First-principles study of B1 to B2 phase transition in PbS

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Abstract. The high pressure structural phase transition in PbS has been studied by means of first-principles total energy calculations which are based on linear combination of atomic orbitals (LCAO) method within local density approximation (LDA). In the present study, the exchange scheme of Becke and correlation functional of von-Barth-Hedin (VBH) are employed. It is observed that more stable phase for PbS is NaCl type (B1) and PbS transforms to the CsCl type (B2) structure under high pressure (22.8 GPa). The calculated value of transition pressure (P\(_t\)) from B1 to B2 structure is found in good agreement with the earlier experimental and theoretical investigations.

1. Introduction

Lead sulfide (PbS) which is known as lead salt has attracted considerable attention because of its direct narrow band gap (0.41 eV), high carrier mobility, high dielectric constant and positive (negative) temperature (pressure) coefficient [1,2]. PbS is very promising material for technological applications in the field of infrared (IR) devices, diode lasers and thermo-photovoltaic energy converters [3]. Knowledge of the electronic and structural properties of PbS under pressure is important in the semiconductor device industry. In the last few decades, structural phase transition in PbS under high pressure attracts new interest. Under normal conditions, PbS crystallizes in the rocksalt (RS) type (B1) structure. Structural phase transformations in PbS compound are reported by Bridgman [4] in 1940. Chattapadhyay et al. [5] have also made high pressure X-ray diffraction study on the structure phase transitions in PbS with synchrotron radiation and found that PbS undergoes structural phase transition from the NaCl type phase to the CsCl type phase at about 21.5 GPa. Knorr et al. [6] have performed an experimental study of the high pressure phase transition in PbS. High pressure structural phase transition in PbS has been reported by R. Ahuja [7] by using full potential linear muffin-tin-orbital (FP-LMTO) method within the generalized gradient approximation (GGA). Recently, using the full potential linearized augmented plane wave (FP-LAPW) method based on density functional theory (DFT) within GGA, high pressure phase transition of PbS has been investigated by Bencherif et al. [8].

2. Method of calculation

The present calculations are performed in the framework of density functional theory (DFT). We have employed the linear combination of atomic orbitals (LCAO) method as implemented in the CRYSTAL06 code [9]. The exchange scheme of Becke [10] and correlation functional of von Barth-Hedin (VBH) [11] are considered in the computation. In the present calculations, the basis sets for Pb and S have been taken from http:// www.crystal.unito.it. Following the standard truncation criteria of the code, the calculations are carried out considering 29 \(\vec{k}\) points in the irreducible wedge of the first Brillouin zone.
Brillouin zone, taking advantage of the symmetry. To achieve self-consistency 55% mixing of successive cycles was considered and the self-consistency was achieved within 8 cycles. Using this method, the total energy as a function of cell volume for the B1 and B2 structure of PbS are computed.

3. Results and Discussion

We have calculated the total energy of PbS in NaCl and CsCl phases as a function of cell volume (figure 1). The energy states of B1 phase is below the B2 phase indicating the stability of B1 phase. In figure 1, the curves represent our computed values and the symbols represent fitting results to the Birch-Murnaghan equation of states [12,13]. The Birch-Murnaghan equation of states is given as follows

\[
E(V) = E_0 + \frac{9V_0B_0}{16} \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] B_0^{2/3} \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^{7/2} \left( 6 - 4 \left( \frac{V_0}{V} \right)^{2/3} \right) \]

(3.1)

where \(E_0\) is minimum energy, \(V_0\) is corresponding volume, \(B_0\) is the bulk modulus at zero pressure and \(B_0' = dB_0/dP\). The equilibrium lattice constant \(a_0\), bulk modulus \(B_0\) and pressure derivative of the bulk modulus \(B_0'\) are computed for both phases at zero pressure by fitting the above equation. These results are summarized in table 1.

In figure 2, enthalpy of PbS in B1 and B2 phases are plotted as a function of pressure. The transition from B1 phase to B2 phase occurs at about 22.8 GPa. The transition pressure is obtained by plotting the difference curve of enthalpy (\(\Delta H\)) in terms of pressure (P). At transition pressure (22.8 GPa) the difference becomes zero. Theoretical and experimental transition pressures are listed in table 2.

![Figure 1](image1.png)

**Figure 1.** The total energy of PbS in NaCl and CsCl phases are plotted as a function of cell volume.

![Figure 2](image2.png)

**Figure 2.** Enthalpy of PbS in NaCl and CsCl phases are plotted as a function of pressure.
### Table 1. Structural properties of PbS.

| structures | a(Å) | B₀ | B₀' |
|------------|------|----|-----|
| B1         |      |    |     |
| Present    | 5.99 | 64.063 | 3.8 |
| Experimental | 5.929<sup>a</sup> | 52.9<sup>a</sup> |   |
|            | 5.936<sup>b</sup> | 62.8<sup>b</sup> |   |
|            | 5.940<sup>f</sup> |   |   |
| Other calculations | 6.000<sup>c</sup> | 54.63<sup>c</sup> | 4.10<sup>c</sup> |
|            | 5.906<sup>d</sup> | 66.3<sup>d</sup> | 4.38<sup>d</sup> |
|            | 6.012<sup>e</sup> | 52.0<sup>e</sup> |   |
|            | 6.006<sup>f</sup> | 56.0<sup>f</sup> | 3.6<sup>f</sup> |
| B2         |      |    |     |
| Present    | 3.649 | 70.714 | 3.8 |
| Experimental | 3.289<sup>g</sup> |   |   |
| Other calculations |   | 59.0<sup>f</sup> | 3.6<sup>f</sup> |

<sup>a</sup> Reference [14]  
<sup>b</sup> Reference [17]  
<sup>c</sup> Reference [8]  
<sup>d</sup> Reference [16]  
<sup>e</sup> Reference [15]  
<sup>g</sup> Reference [7]  
<sup>f</sup> Reference [5]

### Table 2. Phase transition pressure P<sub>t</sub>(GPa) for PbS

|          | P<sub>t</sub> (GPa) |
|----------|--------------------|
| Present  | 22.8               |
| Experimental | 21.5<sup>a</sup> | 21.5<sup>b</sup> |
| Other calculations | 25.30<sup>c</sup> | 25.0<sup>d</sup> |

<sup>a</sup> Reference [5]  
<sup>b</sup> Reference [14]  
<sup>c</sup> Reference [8]  
<sup>d</sup> Reference [7]
4. Conclusions

We have performed the study of structural properties (transition pressure, equilibrium lattice constants and bulk modulus) of PbS using LCAO method within LDA. The total energy of PbS in NaCl and CsCl phases as a function of cell volume are used to estimate the structural parameters. The computed values are found in good agreement with the earlier experimental and theoretical data.

5. References

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