

# Electronic band structure and elastic properties of CdSe by DFT

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## Abstract

The electronic band structure and elastic properties of cubic (B3) cadmium selenide CdSe have been reported using the full potential linearized augmented plane wave (FP-LAPW) method. In this approach, generalized gradient approximation (GGA) and Engel-Vosko generalized gradient approximation (EV-GGA) were used for the exchange correlation potential. The calculated band structure and elastic properties have been compared with the previously reported results. The calculated results are found to be in good agreement with earlier reported results.

**Keywords:** Band structure, elastic properties, FP-LAPW, DFT, GGA

## 1. Introduction

In recent years, there has been a renewed interest in various properties of II-VI binary semiconductor compounds and alloys [1-4]. Among these materials, CdX (where X= S, Se & Te) semiconducting 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 these materials [5-8]. For example, K. O. Magnusson *et.al.* studied electronic band structure of CdSe experimentally by angle-resolved photoemission [7]. Similarly, Su-Huai et al. studied the structural and electronic properties of binary CdX (X= S, Se, Te) semiconductors using LDA [8]. Further, Ab initio calculations based on norm-conserving pseudopotentials and density functional theory using LDA, have been performed to investigate elastic, electronic and lattice dynamical properties of cadmium chalcogenides [9]. In these studies, LDA based theoretical calculated results of band gap are found to be lower than the experimental observed value of band gap which is quit common with such LDA based calculation[10].

This above mentioned problem of underestimating the LDA based calculated band gap may be solved using EV-GGA [11, 22] which motivated us to take up the problem with EV-GGA approach to improve the band gap. Since, we have carried out similar computational work for various materials with different methods [12-15], particularly, recently for some II-VI semiconducting compounds [16-18 ], and so, in the present work, as a part of this series of semiconducting compounds, we have investigated electronic band structure and elastic properties of binary semiconductor compound CdSe using full potential linearized augmented plane wave (FPLAPW) method within a framework of

density functional theory (DFT) with GGA and EV-GGA. The paper is organized as follows: Section 2 describes the method of calculation. Further, results and discussion are presented in section 3. Finally, results are concluded in section 4.

## 2. Method of Calculation

As mentioned above, the calculations are performed using the FPLAPW method within DFT, as implemented in the WIEN2K code [19]. The exchange-correlation potential has been calculated using GGA within the parameterization of Perdew-Burke-Ernzerhof (PBE)[20-21]. Moreover, the Engel-Vosko GGA formalism is applied so as to optimize the corresponding potential for band structure calculations to improve the band gap [11]. 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 interstitial region (IR) of the unit cell. The  $R_{mt}$  for Cd and Se were chosen in such a way that the spheres did not overlap.

To get the total energy convergence, the basis functions in the IR were expanded up to  $R_{mt\_Kmax} = 7.0$  inside the atomic spheres for the wave function. The maximum value of  $l$  were taken as  $l_{max} = 10$ , while the charge density is Fourier expanded up to  $G_{max} = 12 \text{ a.u.}^{-1}$ . The atomic positions for Cd (0, 0, 0) and Se (1/4, 1/4, 1/4) were taken in cubic CdSe B3 phase. For electronic and elastic properties calculation we have used 72 k-points in the irreducible Brillouin zone for structural optimization. The self-consistent calculations are considered to be converged only when the calculated total energy of the crystal converged to less than  $10^{-4} \text{ Ry}$ . In order to obtain the elastic constants of CdSe compound with cubic structure we have used a numerical first-principles calculation by computing the components of the stress tensor  $\epsilon$  for small strains, using the method developed by Charpin and integrated it in the WIEN2K code [19].

## 3 Results and Discussion

### 3.1 Band structure

To get the equilibrium lattice parameter we fitted Murnaghan equation of state which gives the value of equilibrium lattice parameter  $6.21 \text{ \AA}$ . Using this equilibrium lattice parameter, we have calculated and plotted the band structure of cubic B3 phase of CdSe. This self-consistent scalar relativistic band structure of CdSe is obtained within both the GGA and EV-GGA schemes. The electron dispersion curves along the high

symmetry directions in the Brillouin zone for B3 phase at ambient pressure are plotted in Fig. 1(a) &(b) within the GGA and EV-GGA schemes respectively. As mentioned in earlier section, it is well known fact that the LDA and the GGA usually underestimate the energy band gap [8-10, 22-23]. This is mainly due to the fact that LDA & GGA have simple forms which are not sufficiently flexible for accurately reproducing both exchange-correlation energy and its charge derivative. By considering these shortcoming, Engel and Vosko constructed a new functional form of the GGA which was able to reproduce the exchange potential better at the expense of less agreement as regards the exchange energy[11]. This approach, which is called the EV-GGA, yields a better band splitting and some other properties which mainly depend on the accuracy of the exchange-correlation potential. The band structure calculated using the GGA and the EV-GGA for CdSe was similar except for the value of their band gap which was higher within the EV-GGA.

The calculated band structure was found well in agreement with the already available experimental results on band structure [7]. In order to indicate the overall profile of the different bands of CdSe, we have identified the bands with their corresponding electronic states and the Fermi energy ( $E_F$ ) is identified by the dotted line. The lowest lying band shown in the graph arises mainly from Cd-s valence states. The upper valence bands lie above this band are due to p states with the top occurring at the point. The conduction band arises mainly from the Cd-d state with the minimum energy occurring at X points.

Further, the calculated band structures of CdSe indicate a direct band gap equal to 1.12 eV at  $\Gamma$  point. The calculated result of band gap (within E-V GGA formalism) is found better than earlier reported theoretical result and found to be in good agreement with earlier reported experimental result as shown in the table 1. However, the calculated result of the band

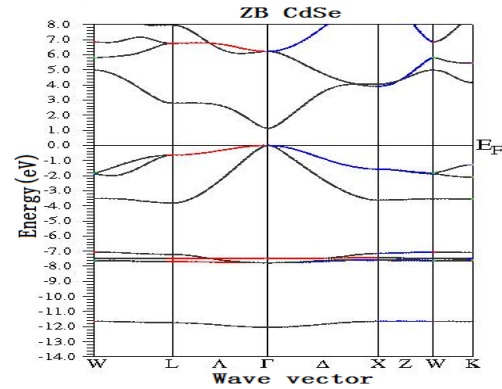


Fig. 1(a) Band structure using GGA; (b) band structure using EV-GGA

Table 1. The calculated direct-band gaps of CdSe (within EV-GGA) compared with the earlier reported theoretical and experimental work.

Material	Calculations	Direct band gap (eV) at $\Gamma$ point
CdSe	This work	1.12
	Theory (Ref. [24])	0.76
	Exp.(Ref.[25])	1.90

gap (within E-V GGA formalism) is still lower as comparatively to that of earlier reported experimental result, but this may be due to the fact that the calculation has been carried out at 0 K while the experiment has been performed at room temperature.

### 3.2 Elastic properties

As mentioned in section 2, in order to obtain the elastic constants of CdSe compound with cubic structure (B3) phase, we have used a numerical first-principles calculation by computing the components of the stress tensor  $\varepsilon$  for small strains [9]. A cubic crystal has only three independent elastic constants,  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ . Hence, a set of three equations is needed to determine all the constants. Therefore, only three types of strain must be applied to the crystal structure. The first equation involves the bulk modulus  $B$  of the crystal. For a cubic crystal, the bulk modulus can be defined as

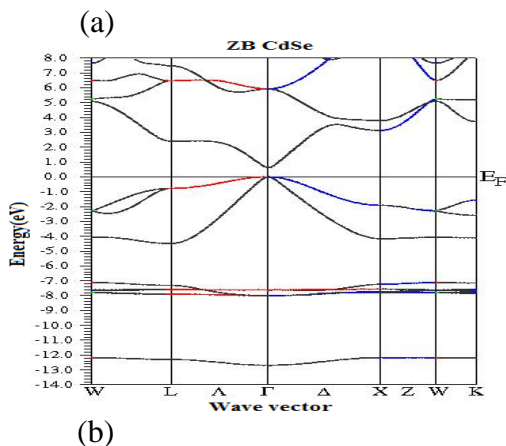
$$B = (C_{11} + 2C_{12})/3 \quad -- (1)$$

The second equation is associated with the relationship between  $C_{11}$  and  $C_{12}$  and can be obtained by applying a volume conserving tetragonal strain to calculate the shear elastic constant,  $C_s = (C_{11} - C_{12})/2$ . The strain tensor is given as

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

Here,  $\delta$  is the deformation parameter. The total energy of the system under the tetragonal shear strain is given by

$$E(\delta) = E_0 + 2C_s V_0 \delta^2 + O(\delta^4) \quad -- (3)$$



Where  $E_0$  is the energy of unstrained state,

$C_s$  is the cubic shear constant,

$V_0$  is the zero strain volume.

And the last equation is associated with  $C_{44}$ . A parabolic fit to the strain energy vs. strain  $\delta^2$  yields the result of shear elastic constant. To determine the pure shear elastic constant,  $C_{44}$  we use volume conserving tetragonal strain tensor which is given by the following relation

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

which yields the total energy as following

$$E(\delta) = E_0 + \frac{1}{2} C_{44} V_0 \delta^2 + O(\delta^4) \quad --(5)$$

Further, Kleinmann parameter is a significant parameter describing the relative position of the cation and anion sublattices using the following relation [26]

$$\xi = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}} \quad --(6)$$

The three elastic constants can be obtained from the second-order derivative of the total energy of the crystal under three type of strains, the volume change, the volume conserved rhombohedral and tetragonal strains. The elastic constants must satisfy the conditions of  $C_{11}-C_{12}>0$ ,  $C_{44}>0$  and  $C_{11}+2C_{12}>0$  for stable cubic phase. The above conditions are satisfied by ZB-CdSe structure, which proves it mechanical stable at ambient pressure. Our GGA calculated values for the elastic constants are compared with the earlier available results in table 2. To, the best knowledge, there is no experimental data available for compare the calculated elastic properties. However, it is clearly seen that our calculated results are found to be in good agreement (with 15-30% difference) with earlier available theoretical results which may due to the different approaches used in the calculations [9, 27].

Table.2 The Calculated elastic constants  $C_{ij}$  (GPa), bulk modulus B (GPa) and Kleinmann parameter  $\xi$  for CdSe in the B3 structure

	Method	C11	C12	C44	B	$\xi$
CdSe	This work	51.7	41.3	55.1	44.7	0.85
	Theory (Ref27)	65	49			
	Theory (Ref. 9)	88.1	53.6	27.4		

#### 4. Conclusions

The first principle calculations based on the density functional theory (DFT) within generalized gradient approximation (GGA) and EV-GGA have been performed to investigate, band structure and elastic properties of CdSe in B3 phase. The calculated band structure was found well in

agreement with the already available experimental results on band structure. The electronic band structure reveals the existence of band gap 1.12 eV at  $\Gamma$  point. Our calculated band gap using EV-GGA approach is found close to the experimental value as compared to other theoretical calculations. The little difference with earlier reported experimental result is explained with the fact that the calculation has been carried out at 0 K while the experiment has been performed at room temperature. For the elastic properties, our calculated results are found in similar to the other available reported results. The predicted values of elastic constants ( $C_{11}$ ,  $C_{12}$ , and  $C_{44}$ ) and bulk modulus B in phase B3 obey generalized elastic stability criteria.

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