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Research Article

Study of structural and electronic properties of $MnTiS_2$ compound

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Abstract

The Density Functional Theory (DFT) based computational work is reported for the intercalated Transition Metal Dichalcogenides (TMDCs) $MnTiS_2$ compound in the present article. The Generalized Gradient Approximation (GGA) and ultrasoft pseudopotential with Perdew-Burke-Ernzerhof (PBE) exchange and correlation effect are considered in Quantum Espresso code. 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), Fermi surfaces and charge density are reported. The effect of charge transfer from guest 3d transition metal Mn-atom to self-intercalated compound TiS_2 has been observed. While, the energy band structure of $MnTiS_2$ compound is computed in the non-magnetic state and found an overlapped band structure, which show metallic nature of the material.

Keywords: Density Functional Theory (DFT); Generalized Gradient Approximation (GGA); Quantum ESPRESSO code; Ultra-soft pseudopotential; Intercalated compound; Transition Metal Dichalcogenides (TMDCs).

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1. INTRODUCTION

Layered compound such as transition metal dichalcogenides are interesting materials with their own properties. Transition metal dichalcogenides are very important as a mother material for intercalation compound. Intercalation means the addition of guest atoms, ions, or molecules between layers of layered compounds, and the resulting substances produced through the intercalation process are called "intercalation compounds" or "intercalates". The central purpose of intercalation is to synthesize materials that have new functions other than those of the mother materials[1]. Different atoms may be intercalated into van der Waals gap with transition metal dichalcogenides TX_2 (T = group IV, V, VI transition metal, X = S, Se, Te) and a great deal of effort has been made to obtain new functional content. The intercalation of 3d-transition metal has also been extensively studied in this work and quite changes have been observed in electronic properties of the host transition metal dichalcogenides, depending on the intercalates[2]. The formulation based on Density Functional Theory (DFT) is commonly used for investigating the structural and electronic properties of materials[3-6]. We have calculated the electronic structure of $MnTiS_2$, by using first principal methods. The effect of charge transfer from guest 3d-transition metal to self-intercalated compound TiS_2 has been reported by[7]. In TiS_2, Ti has a sandwiched layer between two Sulphur layers with very weak van der Waals force. In very weak van der Waals attraction between interlayer, Mn can be easily intercalated in transition metal dichalcogenides TiS_2[8]. Therefore, the Mn-S bonds are stronger than Ti-S bonds[9]. We have concluded that for $MnTiS_2$, the electronic properties depending upon intercalated atom Mn. A strong hybridization takes place in the states like Mn (3d), Ti (3d) and S (3p)[10-13]. However, the titanium disulfide has a very small indirect bandgap as a semiconductor. In $MnTiS_2$ band structure, the energy band lines are overlapped near the Fermi region.

2. COMPUTATIONAL THEORY

Computational study of $MnTiS_2$ compound based on the DFT approach performed with the Quantum Espresso computational code[14] in our laboratory. Using Generalized Gradient Approximation (GGA)[15], the structural optimization, and electronic properties such as band structure, Density of State (DOS), Partial or Projected Density of States (PDOS), Total Density of States (TDOS), Fermi surfaces and charge density are measured for said compounds. In all the computation, we have utilized Perdew-Burke-Ernzerhof (PBE)[16] with

ultra-soft pseudopotential[17]. Also, we have used gnuplot[18] and XCrySDen[19] software for plotting and visualize the different curves.

3. RESULTS AND DISCUSSION

3.1. Structural optimization

The lattice constant is used to calculate the structural properties of said materials. The TiS_2 has a layer with CdI_2 type structure. In which, Ti layer is sandwiched between two layers of sulphur. The unit cell of this structure includes four atoms. In TiS_2 the unit cell position for Ti; the two S atoms are placed in 2d (1/3, 1/3, 0.2501) and (2/3, 1/3, -0.2501) planes. The structure consists of S-Ti-S sandwiches, split by the van der Waals gap in the Z-direction. The guest 3d-atom like Mn can easily be intercalated in pure TiS_2 with very weak van der Waals attraction between the layers Ti and S[20] while Mn atom has lattice position at (0, 0, 0.5) in the structure. The structures of $MnTiS_2$ have hexagonal crystal type with space group $P\bar{3}ml$ [164] as shown in fig. 1. The MnTiS2 the lattice parameters are a = 3.4395 Å and c = 5.9303 Å, respectively. The Brillouin zone (BZ) for hexagonal structure is displayed in fig. 2. The optimizations of lattice parameters are performed for $MnTiS_2$ both compounds. For the relaxation of ground state geometry, following three main steps were carried out.

1. Convergence of total energy with respect to kinetic energy up to an accuracy of 10^{-4} Ry.
2. Convergence of total energy versus k-mesh accuracy of 10^{-4} Ry.
3. Optimization of lattice constants to minimize the total energy.

After this procedure, the ratio of lattice parameters (c/a) was optimized the crystal structure by using the GGA approach with ultrasoft pseudopotentials and displayed in fig. 3.

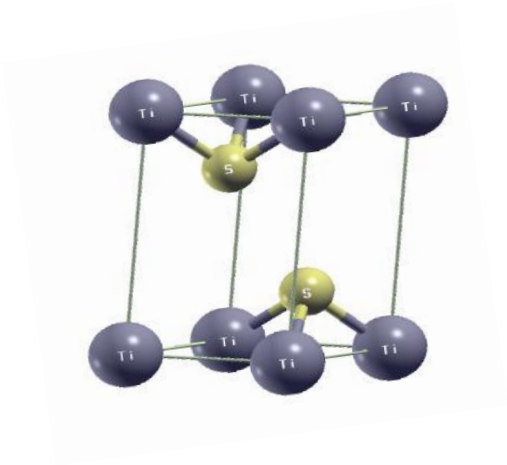


Fig. 1. Crystal Structure of $MnTiS_2$.

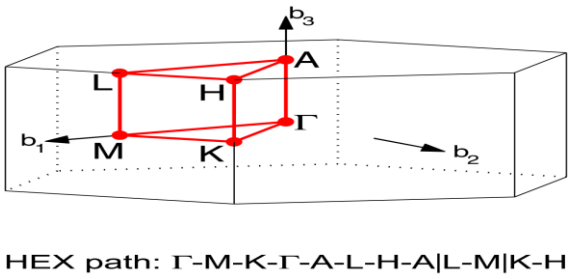


Fig. 2. Brillouin zone for hexagonal structure.

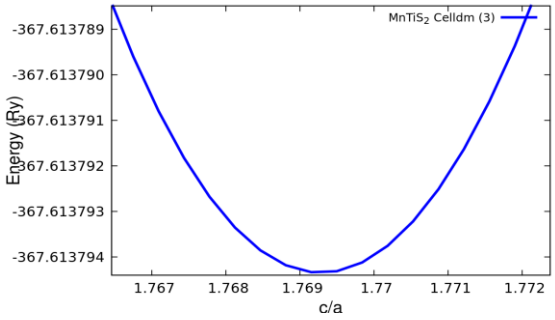


Fig. 3. Optimization curve for $MnTiS_2$.

3.2. Electronic properties

In electronic properties, the energy band structure, DOS, TDOS, PDOS, Fermi surfaces and charge density are reported in this section using DFT based formulation.

3.2.1. Band structure

In the present work, the band structure of $MnTiS_2$ is plotted in fig. 4. The order of high symmetry path direction is Γ→M→K→ Γ→A in irreducible Brillouin zone (IBZ). It is plotted in the energy range of -10.0 to 10.0 eV. Here, the valance band and conduction band both are overlapped in the energy range of -2.5 to 2.5 eV. From that, we have concluded that the $MnTiS_2$ compound has a metallic characteristic.

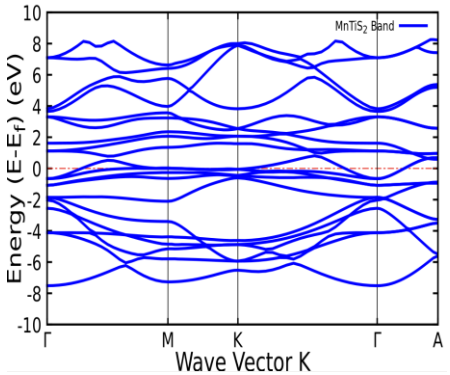


Fig. 4. Electronic band structure of $MnTiS_2$.

3.2.2. 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[21]. We have used here the tetrahedral method for integration over the Brillouin zone to estimate the DOS. Here, figs. 5 and 6, shows the TDOS and PDOS for $MnTiS_2$ compound. They are plotted in the energy range between -15.0 eV to 5.0 eV. In TDOS, below the Fermi region the electron density maximum at 2.0 states/eV at a point -5.0 eV and above the Fermi region the electron density maximum at 2.5 states/eV at a point 1.0 eV. The DOS at Fermi region is 3.0 states/eV show maximum, because of the band overlapping. In PDOS of MnTiS2 is drawn in the states of Mn (3d), Ti (3d) and S (2p). In PDOS, the Mn (3d) and Ti (3d) are mainly contributed in the conduction band, while S (2p) states contribute in the valance band. At the Fermi region, Mn is maximum. We concluded that the $MnTiS_2$ is as a metallic material.

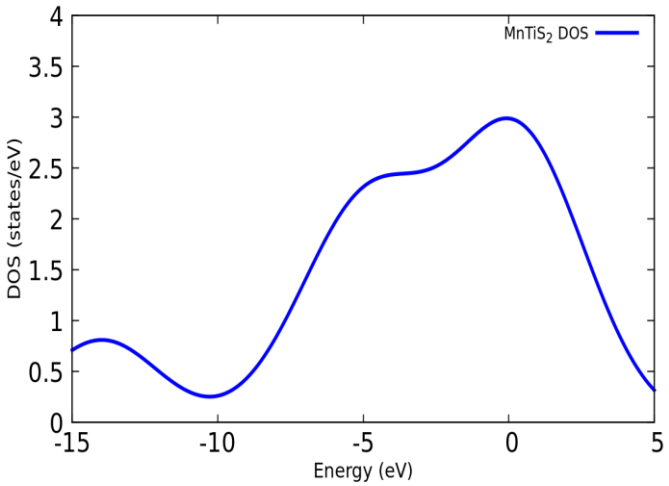


Fig. 5. Total DOS of $MnTiS_2$.

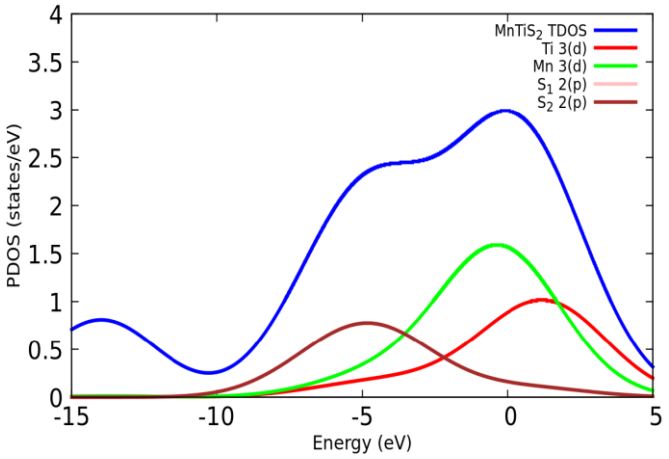
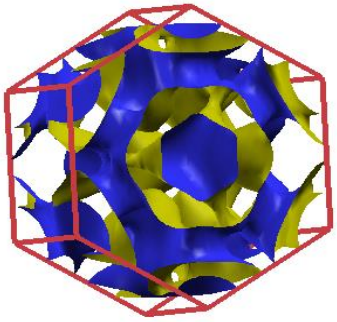


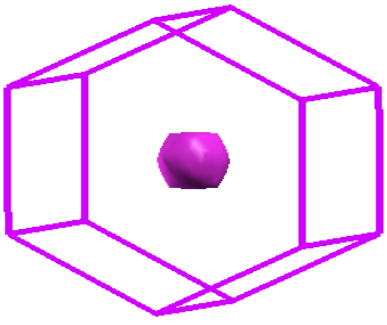
Fig. 6. PDOS for $MnTiS_2$.

3.2.3. The Fermi surfaces

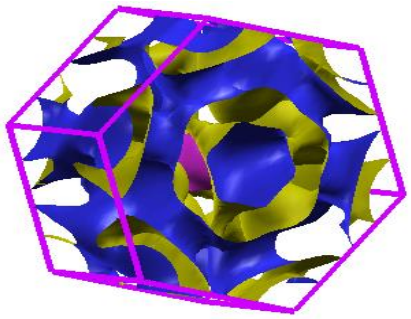
The Fermi energy represents the characteristic energy distinguishes between the occupied and unoccupied energy levels, which helps us to give the relative occupation of the allowed empty lattice bands geometrically in k-space (http://www.quantumespresso.org). The entire Fermi surface has a constant energy E_F in the momentum space. In other words, it is the surface, where all fermion states with momentum $k<k_F$ are occupied and other higher momentum states are unoccupied. Any variation in the unoccupied states around the Fermi surface may lead to the generation of electrical current. Hence, the study of the Fermi surface topology is more important to measure the electronic properties of the materials. While, figs. 7(a)-(d) display the Fermi surfaces for $MnTiS_2$ compound. Here, there are three bands are crossing the Fermi energy level E_F, while, two energy bands are crossing the Fermi surface. The Fermi surface for individual bands passing through the E_F, are shown in figs. 7(a)-(b). For merged bands, the Fermi surfaces are displayed in fig. 7(c). The hole-like concentric cylinders at the zone center (Γ) and the quasi cylinders at the corners of the Brillouin zone in Γ-A direction are given the electron contribution.



(a)



(b)



(c)

Fig. 7. The Fermi surfaces of $MnTiS_2$ for different bands (a) – (b) and for merged band (c).

3.2.4. Charge density

The electron charge density is the density of electron present at a particular time in the electron cloud of any atom per ion per compound. It can be placed where the probability of electron is found maximum at a particular time. The electron charge distribution of the materials is one of the key quantities in computational materials science as theoretically it determines the ground state energy and practically it is used in many material analyses. In the present work, the charge density is computed through DFT approach. To visualize the nature of charge density in $MnTiS_2$ compound is shown in fig. 8. It is minimum at + 0.084 cm^{-2} while maximum near the atom at + 2.782 cm^{-2}.

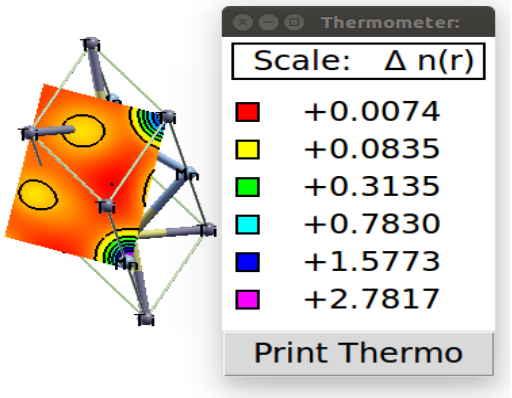


Fig. 8. Charge density of $MnTiS_2$.

4. Conclusions

From the current work, we conclude that, the structural analysis like lattice constants and electronic properties visualized electronic band structure, total and projected density of states (TDOS and PDOS), Fermi surfaces and charge density of $MnTiS_2$ compound is computable using GGA approach including the PBE exchange correlation effects with ultrasoft

pseudopotential under Quantum Espresso code. From the band structure data, the $MnTiS_2$ has an overlapping of the conduction band, and the valance band are seen, which possesses metallic nature of studied materials. Form the TDOS and PDOS graphs of the $MnTiS_2$, it is concluded that, at the Fermi energy level, Mn (3d) and Ti (3d) states are mainly contributed in the conduction band, while S (2p) states are contributed mainly to the valance band only. Also, the TDOS and PDOS of $MnTiS_2$ are found maximum at 3.0 states/eV near the Fermi energy region. The Fermi surfaces corresponding to the energy bands intersecting the Fermi level shows the electronic contribution in the band structure of $MnTiS_2$. While, the electronic contribution shows maximum at point M and K. also, the charge density is increased when guest atom like Mn is introduced in the TiS_2 compound.

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