

## Electronic and elastic properties of alkali-metal sulphides-Li<sub>2</sub>S and Na<sub>2</sub>S

Premlata Pandit\*, Bipul Rakshit & Sankar P Sanyal

Computational Research Laboratory, Department of Physics, Barkatullah University, Bhopal 462 026

\*E-mail: lataprem29@gmail.com

Received 15 December 2008; revised 16 July 2009; accepted 26 August 2009

From first-principles, the electronic and elastic properties of alkali-metal sulphides (Li<sub>2</sub>S, Na<sub>2</sub>S), with emphasis on the plane-wave pseudopotential method and the inclusion of the non-linear core correction for exchange and correlation have been investigated. At ambient condition, these compounds are found to crystallize in cubic anti-fluorite structure. This method is found to describe the properties of these materials rather well. In most of the cases, obtained ground state properties are in good agreement with experimental and theoretical results. From the electronic structure calculations, we found that Li<sub>2</sub>S is indirect band gap semiconductor whereas Na<sub>2</sub>S is direct band gap semiconductor within local density approximation (LDA).

**Keywords:** Plane wave pseudopotential, Alkali-metal sulphides, Semiconductor, Electronic properties, Elastic properties

### 1 Introduction

The alkali-metal sulphides are found to crystallize in the cubic anti-fluorite (anti-CaF<sub>2</sub>-type) structure (Space group no. 225) in ambient condition<sup>1</sup>. This structure is antimorphous to the fluorites (CaF<sub>2</sub>). The cations and anion sublattices of these crystals have different symmetry. In anti-fluorite structure, the small alkali-metal Li<sup>+</sup>, Na<sup>+</sup> ions occupy the tetrahedral (F<sup>-</sup>) sites in fluorites and the larger S<sup>2-</sup> centres occupy the eight-coordinated (Ca<sup>2+</sup>) sites. The sulphides of alkali metal are characterized by their high ionic conductivity and they exhibit large electronic band gap. They have attracted considerable attention due to their technological usefulness and also by their other remarkable and interesting physical properties. These compounds have been used in many technological applications such as solid-state batteries, fuel cells or solid-state gas detectors. Beside the structural aspects, the study of their elastic properties is also important as they are closely related to several fundamental properties such as inter atomic forces, equation of states, phonon spectra, specific heat etc. Due to the development of *ab initio* computer simulation methods, in recent years, it has become possible to predict such crystal properties fairly accurately.

These compounds have been a subject of many experimental and theoretical investigations, focusing on the structural phase transformation<sup>2-5</sup> and electronic properties<sup>6-8</sup> for more than a decade. The elastic constants of Li<sub>2</sub>S and Na<sub>2</sub>S have been determined experimentally by elastic neutron scattering at low temperature<sup>9,10</sup>. Lichanot *et al.*<sup>11</sup> and

Buehrer *et al.*<sup>12</sup> have calculated the elastic constant for Li<sub>2</sub>S and Na<sub>2</sub>S compounds by using the linear combination of atomic orbital (LCAO) method and the shell model, respectively. Recently, Khachai *et al.*<sup>13</sup> have studied the elastic constants and their pressure derivatives of alkali metal sulphide crystals using first principles full potential APW plus local orbital (FP-APW-lo) method with in local density (LDA) and generalized gradient approximations (GGA). These researchers predicted significantly smaller values of  $C_{11}$  and  $C_{12}$  in the case of Na<sub>2</sub>S when compared with experiment. The electronic band structure of these compounds at ambient condition was discussed by Zhuravlev *et al.*<sup>6</sup> using the self-consistent pseudopotential method. The linear combinations of atomic orbital by Hartree-Fock (LCAO-HF) studies<sup>7</sup> were undertaken to determine the valence-band width and density of states for Li<sub>2</sub>S and Na<sub>2</sub>S. The first principles study of electronic structure and ground state properties of these compounds have been investigated by Eithiraj *et al.*<sup>8</sup>.

In the present paper, we have reported the ground state properties such as equilibrium lattice parameter, static bulk modulus, first order pressure derivative of the bulk modulus and the elastic constants of Li<sub>2</sub>S and Na<sub>2</sub>S in anti-fluorite structure calculated using *ab-initio* density-functional theory as incorporated in the plane wave self-consistent field method and compared with corresponding experimental and theoretical data. The electronic structure, density of states and projected density of states for these sulphides have also been studied.

## 2 Computational Methods

We have performed first-principles total energy calculations within the local density approximation (LDA) and generalized gradient approximation (GGA) using the plane wave self-consistent field method computer code<sup>14</sup> (PWSCF). The core electrons are implicitly treated by ultra soft Vanderbilt-type pseudopotentials<sup>15</sup> as supplied by Perdew-Wang<sup>16</sup> and with non-linear core-correction. For each calculation, irreducible k-points are generated according to the Monkhorst-Pack scheme<sup>17</sup>. The Kohn-Sham single-particle functions were expanded on a basis of plane-wave set with a kinetic energy cut-off of 32Ry and 28Ry for Li<sub>2</sub>S and Na<sub>2</sub>S, respectively. Brillouin zone was sampled with 8×8×8 k-point mesh, in order to get well converged ground state energy. The lattice parameter, bulk modulus and pressure derivatives of the bulk modulus for both the compounds were determined by the standard procedure of computing the total energy for different volumes and fitted to Murnaghan's equation of states<sup>18</sup>. The elastic constants were obtained by straining the equilibrium lattice at fixed volumes, using volume-conserving strains and then computing the strained energy as a function of strain<sup>19</sup>.

## 3 Results and Discussion

The total energies as a function of volume are fitted to Murnaghan's equation of states<sup>18</sup>, to determine the ground state properties, such as equilibrium lattice parameter ( $a_0$ ), bulk modulus ( $B_0$ ) and its pressure derivative ( $B'$ ) is presented in Fig. 1(a and b) for Li<sub>2</sub>S and Na<sub>2</sub>S, respectively. All these properties along with the calculated values of elastic constants ( $C_{11}$ ,  $C_{12}$  and  $C_{44}$ ) in anti-fluorite phase for Li<sub>2</sub>S and Na<sub>2</sub>S are presented in Table 1 and compared with available theoretical<sup>7,8,11-13</sup> and experimental<sup>1,9,10</sup> results. The agreement between our calculated results for lattice constant for both the solids using GGA with the experimental data<sup>1</sup> is reasonably good. An analysis of our calculated lattice parameters reveals that there is a good agreement between our results and previously reported work of Khachai *et al.*<sup>13</sup> and Ethiraj *et al.*<sup>18</sup>. In the present case also<sup>20</sup> LDA underestimates the lattice parameter, while GGA values are reasonable. The deviations are 0.5% and 0.8% for Li<sub>2</sub>S and Na<sub>2</sub>S for our GGA calculation, respectively. The calculated values of bulk modulus decrease from Li<sub>2</sub>S to Na<sub>2</sub>S signifying the fact that the compressibility increases from Li<sub>2</sub>S to Na<sub>2</sub>S. As a matter of fact, the present calculated values of bulk modulus (both LDA and GGA), as is observed in other theoretical predictions

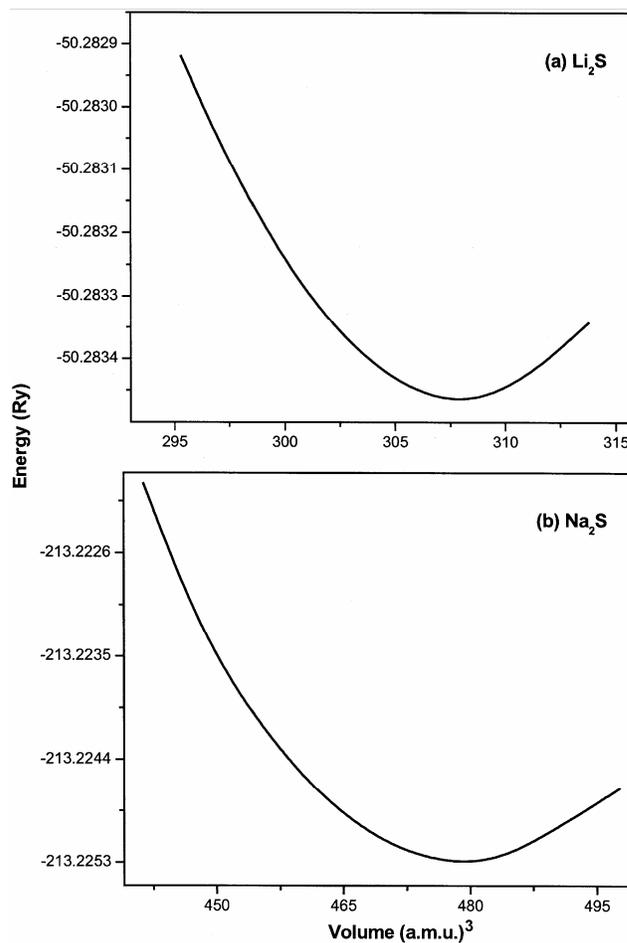


Fig. 1 — Equation of state for (a) Li<sub>2</sub>S (b) Na<sub>2</sub>S

(Table 1), could not compare well with the experimental data. The calculated values of pressure derivatives of bulk modulus ( $B'$ ) for Li<sub>2</sub>S and Na<sub>2</sub>S are in good agreement with recent available theoretical results using first principles full potential APW+lo method<sup>13</sup> with in LDA and GGA. In our case, the calculated values of  $B'$ , fall with in the range of 3-5, which is the case for most solids<sup>19</sup>.

The elastic properties of solids are important because they are related to various fundamental solid state phenomena, such as interatomic potential, equation of state, phonon spectra etc. We have calculated the elastic constants ( $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ ) for Li<sub>2</sub>S and Na<sub>2</sub>S in their anti-fluorite phase, compared them with experimental<sup>9,10</sup> and theoretical results<sup>11-13</sup>. In the case of Li<sub>2</sub>S, our calculated values  $C_{11}$  are higher than the experimental results, from both LDA and GGA, while the GGA value for  $C_{44}$  are reasonable.

The electronic band structures and density of states (DOS) for Li<sub>2</sub>S and Na<sub>2</sub>S are shown in Fig. 2(a and b), respectively. Both the materials show

Table 1 — Calculated lattice parameter  $a_0$  (Å), Bulk modulus  $B_0$  (GPa), its pressure derivatives  $B'$  and elastic constants ( $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ ) (GPa) for  $\text{Li}_2\text{S}$  and  $\text{Na}_2\text{S}$ , compared with the experimental data and theoretical calculations

| Material                       | Present work      |                   | Expt.                         | Other theo work                                                                                                                  |
|--------------------------------|-------------------|-------------------|-------------------------------|----------------------------------------------------------------------------------------------------------------------------------|
|                                | LDA               | GGA               |                               |                                                                                                                                  |
| $\text{Li}_2\text{S}$          |                   |                   |                               |                                                                                                                                  |
| $a_0$ (Å)                      | 5.535             | 5.677             | 5.708 <sup>a</sup>            | 5.645 <sup>c</sup> , 5.572 <sup>d</sup> , 5.715 <sup>d</sup>                                                                     |
| $B_0$ (GPa)                    | 44.9              | 28.3              | 45.7 <sup>b</sup>             | 43.45 <sup>c</sup> , 46.43 <sup>d</sup> , 40.4 <sup>d</sup>                                                                      |
| $B'$                           | 3.58              | 4.57              |                               | 3.47 <sup>d</sup> , 3.46 <sup>d</sup>                                                                                            |
| $C_{11}, C_{12}, C_{44}$ (GPa) | 138.9, 24.4, 42.7 | 113.6, 17.8, 26.6 | 95.4, 21.9, 32.9 <sup>b</sup> | 94.4, 23.3, 34.5 <sup>d</sup><br>83.9, 18.7, 32.2 <sup>d</sup><br>94.1, 13.9, 34.9 <sup>e</sup>                                  |
| $\text{Na}_2\text{S}$          |                   |                   |                               |                                                                                                                                  |
| $a_0$ (Å)                      | 6.532             | 6.570             | 6.526 <sup>a</sup>            | 6.428 <sup>c</sup> , 6.388 <sup>d</sup> , 6.581 <sup>d</sup>                                                                     |
| $B_0$ (GPa)                    | 28.7              | 28.4              | 49.00 <sup>b</sup>            | 32.95 <sup>c</sup> , 33.98 <sup>d</sup> , 28.67 <sup>d</sup>                                                                     |
| $B'$                           | 5.52              | 3.21              |                               | 3.82 <sup>d</sup> , 3.66 <sup>d</sup>                                                                                            |
| $C_{11}, C_{12}, C_{44}$ (GPa) | 92.2, 21.7, 22.9  | 72.8, 41.2, 21.7  | 81.0, 33.0, 21.0 <sup>f</sup> | 61.4, 20.3, 21.4 <sup>d</sup><br>54.1, 15.9, 19.9 <sup>d</sup><br>58.4, 13.6, 20.0 <sup>e</sup><br>64.4, 21.7, 17.9 <sup>g</sup> |

<sup>a</sup> Ref. [1], <sup>b</sup> Ref. [10], <sup>c</sup> Ref. [8], <sup>d</sup> Ref. [13], <sup>e</sup> Ref. [11], <sup>f</sup> Ref [9], <sup>g</sup> Ref [12].s

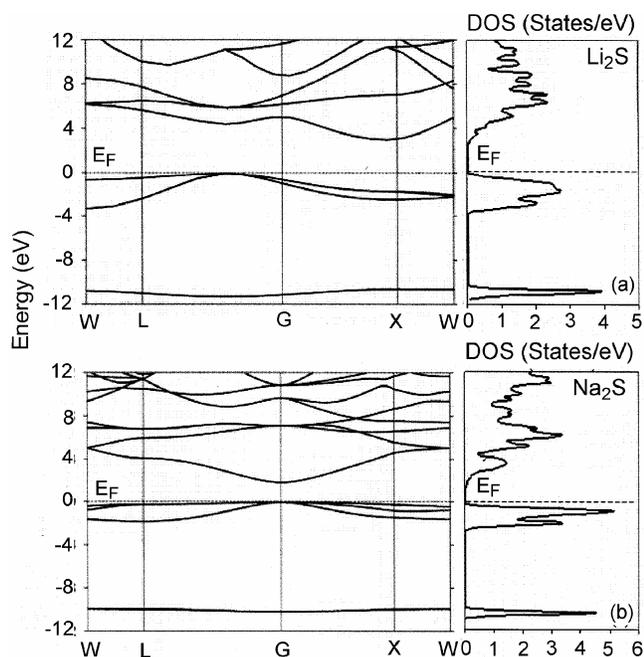


Fig. 2 — Calculated electronic band structure and density of states for (a)  $\text{Li}_2\text{S}$  (b)  $\text{Na}_2\text{S}$  in antifluorite structure. Dotted line shows the Fermi level ( $E_F$ )

semiconducting properties with few eV band gaps, as can be seen from the DOS Fig. 2(a and b). Occupied and unoccupied bands are well separated from each other. From Fig. 2(a), it is seen that an indirect band gap of 3.1 eV (the valence band maximum occurs along the G-L direction and conduction band minimum occur along G-X direction) is obtained for  $\text{Li}_2\text{S}$ , while a direct band gap 2.0 eV is obtained for  $\text{Na}_2\text{S}$  at G point which is shown in Fig. 2(b). From

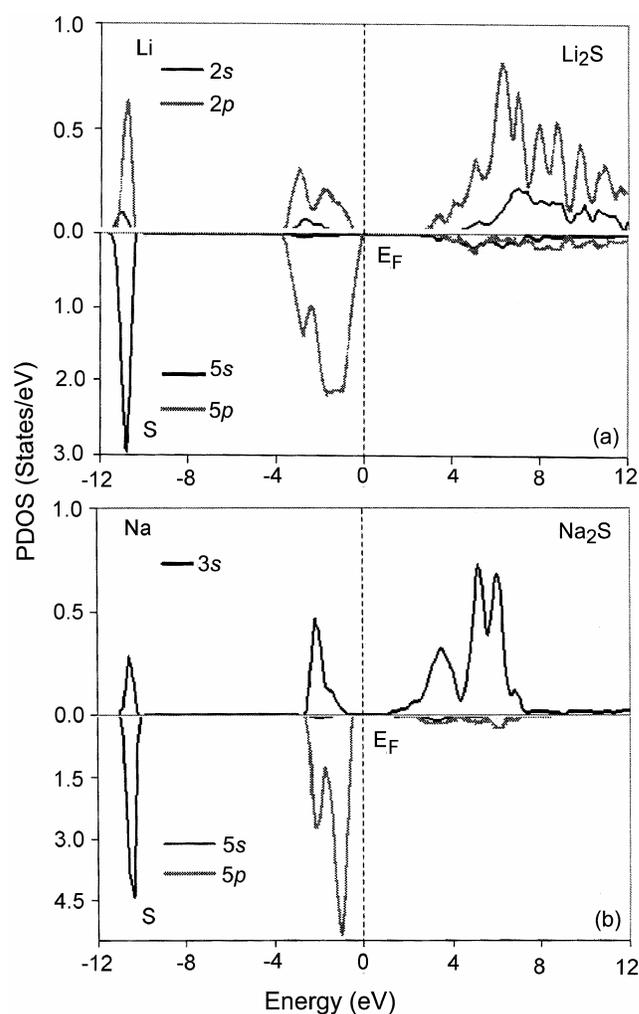


Fig. 3 — Calculated projected density of states (PDOS) for (a)  $\text{Li}_2\text{S}$  (b)  $\text{Na}_2\text{S}$  in antifluorite structure. Dotted line shows the Fermi level ( $E_F$ )

Fig. 2, it is clear that there is no density of states near the Fermi level ( $E_F$ ). These results are in good agreement with the TBLMTO calculations of Ethiraj *et al.*<sup>8</sup> which shows band gap of 3.2 eV for  $\text{Li}_2\text{S}$  and 2.5 eV for  $\text{Na}_2\text{S}$ . It can be seen, clearly from the band structures of Fig. 2(a and b) that there is a shift of bands to higher energy as we move down a group, because of the addition of a shell down a group. The projected densities of state (PDOS) are shown in Fig. 3(a and b) for  $\text{Li}_2\text{S}$  and  $\text{Na}_2\text{S}$ , respectively. The PDOS provide an even clearer picture of the elemental contributions to the electronic structure of  $\text{Li}_2\text{S}$  and  $\text{Na}_2\text{S}$ . The peaks at lower energy level are due to Li-2p and S-5s orbital in  $\text{Li}_2\text{S}$  as shown in Figure 3(a). In  $\text{Na}_2\text{S}$ , the lower energy peaks are due to Na-3s and S-5s orbital in Fig. 3(b). Near the Fermi level ( $E_F$ ) S-5s states and Li-2p states Fig. 3(a) and Na-3s states Fig. 3(b), contribute. Hence, the conduction bands are complex in nature which arises due to the hybridization of Li-2p and S-5s, and 5p states, Li-2p states contribute more in conduction band Fig. 3(a). In  $\text{Na}_2\text{S}$ , the Na-3s states contribute more in conduction band Fig. 3(b).

#### 4 Conclusions

From the present study, we conclude that  $\text{Li}_2\text{S}$  and  $\text{Na}_2\text{S}$  crystallizes in anti-fluorite structure and  $\text{Li}_2\text{S}$  shows wide range indirect band gap semiconductor nature whereas the  $\text{Na}_2\text{S}$  shows direct band gap semiconductor. The ground state and elastic properties are calculated and compared with other experimental and theoretical data. We find good agreement with experimental and other theoretical results and GGA results are more closed to experimental results.

#### Acknowledgement

The authors PP is thankful to MPCST, Bhopal, BR is thankful to BRNS (BARC, Mumbai) for financial support for this work. SPS is thankful to CSIR, New Delhi for financial support to this project.

#### References

- Zintl E, Harder A & Dauth B, *Z Elektrochem*, 40 (1934) 588.
- Grzechnik A, Vagas A, Syassen K, Loa L, Hanfland M & Jansen M, *J Solid State Chem*, 154 (2000) 603.
- Vegas A, Grzechnik A, Syassen K, Loa L, Hanfland M & Jansen M, *Acta Cryst B*, 57 (2001) 151.
- Vegas A, Grzechnik A, Hanfland M, Muhle C & Jansen M, *Solid State Sci*, 4 (2002) 1077.
- Schon J C, Cancarevic Z & Jansen M, *J Chem Phys*, 121 (2004) 2289.
- Zhuravlev Y N, Kosobutskii A B & Poplavnoi A S, *Russ Phys J*, 48 (2005) 138.
- Azavant P, Lichanot A & Repat M, *Acta Crystallogr B*, 50 (1994) 279.
- Eithiraj R D, Jaiganesh G, Kalpana G & Rajagopalan M, *Phys Status Solidi B*, 244 (2007) 1337.
- Buehrer W, Altorfer F, Mesot J, Bill H, Carron P & Smith H J, *J Phys Condense Matter*, 3 (1991) 1055.
- Buehrer W & Bill H, *Helv Phys Acta*, 50 (1977) 431.
- Lichanot A, Apra E & Dovesi R, *Phys Status Solidi (b)*, 177 (1993) 157.
- Buehrer W & Bill H, *J Phys C*, 13 (1980) 5495.
- Khachai H, Khenata R, Bouhemadou A, Reshak Ali H, Haddou A, Rabah M & Soudini B, *Solid State Commun*, 147 (2008) 178.
- Baroni S, A dal Corso S De Gironcoli P Giannozzi, <http://www.pwscf.org>.
- Vanderbilt D, *Phys Rev B*, 41 (1990) 7892.
- Perdew J P & Wang Y, *Phys Rev B*, 45 (1992) 13244.
- Monkhorst H J & Pack J D, *Phys Rev B*, 13 (1976) 5188.
- Murnaghan F D, *Proc Natl Acad Sci U S A*, 30 (1944) 244.
- Mehl M J, *Phys Rev B*, 47 (1993) 2493.
- Haj Hassan F El, Akabarzadeh H & Hashemifer S J, *J Phys Condense Matter*, 16 (2004) 3329.