

First Principle Pseudopotential Study of Zinc Blend to Rock Salt Phase Transition in ZnS

Badal H. Elias¹, Nawzat S. Saadi²

Abstract— Using a first-principles pseudopotential approach and the local-density approximation for the exchange correlation potential, we have calculated the equations of state (EOS's) of the zinc blende (ZB) and rock salt (RS) structures of ZnS. From these EOS's the high-pressure structural phase transformation of ZnS was investigated. These calculations were showed that the pressure for transition from the ZB structure to the RS structure is 14.93 GPa from normalized primitive cell volume V/V_0 –pressure P data, consistent with the experimental data. From the high pressure, we find that the ZB structure ZnS is unstable when the applied pressure is larger than 15 GPa.

Index Terms— Ab-initio calculations, Density functional theory, Electronic structure, High-pressure, Phase Transition, ZnS.

1 INTRODUCTION

ZnS is one of the prototype IIB-VIA semiconductors. Its cubic form, which occurs naturally as a mineral, has given the name zinc blende to the structure (also known as sphalerite or B3) in which most IIB-VIA and IIIA-VA semiconductors crystallize at zero pressure, provided they are not too ionic. At high temperature the hexagonal wurtzite structure, which also has tetrahedral fourfold coordination, is the equilibrium phase and may occur as a metastable form of ZnS at room temperature, as can various polytypes that are intermediate between wurtzite and zinc blende. There has been relatively little work on the properties of ZnS at high pressure, but it is known experimentally [1] that at a pressure in the range 15-18 GPa (150-180 kbar) ZnS adopts the rocksalt (NaCl or B1) structure with the sixfold octahedral coordination typical of ionic solids. This transition, which occurs at sufficient pressure for most binary semiconductors, has been treated theoretically for ZnS in some empirical [2] and semiempirical work [3] and in a density functional calculation [4] by Ves et al., and has been studied experimentally in two papers.[4,5]. The ZnS is a wide band gap semiconductor and an attractive material due to its use in various advanced technological applications in infrared optics, ultraviolet laser devices and electronic image displays, etc. Nanobelts, nanoclusters and various specimens in thin film form have been prepared for this material but the fabrication of large crystal of ZnS is a big problem in many studies due to critical growth condition. Over the past few years, several experimental and theoretical studies have been carried out to understand the mechanical of

ZnS [1-13].

The pressure at which the phase transition from the B3 structure to the B1 structure for ZnS occurs was first reported as 24.5 GPa [2]. It was estimated to be at 18.5 GPa based on the shock data of Rice et al. [6]. Zhou et al. [5], using x-ray diffraction data, reported the phase transition pressure value as 15 GPa. Several research groups have calculated the phase transitions theoretically using different methods recently, Gupta et al. [14] using first principle plane wave pseudopotential (PW-PP) and full potential linear augmented plane wave method (FPLAPW) calculation computed the transition pressure value as 15.2 GPa for (FPLAPW) and 17.2 GPa using (PW-PP) method, Bilge et al. [15] implemented projector augmented wave pseudo potential formalism (PAW) method to study the phase transition value as 18.5 GPa, and Chen et al. [7] computed the transition pressure value as 17.5 GPa from total energy–volume data and 15.4 GPa from equal enthalpies at the transition pressure between two phases.

In this work, we focus on the phase transition of ZnS from the ZB structure (B3) to the RS structure (B1) using a different method. We here adopt a Pseudopotential description of the electron-ion interaction Ultrasoft Pseudopotentials (USP) were introduced by Vanderbilt [8] together with the Perdew–Wang 1991 generalized gradient approximation (GGA) for the exchange–correlation potential [9] in order to allow calculations to be performed with the lowest possible cutoff energy for the plane-wave basis set, the electronic wavefunctions are expanded in a plane-wave basis set with energy cut-off 350 eV. Pseudo-atom calculations are performed for Zn ($3d^{10} 4s^2$) and S ($3s^2 3p^4$). As for the Brillouinzone k-point sampling, we use the $12 \times 12 \times 12$ Monkhorst–Pack mesh (182 points), where the self-consistent converged form of the total energy is 5.0×10^{-7} eV/atom. All electronic structure calculations are implemented through the CASTEP code [10-11].

Applying this theory, we have investigated the first order phase transition of ZnS under constant pressure. The rest of this paper is organized as follows: In Section 2, we make a

1. Faculty of Science, School of Physics, Duhok University, Duhok, Iraq. E-mail: badel_hyder@yahoo.com
2. Faculty of Science, School of Physics, Duhok University, Duhok, Iraq. E-mail: nawzat@uod.ac

brief review of the theoretical method. A detailed description and analysis of our results are presented in Section 3. Finally, a conclusion of the present study is given in Section 4.

2. THEORETICAL METHOD

2.1. Numerical Convergence

We must determine the cut-off energy for the plane wave basis set and the number of k-points at which to calculate wavefunctions. We consider first the truncation of the Fourier series in which the wavefunctions are expanded. We perform a number of simulations at a variety of energy cut-off values, with all other values (such as lattice parameter) kept constant. These simulations tell us the total energy of the system, which we can plot versus the cut-off energy used. The results are shown in figure 1. We see that the total energy is a convergent monotonically decreasing function of the size of the Fourier series used. From these data the cut-off energy of 350eV is achieved for both ZB and RS phases of ZnS. We now consider the discretization of k-space. One of the most popular schemes for generating k-points was proposed by Monkhorst and Pack [12]. This scheme, which was later modified to include hexagonal systems by Monkhorst and Pack [13], produces a uniform grid of k-points along the three axes in reciprocal space. We freeze all parameters except for the number of k-points used. Again we perform a number of simulations at a variety of k-points set then we plot the total energy against the k-points set. The results are shown in figure 2. Using grid size of 12×12×12 k-points is sufficient to provide results with an error of less than 5.0×10⁻⁷ eV/atom for both ZB and RS phases. In our case any further accuracy is not required. And since the computation time required increases with both the above factors, we wish to keep them as low as possible for the desired accuracy. All further simulations have been carried out with the above parameters (i.e. grid size of 12×12×12 k-points and cut-off energy of 350eV).

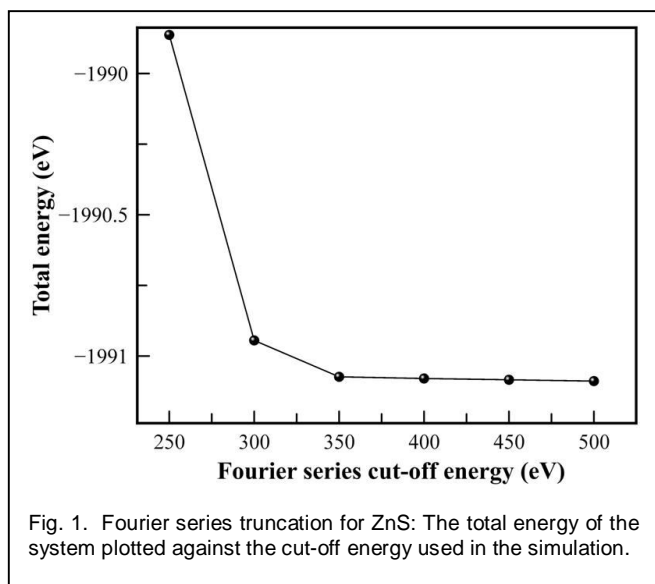


Fig. 1. Fourier series truncation for ZnS: The total energy of the system plotted against the cut-off energy used in the simulation.

2.2 Total energy and lattice Parameters

In all the electronic structure calculation, we adopt the non-

local pseudopotential introduced by Vanderbilt [8] for the interactions of the electrons with the ion cores, together with the generalized gradient approximation (GGA) for exchange-correlation functional in the scheme of Perdew–Burke–Ernzerhof (PBE) [9]. In the present calculations, the electronic wave functions are expanded in a plane wave basis set with energy cut-off of 380 eV, Pseudo-atom calculations are performed for Zn (3d¹⁰ 4s²) and S (3s² 3p⁴). The K-space integration has been performed using 12×12×12 k points in the irreducible Brillouin zone (IBZ), which ensure self-consistent convergence differences of the total energy within 5.0×10⁻⁷ eV/atom. These parameters are sufficient in leading to well converged total energy and geometrical configurations. All total energy electronic structure calculations are implemented through the CASTEP code [10-11].

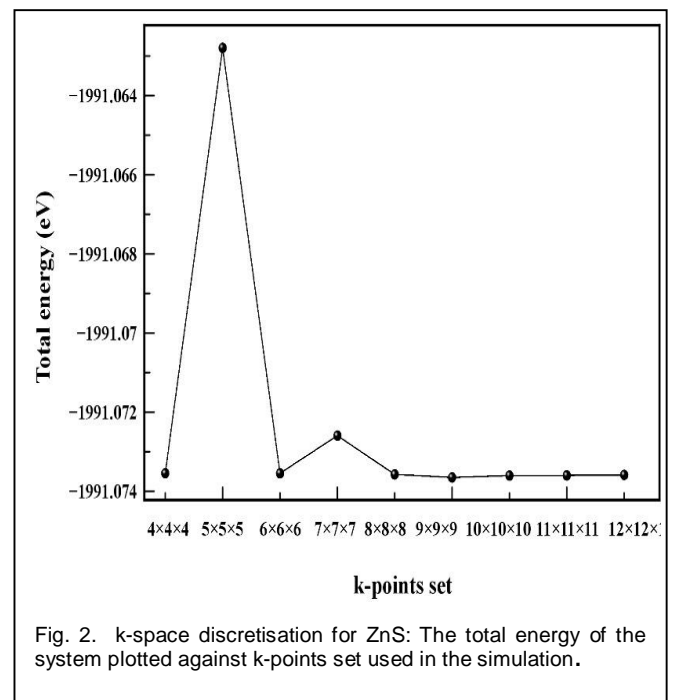


Fig. 2. k-space discretisation for ZnS: The total energy of the system plotted against k-points set used in the simulation.

First of all, we make first-principles calculation to find the most stable structure of both the ZB structure and the RS structure of ZnS, we take a series of lattice constants *a* to obtain the total energy *E* and the corresponding primitive cell volume *V*, which are illustrated in figure 3. The calculations have been carried out on the primitive cell (9-atom) rather than conventional cell (18-atom) to increase the speed of the calculations.

The calculated total energies and pressures as a function of the primitive unit cell volume for ZnS are used to determine the structural properties, phase behavior and isotropic mechanical response functions (bulk modulus and its pressure derivative) of ZnS by fitting the data to a third order Birch-Murnaghan equation of states (EOS). In the 3rd order Birch-Murnaghan equation of state (EOS), the total energy and pressure as a function of volume are given as [16];

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

and

$$P(V) = \frac{3B}{2} \left[\left(\left(\frac{V_0}{V} \right) - \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right)^{\frac{7}{2}} \right] \left\{ 1 + \frac{3}{4} (B_0' - 4) \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\} \quad (2)$$

respectively. In these expressions, E_0 is the total energy, V_0 is the equilibrium volume, B_0 is the bulk modulus at $P=0$ GPa, and B' is the first derivative of the bulk modulus with respect to pressure.

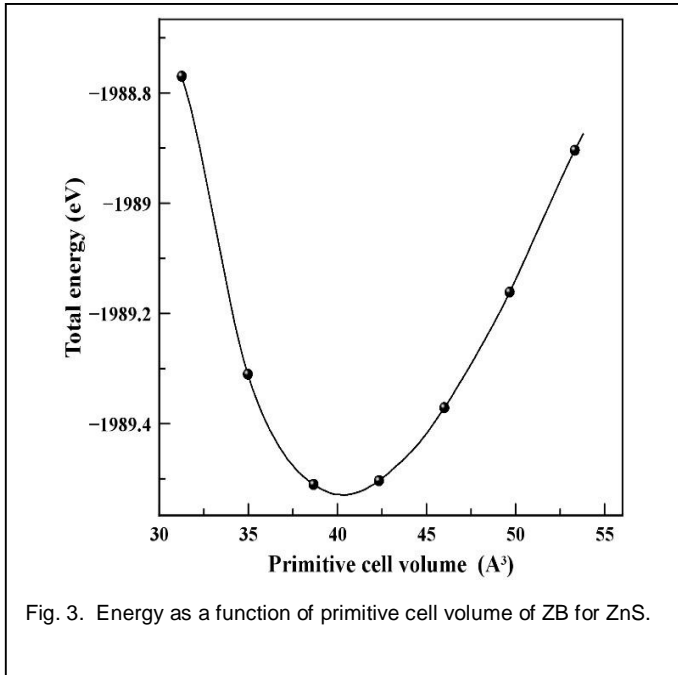


Fig. 3. Energy as a function of primitive cell volume of ZB for ZnS.

3. RESULTS AND DISCUSSION

3.1 Structural properties

The ground-state properties of the rock-salt and zincblende structures of ZnS are obtained by the minimization of the total energy, E , with respect to the unit cell volumes, V . We fit the $E(V)$ of ZnS for RS and ZB phases curves to the third-order Birch-Murnaghan equation of states (EOS). It is possible to obtain the equilibrium lattice parameters, zero-pressure bulk modulus and the pressure derivatives of the bulk modulus. The lattice constant a , the bulk modulus B_0 , its pressure derivative B' , and transition pressure (P_T) calculated at zero pressure are listed in Table 1 as well as other theoretical [16, 19, 20, 22, 23, and 25], and experimental data [20, 21, 25, and 26].

We can see that, for the ZB phase, the calculated lattice constant, bulk modulus and its pressure derivatives are in good agreement with the experimental value and other theoretical. While for the RS phase, the calculated lattice constant and bulk modulus are in good agreement with the experimental and other theoretical value but bulk modulus pressure first derivative is less than the other calculated and evaluated values but still in a reasonable agreement with the experimental value. We see, from this table, that the calculated value of the transition pressure (P_T) is in better agreement with the experimental and other theoretical calculation results.

3.2 Phase transitions

In order to determine the nature of the phase transition in ZnS, we first plot its pressure-volume curve in Fig. 4. The volume monotonically decreases with increasing pressure and the ZB state is still preserved to 14.8 GPa. As the pressure is increased

TABLE 1
THE LATTICE CONSTANTS A (Å), BULK MODULUS B_0 (GPa) AND ITS PRESSURE DERIVATIVE B' AND TRANSITION PRESSURES P_T (GPa) OF ZNS IN THE B3 AND B1 STRUCTURES AT ZERO PRESSURES.

B3 Structure	This work	Other theoretical calculations	Experiments
A	5.3	5.404 ^a , 5.6 ^b , 5.409 ^c	5.41 ^d , 5.409 ^e
B_0	71.75	71.22 ^a , 66.78 ^b , 83.2 ^c	76.9 ^d , 78-75 ^e
B'	4.19	4.705 ^a , 3.95 ^b , 4.43 ^c	4.9 ^d , 4.0 ^e
P_T	14.93	17.5 (15.4) ^a , 14.5 ^f , 16.1 ^d , 19.3 (11.4) ^g	14.7 ^h , 16.0 ⁱ
B1 Structure			
A	5.1	5.07 ^a , 5.24 ^b , 5.02 ^c	5.13 ^d , 5.06 ^h
B_0	80.3	89.54 ^a , 83.11 ^b , 104.4 ^c	85.0 ^d , 103.6 ^h
B'	3.6	4.58 ^a , 4.17 ^b , 4.29 ^c	6.2 ^d , 4 ^h

^aRef. [19], ^bRef. [23], ^cRef. [24], ^dRef. [21], ^eRef. [25], ^fRef. [22], ^gRef. [18], ^hRef. [16], ⁱRef. [26]

from 14.8 to 15GPa, the structural phase transition begins and is accompanied by a sharp volume drop, which is a characteristic of a first-order phase transition. The structural analysis indicates that the ZB structure converts into a RS structure in excellent agreement with experiments.

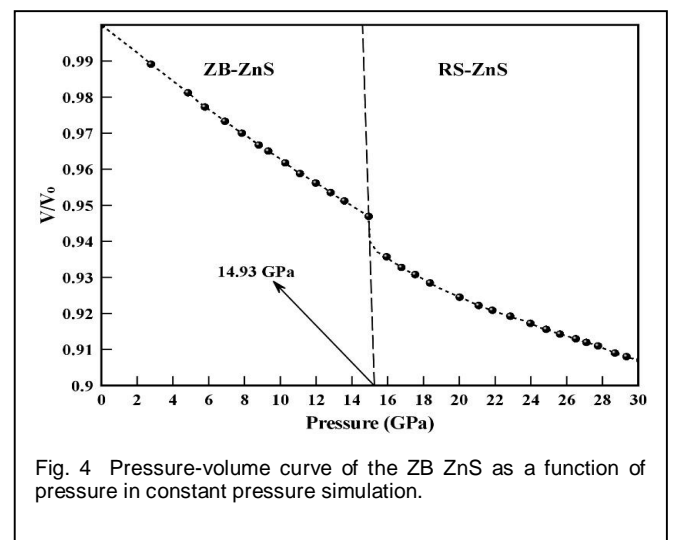


Fig. 4 Pressure-volume curve of the ZB ZnS as a function of pressure in constant pressure simulation.

4. CONCLUSIONS

In summary, first principle calculations based on the density functional theory (DFT) within generalized gradient approximation (GGA) have been performed to investigate the relative stability and the elastic properties of ZnS in the phases of B1 and B3 under different hydrostatic pressures. Our results for lattice parameters are all in agreement with the available experimental and theoretical values at the pressure of 0 GPa. It is shown that the values of the lattice parameter in the phases of B1 and B3 decrease when the pressure is applied to ZnS. The phase transition from B3 to B1 is found as 14.93 GPa accompanying with a volume reduction of about 0.8% which is consistent with the other theoretical and experimental data.

ACKNOWLEDGMENT

Authors would like to thank Faculty of Science, School of Physics; Duhok University in carrying out Computations performed on Theroretical Physics Group (TPG) computers.

REFERENCES

- [1] G. A. Samara and H. G. Drickamer, *J. Phys. Chem. Solids* 23, 457 (1962)
- [2] T. Soma, *J. Phys. C* 11, 2681 (1978) ; T. Soma and H.-M. Kagaya, *Solid State Commun.* 50, 261 (1984)
- [3] J. R. Chelikowsky, *Phys. Rev. B* 35, 1174 (1987)
- [4] Kalarasse S. Ves, U. Schwarz, N. E. Christiansen, K. Syassen and M. Cardona, *Phys. Rev. B* 42, 9113 (1990)
- [5] Y. Zhou, A. J. Campbell and D. L. Heinz, *J. Phys. Chem. Solids* 52, 821 (1991)
- [6] H.G. Drickamer, *Rev. Sci. Instrum.* 41 (1970) 1667
- [7] Chen X Q, Fu C L, Kr̄cmar M and Painter G S 2008 *Phys.Rev. Lett.* 100 196403
- [8] Vanderbilt D 1990 *Phys. Rev. B.* 41 7892
- [9] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* 77 3865
- [10] Payne M C, Teter M P, Allen D C, Arias T A and Joannopoulos J D 1992 *Rev. Mod. Phys.* 64 1045
- [11] Milan V, Winker B, White J. A , Packard C J, Payne M C , Akhmat-skaya E V and Nobes R H 2002 *Int J. Quantum Chem.* 77 85
- [12] H.J. Monkhorst and J.D. Pack, *Phys. Rev.B* 13, 5188 (1976)
- [13] J. D. Pack and H. J. Monkhorst, *Phys. Rev. B* 16, 1748 (1977)
- [14] S.K. Gupta, S. Kumar, S. Auluck, , *Optics Communications*, 284 (2011) 20-26
- [15] M. Bilge, S. Özdemir Kart, H.H. Kart, T. Cagin, *Journal of Achievements in Materials and Manufacturing Engineering* , 31, 1, (2008) 29-34
- [16] F. Birch, *Finite Elastic Strain of Cubic Crystals*, *Phys. Rev.* 71 (1947) 809-824
- [17] Catti M 2002 *Phys. Rev. B* 65 224115
- [18] Ves S et al 1990 *Phys. Rev. B* 42 9113
- [19] Jaffe J E, Pandey R and Seel M J 1993 *Phys. Rev. B* 47 6299
- [20] Miao M S and Lambrecht W R L 2005 *Phys. Rev. Lett.* 94 225501
- [21] Chen X R, Li X F, Cai L C and Zhu J 2006 *Solid State Commun.* 139 246
- [22] Chang E and Barsch G R 1973 *J. Phys. Chem. Solids* 34 1543
- [23] Ali Sahraoui F et al 2007 *Mater. Lett.* 61 1978
- [24] Nazzal A and Qteish A 1996 *Phys. Rev. B* 53 8262

[25] Casali R A and Christense N E 1998 *Solid State Commun.*108 793

[26] Pan Y et al and Zou G 2002 *J. Phys.: Condens. Matter* 14 10487