

# A Study of Electronic and Magnetic Properties of Transition Metal Trihalides

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**Abstract.** We present the electronic and magnetic structure calculations of  $\text{VCl}_3$ ,  $\text{VBr}_3$ ,  $\text{CrCl}_3$  and  $\text{CrBr}_3$ . The results are obtained by density functional theory with plane wave basis sets. The transition metal trihalides generally optimize either in trigonal or monoclinic structures. We have focused on the effect of symmetry on the electronic and magnetic properties of the systems. We have found that magnetic moments change considerably depending on the symmetry. Both  $\text{CrX}_3$  has shown a bandgap  $\approx 2\text{eV}$  while the V based systems have shown half-metallic properties.

## 1. Introduction

The family of transition metal trihalides  $\text{MX}_3$ , where M is a transition metal cation ( $\text{M}=\text{Ti, V, Cr, Fe, Mo, Ru, Rh, Ir}$ ) and X is a halogen anion ( $\text{X}=\text{Cl, Br, I}$ ), have been known for more than 50 years[1, 2]. These compounds have been in spotlight for some amusing electronic and magnetic properties they exhibit in their bulk and monolayer phases such as, intrinsic long-range magnetic order in atomically thin layers[3] as well as its profound applications in spintronics[4]. With lower dimensionalities of  $\text{MX}_3$ , their bandgap can be tuned by doping or changing their stacking orientation. This property of  $\text{MX}_3$  opens up the opportunity in multi-purpose applications.

Structurally an X-ray and neutron diffraction study ascertained that the single  $\text{MX}_3$  crystal adopts a monoclinic  $\text{AlCl}_3$  structure (space group  $C2/m$ ), termed as ( $\beta$  phase)[5].  $\beta$ -phase is found to be lower symmetry crystallographic phase which is most likely to be found at higher temperatures. Upon cooling from higher temperature,  $\text{MX}_3$  layers rearrange themselves from  $\beta$ -phase to  $\text{BiI}_3$ -type trigonal(space group  $R\bar{3}$ ) structure known as  $\alpha$ -phase. The transition has been reported to be a first-order phase transition which does not involve any magnetic changes[6]. This phase transition is believed to result from interlayer interactions among the layers[7, 8]. The interlayer interactions are caused by weak van der Waals(vdW) bonding[7] between halogen(X) anions hence, known as vdW structures. The vdW structures reveal themselves to be truly captivating in the field of materials science due to the presence of intrinsic magnetism and magnetic

anisotropy[9], tunable band gap and high temperature magnetic ordering[4]. This property of tunable band gap leads to new generation spintronics, magnetic and magneto-optic applications[10].

Spintronics is a new generation information technology where spins of electrons are employed as information carriers and also speeds up data processing. Half metals, spin gapless semiconductors and bipolar magnetic semiconductors were proposed one after another as probable property in spintronics[11]. Half metals have been established commendatory in spin current generation and making spintronic and other nano-electronic devices. Dirac half metals exhibit a large bandgap in one spin channel and metallic character in the other. We attempt to figure out half-metals among the family of transition metals in bulk phases.

For many of the  $\text{MX}_3$  compounds downscaling the bulk phase to a stable monolayer is still a challenge. Some studies suggest that monolayers with binding energy smaller than 0.15 eV per atom might be feasible for exfoliation[12]. The physical properties of a

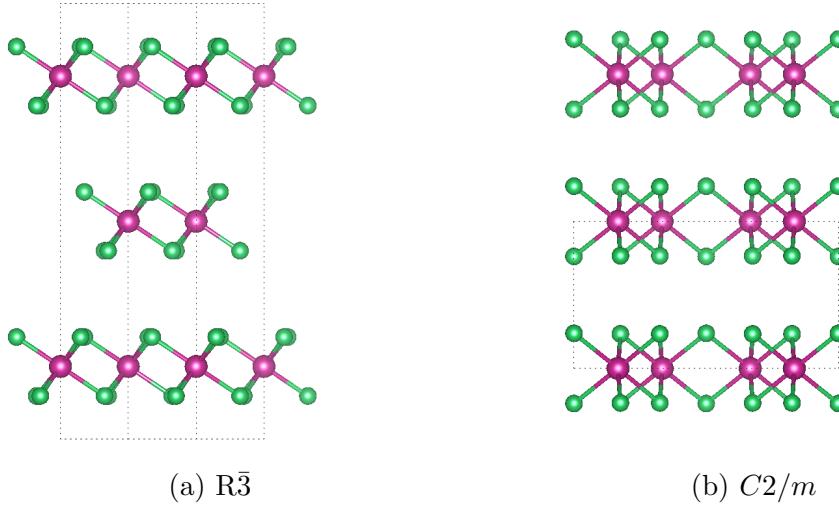


Figure 1: Bulk structures of  $\text{MX}_3$  for (a) $R\bar{3}$  and (b) $C2/m$  space groups respectively

few-layer or monolayer structures of such transition metal  $\text{MX}_3$  are quite different from that of their bulk structures as a result of the different screening environments they experience due to the differences in their effective dimensionality[13].

Various density functional theory(DFT) based studies of bulk and few-layer  $\text{MX}_3$  for the ground-state have been carried out theoretically[6, 14, 15, 16]. The difference in electronic screening for bulk and few-layer  $\text{MX}_3$ [17] results in different electronic bandgaps. These studies cover the interlayer exchange coupling[18] as well as its dependence on the stacking of layers, possible ways to stabilize skyrmions[19], and the electric-field switching of the magnetization[20].

Researchers have detected rich magnetic ground states in the  $\text{MX}_3$  family. Magnetism in the ground state of a material is correlated to interlayer vdW coupling. While vdW coupling originates from distinct stacking orders and the signature Kagome

lattice[21].

In  $\text{MX}_3$ , magnetism originates from the angular momentum associated with partially filled  $d$  orbitals. It has been predicted that the in-plane magnetic interaction among the transition metal cations is a consequence of super-exchange through shared coordinating halogen anions. The super-exchange interaction depends upon factors like orbital occupations and the M-X-M angle[22].

Among the  $\text{MX}_3$  series, the Cr and V-based materials are mainly of importance.  $\text{CrCl}_3$  has recently been shown to have an unusual magnetic easy axis normal to the  $c$ -axis[23]. Further, Ebrahimian *et al.* has recently shown that the magnetism in bilayer  $\text{CrCl}_3$  can be easily controlled by strain and electric field[24]. Ahmad *et al.* has shown magnetism of  $\text{CrCl}_3$  can be controlled by pressure also[25].  $\text{VCl}_3$  has been shown to have half metallicity in 2D[26]. Doping 3d transition metal to  $\text{VCl}_3$  has been shown to tune its electronic and magnetic properties very recently[27]. High tunnel magnetoresistance and spin filtering effect are shown in  $\text{CrBr}_3$ [28]. Grzeszczyk *et al.* has recently shown exciton magnetization in  $\text{CrBr}_3$ [29].

From the above discussion, it is clear that V and Cr-based  $\text{MX}_3$  systems play a significant role in the development of spintronics. Hence, a detailed and systematic study of these systems from the equivalent theoretical field is necessary. In this study, we compare the structural and electronic properties of the possible space groups ( $R\bar{3}$  and  $C2/m$ ) of trichlorides and tribromides of V and Cr using *ab-initio* density functional theory.

## 2. Computational Details

The Density functional theory (DFT) calculations of vdW layered  $\text{MX}_3$  have been brought about with Quantum Espresso[30, 31]. For the exchange-correlation functional general gradient approximation (GGA) was used in the projector augmented wave(PAW)[32] pseudopotential. We used the plane-wave cut-off energy of 320 eV to treat interactions between the valence electrons and ion cores. The calculations are done in  $\Gamma$ -point.

Since  $\text{MX}_3$  is a layered system, vdW corrections were used based on the semiempirical Grimme's DFT-D2[33] approach. We need to account for the strong correlation effects of localized 3d electrons of transition metal atoms to describe their electronic and magnetic properties[34] correctly. In this case, a simplified version of the DFT+U method suggested by Dudarev[35] was employed. We set the effective Hubbard interaction parameter  $U_{eff}$  of metal atoms to 2.7 eV[36, 37]. It is acquired by comparing physical properties directly.

## 3. Results and Discussions

The  $\text{MX}_3$  system stabilizes in  $R\bar{3}$  and  $C2/m$  structures. We have calculated the ground state of both structures with  $\text{M}=\text{V}$ , Cr and  $\text{X}=\text{Cl}$ , Br. The optimized

lattice parameter( $a$ ), optimized M-X bond length( $d_{M-X}$ ), interplanar separation( $d_0$ )and magnetic moment per formula unit( $f.u.$ ) for  $\text{VCl}_3$ ,  $\text{VBr}_3$ ,  $\text{CrCl}_3$  and  $\text{CrBr}_3$  are shown in Table (1), for FM magnetic ordering. The minimal energy ground state of the Bravis lattice are shown in bold.

$\text{MX}_3$	$a(\text{\AA})$	$d_{M-X}(\text{\AA})$	$d_0(\text{\AA})$	magnetic moment( $\mu_B/f.u.$ )
<b><math>\text{VCl}_3(\text{R}\bar{3})</math></b>	6.12	2.40	4.48	2.54(2.0 [38])
$\text{VCl}_3(c2/m)$	6.26	2.40	5.08	2.32(2.96 [5])
<b><math>\text{VBr}_3(\text{R}\bar{3})</math></b>	6.52	2.56	4.60	2.84(2.6 [39])
$\text{VBr}_3(c2/m)$	6.62	2.57	5.15	2.46(2.0 [40])
$\text{CrCl}_3(\text{R}\bar{3})$	6.08	2.38	4.32	3.59(3.0 [41])
<b><math>\text{CrCl}_3(c2/m)</math></b>	6.09	2.38	5.15	5.38 (6.0[42])
$\text{CrBr}_3(\text{R}\bar{3})$	6.46	2.55	4.75	3.91(3.10[43])
<b><math>\text{CrBr}_3(c2/m)</math></b>	6.39	2.56	5.34	3.90

Table 1: Crystal and magnetic structure information of  $\text{MX}_3$  compounds. The magnetic moments in the bracket show their experimental values.

The magnetic moments match closely with their experimental values (given in the bracket and reference therein). The discrepancies come from the fact that we have done a  $\Gamma$ -point only calculation.

In figures (2)-(5), we have discussed the electronic structure of  $\text{MX}_3$  systems.

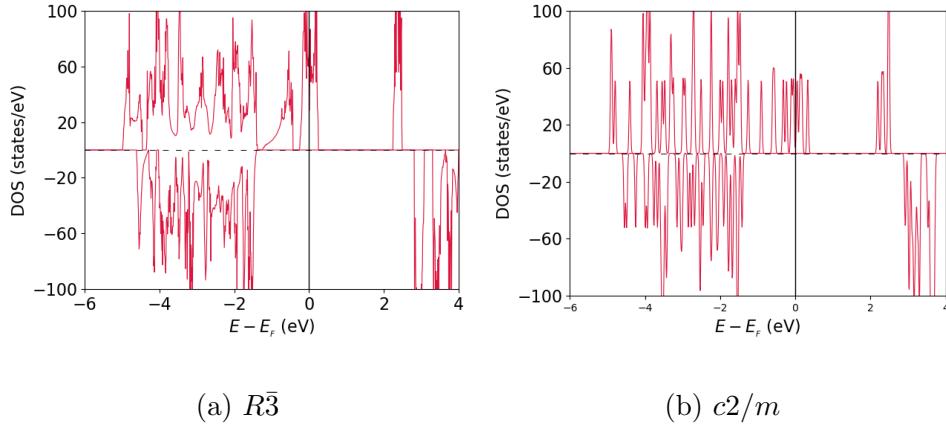
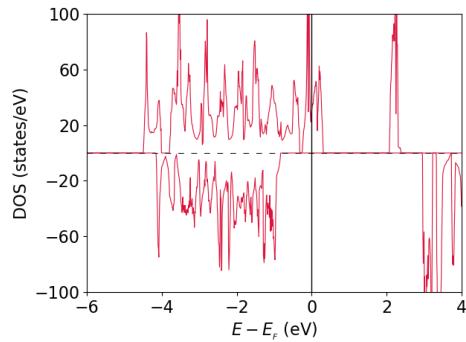
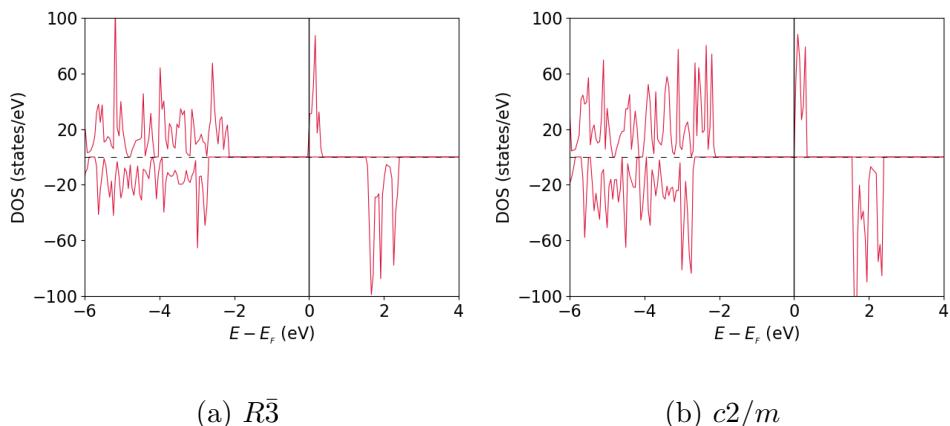
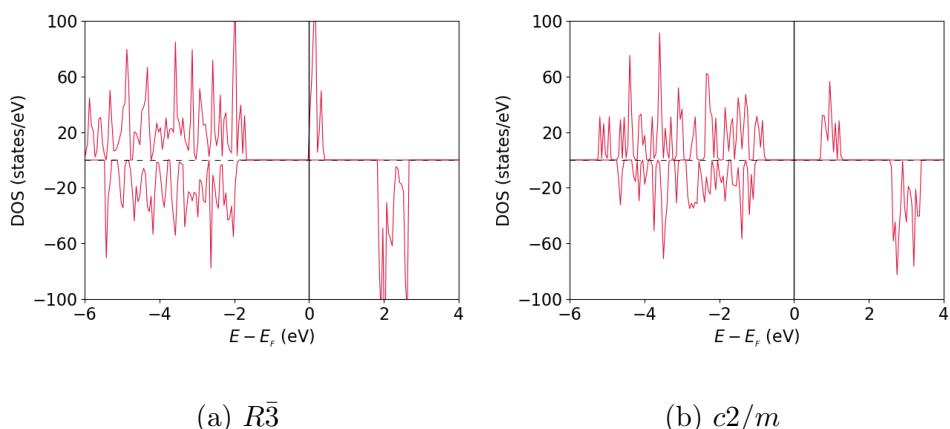


Figure 2: DOS of  $\text{VCl}_3$  for (a)  $R\bar{3}$  and (b)  $c2/m$  structure

The DOS of  $\text{VCl}_3$  shows prominent states in the majority spin channels and a big gap in minority spin channel for both  $R\bar{3}$ (Fig. (2a)) and  $c2/m$ (Fig. (2b)) structure. This resembles the experimental and previous theoretical findings[10].

$\text{VBr}_3$  DOS also shows the same characteristics. These half-metallic behavior of  $\text{VCl}_3$  and  $\text{VBr}_3$  is well known and sustained in bilayer systems[44].

Figure 3: DOS of  $\text{VBr}_3$  for  $R\bar{3}$ Figure 4: DOS of  $\text{CrCl}_3$  for (a)  $R\bar{3}$  and (b)  $c2/m$  structureFigure 5: DOS of  $\text{CrBr}_3$  for (a)  $R\bar{3}$  and (b)  $c2/m$  structure

With our very small  $U_{eff}$ , the story is completely different for Cr-based trihalids. Both  $\text{CrCl}_3$  and  $\text{CrBr}_3$  show bandgap  $\approx 2\text{eV}$  in all the cases. This is also well known feature[45]. Though our position of DOS peaks does not match the existing literature, the characteristics are well produced with the small  $U_{eff}$ . The band gap decreases significantly from  $\text{CrCl}_3$  to  $\text{CrBr}_3$ .

#### 4. Conclusion

Although there are several studies on  $\text{MX}_3$  systems, there is still a gap in understanding their stacking, structure, and electronic and magnetic properties. Due to the recent interest in spintronic applications, it was necessary to study those materials systematically. In this study, we have explored the electronic and magnetic properties of  $\text{CrCl}_3$ ,  $\text{CrBr}_3$ ,  $\text{VCl}_3$  and  $\text{VBr}_3$  in bulk phase using DFT with plane wave basis. We have shown that the stacking and the space group play an important role in their magnetic and electronic properties. We are confident that this will enable us to design better  $\text{MX}_3$  based spintronic devices with bilayer and multilayer.

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