Effect of Temperature on Young’s Modulus of hexagonal Zinc Sulfide

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Abstract
Young’s modulus of Zinc Sulfide at different environment temperatures is studied on the basis of the oscillations of atoms due to the thermal effects. The total energy of the system is a sum over the energies of electrons and phonons which are calculated by the density functional theory and quasi-harmonic approximations, respectively. It is observed that extension of the unit cell decreases phonon energy. The effects of strain on the total energy of hexagonal Zinc Sulfide were investigated. We obtained that, by increasing temperature the minimum of total energy shift to the stretched structures. It is also found that the minimum value of young’s modulus take place at temperature 100K.

Keywords: Zinc-Sulfide; Density functional theory; Young’s modulus; strain

1. Introduction
Semiconductor materials are very important because of enormous technological interest. Zinc Sulfide (ZnS) is an important II-VI compound semiconductor material with a wide direct band gap 3.68 eV [1]. These semiconductor materials can crystallize in either the cubic zinc-blende or the hexagonal wurzite but for each material, one or other of those phases is thermodynamically more stable at 300K, as indicated. Elastic stiffness coefficients are essential for many applications related to mechanical properties of a solid such as internal strain and thermo elastic stress.

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Measure of the deformations is depending on elastic stiffness coefficients that is a very important characterization of the crystals under varying temperature [2,3]. These superlative properties and potential applications make the investigation of electronic and mechanical properties of zinc-sulfide in different environments to be a topic of major concern. Among these properties Young’s modulus is an important parameter it measures the stiffness of a material and represents the ratio between the uniaxial stress and the uniaxial strain. In this work, Young’s modulus of ZnS at different temperatures is theoretically investigated by applying the density functional theory (DFT) and quasi-harmonic approximations (QHA).

2. Model and results
In this work, we assume the total energy of ZnS is a sum over the energies of electrons and phonons. The electronic energy is determined by the Density functional theory and the energy of phonons is determined by the Quasi-Harmonic Approximation [4]. For simplicity, we neglect the expansion of the unit cell due to the thermal expansion of ZnS. In the Bohr-Oppenheimer approximation, the interacting electrons are investigated in the field of fixed ions. The electronic Hamiltonian of system including N electrons and M ions is written as

\[ H = \frac{-\hbar^2}{2m} \sum_{i=1}^{N} \frac{\partial^2}{\partial r_i^2} + \frac{e^2}{2} \sum_{i<j} \left( \frac{1}{|r_i - r_j|} + \sum_{l=1}^{M} \sum_{j=1}^{M} \frac{Z_j}{|R_l - R_j|} \right) \]

where \( r_i \) is the coordinate of the \( I \)-th nucleus. The first term describes the kinetic energy of electrons and the other terms represent the attractive interaction between the nuclei and the electrons and repulsive potential due to the electron-electron interaction. In the DFT theory, the ground state of the many body system is determined by solving the Kohn-Sham equations self-consistently [5].

\[ [-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r)] \Psi_i(r) = \epsilon_i \Psi_i(r), \quad V_{\text{eff}}(r) = V_{\text{H}}(r) + V_{\text{xc}}(r) + V_{\text{ext}}(r) \]

where \( V_{\text{H}}, V_{\text{xc}} \) and \( V_{\text{ext}} \) represent the Hartree (electrostatic), exchange-correlation and external potentials, respectively. The Local Density Approximation (LDA) is the first approximation for exchange-correlation functional. In the LDA, electrons move on a positive background in a neutral ensemble [6,7]. Generalized Gradient Approximation (GGA) is the first step beyond LDA in which the non-homogeneity of the true electron density is accounted for [6,7]. Here, the density functional calculations of ground state energy have been done within the generalized gradient approximation (GGA) and the Perdew–Burke–Ernzerhof (PBE) exchange correlation is adopted. Core electrons are modeled by Non-Relativistic ultra-soft pseudopotentials. The Brillouin zone integration is performed with 20 × 20 × 1 Monkhorst and Pack’s k-point mesh [10] and the cut-off energy for plane wave expansion was taken to be 80 Ry. The DFT calculations are performed with 15 Å distance between layers to avoid the interaction between neighbor layers. The equilibrium position of each nucleus is determined by vanishing the force on nucleus. In the next step, the strained structure is relaxed until the force tolerance of 10–6Ry/au is reached and the electronic ground state energy is calculated. All DFT calculations reported in this paper have been carried out using the Quantum-Espresso code [11]. The phonon energy is calculated by the Quasi-Harmonic Approximation with QHA code [4]. Unfortunately, when we perform these calculations, the QHA code does not work in the case of triclinic structures. So, in the calculation of the phonon energy, the unit cell is considered to conserve its hexagonal shape.

Fig1 shows the phonon energy as a function of energy in the relaxed and strained ZnS. It is observed that the phonon energy increased by temperature and the slope of curve was higher at high temperatures. It means
that the effect of temperature on phonon energy at high temperatures is more than one at low temperatures. It is also seen that by increasing the unit cell dimensions (i.e., with the increase of strain), the phonon energy decreases. So, in the case of strained structure, the minimum of phonon energy is obtained for the structure with the maximum tensile strain. Moreover, according to this figure, the difference between the phonon energies in strained structures diminishes as temperature increases. In other words, it is discerned that the effects of strain on phonon energy is almost negligible at high temperatures. The total energy at different temperatures as a function of strain is shown in Fig 2. It is clear that by increasing temperature up to 100K the minimum of total energy shift to the stretched structures and at higher temperatures shift to the compressed structures. It is also observed that the difference between total energy corresponding to the most tensile and compressive strain due to the phonon energy increases by increasing temperature up to 100K and decreases at higher temperatures. Thus, it can be concluded that the thermal effects corresponding to the phonon energy on Young’s modulus can be neglected at high temperatures. Young’s modulus is defined as the second derivate of the energy with respect to the applied strain [12].

Fig 3 represents the in-plane stiffness as a function of temperature. As it is shown, by increasing the temperature, young modulus decreases but not too much. We also obtained that as the temperature was raised surface Young’s modulus first strongly decreased up to temperature 100K which it reached at a lower rate of variation and at higher temperatures up to 500K young modulus increased and after that decreased again. This all is in good agreement with fig2 which shows the variation of total energy against strain at different energy. The inner curve in Fig. 3 is the first derivative of the stiffness with respect to temperature. It is seen that, by increasing temperature the derivative of young modulus decreases and reaches to its minimum value at 40K. At higher temperatures the young modulus rises and reaches to its maximum at 167K after that by raising temperature the derivative of Young’s modulus tends to zero and Young’s modulus reaches approximately a constant value in the high temperature range.

3. Conclusions
Total energy as a function of energy in the relaxed and strained Zinc Sulfide was studied. The total energy of the system was calculated by the density functional theory and quasi-harmonic approximations, respectively. The effects of strain on the total energy of hexagonal Zinc Sulfide were also investigated. It was found that the effect of strain on the phonon energy at high temperatures is negligible. We obtained by increasing temperature the minimum of total energy shift to the stretched structures and at higher temperatures shift to the compressed structures. The energy-strain curves at high temperatures were found to become closer to the corresponding curve in the absence of phonon energy. The effect of temperature on Young’s modulus of Zinc Sulfide was measured as a function of temperature. As it is shown, by increasing the temperature, young modulus decreases but not too much.

References

Figure captions
Figure 1: Phonon energy as a function of temperature at different strains.
Figure 2: Energy-strain curve at different temperatures.
Figure 3: In-plane stiffness as a function of temperature.

Fig 1. Phonon energy as a function of temperature at different strains
Fig 2. Energy-strain curve at different temperatures

Fig 3. In-plane stiffness as a function of temperature