

First principles calculations of structural, electronic and thermal properties of lead chalcogenides PbS, PbSe and PbTe compounds

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Abstract. The structural, electronic and thermal properties of lead chalcogenides PbS, PbSe and BeTe using full-potential linear augmented plane wave (FP-LAPW) method are investigated. The exchange–correlation energy within the local density approximation (LDA) and the generalized gradient approximation (GGA) are described. The calculated structural parameters are in reasonable agreement with the available experimental and theoretical data. The electronic band structure shows that the fundamental energy gap is direct (L–L) for all the compounds. Thermal effects on some macroscopic properties of these compounds are predicted using the quasi-harmonic Debye model, in which the lattice vibrations are taken into account. The variations of the lattice constant, bulk modulus, heat capacity, volume expansion coefficient and Debye temperature with temperature and pressure are obtained successfully. The effect of spin–orbit interaction is found to be negligible in determining the thermal properties and leads to a richer electronic structure.

Keywords. Lead chalcogenides; band-structure; Debye model.

1. Introduction

During the past decades, the lead chalcogenides, PbX (X = S, Se and Te) have been a subject of a great amount of theoretical and experimental studies, motivated by their importance in infrared technology, and more recently, because of their utility in laser technology and as thermoelectric materials. The PbX compounds are narrow direct gap semiconductors (group IV–VI), which crystallize at ambient conditions in the cubic NaCl structure. The lead salts exhibit properties which are unusual, relative to other semiconductors. Compared for example, with the usual III–V compounds, these IV–VI chalcogens present non-typical electronic and transport properties, such as higher carrier mobilities, higher dielectric constants, narrow band gaps and positive temperature coefficients (Cowley 1965; Dalven 1973; Murase 1980). These properties make them potential candidates for different technological applications. They have been used in thermoelectronic, optoelectronic or spintronic devices, especially in long wavelength imaging (Hummer *et al* 2007), infrared diode lasers (Preier 1979) and in thermophotovoltaic energy converters (Zogg *et al* 1994). The semiconductors PbS, PbSe and PbTe show a small direct gap at the L point of the Brillouin zone. In contrast to most of the semiconductors, this gap decreases with hydrostatic

pressure (Andreev 1968; Besson *et al* 1968; Martinez 1973) and increases with temperature (Tauber *et al* 1966; Andreev 1968; Martinez 1973). Although, considerable progress has been made concerning theoretical description of the structural and electronic properties of lead chalcogenides compounds, there is a real lack of knowledge of their thermal properties. An accurate description of thermal properties of solids is crucial, since, it plays a significant role in determining various material properties. To the best of our knowledge, there are no theoretical reports on the thermal behaviour of these compounds in the literature. Consequently, the primary purpose of this work is to provide some additional information to the existing data on the physical properties of lead chalcogenides using first-principles calculations. The electronic structure calculations are performed to derive the necessary parameters and the effect of spin–orbit interaction is examined. The paper is organized as follows: after a brief introduction in §1, the theoretical framework within which all the calculations have been performed is outlined in §2. In §3, we present and discuss the results of our study. A conclusion of the present investigation is given in §4.

2. Computational method

The calculations reported in this work were done with the WIEN2K programme developed by Blaha *et al* (2008).

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This programme uses the full-potential linearized augmented plane wave (FP-LAPW) method (Anderson 1975) based on density functional theory (Hohenberg and Kohn 1964; Kohn and Sham 1965). In this method, the space is divided into an interstitial region (IR) and non-overlapping (MT) spheres centred at the atomic sites. In order to treat the exchange correlation (x_c) potential, we used both the local density approximation (LDA) as parameterized by Perdew and Wang (1986) and the generalized gradient approximation (GGA) as parameterized by Perdew *et al* (1996). In the FP-LAPW method, the space is divided into an interstitial region (IR) and non-overlapping muffin-tin (MT) spheres centred at the atomic sites. In the IR region, the basis set consists of plane waves. Inside the MT spheres, the basis set is described by radial solutions of one particle Schrödinger equation (at fixed energy) and their energy derivatives multiplied by spherical harmonics. A plane wave cut-off of $k_{\max} = 8/R_{\text{MT}}$ (where R_{MT} is the smallest muffin-tin radius in the unit cell) was used. The valence wave functions inside the muffin-tin spheres are expanded up to $l_{\max} = 10$, while the charge density was Fourier expanded up to $G_{\max} = 14(\text{Ryd})^{1/2}$. The muffin-tin radii are taken to be 2.2 a.u. for Pb atom and 2 a.u. for S, Se and Te atoms. The elastic constants have been calculated using the method recently developed by Charpin and integrated in the WIEN2K package (Blaha *et al* 2008). A mesh of 47 special k -points for PbS, PbSe and PbTe compounds is taken in the irreducible wedge of the Brillouin zone for energy calculation. Both the plane wave cut-off and the number of k -points were varied to ensure total energy convergence. The study of thermal effects was done within the quasi-harmonic Debye model implemented in the Gibbs program (Blanco *et al* 2004). The quasi-harmonic Debye model allows us to obtain all thermodynamic quantities from the calculated energy-volume points. The common thermodynamic parameters that depend on temperature and pressure are used to derive other macroscopic properties.

3. Results and discussion

3.1 Structural and elastic properties

The fitting of the Murnaghan (1944) equation of state to the total energies vs unit cell volumes, yields to the equilibrium lattice parameter (a), bulk modulus (B) and the pressure derivative of the bulk modulus B' . The obtained results for all the systems are presented in table 1, along with some previous theoretical calculations and available experimental measurements. As usual, the obtained lattice parameters are larger for the GGA approach than for the LDA approach. On the contrary, the GGA values for the bulk modulus are smaller than the LDA ones. When we analyse these results, we find that there is a good

agreement between our results and the reported theoretical and experimental investigations. The spin-orbit interaction does not affect the equilibrium properties, in fact, the GGA values obtained for the lattice parameter introducing this interaction in our calculations are 6.009, 6.222 and 6.577 Å, for PbS, PbSe and PbTe compounds, respectively. Albanesi *et al* (2000), using FP-LAPW method within GGA approximation and considering spin-orbit effect, reported lattice parameters for PbSe and PbTe of 6.23 and 6.57 Å, respectively, which are close to our obtained values which confirm the above statement.

Elastic properties of a solid are important because they relate to various fundamental solid-state phenomena such as interatomic bonding, equations of state and phonon spectra. Most importantly, knowledge of elastic constants is essential for many practical applications related to the mechanical properties of a solid: load deflection, thermo-elastic stress, internal strain, sound velocities and fracture toughness. Therefore, knowledge of the elastic properties of PbS, PbSe and PbTe will be of great interest in understanding their behaviour under different constraints. A cubic crystal has three different symmetry elements (C_{11} , C_{12} and C_{44}). The calculated elastic constants for the compounds, within LDA and GGA, are given in table 1, which also contains results of previous calculations as well as the experimental data.

For these lead chalcogenides, the present results for C_{11} are in good agreement with the experimental values, when we use the GGA approximation. The C_{44} , which reflects the resistance to shear deformation, is lower than C_{11} , which is related to the unidirectional compression along the principal crystallographic directions, indicating the weak resistance to shear deformation compared to the resistance to the unidirectional compression. A more extensive comparison can be made for the bulk modulus, B , which is often reported in the literature and which we can calculate from our values of C_{11} and C_{12} . The bulk modulus calculated from the theoretical values of the elastic constants, $B = (C_{11} + 2C_{12})/3$ is also listed in table 1. The bulk modulus calculated from the total energy minimization and from the elastic constants have nearly the same value. The requirement of mechanical stability in a cubic crystal leads to the following restrictions on the elastic constants: $C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$. The elastic constants in table 1 obey these stability conditions, including the fact that C_{12} must be smaller than C_{11} . Our calculated elastic constants also obey the cubic stability conditions, meaning that $C_{12} < B < C_{11}$.

3.2 Electronic properties

We now turn our attention to the electronic properties, such as the direct energy band gaps. For this purpose, the band structures of PbS, PbSe and PbTe compounds were obtained within the GGA. We include the spin-orbit

Table 1. Lattice constant a , bulk modulus B , pressure derivative of bulk modulus B' and elastic constant parameters of PbS, PbSe and PbTe compared with the experimental data and other theoretical works.

	Present work		Experiment	Other theoretical works	
	LDA	GGA		LDA	GGA
PbS					
a (Å)	5.836	6.010	5.929 ^a , 5.936 ^{c,d} , 5.940 ^f	5.860 ^b , 5.906 ^e , 5.854 ^g	6.012 ^{b,g}
B (GPa)	63.926	53.384	52.9 ^a	64.8 ^b , 66.3 ^e , 67.3 ^g	53.3 ^b , 53.2 ^g
B'	4.253	4			
C_{11} (GPa)	169.3	123.4	124 ^a	172 ^b	136 ^b
C_{12} (GPa)	16.70	17.2	33 ^a	11.1 ^b	11.9 ^b
C_{44} (GPa)	21.3	13.1	23 ^a	20.1 ^b	20.1 ^b
$B = (C_{11} + 2C_{12})/3$	67.56	52.46			
PbSe					
a (Å)	6.030	6.210	6.117 ^a , 6.124 ^{c,d} , 6.130 ^f	6.053 ^b , 6.098 ^e , 6.046 ^g	6.196 ^b , 6.222 ^g
B (GPa)	56.692	49.187	54.1 ^a	58.3 ^b , 60.8 ^e , 59.3 ^g	49.1 ^b , 47.5 ^g
B'	3.811	3.660			
C_{11} (GPa)	165.9	110	123.7 ^a	159.5 ^b	120.8 ^b
C_{12} (GPa)	5.4	14.9	19.3 ^a	7.8 ^b	8.9 ^b
C_{44} (GPa)	17.4	21	15.9 ^a	18 ^b	17.2 ^b
$B = (C_{11} + 2C_{12})/3$	58.90	46.40			
PbTe					
a (Å)	6.367	6.560	6.462 ^{a,c} , 6.460 ^f	6.37 ^b , 6.44 ^e , 6.383 ^g	6.565 ^b , 6.57 ^g
B (GPa)	48.897	38.406	39.8 ^a	51.4 ^b , 51.7 ^e , 50.2 ^g	41.4 ^b , 38.7 ^g
B'	4.717	4.462			
C_{11} (GPa)	122	107	105.3 ^a	144.2 ^b	115.7 ^b
C_{12} (GPa)	10.7	3.2	7 ^a	1.5 ^b	4.2 ^b
C_{44} (GPa)	17.6	17.2	13.2 ^a	15.7 ^b	14.3 ^b
$B = (C_{11} + 2C_{12})/3$	47.80	37.8			

^aMadelung *et al* (1983); ^bLach-Hab *et al* (2002); ^cDalven (1973); ^dCohen and Chelikowsky (1989); ^eWei and Zunger (1997); ^fDelin *et al* (1998) and ^gZaoui *et al* (2009).

coupling in our calculations by using the second-variation method programmed in the code WIEN2K. It has a significant influence on the band structures, when heavy elements like lead (Pb) are present. The spin-orbit coupling causes splitting of p - and f -bands and as a consequence, it will influence the other electronic properties. The valence band maximum (VBM) and the conduction band minimum (CBM) occur at the L point in the Brillouin zone for these binary compounds. The calculated band gap values with both GGA and GGA-so for lead chalcogenide compounds are listed in table 2 along with the available theoretical and experimental results. The obtained GGA band gap values are slightly overestimated compared to the available theoretical results. This discrepancy could be attributed to the different functional parameters used in the calculations. The values of the calculated band gaps with spin-orbit interaction show a significant improvement over the results based on GGA compared to the experimental data. Our calculated GGA-so band gap values are comparable to those obtained by Albanesi *et al* (2000) using first principles DFT calculations. The spin-orbit interaction reduces the band gap values for the herein studied compounds, and similar results have been found for HgI₂ and SnI₂ (Ahuja *et al* 1996; Ravindra *et al*

1997). In general, GGA calculations tend to underestimate the main energy gap of semiconductors by 40–50%. In fact, the energy gaps are systematically underestimated in *ab initio* calculations and that is an intrinsic feature of density functional theory, DFT being a ground-state theory not suitable for describing excited-state properties, such as the energy gap. However, it is widely accepted that GGA (LDA) electronic band structures are qualitatively in good agreement with experiments as far as ordering of energy levels and shape of bands.

3.3 Thermal properties

To investigate the thermal properties of PbS, PbSe and PbTe compounds, we apply the quasi-harmonic Debye model (Blanco *et al* 2004), in which the non-equilibrium Gibbs function $G^*(V; P, T)$ can be written as

$$G^*(V; P, T) = E(V) + PV + A_{\text{vib}}[\theta(V); T], \quad (1)$$

where $E(V)$ is the total energy per unit cell, PV the constant hydrostatic pressure condition, $\theta(V)$ the Debye temperature and A_{vib} the vibrational term, which can be

Table 2. Energy band gaps (L → L) in (eV) of PbS, PbSe and PbTe compounds.

	Present work		Experiment	Other works
	GGA-so	GGA		
PbS	0.169	0.496	0.290 ^a	0.380 ^b , 0.448 ^c , 0.074 ^d
PbSe	0.072	0.425	0.17 ^a	0.340 ^b , 0.318 ^c , 0.022 ^d , 0.121 ^f
PbTe	0.182	0.833	0.19 ^e	0.737 ^b , 0.643 ^c , 0.16 ^f

^aGupta and Ravindra (1980); ^bLach-Hab *et al* (2002); ^cZaoui *et al* (2009); ^dZhang *et al* (2009); ^eDalven (1973); ^fAlbanesi *et al* (2000).

written using the Debye model of the phonon density of states as (Blanco *et al* 1996; Flórez *et al* 2002)

$$A_{\text{vib}}(\theta; T) = nk_{\text{B}}T \left[\frac{9\theta}{8T} + 3 \ln(1 - e^{-\theta/T}) - D(\theta/T) \right], \quad (2)$$

where $D(\theta/T)$ represents the Debye integral, n the number of atoms per formula unit.

For an isotropic solid, θ is expressed as (Blanco *et al* 1996)

$$\theta_{\text{D}} = \frac{\hbar}{k_{\text{B}}} [6\pi^2 V^{1/2} n]^{1/3} f(\sigma) \sqrt{\frac{B_{\text{s}}}{M}}, \quad (3)$$

M being the molecular mass per unit cell and B_{s} the adiabatic bulk modulus, approximated by the static compressibility (Blanco *et al* 2004)

$$B_{\text{s}} \cong B(V) = V \left\{ \frac{d^2 E(V)}{dV^2} \right\}, \quad (4)$$

$f(\sigma)$ is given by (Francisco *et al* 2001; Flórez *et al* 2002)

$$f(\sigma) = \left\{ 3 \left[2 \left(\frac{21 + \sigma}{31 - 2\sigma} \right)^{3/2} + \left(\frac{11 + \sigma}{31 - \sigma} \right)^{3/2} \right]^{-1} \right\}^{1/3}. \quad (5)$$

The Poisson ratio σ is taken as 0.25 (Poirier 2000). Therefore, the non-equilibrium Gibbs function $G^*(V; P, T)$ as a function of $(V; P, T)$ can be minimized with respect to volume V

$$\left[\frac{\partial G^*(V; P, T)}{\partial V} \right]_{P, T} = 0. \quad (6)$$

By solving (10), one can get the thermal equation of state (EOS), $V(P, T)$. The isothermal bulk modulus, B_{T} , the heat capacity, C_{V} and the thermal expansion coefficient, α are given by (Blanco *et al* 1996)

$$B_{\text{T}}(P, V) = V \left(\frac{\delta^2 G^*(V; P, T)}{\delta V^2} \right)_{P, T}, \quad (7)$$

$$C_{\text{V}} = 3nk_{\text{B}} \left[4D(\theta/T) - \frac{3\theta/T}{e^{\theta/T} - 1} \right], \quad (8)$$

$$\alpha = \frac{\gamma C_{\text{V}}}{B_{\text{T}} V}, \quad (9)$$

where γ is the Gruneisen parameter, which is defined as

$$\gamma = - \frac{d \ln \theta(V)}{d \ln V}. \quad (10)$$

Through the quasi-harmonic Debye model, one could calculate the thermodynamic quantities of any temperature and pressure of compounds from the calculated $E-V$ data at $T = 0$ and $P = 0$. By using the method above, we can successfully obtain the thermal properties of PbS, PbSe and PbTe compounds. The thermal properties are determined in the temperature range from 0 to 1000 K, where the quasi-harmonic model remains fully valid. The pressure effect is studied in the 0–40 GPa range.

The effect of the spin–orbit interaction is found to be negligible in determining the thermal properties since, the calculations of these properties use $E-V$ data which are not influenced by spin–orbit coupling. The temperature effects at several pressures on the lattice parameters and bulk modulus of the compounds are shown in figure 1. The lattice parameters increase with increasing temperature for a given pressure, but the rate of increase is very moderate, especially at high pressures. At a given temperature, the lattice parameters decrease with increasing pressure. The effect of increasing temperature and decreasing pressure on the lattice parameter are identical. The bulk modulus is related to interatomic potentials because it can be obtained by the second derivatives of the internal energy with respect to strains. The temperature dependence of bulk modulus partially reflects the anharmonic interactions because for a pure harmonic crystal, the bulk modulus would be independent of temperature. At 0 K ($P = 0$), our calculated bulk modulus for PbS, PbSe and PbTe are 47.69, 46.76 and 34.04 GPa, respectively, which are in good agreement with the values obtained by the WIEN2K code. From figure 1, we can see that when $T < 100$ K, B is nearly a constant, which indicates that the lattice parameter nearly keeps constant. When $T > 100$ K, the bulk modulus decreases as T increases. This indicates that the unit cell volume varies significantly as the temperature increases. The bulk modulus increases with pressure at a given temperature,

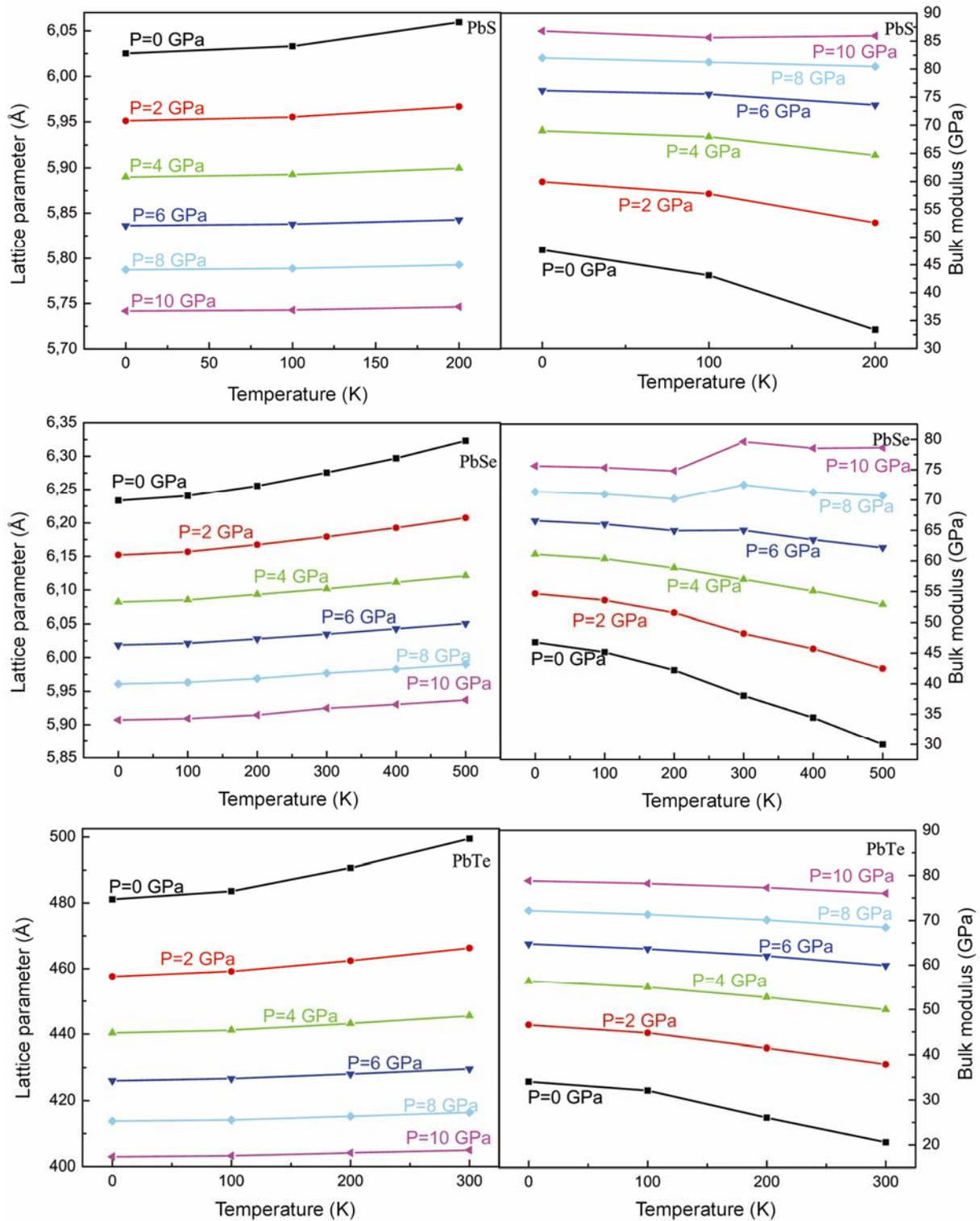


Figure 1. Variation of lattice constant and bulk modulus of PbS, PbSe and PbTe as a function of temperature at several pressures.

which indicates that the hardness of these compounds decreases with the increasing temperature and increases with applied pressure.

The variation of the heat capacities C_v and C_p with temperature in the case of PbSe compound are shown in

figures 2 and 3. Two famous limiting cases are correctly predicted by the standard elastic continuum theory (Debye 1912). At high temperature, the constant volume heat capacity, C_v tends to the Dulong–Petit limit $50 \text{ J mol}^{-1} \text{ K}^{-1}$, whereas C_p follows a linear increase. At

sufficiently low temperature, C_v and C_p are proportional to T^3 . However, at intermediate temperatures, they were governed by the details of vibrations of the atoms and for a long time could only be determined from experiments. For a given temperature, C_v and C_p decrease with increasing pressure. From figures 2 and 3, one can see that the influence of temperature on heat capacity is much more significant than that of pressure.

In figure 4, we present the effect of temperature and pressure on the volume expansion coefficient, α for PbSe and PbTe compounds. It is shown that at a given pressure, α increases sharply with the increase of temperature up to about 100 K and gradually approaches a linear increase at higher temperatures. It can be seen that

thermal expansion coefficient, α decreases dramatically with the increase in pressure. As the pressure increases, the increase of α with temperature becomes smaller, especially at high temperatures.

The calculated properties at different temperatures are very sensitive to the vibrational effects. In the quasi-harmonic Debye model, the Debye temperature is a key parameter. Finally, the pressure dependence of the Debye temperature is calculated and plotted in figure 5. It is found that the Debye temperature, θ_D increases with applied pressure, especially, at low pressure region. Compared with figure 1, one can see that the compressibility increase leads to Debye temperature decrease. This result is in accordance with the fact that Debye temperature is proportional to the bulk modulus and that a hard material exhibits a high Debye temperature. It is also

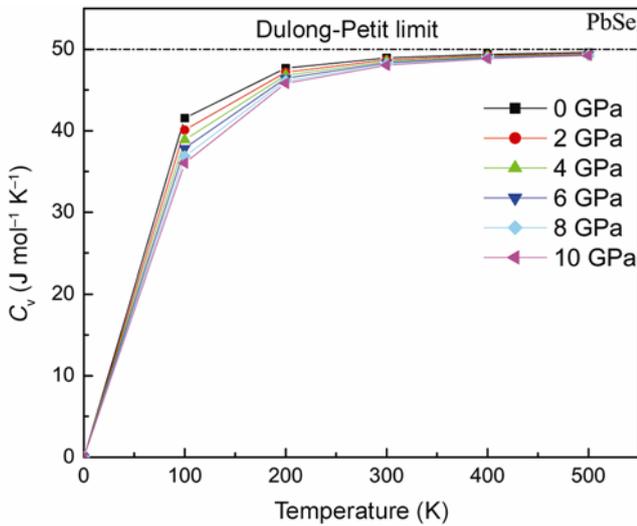


Figure 2. Variation of heat capacity, C_v of PbSe as a function of temperature at several pressures.

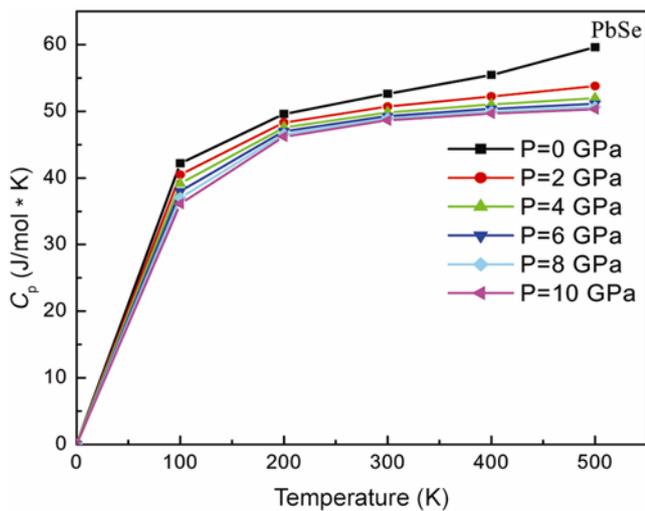


Figure 3. Variation of heat capacity, C_p of PbSe as a function of temperature at several pressures.

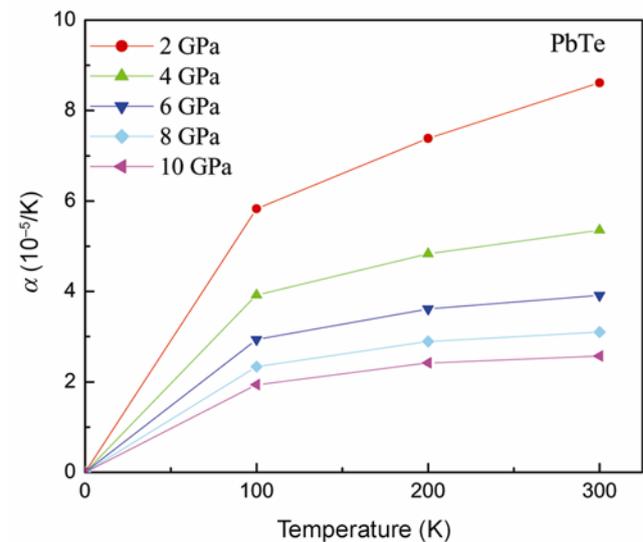
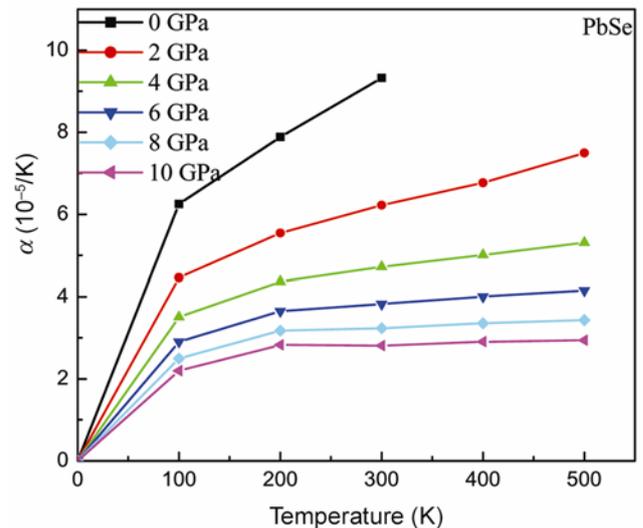


Figure 4. Variation of volume expansion coefficient, α of PbSe and PbTe as a function of temperature at several pressures.

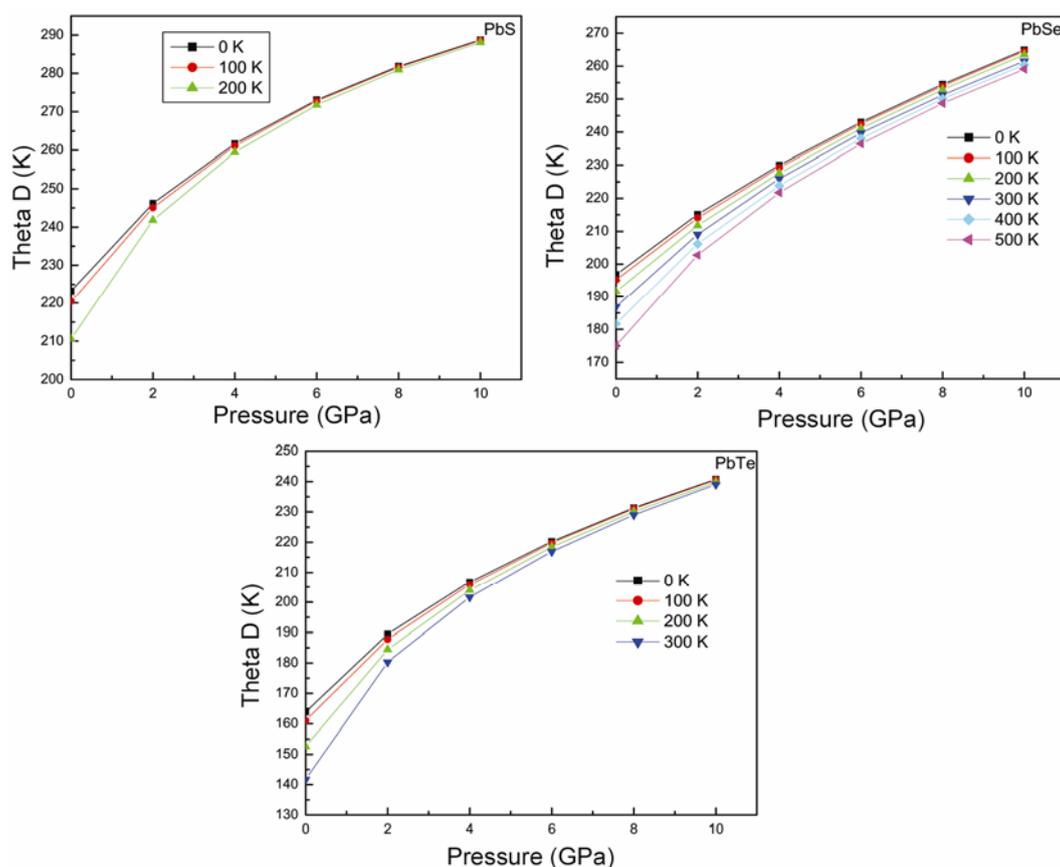


Figure 5. Variation of Debye temperature of PbS, PbSe and PbTe as a function of pressure at several temperatures.

shown that when the pressure is constant, the Debye temperature decreases with temperature.

4. Conclusions

In summary, the present work reports a theoretical study of structural, electronic and thermal properties for lead chalcogenides PbS, PbSe and PbTe by using the FP-LAPW method within DFT. The main results can be summarized as follows:

- (I) The calculated lattice constants and bulk modulus of the compounds are in good agreement with the experimental data and theoretical results.
- (II) Our results regarding the band gap of the binary compounds are found to be in reasonable agreement with the theoretical data.
- (III) Through the quasi-harmonic Debye model, the dependence of the lattice parameter, bulk modulus, heat capacity, volume expansion coefficient and Debye temperature, on temperature and pressure have been obtained successfully.

The present study, especially, thermal properties would be helpful for future experimental and theoretical investigations.

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