

# Structural study of ferromagnetic metal-insulator transition in hollandite chromium oxide, $K_2Cr_8O_{16}$

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The hollandite oxides with the general chemical formula  $A_2M_8O_{16}$  ( $A$  = alkaline metal;  $M$  = transition metal) are a kind of mineral. They are mixed valent oxides with  $M^{3+}/M^{4+} = 1/3$  (an averaged valence of  $M^{3.75+}$ ). The crystal structure consists of the tubular  $M_8O_{16}$ -framework and  $A$ -cations at the tunnel sites of the  $M_8O_{16}$ -framework. The  $M_8O_{16}$ -framework is constructed from the double chains (zigzag-chains) formed by sharing the edges of  $MO_6$  octahedra. The chromium hollandite  $K_2Cr_8O_{16}$ , which at room temperature is tetragonal and a paramagnetic metal (PM), becomes ferromagnetic with  $T_C = 180$  K [1], which is explained by the double exchange mechanism [2], but surprisingly this ferromagnetic metal phase undergoes a transition to an insulator at lower temperature, retaining ferromagnetism. The metal-insulator transition (MIT) at  $T_{MI} = 95$  K is quite unique; 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 (FI). In order to elucidate this unique ferromagnetic MIT, it is crucial to study the crystal structure across the MIT.

The synchrotron X-ray diffraction study for the single crystal has revealed the structural distortion from tetragonal to monoclinic with  $\sqrt{2}a \times \sqrt{2}b \times c$ , where  $a$ ,  $b$  and  $c$  are the lattice parameters in the PM phase (Fig.1). In the FI phase, four Cr sites, two K sites and eight O sites become crystallographically inequivalent. Four Cr sites form the coupled four-chains running in the  $c$ -direction by sharing corner oxygen in the  $Cr_8O_{16}$ -framework. In this geometry, the alternations of Cr-Cr bond and Cr-O bond along the  $c$ -direction exist in the coupled four-chains, resulting in a weak tetramerization of the Cr ions. Such bond alternation could be responsible for the opening of band gap.

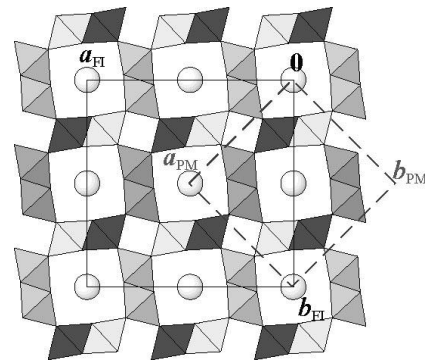


Fig.1 Crystal structure of  $K_2Cr_8O_{16}$  at 20 K viewed from  $c$ -axis.

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[2] Sakamaki M, Konishi T and Ohta Y, *Phys. Rev. B* **80** 024416 (2009).

[3] T. Toriyama, A. Nakao, Y. Yamaki, H. Nakao, Y. Murakami, K. Hasegawa, M. Isobe, Y. Ueda, A. V. Ushakov, D. I. Khomskii, S. V. Streltsov, T. Konishi, and Y. Ohta, *Phys. Rev. Lett.* in press.