Metal-insulator transition in Cr-doped hollandite vanadate K$_2$V$_8$O$_{16}$

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Abstract. The hollandite K$_2$V$_8$O$_{16}$ is a metal with ferromagnetic spin fluctuations in the high temperature (tetragonal I$4/m$) phase and encounters metal-insulator transition (MIT) at 170 K. The mechanism behind the MIT is still controversial due to inadequate information on the electronic structure. Furthermore, substitution of Rb for K or Ti for V increases the transition temperature. We have investigated whether break in the mirror symmetry is responsible for the insulating ground state of K$_2$V$_8$O$_{16}$ and since the Cr counterpart is a robust ferromagnet, whether Cr doping which leads to break in mirror symmetry can help in driving a gap. We find that both 25% and 75% Cr doping break the mirror symmetry but only the former leads to an insulating ground state. Ferromagnetism (FM) remains intact in the insulating phase of K$_2$V$_6$Cr$_2$O$_{16}$. The structural, electronic and magnetic properties of pure and doped K$_2$V$_8$O$_{16}$ were investigated within first-principles calculations using density functional theory (DFT). Electron correlation suppresses orbital fluctuations between the partially occupied Cr and V-3$d^2$ states. Consequently, transfer of charge (electron) from V-3$d$ to Cr-3$d^2$ states is observed which facilitates Cr$^{3+}$-V$^{4+}$ charge ordering. Furthermore, Peierls like structural distortion is associated to the breaking of mirror symmetry in the Cr-V rectangular four chain columns within the crystal. Therefore, the simultaneous effect of Peierls instability, charge ordering and Coulomb correlation is responsible for the MIT in K$_2$V$_6$Cr$_2$O$_{16}$. Besides, Cr-3$d$ O-2$p$ hybridization and Cr-O coupling increases with Cr doping. These two effects are cooperatively responsible for the observed FM in insulating K$_2$V$_6$Cr$_2$O$_{16}$. More interestingly, the strength of FM is augmented with Cr concentration in K$_2$V$_8$O$_{16}$.

1. Introduction

In recent years, studies on electronic and magnetic properties of hollandite crystals have attracted considerable interest in the field of strong electron correlations due to their exotic phenomena such as metal-insulator transition (MIT) as a function of temperature or the degree of doping level. The latter is generally controlled by the degree of chemical substitution. The hollandite oxides [1] have general formula A$_x$B$_8$O$_{16}$ (with 0 $\leq$ x $\leq$ 2), where A represents large tunnel ions such as Na, K, Ba, Sr, Rb, Cs and B represents cations such as Mn, Ti, Al, Cr, V, Si. The hollandite K$_2$Cr$_8$O$_{16}$ is a paramagnetic metal (PM) at room temperature, encounters first step transition from PM to ferromagnetic metal (FM) at 180 K and finally to a ferromagnetic insulator (FI) below 95 K with a supercell structure (monoclinic I2/m) [2, 3]. The ferromagnetism (FM) in the insulating phase is very surprising because it is usually accompanied by metalliclicity and insulating transition metal oxides are normally anti ferromagnetic [4]. Several explanations have been offered to explain the mechanism of MIT in K$_2$Cr$_8$O$_{16}$ [5-8]. Some groups demonstrated that MIT is due to a unique charge ordering [5] or structural distortion due to the formation of Cr- tetramers running in the c-direction [6-8]. In Ti-series,
K,Ti$_x$O$_{16}$ has been reported to be either a dilute ferromagnetic semi-conductor [9] or a paramagnetic metal, depending on the carrier concentration. In the Mn counterpart K$_2$Mn$_8$O$_{16}$, a variety of structural, electronic and magnetic phase transitions have been reported [10, 11]. The concentration of K-ions in this compound is reduced and the actual composition tends toward K$_1$$_8$Mn$_9$O$_{16}$ [12]. The crystal structure of K$_2$V$_8$O$_{16}$ also belongs to the family of hollandite oxides, where one dimensional (1D) double strings of edge shared VO$_6$ octahedron forms a V$_8$O$_{16}$ framework that is assumed to contain V ion in a mixed-valent state +3.75. The crystal contains two planes of V atoms in a unit cell; one is at the topmost plane and the other is at the bottom plane. Any V atom of the topmost plane has two neighbouring V atoms at the bottom plane. One of these two V atoms is linked with the topmost V atom by edge-shared oxygen (O1), while the other is connected by corner-shared oxygen (O2) as can be seen in figure 1(a).

The hollandite vanadate K$_2$V$_8$O$_{16}$ is a metal with ferromagnetic spin fluctuations [13, 14] at the high temperature (HT) tetragonal I4/m structure. It is a mixed valent oxide, which attracts strong attention due to its MIT. The average valence of V atoms in this compound is +3.75 (V$^{3.75+}$). Therefore, the system is in the charge-ordered state of V$^{3+}$ (3d$^2$): V$^{4+}$ (3d$^1$) 1:3. Isobe et al. [14] synthesized a hollandite vanadate K$_2$V$_8$O$_{16}$ by a solid-state reaction method under high pressure and investigated its structural, electronic and magnetic properties. They found that K$_2$V$_8$O$_{16}$ is a ferromagnetic metal at room temperature with tetragonal I4/m symmetry. It encounters MIT at T$_{MI}$ = 170 K with a structural phase transition to monoclinic $\sqrt{2}$a×$\sqrt{2}$b×2c [16]. Different models have been discussed to explain the characteristics of K$_2$V$_8$O$_{16}$ in the insulating phase [15-20]. A recent study reported that half of the V chains are dimerized perfectly, which further form spin singlets that is responsible for the suppression of magnetic susceptibility [16]. Nevertheless, mechanism behind the MIT is still controversial due to inadequate information on the electronic structure (densities of states, band structures). Furthermore, substitution of Rb for K or Ti for V increases the transition temperature (T$_{MI}$). For example, Rb substitution continuously increases T$_{MI}$ and it reaches 220 K for Rb$_2$V$_8$O$_{16}$ [8]. Furthermore, a slight amount of Ti-substitution for V atoms raises the transition temperature up to 270 K at x=0.5 in K$_2$V$_8$xTi$_8$O$_{16}$ from 170 K at x= 0 [9]. However, there have been no reports on the electronic structure till date to realize the electronic structure of Rb or Ti substituted K$_2$V$_8$O$_{16}$. Besides, reports on Cr substitution effect on the structural, electronic or magnetic properties of the present material are not available.

K$_2$V$_8$O$_{16}$ is not a robust ferromagnet, whereas K$_2$Cr$_8$O$_{16}$ is so. Furthermore, K$_2$Ti$_x$O$_{16}$ (x=1.43) is a FM [21]. However, T$_{MI}$ goes on increasing as Cr is replaced by V and then V is replaced by Ti. Our target is to keep ferromagnetism (FM) intact and simultaneously keep T$_{MI}$ near room temperature. This is challenging. In order to test whether FM is robust or not, one has to compare the total energies of particular compound in paramagnetic (PM), FM and antiferromagnetic (AFM) configurations. In case of the compounds under consideration, one has to compare PM and FM energies. Now T$_{MI}$ has not been calculated and it is not possible for us to do that. So our motivation was to assess whether break in the mirror symmetry is responsible for the insulating ground state of K$_2$V$_8$O$_{16}$ and since the Cr counterpart is a robust ferromagnet, whether Cr doping which leads to break in mirror symmetry can help in driving a gap. We find that that both 25% and 75% Cr doping break the mirror symmetry but only the former leads to an insulating ground state. So it would be interesting to see whether robust FM will be observed in this insulating ground state or not and we have explored that FM is augmented markedly with Cr doping.

2. Method of Calculations

In this paper, we performed first-principles electronic structure calculations based on the density functional theory (DFT) [22] as implemented on the linearized-muffin-tin orbital (LMTO) method [23]. The majority spin electrons are metallic whereas minority spin electrons are semiconducting with a band gap. The local density approximation (LDA) is used for the exchange and LDA+U [24], with the inclusion of Hubbard type Coulomb interaction U=4 eV for electron correlations. It should be noted that Kim et al. [19] adopted U$_{eff}$=U-J =3 eV on the V-3d electrons to describe the insulating ground state of K$_2$V$_8$O$_{16}$ in its low-temperature (LT) phase, whereas Toriyama et al. [17] used U=6 eV. Considering the above cases, we have applied an intermediate U value of 4 eV on the V-3d electrons.
of tetragonal $K_2V_8O_{16}$. The spin polarized calculations with and without $U$ have been performed. The unit cell is tetragonal body centred in the space group symmetry $I4/m$. The primitive unit cell contains one K-site, four V-sites and eight O-sites i.e. $KV_4O_8$. The lattice constants are $a=b=9.963$ Å and $c=2.916$ Å [25]. Then, spin-polarized self-consistent calculations were carried out for 25% (the corresponding compound $K_2V_6Cr_2O_{16}$), 50% (the corresponding compound $K_2V_4Cr_4O_{16}$) and 75% (the corresponding compound $K_2V_2Cr_6O_{16}$) Cr-doping, all including electronic correlations.

3. Results and discussion
3.1. Structural investigations
We first investigated the high-temperature structures of pure and doped $K_2V_8O_{16}$ for three different doping levels of Cr at V sites. For $K_2V_8O_{16}$, we observed four V and four corner-shared oxygen (O2) atoms form rectangular four chain columns (RFCCs), running in the $c$-direction [see figures 1(a) and 2(a)]. Two consecutive RFCCs in the ab plane are linked by edge-shared oxygen atoms (O1). In each RFCC, two V atoms are located at one opposite diagonal positions ($z=0$ or $1$), whereas the other two V atoms are located at the other opposite diagonal positions ($z=1/2$).

![Figure1. Crystal structure of $K_2V_8O_{16}$ (a), $K_2V_6Cr_2O_{16}$ (b), $K_2V_4Cr_4O_{16}$ (c) and $K_2V_2Cr_6O_{16}$ (d) in the high-temperature tetragonal $I4/m$ phase. The green, violet, cyan, yellow, red solid spheres represent K, V, Cr, O1 and O2 atoms respectively.](image-url)

As a result, every mirror symmetry is protected in the ab plane, which is responsible for uniform V-O bond distances which further results in uniform V-V distances in the double chains running in the c-direction. Next, we concentrated on the structure of $K_2V_6Cr_2O_{16}$. The primitive unit cell of $K_2V_6Cr_2O_{16}$ consists of one K and Cr atom each, three V, four each of O1 and O2 atoms. The single Cr, three V and four O2 atoms form an RFCC, found in ab plane and running in the c direction. In each RFCC, two V atoms are found at one opposite diagonal positions ($z=0$ or $z=1$), whereas the Cr and another V atoms are found at the other opposite diagonal positions ($z=1/2$). However, every mirror symmetry is preserved by the V atoms at $z=0$ or $z=1$ plane. Thus, V-O2 distances in the c-direction are uniform, which further results in uniform V-V distances in the double chains. Besides, Cr and V atoms at $z=1/2$ plane are shifted from the mirror plane. Indeed this symmetry breaking will result in long/short Cr-Cr and V-V distances in the double chains running in the c-direction as can be seen in low-temperature monoclinic $I2/m$ structure of $K_2V_8O_{16}$ [16-19]. These bond alternations result in the formations of Cr-Cr or V-V dimers in the double chains. The formation of dimers in the Cr/V double chains further results in Peierls instability within the crystal.

The primitive unit cell of $K_2V_6Cr_2O_{16}$ consists of one K, two each of V and Cr, four each of O1 and O2 atoms. In this structure, Cr, V and four O2 atoms form an RFCC in the ab plane [see figures 1(c) and 2(c)]. In each RFCC, two Cr atoms at one opposite diagonal positions and two O atoms are located at the height $z=0$ or $z=1$. Also, two V atoms at the other opposite diagonal positions and the other two O2 atoms are located at the height $z=1/2$ plane [see figure 2(c)]. Therefore, every mirror symmetry is protected in each RFCC. Consequently, all of the Cr-Cr and V-V distances
in the double chains remain uniform, resulting in the non-formation of dimers in the Cr/V double chains.

Figure 2. Schematic illustrations of RFCCs in $K_2V_8O_{16}$ (a), $K_2V_6Cr_2O_{16}$ (b), $K_2V_4Cr_4O_{16}$ (c) and $K_2V_2Cr_6O_{16}$ (d).

Finally, we investigated the crystal structure of $K_2V_2Cr_6O_{16}$. This compound consists of one each of K and V, three Cr, four each of O1 and O2 atoms [see figure 1(d)]. In $K_2V_2Cr_6O_{16}$, RFCCs are also formed by the Cr, V and O2 atoms and found in the ab plane. In each RFCC, the single V and one Cr atom at one opposite diagonal positions in conjugation with two O2 atoms are positioned at the $z=0$ or $z=1$ plane. On the other hand, other opposite diagonal positions contain two Cr atoms. These two Cr atoms and two O2 atoms are positioned at the $z=1/2$ plane. Nevertheless, Cr and V atoms at $z=0$ or $z=1$ are shifted from the mirror plane [see figure 2(d)]. Consequently, Cr or V dimers form in the Cr-Cr or V-V double chains, which further facilitates Peierls distortion within the crystal. Indeed, two Cr atoms at $z=1/2$ plane preserve every mirror symmetry [see figure 2(d)], which results in uniform Cr-Cr distances in the double chains. Therefore, mirror symmetry is practically lost in 25% and 75% Cr-doping for V only. However, structural optimizations were not carried out in the present study, which will be corroborated in our future work.

3.2. Electronic and magnetic properties
We first concentrated on the spin-polarized electronic band structure calculations of pure $K_2V_8O_{16}$ at HT structure. It is found that the system is metallic in the spin majority channel [see figure 3(a)], while insulating in the spin minority channel (not shown in figure 3). Considering both spin channels, the system is a half-metal. The formal valence of V in the present system is +3.75 i.e. the available V-3d electrons is 1.25.

Figure 3. The LDA spin-polarized electronic band structures of $K_2V_8O_{16}$ for the spin majority channel (a). The $d_{x^2-y^2}$, $d_{xy}$ states are illustrated in (b) and (c) respectively. The band structure for the spin majority channel using $U=4$ eV is illustrated in (d). The Fermi level is set at zero in the energy scale.
These electrons are found in V-t\textsubscript{2g} bands, while e\textsubscript{g} bands are found unoccupied (not shown in figure 3). The partial band structures of V-t\textsubscript{2g} states are illustrated in figure 3. It is obvious from this figure that the available 1.25 electrons are shared by V-d\textsubscript{xy}, d\textsubscript{yz}, and d\textsubscript{xz} states. Therefore, none of the V-t\textsubscript{2g} states are completely filled by the available 3d electrons. More interestingly, d\textsubscript{yz} and d\textsubscript{xz} states are exactly degenerate [see figure 3(c)]. The partially occupied t\textsubscript{2g} states results in metallic behaviour of K\textsubscript{2}V\textsubscript{8}O\textsubscript{16}. Accordingly, an orbital fluctuation between d\textsubscript{xy} and d\textsubscript{yz} states is also observed due to the delocalization of electrons in these states. The band structure of the present system using U=4 eV is displayed in figure 3(d). The scenario does not improve, i.e. the system remains in its half-metallic phase. We found that the occupied states become more occupied and unoccupied states become more unoccupied under the influence of U (not shown in figure 3). Nevertheless, no band gap opens upon the application of U=4 eV.

Next, band dispersion calculations of K\textsubscript{2}V\textsubscript{6}Cr\textsubscript{2}O\textsubscript{16} (25% Cr-doping) were carried out in the LDA treatment. The electronic band structures of this compound for the spin majority channel is shown in figure 4(a). The system remains metallic at 25% Cr doping. The partial band structures of Cr/V-t\textsubscript{2g} states are also displayed in figure 4. The available electrons in the Cr and V-t\textsubscript{2g} states are 2.25 and 1.25 respectively. Out of 2.25 electrons, one completely occupies the Cr-d\textsubscript{xy} state [see figure 4(b)], whereas d\textsubscript{yz} and d\textsubscript{xz} states have an equal probability to be occupied by the remaining 1.25 electrons. Thus, these two states are exactly degenerate. Furthermore, all V-t\textsubscript{2g} states share the available 1.25 electrons. Indeed, occupancy of d\textsubscript{xy} states increases significantly [figure 4(d)], whereas that decreases markedly for d\textsubscript{yz/xz} states [see figure 4(e)].

![Figure 4](image.png)

**Figure 4.** The LDA spin-polarized electronic band structures of K\textsubscript{2}V\textsubscript{6}Cr\textsubscript{2}O\textsubscript{16} for the spin majority channel (a). The Cr-d\textsubscript{xy}, d\textsubscript{yz/xz} States are illustrated in (b), (c) and V-d\textsubscript{xy}, d\textsubscript{yz/xz} states are illustrated in (d), (e). The Fermi level is set at zero in the energy scale.

Nevertheless, the electrons in the degenerate states are delocalized near E\textsubscript{F}. These delocalized d electrons are responsible for orbital fluctuations between the partially filled Cr-d\textsubscript{yz/xz} and V-t\textsubscript{2g} states near the close vicinity of E\textsubscript{F}. This sharing of electrons by the partially filled Cr/V-t\textsubscript{2g} states is further responsible for the metallic behaviour of K\textsubscript{2}V\textsubscript{6}Cr\textsubscript{2}O\textsubscript{16}. Besides, double exchange interaction between electrons of the partially occupied Cr/V-t\textsubscript{2g} states facilitates FM in this material. The e\textsubscript{g} states were
observed unoccupied and shifted well above $E_F$ (not shown in figure 4). This material is also insulating in the spin minority channel (not shown in figure 4). Therefore, considering two spin channels, the system is half-metal. More interestingly, Peierls distortion due to the formation of dimers and symmetry lowering is still not capable to open a gap near $E_F$. Figure 5 displays the electronic band structure of the present material for the spin majority channel using $U=4$ eV. The system encounters MIT at $U=4$ eV with a band gap of 0.36 eV. Noteworthy, the bands below $-1.0$ eV are derived from O-$2p$ states which are hybridized with Cr/V-$t_{2g}$ states. To elucidate the origin of MIT in $K_2V_6Cr_2O_{16}$, we further calculated the partial band structures of Cr/V-$t_{2g}$ states as illustrated in figures 5(b)-(d). It is unambiguous from this figure that all the Cr-$d_{xy}$ figure (b), $d_{yz}$ and $d_{xz}$ figure (c) states are occupied by one electron each. The $d_{yz}$ and $d_{xz}$ states are also degenerate in this case. Indeed, the $d_{xy}$ state is more occupied compared to $d_{yz/xz}$ states.

![Figure 5. The LDA+U (U= 4 eV) electronic band structures of $K_2V_6Cr_2O_{16}$ for the spin majority channel (a). The partial band structures of Cr-$d_{xy}$, Cr-$d_{yz/xz}$, V-$d_{xy}$ and V-$d_{yz/xz}$ states are illustrated in (b), (c), (d) and (e) respectively. The Fermi level is set at zero in the energy scale.](image-url)

Noteworthy, $\frac{1}{3}$ of the V-$t_{2g}$ states becomes filled. We found that the V-$d_{xy}$ state is occupied [see figure 5(d)], while $d_{yz}$ and $d_{xz}$ states become unoccupied [see figure 5(e)]. Therefore, out of six available electrons per formula unit ($KV_3CrO_8$), three occupy three Cr-$t_{2g}$ states and remaining three electrons occupy three V-$d_{xy}$ states. It is also observable that O-$2p$ states are hybridized with all the Cr-$t_{2g}$ and V-$d_{xy}$ states, which further stabilize FM in the insulating $K_2V_6Cr_2O_{16}$. Noteworthy, p-d hybridizations for Cr/V-$d_{xy}$ states are much higher in comparison with that for Cr-$d_{yz/xz}$ states. The inclusion of electronic correlations among the degenerate Cr/V-$3d$ states is responsible for reduction in the orbital fluctuations. About 0.25 electron from each of V atoms transfers to the Cr-$t_{2g}$ states such that they become fully occupied. Due to this charge (electron) transfer from V to Cr-$t_{2g}$ states, the number of occupied 3d electrons of Cr and V becomes three (Cr$^{3+}$) and one (V$^{4+}$) respectively. As a result, charge orderings in the fashion of Cr$^{3+}$-V$^{4+}$ and V$^{4+}$-V$^{4+}$ occur, which results in the opening of the band gap when $U$ is included. In particular, each of Cr-$d_{yz}$ and $d_{xz}$ state is now occupied by one electron each. Consequently, all the three Cr-$t_{2g}$ states and only V-$d_{xy}$ state become occupied and are shifted below $E_F$, whereas all the Cr/V-$e_g$ states remain unoccupied (not shown in figure 5). As a
result, a band gap opens near $E_F$ and the system thereby encounters MIT. Therefore, Peierls like structural distortions in conjugation with charge ordering and electrons correlations are accounted for the MIT in $K_2V_4Cr_2O_{16}$. Band gaps observed for $U=4$, 5 and 6 eV are 0.36, 0.59 and 0.79 eV respectively. Occupied Cr-$t_{2g}$ and V-$d_{xy}$ states are directed so much below $E_F$ that they are strongly hybridized with O-$2p$ states. Since Cr-3d O-$2p$ hybridization increases significantly, the occupancy of Cr-$t_{2g}$ bands increases due to band filling effect. Therefore, the insulating phase of $K_2V_4Cr_2O_{16}$ is accompanied by this band filling effect driven by breaking in symmetry. We also observed that Cr-3d O-$2p$ coupling increase significantly due to the application of $U$, which is further responsible for the ferromagnetism in insulating $K_2V_4Cr_2O_{16}$.

In order to complete the study, we investigated the electronic and magnetic properties of $K_2V_4Cr_2O_{16}$ (50% Cr doping). The band structure for the spin majority channel is shown in figure 6(a). The system is metallic in this channel. However, no p-d hybridization is observed in this case. The partial band structures of Cr/V-$t_{2g}$ states are also exhibited in figures 6(b)-(d). It is noticeable that Cr-$d_{xy}$ [figure 6(b)], $d_{yz/xz}$ states [figure 6(c)] are occupied. Besides, V-$d_{xy}$ state [see figure 6(d)] is found partially occupied, whereas $d_{yz/xz}$ states are found unoccupied (not shown in figure 6). It should be noted that the total number of d electrons per f.u. ($K_2V_4Cr_2O_8$) is seven. Now simple electron counting tells us that V-$t_{2g}$ states will be partially occupied which is reflected in the partial band structures of V-$t_{2g}$ states. Out of which, six electrons occupy six $t_{2g}$ states of two Cr atoms and the remaining electron is equally shared by two $d_{xy}$ states of two V atoms. In this sense no charge ordering occurs due to transfer of charge in $K_2V_4Cr_2O_{16}$. Since the number of electrons increases due to Cr doping, electron correlation becomes more important for the FM of the present material. Noteworthy, application of $U=4$ eV is still not able to open a gap at $E_F$ [see figure 6(e)] due to absence of charge ordering. However, the occupied levels become more occupied and shifted far below $E_F$, whereas the unoccupied levels become more unoccupied and shifted far above $E_F$ under the influence of $U=4$ eV, which is also clearly visible from figure 6(e). Furthermore, due to high symmetry of the crystal, Cr-$d_{xy/xz}$ states remain degenerate and thereby none of them become completely occupied. It is worth mentioning that the p-d hybridization increases significantly [figure 6(e)] due application of U. Besides, Cr-O coupling again is responsible for FM of the present material.

![Figure 6. LDA spin-polarized band structure of $K_2V_4Cr_2O_{16}$ (a) for the spin majority channel. The partial band structure of Cr-$d_{xy}$, $d_{yz/xz}$ and V-$d_{xy}$ states are depicted in (b), (c) and (d) respectively. The band structure of this material for $U=4$ eV is also illustrated in (e).](image-url)
Finally, we concentrated on the electronic and magnetic properties of K$_2$V$_2$Cr$_6$O$_{16}$ (75% Cr doping). The band structure for the spin majority channel is shown in figure 7(a). It is evident from this figure that the system remains metallic. The partial band structures of Cr-$d_{xy}$, $d_{yz/xz}$ and V-$d_{xy}$ states are illustrated respectively in figures 7(b), (c) and (d). It is obvious that Cr-$d_{xy}$ states are fully occupied, whereas Cr-$d_{yz/xz}$ states are almost (83%) occupied. It is also evident that V-$d_{xy}$ state is mostly unoccupied. We also found that V-$d_{yz/xz}$ states become completely unoccupied (not shown in figure 7). Consequently, the number of electrons in Cr and V-$t_{2g}$ states become 2.67 and almost zero i.e. Cr$^{3.33+}$, V$^{5+}$ charge ordering occurs. We have also applied of $U = 4$ eV, but no gap opens at $E_F$ [see figure 7(e)], because transferred electrons are not sufficient to completely fill Cr-$d_{yz/xz}$ states. Although the cooperative effect of Peierls instability due to structural distortion and Coulomb interactions is acted upon K$_2$V$_2$Cr$_6$O$_{16}$, it remains metallic due to lack of sufficient electrons to completely occupy Cr-$d_{yz/xz}$ states. Furthermore, p-d hybridization increases markedly as can be seen from figure 7(e). We observed that Cr-O coupling also augmented significantly, which is accounted for the FM of K$_2$V$_2$Cr$_6$O$_{16}$.

![Figure 7. LDA band structure of K$_2$V$_2$Cr$_6$O$_{16}$ (a) for the spin majority channel. The partial band structure of Cr-$d_{xy}$, $d_{yz/xz}$ and V-$d_{xy}$ states are depicted in (b), (c) and (d) respectively. The band structure of this material for $U = 4$ eV is also illustrated (e).](image)

The total ground states energies ($E_{\text{tot}}$) of pure and different Cr-doped K$_2$V$_8$O$_{16}$ as calculated in the PM, AFM and FM configuration are reported in Table 1. It is unambiguous that $E_{\text{tot}}$ is the minimum for FM calculations for all three doping levels. This result indicates that ground state of K$_2$V$_8$O$_{16}$, K$_2$V$_6$Cr$_2$O$_{16}$, K$_2$V$_4$Cr$_4$O$_{16}$ and K$_2$V$_2$Cr$_6$O$_{16}$ are ferromagnetic. Furthermore, $E_{\text{tot}}$ increases significantly with Cr concentration for all three calculations. It should be noted that $E_{\text{tot}}$ enhances significantly about 203, 406 and 608 eV respectively for 25%, 50% and 75% Cr-doping in K$_2$V$_8$O$_{16}$. Therefore, strength of FM is augmented significantly with Cr-concentration in K$_2$V$_8$O$_{16}$. 
4. Conclusion
The presence of Cr at the B-site renders the hollandite $A_2B_8O_{16}$ ferromagnetism but that of V at B-site enhances the $T_{MI}$. We investigated the effect of Cr doping at the vanadium site in a systematic way, i.e. 25%, 50% and 75% doping. It was found that although the first and third led to considerable break in mirror symmetry in the square well but only in the first case, an energy gap opens up when Hubbard-like $U$ is applied. Hence we find the necessary ingredient of obtaining MIT in hollandites is to Peierls instability (dimerization)-driven band filling in the transition metal atoms and Coulomb correlations. It is also explored that strength of FM increases with Cr doping.

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6. References
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Table 1. Total ground state energies (eV) for K2V4O16, K2V6Cr2O16, K2V4Cr4O16, K2V2Cr6O16 and in the PM, AFM and FM configurations.

| Compounds       | K2V4O16 | K2V6Cr2O16 | K2V4Cr4O16 | K2V2Cr6O16 |
|-----------------|---------|------------|------------|------------|
| PM              | -9985.52| -10188.31  | -10391.11  | -10593.90  |
| AFM             | -9985.53| -10188.35  | -10391.18  | -10593.97  |
| FM              | -9985.55| -10188.38  | -10391.22  | -10594.0   |
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