

CHAPTER 6

BAND GAP AND DEBYE TEMPERATURE OF THE ALLOYS OF SbTeSe: AN *ABINITIO* STUDY

6.1 INTRODUCTION

Studies of transport properties of group V semi-metals are interesting due to their technological applications in the field of thermopiles, optical and micro wave detection devices (Alwyn et al 2002, SchilzJ 2000, Lovett 1977). Among them, SbTeSe alloys are of great interest because of their importance in erasable optical recording (Gosain et al 1991, Lostak et al 1989, Waternabe et al 1983) and phase change memory applications (Fung Hsu 2002, Welnic et al 2007). These materials exhibit fast reversible and irreversible transitions which are useful for photonics optical memory, x-ray imaging and electrical conductivity studies. Atomic arrangement determines the electronic properties of the materials (Damodara Das et al 1988, Mehta et al 2004, Dresselhaus et al 1966). The low temperature studies of electron - phonon coupling constant as compared with Boltzmann transport theory (Chih Yuan Wu et al 1998, Wu et al 1998) indicate that SbTeSe alloys may be strongly coupled systems. Electrical and thermal conductivities, and thermo - physical behaviour of these compounds at room temperature were also studied (Lucianada Silva et al 2004, Vibhav et al 2006, Kumar et al 2007) and the results show that addition of Semi-metal Sb as third element in the Se-Te alloy enhances the conductivity. Recently, Ma et al (2012) experimentally determined the high pressure crystal structures of Sb_2Te_3 by synchrotron



angle-dispersive x-ray diffraction (ADXRD) technique and also ab-initio theoretical studies using VASP calculations.

Theoretical calculations of elastic, electronic and optical properties of antimony selenide (Sb_2Se_3) were reported by Koc et al (2012), using SIESTA and VASP codes, and their results are overestimated in comparison with the experimental studies by Abrikosov et al (1969). The present computational work has been carried out by using the results such as Fermi energy, density of states, etc., of first principles electronic structure of these alloys computed by using the well known self-consistent tight-binding linear muffin tin orbital method (Von Barth et al 1972). In the present work, Debye temperatures of the chosen alloys have been estimated.

6.2 CRYSTAL STRUCTURE AND COMPUTATIONAL DETAILS

The SbTeSe family of antimony alloys contains Sb_2Te_3 , $\text{Sb}_2\text{Te}_2\text{Se}$, Sb_2TeSe_2 and Sb_2Se_3 . The electronic configurations of the elements of these chalcogenides are $\text{Sb} = [\text{Kr}] 4d^{10} 5s^2 5p^3$; $\text{Te} = [\text{Kr}] 4d^{10} 5s^2 5p^4$; $\text{Se} = [\text{Ar}] 3d^{10} 4s^2 4p^4$. The first three compounds namely Sb_2Te_3 , $\text{Sb}_2\text{Te}_2\text{Se}$ and Sb_2TeSe_2 belong to the trigonal crystal system with space groups of $R\bar{3}m$ (No.166), $R\bar{3}m$ (No.166) and $R3m$ (No.160) respectively, where as the Sb_2Se_3 is of orthorhombic family with the space group $pbnm$ (No. 62). The basis set included s, p, d and f orbitals for all systems. The ground-state properties were calculated for the lattice parameters that correspond to the minimum of the total energy. The structure is shown in Figure 6.1- 6.4.



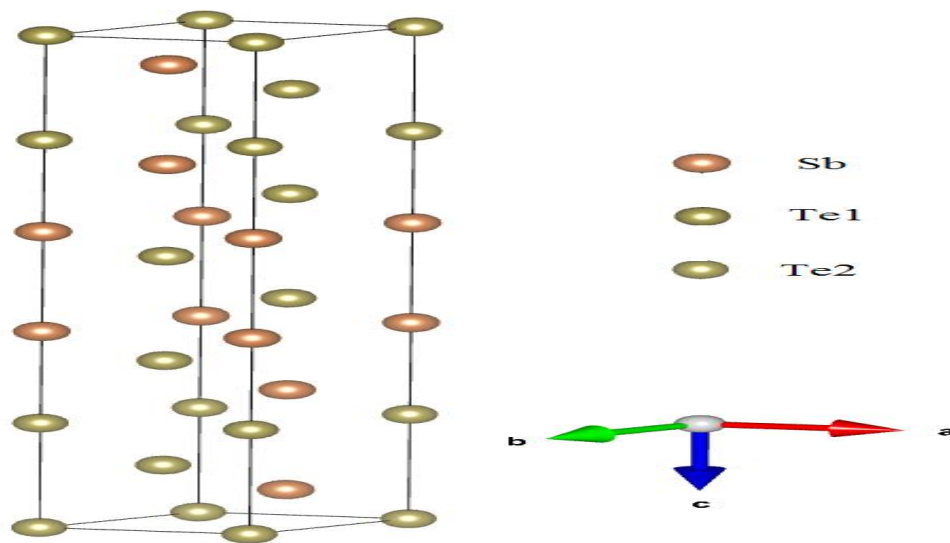


Figure 6.1 Trigonal structure for Sb_2Te_3

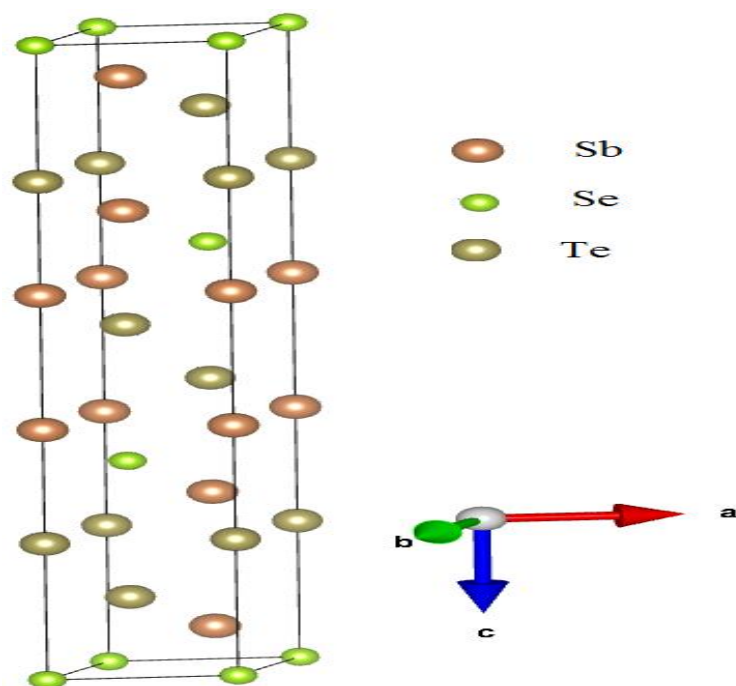


Figure 6.2 Trigonal structure for Sb_2Te_2Se

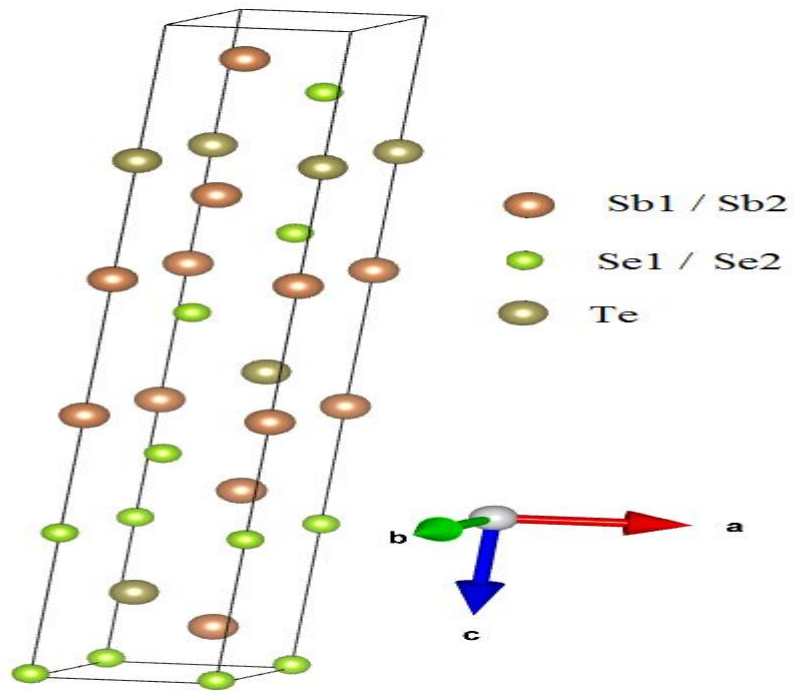


Figure 6.3 Trigonal structure for Sb_2TeSe_2

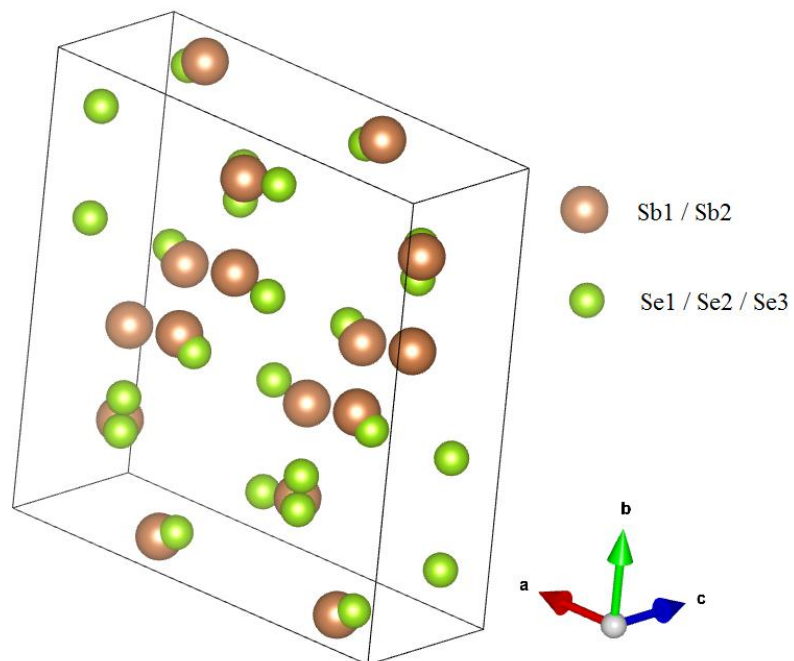


Figure 6.4 Orthorhombic structure for Sb_2Se_3

6.3 TOTAL ENERGY CALCULATION AND RELATED PROPERTIES

The details of crystal structure and lattice parameters are presented in Table 1, (Anderson et al 1987, 1974, Andriamihaja et al 1985, Min et al 1998, Kuganathan 2009, El-Sayad et al 2009, Zheng et al 2002, Hurych et al 1974, Gilbert et al 1974) for all the antimony alloys considered. In order to understand the effect of Se content on the thermal and other related properties of SbTeSe compounds, we intend to study, we need the knowledge of how the electronic total energy, Fermi energy, density of states, etc., vary correspondingly. The electronic total energy values are obtained for various unit cell volumes and fitted to Birch - Murnaghan's equation of state (1944) given by,

$$E(V) = V \frac{B_0}{B_0'} \left[\frac{\left(\frac{V_0}{V}\right)^{B_0'}}{B_0' - 1} + 1 \right] + \text{const.} \quad (6.1)$$

where B_0 , B_0' are the bulk modulus and volume derivative of bulk modulus respectively. A comparison of experimental (Min et al 1998) lattice parameters of Sb_2Te_3 , $\text{Sb}_2\text{Te}_2\text{Se}$, Sb_2TeSe_2 and Sb_2Se_3 are given in Table 6.1. The primitive cell volumes corresponding to the total energy minimum for Sb_2Te_3 , $\text{Sb}_2\text{Te}_2\text{Se}$, Sb_2TeSe_2 and Sb_2Se_3 shows that it is also apparent that the lattice parameters WS volume decreases with the increase of Se content. The plots of total energy as a function of cell volume for Sb_2Te_3 , $\text{Sb}_2\text{Te}_2\text{Se}$, Sb_2TeSe_2 and Sb_2Se_3 are shown in Figure 6.5-6.8.



Table 6.1 Comparison of the calculated lattice parameters with the experimental results. Lattice constant (Å) for Sb_2Te_3 , $\text{Sb}_2\text{Te}_2\text{Se}$, Sb_2TeSe_2 and Sb_2Se_3

Alloys	References	Lattice Parameters		
		a(Å)	b(Å)	c(Å)
Sb_2Te_3	Present	4.27	4.27	30.47
	Theory ^a	4.26	4.26	29.59
	Expt. ^a	4.18	4.18	29.46
	Expt. ^b	4.27	4.27	30.47
$\text{Sb}_2\text{Te}_2\text{Se}$	Present	4.15	4.15	29.67
	Expt. ^c	4.18	4.18	29.94
Sb_2TeSe_2	Present	4.04	4.04	28.99
	Expt. ^d	4.11	4.11	29.49
Sb_2Se_3	Present	11.78	4.02	11.94
	Theory (SIESTA) ^e	11.91	3.98	11.70
	Theory (SIESTA) ^f	11.71	4.14	11.62
	Theory (VASP) ^f	11.52	3.96	11.22
	Expt. ^g	11.79	3.98	11.64
	Expt. ^h	11.59	3.96	11.74
	Expt. ⁱ	11.78	3.99	11.63
	Expt. ^j [30]	11.77	3.96	11.62
	Expt. ^k [31]	11.62	3.69	11.77

a-Ma et al 2012, b- Anderson et al 1987 c- Anderson et al 1974, d-Andriamihaja et al 1985, e-Kuganathan 2009, f-Koc et al 2012, g- El-Sayad et al 2009, h- Min et al 1998, i- Zheng et al 2002, j-Hurych et al 1974, k- Gilbert et al 1974.



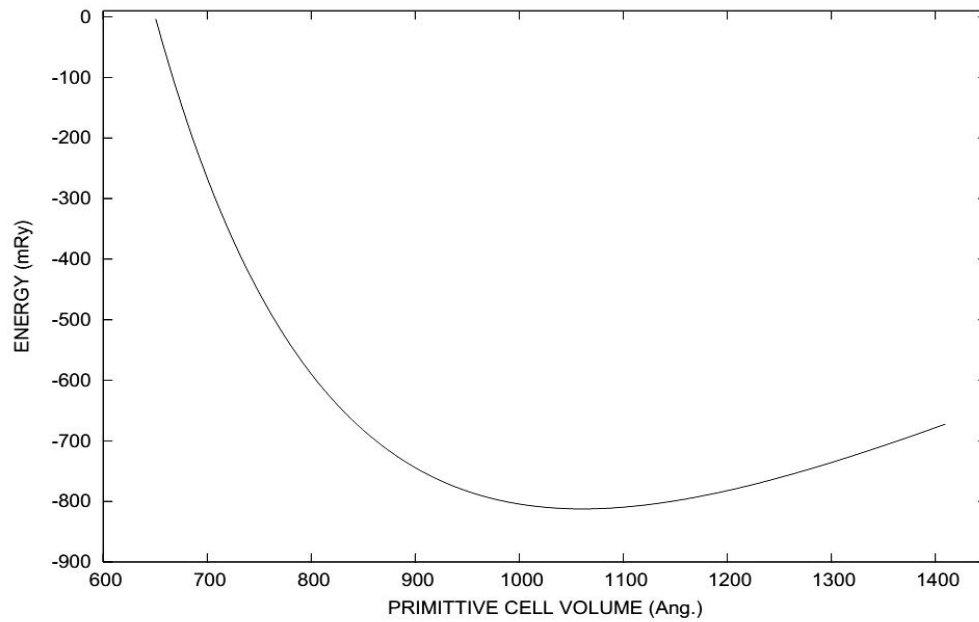


Figure 6.5 Variation of total energy (with reference to -66646.000Ry) with cell volume for Sb_2Te_3

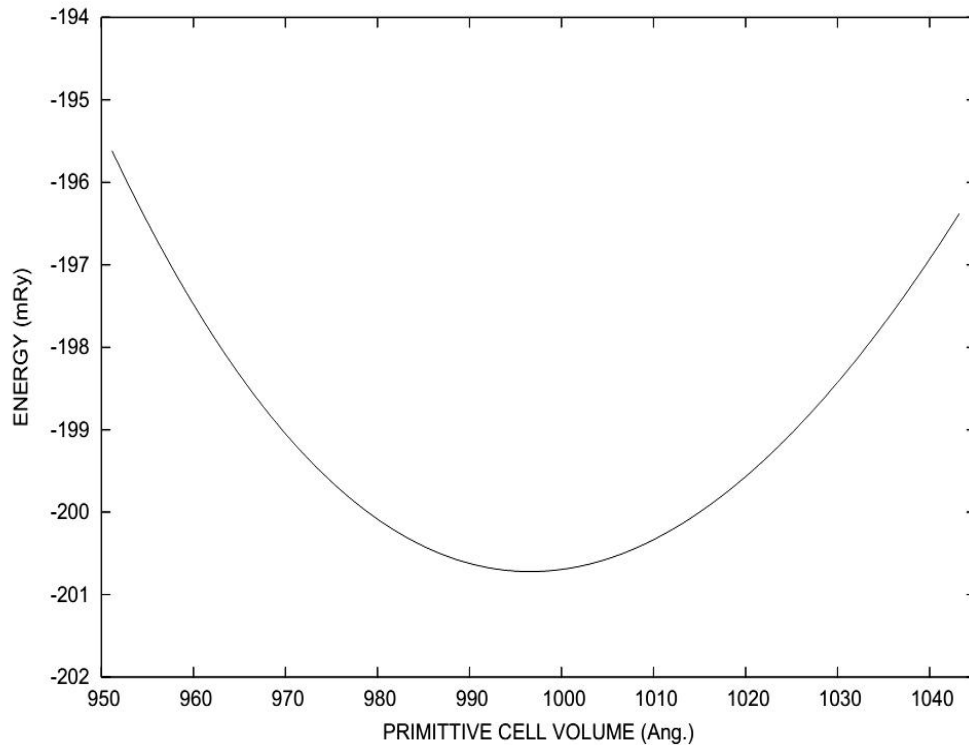


Figure 6.6 Variation of total energy (with reference to -57922.000Ry) with cell volume for $\text{Sb}_2\text{Te}_2\text{Se}$



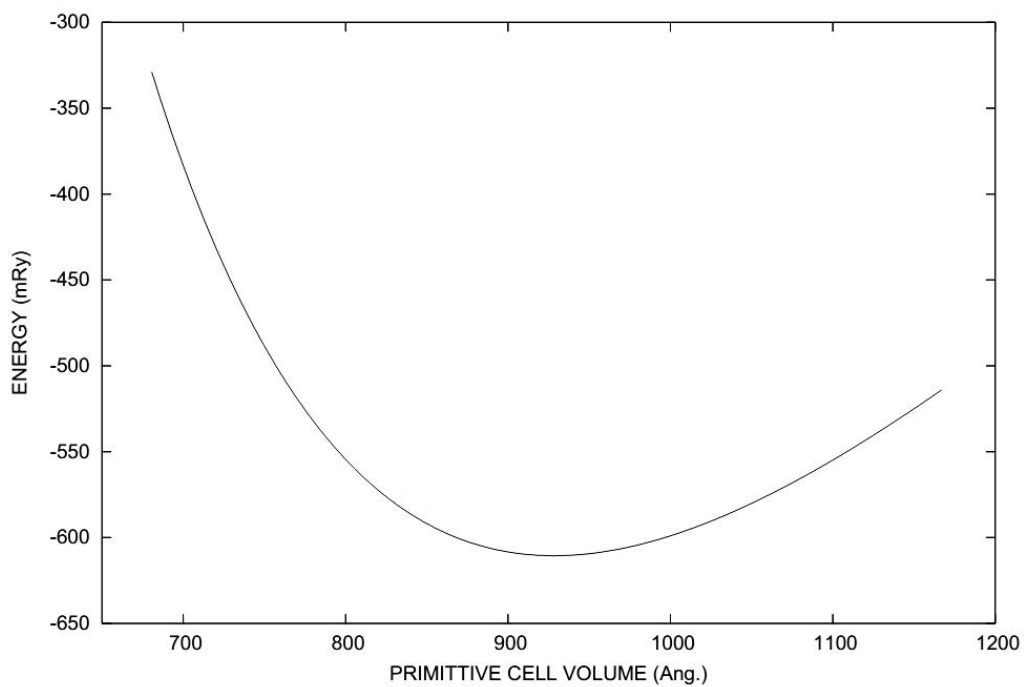


Figure 6.7 Variation of total energy *with reference to -49197.000Ry) with cell volume for Sb_2TeSe_2

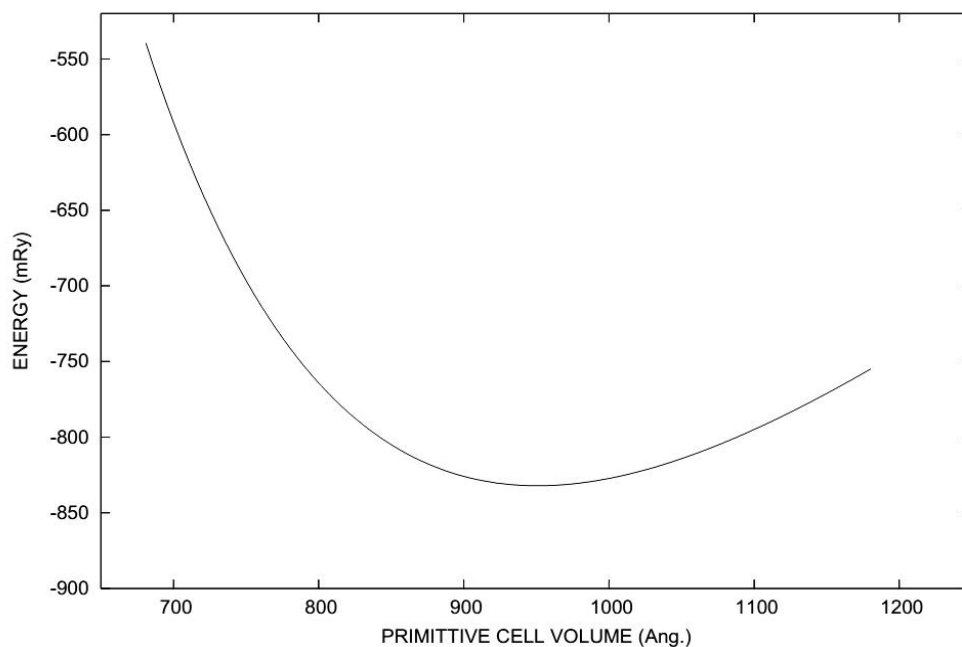


Figure 6.8 Variation of total energy (with reference to -40472.000Ry) with cell volume for Sb_2Se_3

6.4 ELECTRONIC BAND STRUCTURE CALCULATIONS

Ab initio self consistent calculations of these quantities along with the electronic bandstructures, have been carried out through the tight binding linear muffin tin orbital technique within atomic sphere approximation (Andersen et al 1984). The semi-metallic nature of all these alloys is clearly shown by their band structures with nearly filled by valence band, with the Fermi level lying just below the top of the valence band. The electronic bandstructures of (Sb_2Te_3 , $\text{Sb}_2\text{Te}_2\text{Se}$ and Sb_2TeSe_2) and the orthorhombic structure (Sb_2Se_3) along the high symmetry directions of the Brillouin zone are displayed in Figure 6.9–6.12.

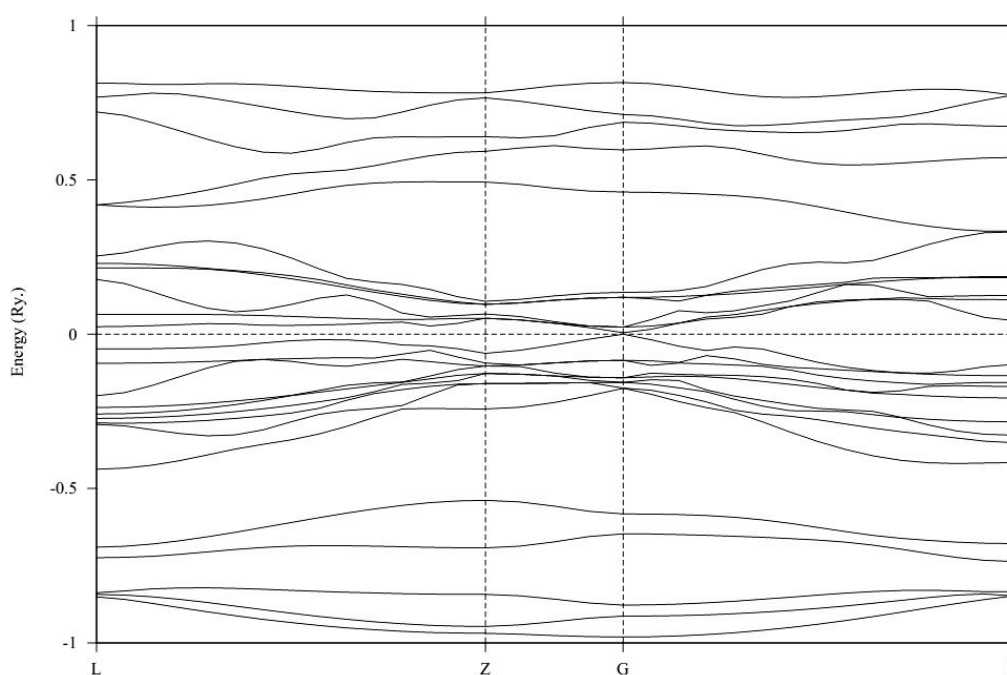


Figure 6.9 Energy band structure for Sb_2Te_3

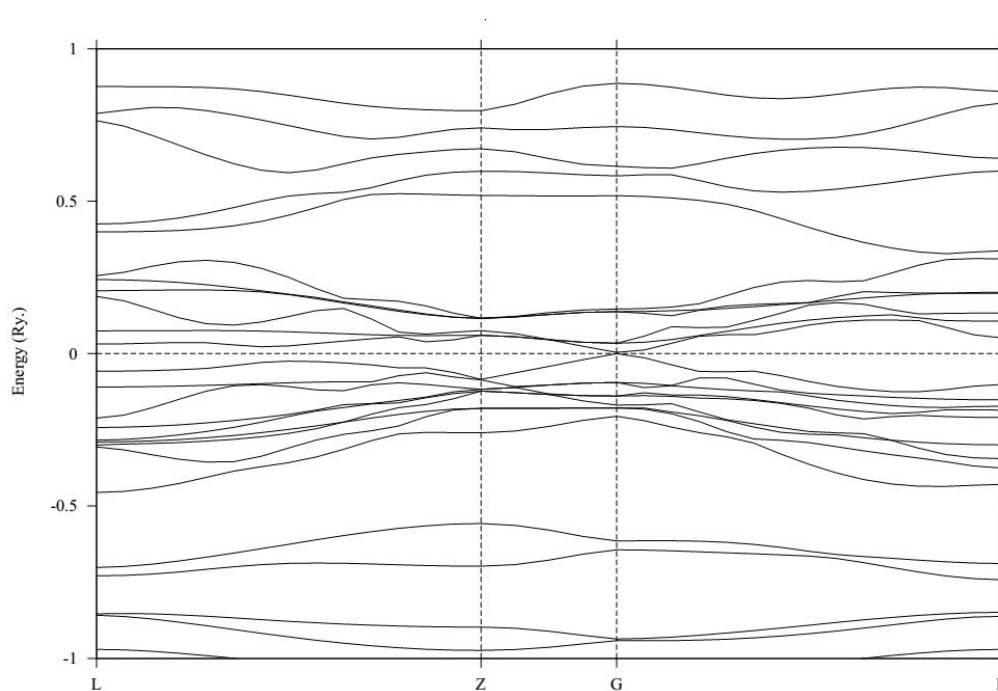


Figure 6.10 Energy band structure for $\text{Sb}_2\text{Te}_2\text{Se}$

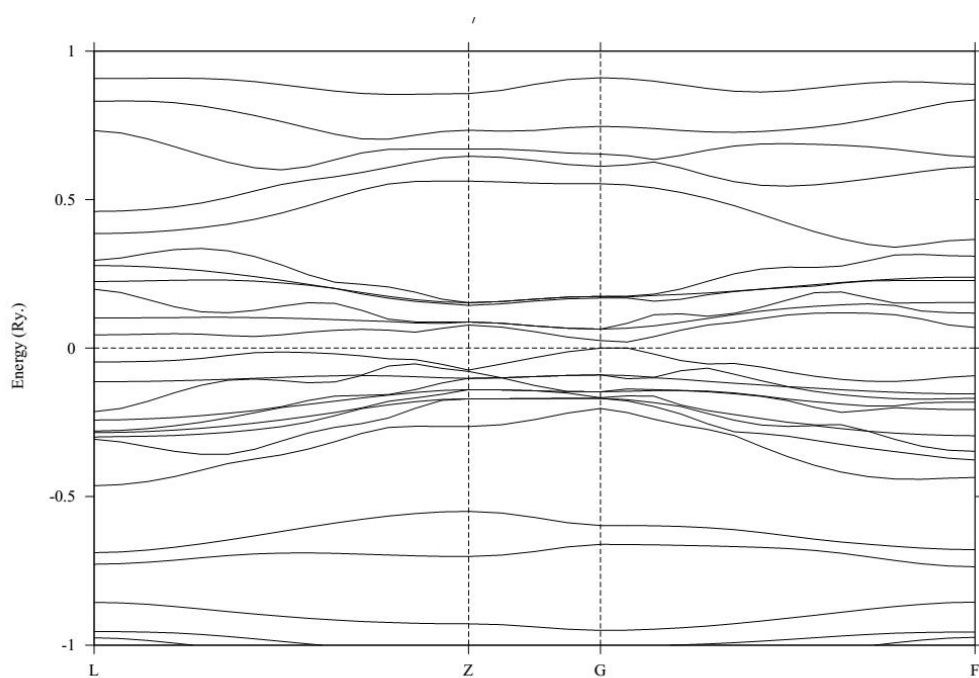


Figure 6.11 Energy band structure for Sb_2TeSe_2

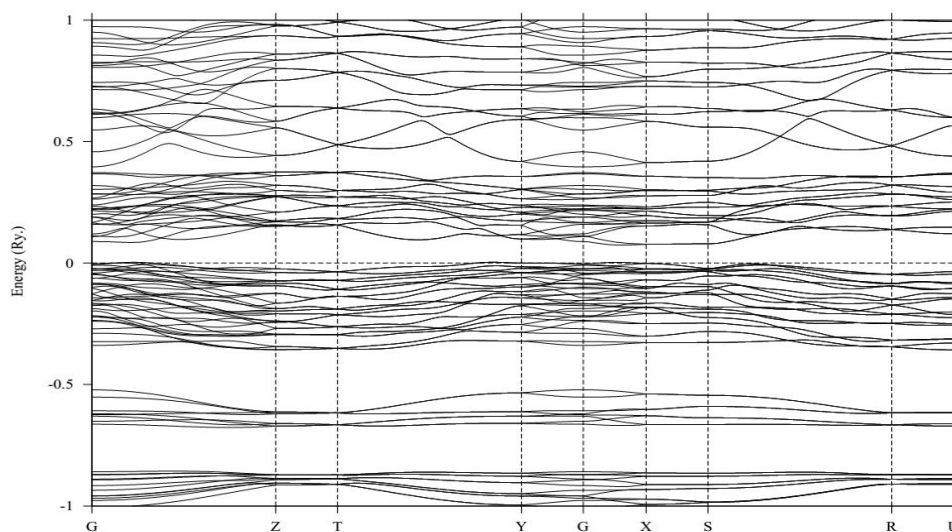


Figure 6.12 Energy band structure for Sb_2Se_3

Table 6.2 provides the Band gap (E_g) and the Fermi energy (E_F) of all alloys of antimony.

Table 6.2 Energy band gap and the Fermi energy of $\text{Sb}_2\text{Te}_x\text{Se}_{3-x}$ ($x=3, 2, 1, 0$) alloys

Alloys	References	E_g (eV)	E_F (eV)
Sb_2Te_3	Present	0.04	5.45
	Expt. ^a	0.03	
	Theory ^b	0.07	
	Expt. ^c	0.23	
$\text{Sb}_2\text{Te}_2\text{Se}$	Present	0.04	5.93
Sb_2TeSe_2	Present	0.38	6.13
Sb_2Se_3	Present	1.03	5.57
	Theory(SIESTA) ^d	1.07	
	Expt ^{e,f}	1.00	

a-Pradyumnan et al 2010, b- Min Sik Park et al 2010, c- Ronnlund et al 1965, d- Koc et al 2012, e- Gilbert et al 1974, f- Arun et al 1998,

6.5 ELECTRONIC DENSITY OF STATES

From the band structures and density of states it is observed clearly that there is a widening of energy gap and downward shifting of Fermi level (E_F) from the top of valence band, thus leading to the increase of density of states of E_F as shown in Figure 6.13 – 6.16.

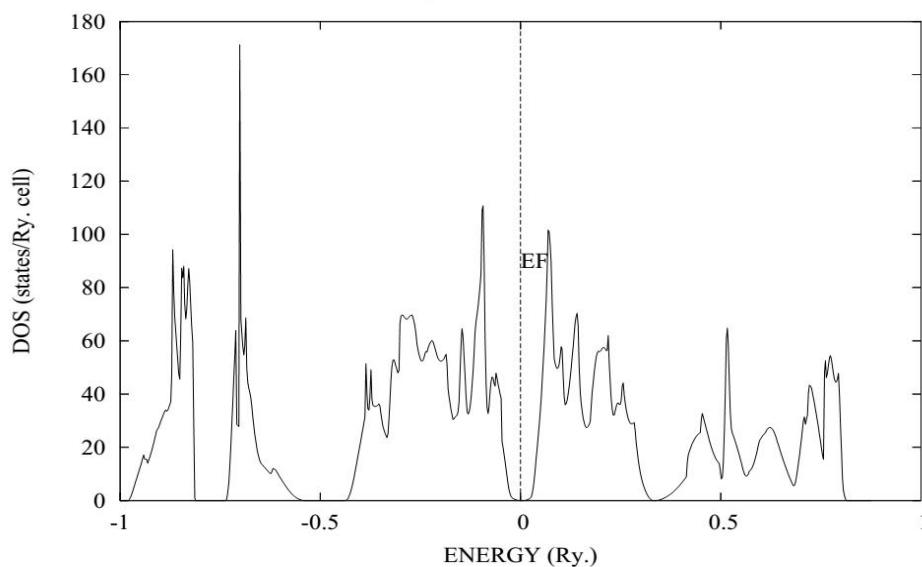


Figure 6.13 Total density of states for Sb_2Te_3

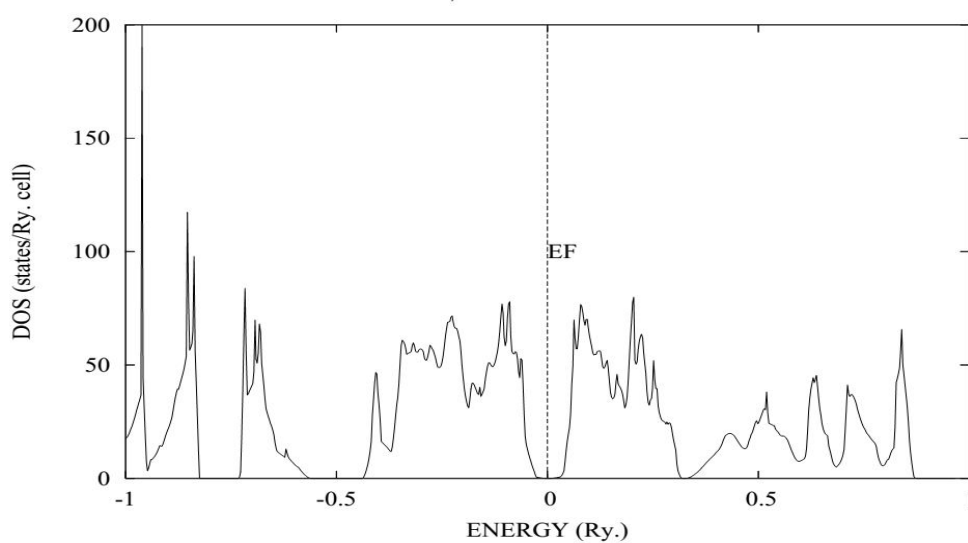


Figure 6.14 Total density of states for Sb_2Te_2Se



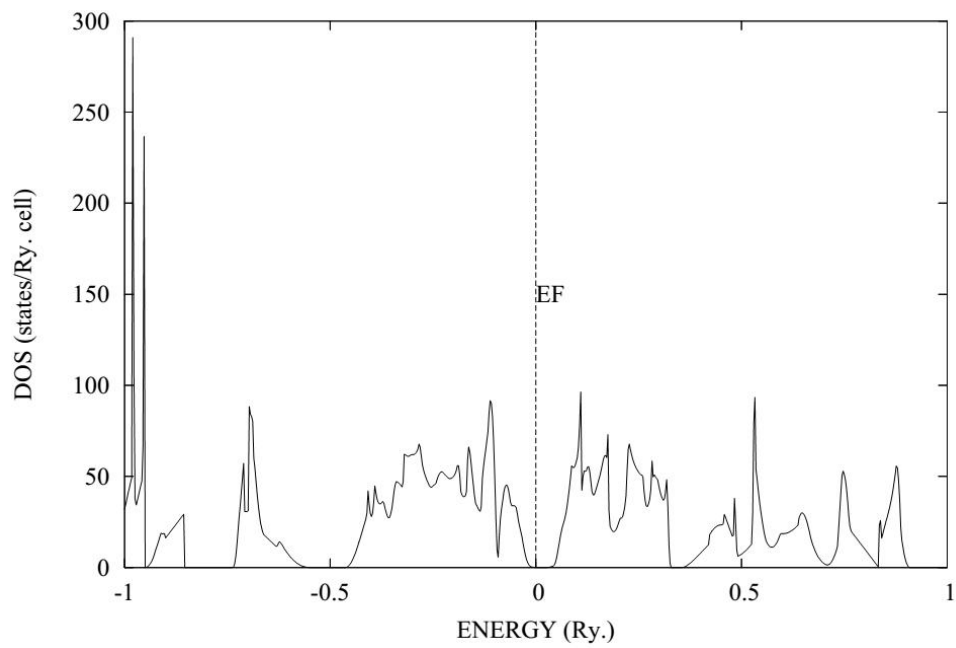


Figure 6.15 Total density of states for Sb_2TeSe_2

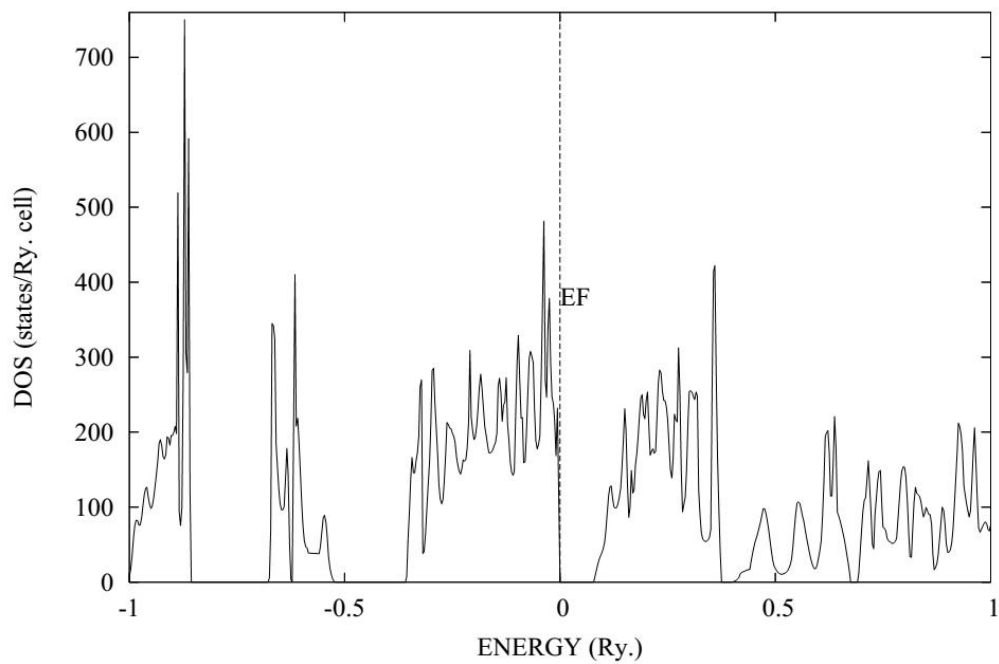


Figure 6.16 Total density of states for Sb_2Se_3

Table 6.3-6.6 Partial and Total electronic density of states for all the four alloys



Table 6.3 Partial and Total electronic density of states for Sb₂Te₃

Band	DOS N(E _F) [(States/Ry/atom)]			
	Sb	Te	E	Total
s	0.1102	0.4493	0.6667	1.2262
p	17.7645	15.189	0.5990	33.5525
d	0.2194	1.2983	0.6597	2.1774
f	0.7349	1.4587	0.0000	2.1936
Total	18.829	18.3953	1.9254	39.1497

Table 6.4 Partial and Total electronic density of states for Sb₂Te₂Se

Band	DOS N(E _F) [(States/Ry/atom)]				
	Sb	Se	Te	E	Total
s	0.3840	0.1661	0.5826	1.0278	2.1605
p	19.2118	3.8580	9.9638	1.2197	34.2533
d	0.3868	0.8933	1.3280	0.6561	3.2642
f	0.6770	0.0000	0.5792	0.0000	1.2562
Total	20.6596	4.9174	12.4536	2.9036	40.9342

Table 6.5 Partial and Total electronic density of states for Sb₂TeSe₂

Band	DOS N(E _F) [(States/Ry/atom)]				
	Sb	Se	Te	E	Total
s	0.6662	0.6749	0.2374	1.0119	2.5904
p	20.9865	8.8085	5.8546	1.2148	36.8644
d	0.6830	2.4101	0.5992	1.1023	4.7946
f	0.4025	0.0000	0.2270	0.0000	0.6295
Total	22.7382	11.8935	6.9182	3.3290	44.8789



Table 6.6 Partial and Total electronic density of states for Sb₂Se₃

Band	DOS N(E _F) [(States/Ry/ atom)]			
	Sb	Se	E	Total
s	0.7167	0.9218	3.0654	4.7039
p	21.6063	14.2532	2.9112	38.7707
d	0.7561	1.6196	1.9983	4.3740
f	0.3832	0.0000	0.0000	0.3832
Total	23.4623	16.7946	7.9749	48.2318

We observe that the total density of states (N(E_F)) at E_F increases with Se content and it is indeed p-dominated. The Fermi energy increases with the increase of Se content while the energy gap (E_g) remains nearly the same; but for Sb₂Se₃, the E_F value has decreased considerably while the energy gap has increased appreciably. Such drastic changes of E_F and E_g values for Sb₂Se₃, when compared to those of other alloys, is attributed to the structural transition from trigonal to orthorhombic structure as Se content (x) in Sb₂Te_xSe_{3-x} increases.

The present energy gap value of Sb₂Te₃ (0.04 eV) is closer that (0.07 eV) of earlier theoretical report by Min Sik Park et al (2010); however, for Sb₂Se₃, the agreement of the present E_g value (1.03 eV) is very good with the earlier experimental reports, (Gilbert et al 1974, Arun et al 1998). In the case of other three alloys, to the best of our knowledge, there are no experimental as well as theoretical reports available in the literature for comparison.



6.6 THERMAL PROPERTIES

The bulk modulus B_0 extracted from the band structure results is immediately used to obtain the Debye temperature θ_D by Moruzzi et al (1988) for the three trigonal system (Sb_2Te_3 , $\text{Sb}_2\text{Te}_2\text{Se}$ and Sb_2TeSe_2) and the orthorhombic structure (Sb_2Se_3) as in 3.50 & 3.51. It may be observed that θ_D values show an increasing trend with the increase of Se content. The Debye temperature (θ_D) values obtained here are found to be closer to the available experimental values than to those of earlier theoretical report by Dyck et al (2002).

Table 6.7 The bulk modulus (B_0), WS-radius (r_o) and the Debye temperature (θ_D) of $\text{Sb}_2\text{Te}_x\text{Se}_{3-x}$ ($x=3,2,1,0$) alloys

Alloys	B_0 (GPa)			WSR r_o (a.u.)	θ_D (K)		
	Present	Literature			Present	Literature	
		Theory	Expt.	Theory		Expt.	
Sb_2Te_3	60.7	54.7 ^a	52.7 ^a	6.33	167	-	160 ^d
$\text{Sb}_2\text{Te}_2\text{Se}$	65.1	-	-	6.20	178	-	-
Sb_2TeSe_2	70.7	-	-	6.05	192	-	-
Sb_2Se_3	61.0	64.78 ^b	-	6.10	232	262.78 ^b	240 ^c

a- Ma et al 2012, b- Koc et al 2012, c-Abrikosov et al 1969, d-Dyck et al 2002

6.7 SUMMARY

The $\text{Sb}_2\text{Te}_x\text{Se}_{3-x}$ ($x = 3, 2, 1, 0$) chalcogenide alloys have been studied theoretically for their thermal properties in terms of the Fermi energy and density of states obtained by using the results of ab-initio computation carried out by the well known self consistent tight binding linear muffin tin orbital method. These studies reveal that the electronic properties are highly



dominated by the p-orbitals, mainly originating from Sb. Semi metallic nature of all the four materials is clearly evident from their band structure and density of states. The energy gap and density of states at E_F increase as Se content increases, while the Fermi energy and bulk modulus values increase as Se content increases, from Sb_2Te_3 to Sb_2TeSe_2 , and then they decrease considerably for Sb_2Se_3 . Such drastic change of these properties for Sb_2Se_3 is therefore attributed to the structural phase change from trigonal to orthorhombic structure.

