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Material CuInSe$_2$ for a Photovoltaic Application

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***Abstract*— currently, interest is focused on semiconductor-based chalcopyrite, mainly group of alloys CuInX$_2$ (X = S, Se, Te) in photovoltaic applications and their principal role in the solar thin cells layers; because of the importance of their electronic and optical properties. We have performed ab initio calculations for semiconductors CuInX$_2$ (X=S, Se, Te) to study the electronic structure and deduce their optical properties, we used the various approximations in calculation from first principle (*ab initio*) with the density functional theory (DFT) to find the band structures, the gaps energies and the states of densities are well defined and are improved by the use of new approximation the Engel-Vosko-generalized gradient approximation EV-GGA , mainly of compound CuInSe$_2$. It is also shown that component have optics properties very significant as (absorption coefficient, index refraction, and extinction coefficient …..) starting from the determination of the dielectric function.**

***Keywords*— *ab inito* calculations, electronic and optical properties of CuInSe$_2$.**

I. INTRODUCTION

Recently, a great deal of interest has been focused on the growth of the ternary I–III–VI$_2$ and II–IV–VI$_2$ semiconductor com-pounds which crystallize in the chalcopyrite type structure. Seen the importance of these semiconductor, among three compound CuInX$_2$ (X = S, Se Te) we choose CuInSe$_2$ to study.

We choose FP-LAPW [1] method because it neither uses approximation on the potential; nor on the total charge density. This has allowed us to calculate the properties of the material using only the positions of atoms and the crystalline structure. Within the framework of this method we used a new approximation which can improve our result, named GGA-EV approximation [2]. While we compare the results obtained with other calculations LDA, we notice that our calculations of the gap energy of the three components are closer to those experimental values especially CuInSe$_2$

II. METHOD of CALCUL

The ternary CuInSe$_2$ semiconducting compounds crystallize in the chalcopyrite structure with tetragonal space group having four formula units in each unit cell.CuInX$_2$ is a ternary analog of diamond structure and essentially a super lattice (or superstructure) of zinc blend. The **Cu** atom is located at (0, 0, 0), (0, 0.5, 0.25), **In** atom at (0, 0, 0.5), (0, 0.5, 0.75), and Se atom at (0.25, 0.25, 0.125); (0 .25, 0.75, 0.125), (0.75, 0 .25, 0.875), (0.4,-0.25, 0.875), See (figure 1). In the present work we used the experimental lattice parameters as listed in following table:

CuInSe$_2$ [3].	5.78	11.56

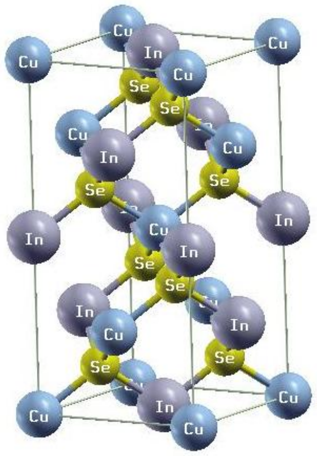

Figure 1: The crystalline structure in phase chalcopyrite of CuInSe$_2$.

In our calculations we use the state-of-the-art full potential linear augmented plane wave (FPLAPW) method in a scalar relativistic version the WIEN2k code [4].

The linear response of system to an external electromagnetic field with a small wave vector is measured through the complex dielectric function ε(ω). The frequency depend on complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ it describe the optical response of the material at all phonon energies $E = \hbar\omega$. The imaginary part, $\varepsilon_2(\omega)$ along wave length limit has been obtained directly from the electronic structure calculation, using the following relation:

$$\varepsilon_2(\omega)=\frac{\pi}{\varepsilon_0}\left(\frac{e}{m\omega}\right)^2\sum_k |M_{vc}|^2\delta(E_c-E_v-\hbar\omega) \qquad (1)$$

Where **ħω** is the photon energy, $\mathbf{M_{vc}}$ the elements of dipolar matrix between initial and final states with their eigenvalues, $\mathbf{E_v(k)}$ and $\mathbf{E_c(k)}$. the real part of the dielectric function $\varepsilon_1(\omega)$ can be extracted using the Kramers-Kronig [5] relation.

$$\varepsilon_1(\omega)=1+\frac{e^2}{\varepsilon_0 m}\sum_k\left(\frac{2}{m\hbar\omega_{cv}}\frac{|M_{vc}|^2}{\omega^2_{cv}-\omega^2}\right) \qquad (2)$$

III RESULTAT and DISCUSSION

A-Electronic structure:

The band structure in the high symmetry direction of The Brillouin zone is shown in figure 2. The band structure, total density of states (TDOS) along with the X-p/s, and Cu-d/p/s partial DOS for $CuInTe_2$ compounds are shown in Figure 3. The maximum valence band (MVB) and the minimum conduction band (MCB) are located at **Γ** in a direct gap energy which has value, 0.6219 eV.

In the bands of conduction, the significant effect of the states "**d**" of **Cu** and the weak effect of the states "**p**" of Te atom influence over the gap width; In the conduction bands **Cu-s** states has a small effect but **In-s** states has a strong effect in enlarging the band gap. In the bands of conduction, the important effect of the states “d” of **Cu** and the weak effect of the states “p” of **Se** atom influence over the gap width. The total reduction of this band is due to the weakening of the hybridization, between the states **d** of Cu and the states **p** of atom Se. By comparing our results with the experimental values and theoretical band gaps given in TABLE I, We notice that our values of energy are underestimated. We also note that our results are closer to the experiment than those obtained by other LDA calculations LDA. We can say than the approximation GGA-EV gives a good improvement for the $CuInSe_2$ compound.

TABLE II : Values of the energy of gap the compound ones calculated with the EV-GGA compared with other calculations and other experimental values.

Component	$CuInSe_2$
Eg (GGA-EV)	0.6219
Eg expérimental (ev)	1.04$^{a.}$, 0.96^{b}
Other calculations of Eg (LDA)	0.424^{c} 0.26^{d}
Theoretical values of Eg	0.01^{e}

^{a}:[6]; ^{b}: [7]; ^{d}:[8]; ^{c}:[9]; ^{e}:[10];

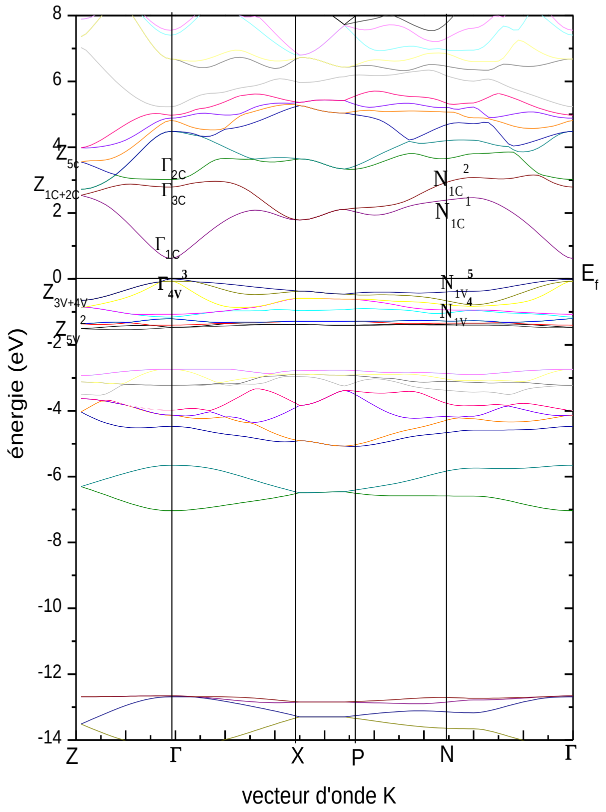

Figure2: Band structure of compound $CuInSe_2$

B. Densities of states (DOS)**:**

We treated the states of copper **Cu_{29}**: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^1$, indium **In_{49}** ($1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $5s^2$ $5p^1$) the selenium Se_{34} ($1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$) as being core states; and states **Cu** ($3d^{10}4s^1$) **In** ($4d^{10}$ $5s^2$ $5p^1$) **Se** ($4s^2$ $4p^4$) as being valence states.
The most important states in each atom are the densities Of states (DOS) total and partial (PDOS) projected, between -10 and 10 eV, Calculated by GGA-EV are respectively illustrated on figure 3, and the level of Fermi is taken as origin of energies.

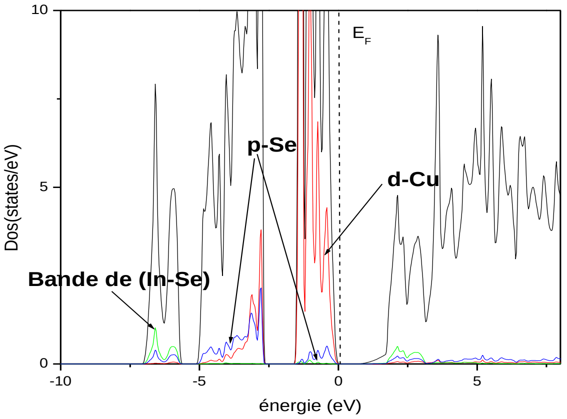

Figure3: Densities of states (DOS) total and partial (PDOS) of $CuInSe_2$

The structure of band, and consequently DOS, can be divided into six following groups:

1- Low group is mainly "d" states of **In**.
2- Second group between -11.0 to -14.0 eV go to significant contributions of the "**s"** states of the atom **X**.
3 - Third groups -6.0 to -7.0 eV is mainly **In-X** bond.
4 - Bands groups between -5.5 eV to energy of Fermi (E_F) are the states "**d**" of **Cu** with a some contribution of the "**p**" states of the **Te** atom.

5- In electronic structure, the higher band of valence is dominated by "**d**" states of **Cu** and p-X. We note that the major part of the character "**d**" of **Cu,** is concentrated in the higher band of valence.

6- the remaining group of the bands of 0.5**eV** until the top comes from the contributions of the "**p**" states of **Se**, the **spd** states (Cu), and the **sp** states (In).

Starting from curves of partial density, we note a strong hybridization between the states **d** of **Cu** and **p of Se** around -1eV. Based on these curves we can say that the hybridization between **d** **(Cu)** and **(p) Se** states becomes weak when replace from S by Te. Thus the width of the gap depends on this hybridization between the states on **d** (Cu) and **p**(Se).

C. Optical properties**:**

The imaginary and real part of the dielectric functions calculated using the Esq (1) and (2) respectively.

$$\varepsilon_2(\omega) = \frac{\pi}{\varepsilon_0}\left(\frac{e}{m\omega}\right)^2 \sum_k |M_{vc}|^2 \delta(E_c - E_v - \hbar\omega) \quad (1)$$

$$\varepsilon_1(\omega) = 1 + \frac{e^2}{\varepsilon_0 m}\sum_k \left(\frac{2}{m\hbar\omega_{cv}}\frac{|M_{vc}|^2}{\omega^2{}_{cv} - \omega^2}\right) \quad (2)$$

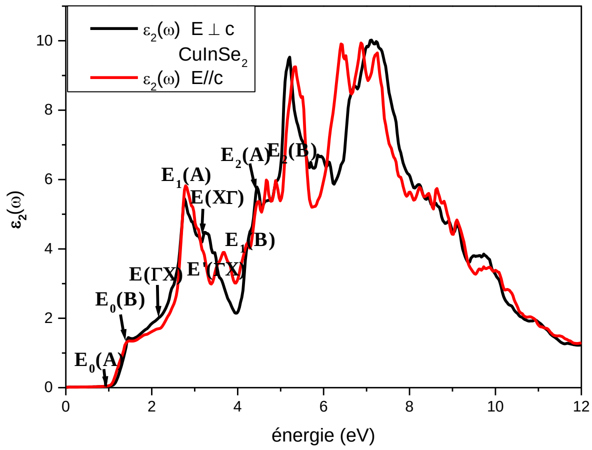

Figure 4: The imaginary part of the dielectric function of $CuInSe_2$.

Generally, the transitions in the optical answer are caused by the transitions from the electrons between the valence band and the band of conduction. These peaks, in the linear optical spectra, correspond to the transitions in the structure of bands. The absorption coefficient is related with the imaginary part of the dielectric function by this relation:

$$\alpha = \frac{2\omega k_e}{c} = \frac{\varepsilon_2\omega}{c} \quad (3)$$

K_e: imaginary part of the index of refraction N.
C: speed of the light

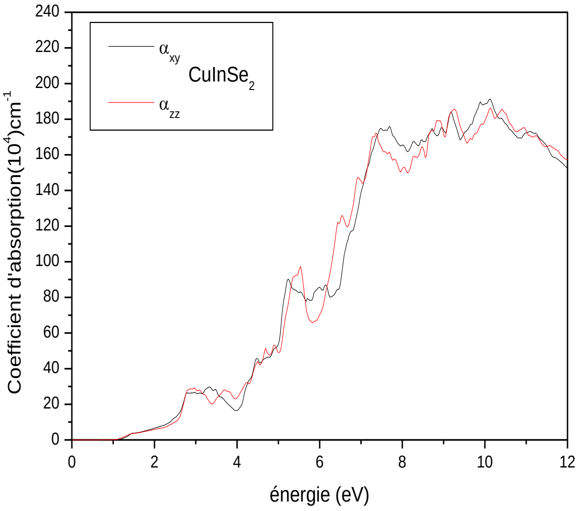

Figure 5: Coefficient of absorption the $CuInSe_2$

IV CONCLUSIONS

In this work using the FP-LAPW, we studied the electronic properties of ternary compound; $CuInSe_2$; According to thus study, we notice that the use of approximation EV-GGA enables us to have a good improvement of calculations of the gap, for compound $CuInSe_2$.

We can conclude that the importance of this semiconductor in the photovoltaic application is due mainly to their appropriate values of the direct gap. The optical properties such as the dielectric function, reflectivity, absorption coefficient, real part of the dielectric function, imaginary part of the dielectric most of the luminous spectrum [0.103µm, 0.826 function and refractive index are correlated with the interband transitions in the respective band structure. Among these properties, absorption coefficient about 10^5cm-^{1}sweeps

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