Effect of K$^+$ de-insertion on the electronic and magnetic properties of K$_2$Cr$_8$O$_{16}$

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Abstract

The hollandite K$_2$Cr$_8$O$_{16}$ undergoes a transition from the paramagnetic metal to ferromagnetic metal (FM) at T$_c$ = 180 K and finally metal-insulator transition (MIT) occurs at the transition temperature T$_{MI}$ = 95 K, preserving ferromagnetism in the low temperature insulating phase. Although ferromagnetism in the insulating phase of K$_2$Cr$_8$O$_{16}$ at low-temperature has been explained using Peierls instability mechanism, the role played by cation Potassium in determining this unique ground state of K$_2$Cr$_8$O$_{16}$ is yet to be explored. In the present study, the effect of a single and full K$^+$ de-insertion on the electronic and magnetic properties of K$_2$Cr$_8$O$_{16}$ for the high-temperature structure is investigated using Density Functional theory. It is imperative that extraction of K$^+$ -ions destroys the K-Cr interaction through the oxygen anions for K$_1$Cr$_8$O$_{16}$/CrO$_2$. This enhances the Cr(d)-O(p) hybridization. The pseudo-gap at Fermi energy in K$_2$Cr$_8$O$_{16}$ shifts to higher energy due to K$^+$ de-insertion. Furthermore, removal of K-ions from the tunnel sites increases the density of states at Fermi level, which is mainly derived from Cr-3d conduction electrons. As the Fermi energy moves more towards the edge of the Cr-d band and away from pseudo gap, T$_c$ increases as it should within the Stoner mechanism governing band ferromagnetism. The strength of ferromagnetism enhances due to increase in the Cr-Cr coupling for isostructural K$_1$Cr$_8$O$_{16}$ and CrO$_2$ as Cr-d and O-p coupling increases with K$^+$ removal.

Keywords: *Hollandite K$_2$Cr$_8$O$_{16}$, First-principles electronic structure calculations, Ferromagnetism, Curie temperature (T$_c$), Stoner mechanism*

1. Introduction

Hollandite compounds have attracted considerable attention in recent years due to some exotic phenomena displayed by them [1-9]. These compounds have general formula A$_x$B$_8$O$_{16}$ ($x \leq 2$), where A is a tunnel cation such as K$^+$, Rb$^+$, Ca^{2+}, Ba^{2+} etc. and B is the transition metal cation such as Cr^{2+}, V^{2+}, Mn^{2+}, Ti^{2+}, Ru^{2+}etc. Typically they are made of double chains of BO$_6$ octahedra forming tunnel in which A-ions reside and the octahedra contain O1 which are edge-shared and O2 which are corner-shared (see Fig. 1). The cation occupation in the tunnel site of the hollandite structure for the transitional metal oxides was extensively studied in the past. For example, adequate efforts have been devoted to investigate the potential applications of Mn-hollandite oxides, A$_x$Mn$_8$O$_{16}$ (A=Ba, Pb etc) as positive electrodes, ionic conductors and oxidation catalysts [10-13].
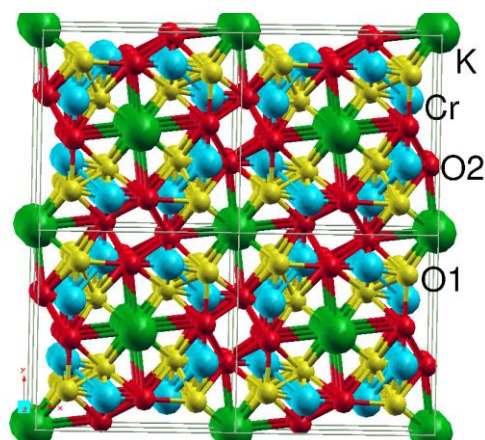
FIG 1. Crystal structure of $K_2Cr_8O_{16}$. The K, Cr, edge-shared oxygen (O1) and corner-shared oxygen (O2) atoms are represented respectively by green, cyan, yellow and red solid spheres.

Recently, some hollandites containing ruthenium ($Ba_{1.33}Ru_8O_{16}$, $BaRu_6O_{12}$) [14] and vanadium ($Bi_xV_8O_{16}$; $1.6 \leq x \leq 1.8$) [15] having one-dimensional (1D) double chains of MO_6 (M=Ru or V) octahedra were found to exhibit anomalous electronic properties. The origin of such electronic properties was thought to be quantum spin fluctuation or geometrical frustration due to their low dimensional structure. The formation of hollandite compounds with different K^+-ion concentrations is possible using different synthesis processes. For example, full occupation of K-sites has been attained by high pressure synthesis methods as in cases of $K_2Cr_8O_{16}$ [16, 22] and $K_2V_8O_{16}$ [23, 24]. Conversely, hollandites with low K^+ concentration were obtained through a soft-chemical process in which a part of K-ions is extracted in conjugation with the oxidation of framework metals [16].

The hollandite $K_2Cr_8O_{16}$ has been explored extensively in both theoretical and experimental studies because of some of its interesting properties [10-22, 25]. $K_2Cr_8O_{16}$ has a tetragonal I4/m structure [8, 21] and exhibits paramagnetic metallic behaviour at the room temperature [11]. This compound encounters a transition from the paramagnetic (PM) metal to a ferromagnetic (FM) metal at $T_c = 180$ K [11]. More interestingly, a metal-insulator transition (MIT) is observed at a temperature of $T_{MI} = 95$ K [11], preserving ferromagnetism (FM) in the insulating phase. However, FM in the insulating phase is very unusual because it is customarily associated with metallic transition metal oxides (TMOs) and antiferromagnetism goes hand in hand with the insulating TMOs [26]. Several explanations have been offered to explain the FM insulating ground state of $K_2Cr_8O_{16}$ [12, 14, 15, 17-22]. Prominent one is the Peierls mechanism [14]. The extraction of K-ions from the tunnel-site increases Cr^{4+} content. Pirrotta *et al.* [16] established the role of K^+ in the experimental investigation of FM behaviour of $K_2Cr_8O_{16}$. They prepared the sample $K_{2-x}Cr_8O_{16}$ ($x \leq 2$) by extraction of K^+-ions from the parent $K_2Cr_8O_{16}$. The maximum removal of K^+ ion corresponds to x=0.8, the corresponding sample is $K_{1.2}Cr_8O_{16}$ for which average Cr-valence is close to 3.85. That means, $K_{1.2}Cr_8O_{16}$ may contain Cr ions in 7:1 ratio of Cr^{4+} (d^2):Cr^{3+}(d^3). In case of $K_1Cr_8O_{16}$, the ratio of Cr^{4+} and Cr^{3+} is 7:1. Ideally total extraction of K-ions may also possible,

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which will produce a new polymorph CrO_2 with the hollandite structure. However, increase of Cr^{4+} content within the crystal will result in changes in the coordination, electronic and magnetic properties of the present material. In this direction, we have systematically removed K-ions from the tunnel site to investigate how the ground state properties deviates from that of pristine $K_2Cr_8O_{16}$.

In most previous works, the role of charge ordering in Cr or dimerization in Cr double chains has been highlighted as being responsible for the insulating FM ground state. Potassium ions, which occupy the empty tunnel did not have their roles investigated or they have been thought to be passive. However, as a result of this de-insertion of K^+-ions, the Curie temperature (T_c) increased by an amount 70 K, leading to $K_{1.2}Cr_8O_{16}$ being a near room temperature FM ($T_c \sim 250$ K) [16]. Therefore, K-ions must be playing a profound intermediary role in the strengthening of FM in $K_2Cr_8O_{16}$. In this study, we have investigated the electronic and magnetic properties of isostructural $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ (50% potassium deficiency) and CrO_2 (full potassium deficiency). At first, we concentrate on the electronic and magnetic properties of $K_2Cr_8O_{16}$. Later, we have investigated the same upon extraction of K^+-ion systematically from the tunnel site, leading to formation of $K_1Cr_8O_{16}$ and Cr_8O_{16}.

2.   Method of Calculation

Here, we performed first-principles electronic structure calculations within the local spin density approximation (LSDA) [27, 28], which is based on the linearized-muffin-tin orbital (LMTO) method in its atomic sphere accounts (ASA) [28, 29], as implemented in the density functional theory (DFT) [30, 31]. The high-temperature structure of $K_2Cr_8O_{16}$ is tetragonal body centred with the space group symmetry I4/m. The primitive unit cell contains one K-ion, four Cr-ions and eight O-ions i.e. KCr_4O_8. The cell parameters used in this purpose were: a=b=9.7627 Å and c=2.9347 Å [32]. We then extracted a K-ion from the tunnel site (the corresponding compound is $K_1Cr_8O_{16}$) and two K-ions from the tunnel site (the corresponding compound is CrO_2 with hollandite structure). Then we comprehensively investigated the electronic and magnetic properties of pristine and K^+ de-inserted $K_2Cr_8O_{16}$.

3.   Results and discussion

3.1 Electronic properties

First of all, we have calculated total densities of states (TDOS) of $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2 in the nonmagnetic (NM) mode. The TDOS for $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2 are illustrated in Fig. 2(a). The calculated TDOS at E_F are 1.3, 1.5 and 2.2 states/eV/formula unit (f.u.) respectively for $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2. Therefore, TDOS increases with the de-insertion of K^+ ions from the tunnel sites. This result suggests that the number of conduction electrons at E_F increases with removal of K^+-ions. We also observed that Fermi level (E_F) is located within a pseudogap for $K_2Cr_8O_{16}$, whereas E_F for $K_1Cr_8O_{16}$ and CrO_2 are shifted more towards the edge of the bands. With the number of electrons at E_F too increasing, delocalization of electrons increases with K-ion removal from the tunnel site. Thus hollandite CrO_2 is the most metallic one and the metallicity of $K_1Cr_8O_{16}$ is lower than CrO_2 but higher than $K_2Cr_8O_{16}$. We also carried out the projected DOS (PDOS) of Cr-3d t_{2g} bands of NM $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$

and CrO_2 [see Fig. 2(b)]. As can be seen in the TDOS, Cr-3d t_{2g} PDOS increases with K^+ de-insertion. Therefore, it can be concluded that removal of K^+-ions from tunnel sites increases Cr-3d conduction electrons.
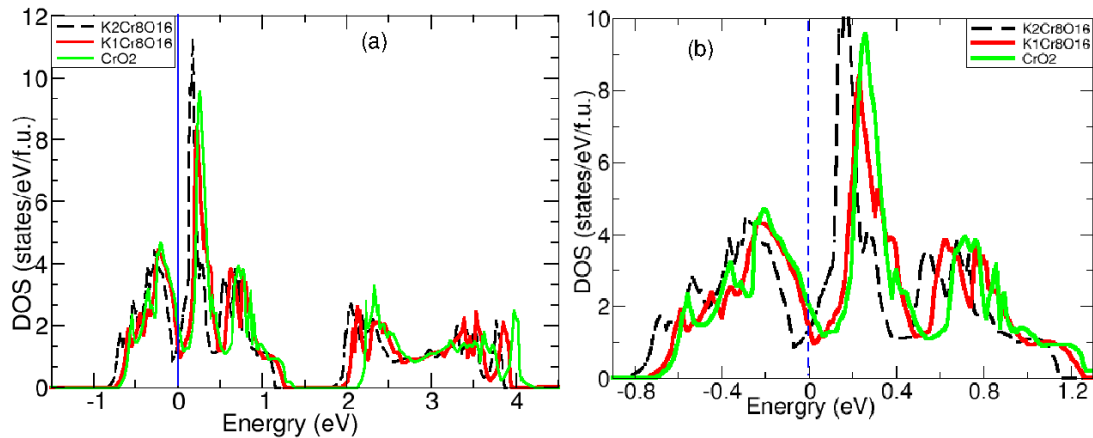

FIG 2. TDOS of isostructural $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2 as calculated in the NM calculations (a). Also, Cr-3d t_{2g} PDOS for the corresponding compounds are illustrated (b). The Fermi level is set at zero of the energy scale.

Furthermore, we have performed a set of spin polarized calculations for PDOS and electronic band structures after extracting K^+ ions from pristine $K_2Cr_8O_{16}$. The above calculations were carried out both in ferromagnetic (FM) and anti-ferromagnetic (AFM) spin configurations to estimate the corresponding self-consistent ground state energies (E_{FM} and E_{AFM}) along with their differences ΔE (=E_{FM}-E_{AFM}) as reported in Table 1. The ground state energies for all the three compounds are minimum for the FM mode, i.e., FM stabilizes in all the three materials. Both E_{FM} and E_{AFM} increase significantly due to K^+-extraction, as expected.

Figures 3(a) displays TDOS of $K_2Cr_8O_{16}$ (black dotted lines), $K_1Cr_8O_{16}$ (green solid lines) and CrO_2 (red solid lines) for all the three compounds in FM phase. The TDOS near E_F is magnified in Fig. 3(b) for the precise understanding of the electronic nature of these three compounds. It is unambiguous from Fig. 3(a) that all the three compounds are half-metals. The low energy physics is determined by the majority spin channel as shown in Fig. 3(b), where the width of 3d band occupying the E_F increases due to increased hybridization. It is evident from these figures that the conduction bands shift higher in energy, leading to E_F moving towards centre of the bands.

Table 1. The PM, FM and AFM energies (E_{PM}, E_{FM} and E_{AFM}), differences between E_{FM} and E_{AFM} ($\Delta E=E_{FM}-E_{AFM}$), effective magnetic moments (μ_{total}) and average magnetic moments of Cr (μ_{Cr}), O1 (μ_{O1}), O2 (μ_{O2}) in μ_B of $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2.

Compounds	$K_2Cr_8O_{16}$	$K_1Cr_8O_{16}$	CrO_2

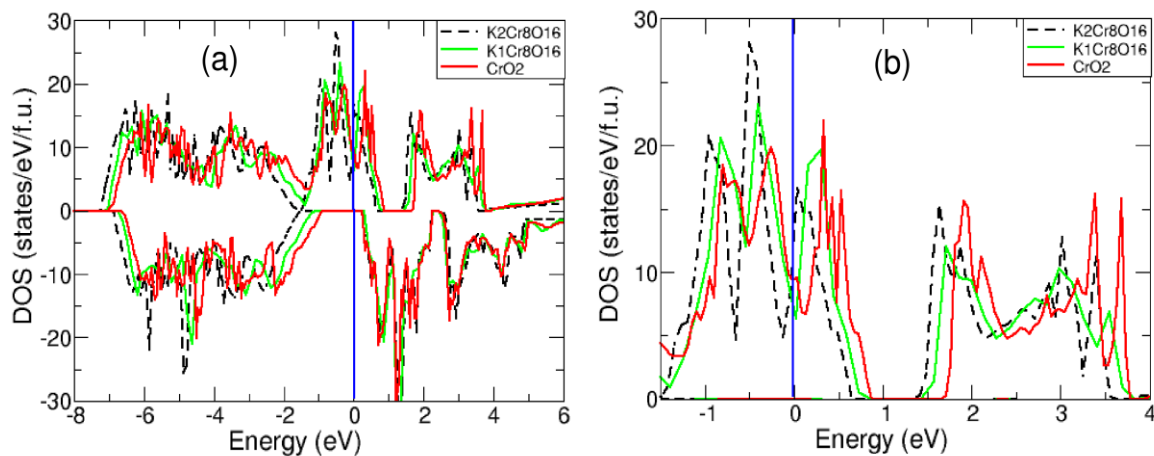| E_{PM} (eV)	-21594.14	-20391.70	-19192.81
E_{FM} (eV)	-21594.40	-20391.94	-19193.12
E_{AFM} (eV)	-21594.38	-20391.88	-19193.03
ΔE (meV)	-20.0	-60.0	-90.0
μ_{total} (μ_B)	-18.0	-17.0	-16.0
μ_{Cr} (μ_B)	-2.25	-2.215	-2.0
μ_{O1} (μ_B)	-0.007	-0.009	-0.006
μ_{O2} (μ_B)	0.044	0.046	0.055

FIG 3. TDOS of $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$, and CrO_2 as calculated in the FM mode. TDOS for both spin channels are illustrated in (a) and for spin majority channel is illustrated in (b). The Fermi level is set at zero of the energy scale.
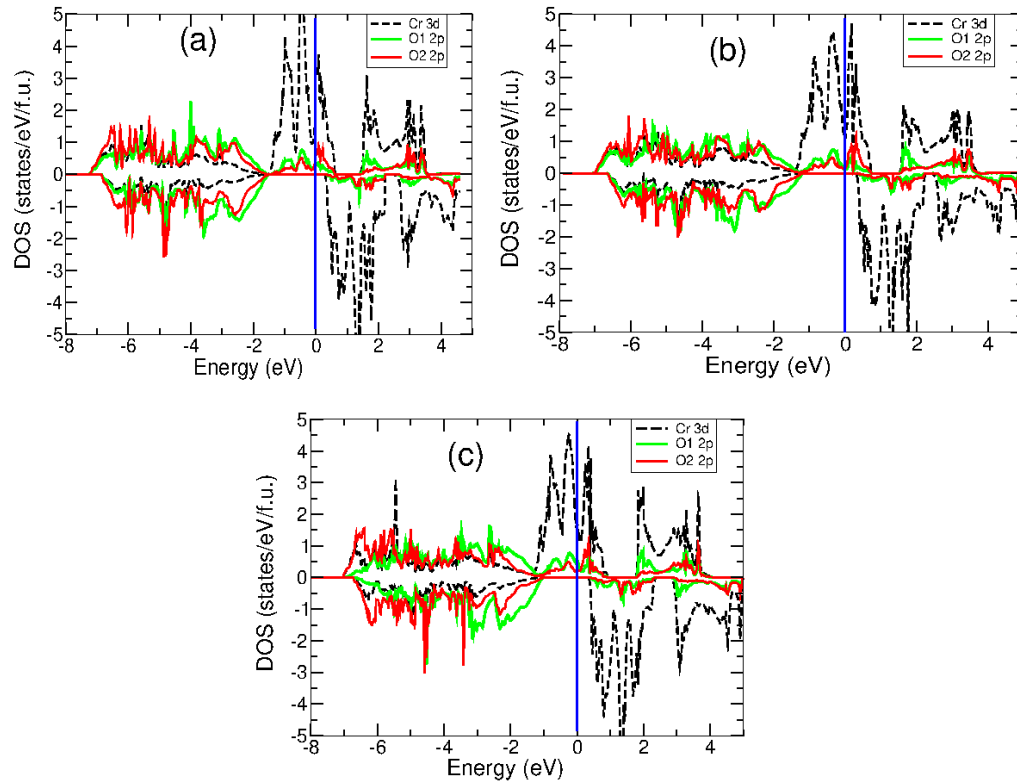
FIG 4. PDOS of Cr-3d, O1 and O2-2p states of $K_2Cr_8O_{16}$ (a), $K_1Cr_8O_{16}$ (b) and CrO_2 (c). The Fermi level is set at zero of the energy scale.

The spin polarized Cr-3d, O1-2p and O2-2p PDOS for $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2 are illustrated in Figs. 4(a)-(c). It is noticeable that TDOS in vicinity of E_F is dominated by the Cr-3d states. The Cr-3d states owing to Cr ion in octahedral coordination with O (both O1 and O2) ions dissociate into lower lying 3-fold degenerate t_{2g} bands and upper lying doubly degenerate e_g bands. In the spin-majority channel, Cr-3d t_{2g} and e_g states of $K_2Cr_8O_{16}$ are observed in the energy ranges -1.5 to 0.6 eV, 1.4 to 3.6 eV respectively [see Fig. 4(a)]. Most importantly, O-2p states are observed mainly from -7.2 to -1.5 eV and -6.8 to -1.5 eV for majority and minority spin channel respectively. For $K_1Cr_8O_{16}$, Cr-3d t_{2g} and e_g states are found between -1.35 to 0.75 eV and 1.55 to 3.75 eV respectively. The O-2p states are observed between -7.0 to -1.35 and -6.6 to -1.35 eV for the spin majority and minority channel [see Fig. 4(b)]. For, CrO_2, Cr-3d t_{2g} and e_g states are found around -1.35 to 0.75 eV and 1.55 to 3.75 eV respectively. The O-2p states are observed between -7.0 to -1.0 and -6.6 to -1.0 eV for the spin majority and minority channel respectively [see Fig. 4(c)].

A closer look at the TDOS reveals that O1 and O2-2p states move higher in energy forwards Cr-t_{2g} bands as K^+ ion is gradually removed. Furthermore, it is evident from Fig. 4 that Cr-3d and O (both O1 and O2)-2p hybridization increases with K^+ removal from the tunnel site. This enhanced Cr-t_{2g} and O-2p hybridization leads to the gain in the carrier density at E_F. We found larger presence of O1-2p electrons at E_F in $K_1Cr_8O_{16}$ and even more in CrO_2. As a proof of this increased contribution of Cr-t_{2g} and O1-2p states, we have shown the fatbands (the contribution of l and m_l specific orbitals to the band) of Cr-t_{2g}, O2-$2p_z$ and O1-$2p_z$ states for $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2 in Fig. 6. In $K_2Cr_8O_{16}$, Cr-t_{2g} bands are

occupied by 2.25 electrons. Upon removal of a single K^+ ion from the tunnel site, Cr-t_{2g} bands become less occupied. And in hypothetical CrO_2 with hollandite structure, Cr-t_{2g} bands become emptier, leading to the Fermi energy occupying a large peak [see Fig. 5(a)]. These Cr-3d bands shift towards higher energy range upon gaining of energy (see Table 1) due to K^+ removal. The shifting of Cr-3d bands for $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2 are illustrated in Fig. 5(a). The PDOS of K-4s states for $K_2Cr_8O_{16}$ and $K_1Cr_8O_{16}$ are also depicted in Fig. 5(b). It is observable that the K-4s PDOS at E_F reduces significantly with K^+ de-insertion, leading the energy domination of O-2p states at E_F.
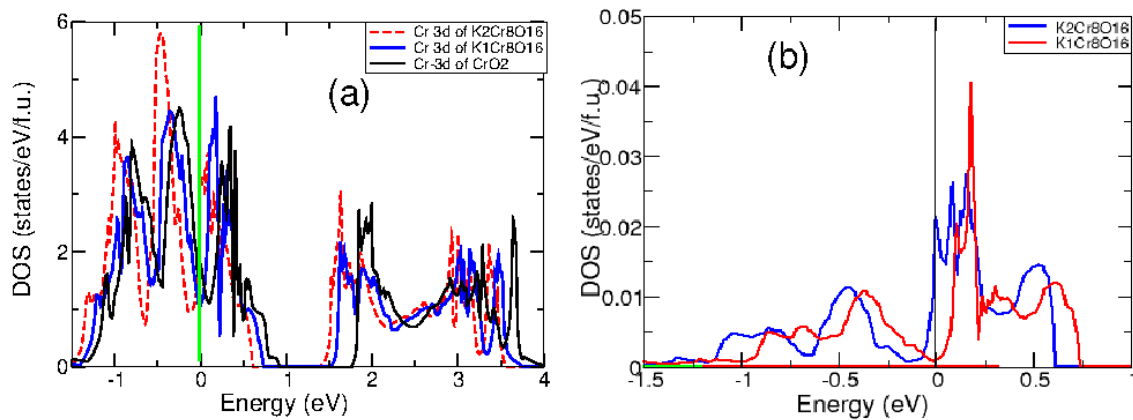

FIG 5. FM (a) Cr-3d PDOS for $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2, (b) K-4s PDOS of $K_2Cr_8O_{16}$ and $K_1Cr_8O_{16}$. The Fermi level is set at zero of the energy scale.

The electronic band structures of Cr-3d t_{2g}, O1-2p$_z$ and O2-2p$_z$ states for $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2 are shown in Figs. 6(a)-(l). The 12 bands originating from Cr-3dt_{2g} states of 4 Cr ions in the primitive unit cell, spread around -1.5 to 0.6 eV, and bands below -1.5 eV are originated from O-2p states. The average valence of Cr in these three materials are +3.75 ($Cr^{3.75+}$), +3.875 ($Cr^{3.875+}$) and +4 (Cr^{4+}) respectively. Hence available valence electrons are 2.25, 2.125 and 2 respectively. For $K_2Cr_8O_{16}$, Cr-d_{xy} state is occupied by an electron, which is localized and shifted below E_F [Fig. 6(a)]. The remaining 1.25 electrons are equally shared by the $d_{yz/xz}$ states [see Fig. 6(b)]. Therefore, quantum orbital fluctuation between these two states is observed, and electrons which are to occupy these two states are therefore delocalized (itinerant) in nature. In addition, Cr 3d-O 2p hybridization in pristine $K_2Cr_8O_{16}$ is observable from Figs. 6(c) and (d).

For $K_1Cr_8O_{16}$, an electron fills d_{xy} state, which localizes and shifts below E_F [Fig. 6(e)]. The remaining 1.125 electrons are equally shared by the $d_{yz/xz}$ states as seen in case of $K_2Cr_8O_{16}$ [see Fig. 6(f)]. Thus, these two states are also degenerate and electrons in these states are itinerant in nature. The occupancy of the $d_{yz/xz}$ state is slightly smaller than that for pristine $K_2Cr_8O_{16}$ (see 1st panel of Fig. 6). A larger p-d hybridization is observed for one K^+ de-insertion [see Figs. 6(g) and (h)] i.e., for $K_1Cr_8O_{16}$ as O-2p states move towards Cr d bands. For CrO_2, d_{xy} state is occupied by an available Cr-3d electron [see Fig. 6(i)] and the remaining electron is equally shared by the $d_{yz/xz}$ states [see Fig. 6(j)]. Therefore, quantum orbital fluctuation of the other electron in the $d_{yz/xz}$ states is also present in CrO_2, making it itinerant.

Simultaneously p-d hybridization also increases in case of full K^+-ion extraction i.e., for CrO_2 [see Figs. 6(k) and (l)].
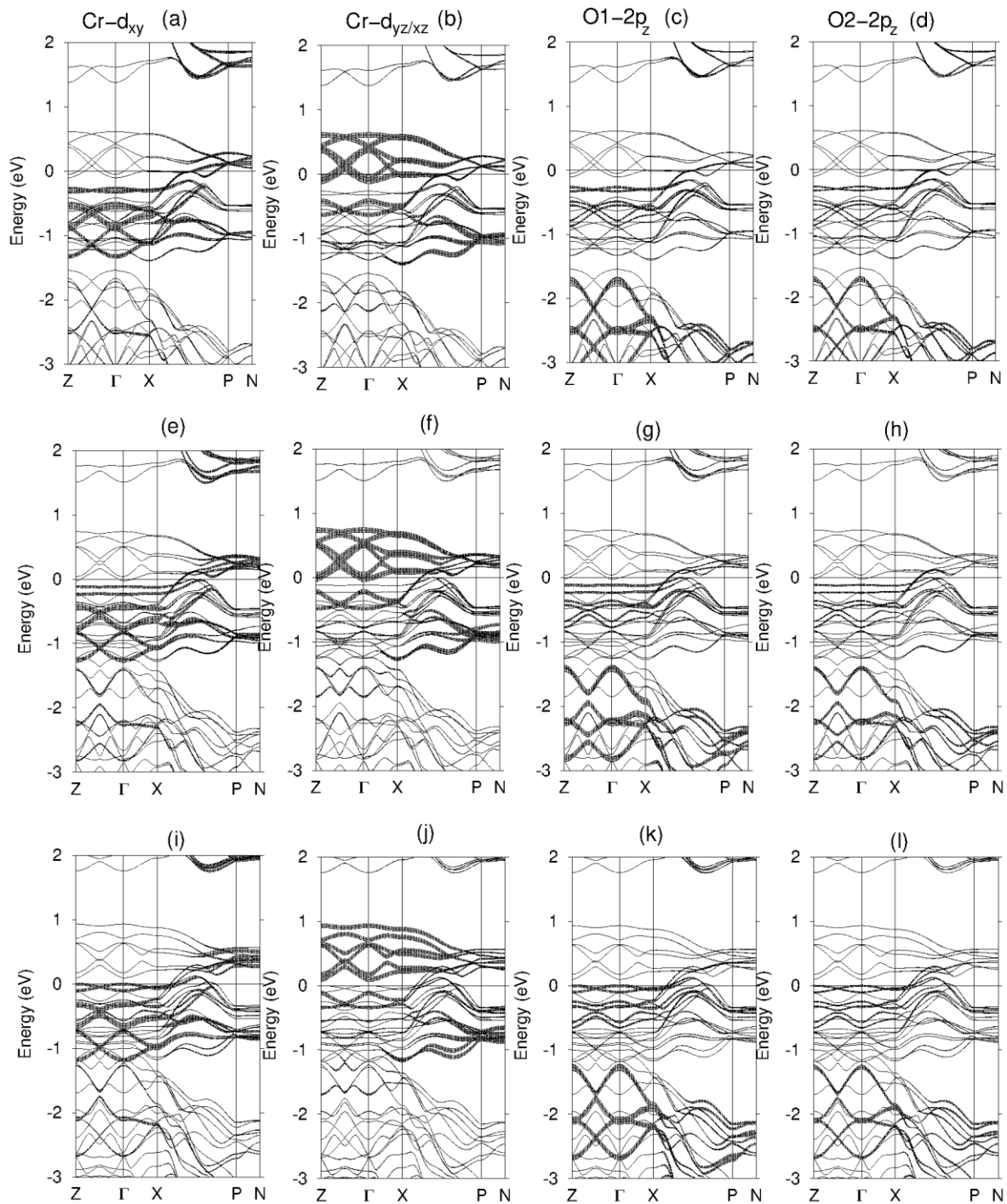

FIG 6. Electronic band structure of Cr-d_{xy}, $d_{yz/xz}$, O1-$2p_z$ and O2-$2p_z$ sates for FM $K_2Cr_8O_{16}$ [(a), (b), (c) and (d)] $K_1Cr_8O_{16}$ [(e), (f), (g) and (h)] and CrO_2 [(i), (j), (k) and (l)] for the majority spin channel. The Fermi level is set at zero of the energy scale.

3.2   Magnetic properties

Let us now concentrate on the magnetic properties for K^+ de-insertion from the pristine compound $K_2Cr_8O_{16}$. The effective magnetic moments calculated for $K_2Cr_8O_{16}$ is 18 μ_B/8Cr i.e., 2.25 μ_B per Cr-ion. The magnetic moment per Cr-ion for $K_1Cr_8O_{16}$ is calculated as 2.125 μ_B corresponding to the effective magnetic moments of 17 μ_B/8Cr. This reductiobn is also reported by Pirrotta *et al.* [16] for $K_{1.2}Cr_8O_{16}$. For full K^+ de-insertion i.e., for CrO_2, the effective magnetic moment is calculated as 16 μ_B/8Cr giving an average Cr-magnetic moments of 2.0 μ_B, which is also observed for rutile CrO_2 as reported by Shim *et al.* [33]. Therefore, K^+ de-insertion enhances Cr-oxidation state, consequently reduces average Cr-magnetic moments (μ_{Cr}). The calculated average magnetic moments of Cr (μ_{Cr}), O1 (μ_{O1}) and O2 (μ_{O2}) of $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2 are reported in Table 1. The exchange integrals between nearest neighbour Cr-ions are known to lead in ferromagnetism [14]. According to Toriyama *et al.* [14], the strongest Cr-Cr coupling is not in the Cr-Cr double chains, but that between the double chains via the corner-shared oxygen atoms. They determined the values of the exchange integrals (J_{eff}) as ~5.3 eV for the first case (Cr-Cr double chains), but double (~10.6 eV) for the latter case. It is evident from Table 1 that μ_{O1} increases/decreases about 0.001 μ_B for $K_1Cr_8O_{16}$/CrO_2, whereas μ_{O2} increases by 0.002 and 0.01 μ_B respectively for one and two K^+ de-insertion, therefore Cr-Cr coupling is enhanced via O2-2p orbitals indicating stronger hybridization. From Table 1, it can be concluded that K^+ removal leads to the strengthening of the Cr-O-Cr interaction which in turn is strengthened by the simultaneous destruction of half of the K-Cr bridges. Hence, K or the alkali ions must be natural choice for Cr_xO_{2x} compounds to be stabilize into singlet states.

3.3   Increase of Curie temperature (T_c)

We have already seen that removal of K-ions from the tunnel sites increase TDOS at E_F (see Fig. 2), which is predominantly derived from increasing Cr-3d conduction electrons due to band emptying effect and increased O-2p hybridization with Cr-3d electrons. The pseudo-gaps at E_F shift to higher energy due to K^+ de-insertion. As the Fermi energy moves more towards the edge of the Cr-d band and away from pseudo gaps, simple Stoner mechanism indicates T_c should increase. In fact, T_c of a system can be crudely estimated from the knowledge of the inter-atomic Coulomb interaction (U), the densities of states at E_F [D(E_F)], the number of atoms (N) and the *d* bandwidth (W) in accordance with the following equation [34]:

$$T_c \propto (\alpha - 1)^\beta \text{----------------(1)}$$

$$\text{and} \quad \alpha = \frac{UD(E_F)}{N}\left(1 - \frac{U}{W}\right)\text{------------(2)}$$

According to the self-consistent renormalized (SCR) theory of Moriya and Kawabata [35, 36], the value of β is taken as 3/4. The SCR results thoroughly interpret the experimental results in the weak ferromagnetic metal [37]. The effective inter-atomic Coulomb interaction is roughly enhanced by the larger bandwidth W. Subsequently, T_c increases as the values of D(E_F) increases and /or W increases. Therefore, the product D(E_F) and W was used to estimate T_c of $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2. For this purpose, NM Cr-3d DOS of these three compounds were calculated and depicted in Fig. 2. Figure 2(b) clearly exhibits Cr-3d DOS at E_F [D(E_F)]. It is clear from Fig. 2 that both D(E_F) and W increase with the

increase of K^+ extraction. Hence we anticipate that FM will become robust as K^+ ions are being gradually de-inserted. This should get reflected in increasing T_c in isostructural $K_1Cr_8O_{16}$ and CrO_2 (Cr_8O_{16}). The calculated values of $D(E_F)$, W and the product of $D(E_F)$ and W i.e., $D(E_F)W$ for $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2 are appended in Table 2. It is evident from this table that the product $D(E_F)W$ increases upon the increase of K-extraction from $K_2Cr_8O_{16}$. The T_c calculated for $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2 is also reported in this table. The T_c increases by 85 K for $K_1Cr_8O_{16}$ and reaches almost the room temperature, which is comparable with the T_c of $K_{1.2}Cr_8O_{16}$ as calculated by Pirrotta *et. al.* [16]. More interestingly, T_c of CrO_2 *i.e*., for full K^+ removal is enhanced almost by ~208 K to attain a value of ~388 K, which is also consistent with the T_c (=390 K) of the naturally abundant rutile CrO_2 [38, 39].

Table 2. Calculated density of states at E_F ($D(E_F)$), d-bandwidths (W), product of $D(E_F)$ and W ($D(E_F)W$) and ferromagnetic Curie temperature (T_c) of $K_2Cr_8O_{16}$, $K_1Cr_8O_{16}$ and CrO_2.

Compounds	$D(E_F)$	W	$D(E_F)W$	T_c (K)
$K_2Cr_8O_{16}$	2.75	4.65	12.79	180
$K_1Cr_8O_{16}$	4.0	4.7	18.8	265
CrO_2	5.4	5.1	27.54	387.6

4. Conclusion

The de-insertion of K^+-ions from the tunnel site has significant effect on the electronic and magnetic properties of $K_2Cr_8O_{16}$. The number of Cr-3d conduction electrons increases due to K^+-ions removal from the tunnel sites, as reflected in increase of $D(E_F)$. Hence the metallicity increases with K^+-de-insertion. The Cr-Cr coupling enhances due to loss of K-Cr bridges which results in increased Cr-O hybridization as compared with $K_2Cr_8O_{16}$, which in turns leads to increase in bandwidth W. This results in the enhancement of the strength of ferromagnetism. The increase of both $D(E_F)$ and W is regarded as the origin of the augmentation of T_c. More interestingly, T_c increases by 85 K for $K_1Cr_8O_{16}$ i.e., almost reaching room temperature. Strikingly, T_c rises by ~208 K to reach 388 K for full K^+ removal i.e., for CrO_2. Hence we find the role played by the A-site cation is not at all passive. It has an indirect effect on the electronic structure and thereby the ferromagnetism in these compounds.

5. Acknowledgements

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