Structural Study of the Unique Ferromagnetic Metal-Insulator Transition in Hollandite $K_2Cr_8O_{16}$

W e have studied the ferromagnetic metal-insulator transition occurring in hollandite $K_2Cr_8O_{16}$ by single crystal X-ray structure analysis. The transition is accompanied by structural distortion from a tetragonal $I4/m$ structure to a monoclinic $P2_1/a$ (or $P2_1/b$) structure with $\sqrt{2} \times \sqrt{2} \times 1$ unit cell. In the low temperature phase, Cr-O bond alternations occur in the rectangular column formed by the four CrO_6 chains (four-chain column), indicating a lattice dimerization with the formation of Cr-tetramer. The spatial arrangement of Cr-tetramer along the c-direction is of the stripe type. Such an arrangement would result from the competition between lattice distortion and coulomb repulsion.

Ferromagnetic insulator (FI) is extremely rare in transition-metal oxides; usually it is found in metallic systems and is caused by double exchange. Insulating ferromagnets are definitely not common among these materials. All the more surprising was the recent discovery [1] that chromium hollandite $K_2Cr_8O_{16}$ first becomes ferromagnetic at $T_c = 180$ K and with decreasing temperature, it experiences a metal-insulator transition (MIT) at $T_{MI} = 95$ K, and remains ferromagnetic at low temperature. $K_2Cr_8O_{16}$ is a mixed-valence oxide with $Cr^{3+}/Cr^{4+} = 1/3$ (an average valence of $Cr^{3.75+}$). In this study, we undertook a structural determination to elucidate this unique ferromagnetic MIT. Synchrotron X-ray diffraction experiments for the single crystal [2] were performed at BL-8A and 8B.

We first confirmed that the structure of the ferromagnetic metallic (FM) phase is isomorphous to that in the paramagnetic metallic (PM) phase, where all the Cr sites are crystallographically equivalent [Fig. 2 (a)]. Next, the structural change at T_{MI} was explored by oscillation photographs. Superlattice reflections with $q = (a^*/2, b^*/2, c^*)$ were clearly observed at 20 K ($< T_{MI}$), indicating that the unit cell becomes $\sqrt{2}a \times \sqrt{2}b \times c$ in the FI phase, where a, b and c are the lattice parameters in the PM and FM phases (Fig. 1). The intensity of superlattice reflections was 10^{-3} times weaker than that of fundamental reflections. Although peak splittings were not observed, the equivalent/inequivalent superlattice reflections showed $I(hkl) = I(\bar{h}k\bar{l}) \neq I(\bar{k}hl) = I(\bar{k}h\bar{l})$, which agrees with

the condition of the Laue class $2/m$, indicating a monoclinic structure. Finally, from a detailed analysis of the reflection conditions we concluded that the space group of the FI phase is $P112_1/a$. The transition is accompanied by symmetry breaking with the loss of the four-fold axis and the mirror plane perpendicular to the c axis.

The structure analysis was performed taking the twining structure which includes domains (a, b, c) and (b, $-a$, c). When the ratio of the twin volume fraction was 0.608(1) : 0.392, we obtained good reliability factors (R-factor = 0.025, R_w = 0.085). In the FI phase, four Cr sites, two K sites and eight O sites become crystallographically inequivalent in contrast to unique Cr and K sites and two O sites in FM and PM phases. The Cr valences estimated via bond valence sum are the same within experimental error ($\leq$0.03 electrons/Cr); the MI transition is accompanied by no charge separation/order. The four Cr sites form three kinds of double chains by sharing octahedral edges Cr1-Cr3, Cr2-Cr2 and Cr4-Cr4, respectively. Three kinds of double chains (A, B and C) are arranged such that the four Cr sites form a rectangular four-chain column by sharing corner oxygen atoms (Fig. 1)

At the same time the four-chain column has Cr-O bond alternations. This structural distortion can be understood as the formation of tetramers of Cr ions in c-direction in each of the four-chain columns; the lattice dimerization occurs in these four-chain columns [Fig. 2(b)].

In each of the four-chain columns short Cr-O bonds occur either at the upper or lower part of the unit cell along the c-direction. The monoclinic structure with $\sqrt{2} \times \sqrt{2} \times 1$ cell is realized as a stripe-like arrangement of these up and down four-chain columns along the diagonal direction (Fig. 3). As a consequence the double chain A has a Cr-Cr bond alternation, while the double chains B and C have no Cr-Cr bond alternation (see Fig. 1).

The observed structural characteristics well coincide with a Peierls mechanism for the metal-insulator transition proposed from electronic structure calculations [3]; one extra electron is weakly localized in the tetramer of Cr1-Cr4 due to a Peierls instability inherent in a one-dimensional electron system characterized by the rectangular four-chain column.

Figure 2
(a) Schematic illustrations of the four-chain columns for (a) the FM phase and (b) the FI phase. In the FI phase, the four-chain columns have Cr-O (Cr-Cr) bond alternations, indicating lattice dimerization with the formation of Cr-tetramers.

Figure 3
Schematic illustrations of structure with stripe-type arrangement.

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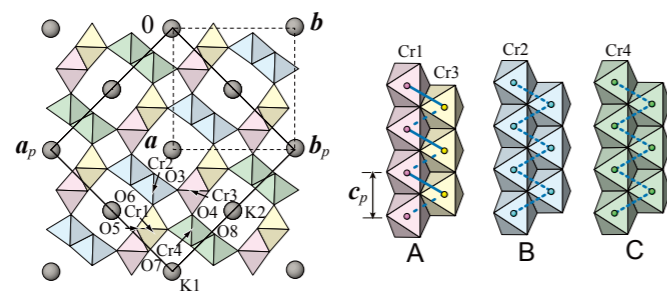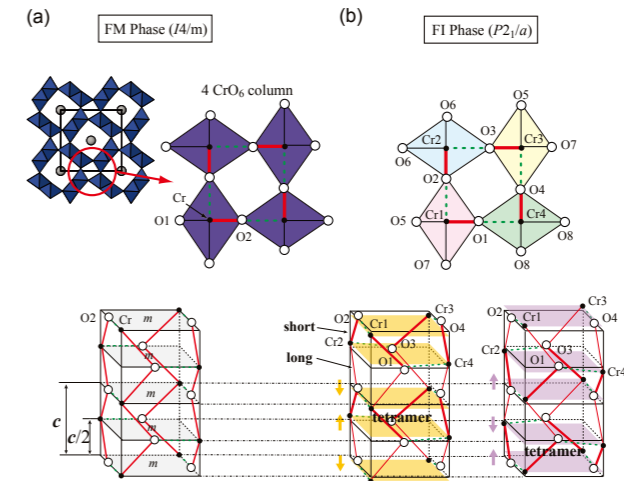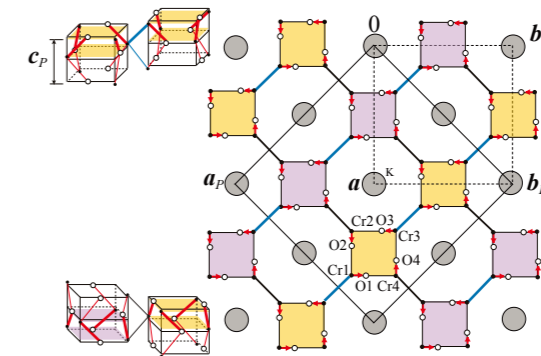

Figure 1
(left) Crystal structure of the ferromagnetic insulator phase in $K_2Cr_8O_{16}$ viewed from the c-axis. (right) Three kinds of double chains. In the structure, there are four Cr sites (Cr1 - Cr4).