Density functional study of the structural, dynamic and Thermodynamic Proprieties of the III-Antimonides semiconductors (BSb, AlSb, GaSb, and InSb)

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***Abstract*— In the present contribution, structural, dynamic, and some thermodynamic properties of the III-Antimonides are studied using the density-functional perturbation theory (DFPT) within the local density approximation (LDA) in combination with the harmonic approximation Our results for the structural properties such as the lattice constant and the bulk modulus were found to agree well with the previous theoretical and experimental works. We have also calculated the phonon dispersion relation, and we found that our phonon calculations show that these compounds are dynamically stable in the zinc blende phase moreover our results of the optical and acoustic phonon frequencies at the high symmetry points Γ, X and L are in good agreement with the available theoretical and experimental data. In addition, the thermodynamic properties, including the free energy, internal energy, entropy, and the heat capacity at constant volume were predicted and discussed.**

***Keywords*— DFPT, III-Sb, Phonon frequencies, splitting LO-TO, Thermodynamic proprieties.**

I. INTRODUCTION

The III–V zinc-blende semiconductor compounds are promising materials for many technological applications because it shows mechanical, thermal and electrical promising properties [1] among them the III-Antimonides BSb, AlSb, GaSb, and InSb, they have considerable interest in high temperature electronic and optical devices [1, 2], recently and because of their uses in rechargeable lithium batteries the III-Sb compounds have attracted more attention [3]. To determine the properties of a material such as phase transition, thermodynamic stability, transport and thermal properties, it is necessary to know the spectrum of phonons, in this context, we opt in this work to explore the structural, dynamic, and some thermodynamic properties of the III-Antimonides by employing the density-functional perturbation theory (DFPT) within the local density approximation (LDA) in combination with the harmonic approximation.

II. COMPUTATIONAL METHOD

Our calculations are performed using the Abinit code based on the density functional theory (DFT) [4] within the local density approximation (LDA). The exchange-correlation potential in the Ceperley–Alder form [5] as parameterized by Perdew and Zunger [6] is used. Electron ion interactions are evaluated using nonlocal, norm-conserving pseudopotentials generated using the scheme proposed by Troullier and Martins [7]. The energy cut off of the plane wave basis was chosen as 80Ha.The special points sampling integration over the Brillouin zone was employed with $8x8x8$ by using the Monkhorst–Pack method [8]. Phonon frequencies were obtained using the linear-response method in the frame of density functional perturbation theory (DFPT) [9-12] as implemented in the ABINIT code, which the expressions are obtained from the second derivatives of the total energy with respect to the phonon displacement. For thermodynamic properties the harmonic approximation has been used [13].

III. RESULTS AND DISCUSSIONS

The structural parameters such us the lattice parameter (a), bulk modulus (B) and its first order pressure derivative (B') can be determined by calculating the total energy for different volumes around equilibrium and fitted by the Murnaghan's equation-of-state [20]. Our results concerning these parameters for the zinc-blend III-Antimonides were presented and compared with the results of previous calculations and the available experimental data in Table I. As can be seen from this table that our results are in good agreement compared with the theoretical [14,15,18] and experimental values [2,16,17,19]. It's remarkable also that the BSb compound have smaller lattice constants and large bulk modulus than the other III-Antimonides AlSb, GaSb, and InSb.

TABLE I
Calculated lattice constants a, bulk modulus B and the pressure derivative of bulk modulus B' for BSb, AlSb, GaSb and InSb zinc-blende compounds, together with available experimental data and results of other calculations

Material	a_0 (A°)	β_0(Gpa)	$\beta_0^{'}$
BSb	5,168	109.73	4.29
Theo.	5.201 [14]	109 [14]	4 [14]
Exp.			
AlSb	6.09	55.56	4.37
Theo.	6.202[15]	51.84[15]	4.45[15]
Exp.	6.135[2]	55.1[16]	
GaSb	5.98	56.44	4.66
Theo.	6.184[15]	49.136[15]	3.88[15]
Exp.	6.096[17]	56.1[17]	
InSb	6,346	46.74	4.74
Theo.	6.48 [18]	45.6 [18]	4.7 [18]
Exp.	6.479 [19]	48.3 [19]	

In figure 1, we report the calculated phonon dispersion curves along several symmetry lines of the zinc-blende BSb, AlSb, GaSb and InSb compounds. As one can see, all the phonon frequencies are positive for BSb, AlSb, GaSb and InSb semiconductors, which confirms the dynamic stability of these compounds in the zinc blende phase. Since all primitive cells contain two atoms, there are six vibrational modes, three of which are acoustic modes and the other three are optical modes. Moreover a small separations between the longitudinal optical modes (LO) and the transverse optical modes (TO) at Γ point (LO-TO splitting) are observed in these spectra, which reflect the strong binding of these compounds. The LO-TO splitting is 17.02, 16.17, 6.94 and 9.35 cm^{-1} for BSb, AlSb, GaSb and InSb respectively, we also note that the optical and acoustic regions are separated for each material and this gap decreases with the increase in the mass of the anion ($B \rightarrow Al \rightarrow Ga \rightarrow In$) due to the difference in mass between anion and cation mass. The phonon frequencies at the points of high symmetry Γ, X and L for BSb, AlSb, GaSb and InSb compounds are presented in Table II compared with the theoretical and experimental results available. Analyzing this table, we observe a decrease in phonon frequencies with the increase of anion mass, and in general, our calculated phonon frequencies are in good agreement with the available theoretical [14, 21] and experimental data[22,23,24].

The temperature dependence of III-Sb's thermodynamic properties was evaluated from the calculated total phonon DOS in harmonic approximation [13]. We studied the evolution as a function of the temperature up to 1000 K of thermodynamic functions such as free energy (ΔF), internal energy (ΔE), entropy (S), and the heat capacity at constant volume (C_v). Our results are illustrated in Figures 2. The temperature dependent $\Delta F(T)$ (see Figure 2-(a)) For the zinc blend III-SB compounds BSb, AlSb, GaSb and InSb show a progressive decrease with the increase of the temperature, while the internal energy $\Delta E(T)$ (Figure 2-(b)) and entropy $S(T)$ (Figure 2-(c)) increase steadily with increasing temperature. In addition, among the four III-Sb, we note that the BSb has the highest free energy and internal energy, and the lowest entropy than the other III-Sb compounds seeing as BSb has a much higher averages phonon frequencies. The heat capacity at constant volume C_v of the studied materials displays two different behaviors according to the temperature in the range considered, at sufficiently low temperatures, C_v increases rapidly with T, and obeys Debye's law [25]. Then at high temperatures, it slowly increases and converges to a limit (≈49.86J.mol^{-1}.maille^{-1}.K^{-1}) in good agreement with the law of Dulong-Petit (3nR).

TABLE III
Calculated phonon frequencies at the points of high symmetry Γ, X and L for BSb, AlSb, GaSb and InSb zinc-blende compounds, theoretical and experimental data are also shown for comparison(all values are in cm^{-1}).

Material	ω_{TO}^{Γ}	ω_{LO}^{Γ}	ω_{TA}^{X}	ω_{LA}^{X}	ω_{TO}^{X}	ω_{LO}^{X}	ω_{TA}^{L}	ω_{LA}^{L}	ω_{TO}^{L}	ω_{LO}^{L}
BSb	*621,32*	604,31	134,20	232 ,46	639,66	566,74	96,10	226,27	589,08	625,45
Theo.[14]	621	611	138	233	644	568	95	226	593	626
AlSb	351.05	367.22	44.70	170.36	334.66	375.2	36.24	162.15	345.52	361.11
Theo.[21]	317	334	82	164	295	343	70	160	310	328
Exp.[22]	318	352	69	154	294	341	56	147	307	320
GaSb	229	235.95	58.48	162.42	208.23	211.41	45.82	158.27	202.54	219.53
Theo.[21]	228	234	64	161	213	214	53	157	223	207
Exp.[23]	224	233	57	166	212	212	46	153	205	216
InSb	*182,96*	182,96	44,42	147,56	156,26	173,36	35,94	135,04	178,45	159,46
Theo.[21]	181	189	27	147	174	174	22	127	177	159
Exp.[24]	179.95	192.1								

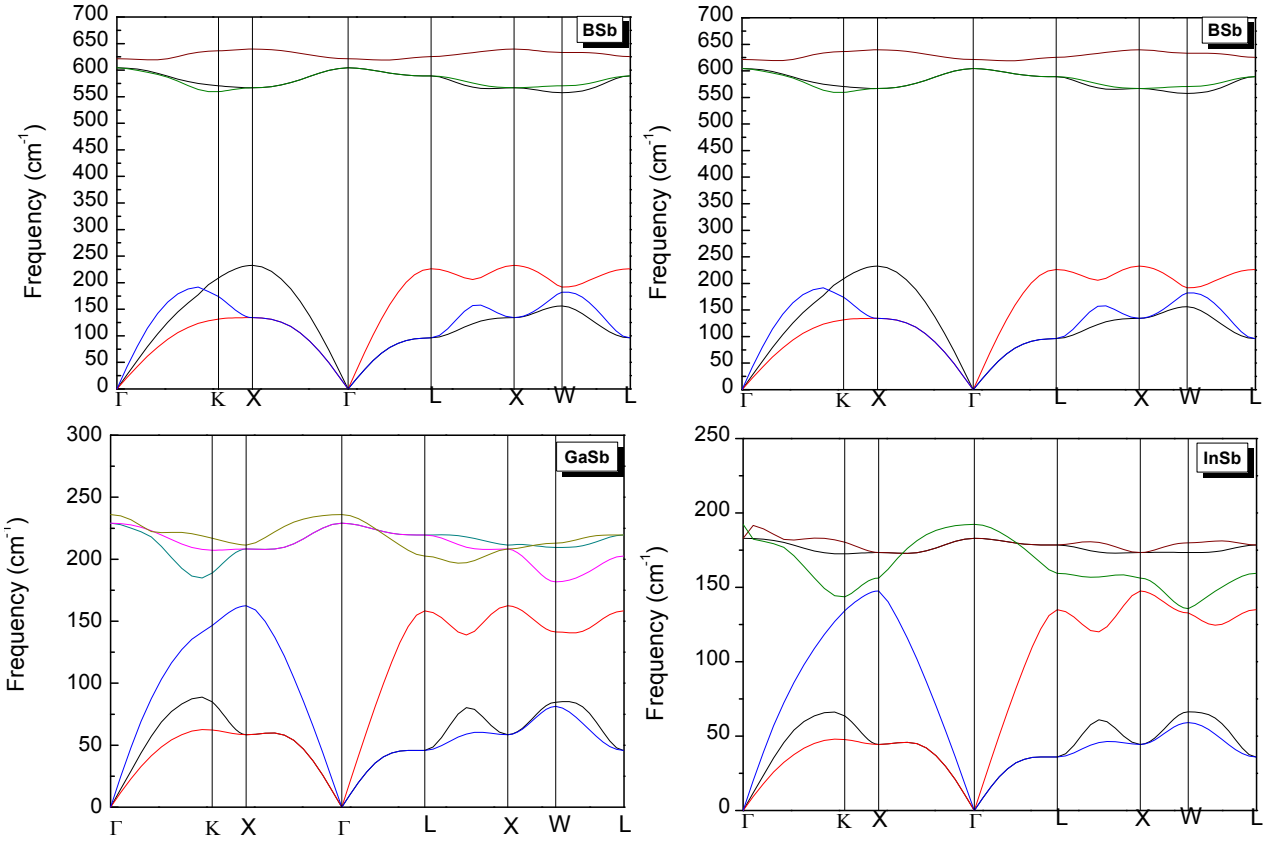

Fig. 1 Phonon frequencies of zinc-blend III-Sb (BSb, AlSb, GaSb, and InSb

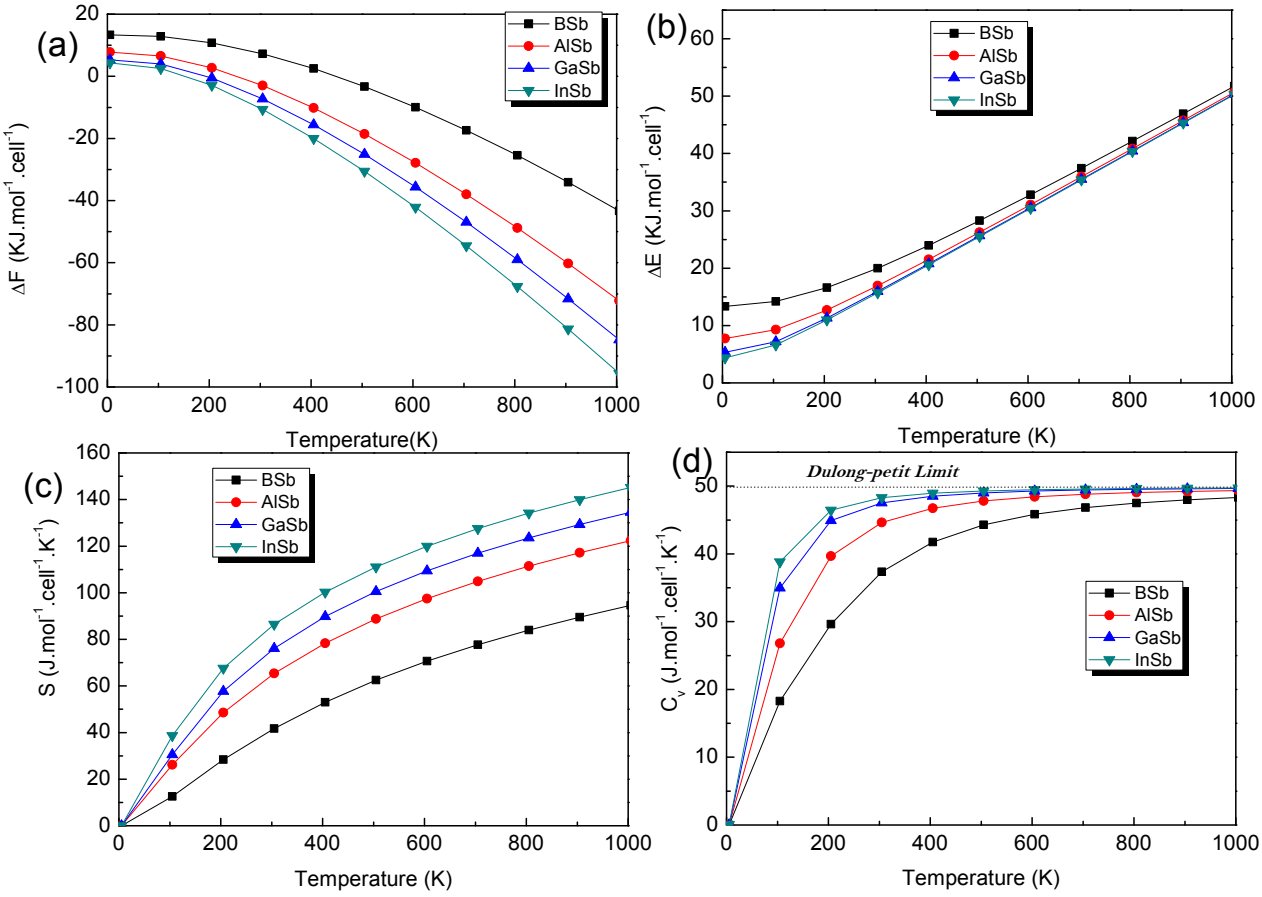

Fig. 2 Temperature dependence of the calculated (a) Free enrgy (ΔF) (b) Internal energy (ΔE), (c) Entropy (S), and (d) Heat capacity at constant volume C_V for III-Sb compounds.

IV. CONCLUSIONS

In summary, we have presented a theoretical study of the structural, dynamic and thermodynamic properties of the zinc-blende III-Sb: BSb, AlSb, GaSb and InSb semiconductors using the density functional perturbation theory DFPT with the LDA approximation. For the structural properties, our calculations of lattice parameter and bulk modulus were found to agree well with the available experimental and theoretical data. The phonon frequencies have been examined and the zinc-blende structure of III-Antimonides is found to be dynamically stable, we also obtained a good agreement with our calculations of the optical and acoustic phonon frequencies at the high symmetry points Γ, X and L with the available theoretical and experimental data. The variation of some thermodynamic proprieties as a function of the temperature have been predicted and discussed such as free energy, internal energy, entropy, and the heat capacity at constant volume the materials of interest.

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