



Calculations of electronic band structure, density of states and elastic properties of ZnTe at high pressure : An ab initio study

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ABSTRACT: Electronic band structure and elastic properties of ZnTe with zinc-blende and rock-salt structures were studied using the density functional theory (DFT) within the local-density approximation(LDA), generalized-gradient approximation and EV-GGA approaches. We have calculated band gap energy in order to determine the electronic and elastic properties. The result indicates that the calculated value of band gap under Engel Vosko (EV-GGA) scheme is in good agreement with the available experimental data. Furthermore, the elastic constants at high pressure RS phase are also calculated and analyzed in details.

KEYWORDS: Band gap, DOS, GGA, elastic properties, LDA.

I. INTRODUCTION

The group II-VI semiconductors and their cubic phases have been the subject of intense investigation under high pressure. Zinc chalcogenides are direct-gap semiconductors with an energy gap ranging from 2.3 eV to 3.7 eV for ZnTe and ZnS [1-3]. Recently the behaviour of zinc chalcogenide has been studied in the context of high pressure investigations for strain effects in the super lattices investigations [4-7]. The effect of pressure on the direct optical band gaps of ZnSe and ZnTe has been investigated for the tetrahedral phases [8-9]. Zinc chalcogenides ZnX (X=S, Se, Te) crystallizes in the zinc-blende(ZB) structure at ambient pressure and rocksalt (RS) structure at high pressure. Various studies have also been reported on zinc chalcogenides in the literature [2, 8-11].

ZnTe has potential applications for development of many semiconductor devices, including blue LEDs, laser diodes, solar cells, and components of microwave generators etc. It can be used for solar cells as a background layer. The ZnTe has been investigated for its uses as visible light-emitting semiconductors laser. The molecular dynamics (MD) simulation presents the transformation from zinc-blende four-fold coordinated structure to a NaCl-type six-fold coordinated structure around 12 GPa [12]. This material has been studied both experimentally and theoretically in last decades at ambient conditions. But the theoretical studies of ZnTe at high pressure are relatively lacking in literature which motivated us to take up this problem as theoretical point of view. So in this paper we report theoretical studies of electronic and elastic properties of ZnTe at ambient and high pressure using the density functional theory with in generalized gradient approximation (GGA) scheme. This paper is organized as follows: The method of calculation is described in section 2. The calculated results are explained in section 3. Finally, section 4 contained the summary and conclusions.

II. METHODOLOGY

The calculations have been carried out using with a self-consistent scheme by solving the Kohn-Sham equations, using a FL-LAPW method in the framework of the density functional theory (DFT), as implemented in the WIEN2K code [13]. The exchange-correlation potential was calculated using the generalized gradient approximation (GGA) for the structural properties. It was observed that the GGA method underestimate the magnitude of the energy band gap below the experimental value, while the energy band gap value calculated by Engel Vosko (EV-GGA) scheme is very near to its experimental value. So in addition to that for the calculation of electronic properties only the

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Engel-Vosko (EV) scheme was applied [14]. The alternative base sets (APW+lo) were used inside the atomic spheres for important l -orbitals (partial waves). For the total energy convergence, the basis functions in the IR were expanded upto $R_{mt} K_{max} = 7.0$. The maximum value of l were taken as $l_{max} = 10$, while the charge density is Fourier expanded up to $G_{max} = 12$. For the calculation of electronic properties we have used 72 k-points in the irreducible Brillouin zone for structural optimization. The alternative base sets (APW+lo) is used inside the atomic spheres for chemically important l -orbitals (partial waves). For all the other partial waves the LAPW scheme is used [15-18]. In the present study, 3p, 3d, 4s orbitals of Zn and 5s, 5p, 5d of Te have been treated as valence states. Moreover, we employ the semi-relativistic approximation (no spin orbit effects included) whereas the core levels are treated fully relativistic [18]. The generalized gradient approximation (GGA) was used for the exchange-correlation potential [19-24]. The unit cell was divided into two regions. The spherical harmonic expansion was used inside the non- overlapping spheres of muffin-tin radius (R_{mt}) and the plane wave basis set was chosen in the interstitial region (IR) of the unit cell. The R_{mt} for Zn and Te were chosen in such a way that the spheres did not overlap with each other.

III. RESULTS AND DISCUSSION ON ZNTE STUDIES

3.1 Electronic Properties

The precise knowledge of the electronic band structures is very important to study many physical and chemical properties of the materials. Electronic band structure of a solid provide the important information about the distribution of electrons in space, momentum and energy which may be represented by a plot depicting the relation between the energy of electron (E) and the wave vector (K). With the help of calculated lattice parameters the electronic band structure was calculated and plotted for ZB phase as well as high pressure RS phase of ZnTe by using the first principal tight-binding linear muffin-tin orbital method (TB-LMTO) within local density approximation (LDA) and FP-LAPW method with in EV-GGA scheme. These electronic band structures were further used to study other semiconductor properties like band gap, DOS, Fermi energy etc. which are described here under this section.

3.2 Band Structure

The band dispersion for (ZB) ZnTe calculated by DFT with in LDA are plotted in the Figure 1(a). In order to indicate the overall profile of the different bands of ZnTe, the different bands are identified with their corresponding electronic states. The detailed electronic band structure of ZB phase of ZnTe by TB-LMTO method has not been reported so far to the best of knowledge and efforts. However, the overall band profile is found to be similar to the band structure of ZnSe in B3 phase [25].

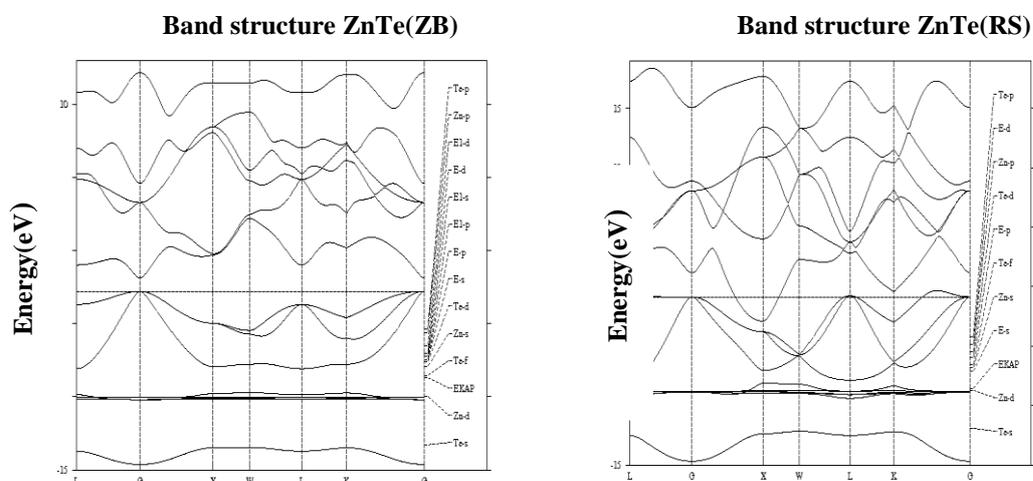


Figure1(a) Band structure of ZnTe
in ZB phase.

Figure1(b) Band structure of ZnTe
in RS phase.

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It can be noticed that the lowest-lying band in the valence band region (which appears at ~ -14 eV) mainly arises from the 5s states of Te while the bands in valence region just below E_F are predominantly due to 4s and 3p orbital of Zn. The conduction band above E_F is mainly due to 3d states of Zn which hybridize with 5p and 5d states of Te. Similarly, the electron dispersion curves along the high symmetry directions in the Brillouin zone for the case of high pressure rock salt (B1) phase of ZnTe are plotted in the Figure 1(b). The electronic band structure of RS (B1) phase of ZnTe by TB-LMTO method has also not been reported to the best of knowledge by other workers. However, the overall profile is again found to be similar to the band structure of RS ZnSe [25]. In this case also Fermi energy is shown by dotted line and it can be seen that the lowest-lying band in the valence band region mainly arises from the 5s states of Te while the bands in valence region just below E_F are predominantly due to 4s and 3p orbital of Zn. The conduction band above E_F is mainly due to 3d states of Zn which hybridize with 5p and 5d states of Te [26].

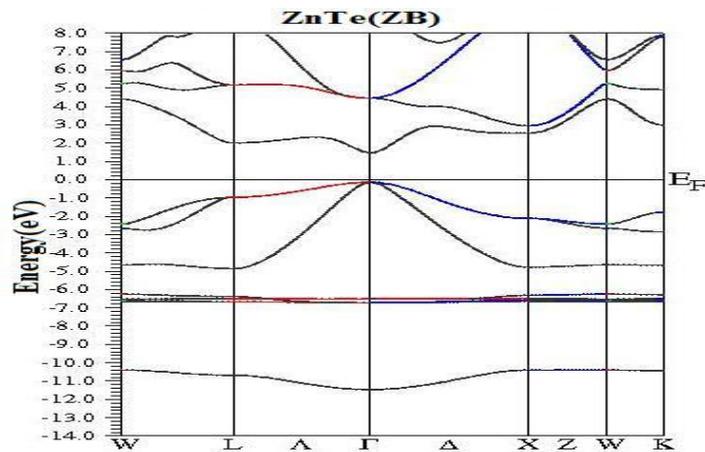


Figure 2(a) Band structure of ZnTe along the high symmetry directions in the Brillouin zone in zinc-blende phase using EV-GGA.

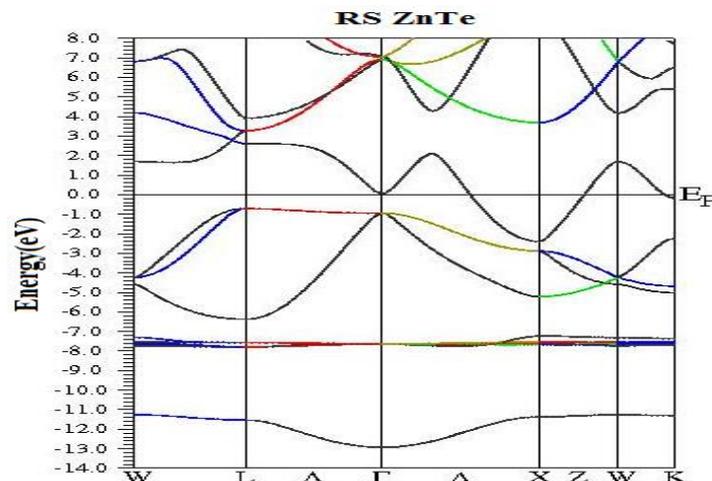


Figure 2(b) Band structure of ZnTe along the high symmetry directions in the Brillouin zone in rock-salt phase .

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Furthermore, the band structure for ZB and RS the phases have also been calculated and plotted using FP-LAPW (WIEN2k) within EV-GGA for perfection in the accuracy of the band gap as shown in the Figures 2(a) and 2(b). The overall band structure profile for both the phases are found similar to the band structure for both the phases calculated by TB-LMTO method as shown in the Figures 1(a) and 1(b). However, little difference in the band position on energy scale may be seen as in the case of ambient phase as the lowest lying band in the valence band region are found at -11.9 eV as compared to the TB-LMTO case which is lying at -14 eV. While the second group of band lies between -6.7 eV to -4.7 eV. The third bands group is found from -2.80 eV upto the Fermi energy.

From the figure 2(b), in high pressure rock salt phase of ZnTe, the hybridization interaction of the d electrons with anion p electrons leads to a repulsion of the involved states. Due to application of pressure the width of the upper valence bands increased and a decrease in the band gap has been observed. It may be occur because of Te- 5p states are pushed up in energy towards the Zn -4s derived conduction bands by p-d interaction. Thus, comparing TB-LMTO - LDA and LAPW-EV-GGA calculations in the zincblende and rocksalt phases, one can see that the band structures are very much similar, except the bandgap at G point for the LDA result is found smaller than EV-GGA result.

3.3 Density of States

Density of state is one of the most important aspects of study in determining the accurate electronic properties of solids. The densities of states (DOS) of a system describe the number of states at each energy level that are available to be occupied. A high DOS at a specific energy level means that there are many states available for occupation. The total and partial DOS are calculated and plotted for ZB and RS phases of ZnTe using FP-LAPW (WIEN2k) within EV-GGA to improve the accuracy in determination of the band gap as shown in the Figure 3(a,b,c,d,e,f). The overall profile of DOS histograms for both the phases are found similar to the DOS histograms for both the phases calculated by TB-LMTO and FP-LAPW methods.

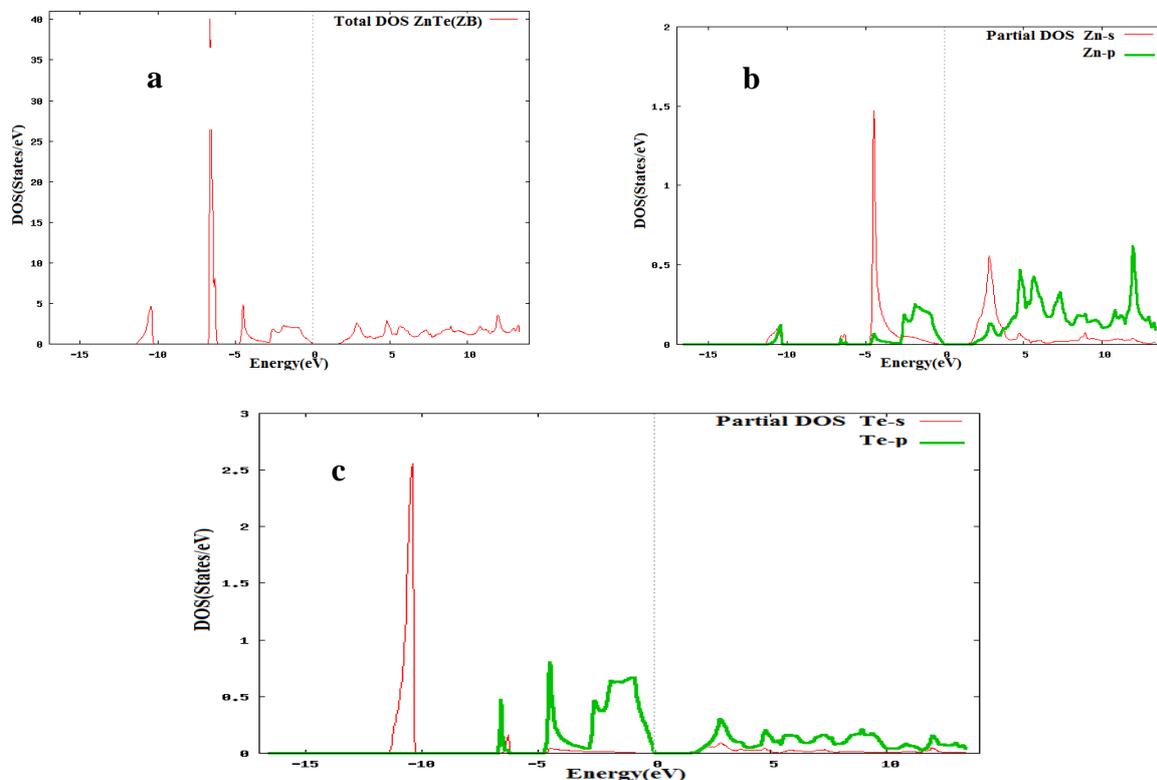


Figure 3 (a-c): Total and partial density of state of ZnTe for ZB phase.

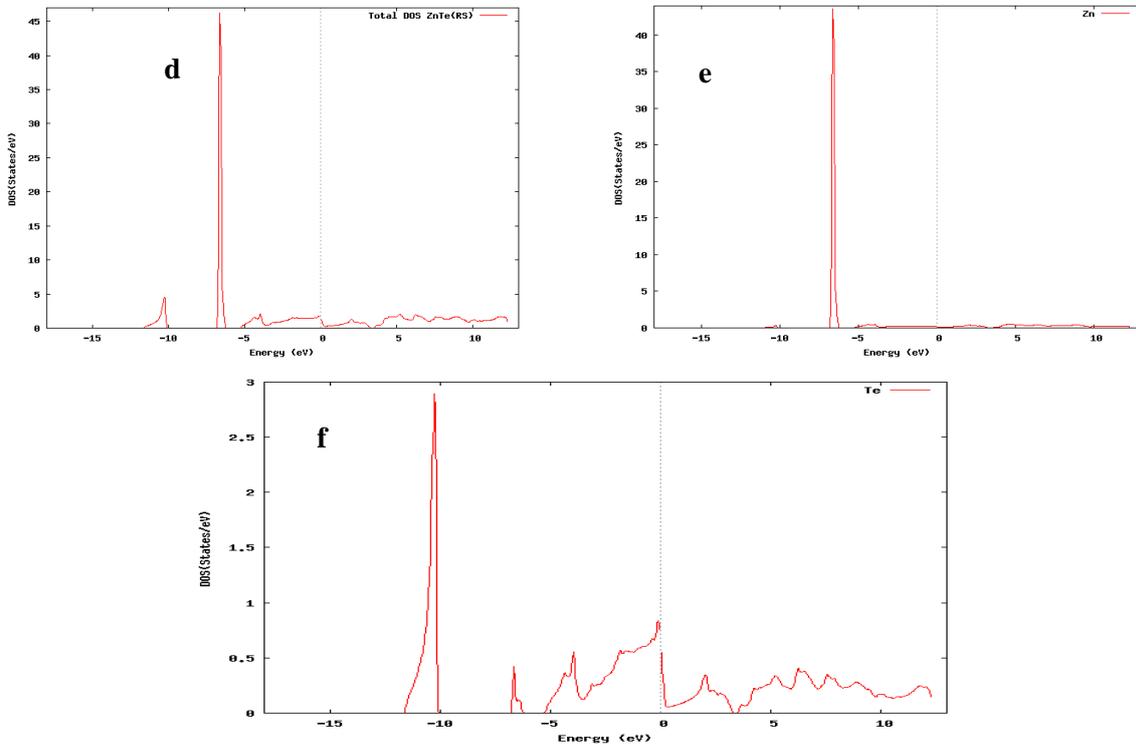


Figure 3(d-f): Total and partial density of state of ZnTe for RS phase.

The lowest energy region mainly arise from 5s states of Te whereas the peaks in next higher energy region just below E_F are predominantly due to 4s and 3p orbital of Zn. The peaks found in the next higher region (in the conduction band above E_F) are mainly due to 3d states of Zn which hybridize with 5p and 5d states of Te. However, in case of RS phase of ZnTe, a strong hybridization interaction of the d electrons with anion p electrons leads to a repulsion of the involved states which is responsible for an increased width of the upper valence band region and hence a decrease in the band gap [26-27]. This fact has also been earlier discussed in the band structure results.

3.4 Band Gap

The band structure of ZnTe has calculated by TB-LMTO and FP-LAPW methods using density functional theory (DFT), as shown in the Figures 1(a) and 2(a) for ZB phase band structures. The band gap is calculated for ZB phase using LDA and GGA schemes and the obtained values of the energy gap are shown in the Table 1 along with the previous reported theoretical work [28-30,12] and experimental values [31-32]. It can be noticed from the calculated results of band gap that both LDA and GGA underestimate the energy gaps as compared to experimental values may be seen in the Table 1. However, GGA yields slightly larger energy gaps than LDA scheme. Further, EV-GGA scheme has been used to improve the band gap value [30]. The band gap value calculated using EV-GGA which is found to be improved and lying closer to the experimental results [31-32]. Similarly, the band gap was checked for high pressure RS phase which is found to be reduced as a function of pressure. One can see from the comparative study of band structures under Figures 1(a-b) and 2(a-b) and partial DOS of both ZB and RS phases shown in Figures 3(a-f). This may be probably due to the fact as mentioned above in high pressure rock salt (B1) phase of ZnTe, the hybridization interaction of the d electrons with anion p electrons leads to a repulsion of the involved states which is responsible for an increased width of the upper valence bands region and hence a decrease in the band gap. It may be believed that this decrease in the band gap is occurred because of Te - 5p states are pushed up in energy towards the Zn 4s derived conduction bands by p-d interaction.



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Table 1: Calculated direct-band gap for zincblende structure of ZnTe, compared with other theoretical calculations and experimental results.

ZnTe	Calculations	Direct band gap (eV) at Γ point
ZB-phase	Present work using EV-GGA	1.60
	Present work using GGA	1.2
	Present work using LDA (TB-LMTO)	0.28
	Theory [Ref.28]	1.32
	Theory [Ref.29]	1.32
	Theory [Ref.30]	1.33
	Theory [Ref.12]	1.02
	Experimental [Ref.32]	2.39
	Experimental [Ref.31]	2.39

Moreover, band gaps are found to be much less than the earlier published experimentally observed values, which may be due the fact that in the present case the calculations have been carried out at 0 K while the reported experiments have been performed at room temperature. This lower value may also be confirmed due to the fact that the LDA underestimates the band gap value in case of TB-LMTO -LDA calculations as compared to GGA and EV-GGA calculations. There are three important independent elastic constants C_{11} , C_{12} , and C_{44} for a cubic crystal to determine the internal properties of material. A stable cubic crystal should match with the conditions: $C_{11}-C_{12}>0$, $C_{44}>0$, $C_{11}+2C_{12}>0$. The calculated elastic constants are also found to obey the cubic stability conditions including the fact that C_{12} must be smaller than C_{11} can be seen in the Table 2. Further, we have also calculated other elastic constants like shear modulus G, Young modulus E, anisotropic parameter A, Kleinmann parameter ξ and Poisson ratio γ for both ZB and RS structures of ZnTe and presented with the published available experimental data and previous theoretical calculations in the Table 2. The calculated values of elastic constants are found in reasonable agreement with the available theoretical and experimental results in ZB phase. Whereas, to the best of knowledge, there is no experimental data for elastic parameters available at high pressure RS phase of ZnTe in the literature and hence comparison could not be possible. However, the calculated results may be very useful for further experimental and theoretical study of the work at high pressure RS phase.

Table 2: The calculated elastic constants C_{ij} (GPa), bulk modulus B (GPa), shear modulus G, Young modulus E, anisotropic parameter A, Kleinmann parameter ξ and Poisson ratio γ for ZnTe in the ZB and RS structures.

ZnTe	Calculations	C_{11}	C_{12}	C_{44}	B	G	E	A	ξ	γ
ZB phase	Present work	56.86	40.60	35.75	46.02	19.92	52.22	0.971	0.796	0.310
	Theory [Ref.33]	71.0	40.3	46.0	-	-	-	-	-	-
	Theory [Ref.34]	64.7	36.0	40.1	45.6	26.6	66.7	2.79	-	0.256
	Theory [Ref.35]	98	31.8	23.3	-	-	-	-	-	-
	Exp. [Ref.36]	71.3	40.7	31.2	-	-	-	-	-	-
RS phase	Present work	95.87	31.60	7.83	53.03	14.38	39.56	-0.50	0.474	0.375
	Others	-	-	-	-	-	-	-	-	-



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IV. CONCLUSIONS

Band structure, DOS and elastic constants for the ZnTe compounds, using the TB-LMTO and FP-LAPW methods are reported. The present calculations show their formation of RS structure at high pressure. The calculated value of direct band gap is compared with the previous results available in the literatures. We also analyzed that it undergo metallization on pressure with the band closure between G and X high symmetry points. The calculated elastic constants are also found in good agreement with the experimental results available.

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