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# Electronic and optical properties of β-HgS

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**Abstract.** Electronic and optical properties of β-HgS have been investigated using the density functional theory. The calculated lattice parameter is 6.043 Å, the bulk modulus is 57.17 GPa, the equilibrium volume is 55.25 $Å^3$. From the band structure, a direct band gap of 0.00002 eV was obtained, which agreed well with other calculations. The plot of the dielectric constant against photon energy indicated several distinctive peaks. The imaginary part has a peak value of 34.99 at 0.47 eV and the real part has a peak value of 29.65 at 0.40 eV. The values obtained for electronic and optical properties of β-HgS are essentially important for applications in optoelectronics.

**Keywords:** mercury sulphide, electronic properties, optical properties, density functional theory, plane-wave pseudopotential method.

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## 1. Introduction

Mercury sulphide (HgS) belongs to the group II-VI compounds. HgS has an ionicity of 0.79, which is the borderline between the ionic rocksalt structure and the covalent zinc-blende structure of $A^NB^{8-N}$ (N = group number) compounds. According to the ionicity, it was defined by [1]. It exhibits two structural modifications in nature, α-HgS (cinnabar, red, trigonal structure) and β-HgS (metacinnabar, black, cubic structure) [2]. β-HgS is metastable and is known to transform to stable α-HgS even at room temperature [3, 4]. β-HgS can also be stabilized at ambient temperature through a couple of percent doping with a transition metal, for example Fe [5], and CdS/HgS/CdS heterostructures [6]. A small addition of Fe helps to crystallize HgS in the zinc-blende structure (β-HgS), both in nature ((~1%) Fe), [7] and in the laboratory [8]. The zinc-blende variety of HgS (β-HgS, metacinnabar) is zero or near zero gap material [9]. The electronic structure of ZB mercury chalcogenides differs in a fundamental way from the electronic structure of the corresponding isoelectronic Zn and Cd systems [10-12]. Wei and Zunger (1988) have noted that the difference among Hg, Zn and Cd chalcogenides is due to the cation *d* band. The incomplete screening of the core by *d* electrons is thought to be the origin of the very different properties of the IIB–VI compounds relative to IIA–VI compounds. Mahapatra and Dash (2006) [13] synthesized well-separated HgS nanocrystals by a wet chemical route and found out that HgS nanocrystals are in cinnabar phase. Xu and Carraway (2012) [14] used solven based approach for the synthesis of β-HgS nanocrystals. Khalilzabeh and Kangarlov (2015) [15] prepared thin layers of HgS by chemical bath deposition techniques. Patil *et al.* (2017) [16] studied HgS doped with chromium by using novel chemical route. β-HgS are useful in ultrasonic transducers, image sensors [17], electrostatic imaging materials [18], photoelectric conversion devices [19, 20] and low-power consumption electronic devices [21]. It is also known to be a technologically important material for its pronounced dichroism [22], birefringence [23] and acoustic-optic properties [24]. In this study, we present electronic and optical properties of β-HgS, namely: lattice parameter, bulk modulus, equilibrium volume, density of states (DOS), band structure, real and imaginary dielectric constant using the first principles method [25-29]. To the best of our knowledge, the plane-wave pseudopotential (PWPP) method [30] has not been used to calculate the electronic and optical properties of β-HgS. Hence, the aim of this study is to investigate electronic and optical properties of β-HgS by using PWPP method as implemented in ABINIT package for the first time.

## 2. Methods of calculations

The first-principles density functional theory (DFT) [25] within Plane-Wave Pseudopotential within the Generalized Gradient Approximation (GGA) [31] implemented in the ABINIT code [32] was used to calculate electronic and optical properties of β-HgS. The Brilloiun zone was performed automatically with

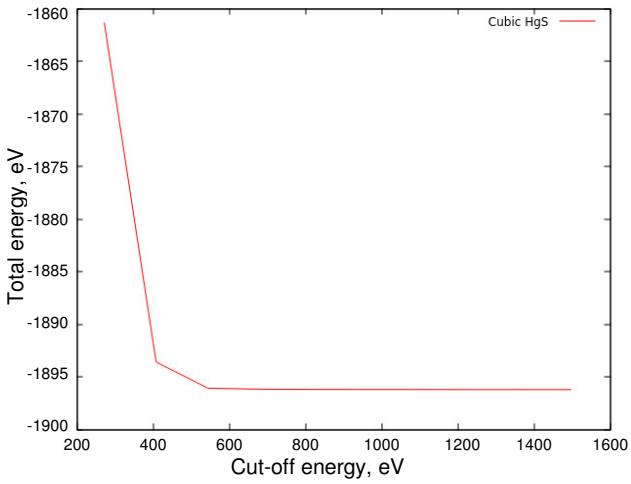


**Fig. 1.** Plot of total energy *vs* the cut-off energy ($E_{cut}$) for β-HgS.

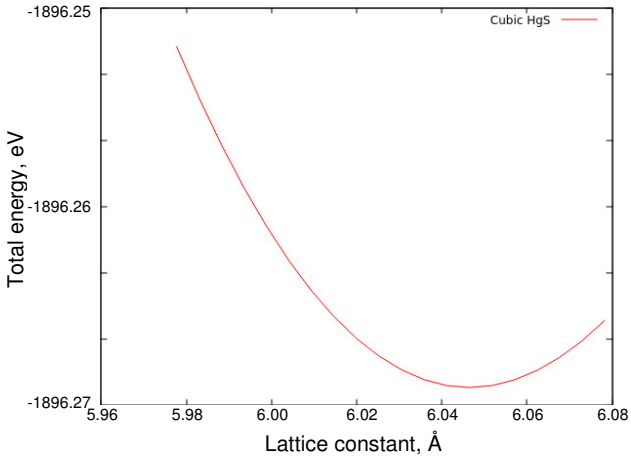


**Fig. 3.** Total energy *vs* lattice constant for β-HgS.

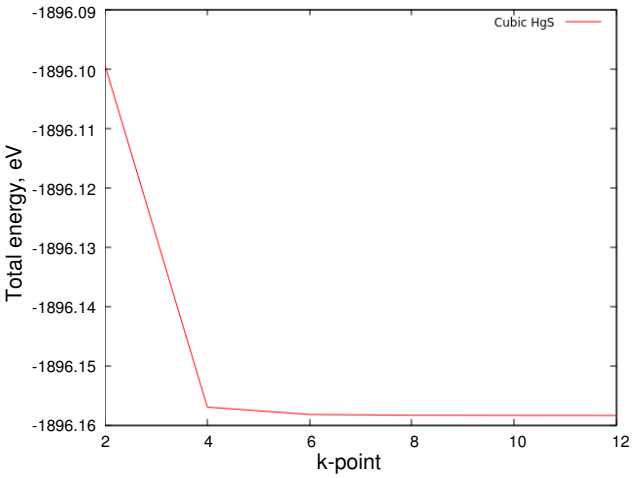


**Fig. 2.** Total energy *vs* k-point for β-HgS.

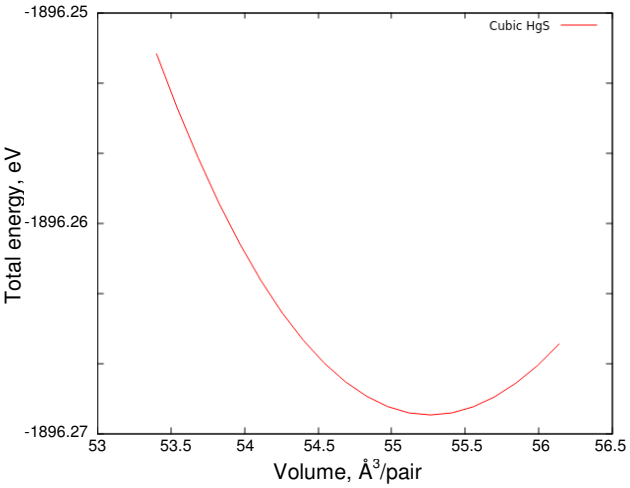


**Fig. 4.** Total energy – volume dependence for unit cells of β-HgS.

6×6×6 k-point mesh according to Monkhorst-pack scheme [33]. Equation of states that consists of mathematical relationship between two or more state functions such as pressure and volume was used to obtain the pressure-volume relationship that allowed us to obtain the equilibrium lattice parameter.

$$P(V)=\frac{B_0}{B_0'}\left[\left(\frac{V}{V_0}\right)-1\right]. \quad (1)$$

Later, we obtained the volume equation from the above pressure as follows:

$$V(P)=V_0\left[1+P\left(\frac{B_0'}{B_0}\right)\right], \quad (2)$$

where $P$ is the pressure, $V$ – volume, $B_0$ – bulk modulus, $B_0'$ – pressure derivative of the bulk modulus and $V_0$ – equilibrium volume.

## 3.Results and discussion

### *3.1. Structural properties*

The results obtained for electronic and optical properties of β-HgS are presented in Figs. 1–11 and Table. The plot of $E_{tot}$ *vs* lattice constants for β-HgS yields a parabolic curve with the minimum energy of β-HgS at 6.043 Å as shown in Fig. 3, which is in good agreement with previous theoretical and experimental results for lattice parameters. Fig. 2 is the plot of $E_{tot}$ vs its k-point sampling curve with monotonic minimum range between 4 and 12. The volume parameter was calculated to be 55.25 Å$^3$ as shown in Fig. 4. Subsequently, the calculated results were used for calculation of all the physical properties of this compound The total energy was investigated as a function of volume in Fig. 4 and as a function of pressure of unit cell for β-HgS crystal as seen in Fig. 5. The total energy vs volume curve is a mirror of total energy versus pressure curve. Fig. 1 is the

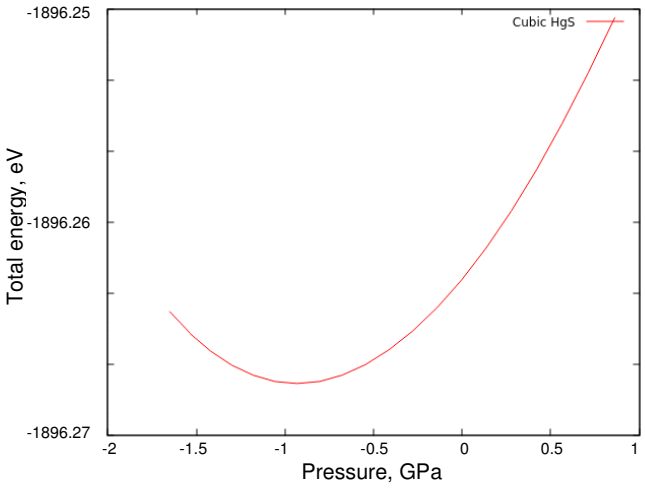


**Fig. 5.** Total energy – pressure dependence for unit cells of β-HgS.

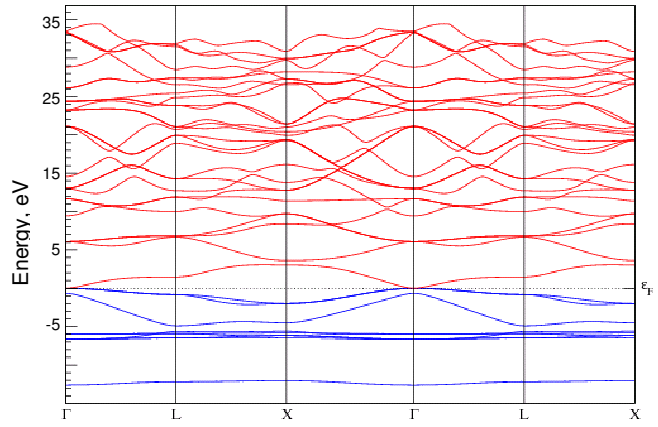


**Fig. 6.** Electronic band structure of β-HgS. The blue solid lines indicate the valence, and the red solid lines are the conduction bands, respectively. For β-HgS $E_g$ (direct) = $2.0 \cdot 10^{-5}$ eV.

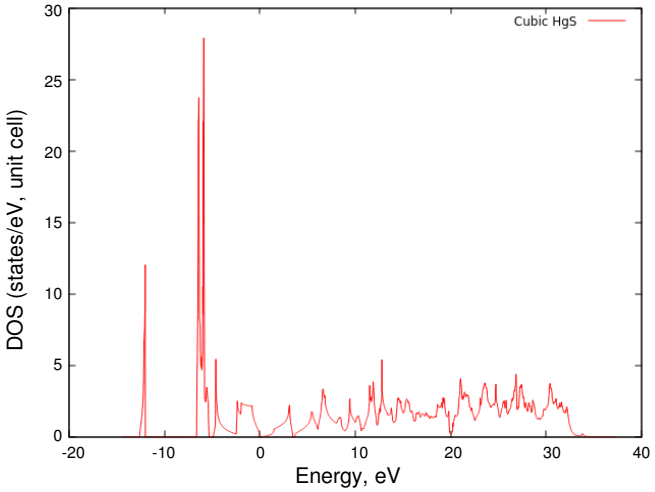


**Fig. 7.** Total density of states for cubic mercury sulphide (β-HgS).

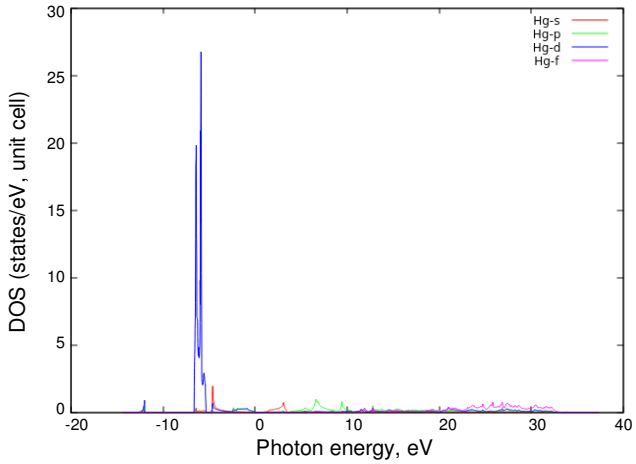


**Fig. 8.** Partial density of states of mercury sulphide (β-HgS) for Hg-constituent.

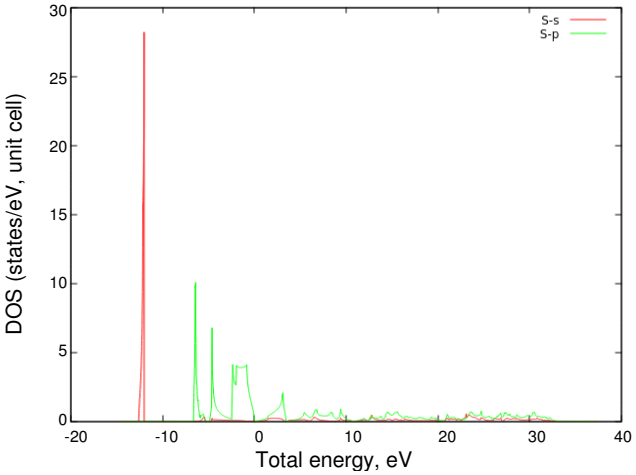


**Fig. 9.** Partial density of states of mercury sulphide (β-HgS) for S-constituent.

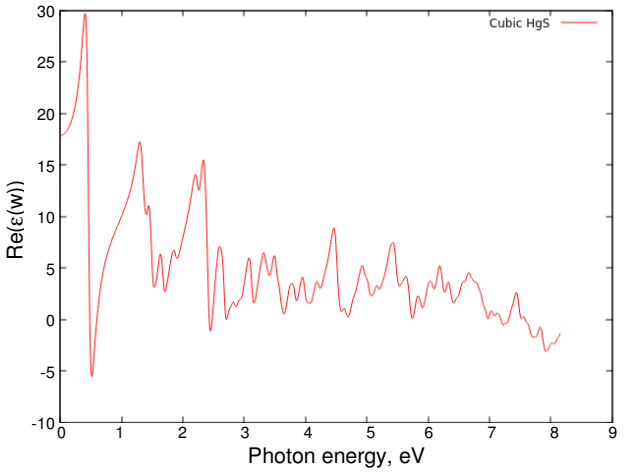


**Fig. 10.** Real part of dielectric function for cubic mercury sulphide (β-HgS).

Table of calculated GGA lattice constant $a_0$, bulk modulus $B$, equilibrium volume $V_0$ and band gap $E_g$ for β-HgS compared to other theoretical studies and experiment.

| Physical parameter | This study GGA:PWPP | Theory | Experimental |
|---|---|---|---|
| Lattice constant $a_0$ (Å) | 6.043 | 5.999 [9], 5.863 [34] | 5.852 [36] |
| Bulk modulus $B$ (GPa) | 57.17 | 59.07 [36], 63.6 [34] | 68.6 [36] |
| Equilibrium volume $V_0$ (Å$^3$) | 55.25 | 54.8 [39] | 50.1 [36] |
| Band gap $E_g$ (eV) | 0.00002 | 0 [34], 0.12 [35] | 0.25 [9], 0.54 [38] |

plot of $E_{tot}$ vs its kinetic energy cutoff ($E_{cut}$) curve with the monotonic minimum range between 600 and 1500 eV. In Fig. 3, it was observed that the minimum value of total energy is –1896.26 eV, and in Fig. 4, it was observed to be –1896.27 eV for this compound.

### *3.2. Electronic properties*

The plane-wave pseudopotential based on density functional theory within the generalized gradient approximation (GGA) was used for electronic structure calculations of β-HgS. The electronic band structure of β-HgS was presented in Fig. 6. The plot displays the energy range between –12.8 and 34.8 eV versus the wave-vectors Γ, L, X, Γ, L and X.

From the electronic band structure of β-HgS, it was observed that it has a direct band gap at high symmetry gamma (Γ) point with the value of $2.0 \cdot 10^{-5}$ eV.

The DOS and partial density of states are presented in Figs. 7, 8, and 9. In Fig. 7, seven main features can distinctly be seen in DOS. Following detailed incite from PDOS of Figs. 8 and 9, the first one is in the energy range from –12.5 to –11.8 eV, which is mainly attributed to S *s*-states; the second one, –6.5 to –5.3 eV, is mainly attributed to the Hg *d*-states; the third one, –4.9 to –2.5 eV, is mainly attributed to the hybridization of Hg *s*-, Hg *d*-, and S *p*-states; the forth one, corresponding to the top valence bands, from –2.5 to 0.0 eV (Fermi level), is mainly due to the hybridization of Hg *d*- and S *p*-states; the fifth one, corresponding to the bottom of the conduction bands, from 0.4 to 3.5 eV, is mainly due to the hybridization of Hg *s*- and S *p*-states with small contribution from S *s*-state; the sixth one, 3.8 to 20.0 eV, is mainly due to the hybridization of Hg *p*- and S *p*-states. Whereas beyond 20 eV, Hg *f*- and S *p*-states contribute mainly.

### *3.3. Optical properties*

β-HgS is an optic crystal that exhibits the symmetry of point group 216. The calculated real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of this compound are as presented in Figs. 10 and 11.

In Fig. 10, the real part of linear dielectric function, $\varepsilon_1$, goes to its maximum value of 29.65 at 0.40 eV. It was observed that β-Hg has a static dielectric constant value 17.74 as shown in Fig. 11. The real part of the complex dielectric constant showed how much the speed of light in this material is slowed down, the imaginary part portrayed how a dielectric material absorbed energy from an electric field due to dipole motion. The real part of the complex dielectric constant obtained for β-HgS is in the photon energy range of 0.0 to 8.2 eV as shown in Fig. 10. Variations in the real part of the complex dielectric constant with photon energy showed several peaks at the energies: 0.40, 1.32, 2.34, 4.48, and 5.43 eV. The peaks are points of inter-band transitions along the high symmetry points in the Brillouin zone. This real part of the complex dielectric constant has the minimum value –5.60 at the photon energy 0.52 eV and also the maximum value 29.65 at the photon energy 0.40 eV. The regions above and below zero indicate that the material behaves as dielectric and semiconductor, respectively. The imaginary part of the complex dielectric constant for β-HgS is in the range 0.00 to 8.17 eV as seen in Fig. 11. Variations in the imaginary part of the complex dielectric constant with photon energy showed several peaks, at the energies: 0.47, 1.49, 2.40, 2.68, and 4.52 eV. The imaginary part of complex dielectric constant has the maximum value 34.99 at the photon energy 0.47 eV.

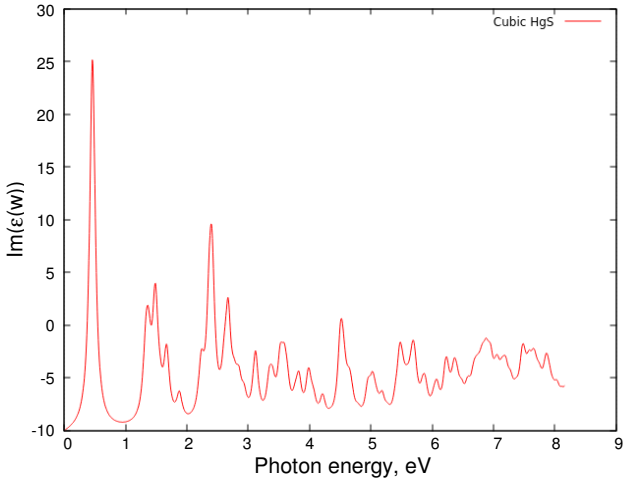


**Fig. 11.** Imaginary part of dielectric function of β-HgS.

## 4. Conclusion

The electronic and optical properties of β-HgS have been investigated using the plane-wave pseudopotential method for the first time. The density functional theory within the generalized gradient approximation was used as the exchange correlation. The ground state properties including equilibrium lattice parameter, pressure and volume derivative and minimized total energy were determined. The obtained results agree with other experimental and theoretical values. It was observed that β-HgS is semiconductor with a direct band gap of $2.0 \cdot 10^{-5}$eV at the gamma (Γ) point.

The real and imaginary dielectric responses of the compound have been also determined. β-HgS is an optic crystal, the compound has a static dielectric constant of 17.74. The results obtained showed that β-HgS exhibits a semi-metallic properties at ambient temperature and pressure, which provides good application in optoelectronic materials.

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