Tight-binding electronic band structure and surface states of Cu-chalcopyrite semiconductors

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Abstract

We report theoretical calculations of the electronic band structure and surface states of Cu-chalcopyrite semiconductors. The systems under consideration are CuGaS₂, CuAlSe₂, and CuGaS₂ doped with Cr. The calculations are carried out using semi-empirical Tight-Binding formalism. By reproducing the band gap of these systems obtained by ab-initio calculations we report the Tight-Binding parameters required for the band structure calculations. We present bulk band structure calculations of the above mentioned semiconductors, and we analyze the (001) and (110) surface states of the corresponding semi-infinite semiconductors.

1. Introduction

Chalcopyrite crystals derived from the I-III-VI₂ (I = Cu, III = Ga, Al, and VI = S, Se) family have received considerable attention as one of the promising materials to be used for thin film solar cells fabrication [1–3]. The energy gap of these materials covers practically all the visible part of the electromagnetic spectrum. The band gap range from 1.7 eV for CuGaSe₂, i.e. from the deep red, to 2.43 for CuGaS₂, and to 2.65 eV for CuAlSe₂, with its main absorption peak located near ultra-violet (UV) region [4–9]. Of course, the energy band gap is the most important parameter owing to the fact that it dominates the main optical-absorption peak in semiconductors. The concept of multiband or intermediate band solar cells has recently attracted renewed attention as a viable approach to achieving high solar power conversion efficiencies [10, 11]. Several approaches have been employed to demonstrate the concept of intermediate band including quantum dots [12, 13] and highly miss-matched alloys [14, 15]. Highly miss-matched alloys are a class of materials whose electronic band structures are dramatically modified through the substitution of a relatively small fraction of host atoms with some dopant. Between these I-III-VI₂ materials, and due to its wide gap, CuGaS₂ is one of most promising candidates to host an intermediate band when it is doped with a transition metal. This is because, as recently suggested, the optimal value of the band gap for a semiconductor that contains an intermediate band, should be around 2.4 eV [14], and CuGaS₂ satisfies this requirement.

The electronic properties of I-III-VI₂ semiconductors have been subject of study for nearly 40 years by different authors using distinct methodologies. As representative examples, we can mention the seminal work of Jaffe and Zunger where they studied self-consistently within the density-functional theory (DFT), the chemical trends in the electronic structure of six Cu-based ternary chalcopyrite semiconductors including CuGaS₂ [16, 17]. They reported 1.65 and 1.25 eV for the energy gap of CuAlSe₂ and CuGaS₂, far from the accepted experimental values 2.65 and 2.43 eV, respectively. Using full-potential linear muffin-tin orbital method based on the local-density approximation and with the Hedin-Lundqvist parametrization for the exchange and correlation potential, R. Ahuja et al, obtained a similar value for the energy gap of CuGaS₂ (1.2 eV) [18]. Band structure and total energy calculations using the density functional theory within the generalized gradient approximation (GGA) for the exchange correlation functional, were carried out by...
Chen et al in 2007, to study what they called ‘band gap anomalies’, due to the unexpected behavior of this parameter with their corresponding lattice constant. Unfortunately, in spite of the methodology used by the authors, they obtained a gap of 0.6932 eV for the CuGaS\(_2\) semiconductor, which is very far from the experimental accepted value (2.43 eV)\(^8,\)\(^9\). As it can be seen from all these results, standard Kohn-Sham DFT fails in describing the band structure of chalcopyrite materials, due to the strong underestimation of the band gap. In order to go beyond the standard Kohn-Sham DFT, new results have been published improving the calculated band gaps. Using a self consisted GW scheme based on Hedin’s Coulomb hole and screened exchange (scCOHSEX) followed by a perturbative G\(_0\)W\(_0\) step, Aguilera et al, reported an energy gap of 2.65 eV for CuGaS\(_2\), in very good agreement with the experimental value\(^20\). Recently, we have done \textit{ab-initio} DFT theoretical calculations using a modified screened hybrid Heyd-Scuseria-Ernzerhof functional (HSE06) to improve the GGA approximation, and we have obtained a band gap of 2.43 eV, which reproduces excellently the experimental value\(^21\).

On the other hand, due to the growing interest of increase the efficiency of a solar cell by considering CuGaS\(_2\) as the active material hosting an intermediate band, a detailed study of the electronic properties of such system becomes necessary, and in this direction many articles have been published exploring such a possibility\(^22–27\). Of course, a precise knowledge of the band structure of such materials requires \textit{ab-initio} calculations. Unfortunately, due to the large unit cells required to manage small doping levels, first principles calculations requires very large time consuming computer calculations, which makes this methodology unfeasible. For systems of such complexity, it is very convenient to have simpler methods available as an alternative tool. The Tight-Binding (TB) method is one such possibility, since it gives solutions showing all the correct symmetry properties of the energy bands, and it is rather easy to get solutions for energy bands at an arbitrary point in the Brillouin zone. The time required by this semi-empirical method depends only on the size of the matrix to diagonalize, which in the worst case is very small compared to the time required for a first principles calculation.

In this paper we present a TB study of the electronic band structure of the CuGaS\(_2\), CuAlSe\(_2\) chalcopyrite semiconductors, together with the corresponding material CuGaS\(_2\) doped with Cr in order to obtain an intermediate band. As a first step, and as a main goal of this paper we adjust all the necessary TB parameters to reproduce the values of the band gap experimentally documented as well as the main features of the band structure obtained from \textit{ab-initio} first-principles calculations recently reported. Using these parameters, we calculate the electronic band structure of the above mentioned chalcopyrite semiconductors along the principal directions of the corresponding Brillouin zone. The knowledge of all these parameters will allow us to tackle more complicated problems which are not possible to consider from \textit{ab-initio} methodology. As an example of this kind of difficult problems, we also calculate the electronic surface states of the semi-infinite chalcopyrite semiconductors along the [001] and [011] directions. This last analysis is carried out by using the Surface Green Function Matching (SGFM) method, which is a successful technique employed to calculate the electronic properties of surfaces, interfaces, quantum wells, and superlattices\(^28,\)\(^29\).

\section*{2. Theoretical model}

Chalcopyrites are tetragonal centered crystalline structures with eight atoms in the unit cell basis and spatial group I\(_4\) 2d. In figure 1 we present the crystal structure for CuGaS\(_2\), and the coordinates of the eight atoms in the unit cell appear in table 1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Unitary cell of CuGaS\(_2\). The unitary cell contains 8 atoms which appear labeled by numbers.}
\end{figure}
According to the TB formalism, the electronic wave function is written as a linear combination of atomic orbitals as,

\[ \Psi_k = \sum_{\nu j} C_{\nu j} \phi_j(r + R_{\nu}) e^{i k \cdot R_{\nu}} \]  

(1)

where \( \nu \) is the atomic orbital, and the sum over \( j \) consider all the atoms in the crystal. The expressions of the TB parameters necessary to diagonalize the matrix appear explicitly in table 20.1 of the book of Harrison \[30\] and they are not given here. For the chalcopyrites considered in this work, the matrix to diagonalize is of order 42 \( \times \) 42, four orbitals (\( sp^3 \)) for each of the two the Ga (Al) atoms and four for each of the four S (Se) atoms, and 9 orbitals (\( sp^3 d^5 \)) for each of the two Cu atoms. The correct form of the Hamiltonian matrix is given in the appendix (A). Similar Hamiltonian has been published before by Rodríguez \[31\] et al, in their study of the electronic properties of a family of chalcopyrites, however small typos appear in the final form of the matrices reported.

### 3. Results

#### 3.1. Electronic structure of CuGaS\(_2\) and CuAlSe\(_2\)

Recently, we have carried out \textit{ab-initio} calculations of the structural and electronic properties of these materials, and the results obtained were reported in reference \[21\]. From the reference of Castellanos \textit{et al} \[21\], we observe that the obtained values for the band gap is 2.43 eV for the CuGaS\(_2\), and 2.65 eV for the CuAlSe\(_2\). Unfortunately if we introduce the values of the TB parameters obtained from the Harrison’s rule, it is not possible to reproduce correctly, neither the experimental values, nor those obtained from first-principle calculations. For example, for the CuGaS\(_2\), chalcopyrite, the band gap obtained using the Harrison’s parametrization, is 6.16 eV, which is very different to the value of 2.43 eV obtained from our \textit{ab-initio} calculations. In order to reproduce the band gap for all the materials considered in this work, we consider a slightly different value for the universal parameters \( \eta_{\alpha \beta \gamma} \), and we carried out as well a fit of the \textit{on-site} parameters. The adjustment of these last parameters is because their values substantially affect the border of the conduction band, and consequently the values of the corresponding band gaps \[16\]. The values of the adjusted universal parameters \( \eta_{\alpha \beta \gamma} \), and the \textit{on-site} parameters used all throughout this work appear in tables 2 and 3, respectively. If we introduced these values in our TB Hamiltonian we reproduce better the band gap for all the semiconductors considered in this work. This can be clearly seen in table 4. In the second

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**Table 1.** Atomic positions in the CuGaS\(_2\) chalcopyrite. The values of the distortion parameter \( \eta = c^2 / 2a \), and the anion displacement \( u \) (in units of \( a \)), used in this work were 0.996 and 0.2332 respectively \[21\].

| Atom number | Atom | Position |
|-------------|------|----------|
| 1           | Cu   | (0, 0, 0) |
| 2           | Ga   | \( a \left( \frac{1}{2}, \frac{1}{4}, 0 \right) \) |
| 3           | S    | \( a \left( \frac{1}{2}, \frac{1}{4}, \frac{1}{2} \right) \) |
| 4           | S    | \( a \left( 1 - u, \frac{1}{4}, \frac{1}{2} \right) \) |
| 5           | Cu   | \( a \left( \frac{1}{2}, \frac{1}{4}, \frac{1}{2} \right) \) |
| 6           | Ga   | \( a \left( \frac{1}{2}, 1, \frac{1}{2} \right) \) |
| 7           | S    | \( a \left( \frac{1}{2}, \frac{1}{4} + u, \frac{1}{2} \right) \) |
| 8           | S    | \( a \left( \frac{1}{2}, \frac{1}{4} - u, \frac{1}{2} \right) \) |

**Table 2.** Parameters \( \eta(\alpha \beta \gamma) \) used to determine the TB parameters.

| \( \eta(\alpha \beta \gamma) \) | Adjusted value |
|------------------------------|----------------|
| \( \eta_{ss \sigma} \)       | -1.40          |
| \( \eta_{sp \sigma} \)       | 1.84           |
| \( \eta_{pp \sigma} \)       | 3.24           |
| \( \eta_{pp \pi} \)          | -0.81          |
| \( \eta_{sd \sigma} \)       | -3.16          |
| \( \eta_{pd \sigma} \)       | -2.95          |
| \( \eta_{pd \pi} \)          | 1.36           |

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In Figure 2 we show the band structure for the chalcopyrite CuGaS$_2$ and CuAlSe$_2$ obtained from our TB calculations using the parameters that better reproduce the experimental values of the band gap appearing in Table 4. We can observe that the band structures are very similar. Both materials are semiconductors with a direct band gap; the value of the band gap is 2.43 eV for CuGaS$_2$ and 2.65 eV for CuAlSe$_2$, and match perfectly well with the experimental results. For both semiconductors, the top of corresponding valence band is nondegenerate. The next deeper band is a doublet. The energy difference between them is due to the crystal field splitting, and we found 0.05 eV and 0.122 eV for the CuGaS$_2$ and CuAlSe$_2$, respectively. This small difference cannot be appreciable due to the scale of the figure; however, these three states are clearly observed by seeing the dispersion relation in the direction Γ-X. The breaking of the degeneration in the valence band is attributed to three main effects: the existence of two different cations; the tetragonal distortion (c/a ≈ 2); and the displacement of the

### Table 3. Adjusted ‘on-site’ parameters in eV, for CuGaS$_2$, and CuAlSe$_2$, used in our calculations. Reported values are included for comparison (a) [30], (b) [31].

| Atom  | $E_{so}$ | $E_{pp}$ | $E_{dd}$ |
|-------|---------|---------|---------|
| Cu (CuGaS$_2$) | −14.55, −6.92$^a$, −14.55$^b$ | −3.22, 1.83$^a$, −2.22$^b$ | −17.64, −20.14$^a$, −16.97$^b$ |
| Cu (CuAlSe$_2$) | −14.775, −6.92$^a$, −14.55$^b$ | −2.22, 1.83$^a$, −2.22$^b$ | −16.65, −20.14$^a$, −16.97$^b$ |
| Ga     | −11.37, −11.37$^a$ | −4.90, −4.90$^a$ |        |
| Al     | −8.92, −10.11$^a$ | −4.97, −4.86$^a$ |        |
| S      | −20.80, −20.80$^a$ | −9.807, −10.27$^a$ |        |
| Se     | −20.32, −20.32$^a$, −20.32$^b$ | −10.289, −9.53$^a$, −8.789$^b$ |        |

Table 4. Band gap (in eV) for the semiconductors considered in this work. The first column shows the results obtained using the TB parameters according to the Harrison’s parametrization [30]; the second column corresponds to the theoretical values obtained from first principles under the approximation of reference [21]; the third column shows the experimental values.

|        | Harrison | scGW | Experimental | Present work |
|--------|----------|------|--------------|--------------|
| CuGaS$_2$ | 6.16     | 2.43 | 2.40 [8]     | 2.43         |
| CuAlSe$_2$ | 5.47     | 2.65 | 2.65 [9]     | 2.65         |

Figure 2. Electronic Band Structure for the (a) CuGaS$_2$, and (b) CuAlSe$_2$ Semiconductors.
anion which does not lies at the center of the tetrahedron. We have taken into account all these three effects in our TB calculations. The effect of the two different cations was considered by the values of the TB parameters corresponding to the Ga and Cu atoms. On the other hand the effect of the tetragonal distortion and the displacement of the anions were considered by introducing the values of the η and μ parameters obtained from our ab-initio calculations [21, 33]. Although the splitting due to these three effects is very small, the obtained values are consistent with recent published results [15].

3.2. Electronic structure of the chalcopyrite CuGaS₂ doped with Cr

In this section we analyze the electronic properties of the chalcopyrite CuGaS₂ doped with Cr atoms. As has been established before, doping this semiconductor could modify the electronic structure of the semiconductor giving rise to an intermediate band [33]. There have been published many results of chalcopyrite semiconductors doped with metallic elements with the purpose to obtain an intermediate band [12, 14, 15, 20–24]. Unfortunately, first principles calculations are very expensive from the computational point of view, because the large number of atoms in the unitary cell needed to manage realistic levels of doping. Due to this tough task, ab-initio calculations are carried out considering large fractions of doping only. Even in this case, these studies are mainly concentrated in calculate the band gap, or the density of states at the Fermi level. Fortunately, the time needed to diagonalize the TB matrix, is very small when compared with any first-principles calculation. If we doped the CuGaS₂ chalcopyrite with Cr atoms, the size of the TB matrix increases due to the presence of the metallic atom in the unitary cell. For a 25% of Cr concentration the size of the TB matrix goes from 42 × 42 to 178 × 178. For this percentage of Cr atoms, the unitary cell contains 16 atoms: 4 Cu atoms (9 atomic orbitals per atom), 3 and 8 atoms of Ga and S, respectively (4 atomic orbitals per atom), and 1 Cr atom with a sp³d⁵ orbital basis. In addition to the above, for this doped chalcopyrite, spin-orbit effect must be taken into account to obtain a correct description of the band structure. This is because, for the doped chalcopyrites, previous ab-initio calculations have demonstrated that the spin with a very definite component contributes to the density of states of the intermediate band [23]. We have adjusted the ‘on site’ parameters for the Cr atom, and the used values appear in table 5. The parameters that take into account the spin-orbit effect λμ have been adjusted to reproduce ab-initio calculations recently reported [21]. The values of these parameters used in the present work, for the d orbitals of the Cu and Cr atoms were 0.012 and 0.2 eV respectively; meanwhile for the p orbitals on the Ga and S atoms were 0.007 and 0.004 eV respectively. In figure 3 we show the local density of states (LDOS) for the CuGaS₂:Cr chalcopyrite as a function of energy at k = (0, 0, 0). We can observe the appearance of the intermediate band located slightly down the center of the band gap. The upper part of figure 3(a) corresponds to the component of the LDOS with spin up, whereas the lower part corresponds to the component of the LDOS with spin down. We include in figures 3(b) and (c), the contributions to the LDOS of the different atoms. The presence of the Cr atoms give rise to the intermediate band with primordially d orbital character. Please note the different scale in figures 3(a) and (b). The general characteristics of the LDOS corresponds very well with those obtained from first principles (see figure 3 of reference by Castellanos et al [33]). We can observe that there is a splitting of degeneration locating the component of spin up of the intermediate band within the band gap. The component of spin down appears located at higher energies as it can be clearly observed. This effect is attributed to the crystal field effect due to the tetrahedral environment on the orbitals d of the Cr atoms, see for example Tell et al [32].

In figure 4 we show the band structure for the CuGaS₂:Cr chalcopyrite doped with 25% of Cr atoms, obtained using the TB parameters adjusted to reproduce the LDOS of reference by Castellanos, et al [33]. For the doped CuGaS₂ chalcopyrite, the symmetry of the unitary cell is tetragonal. The figure 4 shows the band structure along the principal directions of the Brillouin zone. We clearly observe the intermediate band located nearly in the center of the band gap. Both, the states of the intermediate band, and those at the bottom of the conduction

| Element | Eₜ | Eₚ | Eₖ | Eₜₖ |
|---------|----|----|----|------|
| Cr      | −11.83 | −1.87 | −10.60 | −8.35 |
|         |       |     | −10.95 | −8.30 |
|         |       |     | −11.40 | −8.25 |
|         |       |     | −11.50 | −8.05 |
|         |       |     | −11.50 | −8.05 |

*Table 5. Adjusted ‘on-site’ parameters in eV for the Cr atom, the first (second) column corresponds to the parameters for the d orbitals with spin up (down) component.*
Figure 3. (a) Local density of states as a function of energy at \( k = (0, 0, 0) \) for the CuGaS\(_2\):Cr. (b) LDOS projected on the S and Ga atoms; and (c) LDOS projected on the Cr and Cu atoms. The upper (lower) part corresponds to the component of the LDOS with spin up (down), and the vertical dotted line corresponds to the Fermi level.

Figure 4. Electronic band structure for the CuGaS\(_2\):Cr along the principal directions of the Brillouin zone. Note that we have intentionally moved the origin of energy to the position of the Fermi level, and the intermediate band appears at the center of the band gap.
band, correspond to the Cr atom. We observe that the Fermi level appears inside the intermediate band, guaranteeing that the band is partially full. The intermediate band present a small dispersion along the directions of symmetry displayed in the figure. The presence of this intermediate band is very important to ensure the existence of two absorption channels compared with the absorption of only one photon present in conventional solar cells.

3.3. (001) and (110) Surface states

Finally, with the purpose of showing the power of the TB method in the analysis of problems that are difficult to attack by other methodologies, and to have a deep understanding of the electronic properties of the CuGaS\textsubscript{2}, CuAlSe and CuGaS\textsubscript{2}:Cr chalcopyrites, we study the surface states of these materials. The surfaces under study are those along which chalcopyrites are normally grown when they are considered as the active material in a solar cell: (001) and (110). We suppose that the surfaces are ideal surfaces, i.e., the positions of the atoms in the surfaces created by terminating the crystal, are exactly the same than those in the infinite crystal. The study of surface states is carried out using the Surface Green Function (SGFM) method [28, 29], together with the TB Hamiltonian derived here. All the details of the SGFM method appear in the references [28, 29], and they will not repeated here. However, it is worth to writting the explicit form of the Green function for the incomplete crystal:

\[ G^{-1}_s = E - H(0, 0) - H(0, 1)T, \]

(2)

here E is the energy, \( H(0, 0) \) and \( H(0, 1) \) are the Hamiltonians between the principal layers, and T is the transfer matrix. If the surfaces are ideal, as the cases considered here, then, only the outermost atomic layers are affected by the creation of the surface. For the (001) surface, the size of the Hamiltonians, and therefore the size of the Green function of equation (2) is 42 \( \times \) 42, because along this direction the principal layer contains 4 atomic layer with 2 atoms each one. For the [110] the number of atoms in each atomic layer is twice than along the [001] direction, doubling the size of the matrices. In figure 5 we show the dispersion relation along the two-dimensional Brillouin zone for the (001) and (110) surfaces for the CuGaS\textsubscript{2}, CuAlSe\textsubscript{2} and CuGaS\textsubscript{2}:Cr chalcopyrites. For the (001) surface, considering the CuGaS\textsubscript{2} semiconductor, the principal layer contains four atomic layers, two of them containing only anions S, and the other two containing cations Cu and Ga. In this case, the semi-infinite crystal can be obtained by a terminating cation, or termination anion surface. The dispersion relation corresponding to termination cation and anion surface is depicted in figures 5(a) and (b), respectively. Figure 5(c) corresponds to the unique possibility for the (110) surface. The curves denoted with E1 and E2, correspond to the dispersion of the surface states along the high symmetry directions of the 2D Brillouin zone. The top, middle and bottom part of figure 5 correspond to the surface states for the CuGaS\textsubscript{2}, CuAlSe\textsubscript{2}, and CuGaS\textsubscript{2}:Cr chalcopyrites, respectively. From the top and middle part of figure 5, we observe similar behavior of the surface states for the CuGaS\textsubscript{2}, and CuAlSe\textsubscript{2} chalcopyrites: For the anion terminated (001) surface, the E1 and E2 states exhibit similar dispersion, and they tend to be closer to the top of the valence band for the CuAlSe\textsubscript{2} chalcopyrite; whereas for the cation (001) terminated surface, this chalcopyrite exhibits only one surface state (E1), with very similar dispersion compared with the E1 surface state of CuGaS\textsubscript{2}. The anion terminated surface, possesses a surface state located near the top of the valence band. This surface state follows the dispersion relation of the valence band along the \( \Gamma - X \) direction, and appears completely separated along the \( X - M \) direction. For the (110) terminated surface, there are two surface states, one of them located near to the top of valence band, and the other located near the bottom of the conduction band. Apart from the slightly different position in energy, these surface states exhibit similar dispersion in both semiconductors. On the other hand, the dispersion relation of the surface states of the doped chalcopyrite CuGaS\textsubscript{2}:Cr has a completely different behavior. For the cation (001) terminating surface, there are two surface states which appear located closer to the bottom of the conduction band. These states are mainly concentrated in the Ga atoms with predominantly s orbital character. For the anion (001) surface, there are several surface states located in the intermediate band. There is a surface state located inside the lower gap which follows the dispersion of the valence band. This surface state is mainly located in the S atoms, and with predominantly s orbital character. Finally, the (110) surface doped chalcopyrite has four surface states inside each band gap. These surface states exhibit little dispersion compared to previous mentioned terminating layers. The number of surface states for this terminating layer is due mainly to the presence of Cr, and to the number of atoms in the unitary cell and therefore the number of atoms in the (110) surface. To observe the evolution of the surface states, in figure 6 we show the LDOS for the CuGaS\textsubscript{2} and CuGaS\textsubscript{2}:Cr chalcopyrites at the \( \Gamma \) point (\( k = (0, 0) \)) of the 2D surface Brillouin zone for different atomic planes. The LDOS at different atomic layers are numbered with integers, corresponding to the surface and the first inner layers. The atomic layer denoted with 0 corresponds to the surface terminating layer, whereas the layer denoted with 4 corresponds to the LDOS of the bulk semiconductor. From the left column in figure 6, the figure denoted with a) corresponding to cation terminated CuGaS\textsubscript{2} surface, we observe that the surface state at 0.84 eV, marked as E1 in figure 5(a), is mostly concentrated in the surface layer. The LDOS of this surface state mainly comes from the Cu atoms with primarily orbital S character. On the other hand, the surface state at 1.85 eV, is mostly concentrated in the Ga atoms but also with primarily S character. These surface state attenuates very quickly, as...
can be seen into the internal layers. From figure 6(b), corresponding to anion terminated surface, the surface states at 0.80 and 0.93 eV, and denoted as E1 and E2 in figure 5(b), appear mostly concentrated in the S atoms primarily with p orbital character. Finally from figure 6(c), corresponding to the (110) termination surface, we observe that the surface states at 0.32 and 2.05 eV, denoted as E1 and E2 in the top figure 5(c), are mainly localized in the Cu atoms with primarily orbital s character with slightly p orbital character on the S atoms. We observe a quick attenuation of all these states into the internal layers. For the (110) terminating layer, there is a peak at −0.49 eV, i.e. below the top of the valence band. This state is in the continuum and tends to penetrate
into the bulk, as is seen in figure 6(c). The attenuation of the surface states for CuAlSe$_2$ shows similar characteristics as the corresponding cases of CuGaS$_2$. Finally, the right column of figures shows the evolution of the surface states of the CuGaS$_2$:Cr for the same termination layers. For this semiconductor, although we get a completely different behavior, we observe the rapid decay of the surface states when they penetrate into the crystal. This rapid attenuation is clearly seen in the right-hand column of figures of figure 6.

4. Conclusions

We have calculated the electronic properties of the chalcopyrites CuGaS$_2$, CuAlSe$_2$, and CuGaS$_2$:Cr, and their corresponding dispersion relation of the surfaces states along the 2D Brillouin zone for the (001) and (110) terminated surfaces. By adjusting the Tight-binding parameters, we were able to reproduce the band gaps obtained by first-principles calculations, and calculate electronic dispersion relation along the principal directions of the Brillouin zone. For the doped CuGaS$_2$:Cr chalcopyrite, the electronic structure exhibits an intermediate band located inside the band gap, in accordance with previous ab-initio calculations. Using the TB methodology is possible to calculate the dispersion relation for these kind of semiconductors along the whole Brillouin zone without the expensive computational resources required by first principles. For the incomplete crystal, we have found surface states in the gap for both terminated surfaces; for cation or anion (001) terminated surface, as well as cation and anion (110) terminated surface. The attenuation rate of the surface states is always strong and independent of the cation, anion, or cation and anion terminating layers. These surface states do not penetrate more than four atomic layers for all the cases considered in this work. The present study demonstrates
the practical use of the TB method for the study of this kind of systems, where ab-initio methodologies require long time computer calculations.

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Appendix. Tight-binding Hamiltonian for CuGaS2

The general form of the TB Hamiltonian for the chalcopyrite CuGaS2 is,

\[
H = \begin{pmatrix}
H(S_y, S_z) & H(S_y, Ga)_g & H(S_y, Cu)_g & H(S_y, Cu)_g & H(S_y, Ga)_g & H(S_y, Ga)_g & H(S_y, Ga)_g & H(S_y, Ga)_g & H(S_y, Ga)_g \\
0 & H(S_x, S_z) & 0 & 0 & H(S_x, Ga)_g & H(S_x, Ga)_g & H(S_x, Ga)_g & H(S_x, Ga)_g & H(S_x, Ga)_g \\
0 & 0 & H(S_x, S_z) & 0 & H(S_x, Ga)_g & H(S_x, Ga)_g & H(S_x, Ga)_g & H(S_x, Ga)_g & H(S_x, Ga)_g \\
0 & 0 & 0 & H(S_x, S_z) & H(S_x, Ga)_g & H(S_x, Ga)_g & H(S_x, Ga)_g & H(S_x, Ga)_g & H(S_x, Ga)_g \\
H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, Ga)_g \\
H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, S_y)_g & H(Ga, Ga)_g \\
H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, Cu)_g \\
H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, Cu)_g \\
H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, S_y) & H(Cu, Cu)_g
\end{pmatrix}
\]

(A.1)

The diagonal elements of this matrix are in turn 4 × 4 diagonal matrices corresponding to the S and Ga atoms, and 9 × 9 diagonal matrices for the Cu atoms. The upper part of the non-diagonal elements of matrix (A1) contains matrices of 4 × 4 for the interactions between the S and the Ga atoms, and 4 × 9 matrices for the interaction between the S and the Cu atoms. The non-diagonal Hamiltonians of equation (A.1) are in general written as,

\[
H(S_y, Ga)_g = \begin{pmatrix}
V(s, s) & V(s, p_x) & V(s, p_y) & V(s, p_z) \\
V(p_x, s) & V(p_x, p_x) & V(p_x, p_y) & V(p_x, p_z) \\
V(p_y, s) & V(p_y, p_x) & V(p_y, p_y) & V(p_y, p_z) \\
V(p_z, s) & V(p_z, p_x) & V(p_z, p_y) & V(p_z, p_z)
\end{pmatrix}
\]

(A.2)

\[
H(S_y, Cu)_g = \begin{pmatrix}
V(s, s) & V(s, p_x) & V(s, p_y) & V(s, p_z) & V(s, x^2 - y^2) & V(s, z^2 - r^2) \\
V(p_x, s) & V(p_x, p_x) & V(p_x, p_y) & V(p_x, p_z) & V(p_x, x^2 - y^2) & V(p_x, z^2 - r^2) \\
V(p_y, s) & V(p_y, p_x) & V(p_y, p_y) & V(p_y, p_z) & V(p_y, x^2 - y^2) & V(p_y, z^2 - r^2) \\
V(p_z, s) & V(p_z, p_x) & V(p_z, p_y) & V(p_z, p_z) & V(p_z, x^2 - y^2) & V(p_z, z^2 - r^2)
\end{pmatrix}
\]

(A.3)

The matrix elements of equations (A.2) and (A.3) are defined in terms of the direction cosines according to table 20.1 of the book of Harrison [31], and the \(g_i\) appearing in equation (A.1) are defined as,

\[
g_i = e^{i \mathbf{k} \mathbf{d}_i}
\]

(A.4)

being \(\mathbf{k}\) the wave vector, and \(\mathbf{d}_i\) the positions vectors connecting first neighbors only. Because in our calculations we have taken into account the parameter \(c/2a = \eta\) and the displacement of the anion from its ideal position \(a\), the explicit form of the vectors \(d_i\) are,

\[
d_1 = a\left(\frac{1}{4}, -\frac{1}{2}, -\frac{1}{2}\right), \quad d_2 = a\left(-\frac{1}{4}, 0, \frac{1}{2}\right), \quad d_3 = a\left(-\frac{1}{4}, -\frac{1}{2}, \frac{1}{2}\right), \quad d_4 = a\left(-\frac{1}{4}, \frac{1}{2}, \frac{1}{2}\right), \quad d_5 = a\left(0, \frac{1}{2}, 0\right), \quad d_6 = a\left(0, -\frac{1}{2}, 0\right), \quad d_7 = a\left(-\frac{1}{4}, 0, \frac{1}{2}\right), \quad d_8 = a\left(-\frac{1}{4}, -\frac{1}{2}, \frac{1}{2}\right), \quad d_9 = a\left(-\frac{1}{4}, -\frac{1}{2}, -\frac{1}{2}\right), \quad d_{10} = a\left(-\frac{1}{4}, \frac{1}{2}, -\frac{1}{2}\right), \quad d_{11} = a\left(-\frac{1}{4}, \frac{1}{2}, 0\right), \quad d_{12} = a\left(0, -\frac{1}{2}, -\frac{1}{2}\right), \quad d_{13} = a\left(-\frac{1}{4}, 0, -\frac{1}{2}\right), \quad d_{14} = a\left(-\frac{1}{4}, -\frac{1}{2}, -\frac{1}{2}\right), \quad d_{15} = a\left(0, -\frac{1}{2}, 0\right), \quad d_{16} = a\left(0, -\frac{1}{2}, -\frac{1}{2}\right).
\]
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References

[1] Solar Frontier Achieves World Record Thin-Film Solar Cell Efficiency: 22.3% Solar Frontier KK Press Release, December 8 (2015).
[2] Jackson P, Harisidos D, Lotter E, Paetel S, Waerz R, Menner R, Wischmann W and Powalla M 2011 New world record efficiency for Cu(In,Ga)Se2 thin-film solar cells beyond 20% Prog. Photovolta: Res. Appl. 19 894
[3] Maeda T, Takeichi T and Wada T 2006 Systematic studies on electronic structures of CuInSe2 and the other chalcopyrite related compounds by first principles calculations Phys. Stat. Sol. (a) 203 2634
[4] Siebenstritt S 2002 Wide gap chalcopyrites: material properties and solar cells Thin Solid Films 403-404 I
[5] Omata T, Nose K and Otsuka-Yao-Matsuo S 2009 Size dependent optical band gap of ternary I-III-VI2 semiconductor nanocrystals J. Appl. Phys. 105 073106
[6] Chichibu S, Shirakata S, Isomura S, Harada Y, Uchida M, Matsumoto S and Higuchi H 1995 Photoluminescence studies in CuAlSe2 epilayers grown by low-pressure metallocarbo chemical-vapor deposition J. Appl. Phys. 77 1225
[7] Alonso M I, Pascual I, Garriga M, Kikuno Y, Yamamoto N and Wakita K 2000 Optical properties of CuAlSe2 J. Appl. Phys. 88 1923
[8] Chen S, Gong X G, Walsh A and Wei S 2009 Electronic structure and stability of quaternary chalcogenide semiconductors derived from cation cross-substitution of II-VI and I-III-VI2 compounds Phys. Rev. B 79 165211
[9] Shirakata S, Chichibu S and Isomura S 1997 Room-temperature photoreflectance of CuAl1−xGaxS2 alloys Jpn. J. Appl. Phys. 36 7160
[10] Luque A and Marti A 1997 Increasing the efficiency of ideal solar cells by photon induced transitions at intermediate levels Phys. Rev. Lett. 78 5014
[11] Wang W, Lin A S and Phillips J D 2009 Intermediate-band–photovoltaic solar cell based on ZnTe:O Appl. Phys. Lett. 95 011103
[12] Marti A, Antolin E, Stanley C R, Farmer C D, López N, Díaz F, Cánovas E, Linares P G and Luque A 2006 Production of photocurrent due to intermediate-to-conduction band transitions: a demonstration of a key operating principle of the intermediate-band solar cell Phys. Rev. Lett. 97 247401
[13] Shao Q, Balandin A A, Fedoseyev A I and Yuworski M 2007 Intermediate-band solar cells based on quantum dot supercrystals Appl. Phys. Lett. 91 163503
[14] Marti A, Fuertes M D and Luque A 2008 Evaluation of the efficiency potential of intermediate band solar cells based on thin-film chalcopyrite materials J. Appl. Phys. 103 073706
[15] Lucena R, AguilerI A, Palacios P, Wahnón P and Conesa J C 2008 Synthesis and spectral properties of nanocrystalline V-substituted In2Se3, a novel material for more efficient use of solar radiation Chem. Mater. 20 5125
[16] Jaffe J E and Zunger A 1983 Electronic structure of the ternary chalcopyrite semiconductors CuAlSe2, CuGaSe2, CulnSe2, CuGaSe2, CuGaS2, and CuInSe2 Phys. Rev. B 28 5822
[17] Jaffe J E and Zunger A 1984 Theory of the band-gap anomaly in ABC2 chalcopyrite semiconductors Phys. Rev. B 29 1282
[18] Álvarez A, Ruluck S, Eriksson O, Wills J M and Johansson B 1998 Calculated optical properties of a solar energy material: CuGaSe2 Sol. Energy Mater. Sol. Cells 53 357
[19] Chen S, Gong X G and Su-Huai W 2007 Band-structure anomalies of the chalcopyrite semiconductors CuGaX2 versus AsGaX2 (X = S and Se) and their alloys Phys. Rev. B 75 205209
[20] AguilerI A, Vidal J, Wahnón P, Reining L and Botti S 2010 First-principles study of the band structure and optical absorption of CuGaSe2 Sol. Energy Mater. Sol. Cells 94 1933
[21] Castellanos-Aguila J E, Palacios P, Conesa J C, Arriaga J and Wahnón P 2016 Electronic band alignment at CuGaS2 chalcopyrite interfaces Comput. Mater. Sci. 121 79
[22] Palacios P, Sánchez K, Conesa J C and Wahnón P 2006 First principles calculation of isolated intermediate band formations in a transition metal-doped chalcopyrite-type semiconductor Phys. Status Solidi (a) 203 1395
[23] Palacios P, Sánchez K, Conesa J C, Fernández J J and Wahnón P 2007 Theoretical modelling of intermediate band solar cell materials based on metal-doped chalcopyrite compounds Thin Solid Films 515 6280
[24] AguilerI A, Palacios P and Wahnón P 2007 Enhancement of optical absorption in Ga-chalcopyrite-based intermediate-band materials for high efficiency solar cells Sol. Energy Mater. & Solar Cells 91 2033
[25] Yang C, Qin M, Wang Y, Wen D, Huang F and Lin J 2013 Observation of an intermediate band in Sn-doped chalcopyrites with wide-spectrum solar response Sci. Rep. 3 1286
[26] Mohammed L, Saeed M A and Musa A 2016 Electronic confinement for tuning optical properties in β-In2Te3S4 (TM = V, Fe, and Ti): Prospects for intermediate-band materials Sol. Energy 137 621
[27] Andalibi S, Rostami A, Darvish G, Kazem M and Farshi M 2016 Band gap engineering of organo metal lead halide perovskite photovoltaic absorber Opt. Quant. Electron. 48 258
[28] García-Moliner F and Velasco V R 1986 Theory of incomplete crystals, surfaces, defects, interfaces and layered structures Prog. Surf. Sci. 21 93
[29] García-Moliner F and Velasco V R 1992 Theory of Single and Multiple Interfaces (Singapur: World Scientific)
[30] Harrison W A 1989 Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond (Dover Publications)
[31] Rodriguez J A 1999 Hamiltonian tight binding para calcopiritas tipo A1B1C12−x Rev. Mex. Fis 45 584
[32] Bell B, Shyu J L, Kasper H M and Barns R L 1974 Valence-band structure of CuGaIn1−xS2 Phys. Rev. B 10 1748
[33] Castellanos AguilA J E, Palacios P, Conesa J C, Arriaga J and Wahnón P 2017 Theoretical band alignment in an intermediate band chalcopyrite based material 242 132