

Investigation of the Optical Properties of CdBr₂

Hamdollah Salehi, Nastaran Asareh

Department of Physics, Shahid Chamran University of Ahvaz, Ahvaz, Iran

E-mail: salehi_h@sua.ac.ir

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Abstract

The optical properties of CdBr₂ were studied by first principle using the density functional theory. The dielectric functions and optical constants are calculated using the full potential-linearized augmented plane wave (FP-LAPW) method with the generalized gradient approximation (GGA). The theoretical calculated optical properties and energy Loss (EEL) spectrum yield a static refractive index of 2.1 and a plasmon energy of 13eV for hexagonal phase. The results, in comparison with the published data, are in good agreement with the experimental and previous theoretical results.

Keywords: Optical Properties, CdBr₂, WIEN2k, FP-LAPW, DFT, GGA

1. Introduction

Cadmium halogenides are widely uses as radiations. The lattice of these complicated crystals are strongly anisotropic. The CdBr₂ structure is of the CdCl₂ type, namely, the rhombic lattice with D_{3d}^5 symmetry [1]. Cadmium bromide Crystallise with layer structures in which banding within the layer is strong with a large ionic contribution, while bonding between the layers is weak. The basic structure of these materials is an infinite hexagonal sheet of Cd atoms sandwiched between two similar sheets of halogen atoms, the Cd atoms being Octahedrally coordinated. These three-sheet sandwiches (or layers) are then stacked to form the three-dimensional compound. Because of the weak binding between the layers, different stacking sequences represent only slight differences in total energy and so several such sequences are possible. There is relatively little information available about the electronic and optical properties of the cadmium halides as a whole. Band structure calculations have recently been made for CdI₂ (McCanny *et al* 1977, Bordas *et al* 1978, Robertson 1979). Optical experiments in the main have been concerned with the strong excitons exhibited by all three materials [2]. Cadmium bromide is known as a photochromic crystal and is widely used as window for Infrared applications [3].

In the present work the optical properties of CdBr₂ have been studied using the full potential linearized augmented plane wave method (FP-LAPW). The results, in comparison with the published data, are in good agreement with the experimental and previous theoretical results.

2. Method of Calculation

Calculation of the optical properties, of CdBr₂ were carried out with a self-consistent scheme by solving the Kohn-Sham equation using a FP-LAPW method in the framework of the DFT along with the GGA method [4,5] by WIEN2k package [6]. In the FP-LAPW method, space is divided into two regions, a spherical “muffin-tin” around the nuclei in which radial solutions of Schrödinger Equation and their energy derivatives are used as basis functions, and an “interstitial” region between the muffin tins (MT) in which the basis set consists of plane waves. There is no pseudopotential approximation and core states are calculated selfconsistently in the crystal potential. Also, core states are treated fully relativistically while valence and semi-core states are treated semi-relativistically (*i.e.* ignoring the spin orbit coupling). The cut-off energy, which defines the separation of the core and valence states, was chosen as -6 Ryd.

The complex dielectric tensor was calculated, in this program, according to the well-known relations [7].

$$\text{Im } \varepsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2 \omega^2} \sum_{c,v} \int dk \langle c_{\mathbf{k}} | p^{\alpha} | v_{\mathbf{k}} \rangle \langle v_{\mathbf{k}} | p^{\beta} | c_{\mathbf{k}} \rangle \delta(\varepsilon_{c_{\mathbf{k}}} - \varepsilon_{v_{\mathbf{k}}} - \omega) \quad (1)$$

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

and the optical conductivity is given by:

$$\text{Re } \sigma_{\alpha\beta}(\omega) = \frac{\omega}{4\pi} \text{Im } \varepsilon_{\alpha\beta}(\omega) \quad (3)$$

In Equation (1), $c_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are the crystal wave functions corresponding to the conduction and the valence bands with crystal wave vector \mathbf{k} . In Equation (3) the conductivity tensor relating the inter band current density j_{α} in the direction α which flows upon application of an electric field E_{β} in direction β in which the sum in Equation (1) is over all valence and conduction band states labeled by v and c . Moreover, the complex dielectric constant of a solid is given as:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (4)$$

Here, real and imaginary parts are related to optical constants $n(\omega)$ and $k(\omega)$ as:

$$\begin{aligned} \varepsilon_1(\omega) &= n^2(\omega) - k^2(\omega) \\ \varepsilon_2(\omega) &= 2n(\omega)k(\omega) \end{aligned} \quad (5)$$

The other optical parameters, such as energy-loss spectrum and oscillator strength sum rule are immediately calculated in terms of the components of the complex dielectric function [8].

3. Results and Discussion

The calculations first were carried out using the experimental data for lattice constants, $a = 3.954 \text{ \AA}^0$, $c = 18.672 \text{ \AA}^0$ in the hexagonal phase. Then by minimizing the ratio of the total energy of the crystal to its volume (volume optimizing) the theoretical lattice constants were obtained = 4.039 and $c = 19.328 \text{ \AA}^0$.

In order to reduce the time of the calculations we used the symmetries of the crystal structure and some other approximations for simplicity. The calculation was performed with 6000 k-points in the hexagonal phase.

The self-consistent process, for both phases, after 11 cycles had convergence of about 0.0001 in the eigenvalues in which for the hexagonal phase 1612 plane waves were produced. Under these conditions the values of the other parameters were $G_{\text{max}} = 14$, $R_{\text{MT}}(\text{Cd}) = 2.5 \text{ au}$, $R_{\text{MT}}(\text{Br}) = 2.4 \text{ a.u.}$ The iteration halted when the total charge adjustment was less than 0.0001 between steps.

3.1. Dielectric Function

We calculated optical properties of CdBr_2 in the hexagonal phase, but here we only present the optical properties. The real and the imaginary parts of the dielectric functions are shown in **Figure 1** for CdBr_2 in the hexagonal phase. The value of the main peak of $\varepsilon_1(\omega)$ curve is 8.6 at energy of 5.5 eV and for $\varepsilon_2(\omega)$ is 8.2 at the energy equal 7.6 eV.

The real and the imaginary parts of optical conductivity are shown in **Figure 1** for CdBr_2 in hexagonal phase.

In **Figure 2** the optical constant $n(\omega)$ and Extinction coefficient $k(\omega)$ is shown for CdBr_2 in hexagonal phase. The static refractive index value for CdBr_2 in the hexagonal phase calculated in this work, and the values obtained by other methods are summarized in **Table 1**.

Referring to **Table 1**, it can be seen that the calculated refractive index in this work is equal with the values measured experimentally.

3.2. Electron Energy Loss Spectroscopy

EELS is a valuable tool for investigating various aspects of materials [8]. It has the advantage of covering the complete energy range including non-scattered and elastically scattered electrons (Zero Loss). At intermediate energies (typically 1 to 50 eV) the energy losses are due primarily to a complicated mixture of single electron excitations and collective excitations (plasmons). The positions of the single electron excitation peaks are related to the joint density of states between the conduction and valence bands, whereas the energy required for the

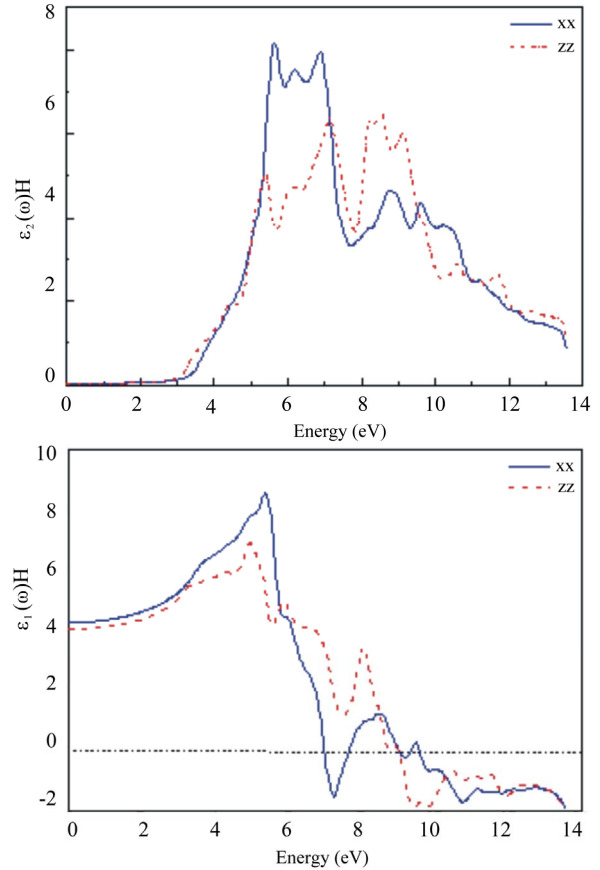


Figure 1. Real and imaginary part of the dielectric function for CdBr_2 in hexagonal phase.

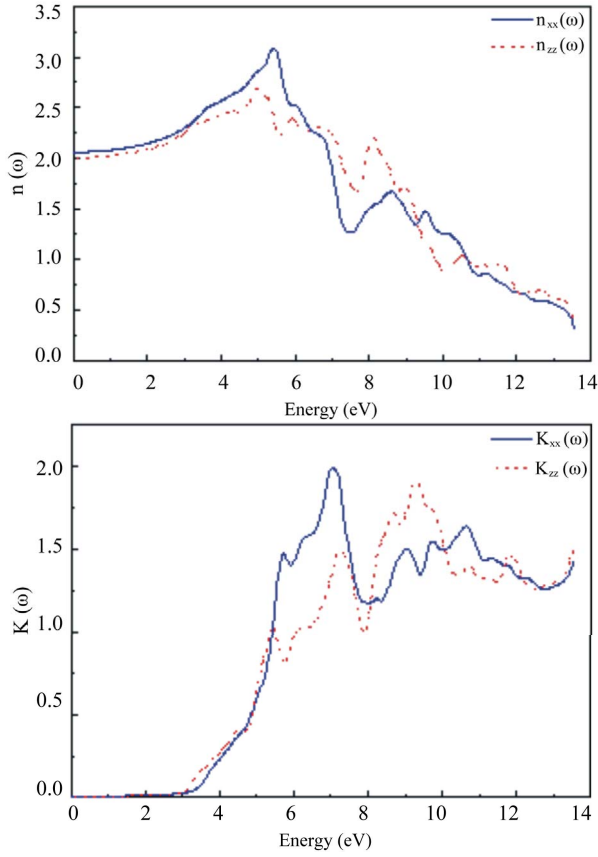


Figure 2. The optical constant $n(\omega)$ and $k(\omega)$ is CdBr_2 in hexagonal phase.

excitation of bulk plasmons depends mainly on the electron density in the solid. Here electrons, which excite the atoms electrons of the outer shell is called Valence Loss or valence interband transitions (**Figure 3**). At higher energies, typically a few hundred eV, edges can be seen in the spectrum, indicating the onset of excitations from the various inner atomic shells to the conduction band. In this case the fast electrons excite the inner shell electrons (Core Loss) or induce core level excitation of Near Edge Structure (ELNES) and XANES. The edges are characteristic of particular elements and their energy and height can be used for elemental analysis.

Table 1. The CdBr_2 static refractive index in hexagonal phase calculated by various methods.

Method	FP-LAPW (GGA96)	Experimental	Theoretical
n	5.5	5.17,5.68[1]	-
Difference with experimental (%)	6,-3.27	-	-
$\epsilon(0)$	4.2	4.1[1],4[2]	-
Difference with experimental (%)	2.38	-	-

In the case of interband transitions, which consist mostly of plasmon excitations, the scattering probability for volume losses is directly connected to the energy loss function. One can then calculate the EEL spectrum from the following relations.

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_1 + i\epsilon_2$$

$$\text{and EELSpectrum} = \text{Im}[-1/\epsilon_{\alpha\beta}(\omega)] = \frac{\epsilon_2}{\epsilon_1^2 + \epsilon_2^2}$$

(6)

In **Figure 3** the energy loss function is plotted for CdBr_2 in hexagonal phase. These peaks can, however, have different origins such as charge carrier plasmons and interband or intraband excitations. The energy of the maximum peak of $\text{Im}[-\epsilon^{-1}(E)]$ at 13 eV is assigned to the energy of the volume plasmon $\hbar\omega_p$. The first peak at 8 eV and second peak at 10 eV originates from orbitals d atom Br. The value of $\hbar\omega_p$ obtained in this work and for free electron is given in **Table 2**.

For free electrons the plasmon energy is calculated according to the following model:

$$\hbar\omega_p^e = \hbar \sqrt{\frac{ne^2}{\epsilon_0 m}} \quad (7)$$

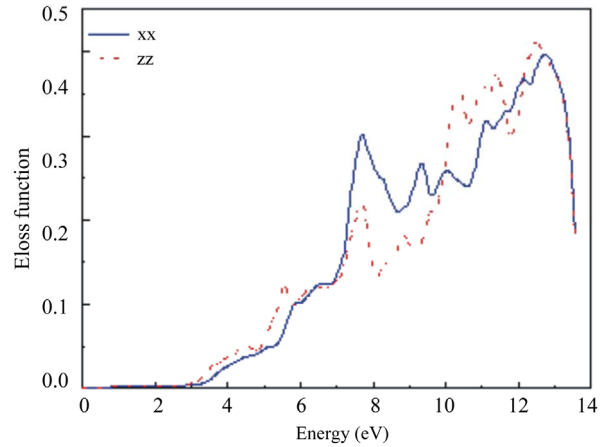


Figure 3. Electron energy loss spectrum $\text{Im}[-\epsilon^{-1}(E)]$ for CdBr_2 in hexagonal phase.

Table 2. The CdBr_2 plasmon energy $\hbar\omega_p$ of the energy loss function in hexagonal phase calculated by this method and free electron.

Methods	Plasmon energy $\hbar\omega_p$ (eV)
FP-LAPW (GGA96) (this work)	13
Free electron (ignoring Cd-4p and Br-3d states)	18.7
Free electron	15.8

If we use this model, then what should be the number of valance electrons per CdBr_2 molecule, N , used to calculate the density of valance electrons, n , and thus the plasmon energy in Equation (7).

4. Conclusions

We have calculated the optical properties of (PT) in hexagonal and tetragonal phases using the full potential-linearized augmented plane wave (FP-LAPW) method with the generalized gradient approximation (GGA). The calculations show a static refractive index of 2.1 and an EEL spectrum of 13eV for the hexagonal phase.

5. References

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