



ELECTRONIC AND OPTICAL PROPERTIES OF CDSE AT HIGH PRESSURE

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ABSTRACT

Ab-initio calculations of some electronic & optical properties of CdSe at high pressure have been performed using the density functional theory (DFT) based full-potential linear augmented plane wave (FP-LAPW) method within generalized-gradient-approximation (GGA). Initially, the structural properties viz. total energy and lattice parameters of Cd Se are calculated for both the ambient and high pressure phases and are compared with earlier obtained results. Then using these structural parameters we carried out electronics structural and optical properties of Cd Se (like electronic band structure, density of states, optical conductivity etc) at ambient & high pressure. The calculated parameters are found to be in good agreement with the available experimental and other theoretical results at ambient pressure, whereas at high pressure some of our high pressure results could not be compared because of unavailability of experimental data.

Keyword: *Electronic band structure, DFT, FP-LAPW, CdSe, optical properties*

I. INTRODUCTION

Cadmium Selenide (CdSe) semiconductor material has been of interest because of its enormous technical importance, particularly in solar cells and in fabrication of other optoelectronics devices [1-7]. Depending on growth condition, this material exists in hexagonal wurtzite structure (WZ) or cubic zincblende (ZB) structure almost at ambient pressure, but transforms to rock salt (RS) structure and other phases at high pressure [8-14]. Although due to its technological applications, this material has been studied both experimentally and theoretically in last decades, but more of them are experimental and or theoretical at ambient conditions. The Ab-initio theoretical studies of CdSe at high pressure for such properties are relatively lacking in the literature which motivated us to take up this problem. And so, in the present work, we report theoretical studies of electronic and optical properties of CdSe at high pressure using the density functional theory (DFT) based full-potential linear augmented plane wave (FP-LAPW) method within generalized-gradient-approximation (GGA). This paper is organized as follows. The method of the calculation is described in section II. The calculated results are described and discussed in the Section III. Finally, section VI contains the summary of obtained results and conclusion.

II. METHODOLOGY

We have carried out the computational work using the density functional theory (DFT) based full-potential linear augmented plane wave (FP-LAPW) method [15-20]. The exchange-correlation potential has been



calculated using GGA within the parameterization of Perdew-Burke-Ernzerhof (PBE) [20-21]. The unit cell is partitioned into non-overlapping muffin-tin spheres around the atomic sites and in interstitial region. In these two types of regions, different basis sets are used. The wave function and potential are expanded in spherical harmonic functions inside non overlapping spheres and a plane wave basis set in the remaining space of the unit cell (interstitial region) is used. We have chosen the R_{MT} for Cd=2.38 a.u., and for Se= 2.33 a.u. respectively which were chosen in such a way that the spheres did not overlap. The plane wave cut off of $K_{max} = 8.0/R_{MT}$ (R_{MT} is the smallest muffin-tin radius) is chosen for the expansion of the wave functions in the interstitial region. A mesh of 72 special k-points was taken in the irreducible wedge of the Brillouin zone for both ambient & high pressure phases of CdSe. In the present calculations, the core states are treated fully relativistically while the valence and semi core states are treated semi-relativistically (ignoring the spin-orbit coupling). The self-consistent is considered to be converged when the total energy of the system is stable within 10^{-5} eV. We have done our calculations by specifying the atomic positions, for zinc-blende structure, Cd atom is at the position of (0,0,0) and Se atom sitting at the position of (1/4,1/4,1/4) in primitive unit cell while for the case of rock-salt structure, Cd atom is at the position of (0,0,0) and Se atom is at the position of (1/2,1/2,1/2) in the primitive unit cell. Further, the optical properties can be obtained from the complex dielectric function. It can be expressed as

$$\epsilon_{\alpha\beta}(\omega) = \text{Re}\epsilon_{\alpha\beta}(\omega) + i\text{Im}\epsilon_{\alpha\beta}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (1)$$

The imaginary part of the dielectric tensor can be computed from the electronic band structure of solid. The dielectric function, $\epsilon_2(\omega)$, is strongly correlated to the joint density of states (DOS) and transition momentum matrix elements. The following real and imaginary parts of dielectric functions can be used to calculate the other optical parameters [22-24].

$$\text{Im}\epsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2\omega^2} \sum_{c,v} \int_0^\infty dk \langle c_k | P^\alpha | v_k \rangle \langle v_k | P^\beta | c_k \rangle (\epsilon_{c_k} - \epsilon_{v_k} - \omega) \quad (2)$$

$$\text{Re}\epsilon_{\alpha\beta}(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \text{Im}\epsilon_{\alpha\beta}(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (3)$$

Where c_k and v_k are the electron states in the conduction and valence bands, respectively, with the wave vector k . The optical conductivity is given by the relation

$$\text{Re} \sigma_{\alpha\beta}(\omega) = \frac{\omega}{4\pi} \text{Im}\epsilon_{\alpha\beta}(\omega) \quad (4)$$

A denser sampling of the BZ was required to calculate the optical properties of the sample and so a mesh of 3000 k-points was used.

III. RESULTS& DISCUSSIONS

In order to investigate the electronic and optical properties of CdSe at ambient & high pressure, first of all to determine ground state properties, the total energies are computed for different cell volumes. The calculated total energies are then fitted to Murnaghan or Birch's equation of state (EOS) [25] to obtain the equilibrium lattice constants. The variations of the calculated total energy with volume for CdSe at ambient and high pressure phases are shown in Fig. 1(a) & 1(b) respectively.

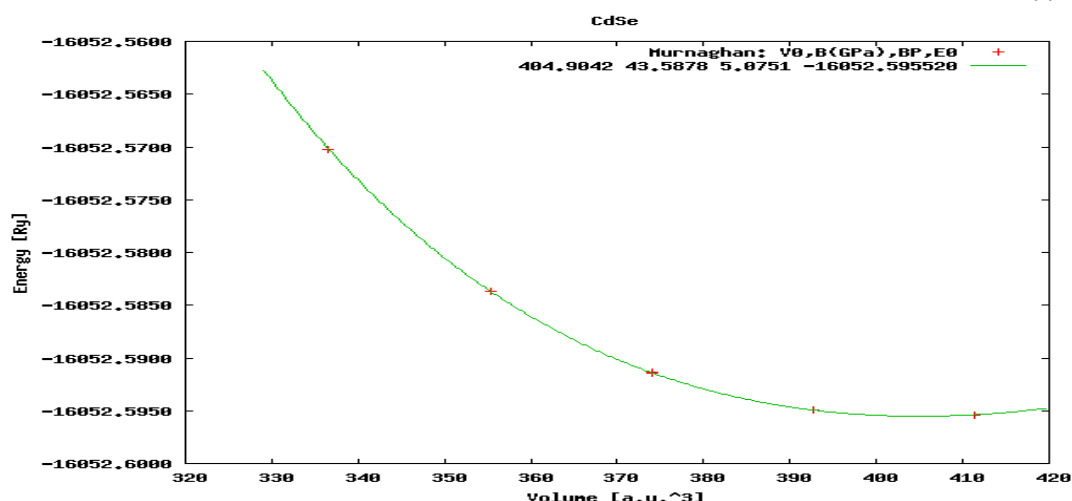


Fig. 1(a): Energy vs volume for CdSe ambient pressure ZB phase

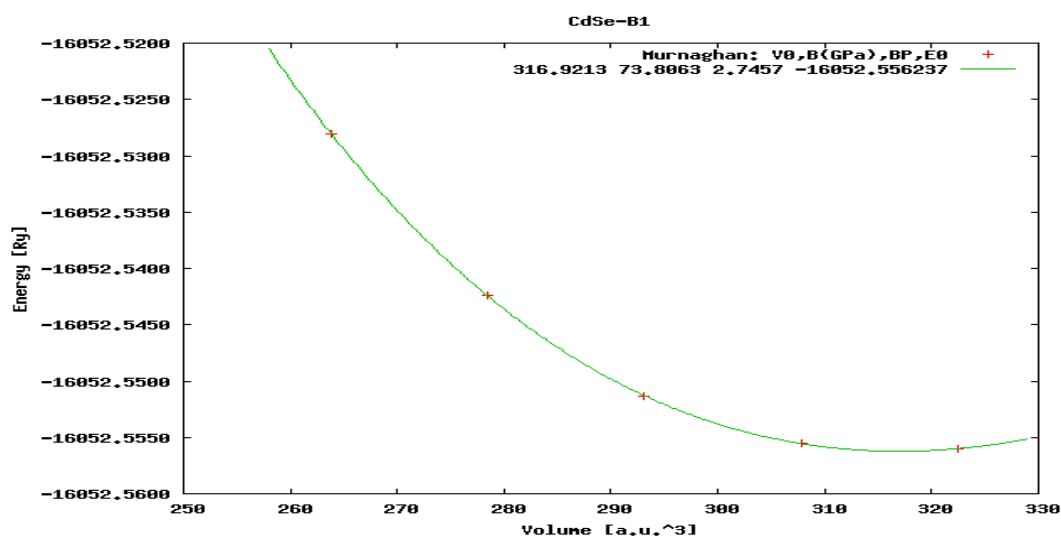


Fig.(1b): Energy vs volume for High Pressure RS Phase of CdSe

Our calculated optimized equilibrium lattice constant for CdSe is 6.21 Å in ambient pressure ZB phase and 5.72 Å for high pressure RS phase which agree well with general trend (i.e. it decreases with increase in pressure). When we compared our results with earlier reported results, it is found that these results are in good agreement with the earlier reported experimental results as comparatively to earlier reported theoretical results [26-28]. However, still earlier reported experimental results are found slightly underestimated as comparatively to our calculated results and earlier reported theoretical results which may be explained on the fact that GGA calculated structural results always overestimate the values [27-28].

Further, using our above mentioned optimized structural parameters we have calculated and plotted the electronic band structure for ambient and high pressure phases of CdSe. The calculated electronic band structure for ambient pressure zinc blende (ZB) phase of CdSe using FP-LAPW within GGA for which the corresponding electron dispersion curves along the high symmetry directions in the Brillouin zone are plotted in Fig. 2.0(a). The energy zero is taken at the valence band maximum for reference. The overall profile of our calculated electronic band structure of ambient pressure ZB phase of CdSe is found to be similar to the band structure of ambient pressure phase of CdSe calculated by first principles orthogonalized linear-combination of

atomic-orbitals (OLCAO) method [29]. However, to the best our knowledge there is no experimental data to compare. In order to indicate the overall profile of the different bands of CdSe, we have identified the bands with their corresponding electronic states. It can be seen that the lowest-lying band in the valence band region (which appears at ~ -11.6 eV) mainly arises from the 4s states of Se while the bands in valence region just below E_F are predominantly due to Cd-5s and Se-4p orbitals. The conduction band above E_F is mainly due to 4d states of Se which hybridize with 5p and 5d states of Cd. Fermi energy is shown by dotted line.

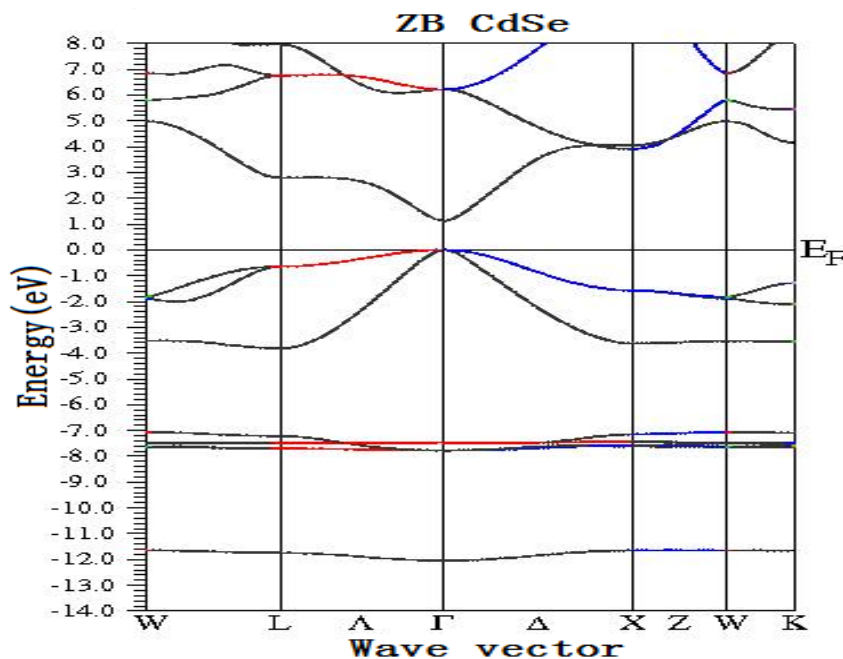


Fig.2(A) Electronic Band Structures For Ambient Pressure Zinc- Blende Phase of Cdse

Similarly, we calculated the electronic band structure for high pressure rock salt (RS or B1) phase of CdSe using FP-LAPW within GGA for which the corresponding electron dispersion curves along the high symmetry directions in the Brillouin zone are plotted in Figure 2(b). In this case overall profile of electronic band structure is found to be similar to the band structure of ambient pressure ZB phase of CdSe (calculated by pseudo-potential approach) with little change in the positions of the different bands [29]. However, to the best our knowledge there is no experimental or theoretical data of high pressure RS phase CdSe to compare. Here also Fermi Energy is shown by dotted line and it can be seen that the lowest-lying band in the valence band region (which appears at ~ -12.0 eV) mainly arises from the 4s states of Se while the bands in valence region just below E_F are predominantly due to Cd-5s and Se-4p orbitals. The conduction band above E_F is mainly due to 4d states of Se which hybridize with 5p and 5d states of Cd. However, in this case, high pressure effect leads in increased width of the upper valence bands region due to which Se-4p states are pushed up in the energy towards the Cd-5s changing the band gap.

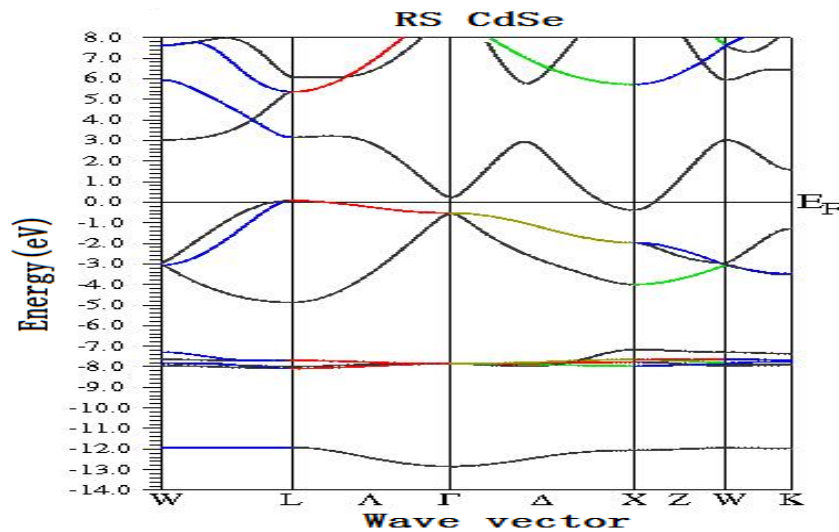


Fig. 2 (b) Electronic band structures for ambient pressure zinc-blende phase of CdSe

Further, to calculate optical properties of CdSe in both ambient & high pressure phases, the imaginary part of dielectric tensor is computed from the electronic band structure of CdSe for both the cases. The real part of the dielectric function is extracted from the imaginary part using the Kramers-Kronig relation. And finally, the optical conductivity is calculated using dielectric function which is derived from electronic properties. Calculated optical conductivity is shown in Fig. 3(a) and 3(b) for ambient & high pressure phases of CdSe respectively.

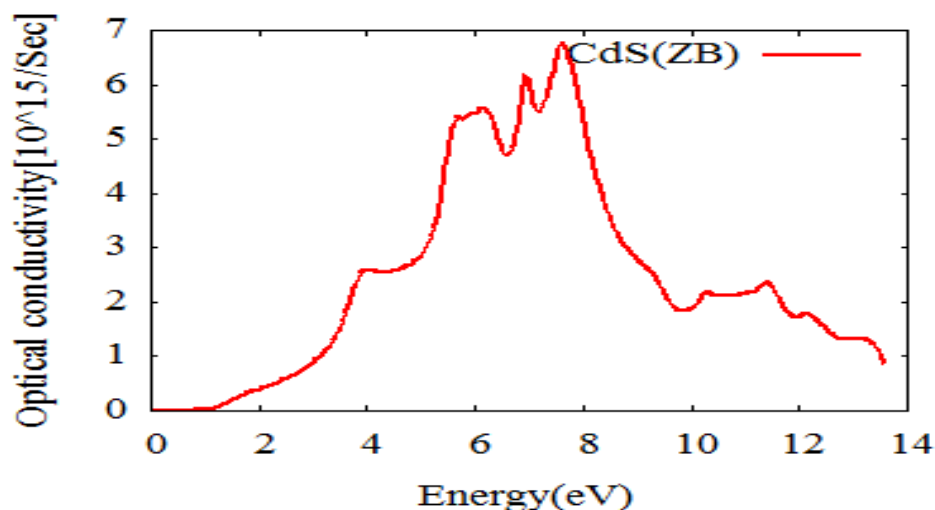


Fig. 3(a): Optical conductivity for ambient pressure ZB phase of CdSe

Occupied electron states are excited to unoccupied electron states by absorbing photons. This interband transition is called optical conduction (also called Drude transition) and photon absorption by electron is called interband absorption. As shown in the Figure 3(a), the optical conduction starts with energy of about 1.12 eV for CdSe in the ZB phase and by increasing photon energy, the optical conduction will rise. The reason of starting optical conduction $\sigma(\omega)$, from above said energy range, is the energy gap (as the excited electrons have not enough energy to pass the energy gap and transfer to the conduction band). To the best of our knowledge, there is no any earlier reported experimental results of the optical conduction $\sigma(\omega)$ of the CdSe compound in ambient

pressure phase and so comparison is not possible. Further, the Figure 3(b) shows the optical conduction $\sigma(\omega)$ for CdSe in the RS phase in which it can be seen that the overall structures in $\sigma(\omega)$,

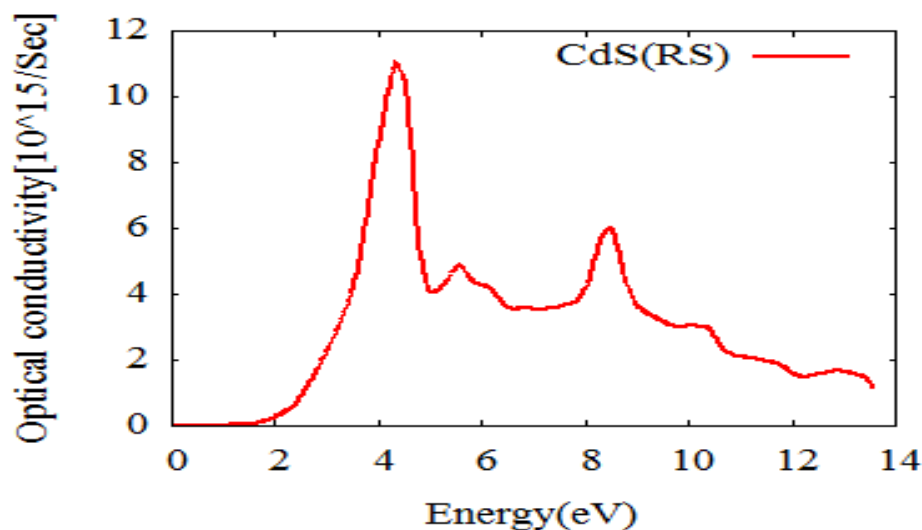


Fig.3(b): Optical conductivity for high pressure RS phase of CdSe

are shifted little towards the lower energies with increase in the peak heights as comparatively to that of ZB phase. It may be due to change in electronic band structure under high pressure as described in section 2. To the best of our knowledge, there is no any earlier reported experimental results of the optical conduction $\sigma(\omega)$ of the CdSe compound in RS phase and so comparison is not possible.

IV. CONCLUSIONS

The electronic and optical properties of CdSe have been investigated using the density functional theory (DFT) based FPLAPW method within GGA for both ambient & high pressure phases. Firstly, the structural properties like total energy and equilibrium lattice parameters have been calculated for both ambient and high pressure phases which are found in very well agreement with the earlier results and then using these structural parameters, we carried out electronics and optical properties of CdSe at ambient and high pressure. The calculated parameters are found in good agreement with available earlier reported experimental and other theoretical results. However, in some cases, there were no earlier reported results and so comparison could not be possible. These results may provide significant guidelines for further experimental investigation.

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