sample at 5 and 300 K. The magnetization curve at 300 K consists of a paramagnetic component of $K_2Cr_8O_{16}$ and a ferromagnetic component of impurity CrO_2 .

is much larger than the calculated value of 1.19 [emu/(Cr mol)]K (2.25 μ_B/Cr) from the averaged valence of Cr^{3.75+}. Such enhanced Curie constants have often been observed in itinerant ferromagnetic systems and understood in terms of ferromagnetic spin fluctuation [17]. As described below, the present study reveals that $K_2Cr_8O_{16}$ is a ferromagnetic metal (or half-metal). The ratios of magnetic moments $7\mu_B/2.25\mu_B = 3.1$ and $T_C = 180$ K for K₂Cr₈O₁₆ are comparable to those of the ferromagnetic metal Pd-Co or Pd-Fe alloy and are located on the universal line in a Rhodes-Wohlfarth plot, suggesting ferromagnetic spin fluctuation as an origin for the observed enhancement of the Curie constant [17]. The large temperature independent term $\chi_0 = 9.5 \times$ 10^{-3} emu/(Cr mol) would be associated with the itinerant band in a two-band system which is predicted from the band calculation [18]. However, it should be noted that these obtained magnetic parameters include considerable ambiguity due to the small absolute value of magnetization with a small amount of samples and due to the narrow fitting temperature range.

The electric resistivity $\rho(T)$ measured along the *c* axis by using a needlelike single crystal is shown in Fig. 3. The $\rho(T)$ at room temperature is less than $10^{-2} \Omega$ cm. On cooling from 300 K, the $\rho(T)$ once decreases, then turns to a gradual increase around 250 K, and shows a jump around 95 K, followed by the sharp increase up to $\sim 10^3 \Omega$ cm (the upper limit in our measurement system) at 30 K. There is no observable hysteresis around 95 K. The $\rho(T)$ between 95 and 250 K does not obey any activation type, indicating that the electronic state is not semiconductive. The absolute value of $\rho(T)$ is comparable to that of a half-metal, as predicted from the band calculation [18]. Although the origin for its negative temperature depen-



FIG. 3 (color online). Temperature dependence of resistivity (ρ) measured along the *c* axis, which clearly indicates a metal (or half-metal)-to-insulator transition at 95 K. The inset shows the magnetoresistance effect around the ferromagnetic transition temperature $T_C = 180$ K, where the resistivities at various fields are normalized to that at zero field (H = 0 T).

dence is still unknown, the behavior might be understood as a polaronic conductivity or a quasi-one-dimensional conductivity influenced by inevitable defects in the crystal. Now the $\rho(T)$ behavior clearly shows a M-I (or half-metalto-insulator) transition at $T_{M-I} = 95$ K. To elucidate any relation between magnetic and electrical properties, we carefully inspected M(T) and $\rho(T)$ around $T_C = 180$ K and $T_{M-I} = 95$ K. The $\rho(T)$ curve of K₂Cr₈O₁₆ does not show any anomaly around T_C under no magnetic field; however, a slight magnetoresistance effect has been observed around T_C , as shown in the inset in Fig. 3. On the other hand, the M(T) curve at H = 0.05 T shows a clear bend around 95 K, as shown in Fig. 1, signifying any relation to the M-I transition.

To investigate any structural transition at T_{M-I} or T_C in K₂Cr₈O₁₆, powder x-ray diffraction was measured as a function of temperature. Neither splitting of the diffraction peak nor additional peak has been observed. X-ray diffraction patterns can be indexed by a tetragonal *I*4/*m* symmetry in the whole temperature range measured (10–300 K). The temperature dependence of lattice parameters is shown in Fig. 4. The *a* axis smoothly decreases on cooling, and the *c* axis is almost constant in the measured temperature range. However, the sudden change $\rho(T)$ at 95 K suggests any structural modifications, and therefore synchrotron x-ray diffraction by using a single crystal is now planned to elucidate any local structure modification and/or any superstructures.

Now an anomalous FM-FI transition compound, the hollandite $K_2Cr_8O_{16}$, has been unveiled. M-I transitions as a function of temperature, in general, are coupled with charge, orbital, spin, and/or lattice degrees of freedom. $K_2Cr_8O_{16}$ with a mixed valence of $Cr^{3+}/Cr^{4+} = 1/3$ has both charge and orbital degrees of freedom in addition to spin and lattice degrees of freedom. Thermodynamics tells us that charge, orbital, and spin degrees of freedom on electrons freeze as the temperature is lowered. In most cases, the charge and/or orbital degrees of freedom first freeze, and at the same time or next the spin degree of



FIG. 4. Temperature dependences of lattice parameters (a, c, and unit volume) in a tetragonal structure with I4/m symmetry.

freedom freezes in insulating phases. The magnetic transition followed by a M-I transition in $K_2Cr_8O_{16}$ is a very rare case. One exception is a FM to charge ordered insulator transition in perovskite manganites [2]. Here it should be emphasized that this M-I transition in perovskite manganites is accompanied by a drastic structural change, and the resulting charge ordered insulator phase has an antiferromagnetic order [2]. The M-I transition in the ferromagnetic state of $K_2Cr_8O_{16}$ is a very rare case. In this case, the possibility of charge order as an origin of the M-I transition might be ruled out by the experimental results of the surviving ferromagnetic order and the absence of apparent structural change across the M-I transition. Furthermore, the difficulty of charge separation into Cr³⁺ and Cr^{4+} may arise from the chemical reason that the stable atmosphere is very different between Cr³⁺ and Cr^{4+} . $K_2Cr_8O_{16}$ is a rare oxide in which the thermodynamical demand to charge order is depressed by the chemical (valence) instability. As another origin, the sudden M-I transition seems to call any orbital order to mind. Orbital ordering often leads the system to insulator. Almost all orbital order driven M-I transitions, however, are firstorder structural transitions, and they are often accompanied by the sudden reduction of $\chi(T)$, indicating the spingapped low-temperature insulator phases [19-21]. The M-I transition of K₂Cr₈O₁₆ does not have such characteristics; nevertheless, a possibility of an orbital order driven M-I transition would not be entirely ruled out for the limited examples. If the origin for the M-I transition in K₂Cr₈O₁₆ is an orbital order, it is a very challenging problem what orbital order guarantees the electron localization retaining ferromagnetic order.

Finally, we compare three hollandite compounds with the isostructure: $K_2Ti_8O_{16}$, $K_2V_8O_{16}$, and $K_2Cr_8O_{16}$. $K_2 Ti_8 O_{16}$ is a Pauli-paramagnetic metal and does not show any transition down to the lowest temperature [22]. $K_2V_8O_{16}$ shows a M-I transition with the structural change; the high-temperature metallic phase shows a CW-type $\chi(T)$ with an antiferromagnetic interaction, and the lowtemperature insulator phase is a spin-liquid state with $V^{4+} - V^{4+}$ spin-singlet pairs [11]. $K_2Cr_8O_{16}$ shows a CW-type $\chi(T)$ with a ferromagnetic interaction and actually exhibits a ferromagnetic order followed by the unexpected M-I transition. The compounds have the same mixed valence of $M^{3+}/M^{4+} = 1/3$ but have a different number of d electrons: 2 ($K_2Ti_8O_{16}$), 10 ($K_2V_8O_{16}$), and 18 ($K_2Cr_8O_{16}$), respectively. Therefore, similar band structures with a different filling level can be expected. Assuming a simple band structure (t_{2g} band), the low filling level in K₂Ti₈O₁₆ explains the Pauli-paramagnetic metal with a weak electron correlation. Further increase of the filling level may lead to a strong (antiferromagnetic) electron correlation in K₂V₈O₁₆, resulting in the M-I transition. On the other hand, K₂Cr₈O₁₆ can be regarded as a hole-doped system to a hypothetical band insulator with full occupancy of 24 electrons, and the FM can be understood from the double exchange mechanism. In this context, the transition to insulator keeping ferromagnetism is a surprising and unexpected phenomenon, because the ferromagnetism should guarantee the metallicity in the double exchange mechanism.

In summary, the hollandite chromium oxide $K_2Cr_8O_{16}$ has been synthesized in both powder and single-crystal form under high pressure. Combining electrical resistivity, magnetic susceptibility, and x-ray diffraction, we found that $K_2Cr_8O_{16}$ is a ferromagnetic metal (or half-metal) with $T_C = 180$ K and shows a metal (or half-metal)-to-insulator transition at $T_{M-I} = 95$ K without any apparent structural change but retaining ferromagnetism. To the best of our knowledge, this is the first example of a FM to FI transition. To understand this anomalous FM-FI transition, further investigation should be done both experimentally and theoretically.

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*yueda@issp.u-tokyo.ac.jp

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