

Elastic and Electronic Properties and the (B3-B1) Phase Transition of ZnO

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Abstract. Based upon the density functional theory (DFT) within the generalized gradient approximation (GGA) in this paper, the first-principles approach is used to study the electronic band structure, density of state(DOS) and elastic properties of ZnO in the phases of B3 (zincblende) and B1 (rock salt). Phase transition from B3 to B1 is also predicted from enthalpy-pressure data. The results show that ZnO undergoes a structural phase transition from B3 phase to B1 phase at a pressure around 10.249 GPa. The calculated result of the ground-state energy, the lattice constant, the bulk modulus, the pressure derivative, the elastic stiffness coefficients (C_{11} , C_{12} , C_{44}) and phase transition of B3 and B1 phases are generally in good agreement with the other theoretical and experimental data.

Keywords: ZnO; density functional theory, generalized gradient approximation, phase transition; elastic constants

1. INTRODUCTION

ZnO is one of the most important II-VI binary compound, being a wide and direct band gap semiconductor, has many potential applications in electronics and optoelectronic devices. It has been investigated already in 1912. With the beginning of the semiconductor age after the invention of the transistor [1], systematic investigations of ZnO as a compound semiconductor were performed. In 1960, the good piezoelectric properties of zinc oxide were discovered [2], which led to the first electronic application of zinc oxide as a thin layer for surface acoustic wave devices [3]. Currently, research on zinc oxide as a semiconducting material sees a renaissance after intensive research periods [4, 5].

The results of these earlier activities were summarized in reviews of [6,7,8], Since about 1990 an enormous increase of the number of publications on ZnO occurred and more recent reviews on ZnO have been published [9-11]. The renewed interest in ZnO as an optoelectronic material has been triggered by reports on p-type conductivity, diluted ferromagnetic properties, thin film oxide field effect transistors, and considerable progress in nanostructure fabrication. ZnO, crystallizes in either the structure of hexagonal wurtzite (B4) or the cubic zinc-blende structure (B3) or both at ambient pressure. It undergoes a crystallographic phase transition into the sixfold-coordinated rock salt (B1) structure [12,13] at high pressure and also exist in the eightfold-coordinated CsCl (B2) structure, in analogy to the alkali halides and alkaline-earth oxides[14].

The structural properties of ZnO crystals under hydrostatic

pressure have already been studied for many years [15-34]. It

is known that at hydrostatic pressures of about 9-13 GPa It is well known that there are phase transitions from B4 structure to B1 structure, from B3 to B1 of ZnO when the pressure is applied.

Therefore, the main aim of the this work is to present a detailed study of behavior of structural and mechanical properties of ZnO in the phases of B1 and B3 under hydrostatic pressure by using first-principle calculations based on density functional theory (DFT) within generalized gradient approximation (GGA).

The paper is organized as follows: In §2, we briefly describe the computational techniques used in this work. Results and discussions are presented in §3. Finally, conclusions and remarks are given in §4.

2. COMPUTATIONAL DETAILS

The present quantum-mechanical calculations are performed based on the density functional theory and pseudopotential methods, which are implemented in the first-principles calculation program CASTEP software package,[35]. Interactions of electrons with ion cores are represented by the Vanderbilt-type ultrasoft pseudopotential for Zn and O atoms. Electronic exchange-correlation energy is treated under generalized gradient approximation (GGA) with the Perdew Burke Ernzerhof functional [36].

To estimate the optimal conditions to optimization and calculation the two parameters that affect the accuracy of calculations are the kinetic energy cut-off which determines the number of plane-waves in the expansion and the number of special k-points used for the Brillouin zone (BZ) integration. The BZ integrations were replaced by discrete summations over a special set of k-points, using the standard k-point technique of Monkhorst and Pack [37] where the k-point mesh used is $(6 \times 6 \times 6)$ the results are shown in Figure (1). The plane-wave energy cut-off to expand the wave functions is set to be 500 eV for ZnO in the structures of rock salt (B1) and zinc blende (B3) the results are shown in figure(2).. Careful

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convergence tests show that with these parameters, the relative energy is converged to better than 10^{-5} eV/atom.

The calculated total energies and pressures as a function of the primitive unit cell volume for ZnO are used to determine the structural properties, phase behavior and isotropic mechanical response functions (bulk modulus and its pressure derivative) of ZnO by fitting the data to a third order Birch-Murnaghan equation of states (EOS), the total energy and pressure as a function of volume are given as [38];

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B_0' + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\} \quad (1)$$

and

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

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.

To obtain the elastic constants of ZnO compound with cubic structure, we have used a numerical first-principles calculation by computing the components of the stress tensor δ for small strains, using the method developed recently by Thomas Charpin [39] and integrated in the CASTEP package, there are only three independent elastic constants, namely, C_{11} , C_{12} and C_{44} . Hence, a set of three equations is needed to determine all the constants, which means that three types of strain must be applied to the starting crystals. The first equation involves calculating the bulk modulus (B), which is related to the elastic constants, by

$$B = (C_{11} + 2C_{12})/3$$

The second one involves performing volume-conservative tetragonal strain tensor:

$$\varepsilon = \begin{pmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \delta^2/(1-\delta^2) \end{pmatrix} \quad (3)$$

Here, δ is the deformation parameter. Under the tetragonal shear strain, the total energy of the system is given by;

$$E(\delta) = E_0 + 2C_s V_0 \delta^2 + O(\delta^4). \quad (4)$$

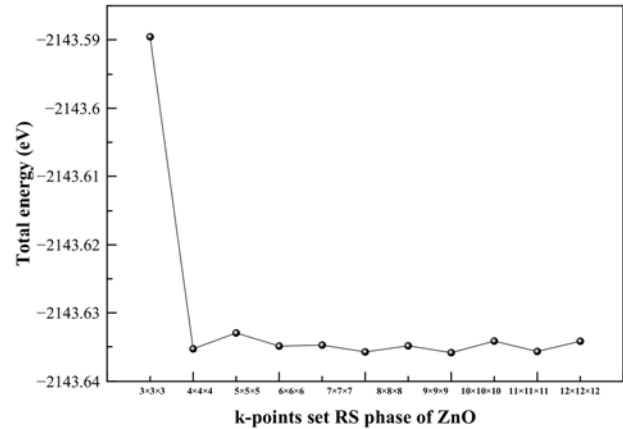
Here, E_0 is the energy of unstrained state, C_s is the cubic shear constant and V_0 is the zero strain volume. A parabolic fit to the strain energy vs. strain δ^2 yields the result of shear elastic constant.

Finally, the remaining independent modulus, C_{44} , was found by shearing the crystal with monoclinic strain

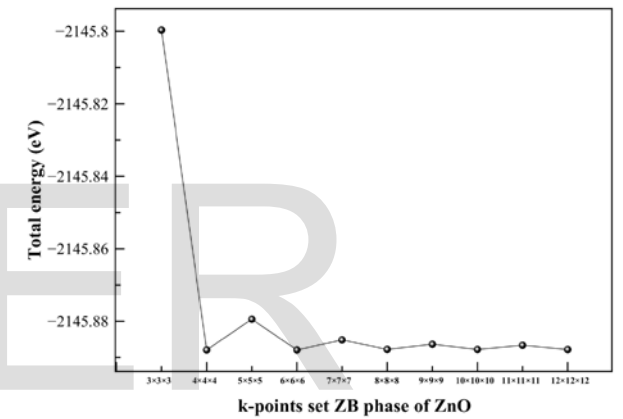
$$\varepsilon = \begin{pmatrix} 0 & \delta/2 & 0 \\ \delta/2 & 0 & 0 \\ 0 & 0 & \delta^2/(4-\delta^2) \end{pmatrix} \quad (5)$$

Which yields the total energy following as

$$E(\delta) = E_0 + \frac{1}{2} C_{44} V_0 \delta^2 + O(\delta^4). \quad (6)$$

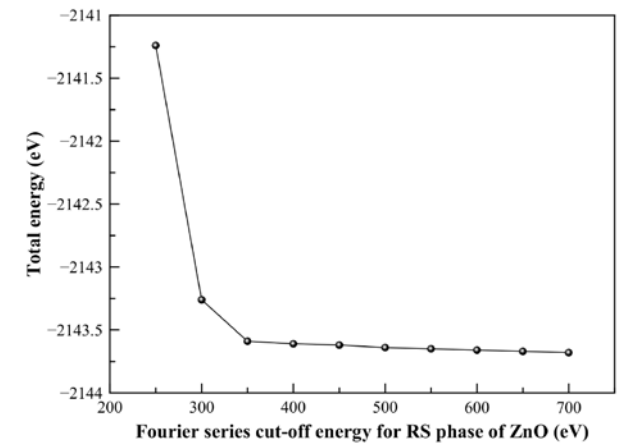


(a)

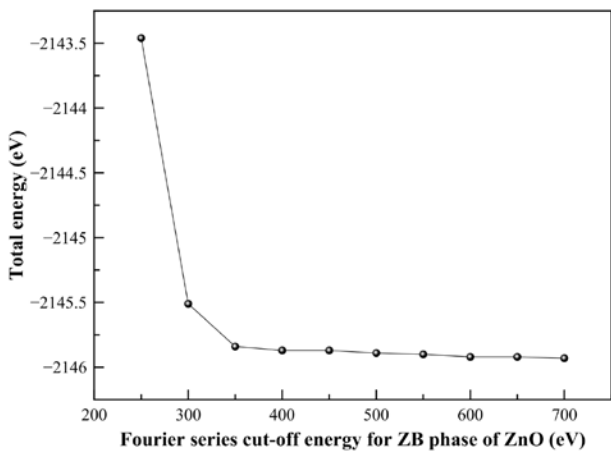


(b)

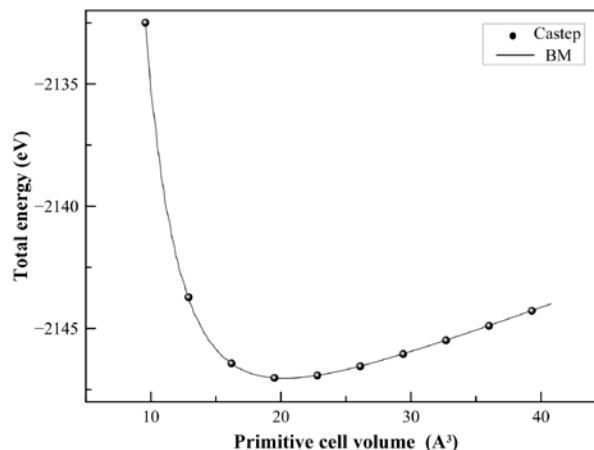
Figure (1): k-space discretization for ZnO a(RS), b(ZB): The total energy of the system plotted against k-points set used in the simulation



(a)



(b)



(b)

Figure (2): Fourier series truncation for ZnO a(RS),b(ZB): The total energy of the system plotted against the cut-off energy used in the simulation

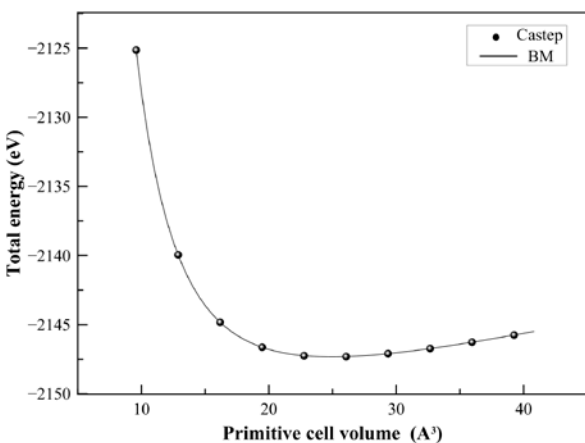
Figure (3): Energy as a function of primitive cell volume of (a)ZB and (b) RS for ZnO.

3. RESULTS AND DISCUSSIONS

3.1 STRUCTURAL PROPERTIES AT ZERO PRESSURE

After determining the kinetic energy cut-off and the number of special k-points which give the best possible convergence of total energy for the rock salt and zincblende structures of ZnO, they are used to calculate the total energy for various lattice constants. Energies were calculated for various lattice constants and the different values obtained were then traced as functions of unit cell volume. One can deduce the static structural properties such as the equilibrium lattice constant from the volume which gives the minimum energy the results are shown in Figure (3).

We fit the $E(V)$ curves to the third-order Birch-Murnaghan equation of states (EOS) equation (1). It is possible to obtain the lattice parameters, bulk modulus and the pressure derivatives of the bulk modulus. The lattice constant a , the bulk modulus B , its pressure derivative B' , and elastic constants (C_{11} , C_{12} , C_{44}) calculated at zero pressure are listed in Table1 as well as other theoretical and experimental data. Through this table, our lattice parameter for rock salt structure, $a=4.3277 \text{ \AA}$, is in excellent with the experimental value of $a=4.271 \text{ \AA}$ [41] and 4.283 \AA [40] and the theoretical results of $a= 4.3379 \text{ \AA}$ [19] and 4.223 \AA [22], respectively. For the B3 phase, the predicted lattice parameter, $a=4.6329 \text{ \AA}$, is also good agreement with the experimental value of 4.62 \AA [43] and other theoretical calculations [19,22]. The values of elastic constants for B3 and B1 structures can not be compared with the experimental data due to scarcity in the literature. Our predicted values of elastic constants for B1 and B3 structures are compatible with the other theoretical calculations [19,22]. The values of the lattice parameter decrease as the pressure increases.



(a)

TABLE I

The lattice constants a (Å), bulk modulus B_0 (GPa) and its pressure derivative B' and elastic constants C_{ij} and transition pressures P_T (GPa) of ZnO in the B3 and B1 structures at zero pressures.

B3 Structure	This work	Other theoretical calculations	Experiments
a	4.6369	4.52 ^a , 4.6329 ^b	4.62 ^c
B_0	129.42	168 ^a , 139.32 ^b	
B'	4.4782	4.6 ^a , 3.7586 ^b	
C_{11}	151.431	358 ^a , 167.363 ^b	
C_{12}	110.581	158 ^a , 125.304 ^b	
C_{44}	74.152	128 ^a , 112.883 ^b	
P_T	10.249	11.81 ^b , 8.57 ^e	2.0-8.7 ^d
B1 Structure			
a	4.3277	4.223 ^a , 4.3379 ^b	4.271 ^d , 4.283 ^f
B_0	164.04	209.6 ^a , 164.91 ^b	.5228 ^d , 202 ^f
B'	4.5227	4.46 ^a , 4.5318 ^b	4 ^d , 3.54 ^f
C_{11}	213.728	279 ^a , 237.319 ^b	
C_{12}	136.291	112 ^a , 145.183 ^b	
C_{44}	81.904	101 ^a , 82.185 ^b	

^aFrom Ref. [22], ^bFrom Ref. [19], ^cFrom Ref. [43] ^d,From Ref. [41], ^eFrom Ref. [40]

3.2. ELASTIC PROPERTIES

In order to further confirm the structure stability under strain, we calculated the elastic constants of the two structures, which were shown in (Table 1). There are three independent elastic constants, C_{11} , C_{12} , and C_{44} for a cubic crystal. A stable cubic crystal should match with the conditions: $C_{11}-C_{12}>0$, $C_{44}>0$, and $C_{11}+2C_{12}>0$. The three elastic constants can be obtained from the second-order derivative of the total energy of the crystal under three type of shear strains: the volume change, the volume conserved tetragonal and rhombohedral strains. The bulk moduli evaluated from the elastic constants (Table 1) were consistent with those obtained from Murnaghan equation (Table 1) for the two structures of ZnO. The rock salt bulk modulus we calculated from the Murnaghan equation is

164.04 GPa which is smaller than the experimental values such as 5228 and 202 GPa.

3-3 PHASE TRANSITIONS

The forces that act on the nuclei causes optimization of the unit cells which means that the lattice parameters change into new values and this causes the structure to come into new structure, this happen at embedded pressure with certain values called the transition pressure. Since all our calculations are performed at $T = 0$ K, then the Gibbs free energy, $G = E_0 + PV - TS$, becomes equal to the enthalpy, $H = E_0 + PV$. In order to determine the nature of the phase transition in ZnO, we first plot its Enthalpy (H_y) ($1H_y=27.2114$ eV) as a function of pressure of ZnO in the (RS) B1 and (ZB) B3 structures The transition pressure (P_T) from B3 phase to B1 phase is calculated at the precise point where the enthalpies of B3 and B1 phases are equal. The transition pressure from B3 to B1 is predicted as 10.249 GPa as given in Figure (4).

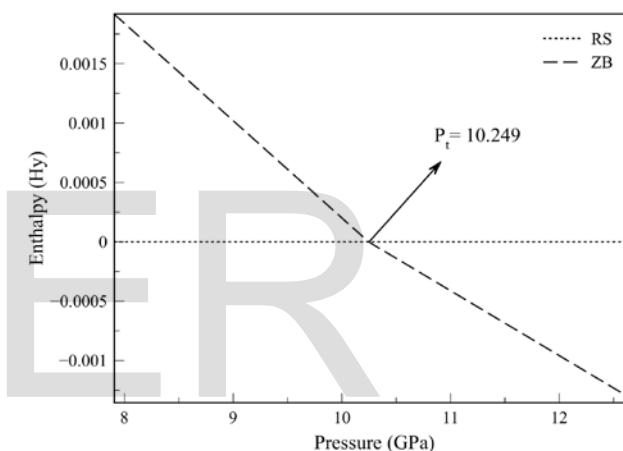
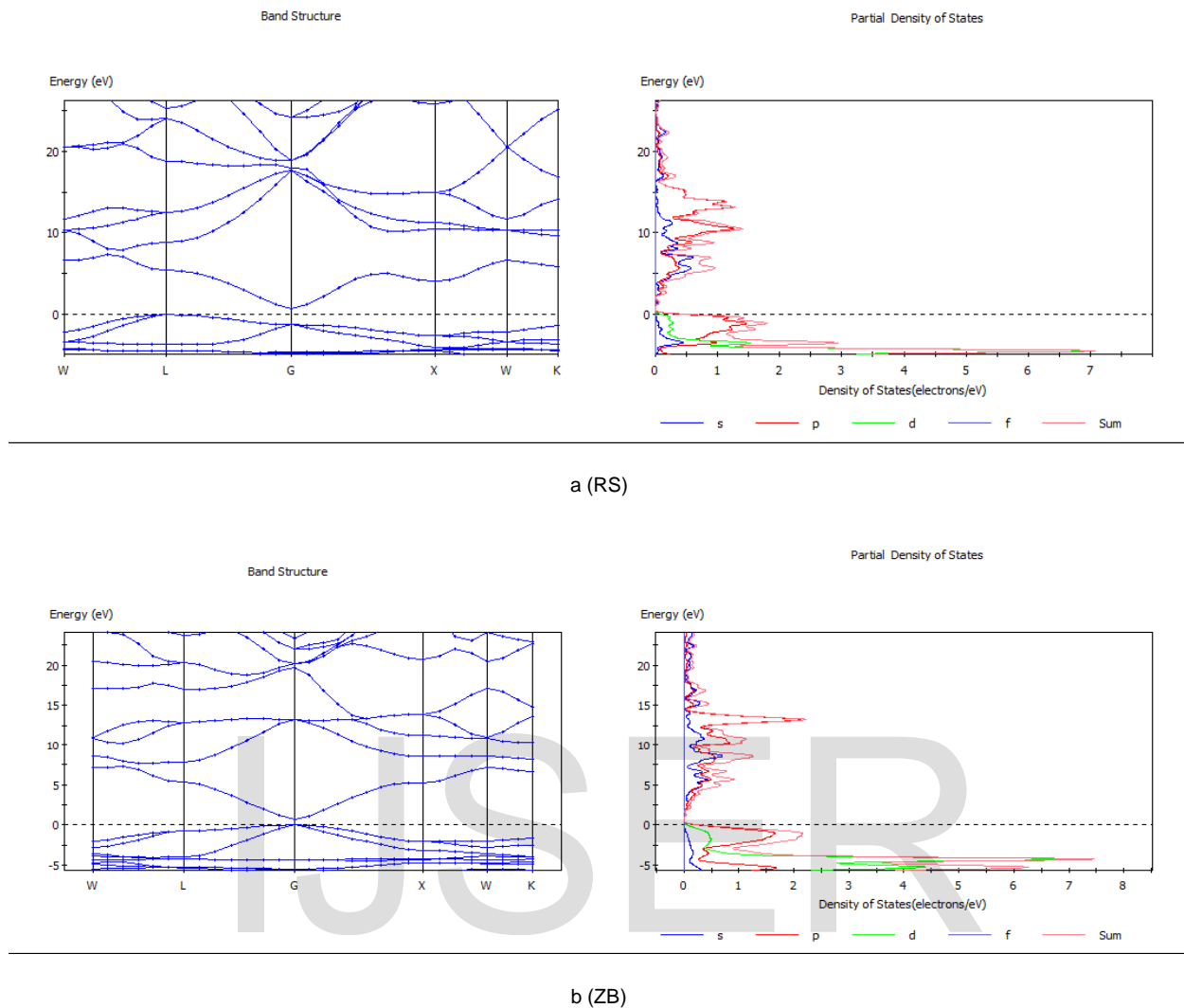


Figure (4): Enthalpy as a function of pressure of ZnO in the (RS) B1 and (ZB) B3 structures

3.4. BAND STRUCTURE AND DENSITY OF STATES

The study band structure and calculate the band gap for each structure of ZnO compound, is very important because by calculating it we can determine whether the compound is metal, semiconductor or insulator. The electronic band structure of a crystal describes the allowed states for electrons in the periodic potential of the solid. The band structure is usually calculated in the so called 1st Brillouin zone (FBZ) of the reciprocal space along special paths connecting high symmetry points. We can use the smallest possible real space unit cell of the crystal to calculate the band structure.

The density of states (DOS) including total DOS, partial DOS (PDOS) and the band structure of ZnO were firstly calculated after geometry optimization. The calculated results are shown in Figure (5), which are in agreement with the results calculated using other theoretical methods.[45-47]



Figure(5)The band structures(left panel)and density of states(right panel) of ZnO (a) RS and (b) ZB structures

Figure (5a) shows energy band gap for RS which found to be 0.734 eV which correspond to indirect transition at Γ point., and figure (5b) shows the energy band gap for ZB which found to be 0.631 eV which correspond to direct transition at Γ point , which is in accordance with other computed values using DFT, such as 0.73 eV by Schleife [47] and 0.80 eV by Janotti [48] and it is far less than the experimental value of 3.37 eV. It is well known that the underestimated band gap can be due to neglect of correlation between excited-state electrons.

4. CONCLUSION

In summary, using the first-principles calculation of plane wave ultra-soft pseudopotential technology based on the density functional theory within generalized gradient approximation (GGA).

The main results and conclusion of this study can be summarized as follows:

- 1- The calculated structural parameters (a, B, B`,) using CASTEP software package are found to be in good

agreement with the available experimental data and other theoretical results.

- 2- The 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 ZnO.
- 3- The pressure phase transition from the zinc-blende phase (B3) to rock salt phase (B1) of this compound is obtained it is at around 10.249 GPa, which is in good agreement with the available theoretical data reported in the literature.
- 4- The energy band gap for ZnO compound was calculated for ZB and RS structures and found to be 0.631eV for ZB and 0.734eVfor RS using GGA approximations.
- 5- ZnO behaves as semiconductor in the zinc-blende since it has a large energy gap in this structure. For rock salt it has energy band gap about 0.734eV GGA approximation which lead to non-metallic behavior.

- 6- For the elastic properties (C_{ij}), we have achieved good agreement between the calculated elastic constants with other available data for the zincblende and rock salt structures at zero pressure.

ACKNOWLEDGMENTS

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

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