

Calculations of electronic band structure and optical properties of HgTe under pressure

P K Saini^{a,*}, D Singh^c & D S Ahlawat^a^aDepartment of Physics, Chaudhary Devilal University, Sirsa 125 055, India^bDepartment of Physics, Government P G College, Hansi 125 033, India^cDepartment of Physics, M M University, Ambala 133 203, India*Received 17 March 2017; accepted 21 May 2017*

The electronic band structure and optical properties of HgTe have been reported using the full potential linearized augmented plane wave (FP-LAPW) method based on density functional theory. In this approach, generalized gradient approximation (GGA) and Engel-Vosko generalized gradient approximation (EV-GGA) have been used for the exchange correlation potential in the calculations. The electronic band structures have been calculated to discuss the electronic properties and optical properties of the compound. Moreover, optical properties including dielectric functions, absorption, optical conductivity, refractive index, reflectivity and energy loss spectrum have been obtained and analyzed in details within the energy range up to 14 eV. The obtained results have been compared with the previous calculations and available experimental data. Overall good agreement is found.

Keywords: Electronic band structure, Elastic constants, Optical properties, WIEN2k

1 Introduction

Recently, there has been much interest in various properties of II-VI binary semiconductor compounds and alloys¹⁻⁴. Among these materials, HgX (where X= S, Se and Te) compounds are found to be very important materials due to their technological applications particularly in optoelectronics devices. There have been several experimental and theoretical studies on this materials⁵⁻⁹. Although density-functional theory DFT methods have proved important for studying high-pressure phases¹⁰, only a few such studies of mercury chalcogenides have been reported up to now¹¹⁻¹³. In this paper we have presented the results of a first-principles DFT study of electronic band structure and optical properties of the zinc blende and rocksalt structure of HgTe, to the best of our knowledge, have not been considered theoretically before, particularly at high pressure. In addition to this work, we also have discussed the common trends and the differences in band structures and optical properties of HgTe at ambient and high pressure.

2 Method of Calculation

The calculations are performed using the scalar relativistic FP-LAPW approach within DFT, as

implemented in the WIEN2K code¹⁴. The exchange-correlation energy of electrons is described in the generalized gradient approximation (GGA) within the parameterization of Perdew-Burke-Ernzerhof^{15,16} (PBE) to calculate the total energy. Moreover, the Engel-Vosko generalized gradient approximation (EV-GGA) formalism is also applied so as to optimize the corresponding potential for electronic band structure calculations in order to improve the band gap¹⁷. In these calculations, 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 remaining space of the unit cell (interstitial region). The R_{MT} for Hg and Te were chosen for the expansion of the wave functions in the interstitial region in such a way that the spheres did not overlap. The basis functions in the interstitial region were expanded up to $R_{MT} \cdot K_{MAX} = 7.0$ inside the atomic spheres for the wave function to get the total energy convergence. The maximum value of l was taken as $l_{max} = 10$ in the muffin-tin spheres, while the charge density is Fourier expanded up to $G_{max} = 14 \text{ a.u.}^{-1}$. The atoms are taken at the positions of Hg(0,0,0) and Te(1/4,1/4,1/4) for ZB phase and Hg(0,0,0) and Te(1/2,1/2,1/2) for RS phase of HgTe, respectively. Accurate convergence

*Corresponding author (E-mail: pawansaini2005@gmail.com)

criteria have been considered for all the above mentioned parameters.

3 Results and Discussion

3.1 Band structure

The calculated total energies are fitted according to Murnaghan equation of state¹⁸ (EOS) to obtain the equilibrium lattice constant. The optimized lattice constant of HgTe is obtained as 6.67 Å in zinc blend phase whereas it is found 5.78 Å for RS phase under the application of high pressure at about 17.09 GPa. Using these equilibrium lattice parameters, we have calculated and plotted the band structure at ambient pressure ZB phase as well as high pressure RS phase of HgTe by use of FP-LAPW method with in EV-GGA scheme. The derived electronic band structures were further used to study other properties like band gap and optical properties etc. The electron dispersion curves along the high symmetry directions in the brillouin zone for zinc blende and rocksalt phase of HgTe are plotted in Fig. 1(a) and 1(b) within the EV-GGA schemes, respectively. The Fermi level (E_F) was selected to position at 0 eV and coincides with the top of the valence band. The calculated band structure profiles for both the phases have been found similar. However, a little difference in the band location on energy scale may be seen as in the case of ambient phase. It can be seen that the lowest lying band in the valence band region are positioned at -11.0 eV for both the phases. It mainly arises from the s states of Te while the bands in valence region just below E_F

are predominantly due to s and p orbital of Hg. The conduction band above E_F is mainly due to d states of Hg which hybridize with p and d states of Te.

Similarly, the electron dispersion curves along the high symmetry directions for high pressure rock salt (B1) phase of HgTe is plotted and analyzed in Fig. 1(b). The band structure of B1 phase of HgTe by FP-LAPW method has also not been reported to the best of our knowledge. It can be seen that the lowest-lying band in the valence band region mainly arises from the s states of Te while the bands in valence region just below E_F are predominantly due to s and p orbital of Hg. The conduction band above E_F is mainly due to d states of Hg which hybridize with p and d states of Te. Furthermore, as we can see from the figure, in high pressure rock salt (B1) phase of HgTe, this hybridization interaction of the d electrons with anion p electrons leads to a repulsion of the involved states. An increased width of the upper valence bands and a decrease in the band gap has been observed. The later may occur because of Te- p states are pushed up in energy towards the Hg - s derived conduction bands by p - d interaction. Therefore the d bands show remarkable dispersion and separate against in two groups of bands. When there is stronger p - d interaction in HgTe then there is increase in the d band width. The metallic character increases under high pressure RS phase due to crossing of conduction band at Fermi level in different high symmetric directions in band structures. Thus, comparing LAPW-EV-GGA calculations in the zincblende and rock salt

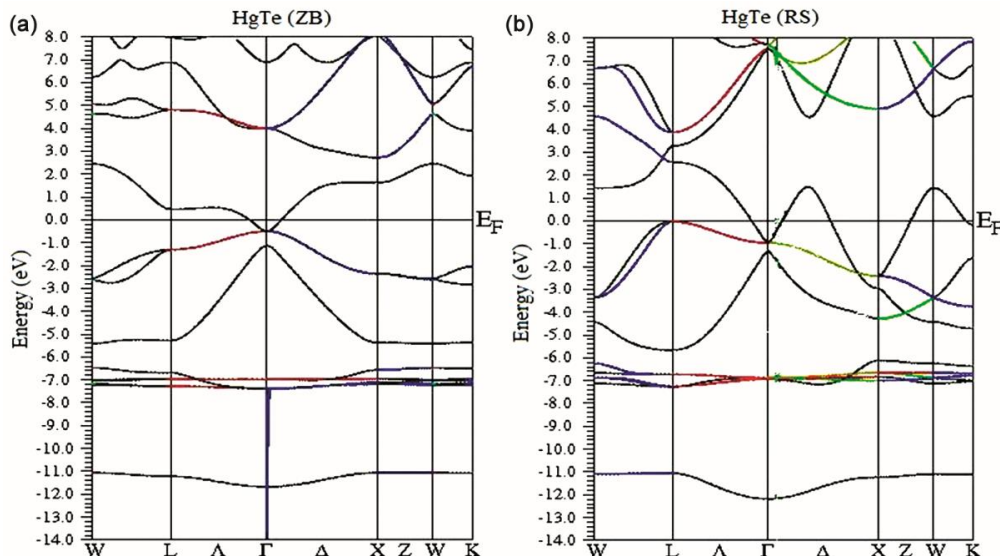


Fig. 1 – (a) Band structure of HgTe in zinc-blende phase using EV-GGA and (b) band structure of HgTe in rocksalt phase using EV-GGA

phases, one see that the band structures are very similar, except the bandgap at Γ point. The calculated value of band gap for ZB phase using EV- GGA schemes are shown in the Table 1 along with the previous theoretical reported work¹⁹ and experimental values^{20,21}. Our calculated band structure of HgTe indicate a negative direct band gap equal to -0.543 eV and has been found in good agreement with the available experimental results.

3.2 Optical properties

The optical properties are obtained from the complex dielectric function $\epsilon_{\alpha\beta}(\omega) = Re \epsilon_{\alpha\beta}(\omega) + i Im \epsilon_{\alpha\beta}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, which is related mainly to the electronic structure of solid. The imaginary part $\epsilon_2(\omega)$ of the dielectric function is calculated from the total density of states and the momentum matrix elements between the occupied and unoccupied Eigen states of the material. The real part $\epsilon_1(\omega)$ of the frequency dielectric function can be computed from $\epsilon_2(\omega)$ using the Kramer-Kronig relationship^{22,23}. Using the dispersion of real and imaginary parts of dielectric functions one can calculate dispersion of other optical parameters such as, optical conductivities, absorption

coefficient, reflectivity, dielectric constant, refractive index, extinction coefficient and loss function. Figure 2(a) displays the dispersion of the real and imaginary parts of dielectric function, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, for ZB HgTe. The observed spectra $\epsilon_2(\omega)$ show the threshold energy occurring at 0.12 eV. It may be seen that the three major energy spectral peaks situated at 2.01, 3.9 (principal peak), and 6.21 eV. The maximum peak height in $\epsilon_2(\omega)$ at about 2.01 eV is lying at 13.3, which corresponds to the transition from occupied Hg-*s* to unoccupied Te-*s* band states. The calculated static dielectric constant $\epsilon_1(0)$ without any contribution from lattice vibration is equal to about 18.4 as shown in Fig. 2(a) The wide band energy gap yields a smaller value of $\epsilon_1(0)$. Our calculated value of static dielectric constant is presented in Table 2. It may be observed that a smaller energy gap yields a larger $\epsilon_1(0)$ value. Figure 2(b) displays the calculated real $\epsilon_1(\omega)$ and imaginary dielectric function $\epsilon_2(\omega)$ for the RS HgTe compound. It may be seen that the $\epsilon_2(\omega)$ shows a large peak (positioned at 2.3 eV) for HgTe for the RS phase.

Figure 3(a) displays the calculated absorption spectrum $\alpha(\omega)$, for the HgTe compound in ZB phase and RS phase. The absorption edge starts at about 0.19 eV in the spectrum. The absorption spectrum $\alpha(\omega)$, shows a very intense absorption at about 6.49 eV, which may be due to excitations of photons. In case

Table 1 – Calculated direct-band gap for zinc blende phase of HgTe along with the other theoretical and experimental work

Material	Calculations	Direct band gap(eV) at Γ point
HgTe	Present work (using EV-GGA)	-0.543
	Theory ^a	-0.84
	Experimental ^b	-0.30
	Experimental ^c	-0.3

^aRef¹⁹, ^bRef²⁰, ^cRef²¹

Table 2 – Calculated values of static dielectric constant for zincblende and rocksalt phases of HgTe

Compound	Phase	Calculation	Static dielectric constant, $\epsilon_1(0)$
HgTe	ZB	Present work	18.4
		Others	-
	RS	Present work	30.2
		Others	-

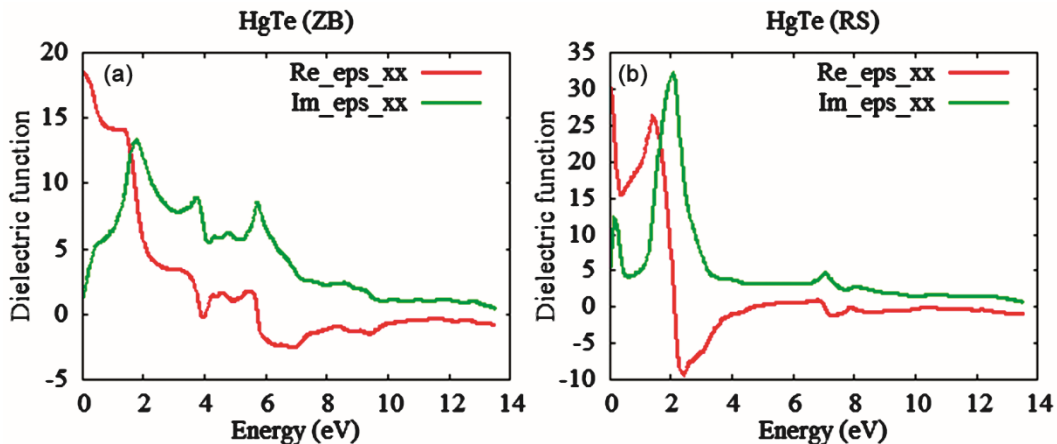


Fig. 2 – (a) Real $\epsilon_1(\omega)$ and imaginary $\epsilon_2(\omega)$ dielectric function of ZB HgTe and (b) real and imaginary $\epsilon_2(\omega)$ dielectric function of RS HgTe

of RS phase, the absorption edge starts at about 0.67 eV in the spectrum. The highest peaks located in the spectrum are due to the transition of electrons along high symmetry directions. It was observed that the occupied electron states are excited to unoccupied electron states in upper Fermi level by absorbing photons or by application of high pressure. This inter-band transition is called optical conduction also known as Drude transition. The spectrum in Fig. 3(b) shows that the optical conduction starts with energy of about 0.22 eV and 0.98 eV for ZB and RS phases of HgTe, respectively. The optical conductivity is found to be increased with the increase of photon energy. After attaining the maximum value of optical conductivity at 6.5 eV for ZB and 2.3 eV for RS phase, it starts to decrease with increase of photon energy. The excited electrons have no enough energy to pass the energy gap, and transfer to the conduction band. Thus, the band gap energy is the main reason of starting optical conduction $\sigma(\omega)$.

Further, Fig. 4(a) shows the calculated frequency dependent reflectivity $R(\omega)$ for the HgTe compound in

ZB and RS phase. A strong reflectivity maximum has been observed between the energy range 6.2 eV–10.3 eV and 2.1 eV–3.3 eV for ZB and RS phase, respectively, which may be arises due to the inter-band transitions. Further, A strong reflectivity minimum is seen at energies ranging from about 8.1–10 eV and 5.2–10.6 for ZB and RS phase, respectively, which representing a collective plasma resonance. The depth of the plasma minimum can be calculated by the imaginary part of the dielectric function at the plasma resonance and gives the degree of overlap between the inter-band absorption regions. The calculated refractive index for the ZB and RS HgTe compound are shown in Fig. 4(b). It can be noticed that the refractive index is significant only up to 1.7 eV for ZB and 1.62 eV for RS phase, beyond these energy range it drops sharply. The theoretically calculated static refractive index 4.3 for ZB and 5.5 for RS HgTe are displayed in Table 3. There are no experimental and theoretical results available on refractive index in the literature for comparison of our calculated values of refractive index of ZB and RS HgTe. The electron

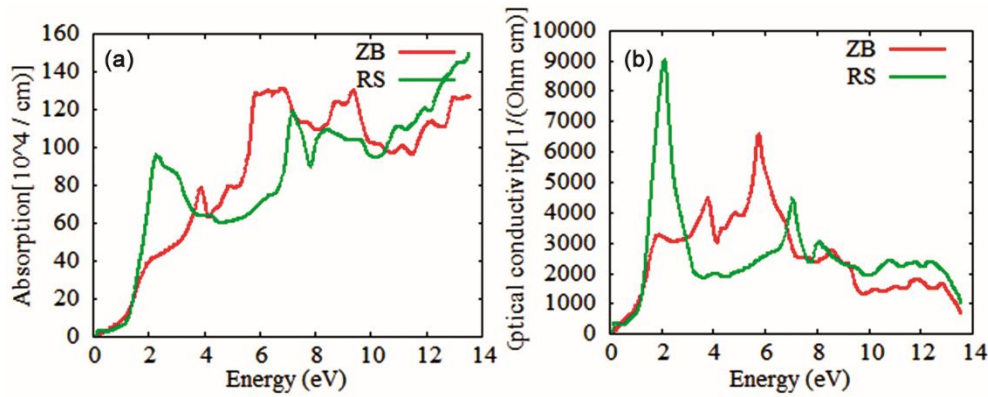


Fig. 3 – (a) Absorption $\alpha(\omega)$ of HgTe in ZB and RS phase and (b) optical conductivity of HgTe in ZB and RS phase

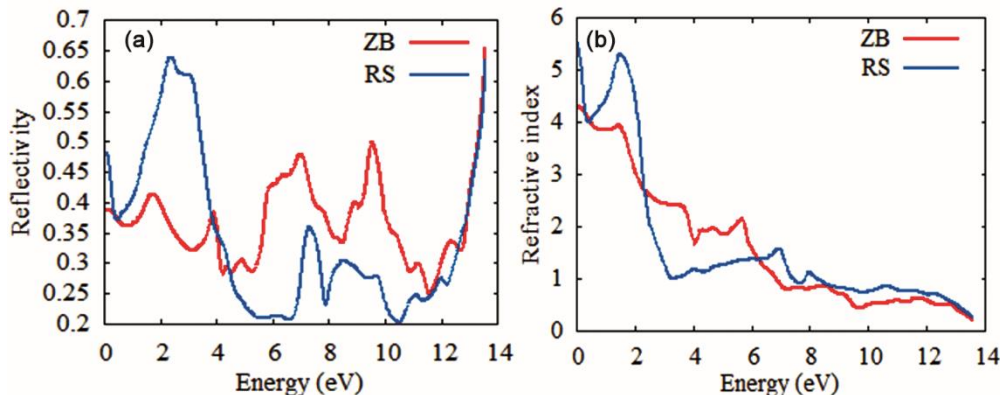


Fig. 4 – (a) Reflectivity $R(\omega)$ of HgTe in ZB and RS phase and (b) refractive index of HgTe in ZB and RS phase

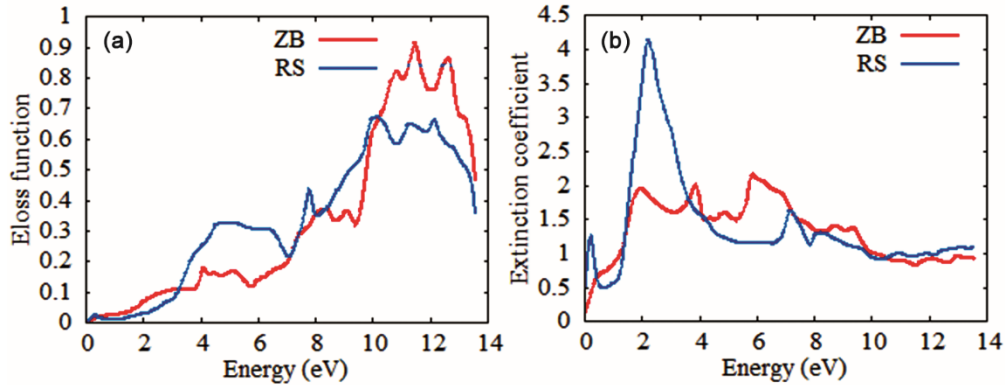


Fig. 5 – (a) Eloss function of HgTe in ZB and RS phase and (b) extinction coefficient of HgTe in ZB and RS phase

Table 3 – Calculated static refractive index for zincblende and rocksalt phases of HgTe

HgTe	Calculations	Static refractive index
ZB phase	Present work	4.3
	Others	-
RS phase	Present work	5.5
	Others	-

energy loss spectroscopy (EELS) is very useful technique for investigating various aspects of study for the materials including non-scattered and elastically scattered electrons (zero Loss). The energy losses are mainly due to a complicated mixture of single electron excitations and collective excitations (plasmons) at some intermediate energy range (typically 1 to 50 eV). The single electron excitation peaks positions are related to the joint density of states between the conduction and valence bands, whereas the energy required for the excitation of bulk plasmons depends on the electron density. The electrons, which are responsible to excite the atomic electrons of the outer shell is called valence loss or valence inter-band transitions. Inter-band transitions consist mostly of plasmon excitations and the scattering probability for volume losses is directly associated to the energy loss function. Figure 5(a) shows that the most prominent peak in the energy loss spectrum is associated with the Plasmon peak and located at 11 eV for ZB phase and 12.1 eV for RS phase of HgTe. The corresponding frequency associated to Plasmon peak is called plasma frequency²⁴, $\hbar\omega_p$.

The extinction coefficient $k(\omega)$ is calculated and plotted in Fig. 5(b) of HgTe for both ZB and RS phase, respectively. The local maxima of the extinction coefficient $k(\omega)$ corresponds to the zero of $\epsilon_1(\omega)$ (6.1 eV) for HgTe in ZB phase and 2.2 eV for HgTe in

RS phase, respectively. The difference in the spectra of the extinction coefficient for ZB and RS indicates that there is a shifting of the maxima peak towards lower energy side for RS and increase in peak height. To the best of our knowledge, we have not found any experimental and theoretical data available in the literature especially at high pressure RS phase to compare our results of HgTe for optical dispersions. However, the calculated results of optical dispersion may be helpful for future predictions about HgTe compound at ambient as well as high pressure RS phase and perform more suitable experiments in this direction for further research work on this material.

4 Conclusions

In this work we have studied the band structure and optical properties of HgTe compound using the first principles calculations. The calculated results for electronic band structures show that these compounds have inverted band structures. It is also observed that HgTe compound having semi-metallic nature in ZB phase. The metallic character is found to be increased under high pressure RS phase due to crossing of conduction band at Fermi level in different high symmetric directions in band structures. The theoretically obtained values of static dielectric constants $\epsilon_1(0)$ and static refractive index are found to be increased with the increasing metallic behavior of the compound. Furthermore, we have also calculated the other optical properties like dielectric function, absorption, optical conductivity, reflectivity, refractive index, loss function and extinction coefficient for ZB and RS HgTe in details. The calculated results could be useful for further experimental investigations about this compound.

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