Computational Predictions of the Electronic and Magnetic Properties of Alkali Metal Chlorides A$_2$MCl$_6$ (A= Alkali Metal, M = Mn, Mo): A Density Functional Theory Study

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Abstract

Detailed first-principles calculations of the electronic structure inclusive of magnetic properties of alkali metal chlorides of the type A$_2$MCl$_6$ (A = Alkali metal, M= Mn, Mo) have been performed using the density functional theory (DFT). The calculated optimized lattice constants show close agreement with experimental results. The electronic band structure and density of states were investigated for the first time using different schemes of generalized gradient approximation (GGA) such as Wu-Cohen GGA, modified Becke Johnson potential and GGA plus Hubbard $U$ parameter method. We found that the Hubbard $U$ correction significantly improves the current DFT results. The calculated band structures of K$_2$MoCl$_6$ or Cs$_2$MoCl$_6$ indicate that the spin up electrons have metallic structure while the spin down configurations have semi-conducting nature together resulting in a half-metallic behavior. Finally, the analysis of magnetic properties indicates a ferromagnetic nature for all these compounds. These findings indicate that the alkali metal chlorides K$_2$MoCl$_6$ and Cs$_2$MoCl$_6$ are potentially promising candidates for future applications in the field of spintronics.

Keywords: First principles calculations; alkali metal chlorides; Hubbard U parameter; half metallic; spintronics

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1. Introduction
The so-called half-metallic compounds, whose one state is metallic and the other insulator (or semiconductor) has attracted growing interest in the recent past due to their use in spin based electronics [1]. However, most of these materials are inherently non-magnetic, restricting their applications to the field of spintronics [2]. For possible applications in spintronics, it is necessary to discover materials with ferromagnetism at room-temperature and complete (100%) spin polarization at Fermi level [3]. Half-metallic magnets, having a metallic state in one spin direction and a semiconducting/insulating nature in the other spin direction, are proved to be the favorable materials for spintronics [1]. These materials possess large magnetoresistance (MR) and can be practically used as spin valves, spin filters, and magnetic sensors [4, 5]. In these materials, we not only consider charge of the electron but also its spin in order to produce faster processing speed in high-tech electronic devices [6]. The successful use of the electronic charge with its spin makes spintronic devices ideal and more useful than the ordinary devices. De Groot and Mueller first discovered half-metallicity in magnetic half-Heusler alloys NiMnSb and PtMnSb [7]. Since then, many reports have been published in the literature predicting half metallic characteristics in most of the new compounds. A large number of half metallic compounds have been predicted theoretically and confirmed experimentally including half and full-Heusler alloys, perovskite compounds, metallic oxides, chalcogenides, and transition metal pnictides [4, 8-10].

Here we present a detailed study of another kind of half metallic compounds, the alkali metal halides with anti-fluorite structure of the type A₂MCl₆ (A= Alkali metals and M = Mn, Mo). In these compounds, half metallicity arises due to the strong spin polarization of transition metal d-state and halogens ion p-state [3]. A lot of literature data has been published on the structural properties of this important group of compounds [11-16]. However, very limited amount of data is available about the electronic properties of these compounds. Donald et al. [11] systematically studied the lattice energies and thermo-chemistry of hexachloromolybdates K₂MoCl₆ and Rb₂MoCl₆. They found that the lattice energies of K₂MoCl₆ and Rb₂MoCl₆ are 1418 kJ/mol and 1347 kJ/mol, respectively. By performing first principles calculations, Deeth and Jenkins [12] predicted the heterolytic bond enthalpies E(M-X), bond lengths, and energies of hexahalometallate (IV) complexes. The calculated lattice energies are in fair agreement with the data published elsewhere [11]. Another extensive review by Douglas et al. [13] focuses on the structure of [MoCl₆]²⁻ complexes. Based on their study, it is confirmed that A₂MCl₆(A=K, Rb,
Cs; M = Mn, Mo) possesses cubic structure with space group $Fm\bar{3}m$. Moews [14] successfully synthesized the crystal, as well as performed studies related with the visible and ultraviolet spectra of the single crystal $K_2MnCl_6$. They concluded that the compound exhibit anti-fluorite cubic structure with unit cell length of 9.6445 ± 0.0020 Å. The bond length for Mn-Cl is 2.276 Å while for K-Cl it is 3.412 Å. The rubidium and cesium hexachloride complexes (Rb$_2$MnCl$_6$ and Cs$_2$MnCl$_6$) were also prepared and are known to have the same structures as reported for $K_2MnCl_6$. Norman carried out magnetic susceptibility measurements of $K_2MnCl_6$, $K_3Cr(CN)_6$, and V(bipy)$_3$(ClO$_4$)$_2$ in the low-temperature range from 76 K to 295 K [15]. The susceptibilities were found to increase upon decreasing the temperature. Furthermore, the magnetic moments were also measured and found in reasonable agreement with the spin only moment. Another group of researchers [16] successfully measured the magnetic susceptibility of $A_2MnCl_6$ ($A = NH_4^+, K^+, Rb^+$) salts at different temperatures. The same group also determined the crystal structure of hexametallates by powder X-ray diffraction technique.

The above discussion shows that considerable efforts have been made in the past to know the structural properties of alkali metal halides. However, the electronic and magnetic properties of these compounds are still largely unexplored. We hereby present the results of our computational investigation of the electronic and magnetic properties of alkali metal halides using the rapidly developing approach of density functional theory. Here we focus on calculating the lattice constant, bond length, band structure, electronic density of states, and magnetic properties of four different compounds, namely $K_2MnCl_6$, $K_2MoCl_6$, $R_2MnCl_6$, and $Cs_2MoCl_6$.

2. Calculations Method

The calculations presented in this work are based on the Kohn-Sham formalism of the density functional theory as implemented in the computer code Wien2k [17]. The exchange-correlation energy ($E_{XC}$) are treated with the Wu-Cohen GGA [18], Tran-Blaha modified Becke Johnson potential [19] and GGA plus Hubbard $U$ functional [20] with spin polarization. The optimized crystal structure and lattice parameters are obtained using the Wu-Cohen GGA functional. The optimized structure geometry is then used to investigate the electronic band structure, the total and partial density of states, the elastic constants, different elastic moduli, and total cell magnetic moment. Due to the well-known underestimation problem of standard LDA/GGA in describing complex systems we use the on-site Coulomb energy ($U$) in our calculations for the transition
metals (TMs) Mn and Mo which have partially filled \( d \) and \( f \) orbitals. In GGA scheme, the exchange-correlation energy \( (E_{XC}) \) is a functional of localized charge densities and their gradients:

\[
E_{XC}^{\text{GGA}}[\rho_\uparrow, \rho_\downarrow] = \int \varepsilon_{xc}(\rho_\uparrow, \rho_\downarrow, \nabla \rho_\uparrow, \nabla \rho_\downarrow) \rho(r) \, d^3r
\]  

(1)

Where \( \rho_\uparrow, \rho_\downarrow \) are electron charge densities for the spin up and spin down configurations and \( \nabla \rho_\uparrow, \nabla \rho_\downarrow \), are the corresponding gradients corrections. Further details about the spin polarized method (\( \sigma\)-GGA) and their formulas used in the present calculations were reported in earlier works [17,21]. To account for the self-interaction error in TMs \( d \) and \( f \) states we used the DFT+\( U \) method introduced by Anisimov and co-workers [22-24], which meet the high proficiency of LDA/GGA and treatment of the electron correlation with Hubbard model. The parameter \( U \) can be determined with the help of linear response theory [25].

In the full-potential scheme, the core orbitals are treated fully relativistically, whereas the valence orbitals are treated semi-relativistically. All the calculations have a kinetic energy cutoff of 400 eV, which is fairly large for the compounds studied here. The size, shape, and the relative atomic positions of the unit cell are relaxed to the point when the force acting on each atom is less than 0.05 eV/Å. For self-consistent calculations, the charge convergence criteria were selected as 0.01 me/a.u\(^3\) and that of the energy is 0.001 Ry. In all the calculations, the plane wave parameters, \( K_{\text{max}} = 8 \) and \( G_{\text{max}} = 12 \) a.u\(^{-1}\), are used for wave-function expansion in the interstitial region. The Hubbard \( U \) value is varied from 0.46 Ry to 0.61 Ry for Mn and Mo \( d \) states in the DFT+\( U \) calculations. The radial wave-functions inside the non-overlapping spheres were expanded up to \( l_{\text{max}} = 12 \). We used 2000 k-points over the first Brillouin zone (BZ) to compute the band derivatives and the density of states (DOS). The muffin-tin radii for K, Rb, Cs, Mn, Mo and Cl atoms are selected in such a manner that the corresponding muffin-tin spheres did not overlap. Therefore, we have chosen 2.5 Bohr atomic a.u for K, Rb, and Cs, 2.31 for Mn, 2.35 for Mo, and 2.01 for Cl.

3. Results and Discussion

3.1 Structural Properties
As a first step towards analysis of the structural properties of the compounds, all the lattice structures and atomic positions were optimized by minimizing the forces acting on the respective atoms using the WC-GGA approach. The optimized unit cell structure (a view along a-axis) is shown in Fig. 1a. The monovalent cation (K/Rb/Cs) is coordinated by twelve halogen ions, whereas each tetravalent cation (Mn/Mo) is coordinated by six halogen ions (Fig. 1b), forming an octahedron. The anion Cl is 6-fold coordinated. All the compounds investigated in the present study crystallize in anti-fluorite type structure with space-group Fm\(\overline{3}m\) (No. 225). In the structure, the K/Cs/Rb atom is located at Wyckoff site 8c (1/4, 1/4, 1/4) and MnCl\(_6\)/MoCl\(_6\) octahedra are centered on Mn/Mo at 4a (0, 0, 0) site. The Cl neighbors are located at 24e (x, 0, 0) site, where the variable parameter x lies around 0.2 for each of the compounds, as summarized in Table 1. The summary of our optimized structural parameters (lattice constants, ground state energy, unit cell volume, and bond length) is assembled in Table 2. A quick look at the table shows that the lattice constant seems to be increased by varying the monovalent cation, i.e. in the order \(K \rightarrow Rb \rightarrow Cs\); it is 9.74 Å for K\(_2\)MnCl\(_6\), 9.89 Å for K\(_2\)MoCl\(_6\), 10.97 Å for Rb\(_2\)MnCl\(_6\), and 10.42 Å for Cs\(_2\)MoCl\(_6\). Further, it can be noticed that the lattice constant for all the compounds slightly overestimates the experimentally measured data\[14, 27\]. This would be due to the use of GGA functional which to some extent increases the lattice constant \[18\]. The table shows that the ground state energy, \(E\) (Ry), for Cs\(_2\)MoCl\(_6\) is greater than that of the rest of the compounds. The Mn-Cl chemical bonds are 2.327 Å in K\(_2\)MnCl\(_6\) and 2.332 Å in Rb\(_2\)MnCl\(_6\). Similarly, Mo-Cl chemical bonds are 2.354 Å in K\(_2\)MoCl\(_6\) and 2.443 Å in Cs\(_2\)MoCl\(_6\) which is consistent with experimental results \[14, 16, 27, 28\]. The increase in bond length, Mn-Cl and Mo-Cl, is observed as we move from K to Rb to Cs which is attributed to the larger atomic size of Cs than K and Rb.

### 3.2 Electronic Properties

To predict the electronic properties of A\(_2\)MoCl\(_6\) (A=K, Cs) and A\(_2\)MnCl\(_6\) (A=K, Rb) systems, the spin dependent electronic band structure and density of states are calculated using the optimized geometry. Different exchange-correlation energy functionals namely, spin polarized WC-GGA, TB-mBJ, and GGA+\(U\) accompanied with spin polarization are used in order to get the detailed information of the electronic nature for all these compounds. We also checked the electronic properties of the above compounds using non-spin GGA calculations. In simple GGA calculations, the band structures profile shows overlapping bands across the Fermi level (not
shown for brevity), suggesting these compounds as metallic solids. Upon adding spin of the electron, the three different methods (GGA, TB-mBJ, and GGA+U) reveal an intriguing half-metallic character of the compounds K₂MoCl₆ and Cs₂MoCl₆. The majority spin-channel shows metallic character with zero bandgap, while the minority spin-channel shows a semiconducting nature with wide bandgap. The band structure plot of A₂MoCl₆ obtained at GGA+U level is shown in Fig. 2(a, b). From the plot, it can be seen that the valence-band maximum (VBM) of K₂MoCl₆ lie at the Γ symmetry point of 0.29 eV and the conduction-band minimum (CBM) is located at X position of 2.18 eV in the first BZ, whereas for Cs₂MoCl₆ the VBM lie at Γ symmetry point of 0.03 eV and the CBM is located at X position of the 1.56 eV in the spin down mode. Thus, the GGA+U calculations predicted that both the compounds K₂MoCl₆ and Cs₂MoCl₆ exhibit an indirect bandgap of 2.47 eV and 1.59 eV, while in the case of mBJ the corresponding values are 3.14 eV and 2.83 eV, respectively. Table 3 shows that in both the calculations the bandgap decreases with replacing K by Rb or Cs. According to our calculations, the mBJ and GGA+U method produces quite better results as compared with simple GGA. As still there is no experimental and theoretical data available for comparison, we hope that our results may offer useful guidance for further experimental and theoretical research in this direction in the future.

For A₂MnCl₆ (A=K, Rb) compounds, the band structure plots are obtained using exactly the same approach as described above for A₂MoCl₆. The WC-GGA and mBJ calculations predict the compound Rb₂MnCl₆ as half metallic. However, when GGA+U method is employed, the compound shows spin polarized semiconducting nature. For K₂MnCl₆, the plots are shown in Fig. 2(c). In both the spin states, the VBM and CBM reside at the Γ − X line indicating an indirect bandgap character. The band gap is considerably larger in the spin down state (3.97 eV) than spin up state (0.50 eV), making K₂MnCl₆ a spin-polarized semiconductor. For Rb₂MnCl₆, the spin dependent band structure profile (shown in Fig. 2(d)) is identical to that of K₂MnCl₆ except a little difference of the band gap energy in both the spin configurations.

To gain further insight into the electronic properties of A₂MoCl₆/A₂MnCl₆ frameworks, we analyzed the orbital projected total density of states (DOS) and the partial density of states (PDOS). Details of the DOS calculated by GGA+U method for all the compounds are illustrated in Fig. 3 and Fig. 4. We have also plotted the spin polarized partial DOS for K/Rb/Cs, Mo, Mn, and Cl atoms in order to predict the contribution of individuals atom in the total DOS. From Fig.
3a, it is clear that the upper valence band (nearly at −4 eV) of K₂MoCl₆ contains primarily Cl-\(p\) and Mo-\(d\) states. In spin up state, we find some overlap across the Fermi level between the delocalized Mo-\(d\) and Cl-\(p\) states presenting metallic characteristics of K₂MoCl₆, while in spin down state, the half-metallic behavior is observed with half-metallic bandgap of 2.18 eV. The bottom of conduction band is predominantly formed by Mo-\(d\) state in both the spin directions, whereas the upper part of conduction band (7 eV to 18 eV) is mainly contributed by K-\(d\), Cl-\(p\), and Cl-\(d\) states, respectively.

A similar scenario is seen in the case of Cs₂MoCl₆ (Fig. 3b) where the half-metallicity is observed in the spin down state with a half-metallic bandgap of 1.56 eV. There is also a sharp peak in the lower valence band region (−5.6 eV) due to the Cs-\(p\) state in both the spin configurations.

Similarly, for Mn containing compounds A₂MnCl₆ (A = K, Rb), the total DOS obtained from GGA+\(U\) calculations are depicted in Fig. 4. First, for K₂MnCl₆ compound, a narrow band is observed at an energy of −5.5 eV in the lower part of the valence band. The next band with different maxima (from −3 eV to 0 eV) in both the spin states is made of Cl-\(p\) state with some contribution from Mn-\(d\) state. In the spin up configuration, there is a narrow gap of 0.50 eV across the Fermi level, while in spin down state a wide band gap of 3.97 eV is present, suggesting a spin polarized semiconducting nature of the under study compounds. Above the Fermi level, there is mixed contribution of K-\(d\), Cl-\(p\), and Cl-\(d\) states in the upper region of the conduction band. In Fig. 4b, the atom projected DOS are shown for Rb₂MnCl₆ compound. It has nearly the same profile as obtained earlier for K₂MnCl₆ with little difference of the bandgap energy in both the spin configurations.

### 3.4 Magnetic Properties

The magnetic properties of the selected compounds were investigated using the spin polarized calculations based on the DFT. The magnetic moments and spin-resolved density of states (DOS) were calculated in order to explain the complete magnetic nature of the compounds. Our calculations reveal that both the systems, A₂MoCl₆ (A= K, Cs) and A₂MnCl₆ (A= K, Rb), are in ferromagnetic state. Table 4 shows the total cell magnetic moment, partial magnetic moment, and interstitial region magnetic moments of A₂MoCl₆ and A₂MnCl₆, calculated using GGA, mBJ, and GGA+\(U\) method. From the table, it is obvious that the total cell magnetic moment of
the compounds calculated with mBJ method is an integral value, which meets the criteria of a half metal as suggested by Slater–Pauling rule [37]. The positive value of the magnetic moment indicates that the magnetic ground state is ferromagnetic for $A_2\text{MoCl}_6$ and $A_2\text{MnCl}_6$. As addressed in Table 4, the magnetic moment of Mo is $1.9192\mu_B$ and $2.3900\mu_B$ in the compounds $K_2\text{MoCl}_6$ and $Cs_2\text{MoCl}_6$ while the magnetic moment of Mn is $3.0934\mu_B$ and $3.8928\mu_B$ in $K_2\text{MnCl}_6$ and $Rb_2\text{MnCl}_6$, respectively. In all the compounds, the magnetic moment seems to be mostly contributed by Mo and Mn, while the remaining atoms i.e. K, Rb, and Cs have little contribution to the total cell magnetic moment. Further, the Cl-atom is polarized antiparallel with a negative value of the magnetic moment.

In order to gain more information about the magnetic moments shown in Table 4, we calculated the spin-resolved density of states (Fig. 3 - 4) for $A_2\text{MoCl}_6$($A=K,\, Cs$) and $A_2\text{MnCl}_6$($A=K,\, Rb$) compounds. Both the valence and conduction bands are contributed by the TM-$d$ and Cl-$p$ states near the Fermi level (in spin up state). In spin down state, the VBM and the CBM overlap across the Fermi level giving rise to half metallic bandgap nature. In addition, it is evident from the spin-polarized DOS plots that the magnetism mainly arises due to the strong spin coupling of the TM-$d$ and Cl-$p$ states near the Fermi level. Further insight into the TMs (Mn and Mo) revealed that it is the partially filled $3d/4d\, (t_{2g},\, e_g)$ orbitals that play the key role in the magnetic nature of the selected compounds. The $d$-orbitals usually split into $t_{2g}(d_{xy},\, d_{xz},\, d_{yz})$ and $e_g(d_{x^2-y^2},\, d_{z^2})$ states [3, 38]. For $A_2\text{MoCl}_6$ (Mo: $4d^5$) system, the PDOS are shown in Fig. 3(c) and 3(d). Such electronic configuration will lead to five valence electrons filling the lower $d$-orbitals, giving rise to a total magnetic moment of $2\mu_B$. For $A_2\text{MnCl}_6$ (Mn: $3d^5$), as shown in Fig. 4(c) and 4(d) the four spin up and one spin down states are filled by five valence electrons leading to a total magnetic moment of $3\mu_B$ for each of the compounds.

4. Conclusions

We have systematically performed electronic structure calculations of the alkali metal chlorides of the type $A_2\text{MCl}_6$ ($A=$ Alkali metals and $M=$ Mn, Mo) using density functional theory. We used the spin-polarized WC-GGA, mBJ, and GGA+$U$ method in order to accurately determine the structural, electronic, and magnetic properties of these compounds. The lattice constants and bond length achieved with WC-GGA are found in reasonable agreement with experimentally reported data. The Hubbard $U$ parameter improves the energy bandgap categorizing $K_2\text{MoCl}_6$.
and Cs₂MoCl₆ as half-metallic compounds. Surprisingly, the manganese containing compounds, K₂MnCl₆ and Rb₂MnCl₆, show up to be spin-polarized semiconductors. The elastic constants (C₁₁, C₁₂, and C₄₄) satisfy the mechanical stability criteria suggesting these compounds as mechanically stable. Furthermore, according to our calculations, these compounds are ferromagnetic. The unique half-metallic features along with ferromagnetism of K₂MoCl₆ and Cs₂MoCl₆ hold great promise for future applications in spintronics.

Notes

The authors state no conflict of interest.

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Captions

Table captions
Table 1 Atomic coordinates for A₂MnCl₆/A₂MoCl₆ systems (SG Fm̅3m) along with the optimized structure coordinates obtained through WC–GGA.

Table 2 Optimized crystal parameters (lattice constant, volume, Energy, bond length) of K₂MnCl₆, K₂MoCl₆, Rb₂MnCl₆, and Cs₂MoCl₆ compared with experimental results.

Table 3 The calculated energy bandgap (in eV) for K₂MoCl₆, Cs₂MoCl₆, K₂MnCl₆, and Rb₂MnCl₆ using WC-GGA, mBJ, and GGA+U method.

Table 4 The calculated partial and total magnetic moments for the family of the compounds A₂MoCl₆/A₂MnCl₆.

Figure captions

Fig. 1 (a) The unit cell structure of A₂MCl₆ (A= K, Rb, Cs; X = Mn, Mo) (b) Schematic view of MCl₆ octahedra. The color scheme is shown in the figure.

Fig. 2 The calculated band structures of the (a) K₂MoCl₆ (b) Cs₂MoCl₆, (c) K₂MnCl₆ (d) Rb₂MnCl₆ compounds. The red and blue lines represent spin-up and spin-down states, respectively. The Fermi level (dashed line) is set to 0 eV.

Fig. 3 Total DOS of the (a) K₂MoCl₆, (b) Cs₂MoCl₆, (c) PDOS of K₂MoCl₆, (d) PDOS of Cs₂MoCl₆ frameworks. The vertical dotted line in plot represents Fermi level.

Fig. 4 Total DOS of the (a) K₂MnCl₆, (b) Rb₂MnCl₆, (c) PDOS of K₂MnCl₆, (d) PDOS of Rb₂MnCl₆ frameworks. The vertical dotted line in plot represents Fermi level.

Table 1

Atomic coordinates for A₂MnCl₆/A₂MoCl₆ systems (SG Fm̅3m) along with the optimized structure coordinates obtained through WC–GGA.

| K₂MnCl₆  | Wyckoff | x     | x(opt.) | y     | y(opt.) | z     | z(opt.) |
|----------|---------|-------|---------|-------|---------|-------|---------|
|       | a₀ (Å) | V    | E      | d_A (Å) | d_B (Å) |
|-------|--------|------|--------|---------|---------|
| **K₂MnCl₆** |        |      |        |         |         |
| This work: | 9.74   | 827.05 | -10251.11 | 2.327 [Mn-Cl] | 3.564 [K-Cl] |
| Experiment: | 9.64₁⁴ | ---- | ---- | 2.276₁⁴ | 3.412₁⁴ |
| **K₂MoCl₆** |        |      |        |         |         |
| This work: | 9.89   | 864.57 | -16030.87 | 2.354 [Mo-Cl] | 3.492 [K-Cl] |
| Experiment: | 9.85₂⁷ | ---- | ---- | 2.31₂⁷ | 3.48₂⁷ |
| **Rb₂MnCl₆** |        |      |        |         |         |
| This work: | 9.97   | 886.38 | -19764.35 | 2.332 [Mn-Cl] | 3.659 [Rb-Cl] |
| Experiment: | 9.82₁⁴ | ---- | ---- | 2.282₁⁶ | 3.483₁⁶ |

Table 2

Optimized crystal parameters (lattice constant, volume, Energy, bond length) of K₂MnCl₆, K₂MoCl₆, Rb₂MnCl₆, and Cs₂MoCl₆ compared with experimental results.
Table 3

The calculated energy bandgap (in eV) for $K_2MoCl_6$, $Cs_2MoCl_6$, $K_2MnCl_6$, and $Rb_2MnCl_6$ using WC-GGA, mBJ, and GGA+U method.

| Compounds    | WC-GGA | mBJ | GGA+U |
|--------------|--------|-----|-------|
|              | Up spin | Down spin | Up spin | Down spin | Up spin | Down spin |
| $K_2MoCl_6$  | 0       | 1.93 | 0     | 3.14     | 0       | 2.47      |
| $Cs_2MoCl_6$ | 0       | 1.38 | 0     | 2.83     | 0       | 1.59      |
| $K_2MnCl_6$  | 0.73    | 1.40 | 1.66  | 2.65     | 0.5     | 3.97      |
| $Rb_2MnCl_6$ | 0       | 1.41 | 0     | 2.39     | 0.6     | 4.04      |

Table 4

The calculated partial and total magnetic moments for the family of the compounds $A_2MoCl_6/A_2MnCl_6$.

| Compound     | $m^{K/Rb/Cs}$ | $m^{Mo/Mn}$ | $m^{Cl}$ | $m^{Inst}$ | $m^{Cell}$ |
|--------------|---------------|-------------|----------|------------|------------|
| $K_2MoCl_6$  | 0.0009        | 1.7180      | -0.0226  | 0.4331     | 2.0175     |
| GGA          | 0.0001        | 1.9192      | -0.0484  | 0.3710     | 2.0000     |
| TB-mBJ       | 0.0032        | 1.5654      | 0.0005   | 0.3610     | 1.9356     |
| $Cs_2MoCl_6$ |               |             |          |            |            |
|        |        |        |        |        |
|--------|--------|--------|--------|--------|
|        | GGA    | TB-mBJ | GGA+U  |        |
|        | -0.0002 | -0.0012 | -0.0014 |        |
|        | 2.1919  | 2.3900  | 2.0146  |        |
|        | -0.0959 | -0.1324 | 0.0443  |        |
|        | 0.3762  | 0.4058  | 0.3134  |        |
|        | 1.9922  | 2.0000  | 2.0593  |        |
|        | K₂MnCl₆ |        |        |        |
|        | GGA    | TB-mBJ | GGA+U  |        |
|        | 0.0005  | 0.0004  | 0.0004  |        |
|        | 3.8656  | 3.0934  | 1.7066  |        |
|        | -0.1234 | -0.0263 | 0.1542  |        |
|        | -0.0599 | 0.0638  | 0.3601  |        |
|        | 3.0663  | 3.0001  | 2.9927  |        |
|        | Rb₂MnCl₆|        |        |        |
|        | GGA    | TB-mBJ | GGA+U  |        |
|        | 0.0010  | -0.0002 | 0.0015  |        |
|        | 3.9700  | 3.8928  | 1.1876  |        |
|        | -0.3251 | -0.1508 | 0.2223  |        |
|        | -0.4138 | 0.0123  | 0.4777  |        |
|        | 1.6076  | 3.0001  | 3.0023  |        |
Fig. 1. (a) The unit cell structure of $\text{A}_2\text{MCl}_6$ ($\text{A} = \text{K, Rb, Cs}; \text{M} = \text{Mn, Mo}$) (b) Schematic view of $\text{MCl}_6$ octahedra. The color scheme is shown in the figure.
Fig. 2. The calculated band structures of the (a) $\text{K}_2\text{MoCl}_6$ (b) $\text{Cs}_2\text{MoCl}_6$, (c) $\text{K}_2\text{MnCl}_6$ (d) $\text{Rb}_2\text{MnCl}_6$ compounds. The red and blue lines represent spin-up and spin-down states, respectively. The Fermi level (dashed line) is set to 0 eV.
Fig. 3. Total DOS of the (a) K$_2$MoCl$_6$, (b) Cs$_2$MoCl$_6$, (c) PDOS of K$_2$MoCl$_6$, (d) PDOS of Cs$_2$MoCl$_6$ frameworks. The vertical dotted line in plot represents Fermi level.
Fig. 4. Total DOS of the (a) K₂MnCl₆, (b) Rb₂MnCl₆, (c) PDOS of K₂MnCl₆, (d) PDOS of Rb₂MnCl₆ frameworks. The vertical dotted line in plot represents Fermi level.