Tuning of Magnetism and Band Gap in 2D-Chromia via Strain Engineering

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The area of intrinsic two-dimensional (2D) materials is spreading widely day by day due to their easily availability and interesting applications. As a newly exfoliated 2D material from bulk Cr_2O_3 mineral, 2D-Chromia is most far ultrathin magnetic indirect band gap semiconductor with low Curie Temperature (T_C). For the present work, we have carried out the detailed structural analysis of 2D-Chromia by prefacing strain via means of density functional theory (DFT). 2D-Chromia in pristine form comes out to ferromagnetic with considerable total spin magnetic moment of 12 μ_B per unit cell and large band gap (0.72/3.71 eV in majority/minority spin channel). But the presence of low T_C and large band gap limits its applications. Thus, in present work, we have checked the dependence of magnetic state and band gap on tensile and compressive strains. Our results indicate that band gap depends strongly on both the strains but magnetic ground state remains unaffected on applying strain. These findings summarize that the resulting 2D-Chromia under study has broad application prospective in spintronics, transistors, and memory-based devices.

Keywords: DFT; Ferromagnetism; Spintronics

1 Introduction

Advanced magnetism in two dimensional (2D) materials is currently one of the most fascinating and hot topics for materials science community due to their wide spectrum of applications in almost every field such as spintronics, quantum computers, random access memory-based devices, magneto-resistive tunnelling, electrolysis, optoelectronics and advanced rechargeable batteries[1-2]. With the passage of time, a number of studies have been performed to originate and understand magnetism in these 2D materials at nano scale through advanced theoretical calculations and experimental techniques[3-5]. However, there are still so many challenges left to tackle such the long-range magnetic order which is maintained in bulk but can be easily destroyed in these 2D materials as they are too thin to handle thermal fluctuations[6]. Thus, it is important to offer some effective and important perspectives in this direction that may be helpful further to originate magnetism in them and to enhance their potential for technological applications. Now a days, CrI_3, $Cr_2Ge_2Te_6$, 2Danalog of transition metal oxides such as hematene (2D analog of iron-ore hematite Fe_2O_3), 2D-Chromia (2D analog of bulk Cr_2O_3 mineral) have emerged as exciting intrinsic 2D materials as far as collective magnetism is concerned[7-9]. Also, in these materials, depending upon the requirement for a particular application, it is very easy to tune their electronic and magnetic properties by applying strain, defects and electric field. Further, these 2D materials can handle large strain as compared to their bulk analog. Like, FeSe monolayer can handle large strain as 6%, whereas MoS_2 monolayer can sustain strain as high as 11%[10]. Thus, strain engineering can be one of a practical approach to tune their various properties. Chen *et al.*[11] made an attempt to tune the magnetism in hematene by ferroelectric polarization. Their results indicated that the magnetism in it can be controlled easily by changing bond length of Fe-O. Previously, our group[12-13] also studied the effect of strain on the structural, electronic and magnetic properties of hematene. It was found that pristine hematene is ferrimagnetic in nature and its T_C is 298 K. Upon applying compressive and tensile strain, band gap and magnetic state remain same but Curie temperature (T_C) gets affected to a great extent. This T_C gets

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increased on increasing compressive strain and this increase in T_C is up to 33% at strain of -6%. Also, it gets decreased by increasing tensile strain. Further, our group[14] also studied the structural, magnetic and electronic properties of 2D-Chromia (2D-Cr_2O_3) which is exactly similar to hematene just with one difference that Cr atom is present in 2D-Chromia instead of Fe atom in hematene at the same positions. Thus, working on the same line, we wish to further extend our study of 2D-Chromia by introducing compressive and tensile strain up to 6% on the band gap and magnetic state. To our belief, this is the first report on the prediction of its strain-induced magnetic state and band gap of 2D-Chromia.

2 Computational Details

All the first-principles calculations of pristine and strain induced structures were performed using density functional theory (DFT) approach as implemented in Quantum Espresso[15]. The coordinates of atoms of all strain induced structures were optimized by incorporating conjugate-gradient algorithm and the
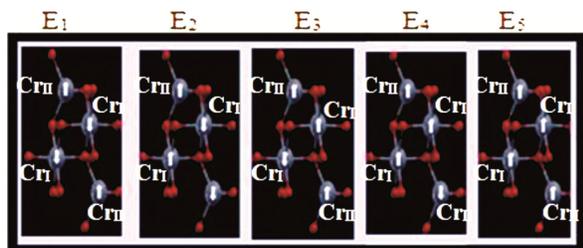
Fig. 1 — Optimized 2D-Chromia unit cell in five possible configurations depending upon different spin alignments

electronic relaxations were done using a very tight convergence criteria of 10^{-8} eV. The Coulomb corrected generalized gradient approximation (GGA+U) was used as the exchange-correlation potential under Perdew-Burke-Ernzerhof (PBE) parameterization[16-17]. In addition, the strong correlations between d-orbitals of Cr-atom in 2D-Chromia were handled by selecting a proper value of Hubbard parameter (U=5eV)[14]. A k-points mesh of 15×15×1 was used to sample the brillouin zone. The periodic interactions were avoided by adding a vacuum layer of 15 Å thickness along c-axis. The tetrahedron method with Blöchl corrections was used to calculate total and partial density of states of all the cases.

3 Results and Discussion

2D-Chromia has an interesting crystal structure as it is exfoliated from a natural bulk mineral α phased Cr_2O_3. Its unit cell is composed of ten (four Cr and six O) atoms. But the environment of all four Cr atoms is not same. Out of four, two Cr atoms (Cr_I) atoms are surrounded by six O atoms whereas the remaining two (Cr_{II}) are enclosed by three O atoms. Depending upon the different spin alignment of these Cr_I and Cr_{II} atoms, five different spin configurations (E_1, E_2, E_3, E_4, E_5) are possible.

Our results indicate that out of these five configurations (Fig. 1), E_5 in which all Cr_I and Cr_{II} atoms align parallel comes out to be ground state with total spin magnetic moment of 12 μ_B per unit cell. Also, 2D chromia has an indirect band gap with values of 0.723/3.710 eV in majority/minority spin channel in this E_5 configuration (Fig. 2).
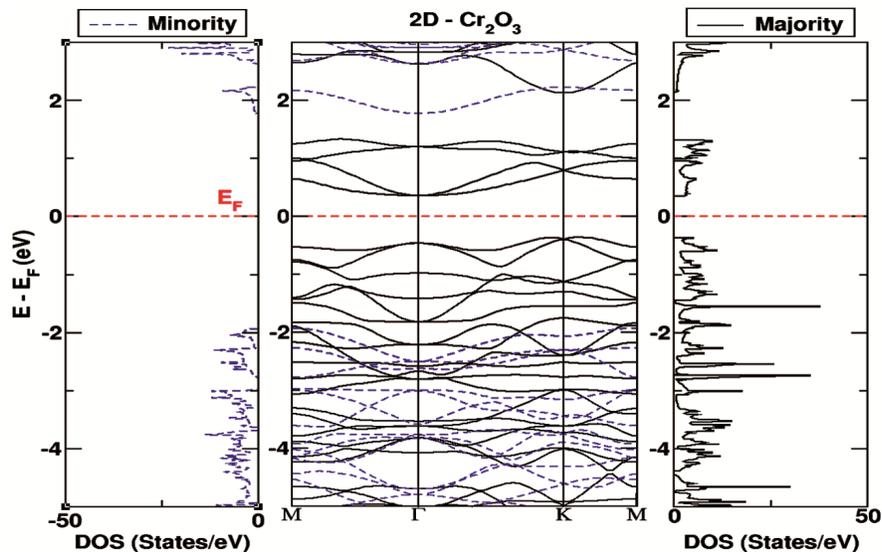
Fig. 2 — Spin resolved bandstructure and density of states of pristine 2D-Cr_2O_3. E_F represents the Fermi level and is shifted to zero.

The large difference in the band gap values in majority spin channel (MAC) and minority spin channel (MIC) is due to the fact that for MAC, the main contribution to valance band arises from the hybridization of d orbitals of Cr_I, Cr_{II} atoms and p-orbitals of O atoms, whereas for MIC, it mainly arises from p-orbitals of O-atoms. Also, the conduction band for MAC consists of d-orbitals of Cr_I and Cr_{II} in the close proximity of Fermi level (E_F) whereas for MIC, the occupancy of d-orbitals of Cr_I and Cr_{II} is far away from E_F. The large value of band gap limits its worth in various applications such as transistors and semiconductors. Thus, in order to tune the band gap and magnetic states, we made an attempt to introduce the biaxial strain *i.e* compressive ranging from -2% to -6% and tensile ranging from +2% to +6% in it. After that, atomic coordinate of all the strain induced structures were relaxed keeping the lattice constant same. This optimization did not cause any type of distortion in the shape of 2D-Chromia. The stability of all these cases was ensured by calculating formation energy (E_{For}) by using formula as under:

$$E_{For}= E_{2D\text{-}Chromia}-4E_{Cr}-6E_O \qquad \ldots(1)$$

where $E_{2D\text{-}Chromia}$ stands for energy in respective strained case. E_{Cr} and E_O represent ground state energy for isolated Cr and O atoms, respectively.

Our results shows that E_{For} comes out to be negative for all cases confirming their stability (Table 1).

From Table 1, it is clear that all compressive strained structures are more stable as compared to all tensile strained cases. Out of all compressive strained cases, one with -6% comes out to be most stable. Also, there is a little difference in energy for -4% and -6% cases which indicates that strain percentage cannot be more than -6%. Our DFT+U simulations predict that ground state for all the strain induced structures remains ferromagnetic with total magnetic moment of 12 μ_B per unit cell. It means that magnetic state is robust under both strains for all cases. However, the total DOS in the proximity of E_F get affected highly for all cases of tensile and compressive strain (Fig. 3).

Further, there is an appreciable change in the values of band gap for both spin channels of all the strain cases, implying that this band gap is tunable under the effect of strain. But the band gap comes out to be indirect for all the cases. The value of band gap gets reduced in both the spin channel for both compressive and tensile strain [Table 2]. Also, the band gap keeps on decreasing with increase in both types of strains. But

Table 1 — Calculated Formation energy (E_{For}) of all compressive and tensile strain induced cases in range (-6% to +6%)

Strain	-6%	-4%	-2%	+2%	+4%	+6%
E_{For}(eV)	-0.359	-0.358	-0.242	-0.098	-0.071	-0.066
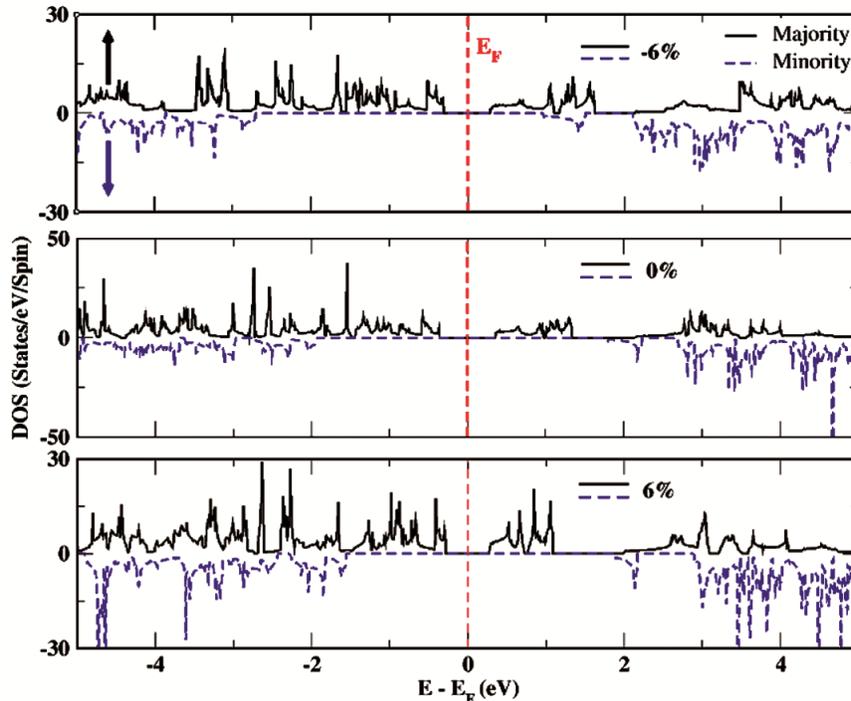
Fig. 3 — Calculated spin polarized total density of states (TDOS) of strained induced 2D-Chromia Monolayer.

Table 2 — Calculated Spin polarized band gap values for pristine and strained induced (compressive and tensile strain ranging from -6 to +6%) of 2D-Chromia monolayer.

Strain	-6%	-4%	-2%	0%	+2%	+4%	+6%
Band Gap($\uparrow$)(eV)	0.597	0.598	0.601	0.723	0.586	0.576	0.557
Band Gap($\downarrow$)(eV)	3.601	3.601	3.620	3.710	3.492	3.406	3.428

the reduction is more for tensile strain as compared to compressive strain. This may be due to the fact that compressive strained structures are more stable as their ground state energies are closer to that of pristine case. Thus, tensile strain affects 2D-Chromia monolayer more as compared to compressive strain because of large difference in their ground state energies. The maximum reduction in band gap (22%/7% for majority/minority spin channel) is for +6% case of tensile strain.

4 Conclusion

The effect of compressive and tensile strain was examined on 2D-Chromia monolayer in order to tune the band gap and magnetic state by DFT simulations. Our results indicate that the magnetic ground state of pristine as well as strained Chromia monolayer remain ferromagnetic with same magnetic moment and all the pristine and strained systems come out indirect semiconductor with different band gaps for the majority and minority spin channels. On applying compressive and tensile strains, the structural and magnetic properties do not change much but the value of band gap gets reduced around 22% for majority spin channel and 7% for minority spin channel as compared to that of the pristine case. We are hoping that our results will promote experimental studies for

2D-Chromia and find out the way for its application in spintronics, transistors, and memory-based devices.

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