

The structural study on the ferromagnetic metal-insulator transition of $\text{K}_2\text{Cr}_8\text{O}_{16}$

Akiko NAKAO¹, Yuki YAMAKI², Hironori NAKAO¹, Yoichi MURAKAMI¹, Kunihiro HASEGAWA³, Masahiko ISOBE³, Yutaka UEDA^{*3}

¹Institute of Materials Structure Science, KEK, Tsukuba, Japan

²Department of Physics, Tohoku University, Sendai, Japan

³Institute for Solid State Physics, University of Tokyo, Kashiwa, Japan

Introduction

$\text{K}_2\text{Cr}_8\text{O}_{16}$ is a ferromagnetic metal (FM) with $T_C = 180$ K and surprisingly this FM phase undergoes a transition to an insulator (FI) at $T_{\text{MI}} = 95$ K, retaining ferromagnetism [1]. We have performed X-ray diffraction experiments for the single crystal using synchrotron radiation source to detect any structural change associated with this unique ferromagnetic metal-insulator (MI) transition.

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The structure changes from a tetragonal $I4/m$ structure of the high temperature FM phase to a monoclinic $P112_1/a$ (or $P112_1/b$) structure of the low temperature FI phase at $T_{\text{MI}} = 95$ K. The unit cell becomes large as $\sqrt{2}a \times \sqrt{2}b \times c$, where a , b and c are the lattice parameters in the FM phases. In the FI phase, four Cr sites (Cr1 - Cr4), two K sites (K1 and K2) and eight oxygen sites (O1 - O8) become crystallographically inequivalent in contrast to unique Cr and K site and two O sites in the FM phase. Figure 1 shows the schematic structure of the FI phase. It is made of three kinds of double-chains (A, B and C) which are formed by edge sharing Cr1O_6 - Cr3O_6 (for A), Cr2O_6 - Cr2O_6 (for B) and Cr4O_6 - Cr4O_6 (for C) octahedra, respectively. These double-chains are interconnected each other through common corners (O1 - O4) of CrO_6 (Cr1O_6 - Cr4O_6) octahedra to form the Cr_8O_{16} -framework with tunnels. The hollandite structure has both large tunnels and narrow rutile-like tunnels running along the c -axis. There are two types of large tunnels occupied by K ions; one is surrounded by the double chains A and B, and the other is surrounded by the double chains A and C. These two types of large tunnels are arranged in a stripe manner along the a -axis, as shown in Fig. 1(a). On the other hand, all the narrow rutile-like tunnels (columns) are surrounded by common four CrO_6 (Cr1O_6 - Cr4O_6) chains, as shown in Fig. 1(b).

The average values of the Cr-O bond lengths for four Cr sites (Cr1-Cr4) are almost the same and the Cr valences estimated via the bond valence sum are the same within the experimental errors (≤ 0.03 electrons/Cr). This means that the metal-insulator (MI) transition in $\text{K}_2\text{Cr}_8\text{O}_{16}$ is accompanied by no charge separation/order. Instead, the characteristic Cr-O bond alternations along the c -axis are observed in the rectangular column formed by four CrO_6 (Cr1O_6 - Cr4O_6) chains. Such bond alternations indicate the tetramerization of Cr ions in the rectangular

column. These observed structural characteristics well coincide with a Peierls mechanism for the MI transition in the band calculations [2]; one extra electron is weakly localized in the Cr1 - Cr4 tetramer due to Peierls instability inherent in one dimensional electron system characterized by the rectangular column. The spatial arrangement of the rectangular columns with the tetramers has neither uniform type nor checkerboard type, but it has an unexpected stripe type, as shown in Fig.1(c). Such a stripe type arrangement would result from the competition between ferro-arrangement from lattice distortion and antiferro-arrangement from coulomb repulsion.

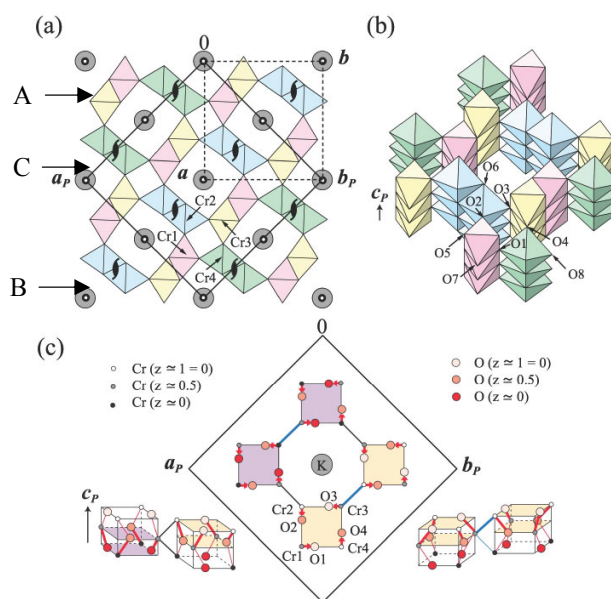


Fig. 1. (a) Crystal structure of $\text{K}_2\text{Cr}_8\text{O}_{16}$ at 20 K viewed from the c -axis. (b) Part of the crystal structure showing connection of the double Cr chains running along the c -axis. (c) Schematic illustration of the tetramerization. Thicker lines represent shorter Cr-O or Cr-Cr bonds.

References

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