A Newly Developed Dispersive Interaction Approach, DFT-D3, To The Three-Dimensional Topological Host Material Sb_2Te_3

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Abstract

Antimony Telluride (Sb_2Te_3), a topological insulator is a layered semiconductor material with hexagonal unit cell similar to graphene. The characteristic presence of their conducting edges or surfaces with self-induced protection, promise for remarkable future applications. In this exertion based on the first principle approach, the structural and electronic properties of Sb_2Te_3 compound have been investigated for both without and with spin orbit coupling (SOC). Lattice structure, band structure, total density of states (TDOS), partial density of states (PDOS), energy bands of surface states are determined within Quantum Espresso simulation package. Furthermore, dispersive interactions, induced due to the presence of van-der-Waals forces have also been taken care of. The newly developed method of *DFT-D3* has been incorporated for accurate predictions of band gap and lattice parameters. A proficient model, *The Slab Model*, has been used to observe the presence of single Dirac cone on the surface. To our knowledge, our theoretical investigations are valid and are found to be congruous with the observed data.

Introduction

Topological Insulators (TI) [1]-[6] are a new class of narrow band gap materials with their wave functions that describe their electronic states, spanning a Hilbert space with a non-trivial topology [7]-[9]. For such bulk insulators, the strength (strong) of the spin-orbit coupling tends the conduction and valence bands to invert. In this topological regime there then develops a linear dispersion relation between the surface states and the surface momentum causing variation of the spin polarization with respect to the momentum [10, 11]. These materials are of considerable interest for applications like in optoelectronics [12, 13], thermoelectric [14], broadband photodetectors [15], quantum computing [16], spintronics [17], etc. [18, 19].Their importance have also been realized in the field of superconductors where one expects the proximity effect when topological superconductors are constructed through its proper interfacing with conventional superconductors [20].This rapidly developing subfield of condensed matter physics has recently lead to the discovery of dissipationless spin-currents which manipulates through spin degrees of freedom and in the upcoming years can prove to be revolutionary in the field of information technology [21]. Recent developments in the designing of hard-disks in industries have already brought prolific boost in the field of capacity and size of the storage devices. The studying of these effects with TIs scientifically enriches the whole of the subject [22, 23]. Apart from this non-interacting band theory, there also exists material realizations with strong electron-electron interactions defining topological Kondo [24] and Mott [25] insulators. When researched with deeper understanding mysterious Majorana fermions have been detected which can help in the development of topological quantum computations. Among the recently increased research in the field of this novel state of quantum matter there does not exist a unique one such material that may efficiently meet all or various requirements in experimental observations. Recently, Sb_2Te_3 has been studied for special electronic properties due to its natural presence as a material with non-conducting bulk, and protected characteristic surface conduction attribute, emanated from the presence of massless Dirac-cone [26, 27]. Therefore, in order to sympathetically acknowledge its promising complexion, a detailed knowledge of its structure and electronic identity is required.

With its known rhombohedral crystalline structure, Sb_2Te_3 belongs to R-3m (166) space group comprising five atomic layers structure held together by van-der-Waals attraction and atoms covalently bonded to each other. Alternatively, in its conventional cell form it forms unit cell of hexagonal structure with 15 atoms configurating sandwiched layer structures called Quintuple layers (QL), forming a slab of 5 atomic layers. Most of the electrons and structure calculations for Sb_2Te_3 are performed with experimental data without full relaxation and the absence of van der Waals interacting forces [15, 28, 29]. Distinct from the perceptible works previously performed we explore the calculations here with full relaxations. We also provide the new method of incorporating the van-der- Waals interaction property to our study of the crystal. The calculated structure and electronic properties in this work are useful to qualitatively est

Computational Methods

We have performed structural optimization and electronic structure calculations using the plane wave self-consistent field (PWscf) program with density functional theory (DFT), and the generalised gradient approximation (GGA) of Perdew et al. [30] for the exchange and correlation potentials. Full relativistic and scalar relativistic pseudopotentials were used which is essential for the calculation of electronic structure of Sb_2Te_3 with and without the inclusion of SOC respectively. Plane wave kinetic cut-off were set at 40 Ry with charge density of 320 Ry. The Brillouin zone were sampled with 8x8x8 Monkhorst-Grid of k-points [31]-[32] for self-consistent field calculations. For the density of states denser values of 12x12x12 k-points were provided. Further for the slab calculation 8x8x1 k-point grid were introduced. For the inclusion of inter-layered forces within the QL a newly modified empirical van-der-Waals parameter, semi empirical Grimme's DFT-D3 van-der-Waals (DFT-D3) corrections were considered. Broyden-Fletcher-Goldfarb-Shanno algorithm was used for the geometry relaxation calculations as a result of the Born-Oppenheimer approximation. All calculations were performed within the Quantum-espresso simulation package.

Results And Discussion

a. Structural properties

Sb_2Te_3 in its conventional cell form is a hexagonal structure and its primitive cell is a rhombohedral(R-3m) structure as shown in Fig. I. This centrosymmetric structure has a three-fold rotation symmetry, a binary axis and a bisectrix axis defined as the z-, x-, and y-axis respectively. For the accurate analysis of properties such as band structure, geometrical optimization of Sb_2Te_3 was first performed. The steps adopted are following. Experimental lattice parameters and the angle between the rhombohedral basis vectors of the length **[33]-[34]** were taken to build cell of required volume. We then performed the convergence test both cut-off energy optimization as well as cohesive energy optimization to obtain the lowest energy $E_{min.}$ The theoretical optimized lattice parameters together with previous first principle calculations and experimental values are shown in Table I. Comparing with the experimental values it can be observed that the value for the lattice parameter a exceeds by approximately 1% while LDA+SOI underestimates it by approximately the same percentage. For the lattice constant c, LDA+SOI

underestimates it by 1.02% and PBE+SOI overestimates it by 1.03%. The inclusion of van-der-Waals modification, DFT-D3 proves out to provide accuracy to the calculated values. Thus, for the structural parameters' calculation vdW correction is more important than the SOC effects. Next, if we consider the electronic structure calculations the SOC plays prominent role as it inverts the occupation states and creates band gap reflecting the topological nature of this material. Following the outputs in the Table II one observes the variation in the values of E_g when compared with the experimental values. The reason behind this underestimation is the limitation of the approximated exchange-correlation potentials.

Table 1 Calculated lattice parameters for Sb2Te3

Work	Method	Lattice Parameters		
		a(A^0)	c(A^0)	c/a
Our work	LDA	4.165	29.260	7.025
	LDA+SOI	4.236	29.590	6.985
	PBE	4.342	30.932	7.123
	PBE+SOI	4.332	31.351	7.237
	DFT-D3	4.256	29.960	7.039
	DFT-D3(SOI)	4.258	30.376	7.133
Experimental	Expt. **[33]**	4.264	30.458	7.143

Table II Sb_2Te_3 band gap results.

Work	Methods	Band gap value (eV)
Our work	LDA	0.000
	LDA+SOI	0.055
	PBE	0.077
	PBE+SOI	0.127
	DFT-D3	0.091
	DFT-D3(SOI)	0.138
Experiment	Exp. **[35]**	0.150

b. Electronic Properties

The calculation of electronic band structure is theoretically very important as it helps in understanding the orbital contributions in the behaviour of a material. We have performed TDOS and PDOS of Sb_2Te_3 here. For the band structure calculation both LDA and PBE approximation based on DFT was used along special symmetric directions of the Brillouin zone. For a better and accurate results band structure modified with vdW has also been obtained. The computed distributions can be seen in Fig. II.

Analysing the PDOS structure of DFT+DW(SOC) we find that from the Sb- part some contribution is provided by the s-orbitals to the lowest valence band (-13.2740 eV to -10.9147 eV) while a large part of its contribution can be observed in the valence band (-5.9794 eV to -0.27470 eV) near to the Fermi level with a maximum to the conduction band (0.00530 eV to 3.7453 eV). Observing the Te - contribution, we find that the maximum contribution by its s-orbitals can be observed in the lowest valence band, while the p-orbital contributes its maximum to valence band (-5.9794 eV to -0.27470 eV) about the Fermi level. Conclusively, we find that for the material properties of Sb_2Te_3 near the Fermi level the p-orbitals play a huge role. The presence of hybridizations between s- orbital and p- orbital in the valence bands help in understanding the presence of an interatomic force in Sb_2Te_3 material.

c. Topologically Protected States at the (111) Surface of Sb_2Te_3

Antimony Telluride is a second-generation 3D topological insulator material with protected states at the surfaces **[36]**. For the observation of its characteristic signature, a single Dirac cone, one requires models that can account explicit presence of the surfaces. We in our work have used the so-called slab models **[37]**. In this model the slab is placed such that their periodic lattice placement prevents the mutual interactions between the different slab surfaces. One finds good models for studying topological surface states through a few-QL-thick slabs of bismuth-chalcogenide TIs **[38]**.

A 2D slab-model was formed by slicing a bulk lattice across the (111) directions. We then applied the PBE- standard form non-linear core-correction full relativistic pseudopotential. The required self-consistent treatment was also performed to achieve the correct screening of the neighbourhood surfaces' atoms. Fig.4 shows the band structure of such slab models of 3 QL calculated for Sb_2Te_3. It can be clearly observed that there is a presence of a Dirac cone at the (gamma)-point which correspond to the surface-localized states. These Dirac cones are degenerate due to the inversion symmetry. We can thus conclusively observe that the electronic structure of Sb_2Te_3 has a bulk insulating band structure strongly influenced with SOC and a single Dirac cone at its (111) surface.

Conclusion

In this paper, structural characterizations and electronic investigations of Sb_2Te_3 TI were performed theoretically. With the inclusion of van-der-Waals modification (DFT-D3) the values for band gap and lattice parameters were found to be more accurate. Through their investigations we have found that SOI effect have very small effect and the vdW correction is more important. The analysis of PDOS structure indicates that while p-orbitals play important role in defining the material properties near the Fermi level,

the hybridizations between s- and p- orbitals in the valence band justifies the presence of interatomic forces in the material. Topologically protected state with single Dirac cone was then observed with a 2D slab-model technique. The band structure obtained under standard non-linear full relativistic PBE concludes the bulk insulating structure of Sb_2Te_3 with a single Dirac cone at the surfaces. Consistencies with the experimental data provide effectiveness to our theoretical investigation for proficient future applications.

Declarations

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Figures

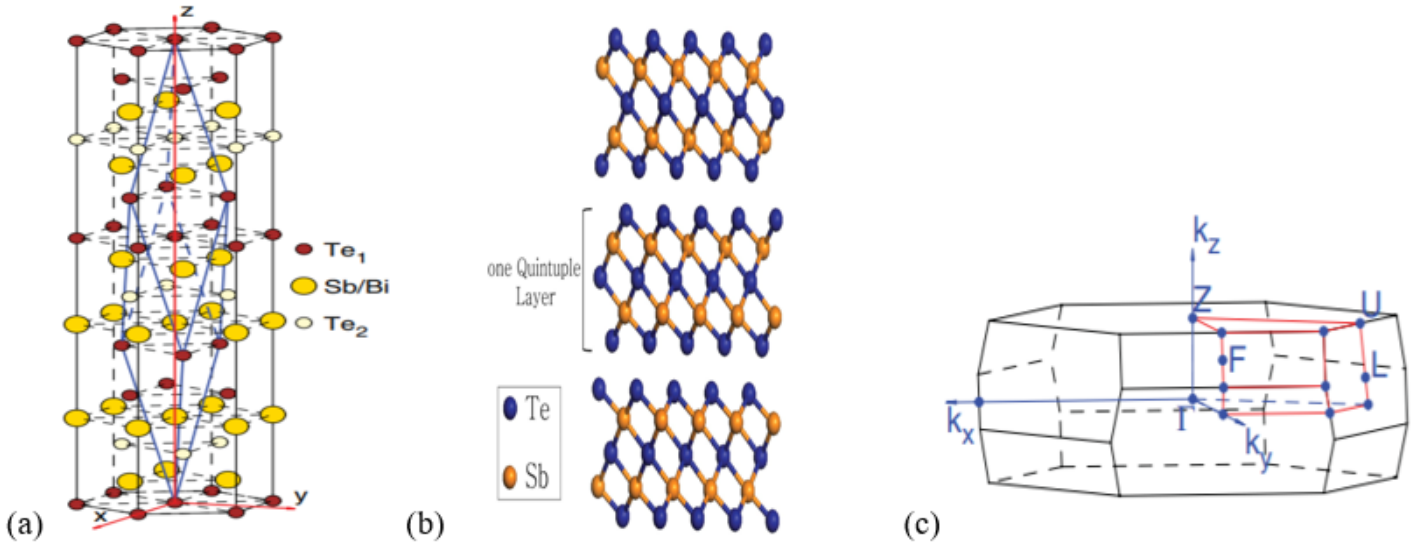

Figure 1

(a) Bulk crystal structure of Sb2Te3/Bi2Te3 (b) Side view of a 3-quintuple-layer slab of Sb2Te3 (c) Bulk Brillouin zone of a two-dimensional slab of Sb2Te3.

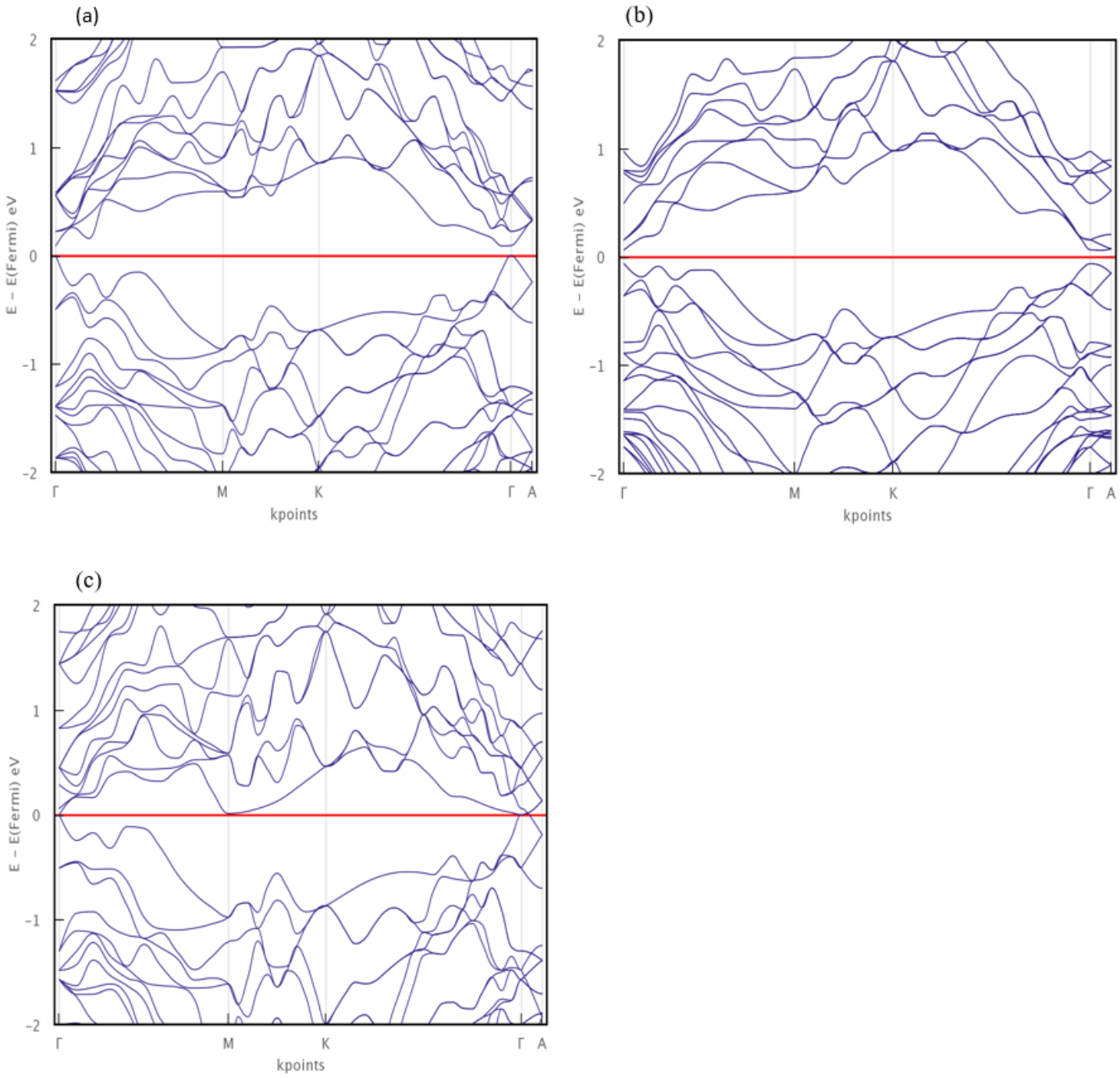

Figure 2

Band structure of bulk Sb2Te3 calculated by (a) DFT-D3 (b) DFT-D3(SOC) (c) LDA

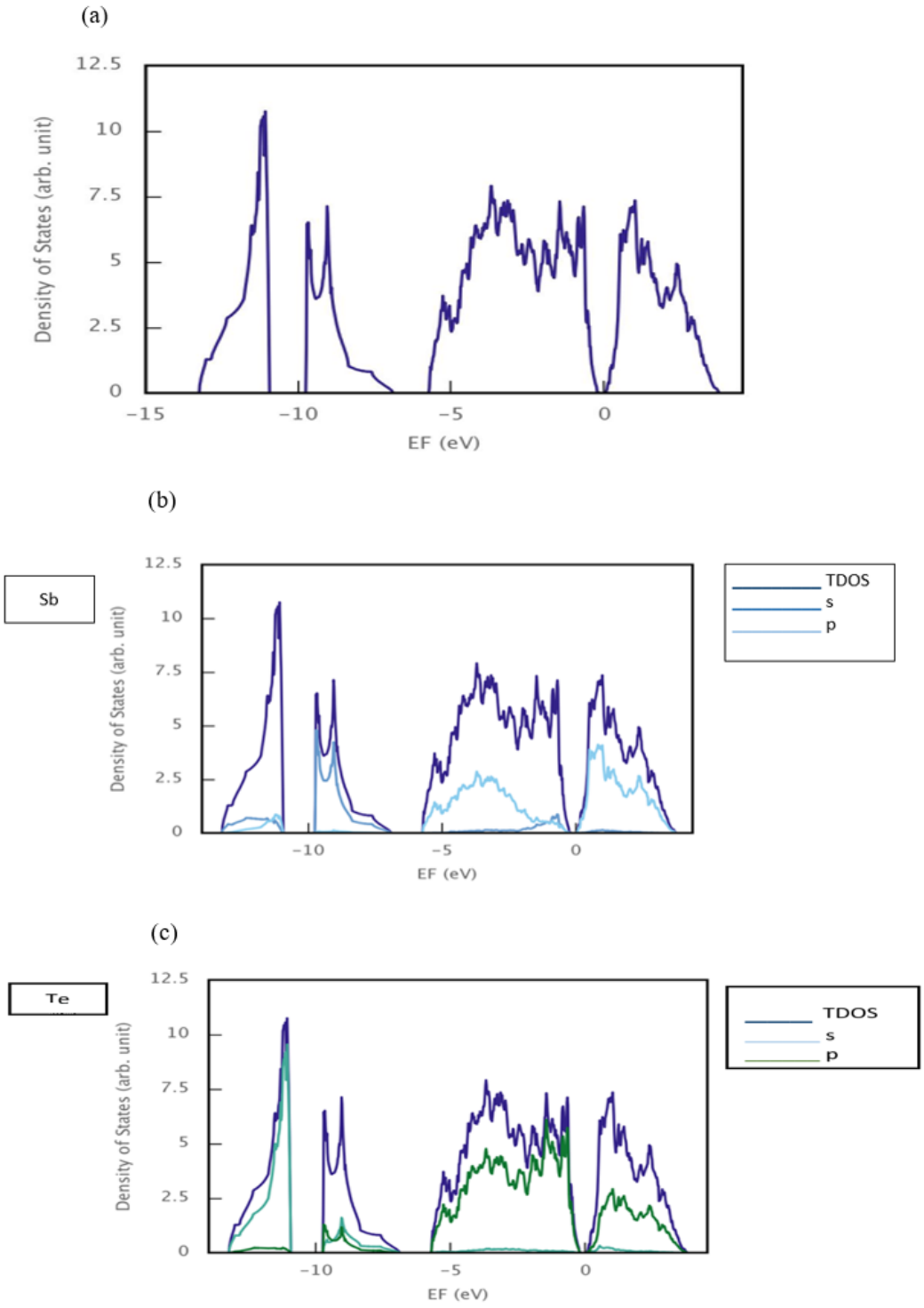

Figure 3

Density of states (a) Total DOS (b) Partial DOS -Sb (c) Partial DOS -Te

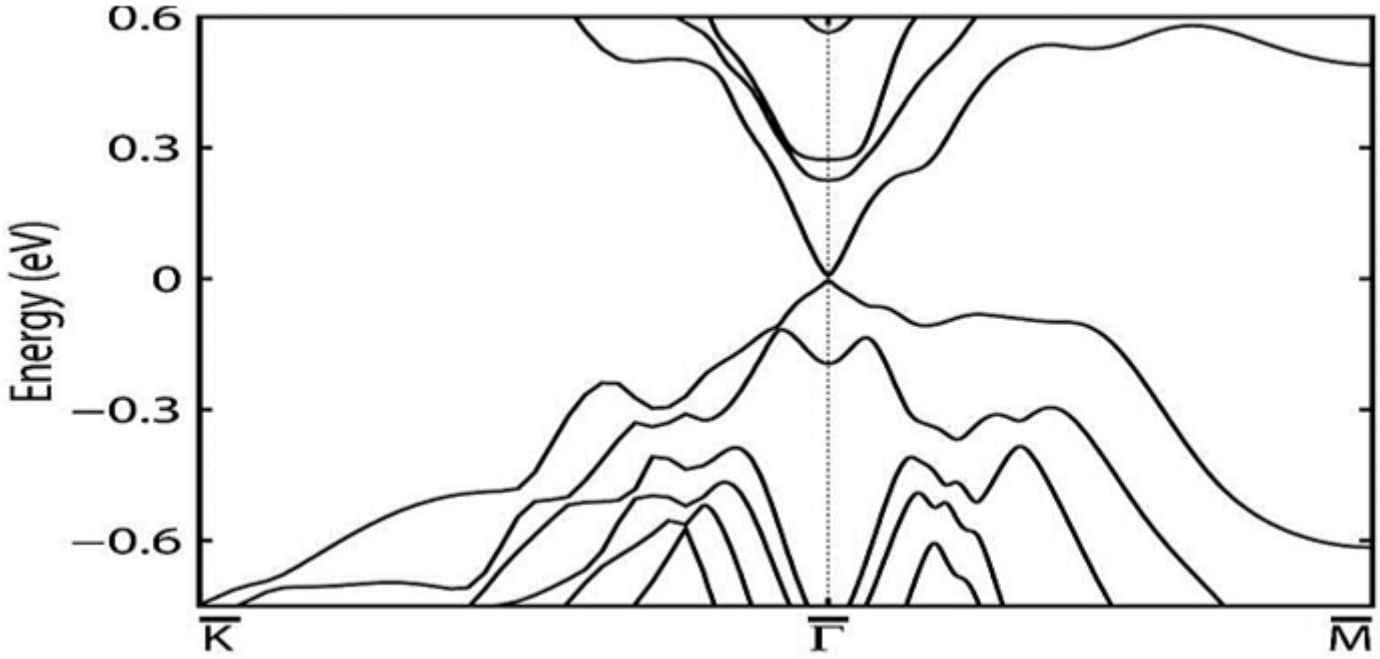

Figure 4

Band structure of a 3QL Antimony Telluride