High Pressure Study of Structural and Electronic Properties of PbSe

P. Bhambhani, 1 K. Kabra, 2 B. K. Sharma, 3 and G. Sharma 2

1 Department of Physics, Banasthali University, Banasthali 304022, India
2 Department of Pure & Applied Physics, University of Kota, Kota 324010, India
3 Faculty of Sciences, Manipal University Jaipur, Jaipur 303007, India

Correspondence should be addressed to G. Sharma; gspphysics@gmail.com

Received 30 August 2014; Revised 22 November 2014; Accepted 1 December 2014; Published 30 December 2014

High pressure structural phase transition and electronic properties have been investigated using the linear combination of atomic orbitals (LCAO) method with two exchange-correlation approximations, the generalized gradient approximation (GGA) and local density approximation (LDA). The present study shows phase transitions from B1 to B27 and B27 to B2 at 6.24 GPa and 16.39 GPa, respectively. Lattice constant, bulk modulus, and energy gap of pressure-induced PbSe are found to be in good agreement with previous theoretical and experimental results. Variation of electronic band structure with pressure shows direct band gap along L point of the Brillouin zone.

1. Introduction

Systematic studies of IV–VI semiconductor compounds on theoretical as well as experimental background have given overwhelming properties which not only are important for the scientific inquest but have wide scale technological applications [1–9]. These compounds possess intriguing array of narrow energy gap, high carrier mobilities, high dielectric constant, positive temperature coefficient of the band gap and negative pressure dependence of the band gap, and high anisotropy, which are the basic requirements for the applications in the branch of the thermoelectronics, optoelectronics, and spintronics [10–15].

Such fascinating properties of the IV–VI semiconductor compounds become a subject of extensive research on the lead chalcogenides PbX (X = S, Se, Te). On account of narrow forbidden gap of PbSe ~ 0.26 eV (300 K), anomalous order of band gap, and low thermal conductivity, it appeared to be a potential candidate for the technological applications in the field of thermoelectric devices [10, 16–18]. Further, low transition pressure and narrow energy gap of the intermediate phase of this compound make it a suitable candidate for the fabrication of other electronic devices [18, 19]. The anomalous properties of PbSe and IV–VI semiconductor compounds as compared to III–V and II–VI semiconductors are due to interaction of Pb s-electron valence bands with the Se p-electrons valence band [12].

Excellent properties of this material were aggravated to investigate pressure-induced structural and electronic properties. In the last few decades, a number of investigations on its pressure-induced phase transition and structural properties have been reported; see, for example, [9–12, 18–23]. At ambient conditions, PbSe crystallizes in sixfold-coordinated rock-salt type B1 structure, with space group Fm3m. At pressure between 3 and 5 GPa, it transforms from B1 phase to an orthorhombic intermediate phase [11]. The intermediate phase may be GeS (B16, Pbnm), FeB (B27, Pnma), and CrB/TI1 (B33, Cmcm) [19, 21, 24, 25]. Further, with increasing pressure between 15 and 16 GPa, structural phase transition takes place from the orthorhombic phase to eightfold coordinated CsCl B2-type phase (space group Pm3m) [8–11, 19, 21]. The phase transition from low to high pressure, that is, from intermediate to B2-type phase, is reported as semiconducting to metallic transition [II, 25–27]. Chattopadhyay et al. [8, 9] from X-ray diffraction studies using synchrotron radiation reported TII, B33-type structure for the intermediate phase of
PbSe, while Ovsyannikov et al. reported it to be of GeS-type [22]. This intermediate phase has also been experimentally proposed to be orthorhombic Pnma structure [28]. The theoretical investigations on the intermediate phase of PbSe have less attention in the literature. Thus, the present paper deals with the pressure-induced structural phase transition and electronic properties of PbSe at different pressures using LCAO method.

2. Computational Details

Quantum mechanical periodic LCAO calculations for the ground state total crystal energy are performed using the computer code CRYS\textsc{tal}06 [29]. There are two fundamental schemes to compute the electronic structure and related properties of solids: one is the Hartee-Fock (HF) approximation and the other is the DFT [30, 31]. In HF, the exchange potential is included exactly and additional terms describe the correlation effects approximately but, in the DFT, both exchange and correlation effects are included. To gain the quantitative validity of results, we have used both the GGA and LDA approximations. The Kohn-Sham Hamiltonian for GGA is constructed by considering the exchange and correlation scheme of Becke [32] and Perdew-Burke-Ernzerhof (PBE) [33], respectively, while LDA approximation is based on Becke [32] and von Barth-Hedin (VBH) [34] schemes, respectively. The basis sets for the S were taken from [35] and due to nonavailability of all electron basis sets of Pb, only its valence part was considered in the present computations [36]. The self-consistent calculations are performed using 29, 35, and 343 k-points in the irreducible Brillouin zone (BZ) for B1, B2, and B27 phases, respectively, with sufficient tolerances. The level of numerical approximation in evaluating the Coulomb and exchange series appearing in the SCF equations for periodic systems is controlled by five tolerances [29]. In the present calculations, tolerances of the order of $10^{-6}$, $10^{-5}$, $10^{-4}$, $10^{-3}$, and $10^{-10}$ were considered. To achieve self-consistency, 70% mixing of successive cycles is considered and self-consistency is achieved within 10, 12, and 18 cycles for B1, B2, and B27 phases, respectively.

The cohesive energy [37] from the Compton profile data can be derived as follows:

\[
E_{\text{coh}} = \int_{0}^{\infty} p_{z}^{2} \left[ J_{s}(p_{z}) - J_{s,f}(p_{z}) \right] dp_{z},
\]

where \(p_{z}\) is component of electron momentum along the \(z\)-axis and \(J_{s}\) and \(J_{s,f}\) represent Compton profiles of solid and free atoms, respectively. The solid Compton profile \((J_{s})\) values are calculated from DFT-LCAO method and the free-atom Compton profile \((J_{s,f})\) values are taken from Biggs et al. [38–40].

3. Results and Discussion

3.1. Phase Transition and Structural Parameters. The structural parameters were theoretically evaluated first by calculating the total lattice energies over a set of different volumes around the equilibrium values and then were fitted to the third order Birch-Murnaghan equation of state (EOS) using the following relations:

\[
E(V) = E_{0} + \frac{9V_{0}B_{0}}{16} \left\{ \left[ \left( \frac{V_{0}}{V} \right)^{2/3} - 1 \right]^{3} B'_{0} \\
+ \left[ \left( \frac{V_{0}}{V} \right)^{2/3} - 1 \right]^{2} \left[ 6 - 4 \left( \frac{V_{0}}{V} \right)^{2/3} \right] \right\},
\]

where \(E_{0}\) is minimum energy, \(V_{0}\) is corresponding volume, and \(B_{0}\) is the bulk modulus at zero pressure and \(B'_{0} = dB_{0}/dP\). The third order Birch-Murnaghan isothermal equation of state [41, 42] relating pressure and volume is given by

\[
P(V) = \frac{3B_{0}}{2} \left[ \left( \frac{V_{0}}{V} \right)^{7/3} - \left( \frac{V_{0}}{V} \right)^{5/3} \right] \\
\times \left\{ 1 + \frac{3}{4} \left( B'_{0} - 4 \right) \left[ \left( \frac{V_{0}}{V} \right)^{2/3} - 1 \right] \right\}.
\]

Calculations were performed in both GGA and LDA frameworks and the respective parameters, that is, lattice constant \((a)\), bulk modulus \((B_{0})\), and pressure derivative of bulk modulus \((B'_{0})\) for B1, B27, and B2 phases of PbSe, are given in Table 1. As per the device application, high bulk modulus and its pressure derivative are essential parameters for photovoltaic applications in optoelectronic devices [43, 44]. The bulk modulus also defines resistance to change in volume against any mechanical deformation [44]. Therefore, we computed the values of bulk modulus and its derivative using Birch-Murnaghan EOS and summarized them in Table 1. The value of bulk modulus obtained from Birch-Murnaghan EOS agrees well with the value reported by Rached et al. [45]. This variation of \(B_{0}\) in accordance with the theory of Cohen [46] who obtained an empirical expression for the bulk modulus based on the nearest-neighbor distance. As seen from Table 1, the pressure derivative of bulk modulus \((B'_{0})\) is almost the same for all the three phases with average value of 4.0. On comparing the structural parameters obtained from two different schemes, that is, GGA and LDA, we observed that lattice parameter obtained from LDA approach is larger than GGA while the bulk modulus obtained from GGA is higher as compared to the one obtained from LDA. Figures 1(a) and 1(b) show the variation of the total energy versus volume computed for PbSe in B1, B27, and B2 phases obtained from both GGA and LDA approximations together with EOS data. As evident from Figures 1(a) and 1(b), the energy state of B1 phase is lower than that of the other two phases. This phase could be regarded as a stable phase of PbSe system [26].

In order to investigate the phase transition pressure \((P_{t})\) for intermediate and CsCl-type phase, we computed variation in enthalpy with pressure using GGA and LDA approximations considering certain constraint of temperature for all the three phases of PbSe compound. Since a stable phase
### Table 1: Calculated equilibrium lattice parameter \(a\), bulk modulus \(B_0\), pressure derivatives of bulk modulus \(B'_0\), and cohesive energy \(E_{coh}\) for PbSe.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Present calculations</th>
<th>Experimental results</th>
<th>Other calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_0) (Å)</td>
<td>6.08 GGA 6.17 LDA</td>
<td>6.117 [29], 6.133 [9], 6.124 [56], 6.117 [57]</td>
<td>6.211 [10], 6.098 [23], 6.226 [12], 6.214 [12]</td>
</tr>
<tr>
<td>(B_0) (GPa)</td>
<td>66.96 GGA 64.72 LDA</td>
<td>28.8 [8], 54.1 [56], 54.1 [58]</td>
<td>48.27 [10], 60.8 [23], 44.5 [12], 49.5 [12], 66.0 [42]</td>
</tr>
<tr>
<td>(B'_0)</td>
<td>4 GGA 3.7 LDA</td>
<td>4.1 [8]</td>
<td>4.35 [10], 4.56 [23], 3.64 [12], 3.8 [12]</td>
</tr>
<tr>
<td>(E_{coh}) (eV)</td>
<td>6.95 GGA</td>
<td>—</td>
<td>7.39 [44]</td>
</tr>
</tbody>
</table>

#### Orthorhombic Pnma phase (B27, FeB type)

| \(a_0\) (Å) | \(a = 11.38\) GGA \(a = 11.48\) LDA |
| \(b_0\) (Å) | \(b = 4.374\) GGA \(b = 4.474\) LDA |
| \(c_0\) (Å) | \(c = 4.259\) GGA \(c = 4.359\) LDA |
| \(B_0\) (GPa) | 68.94 GGA 65.5 LDA |
| \(B'_0\) | 4.9 GGA 4.9 LDA |

#### CsCl-type, B2 phase

| \(a_0\) (Å) | 3.709 GGA 3.74 LDA |
| \(B_0\) (GPa) | 70 GGA 64.72 LDA |
| \(B'_0\) | 3.9 GGA 3.7 LDA |

**Figure 1:** The calculated energy versus volume for B1, B27, and B2 phases of PbSe: using the PBE (a) and VBH (b) correlation functional. The scattered points show calculated energies and the solid lines show the fitted \(E(V)\) curves according to Birch-Murnaghan equation of state (EOS).

of any crystal is coupled with its minimum free energy, we have constrained the temperature to zero in order to obtain a thermodynamically stable phase which has lowest enthalpy, \(H = E + PV\), under given pressure [26, 47]. At \(P\), enthalpy of the two consecutive phases is equal [16, 48]. Difference in enthalpy of high pressure phases (B27 and B2) and that in stable phase (B1) for both GGA and LDA approximations are plotted in Figures 2(a) and 2(b), respectively. From GGA approach, the transition from the stable B1 phase to Pnma intermediate phase is predicted to be 6.24 GPa and the transition from intermediate to CsCl-type phase is 16.39 GPa, while the \(P\) evaluated from LDA approach is 7.97 GPa for transition from NaCl phase to an orthorhombic Pnma (B27, FeB type) phase and 18.25 GPa for transition from Pnma (B27) phase to the CsCl-type (B2) phase.

These investigated transition pressures are reported in Table 2. Since the transition pressures derived from GGA approximation are closer to the experimental results as compared with the transition pressures derived from LDA approximation, for this reason further investigation is done...
Figure 2: Enthalpy versus pressure calculated from first-principles total energy for the B1, B27, and B2 structures of PbSe using the PBE (a) and VBH (b) correlation functional.

Table 2: Transition pressure (in GPa) for PbSe.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Present GGA</th>
<th>LDA</th>
<th>Experimental</th>
<th>Other calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1 → B27</td>
<td>6.24</td>
<td>7.97</td>
<td>4.5 [9], 4.5</td>
<td>7.45 [10], 10.0</td>
</tr>
<tr>
<td>B27 → B2</td>
<td>16.39</td>
<td>18.25</td>
<td>16.0 [9], 16.0</td>
<td>18.76 [10], 20.0</td>
</tr>
</tbody>
</table>

with GGA approximation. The recent investigations of Li et al. [49] on the pressure-induced structure transitions of PbSe using density functional theory are in agreement with the present data. The calculation of cohesive energy from the experimental Compton profile is a difficult task due to weighting of $p^2$ in the high momentum region [50, 51]. Therefore, we have used the DFT-PBE profile for the calculation of cohesive energy of PbSe. The calculated cohesive energy along with available data are given in Table 1. From this table, it is evident that our calculated value of $E_{coh}$ shows fairly good agreement with earlier data [44].

The pressure versus volume data for B1, B27, and B2 phases were computed, using the calculated values of $B_0$ and $B'_0$ using (3), and plotted in Figure 3. The curve shows that at $P_t$ there is sudden collapse in volume.

3.2. Pressure Dependent Electronic Properties. Knowledge of energy band gaps at different pressures is important to provide the information about their potential efficiency in fabricating various optoelectronic and thermo electronic devices. In order to compute the energy band gap at different pressures, the equilibrium lattice constants are used and different symmetry points like $W (0.5, 0.25, 0.75), L (0.5, 0.5, 0.5), \Gamma (0.0, 0.0, 0.0), X (0.5, 0.0, 0.0), W (0.5, 0.25, 0.75),$ and $K (0.375, 0.375, 0.75)$ are considered in the BZ. The energy band gaps of PbSe in B1 phase at different hydrostatics pressures are reported in Table 3.
Table 3: Band gap of PbSe in B1 phase at different pressures.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Present calculation</th>
<th>Other calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>−4</td>
<td>0.338</td>
<td>—</td>
</tr>
<tr>
<td>−2</td>
<td>0.252</td>
<td>—</td>
</tr>
<tr>
<td>0</td>
<td>0.185</td>
<td>0.21 [13], 0.15 [12], 0.16 [52]</td>
</tr>
<tr>
<td>2</td>
<td>0.118</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>—</td>
</tr>
</tbody>
</table>

Figure 4: Energy band structure of PbSe in B1 phase.

As seen from Figure 4, the valence band maximum and the conduction band minimum lie at $L$ point of the BZ. The occupied 6s-band of Pb atom lies close to the valence band of Se atom which is of p-type. Since the symmetry of Pb 6s band is the same as that of the highest valence band at the $L$ point, there exists strong level repulsion which determines the feature of band structure and gives direct band gap along $L$ point of the BZ at all considered pressures [12].

Since the band structures at all considered pressures are similar with only a small change around the Fermi level, it is desirable to present band structure of B1 phase only at zero pressure (Figure 4). The variation of band gap with pressure for B1 phase is plotted in Figure 5. It shows that with increasing pressure minima of conduction band come closer to the Fermi energy level and thus reduce the band gap. A similar feature of energy gap with pressure is reported by Nabi et al. [52]. A number of groups have observed the zero pressure band gap of PbSe $\sim$0.26–0.28 eV computationally and $\sim$0.27–0.31 eV at ambient temperature, experimentally [53–55]. Thus, the present zero pressure value, that is, 0.185 eV of PbSe, is lower than these values.

4. Conclusions

The pressure-induced phase transition and electronic properties of PbSe investigated using LCAO method were found to be in good agreement with previous theoretical and experimental results. The intermediate phase of PbSe between B1 and B2 phases is found to be B27 phase. The variation of energy band gap of PbSe under pressure is reported and it is found that, unlike II–VI and III–V compounds, PbSe shows direct band gap at $L$ point of BZ.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

This work is financially supported by the CSIR, New Delhi, through the major Research Project no. 03 (1205)/12EMR-II, dated 12 April, 2012.

References


