Electronic and magnetic properties of CdI$_2$-type MX$_2$ (M = V, Nb; X = Al, Ga and In) compounds

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Abstract. First-principle calculations within the density-functional theory is used to investigate the possibility of existence of ferromagnetism in hypothetical CdI$_2$-type MX$_2$ (M = V, Nb; X = Al, Ga and In) compounds. The TBLMTO-ASA program is used for this purpose. Both spin-polarization and non-spin-polarization calculations are carried out for each compound. The spin-polarization calculation shows that VX$_2$ (X = Al, Ga and In) compounds are ferromagnets whereas NbX$_2$ (X = Al, Ga and In) compounds are non-magnets because no effective polarization of the energy states occurs at their equilibrium volume. However, the NbX$_2$ (X = Al, Ga and In) compounds become ferromagnets under large volume expansion. Ferromagnetism in these compounds is predicted for the first time. The variation of lattice constant with magnetic moment for VX$_2$ (X = Al, Ga and In) compounds are also analysed. The magnetism arises mainly from the cation $d$-like states. This result is similar to other transition-metal based pnictide and chalcogenide compounds. The ground-state properties like equilibrium lattice parameters, bulk modulus, heat of formation and total and partial magnetic moments are calculated.

1. Introduction
Several layered transition-metal compounds have interesting magnetic properties [1, 2]. In this work, we have systematically studied the electronic band structure calculations for the hypothetical layered CdI$_2$-type MX$_2$ (M = V, Nb; X = Al, Ga and In) compounds in the ferromagnetic and nonmagnetic phases. To the best of our knowledge, there are no experimental and theoretical studies on these compounds. The motivation of the present work is to investigate the ferromagnetism in these compounds by performing first principles electronic structure calculations by means of TBLMTO method within the density functional formalism. Ferromagnetism in these compounds is predicted for the first time. The obtained results are compared with other transition-metal ferromagnets [3].

2. Crystal Structure and Method of Calculations
Within the framework of DFT, the electronic structure calculations are performed using the TBLMTO method. The potential and charge density inside each atomic sphere are assumed to have spherical symmetry. This method has been described well in the literature [4-6]. In the CdI$_2$-type structure (space group: P-3m1, No.: 164), the M and X atoms occupy the (0, 0, 0) and (0.33, 0.66, z) positions. The LMTO method gives accurate results only for close packed structures. Hence, an empty sphere is placed at the appropriate position, E: (0, 0, 0.82). For the titled compounds, the cell parameter values are optimized using the experimental cell parameter values of CdI$_2$-type Vanadium di halide compounds [2].
3. Result and discussion

Spin-polarization (Ferromagnetic phase) and non-spin-polarization (Nonmagnetic phase) calculations were carried out for the titled compounds in the hypothetical CdI$_2$-type structure in a manner similar to our earlier work [7, 8]. The total energy as a function of molecular volume is calculated for all these compounds. As an example, the result for CdI$_2$-type VAl$_2$ and NbAl$_2$ compounds are shown in figure 1. From the total energy calculations, it is observed that VX$_2$ compounds have lower energies in ferromagnetic phase compared with non-magnetic phase whereas NbX$_2$ compounds does not occur effective spin-polarization. Heat of formation or formation energy is calculated in order to study the stability of phase. The calculated ground-state properties and heat of formation of these compounds are listed in Table 1.

![Figure 1. Calculated total energy per formula unit vs. Volume (Å$^3$).](image)

The calculated spin-dependent density of states for VAl$_2$ compound at their equilibrium volume is shown in Figure 2. This compound exhibit ferromagnetic property with small magnetic moment and both the spins have metallic nature. In this compound, the states which are lying around -10 eV are mainly due to the anion s-like states. The states lying above this are mainly contributed by anion p-like states and cation s- and d-like states. The hybridized states of anion p-like and cation d- and s-like states lie close to the Fermi level. The density of states profiles of majority spin and minority spin for these compounds are slightly different. This may be one of the reasons why there is small magnetic moment induced in the anion p-like states. The overall density of states profiles for VGa$_2$ and Vi$_2$ compounds are similar. The calculated total magnetic moments for these compounds are given in Table 2 along with partial magnetic moments at each atomic site.

| Compounds | Lattice constants (a, c) in Å, bulk modulus ($B_0$) in GPa and heat of formation (H) in kJ/mol. in FM phase. The values in the parenthesis are for NM phase. |
|-----------|------------------------------------------------------------------------------------------------------------------------------------|
| VAl$_2$   | $a = 3.389$, $c = 5.492$, $B_0 = 471.57$, $H = 124.891$ in kJ/mol.                                                                  |
| VGa$_2$   | $a = 3.473$, $c = 5.637$, $B_0 = 399.71$, $H = 120.987$ in kJ/mol.                                                               |
| Vi$_2$    | $a = 3.561$, $c = 5.779$, $B_0 = 313.53$, $H = 91.286$ in kJ/mol.                                                               |
| NbAl$_2$  | $a = 3.445$, $b = 5.594$, $B_0 = 585.96$, $H = 98.631$                                                                      |
| NbGa$_2$  | $a = 3.517$, $b = 5.707$, $B_0 = 503.55$, $H = 89.343$                                                                      |
| NbIn$_2$  | $a = 3.621$, $b = 5.878$, $B_0 = 484.64$, $H = 68.731$                                                                      |
Figure 2. Spin-dependent total (left) and partial (right) DOS’s of VAl₂ compound at their equilibrium volume.

From the table, it can be observed that the main contribution to the magnetic moment comes from the transition-metal atom. From the Figure 3, it can be seen that the magnetic moment for VX₂ compounds is slowly decreasing with reducing the cell volumes, finally it becomes non-magnetic.

Table 2. Calculated magnetic moments (µ) in µB.

|         | Cation | Anion | Empty site | Total  |
|---------|--------|-------|------------|--------|
| VAl₂    | 2.3302 | 0.1315| 0.0197     | 2.4814 |
| VGa₂    | 2.1606 | 0.1001| 0.0149     | 2.2756 |
| VIn₂    | 2.7203 | 0.0868| 0.0111     | 2.8182 |

Figure 3. Volume vs. magnetic moment of VX₂ compounds.

Both spin-polarization and non-spin-polarization calculations are carried out for NbX₂ compounds. The overall density of states profiles for these compounds at their equilibrium volume are similar to majority spin density of states of VX₂ compounds. These compounds exhibit non-magnetic behavior. In these compounds, both the spin bands are metallic. For expanded volume, these compounds exhibit ferromagnetic property with small magnetic moment. Both spins have metallic character. The difference between majority spin and minority spin states is that, around the Fermi level, the hybridized states of anion p-like and cation d-like states shifts towards the lower energy and lies below the Fermi level in the spin up states. With increasing volume, the cation d-electrons transfer from minority spin to majority spin. The spin-dependent total and partial density of states for NbAl₂ compound at their critical or expanded volume is given in Figure 4. The critical lattice constants and magnetic moments for NbX₂ compounds are given in Table 4.

Figure 4. Spin-dependent total (left) and partial (right) DOS’s of NbAl₂ at their expanded volume.
Table 4. Calculated critical lattice constants (a$_{cri}$, c$_{cri}$) in Å, magnetic moments (µ) in µ$_B$ for NbX$_2$ compounds.

|          | a$_{cri}$ | c$_{cri}$ | Magnetic moments |
|----------|-----------|-----------|------------------|
|          | Cation    | Anion     | Empty            | Total            |
| NbAl$_2$ | 3.836     | 6.216     | 1.3335           | 0.1604           | 0.0134           | 1.5075           |
| NbGa$_2$ | 3.775     | 6.127     | 1.2672           | 0.1391           | 0.0149           | 1.4212           |
| NbIn$_2$ | 3.879     | 6.215     | 0.1547           | 0.0110           | 0.0006           | 0.1663           |

4. Summary and Conclusion

To summarize, the electronic band structure calculations have been carried out for titled compounds in hypothetical CdI$_2$-type structure in order to find ferromagnetism. From the total energy calculations, one can observe easily that VX$_2$ (X = Al, Ga and In) compounds have lower energies in ferromagnetic phase compared with nonmagnetic phase whereas NbX$_2$ (X = Al, Ga and In) compounds are nonmagnets at their equilibrium volume. In these compounds, the magnetism arises mainly from the cation d-like states. VX$_2$ (X = Al, Ga and In) compounds exhibit ferromagnetic property with small magnetic moment at their equilibrium volume. However, NbX$_2$ (X = Al, Ga and In) compounds exhibit ferromagnetism under large volume expansion. In these compounds, unit cell volume plays an important role in exhibiting ferromagnetism. This result is similar to other transition-metal based group V compounds [3, 9].

Acknowledgement

The first author (G. J.) gratefully acknowledges the financial support from University Grant Commission (UGC), India.

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