East Eur. J. Phys. **1**. 93-98 (2021)
DOI:10.26565/2312-4334-2021-1-12

PACS: 71.15.Mb, 71.20.-b, 71.20

STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF INTERCALATED TRANSITION METAL DICHALCOGENIDES COMPOUND MTiS$_2$ (M = Cr, Mn, Fe) BY DENSITY FUNCTIONAL THEORY

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Received December 31, 2020; accepted February 26, 2021

In the present work, we have studied intercalated Transition Metal Dichalcogenides (TMDC) MTiS$_2$ compounds (M = Cr, Mn, Fe) by Density Functional Theory (DFT) with Generalized Gradient Approximation (GGA). We have computed the structural and electronic properties by using first principle method in QUANTUM ESPRESSO computational code with an ultra-soft pseudopotential. A guest 3d transition metal M (viz; Cr, Mn, Fe) can be easily intercalated in pure transition metal dichalcogenides compound like TiS$_2$. In the present work, the structural optimization, electronic properties like the energy band structure, density of states (DoS), partial or projected density of states (PDoS) and total density of states (TDoS) are reported. The energy band structure of MTiS$_2$ compound has been found overlapping energy bands in the Fermi region. We conclude that the TiS$_2$ intercalated compound has a small band gap while the doped compound with guest 3d-atom has metallic behavior as shown form its overlapped band structure.

KEYWORDS:-Density Functional Theory (DFT), Transition metal dichalcogenide compounds (TMDCs), Generalized Gradient Approximation (GGA), Quantum ESPRESSO code, Intercalated compound, ultra-soft pseudopotential.

During several years, the Transition Metal Dichalcogenides (TMDC) materials of group IV-b,V-b and VI-b have received significant consideration because of their uses particularly as electrodes in photoelectrochemical (PEC) solar ce1l for conversion of solar energy into electrical energy as well as photonic devices in numerous electronic applications. We have work on MTiS$_2$ intercalated compound [1]. While, different atoms may be intercalated into van der Waal's gap with TMDC TX$_2$ (T = group IV, V, VI transition metal, X = S, Se, Te) compounds and a great deal of effort has been made to obtain new functional content. In TiS$_2$, Ti has a sandwiched layer between two Sulphur layers with very weak van der Wall's force. Because of such weak attraction between interlayer, a guest 3d atom can be easily intercalated in the TMDC TiS$_2$ [2]. The effect of charge transfer from guest 3d-transition metal to self-intercalated compound TiS$_2$ has been studied by Kim *et al.* [3]. Also, based on self-consistent APW method the d-orbitals of intercalant M atoms hybridize strongly with p-orbitals of 'S' in such a way that the Ti-S bonds become weaker than the M-S bonds [4, 5]. Therefore, the M-S bonds are much stronger than Ti-S bonds [5]. Also, a strong hybridization takes place in the states like 3d states of M, 3d-states of Ti and 3p-states of S [6-8]. However, the TiS$_2$ has a very small indirect bandgap as a semiconductor [4]. Also, in the band structure of MTiS$_2$, the energy band lines are overlapped near at the Fermi region.

The Density Functional Theory (DFT) based formulation is commonly used for investigating the structural and electronic properties of the materials and found successful [9-12]. The molecular-orbital (MO) method is found useful to examine the nature of chemical bonding in intercalated MTiS$_2$ compound [3]. The intercalates MTiS$_2$ (M = Cr, Mn, Fe) compounds depending on the guest atom M (viz; Cr, Mn, Fe), which are supported by various experimental techniques such as X-Ray photoemission spectroscopy (XPS), Angle Resolved Resonant Photoemission Spectroscopy (ARPES), Angle Resolved Inverse Photoemission Spectroscopy (ARIPES) and high field magnetization measurements [13,14].

Very recently, Sharma *et al.* [6] have reported transport properties and electronic structure of intercalated compounds CrTiS$_2$ by employing full potential linearized augmented plane wave (LAPW) with local orbitals (LO) method, in the outline of DFT with Generalized Gradient Approximations (GGA) [15] under Wien2K code [16] environment. They have constrained their studies up to band structure, density of states (DOS), charge density and specific heat calculations only. But, they have not reported theoretical fallouts of MnTiS$_2$ and FeTiS$_2$ compounds in their research work thoroughly. Also, they concluded that all CrTiS$_2$, MnTiS$_2$ and FeTiS$_2$ compounds have same electronic band structure and DOS. However, all above mentioned materials have different band structure and DOS.

Hence, looking to the technological aspects of the said materials, we though it undertakes in the present work, the structural optimization and electronic properties like energy band structure, density of states (DOS), partial or projected density of states (PDOS), total density of states (TDOS) of MTiS2 compounds using GGA [15] with Perdew-Burke-Ernzerhof (PBE) exchange and correlation effect [17] and ultra-soft pseudopotential [18] through Quantum ESPRESSO code [19] under DFT environment. The prime novelty of our current work is that, we have compared our computed results of the studied materials and their properties after and before the interaction process, which gives us good assessments and nature of aforementioned materials briefly.

COMPUTATIONAL METHODOLOGY

All the calculations are performed in our computational laboratory based on density functional theory (DFT) of intercalated compound $MTiS_2$ by solving Kohn-Sham equations [20] with Burai software [21]. Here, we have adopted Generalized Gradient Approximations (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange and correlation effect [17] and ultra-soft pseudopotential [18] through Quantum ESPRESSO code [19]. The structural optimization and the electronic properties such as band structure, density of states (DOS), partial density of states (PDOS) and total density of states (TDOS) are reported for intercalated $MTiS_2$ compound.

RESULT AND DISCUSSION

Structural Optimization

The $MTiS_2$ has the CdI_2-type layer structure, in which, Ti layer is inserted among two Sulfur layers. In this structure, the unit cell of it comprises four atoms with the unit cell positioned for Ti is a 1a; the two S atoms are positioned in 2d (1/3, 1/3,0.2501) and (2/3,1/3,-0.2501), respectively. The structure consists of S-Ti-S sandwich, separated in Z-direction by the van der Wall's gap [22]. In very weak van der Wall's attraction between the Ti and S layers, guest 3d atom like Cr, Mn and Fe can be easily intercalated in pure TiS_2. In the $MTiS_2$ atom, the lattice position is 1b (0, 0, 0.5) in the structure and also has a hexagonal crystal structure with space group $P\bar{3}ml$ [164] as shown in Fig. (1), (2) and (3). In $MTiS_2$ has the lattice parameters a = 3.4395Å and c = 5.9303Å. The Brillouin zone (BZ) for hexagonal structure is shown in Fig. (4).

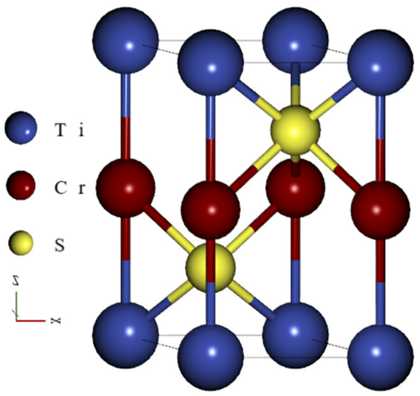


Figure 1. Crystal structure of $CrTiS_2$

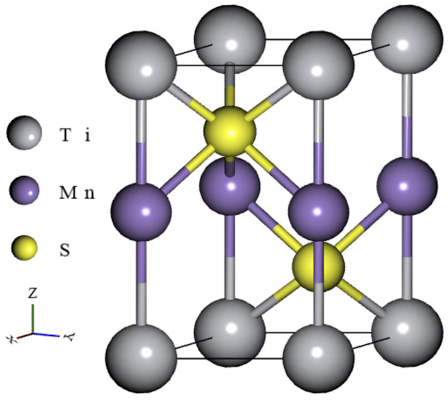


Figure 2. Crystal structure of $MnTiS_2$

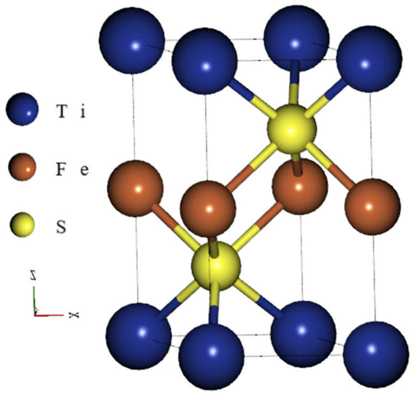


Figure 3. Crystal Structure of $FeTiS_2$

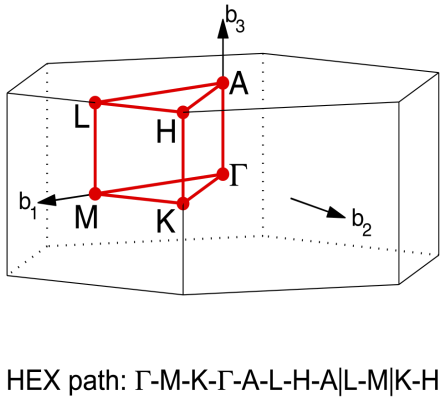


Figure 4. Brillouin zone for Hexagonal structure

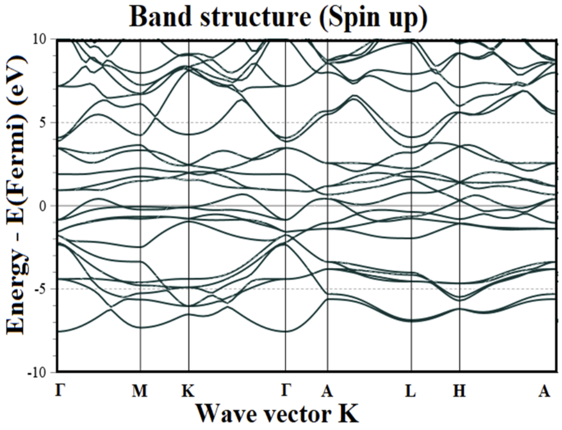
Electronic properties

In electronic properties, the energy band structure, density of states (DOS), total density of states (TDOS) and partial or projected density of states (PDOS) are computed and studied.

Band Structure

In the energy band structure calculation, the path of **k**-points is considered at the high symmetry path viz; Γ→M→K→ Γ→A→L→ H→A in irreducible Brillouin zone (IBZ). The Band structures of the said materials are plotted in the energy range of -10.0 eV to 10.0 eV. Also, we have calculated the energy band structure with spin polarized calculation of said material with spin up and spin down band structure as shown in the same figure.

In Fig. (5) and (6) shows the electronic band structure of $CrTiS_2$ compound with spin up and spin down configuration for taking K path is Γ→M→K→ Γ→A→L→ H→A. The valance band and the conduction band are overlapped in the energy range of -5.0 eV to 5.0 eV. From that, we have concluded that the intercalated compound like $CrTiS_2$ has a metallic characteristic. Here, the maximum band is overlapped at the Fermi level. According to the spin up and spin down band structure of $CrTiS_2$, the paramagnetic nature of the studied compound successfully observed.



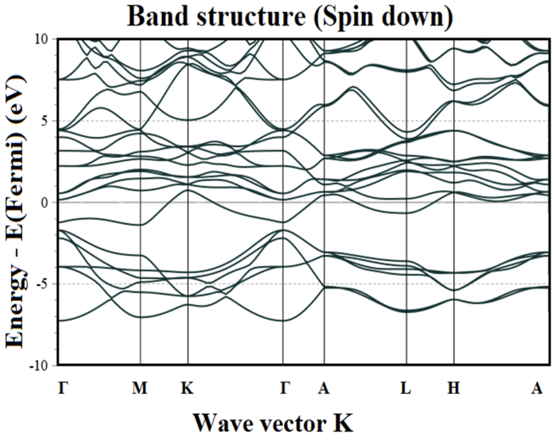
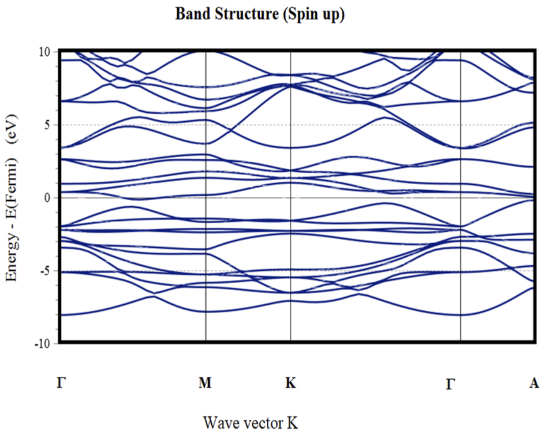


Figure 5. Electronic band structure of $CrTiS_2$ Spin up

Figure 6. Electronic band structure of $CrTiS_2$ Spin down

Fig. (7) and (8) shows the electronic band structure with spin up and spin down configuration for $MnTiS_2$ compound for K path taking is Γ→M→K→ Γ→A. The valance band and the conduction bands are overlapped in the energy range between -5.0 eV to 5.0 eV. In $MnTiS_2$, the energy band lines are overlapped more than that of the $CrTiS_2$ material. From that, we have concluded that the intercalated compound like $MnTiS_2$ has a metallic characteristic. Here also, one can observe the maximum band is overlapped at the Fermi level. According to the spin up and spin down band structure of $MnTiS_2$, it is having a paramagnetic material in nature.



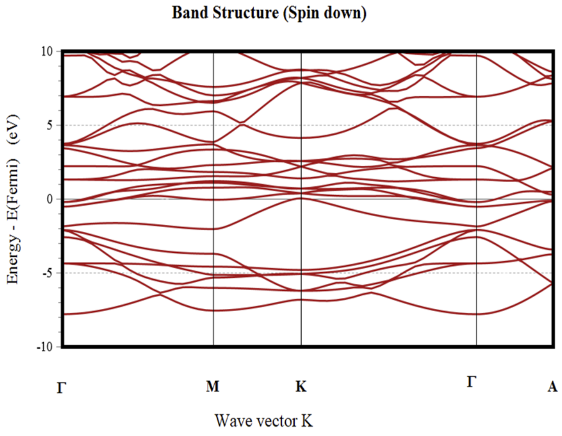
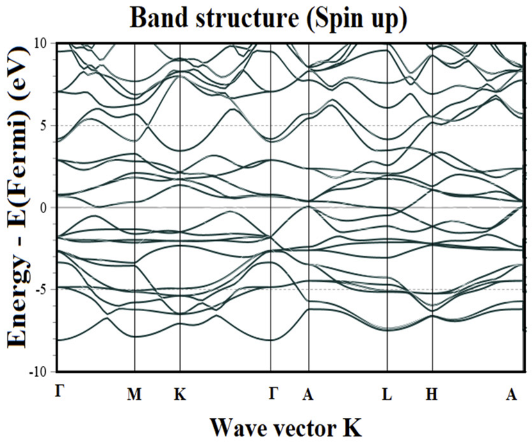


Figure 7. Electronic band structure of $MnTiS_2$ Spin up

Figure 8. Electronic band structure of $MnTiS_2$ Spin down

Fig. (9) and (10) shows the electronic band structure with spin up and spin down configuration in the K path of Γ→M→K→ Γ→A→L→ H→A.



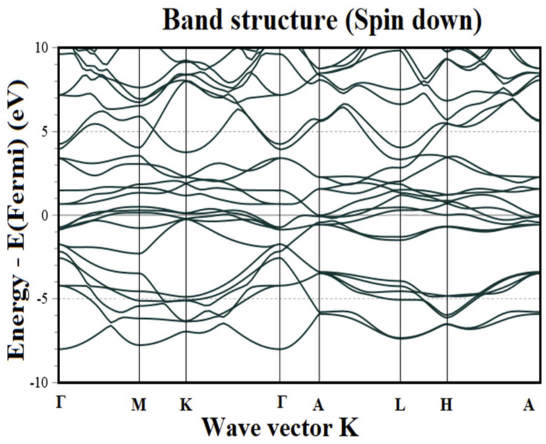


Figure 9. Electronic band structure of $FeTiS_2$ Spin up

Figure 10. Electronic band structure of $FeTiS_2$ Spin down

The valance band and the conduction bands are met in the energy range of -5.0 eV to 5.0 eV. In $FeTiS_2$, the energy band lines are overlapped more than that of $CrTiS_2$ and $MnTiS_2$ compounds. From that, we have noted that, $FeTiS_2$ intercalated compound has a metallic nature. Here also, the band is overlapped maximum at the Fermi level. From the spin up and spin down band structures of $FeTiS_2$, one can say that, the materials has a ferromagnetic in nature.

Density Of States (DOS)

From the partial or projected DOS, the contributions from the individual orbitals of different materials like s, p, d and f can be checked [19]. We have used here the tetrahedral method for integration over the Brillouin zone to estimate the DOS. Both DOS and PDOS are computed for spin up and spin down configuration.

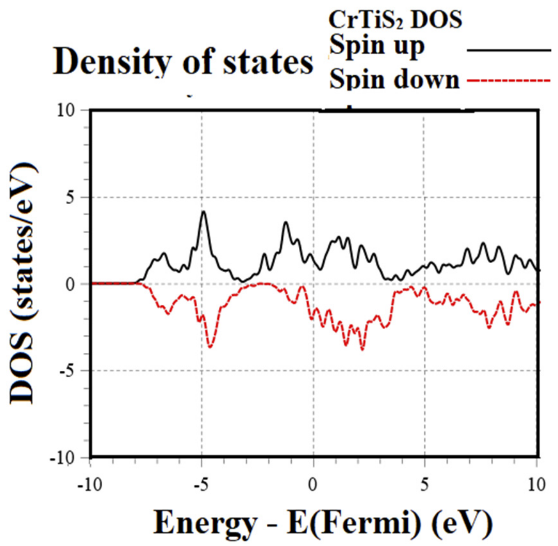


Figure 10. Total DoS of $CrTiS_2$

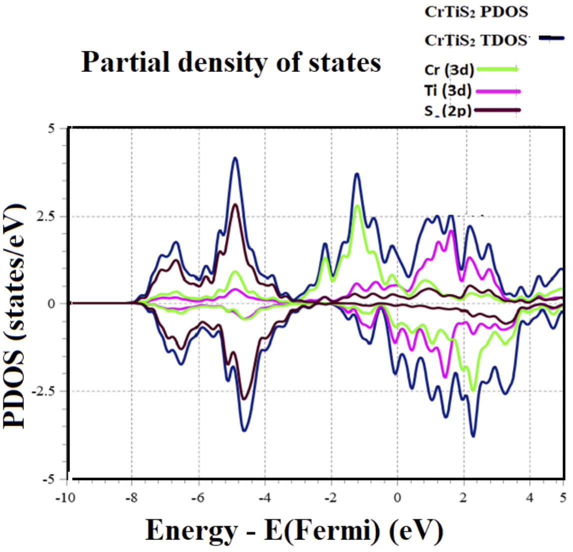


Figure 11. Partial DOS of $CrTiS_2$

The TDOS of $CrTiS_2$ is shown in Fig. 10. While, Fig. 11 displays the energy contributions from the individual orbitals like s, p, d and f in PDOS for $CrTiS_2$ compound. It is plotted in the energy range between -10.0 eV to 10.0 eV in both spin up and spin down energy states. In TDOS below the Fermi region, the electron density shows maximum at 6.0 states/eV at a point -5.0 eV in spin up DOS and 3.5 states/eV at a point -4.5 eV in spin down DOS. Above the Fermi region, the electron density maximum at 1.0 states/eV at a point 2.0 eV in spin up and 1.5 eV in spin down DOS. However, the DOS at the Fermi region is 1.5 states/eV. In PDOS of $CrTiS_2$ is drawn in the states of Cr (3d-state), Ti (3d-state) and S (2p-state), respectively. Such 3d-states are mainly paid attention to the conduction band, while S-2p states are mainly contributed to the valance band. Because of these, the $CrTiS_2$ is having a metallic compound.

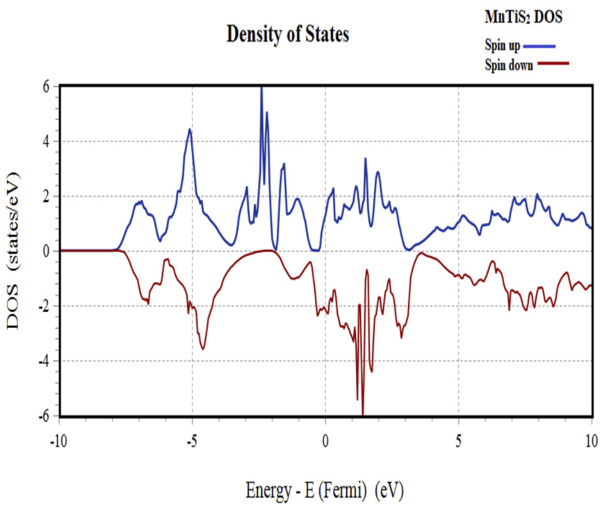


Figure 12. Total DoS of $MnTiS_2$

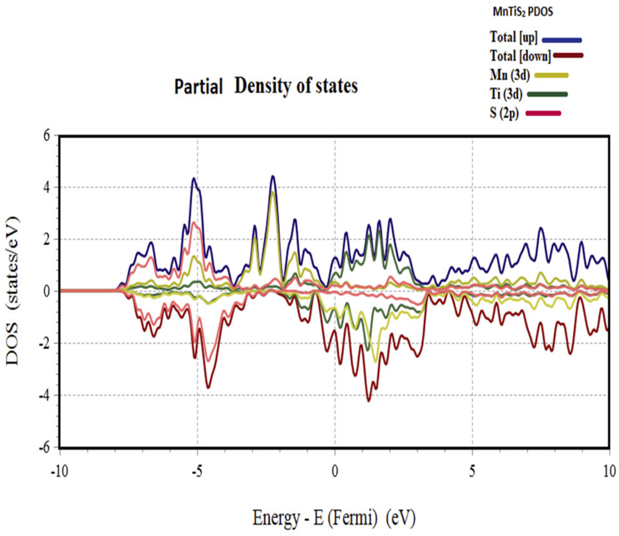


Figure 13. Partial DOS of $MnTiS_2$

Figs. 12 and 13, show the TDOS and PDOS for $MnTiS_2$ compound, which are plotted in the energy range between -10.0 eV to 10.0 eV in both spin up and spin down energy states. In TDOS below the Fermi region, the electron density shows maximum at 6.0 states/eV at a point -5.0 eV in spin up DOS and 3.5 states/eV at a point -4.5 eV in spin down

DOS. Above the Fermi region, the electron density maximum at 1.0 states/eV at a point 2.0 eV in spin up and 1.5 eV in spin down DOS graphs. The DOS at the Fermi region is shown at a 1.5 states/eV. In PDOS of $MnTiS_2$ is drawn in the states of 3d-state of Mn, 3d-state of Ti and 2p-state of S, respectively. In PDOS, 3d-states of Mn and Ti are mainly contributed to the conduction band, while 2p-state of S is mainly contributed to the valance band. Hence, the $MnTiS_2$ is showing a metallic nature.

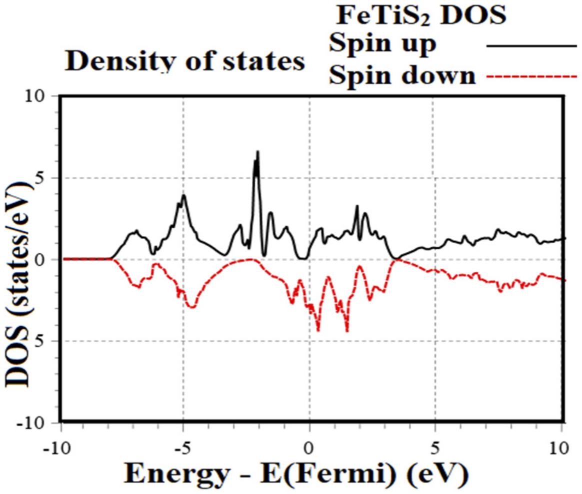


Fig. 14. Total DoS of $FeTiS_2$

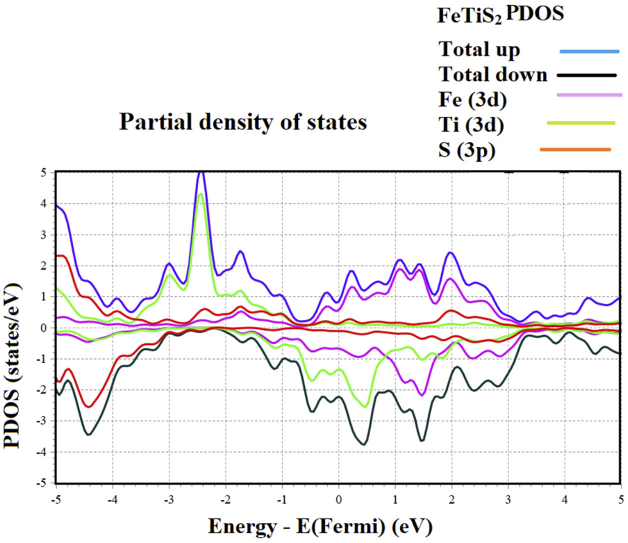


Fig. 15. Partial DOS of $FeTiS_2$

Figs. 14 and 15, display the TDOS and PDOS for $FeTiS_2$ compound with spin up and spin down configuration. It is drawn in the energy range between -10.0 eV to 10.0 eV in both spin up and spin down energy states. In TDOS below the Fermi region, the electron density found maximum at 6.0 states/eV at a point -5.0 eV in spin up DOS and 3.5 states/eV at a point -4.5 eV in spin down DOS. While, above the Fermi region, the electron density shown maximum at 1.0 states/eV at a point 2.0 eV in spin up and 1.5 eV in spin down DOS. However, the DOS at the Fermi region is found at 1.5 states/eV. The 3d-states Fe, Ti and 2p-state of such compound is represented in PDOS, in which 3d-states are mainly donated to the conduction band, while 2p state is mainly contributed to the valance band only, which shows a metallic nature.

Above the reference paper, Sharma, Y., Shukla, S., Dwivedi, S., Sharma, R.: Transport properties and electronic structure of intercalated compounds $MTiS_2$ (M = Cr, Mn and Fe), she says all the materials have same electronic properties. In our research paper calculation, we can say all the material have not same electronic properties. Some changes in energy band lines and density of states shown the above figure.

CONCLUSION

Lastly, we conclude here that, the DFT based simulation is used to compute the structural analysis, eelectronic properties like electronic band structure, total and projected density of states (TDOS and PDOS) of $MTiS_2$ (M = Cr, Mn and Fe) intercalated compound using GGA and PBE exchange correlation effects. Whole computations are performed with Quantum Espresso code. From the structural optimization, the guest atom is placed between the interlayer of TiS_2 and shows significant variations in the studied properties. From the electronic band structure data of the all the compounds, it is noticed that the conduction and valance bands are overlapped with each other and shows metallic nature. Also, spin up and spin down natures are easily reported from the band structure data and DOS data of the aforementioned materials. Such type of results is not reported by Sharma et al. [6] earlier. Also, it is observed that, 3d-states of M and Ti atoms are mainly contributed to the conduction band and 2p-state of S atom is mainly contributed to the valance band, respectively. While, metallic nature of $FeTiS_2$ material is found more than $MnTiS_2$ and $CrTiS_2$ compounds. Also, spin polarized configuration with spin up and spin down electronic band structure are observed for aforesaid compounds. It is concluded from that, the $CrTiS_2$ and $MnTiS_2$ compounds are having paramagnetic in nature, while $FeTiS_2$ is having ferromagnetic in nature. According to their such type of properties, the TiS_2 compound is used for making rechargeable lithium batteries and fabrication of photo electronic devices. The prime novelty of this compound is that, it can be easily intercalated by any guest 3d atom.

ACKNOWLEDGMENTS

We sincerely acknowledge the computational facility developed under DST-FIST programme from the Department of Science and Technology, Government of India, New Delhi, India and financial assistance under DRS-SAP-II from University Grants commission, New Delhi, India.

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ВИВЧЕННЯ СТРУКТУРНИХ І ЕЛЕКТРОННИХ ВЛАСТИВОСТЕЙ ІНТЕРКАЛЬОВАНИХ ДИХАЛКОГЕНІДНИХ КОМПАУНДІВ ПЕРЕХІДНИХ МЕТАЛІВ MTiS$_2$ (M = Cr, Mn, Fe) ЗА ТЕОРІЄЮ ФУНКЦІОНАЛЬНОЇ ЩІЛЬНОСТІ

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У цій роботі ми вивчали інтеркальовані дихалкогеніди перехідних металів (TMDC) MTiS2 (M = Cr, Mn, Fe) за допомогою теорії функціональної щільності (DFT) із узагальненою апроксимацією градієнта (GGA). Ми обчислили структурні та електронні властивості, використовуючи метод першопринципу в обчислювальному коді QUANTUM ESPRESSO з надм'яким псевдопотенціалом. 3d-перехідні метали M (а саме; Cr, Mn, Fe) можуть бути легко інтеркальовані у сполуку чистого дихалькогеніду перехідного металу, як TiS$_2$. У цій роботі повідомляється про структурну оптимізацію, електронні властивості, такі як: структура забороненої зони, щільність станів (DoS), часткова або прогнозована щільність станів (PDoS) та загальна щільність станів (TDoS). Було виявлено, що структура забороненої зони сполуки MTiS2 перекриває енергетичні смуги в регіоні Фермі. Ми прийшли до висновку, що інтеркальована сполука TiS$_2$ має малу заборонену зону, тоді як легована сполука з 3d-атомом має металеву поведінку, як видно з забороненої зони що перекривається.

КЛЮЧОВІ СЛОВА: теорія функціональної щільності (DFT), дихалкогенідні сполуки перехідних металів (TMDC), узагальнене градієнтне наближення (GGA), квантовий код ESPRESSO, інтеркальований компаунд, надм'який псевдопотенціал.