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Elastic Properties of Zinc Sulfide by Using Generalized Gradient Approximations

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Abstract. The plane-wave pseudo-potential (PW-PP) technique is used to explore the elastic characteristics of Zinc sulfide based on "first-principle density functional theory (DFT) with generalized gradient approximation (GGA)". The computed parameters match the experimental and other theoretical results quite well. The Bulk modulus B, compressibility K, Young's modulus Y, shear modulus G, and Poisson's ratio σ, as well as the optimised lattice parameters, independent elastic constants (C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, and C_{66}), have all been evaluated and discussed. Valuable information on structural and elastic properties needs understanding of properties of materials for microscopic perspective. The rationale for this is because structural characteristics can reveal a lot about the nature of interatomic binding interactions in solids in great detail.

KEY WORDS: density functional theory, density of states, pseudo-potentials, generalized gradient approximation, elastic constants.

1 Introduction

In order to study the elastic properties of Zinc sulfide (ZnS) II–VI compound semiconductor, various attempts have been made in the recent past [1]. This is because they have a wide range of technological applications in modern technology. Light-emitting diodes (LEDs), electroluminescence, flat panel displays, infrared windows, sensors, lasers, and biodevices are just a few of the many applications of ZnS [2]. Because cubic zinc blende (ZB) and hexagonal wurtzite (WZ) ZnS have a higher direct band gap of 3.72 eV and 3.77 eV, respectively, it is more suited for visible-blind ultraviolet (UV)-light based devices like sensors/photo detectors.

The elastic constant of ZnS allows us to construct fundamental principles about semiconductor materials' physical properties. With rapid development of high

technology, extensive experimental works have been done to discuss the behaviour of ZnS in the past few years. Theoretically, the investigation of the behaviour of ZnS have made remarkable progress by using the ab initio method [3, 4]. Gupta et al. performed a theoretical study of the structural of ZnS using first principle plane wave pseudo potential (PW-PP) and full potential linear augmented plane wave (FPLAPW) method [5]. However, when compared to the exact experimental data available, a sufficient understanding of the microscopic physical origin of ZnS under is still lacking, particularly in the elastic properties we have adopted. To study the structural and elastic properties by density functional theory (DFT), the GGA exchange and correlation potential is used here.

2 Computational Method

The plane-wave pseudo-potential approach based on the density-functional theory [6] was incorporated in the BIOVIA material studio's CASTEP module for first-principles research. BIOVIA, a brand of Dassault systems, is a scientific tool that can be used for research work. The exchange-correlation energy is addressed using the Perdew-Burke-Ernzerhof (PBE) scheme under the generalised gradient approximation [7]. The non-conservative pseudo-potentials have been utilised in the computations, and the plane-wave cutoff energy for ZnS at 650 eV.

The Coulomb potential energy induced by electron–ion contact is described using valence electrons from the Zn ($3d^{10}$ $4s^2$) and S ($3s^2$ $3p^4$) orbitals. The Monkhorst–Pack method with a $5 \times 5 \times 5$ special k-point mesh is used to integrate special points sampling over the Brillion zone.

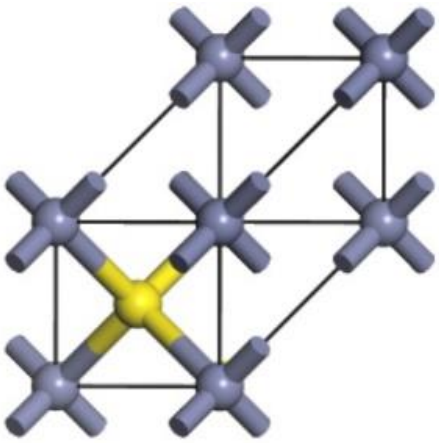

Figure 1. Primitive cell of ZnS. Grey balls represent Zn and yellow represents Sulphur.

Figure 1 represents the primitive cell of ZnS used for our calculations. Yellow colour represents the Sulphur atom and grey color represents the Zn atoms. Zinc sulphide occurs in two types of structures, cubic zinc blende and hexagonal wurtzite. Out of these we have considered the more stable one i.e., zinc blende ZnS for our calculations. It is also preferable from a thermodynamic point of view. Figure 2 shows the crystal structure with the Zinc atom represented by grey color and sulphur atoms by yellow color. it is a cubic close pack structure also known as face-centered-cubic. The lattice constant of this structure is 5.4093 Å. Using density functional theory (DFT) computational method the zinc blende phase of ZnS is shown in Figure 2.

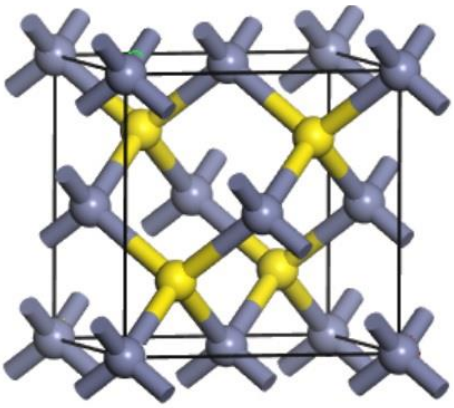

Figure 2. Cubic crystal structure of ZnS. Grey balls represent Zn and yellow represents Sulphur.

Tolerances for geometry optimization are specified at a total energy difference of less than 10^{-5} eV/atom. The elastic constants C_{ij} and elastic compliance constants S_{ij} for ZnS, using the CASTEP algorithm, have been directly calculated. The Debye temperature is computed systematically using the derived elastic constants.

3 Results and Discussions

Materials' elastic characteristics provide useful information on the bonding character between neighboring atomic planes, the anisotropic nature of the bonding, structural stability, and stiffness. Interatomic potentials, thermal expansion, Debye temperature, phonon spectra, and specific heat capacity are all revealed by these properties. A Taylor expansion of the total energy as a function of lattice strain is used to calculate elastic constants. The elastic constants C_{ij}, bulk modulus B, shear modulus G, Young's modulus Y, Poisson's ratio σ, and the anisotropic factor A were calculated to explore the elastic characteristics of ZnS.

The data have been presented in Table 1. We have listed the calculated elastic constants.

Table 1. The calculated elastic constants C_{ij} (in GPa), and elastic compliance constants S_{ij} [GPa = 1] for ZnS at zero pressure and the shear anisotropic factors A.

C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	S_{11}	S_{12}	S_{44}	A
110.402	83.594	83.594	110.402	36.698	36.698	0.0261	-0.011	0.0272	1.324

The six independent elastic constants C_{ij} must meet the Borne Huang criterion for a stable structure [8].

$$C_{11} > 0;\ C_{33} > 0;\ C_{44} > 0;\ C_{66} > 0\,, \tag{1}$$

$$C_{11} - C_{12} > 0;\ (C_{11} + C_{33} - 2C_{13}) > 0\,, \tag{2}$$

$$2\left[(C_{11} + C_{12}) + C_{33} + 4C_{13}\right] > 0\,. \tag{3}$$

For a ZnS semiconductor, the stiffness and compliance constants are related by

$$S_{11} = \frac{1}{3}\left(\frac{1}{C_{11} + 2C_{12}} + \frac{2}{C_{11} - C_{12}}\right), \tag{4}$$

$$S_{12} = \frac{1}{3}\left(\frac{1}{C_{11} + 2C_{12}} - \frac{1}{C_{11} - C_{12}}\right), \tag{5}$$

$$S_{44} = \frac{1}{C_{44}}\,. \tag{6}$$

Table 1 shows that the estimated elastic constants are positive and meet the following criteria. This indicates that the semiconductor compounds are mechanically stable. The orientation dependency of the elastic moduli or sound velocities is the elastic anisotropy of a crystal. An accurate explanation of such anisotropic behaviour has fundamental implications in both engineering and solid state crystal physics.

We used the anisotropic factor specified by

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \tag{7}$$

to calculate the elastic anisotropy of ZnS. Table 1 shows the computed anisotropic factor of ZnS, as well as other data. A is a term used to describe the degree to which ZnS is twisted. The degree of elastic anisotropy in solids is measured using the formula A. If $A = 1$ it is isotropic completely and if A is smaller or greater than one, it implies the material is anisotropic. Table 1 shows that, A for ZnS is greater than unity, suggesting that the material under investigation is elastically anisotropic.

In the Voigt approximation, the bulk modulus B_{V} and shear modulus G_{V} are represented as

$$B_{\mathrm{V}} = \frac{1}{9}\left[2\left(C_{11}+C_{12}\right)+4C_{13}+C_{33}\right], \tag{8}$$

$$G_{\mathrm{V}} = \frac{1}{30}\left(C_{11}+C_{12}+2C_{33}-4C_{13}+12C_{44}+12C_{66}\right). \tag{9}$$

The bulk modulus B_{R} and shear modulus G_{R} are given in the Reuss approximation as

$$B_{\mathrm{R}} = \frac{(C_{11}+C_{12})C_{33}-2C_{13}^2}{C_{11}+C_{12}+2C_{33}-4C_{13}}, \tag{10}$$

$$G_{\mathrm{R}} = \frac{5C_{44}C_{66}[(C_{11}+C_{12})C_{33}-2C_{13}^2]}{2[3B_{\mathrm{V}}C_{44}C_{66}+\{(C_{11}+C_{12})C_{33}-2C_{13}^2\}(C_{44}+C_{66})]}. \tag{11}$$

The bulk modulus B and shear modulus G are calculated using the Hill approximation

$$B = \frac{1}{2}\left(B_R+B_{\mathrm{V}}\right), \tag{12}$$

$$G = \frac{1}{2}\left(G_R+G_{\mathrm{V}}\right). \tag{13}$$

Table 2. In contrast to existing data, the estimated bulk moduli (B_{R}, B_{V}, B in GPa), shear moduli (G_{R}, G_{V}, G in GPa), Young's modulus (Y in GPa), compressibility (K in GPa^{-1}), G/B, and Poisson's ratio (σ)

B_{R}	B_{V}	B	G_{R}	G_{V}	G	Y	K	G/B	σ
92.530	92.530	92.530	21.649	27.380	24.514	67.576	0.010	0.264	0.378

We can estimate Young's modulus Y and Poisson's ratio σ using the following relationships based on the computed bulk modulus B and shear modulus G.

$$Y = \frac{9BG}{3B+G} \quad \text{and} \quad \sigma = \frac{3B-2G}{2\left(3B+G\right)}.$$

A material should be brittle if $G/B > 0.5$, else it should be ductile, according to Pugh's criterion [9]. Our calculations show that $G/B < 0.5$, implying that the materials will be flexible. This value is 0.26493 in our case. As a result, ZnS has the trend of flexible. For industrial and technical applications, understanding of Young's modulus and Poisson's ratio is crucial. The Young modulus is a helpful tool for determining the stiffness of solids. The greater the value of Y, the stiffer the material. For brittle materials, the Poisson's ratio is low. The Debye temperature (θ_D) is an important thermodynamic parameter

for determining physical characteristics of crystals such as specific heat, thermal expansion, melting point, etc. The Debye temperature is the temperature of a crystal's greatest normal mode of vibration. According to Debye theory. As a result, the Debye temperature (θ_D) is the maximum temperature that a single normal lattice vibration may achieve [10–12], the value becomes elastic Debye temperature $= 301.67$ K with averaged sound velocity $= 2768.489$ m/s.

4 Conclusions

Thus we have investigated the elastic characteristics of semiconductor ZnS using first-principle calculations based on density functional theory with generalized gradient approximation (GGA). We have also computed these compounds, Debye temperatures, bulk modulus, shear modulus, Young's modulus, Poisson's ratio, compressibility, and elastic anisotropy factor independently. The value of bulk modulus of ZnS is found to be 92.53012 GPa while the shear modulus is found to be 24.514 GPa. From these we calculated the values of Young's modulus as 67.57610 GPa and Poisson's ratio as 0.37828. The value of G/B ratio obtained in this study suggests that ZnS is flexiable. The results reveal that the compounds are mechanically stable and have significant anisotropy in terms of elasticity and flexible.

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