First-principle investigations of structural and optical properties of CdSe

Y. Benkrima[a,*], D. Belfennache[b], R. Yekhlef[b,c], A. M. Ghaleb[d]
[a]*Ecole Normale Supérieure de Ouargla, 30000 Ouargla, Algeria*
[b]*Research Center in Industrial Technologies CRTI, P.O. Box 64, Cheraga, 16014 Algiers, Algeria*
[c]*Laboratory of Electrochemistry, Molecular Engineering and Redox Catalysis (LEIMCR) Department of Engineering Process, Faculty of Technology, Ferhat Abbas University Setif-1, Setif 19000, Algeria*
[d]*Department of Physics, College of Sciences, University of Kirkuk*

Our calculations have been done using the density functional theory (DFT). In fact, we were able to find the optical and structural properties of CdSe compound of cubic phase by using the previously mentioned theory. The pseudo-potential linearised augmented plane wave (PP-LAPW) method is applied to solve the Kuhn-Sham equations. The results are obtained using Generalized Gradient Approximation according to the scheme described by Perdew-Burke-Ernzerhof (GGA-PBE) as a types of exchange-correlation. Convergence of energy and charge has been verified, this is for the study of properties basic state of the compound. It was found that the calculated initial cell constants at equilibrium are very close to previous theoretical and experimental works. The electronic properties of the energy band structure and the total density of states confirmed that the CdSe compound has a direct energy gap estimated at 1.52 eV, which is very close to the previous applied results. The general results of the calculated optical properties including the imaginary part of the dielectric constant, absorption coefficient, reflectivity, optical conductance, refractive index, and extinction coefficient of cubic phase CdSe under the imposed conditions are discussed and compared with previous works. Through our results, new and important optical properties of the compound were highlighted, and then determine the areas of its use in the appropriate technological industries.

1. Introduction

Semiconductors are among the most common materials in various fields [1–3], especially those belonging to the cadmium chalcogenide family (CdS, CdSe and CdTe) which are very important materials to be used in various optoelectronic devices [4,5].It has two phases. The first has a cubic phase, which we call (sphalerite), while the second is a hexagonal phase, which we call (Wurtzite) [6, 7]. The first phase is unstable as it is mainly formed by the electrochemical process, while the other phase has a stable thermodynamic structure; it is formed either indirectly by cubic phase annealing or directly by using other methods of preparation [8]. In the compound, we find four cadmium (Cd) atoms linked to one selenium (Se) atom according to bonds of equal length between Cd and Se, the first successful attempt to develop CdSe crystals was by Frerichs, who made a gas-phase reaction between cadmium halide (Cd) and selenium (Se) [9].

CdSe is a promising photovoltaic material due to its direct energy gap and high absorption coefficient for absorbing light very efficiently and converting it into electrical energy. The CdSe compound has interesting properties and is suitable for many potential applications such as in solid-state devices such as solar cells, high-efficiency thin-film transistors, light-emitting diodes, and also gamma-ray detectors, as well as photoanodes in photoelectronchemical cells (PEC) and Electric lighting devices [10-12]. Most of theoretical investigations have focused on the properties resulting from the quantum confinement effect [13], in 1996, through photometric measurements

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on CdSe quantum dots, Ephroso's spherical confinement models and Wang's atomic models were revealed. In another study, Engelhardt et al. [14] studied room temperature laser structures of strain-compensated CdSe quantum island lasers. EranRabbani [13] reported in 2001 about static electricity of the passivatedCdSe nanoparticles. On the other hand, a significant number of works have also been done to study different properties of CdSe [13, 15, 16].

In this work, we will investigate the electronic properties and optic properties of CdSe by using the plane-wave pseudopotential density functional theory method through the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) program [17]. The results obtained are in agreement with the available experimental data and other theoretical results. In Sec. 2, we make a brief review of the theoretical method. The results and discussions are presented in Sec. 3.

2. Detail of calculations

These calculations are based on the first principles pseudopotential method in the frame work of DFT [18,19] the description of the interactions of the electronic exchange-correlation were treated by the (PBE) functional of the Generalized Gradient Approximation (GGA)[20] Which was implemented in the SIESTA code[17]. The input variables used are estimated to be about 400 eV chosen to cut off the power from the planar wave, and the Brillouin zones model is sampled through very dense ($6 \times 6 \times 6$) Monkhorst Pack K point grids. Our calculations of the self-consist field (scf) in the convergence criteria of total energy were set about 5×10^{-6}eV, and 0.005 Å is taken for the greatest ionic movement tolerance within the atoms. Since the atomic forces were less than 0.005 eV/Å, we also used the conjugate gradient technique to relax the structure. Our calculation of the parameters for the bulk CdSe constants are a = b = c= 6.18 Å, and that after the network parameters were left to relax to finally stabilize at the previously mentioned values, which agree very well and approach the theoretically or experimentally calculated values.

3. Results and discussion

3.1. Structural properties

We used density function theory (DFT) and Siesta code to calculate the initial cell constants. Where we found the following values: 6.18 Å for constant a, b and c, because it is a cubic structure, and the angle constants α = β = γ = 90.0°(Fig. 1). It is clear from the table 1, that the results we obtained are in agreement with the theoretical and experimental results mentioned in this table, which are described in the works [21-24]. We also calculated the percentage of error in the obtained values, in order to compare them to the experimental values taken as a reference. We found the error value in calculating the constant a is small, we notice through the calculated error values that we find that they are very small, which indicates the method of calculation is very accurate.

Table 1. Lattice constant (Å), bulk modulus B_0 (GPa), and its pressure derivative B_0' (GPa) of CdSe at 0 K and 0 GPa.

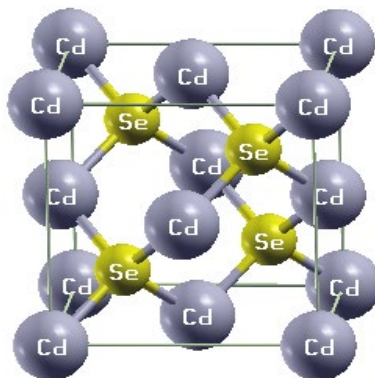| Works	a (Å)	B_0 (GPa)	B_0' (GPa)
Our work	6.18	58.962	4.73
Theoretical works	6.017 [21]	61.6	4.80
	6.178 [21]	47.6	4.70
	6.07 [22]	59.2	4.67
	6.05 [23]	65.12	4.20
Experimental work	6.05 [24]	53	/

Fig. 1. Cubic crystal structure of CdSe.

3.2. Electronic properties
3.2.1. Structure of energy bands

The Brillouin region defined in the cubic structure of the compound is the first building block in the study of the electronic properties of the physical body. The below graph shown in Figure 2 shows the results of the computed electronic study of the Brillouin region associated with the cubic phase of CdSe, After that, the study will be generalized to all parts of the compound.
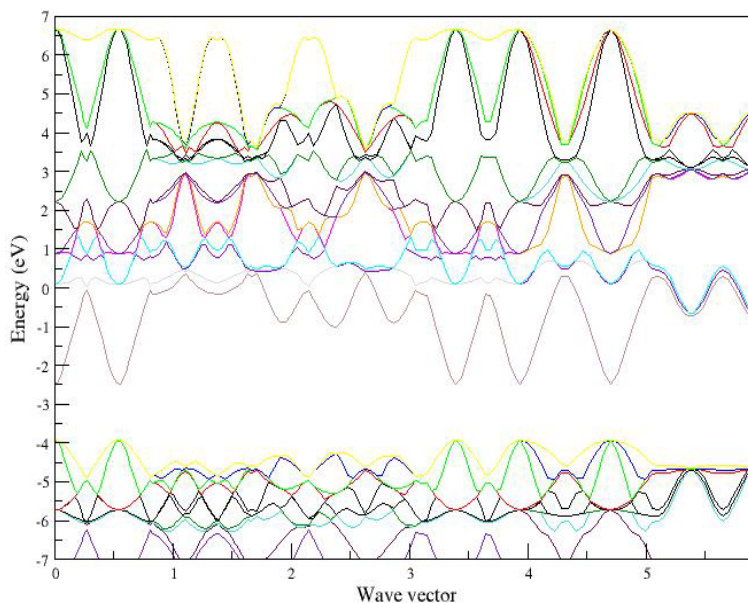

Fig 2. The structure energy band of CdSe phase.

Density functional theory (DFT) and generalized gradient approximation GGA were both used to determine the energy gap of the CdSe, This method, as the most recommended method, is also specialized for studying electronic structures of materials. The structure of the energy band for the CdSe compound shown in Fig. 2 was calculated

According to the previous figure, the highest peak in the valence band and the lowest in the conduction band are placed practically on the same line as the point τ (gamma), showing that CdSe has a direct gap of 1.52 eV using GGA approximation .The energy gap value was calculated based on the GGA approximation and compared with previous theoretical and experimental results as shown in Table 2.

Table 2. The energy gap Eg (eV).

Works	Eg (eV)
Our work	1.52
Theoretical works	0.417 [25]
	1.08 [26]
Experimental work	1.90 [24]

What can be seen is that the energy gap value was close to the experimental results shown in Table 2, while the results calculated for the energy bands structure based on the approximate GGA were larger than the previous theoretical results. This indicates that this simulation method used provides results that are close to reality. Although the theory of density function minimizes the value of the energy gap for compounds, in our calculations we were able to obtain good values close to reality, which indicates the precise program that was used in the study of the compound.

3.2.2. Electronic Density of States

In order to know the reason for the presence of states that formed the valence and conduction bands and to understand the nature of interactions between atoms of the studied compound, the total density of states (TDOS) of the CdSe compound were analysed using GGA, as shown in Fig.3.
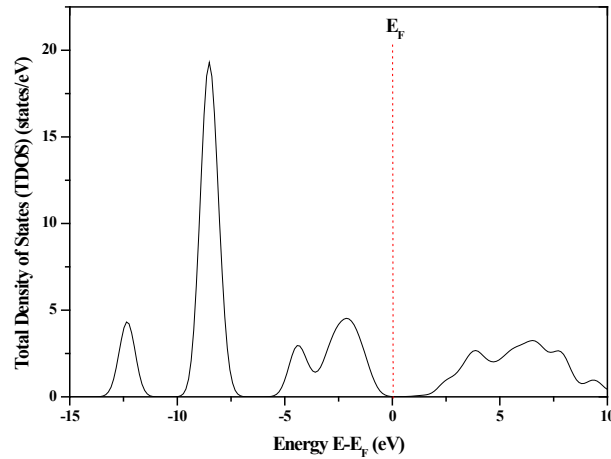

Fig. 3. Total density of states (TDOS) for CdSe.

Figure 3 shows that the calculated total density of states (TDOS) for CdSe has high values in the region near the fermi level. This means that the valence band is rich in electrons. The region extending from -10 to 0 eV is considered an active region and enjoys the mobility of electrons. In this region, two prominent peaks are recorded for the density of states, which are estimated at 4.92 (states/eV) and 19.84 (states/eV) corresponding to energies 2.39 eV and 8.73 eV respectively. The value of the energy gap can also be seen on the figure, which is estimated at 1.52 eV.

3.3. Optical properties

Ab Initio Calculations on Structural electronic and Optical Properties of CdSe in cubic Phase It is important to resort to optical properties in order to understand the nature of material and its usage in opto-electronic devices. The following function ε (w) can serve to describe the optical response of a material to the electromagnetic field at all energy levels:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \tag{1}$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$: real and imaginary part of the dielectric function. Real part of the dielectric function $\varepsilon_1(\omega)$ mentions to the dispersion of the incident photons by the material, while the imaginary part $\varepsilon_2(\omega)$ means the energy absorbed by the material. The imaginary part $\varepsilon 2(\omega)$ is calculated based on the contribution of the direct interband transitions from the occupied to unoccupied states, and the calculation is associated with the energy eigen value and energy wave functions, Concerning the real part $\varepsilon 1(\omega)$, it can be found from its corresponding $\varepsilon_2(\omega)$ by Kramers-Kronig transformation in the form [27].

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega') d\omega'}{\omega'^2 - \omega^2} \qquad (2)$$

where, P is principle value of the integral.

3.3.1. Imaginary part of dielectric function
The imaginary part is calculated theoretically using the following relation:

$$\varepsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2 \omega^2}\right) \sum_{i,j} \int i \, |M|j^2 f_i (1 - f_i) \delta(E_f - E_i - \omega) d^3 K \qquad (3)$$

where M is the dipole matrix; i and j are initial and final states respectively; f_i is the Fermi distribution function for its state; E_i is the energy of electron in the its state and ω is the frequency of the incident photon. Figure 4 shows imaginary part of the dielectric constant of CdSe in terms of energy. We note that the first peak was recorded at the absorption edge estimated at 6.1 eV, which reaches peak value 13, this results from the movement of electrons from the highest valence band to the lowest point in the conductivity band. We also notice in general a fluctuating curve between the increase and decrease, and we also distinguish through the figure the energy gap estimated at 1.52 eV.
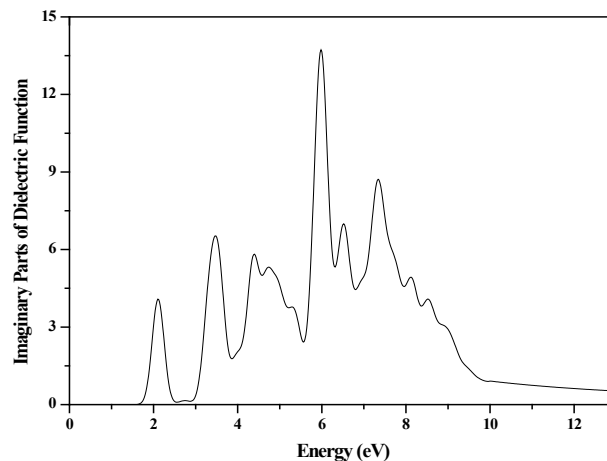

Fig. 4. Imaginary part of the dielectric constant of CdSe.

3.3.2. Absorption coefficient
It is the phenomenon of light propagation inside the material due to its absorption of the incident light ray, which is given by the following relation:

$$\alpha(\omega) = \frac{\varepsilon_2(\omega).\omega}{c.n} \qquad (4)$$

where ω is the frequency, c: the speed of light in vacuum, n: the refractive index. Fig.5 represents the absorption coefficient of CdSe using GGA.
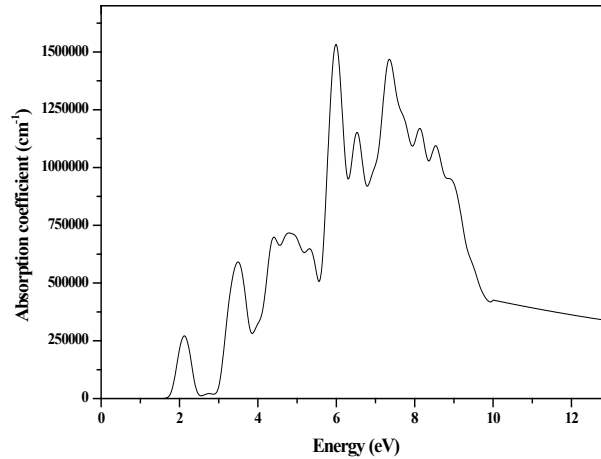
Fig. 5. The absorption coefficient of CdSe.

Figure 5 highlights the changes in the absorption coefficient in terms of energy, for example (eV). The curve can be divided into three regions:

- Basic absorption region: It is in the range between (0 to 1.52) eV, where no absorption values appear, but rather rapid absorption occurs when the absorbed radiation energy is equal to the energy gap, which represents the lowest energy difference between the highest level in the valence band and the lowest level in The conduction range, which is called Eg.

- Minimum absorption area: Found in the two ranges going from (1.52 to 5.8) eV and

(9 to 12) eV, which corresponds to the absorption values ranging from (0 to 700000) cm^{-1}, and (3750000 to 8750000) cm^{-1} respectively. This absorption is very weak, which makes it difficult for usto study the absorbency, as the electrons are moving from one level to another.

- Maximum absorption area:This region is limited to (5.8 to 9) eV, which corresponds to the following absorption values from (700000 to 1500000) cm^{-1}, which represents the maximum intensity of absorption, meaning that electrons in it move from the valence band to the conduction band in the levels extending between them, where is the highest absorption value recorded in this area, which is estimated at 1500000 cm^{-1}.

3.3.3. Extinction coefficient

The extinction coefficient k is the amount of energy, absorbed by the material electrons, of the incident light ray photons. This coefficient is given according to the following relation:

$$K(\omega) = \left[-\frac{\varepsilon_1(\omega)^{1/2}}{2} + \frac{\sqrt{\varepsilon_1{}^2(\omega) + \varepsilon_2{}^2(\omega)}}{2} \right]^{\frac{1}{2}} \tag{5}$$

whereas: $\varepsilon_1(\omega)$: real part of the dielectric constant, $\varepsilon_2(\omega)$: the imaginary part of the dielectric constant. The figure (6) hereunder shows the changes of the extinction coefficient k of CdSe in terms of energy.
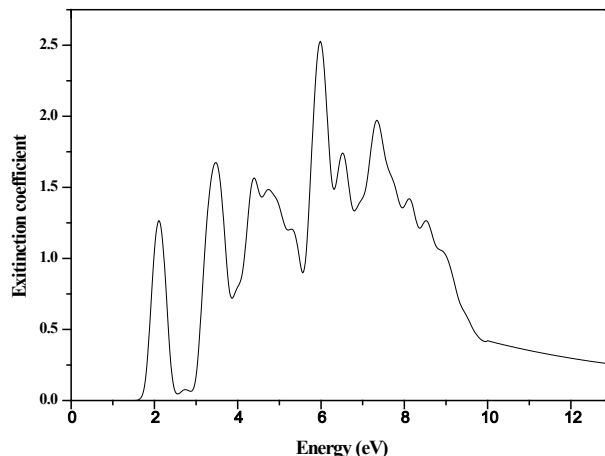
Fig. 6. Extinction coefficient K of CdSe.

Figure 6 represents the changes of the extinction coefficient in terms of energy in (eV) unit, using the approximations GGA. In the range (0 to 1.52) eV, we note that no value of the extinction coefficient was recorded, due to its presence in the energy gap region, but in the range from (1.52 to 2) volts, we notice that the extinction coefficient gradually increases with the increase in energy and reaches to its greatest extent in the primary absorption region. But in the range extending from (1.52 to more) eV, we notice that the extinction coefficient gradually fluctuates, increasing at times and decreasing at other times, to reach its maximum value in the basic absorption region, with an estimated value of 2.5 . This oscillation is due to the behaviour of light at the level of semiconductors [28].

3.3.4. Optical conductivity

Defined as the increase in the number of carriers (electron holes), as a result of the light beam incident on the material, and denoted by: σ(w), Figure 7 shows the optical conductance results for CdSe compound.
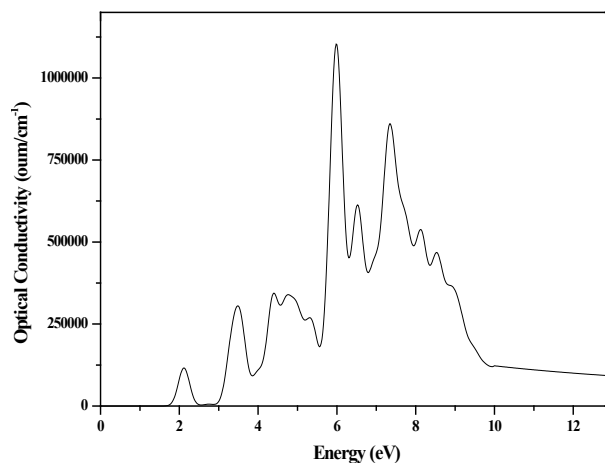

Fig. 7. Optical conductivity of CdSe.

Figure 7 represents the changes in the optical conductivity values in terms of energy in (eV) unit, by using GGA approximation. We note that in the region extending from (0 to 1.52) eV, no optical conductivity value is recorded, because it is located in the energy gap region. while in the range extending from (1.52 to 6.2) eV, we see that the values of the optical conductivity are in a noticeable increase until they reach the peak at energy of 6.2 eV, which corresponds to 1235000

(oum/cm^{-1}). The values of conductivity are constantly decreasing based on the amount of energy 9 eV.By analyzing the absorbance and optical conductivity curves, we concluded that this compound confirms the fact that CdSe is a semiconductor [29].

3.3.5. Reflectivity

The reflectivity R is defined as the ratio of the reflected light (ray) IR of the incident light beam with a given wavelength on a given surface, and the incident light (ray) IR.

$$R=\frac{(n-1)^2+K^2}{(n+1)^2+K^2} \tag{6}$$

where: n is the real part of the complex refractive index, k: is the imaginary part of the refractiveindex, When k=0 we find that:

$$R=\frac{(n-1)^2}{(n+1)^2} \tag{7}$$

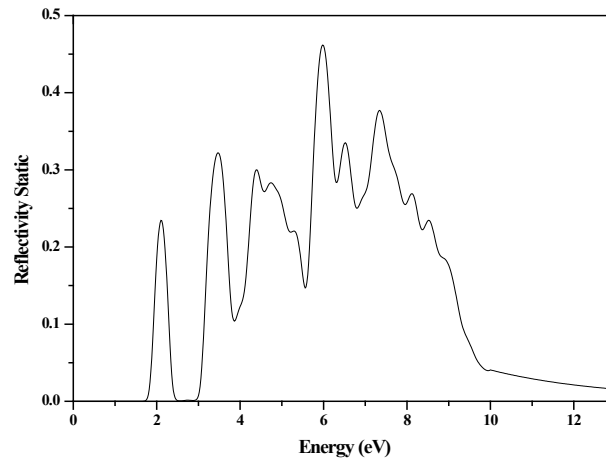when n=0, we find that R= 1. Fig. 8 represents the reflectivity curve of CdSe.

Fig. 8. The reflectivity of CdSe.

Figure 8 represents the reflectivity curve R (ω) in terms of energy, It is noted that the reflectivity is non-existent in the following two ranges from the value 0. To 1.52 eV and 2.5 to 3 eV. So that the reflectivity values witness a fluctuation in the value between the increase and decrease in the entire remaining energy field, except for its continuous decrease starting from energy value 9 eV. This means that CdSe behaves like a semiconductor [30].

4. Conclusion

We have analysed both the structural, electric and optical properties of the cubic phase CdSe using PP-LAPW method and the Siesta code. Besides, the exchange-correlation effects have been treated by GGA-PBE approximations. The results of the structural study show a great consistency with the previously calculated theoretical and experimental values. The electronic properties of the energy band structure and the total density of states confirmed that the CdSe compound has a direct energy gap estimated at 1.52 eV, which is very close to the previous applied results. all the optical properties that were calculated, such as the imaginary part of the dielectric constant, the reflectivity R(ω), the extinction coefficient k(ω), the absorption coefficient α (ω), and the optical conductivity (ω), confirmed the unique properties of CdSe that were shown

by previous experimental results. This compound also has promising electronic and optical uses due to its aforementioned properties.

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