Peierls Mechanism of the Metal-Insulator Transition in Ferromagnetic Hollandite \( \text{K}_2\text{Cr}_8\text{O}_{16} \)

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Synchronous x-ray diffraction experiment shows that the metal-insulator transition occurring in a ferromagnetic state of a hollandite \( \text{K}_2\text{Cr}_8\text{O}_{16} \) is accompanied by a structural distortion from the tetragonal \( I4/m \) to monoclinic \( P112_1/a \) phase with a \( \sqrt{2} \times \sqrt{2} \times 1 \) supercell. Detailed electronic structure calculations demonstrate that the metal-insulator transition is caused by a Peierls instability in the quasi-one-dimensional column structure made of four coupled Cr-O chains running in the \( c \) direction, leading to the formation of tetramers of Cr ions below the transition temperature. This provides a rare example of the Peierls transition of fully spin-polarized electron systems.

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Low-dimensional solids have attracted considerable attention in recent years. An interesting class of these materials, which has just started to be explored, is the so-called tunnel compounds. Typically, they are made of double MO chains (\( M \) is, e.g., a transition-metal element) with edge-sharing \( MO_6 \) octahedra, forming zigzag chains (triangular ladders). These double chains are connected via corner-sharing octahedra into particular structures, e.g., hollandites, ramsdellites, romanechites, todorokites, or systems with the calcium-ferrite structure. The large tunnels thus formed are filled by ions such as \( \text{K}^+ \), \( \text{Rb}^+ \), \( \text{Ca}^{2+} \), \( \text{Ba}^{2+} \), etc. These materials display a wide range of magnetic, charge, and orbital orderings, metal-insulator transitions (MIT), etc. \([1–4]\). They are usually considered as quasi-one-dimensional, the 1D building blocks being the double chains \([4,5]\).

Perhaps the most surprising phenomenon was discovered recently in a Cr hollandite \( \text{K}_2\text{Cr}_8\text{O}_{16} \) \([2]\). This material, which is tetragonal (space group \( I4/m \)) \([6]\) and metallic at room temperature, becomes ferromagnetic below \( T_c = 180 \text{ K} \). But at lower temperatures it experiences a MIT at \( T_{\text{MI}} = 95 \text{ K} \) remaining ferromagnetic in the insulating phase. This is very unusual: typically, insulating transition-metal oxides are antiferromagnetic, and ferromagnetism usually goes hand in hand with metallic properties \([7]\).

Among the several explanations offered, a proposal was made that charge ordering is responsible for the low-temperature behavior \([8]\).

The clue to understanding the nature of MIT in \( \text{K}_2\text{Cr}_8\text{O}_{16} \) can be obtained from structural studies, which should show the signatures of eventual charge or orbital order, or some other structural distortions. Conventional powder x-ray studies \([2]\) did not detect any structural distortions, which nevertheless should be present.

Therefore, in the present study, we undertook careful structural determination, using synchrotron radiation, and we combined it with the detailed electronic structure calculations to obtain a complete picture of the phenomena occurring in \( \text{K}_2\text{Cr}_8\text{O}_{16} \) at the MIT.

The picture which emerged out of our study is rather unexpected: one can indeed consider this material as quasi-1D, but the 1D building blocks are not the usually considered double chains, but rather the four corner-sharing chains around small squares, forming vertical “chimneys” in the \( c \) direction (columns Cr1-Cr2-Cr3-Cr4 in Fig. 1). To the best of our knowledge, this is the first example of the 1D structure made in such a way. The MIT in \( \text{K}_2\text{Cr}_8\text{O}_{16} \) is caused by the Peierls instability in this four-chain column. This mechanism provides a natural explanation for the observed structural distortions, i.e., the lattice dimerization in each of the four-chain columns below \( T_{\text{MI}} \). Importantly, we detected no charge ordering at the MIT; charge density is found to be the same at all Cr ions.

The synchrotron x-ray diffraction experiment was carried out on the imaging-plate diffractometer at beam lines 8A and 8B of Photon Factory in KEK. The reflection data sets for the structural analysis on single crystals were collected in the ferromagnetic metallic (FM) and ferromagnetic insulating (FI) phases using the x-ray energy of 18 keV \([9]\).

To elucidate the origin of the FI phase, the crystal structure was explored by oscillation photographs.
concluded that the space group of the FI phase is \( P_{2}2_{1}2_{1} \). From a detailed analysis of the reflection conditions \([9]\), we arranged in a stripelike pattern. We nevertheless found that the results do not change qualitatively for different values of \( U \) between 2 and 5 eV. We also note that the value \( U \approx 2–3 \text{ eV} \) we used is standard and accepted for Cr oxides with \( \text{Cr}^{3+} \) and \( \text{Cr}^{4+} \) \([13,14]\); we actually confirmed that the results do not change qualitatively for different values of \( U \) between 2 and 5 eV.

We then found that the electronic structure of the high-temperature phase is that of a half-metal, but with the substantial dip, almost a pseudogap at the Fermi level (see Ref. \([15]\) for the result at \( U = 0 \text{ eV} \)). Thus, one may anticipate that relatively minor changes in structure can push the occupied states down and empty states up, opening a gap in the spectrum and giving the gain in energy. This is indeed what happens in \( \text{K}_2\text{Cr}_3\text{O}_{16} \), as shown in Figs. 2(a)–2(d), the calculations using the experimentally observed structure of the FI phase show that a gap of \( 0.03–0.13 \text{ eV} \) opens, depending on the value \( U = 2–3 \text{ eV} \). This is in reasonable agreement with the gap \( \approx 40 \text{ meV} \) found recently by laser photoemission \([16]\).

Superstructure reflections associated with the unit cell of \( \sqrt{2}a \times \sqrt{2}b \times c \) were clearly observed in the FI phase (20 K). The intensity of the superlattice reflections is \( \sim 10^{-3} \) of the fundamentals, continuously increasing with decreasing temperature, suggesting a second-order phase transition. The distribution and intensity of the superlattice reflections are consistent with the Laue class \( 2/m \); although peak splittings due to distortion of the lattice from 90° were not observed, the intensities of equivalent and inequivalent superlattice reflections showed \( I(hkl) \neq I(h\bar{k}\bar{l}) \neq I(\bar{h}k\bar{l}) \neq I(\bar{h}\bar{k}l) \) with the monoclinic domain ratio of 6:4. Thus, the system is monoclinic in the FI phase. From a detailed analysis of the reflection conditions \([9]\), we concluded that the space group of the FI phase is \( P1\overline{1}2_{1}/a \). The transition is accompanied by a symmetry breaking with the loss of the fourfold axis and the mirror plane perpendicular to the \( c \) axis.

The structure analysis of the FI phase was performed on the basis of the space group \( P1\overline{1}2_{1}/a \), where four Cr sites, two K sites, and eight O sites become crystallographically inequivalent \([9]\). From the result, we nevertheless found that the Cr valences estimated from the bond valence sum are the same at all the Cr sites within the experimental error \( (\approx 0.03 \text{ electrons}/\text{Cr}) \), i.e., no evidence of charge ordering. The resulting crystal structure of the FI phase is shown in Fig. 1.

The observed structural distortions can be explained as follows: The four Cr sites form three types of double chains \([\text{Cr}1-\text{Cr}3, \text{Cr}2-\text{Cr}2, \text{and Cr}4-\text{Cr}4 \text{ double chains, see Fig. 1(a)}] \), a half of which (\text{Cr}1-\text{Cr}3) has a Cr-Cr bond alternation. Simultaneously, there occurs a lattice dimerization in all the four-chain columns made of \text{Cr}1-\text{Cr}2-\text{Cr}3-\text{Cr}4 chains, leading to the formation of tetramers of Cr ions \([\text{shown in Fig. 1(c)} \text{ by shading}] \). This dimerization takes place within the unit cell in the \( c \) direction, without doubling the \( c \) lattice parameter. The degree of dimerization is \( \delta = 0.025 \) at 20 K, where \( \delta \) is defined in Fig. 1 and is zero in the FM phase. As we show below, it is this lattice dimerization in the four-chain columns which plays a crucial role and drives the structural and metal-insulator transition. The relative stacking of column distortions is in such a way that they form stripes in the \( a_p \) direction \([\text{see Fig. 1(c), middle}] \), with the distortions in phase along these stripes, but opposite (shifted by a half of the period) in the neighboring stripes. This leads to the net monoclinic symmetry. This also explains the occurrence of the bond alternation in the double chains made of \text{Cr}1-\text{Cr}3 in these stripes \([\text{see Fig. 1(c), right}] \), but no dimerization in double chains made of \text{Cr}2-\text{Cr}2 and \text{Cr}4-\text{Cr}4 which are sandwiched between the stripes with opposite distortions \([\text{Fig. 1(c), left}] \).

To clarify the mechanism of the MIT further, we carried out the electronic structure calculations using different methods: local-density approximation (LDA) and generalized gradient approximation (GGA), taking into account the Hubbard-type repulsion \((\text{LDA/GGA} + U)\), in the FLAPW \([10]\) and LMTO-ASA \([11]\) implementations. The double counting corrections were taken in the form of the fully localized limit \([12]\) both for the FLAPW and LMTO-ASA calculations. We also checked the around-mean-field correction \([12]\) in the FLAPW calculation and confirmed that the results are almost the same. We also note that the value \( U \approx 2–3 \text{ eV} \) we used is standard and accepted for Cr oxides with \( \text{Cr}^{3+} \) and \( \text{Cr}^{4+} \) \([13,14]\); we actually confirmed that the results do not change qualitatively for different values of \( U \) between 2 and 5 eV.
Our calculations confirmed that the ground state of K₂Cr₅O₁₆ is ferromagnetic both in the metallic and in the insulating phase. Calculations of the exchange coupling constants using the procedure of Ref. [17] demonstrate that all the exchange integrals between nearest-neighbor Cr ions are indeed ferromagnetic, where, surprisingly, the strongest Cr-Cr coupling is not that in the double chains, but that between the double chains, via corner-shared oxygens (O1, O2, O3, and O4): in the metallic state, the values are $J \sim 5.3$ meV in the double chain, but twice as large between the double chains, $\sim 10.6$ meV. The mechanism of ferromagnetism here is similar to that in CrO₆ [14] and is in fact due to a double exchange [15]. Indeed, one electron with the symmetry $d_{xy}$ in the local coordinate system of Fig. 3 (with the $z$ axis directed towards the corner oxygen connecting double chains) is practically localized, whereas the remaining electrons are in delocalized states formed by the $d_{yz}$ and $d_{zx}$ orbitals [15,18]. The opening of a small gap ($\sim 0.1$ eV) at the Fermi level in the low-temperature phase, which is much smaller than the bandwidths $\sim 2$ eV, does not significantly modify the exchange mechanism.

The stronger coupling between the corner-sharing Cr ions of different double chains is clear from the orbital-projected density of states (DOS) shown in Figs. 2(b)–2(d); the states at the Fermi level are predominantly made up of the $d_{yz}$ and $d_{zx}$ orbitals of Cr with strong admixture of the $p_z$ orbitals of corner oxygens (O4) connecting two double chains, reflecting a negative charge-transfer-gap situation [15]. Thus, it is natural to treat K₂Cr₅O₁₆ as consisting primarily of strongly coupled four corner-sharing Cr chains. In this sense, K₂Cr₅O₁₆ can in the first approximation be treated as a quasi-1D system, but with the 1D blocks quite different from what is usually assumed in the tunnel compounds of this type.

The quasi-1D character of the electronic states is further confirmed by the Fermi surface calculated in the FM phase [see Fig. 2(e)]; the result also serves as the explanation of the nature of the MIT in this system. As one sees from Fig. 2(e), there exists strong nesting in the electron spectrum, with the nesting wave vector $Q_z = 2\pi/c$. Correspondingly, we may expect that there will occur a Peierls transition in this system. The structural data presented above agree with this picture: they demonstrate that indeed a lattice dimerization in the $c$ direction corresponding to $Q_z$ occurs, after which the tetramers of Cr ions are formed in the four-chain columns. This opens a gap at the Fermi level, but, as there are four Cr ions in a four-chain column per unit cell in the $c$ direction, it does not double the unit cell along $c$. On the other hand, the arrangement of these distorted four-chain columns leads to an increase of the unit cell in the $ab$ plane, with the unit cell becoming $\sqrt{2} \times \sqrt{2} \times 1$.

The presence of 1D columns consisting of four Cr chains explains the existence of a Peierls transition for the average valence Cr$^{3.75+}$ in K₂Cr₅O₁₆. This value, with one extra electron per four Cr ions on top of the Cr$^{4+}$ background, seems at first glance to be unfavorable for Peierls dimerization. However, for the 1D system of four chains, the spectrum for the undimerized case has four fully spin-polarized bands near the Fermi level, touching at band edges (see Fig. 5 of Ref. [15] for the bands at

\[\text{FIG. 2 (color online). Calculated GGA + U partial DOS in the FI phase of K}_2\text{Cr}_5\text{O}_{16} \text{ at } U = 3 \text{ eV: (a) the majority- and minority-spin DOS in a wide energy range, (b) the majority-spin 3d t_{2g} orbitals of Cr}_4, \text{ (c) the majority-spin 2p orbitals of corner O4 and edge O8 oxygens, and (d) the orbital decomposition for the majority-spin band of O4. The Fermi level is indicated by a vertical line. In (e), the calculated Fermi surface in the FM phase at } U = 2.9 \text{ eV is shown.} \]
via the Peierls mechanism, although the electron correlations among both-spin electrons are definitely important for preparing the state with a Peierls instability, i.e., the FM state of the double-exchange origin. We may therefore say that the present MIT is the realization of a unique Peierls transition of fully spin-polarized electrons (or "spinless" fermions) where the spin degrees of freedom of electrons essentially play no role in the transition itself.

In conclusion, we performed the synchrotron x-ray diffraction experiment on the low-temperature FI phase of K₂Cr₃O₁₆ and reported the structural changes causing the MIT of this material. The structural distortions observed consist of dimerization in the four-chain columns of corner-sharing CrO₆ octahedra and formation of a stripleik pattern of the dimerized columns. These structural data, together with our electronic structure calculations, lead us to a model of the MIT in this system caused by the Peierls transition in the quasi-1D four-chain columns, which form the natural 1D building blocks. The 1D units in K₂Cr₃O₁₆ are thus different from the usually considered double chains. The system remains ferromagnetic in the FI phase; the double-exchange ferromagnetism is not altered by the opening of the small gap. We thus demonstrated that the uncommon FI phase of materials can be realized in K₂Cr₃O₁₆ via the MIT due to Peierls mechanism in a system of fully spin-polarized electrons, which is indeed a very rare phenomenon. In addition to specific importance for K₂Cr₃O₁₆, our results demonstrated that, in tunnel compounds like hollandites and similar materials, the coupling between the double chains via corner-shared oxygens may be as strong as, and sometimes even stronger than, that within these chains. This result may change the usual interpretation of the properties of the whole big class of these materials, which may have general and important implications for future research.

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