(100) ideal-surface band structure for the series of Cu-based $A^{I}B^{III}C_{2}^{VI}$ chalcopyrites.

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Abstract

We use the Surface Green’s Function Matching (SGFM) method and a tight-binding hamiltonian to calculate the (100)-surface electronic band structure and local density of states of the series of Cu-based $A^{I}B^{III}C_{2}^{VI}$ chalcopyrites. We find four surface states in the optical gap energy region of s-p character and three surface states in the conduction band region of p-character. We show the trends of different characteristics within the series by means of figures and tables so that the quantitative behavior can be evaluated as well. We did not find Frontier Induced Semi-Infinite states of non-dispersive character in the studied range of energy within the valence band as we found in the case of the (112) surface electronic band structure for $CuInSe_{2}$.

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I. INTRODUCTION

Semiconducting chalcopyrites are interesting for their non-linear optical properties and for their possible technological applications [1, 2]. Chalcopyrites are used in processes as chemisorption, catalysis and bioleaching [3], solar cells [4] and other applications [5, 6]. Surfaces, interfaces, quantum wells and superlattices with chalcopyrites as one of the elements are of interest in this context.

At the basis of a proper description of these systems is an accurate enough calculation of the electronic band structure. The first calculation of the electronic structure for the series of ternary Cu-based chalcopyrites was presented by Jaffe and Zunger [7]. It was calculated self-consistently within the density functional formalism. They present a generic diagram of the bulk electronic band structure for the Cu-based chalcopyrites. The electronic band structure of bulk CuInSe$_2$ and of its (112) surface has been studied later on by Rodríguez et al. [8] using the tight-binding method. They implemented a set of tight-binding parameters for the series of chalcopyrites $CuB^{II}C^{VI}$ with $B = Al, Ga, In$ and $C = S, Se, Te$ that describe quite accurately the bulk electronic band structure and have been used successfully [9, 10] as input to calculate the surface electronic band structure using the Surface Green’s Function Matching (SGFM) method [11]. Interfaces [12] and superlattices [13] can also been described successfully by this method.

Ab initio methods have been used to calculate the bulk electronic band structure although sometimes the semiconductor optical gap is not reproduced accurately. Recently these methods have been used successfully to study ferromagnetism of Mn-substituted Cu-based chalcopyrites [14]. The main interest of these works is related to spintronics. Mn-doped II-IV-V$_2$ chalcopyrites have been studied in ref. [15]. Comparison of predicted ferromagnetic tendencies of Mn substituting the Ga site in II-V’s and I-III-VI$_2$ chalcopyrites semiconductors is done in [16] and the site preference for Mn substitution in spintronic chalcopyrite semiconductors is explored in [17]. Other recent studies on chalcopyrites are on magnetic defects in a photovoltaic material (Fe-doped CuInSe$_2$) [18] and the effect of hydrogen (H) on Cu-based chalcopyrites. Actually, for CuGaSe$_2$ it is found that H is a deep donor while for CuInSe$_2$ it is a shallow one. The conductivity can be changed from p-type to n-type either by introducing hydrogen to the sample as a dopant or by passivating the defects. The final result depends on details of the minimum of the conduction band of the chalcopyrite and
on stoichiometry \[19\]. \textit{Ab initio} methods have also been used to study other bulk properties as intrinsic point defects in \textit{CuInSe}_2 \[20\], anion vacancies as a source of persistent photo-conductivity in \textit{CuGaSe}_2 and \textit{CuInSe}_2 \[21\], and to establish the existence of an energetic barrier for holes arriving from the grain interior to the grain boundaries in \textit{CuInSe}_2 \[22\].

There are in the literature several other studies on chalcopyrites of the type \textit{A}^I\textit{B}^{III}\textit{C}^{VI}. The stability of this crystal phase has been studied and its possible coexistence with a phase of \textit{CuAu-type} has been predicted in some cases \[23\]. Structural and dynamic properties of the lattice of some chalcopyrites using the perturbation method to the density functional are presented in reference \[24\]. They calculate the static and high frequency dielectric tensor and get a good agreement with infrared and Raman experimental results. Order-disorder transitions can be induced by doping the sample with a magnetic ion as \textit{Mn} to a dilute magnetic semiconductor with a slightly modified crystal structure \[25\].

Reference \[26\] deals with a systematic treatment of the stability as a function of the concentration of the components in \textit{ZnGeAs}_2 / \textit{GaAs} in the (001) direction. The effect of anion and tetragonal distortions on the (112) surface has been recently studied for a series of \textit{Cu}-based chalcopyrites by Tototzintle \textit{et al.} \[27\]. For \textit{CuInSe}_2, the electronic states of the ideal surfaces (100) and (112) has been calculated by Rodríguez \textit{et al.} \[28\], the reconstruction of the polar (112) and (-1-1-2) surfaces versus the non-polar (220) one has been studied by Zhang and Wei \[29\]. Also the defect induced non-polar to polar transition at the (112) surface is considered in reference \[30\]. On the basis of atomic chemical potentials, they show that the (112) surface is the more stable. No extensive calculation on the (100) surface for the series we deal with in this work is known to us. The mechanism of linear and non-linear optical effects of \textit{AgGaX}_2 (\textit{X} = \textit{S}, \textit{Se}, \textit{Te}) has been recently studied by Bai \textit{et al.} \[31\].

Recent experiments on \textit{Cu}-based chalcopyrites include the study of the influence of hydrogen \[32\], Raman \[33\], atomic defects and non-stoichiometry \[34\] and muon charge states \[35\] all in \textit{CuInSe}_2; quasi real-time Raman studies on the growth of \textit{Cu-In-S} thin films \[36\] and temperature dependent Hall measurements of intrinsic defects in \textit{CuGaSe}_2 \[37\].

In this paper we use the tight-binding hamiltonian and the parameters previously constructed \[8,9,10\] and the Surface Green’s function matching method (SGFM) \[11\] to study the electronic band structure of the ideal (001) surface for the series of the \textit{Cu}-based chalcopyrites \textit{CuB}^{III}\textit{C}^{VI} where \textit{B} = \textit{Al}, \textit{Ga}, \textit{In}; \textit{C} = \textit{S}, \textit{Se}, \textit{Te}. The method has been proved
accurate enough to describe other systems as II-VI \[38, 39\] and III-V zincblende \[40\] and wurzites \[41\] semiconductors. The Surface Green’s function matching method \[11\] starts with the bulk tight-binding parameters as input and takes care by itself for the proper matching condition that describes the surface.

The tight-binding method \[44\], the construction of the hamiltonian and the Surface Green’s function matching method are described extensively enough elsewhere \[8, 10, 11, 27, 42, 43\]. We therefore limit ourselves in the rest of the paper to our new results.

II. THE (100) BULK PROJECTED BANDS FOR THE SERIES CuB\(^{III}\)C\(^{VI}\) WHERE \(B = Al, Ga, In; C = S, Se, Te\).

Previous to the electronic density of states for the (100) ideal surface, it is convenient to describe the general trends in the (100) bulk-projected electronic band structure for the series. A generic diagram emerges from the bulk electronic band structure \[45\] similar to the one elaborated previously by Jaffe and Zunger \[7\]. As we already mentioned, we used the SGFM method \[11\] to calculate the (100)-surface Green’s function and from the poles of its real part we calculated the band structure that we present on Figs.1-3. The shaded areas are the bulk bands. The origin is at the top of the valence band. Notice that we have drawn the bands from -6 eV to +10 meV. The bulk bands presented here as shaded areas are obtained from the (100)-electronic band structure projected into the bulk (fifth layer). The bands are drawn through the high-symmetry points \(X - \Gamma - M\) in the irreducible part of the two dimensional First Brillouin Zone. In the range of energy that we have considered for this calculation, the valence band is characterized by a lens at the top of the valence band at \(\Gamma\) that gets wider as the \(C^{VI}\)-cation gets heavier. The width of the upper valence band (UVB) shrinks as the mass of the \(B^{III}\) cation enhances. For \(B^{III} = In\) the small gap that separates the UVB from the intermediate valence band (IVB) appears in the region around -5 eV. It is evident that the UVB-width shrinks also with a bigger \(C^{VI}\)-anion mass as the optical gap does in the whole series. In the conduction band (CB) energy region three sub-bands are apparent separated by inner gaps. The gap around 7eV is of particular interest as states appear within this energy region. We will comment further on the behavior of these states below.
III. THE (001) IDEAL SURFACE ELECTRONIC BAND STRUCTURE FOR THE SERIES OF CHALCOPYRITES $CuB^{III}C^{VI}$ ($B = Al, Ga, In; C = S, Se, Te$).

In Fig.1, we present the bands for $CuAlC^{VI}_2$, in Fig.2 for $CuGaC^{VI}_2$ and in Fig. 3 for $CuInC^{VI}_2$. Electronic states appear in the optical gap region and from 6-8 eV in the conduction band (CB). We label the four states that we have found in the optical gap region as $E_1$, $E_2$, $E_3$, $E_4$ and the three in the upper part of the CB as $E_5$, $E_6$, and $E_7$.

A. States within the optical gap energy-region.

In the optical gap energy region of all the Cu-based chalcopyrites four states occur. Two, $E_1$ and $E_2$, are truly surface states and remain within the gap energy region for the whole series. $E_3$ and $E_4$ behave differently. Notice that the heavier the anion, the smaller the energy difference between the top of the valence band and the surface states $E_1$ and $E_2$. Nevertheless these two states remain well within the gap for the whole series and almost at the middle of this energy interval. That is to say that the gap also shrinks as the mass of the anion gets bigger for the same cations in the perovskite. Also as the mass of the $B^{III}$ cation is heavier, the gap decreases and the distance between the states $E_1$ and $E_2$ and the top of the valence band is shorter in energy. These features are universal and can be appreciated quantitatively in Table I where we present the energy of the four states within the optical gap at three high-symmetry points in the two dimensional first Brillouin zone, namely, $\Gamma$, $X$ and $M$. 


CuAlS$_2$ 1.29 1.26 1.26 1.62 1.41 1.41 3.21 3.21 3.21 3.30 3.48 3.48
CuAlSe$_2$ 1.04 0.99 0.99 1.26 0.99 0.99 2.67 2.74 2.74 2.67 2.74 2.74
CuAlTe$_2$ 0.63 0.57 0.57 0.84 0.57 0.57 2.01 1.98 1.98 2.01 2.22 2.22
CuGaS$_2$ 0.81 0.81 0.81 1.14 0.87 0.87 1.71 1.74 1.71 1.89 1.98 1.98
CuGaSe$_2$ 0.69 0.63 0.57 0.81 0.63 0.57 1.44 1.41 1.41 1.44 1.62 1.62
CuGaTe$_2$ 0.41 0.35 0.35 0.54 0.35 0.35 0.98 0.92 0.92 0.98 1.13 1.13
CuInS$_2$ 0.57 0.48 0.48 0.75 0.48 0.48 1.62 1.71 1.71 1.74 1.98 1.98
CuInSe$_2$ 0.39 0.18 0.18 0.48 0.33 0.33 1.23 1.50 1.50 1.53 1.68 1.68
CuInTe$_2$ 0.30 0.15 0.15 0.42 0.24 0.24 1.18 1.29 1.29 1.32 1.50 1.50

Table I- The energies at the high symmetry points $\Gamma$, $X$, and $M$ for the four states that appear in the optical gap region.

The states $E_3$ and $E_4$ lie very close to the bottom of the CB and remain truly surface states for the whole series except for CuInSe$_2$. There the two states become a resonance around $\Gamma$. The surface state $E_4$ enters into the CB at $X$ and $M$ for the three chalcopyrites CuAlC$_{VI}$ studied here.

The composition of the surface states $E_1$ and $E_2$ is mainly of $s$ and $p$ character. We also find a small contribution (less than 3%) from states of $d$-symmetry. This contribution decreases as the anion mass gets heavier while at the same time the $p$-character of the state increases and its $s$-character diminishes. The surface states $E_3$ and $E_4$ are more of $s$-character but its $p$-contribution enhances as the anion mass gets bigger. The $d$-contribution to this two states is very small or absent at all. We quote the composition of these states for some cases in Table II.

| element  | E1 [%] | E2 [%] | E3 [%] | E4 [%] |
|----------|--------|--------|--------|--------|
|          | $s$ $p$ $d$ | $s$ $p$ $d$ | $s$ $p$ $d$ | $s$ $p$ $d$ |
| CuAlS$_2$ | 43 56 1.7 | 47 50 2.8 | 67 32 0.0 | 78 21 0.2 |
| CuGaSe$_2$ | 32 67 1.2 | 38 59 2.5 | 55 45 0.0 | 62 37 0.3 |
| CuInTe$_2$ | 22 78 0.7 | 28 71 1.0 | 55 45 0.0 | 55 45 0.0 |

Table II- Composition of some of the (100) surface states at $\Gamma$. The percentages are rounded so that they do not exactly sum to 100% in some cases.
Notice that as the mass of the cation ($B^{III}$) gets heavier a lens develops around $\Gamma$ at the bottom of the CB. Of special interest in this context is $CuInSe_2$ since the two states $E_3$ and $E_4$ lie in the lens space. For $CuInTe_2$ we find the $E_4$ state in the lens while the $E_3$ state is not.

B. States in the conduction-band-gaps energy region.

Above the optical gap, within 10 eV from the top of the valence band (the origin), there are two gaps in the CB. They do not shrink very much with the enhancement of the anion mass conserving the cation ($B^{III}$) fixed but the whole bulk band structure moves downwards to the origin so that the net effect is that the optical gap diminishes as we already mentioned above. As a consequence a third small gap appears around 10 eV. Notice also the displacement of the structure towards lower energies as the anion gets heavier for fixed cations. Three new surface states develop in this range of energy, namely, $E_5$, $E_6$, and $E_7$. The energy at which these states occur is smaller as the anion mass or as the cation $B^{III}$ gets bigger. We have produced Table III to report on the energy at which these states appear.

| element     | E5 [eV] | E6 [eV] | E7 [eV] |
|-------------|---------|---------|---------|
|             | $\Gamma$ | $X$ | $M$ | $\Gamma$ | $X$ | $M$ | $\Gamma$ | $X$ | $M$ |
| CuAlS$_2$   | 7.05    | 6.90   | 6.90 | 7.05    | 6.99 | 6.99 | 8.28 | 8.34 | 8.34 |
| CuAlSe$_2$  | 6.39    | 6.40   | 6.40 | 6.52    | 6.52 | 6.52 | 7.64 | 7.66 | 7.66 |
| CuAlTe$_2$  | 5.52    | 5.52   | 5.52 | 5.64    | 5.64 | 5.64 | 6.72 | 6.69 | 6.72 |
| CuGaS$_2$   | 6.09    | 5.91   | 5.91 | 6.09    | 6.06 | 6.06 | 7.38 | 7.38 | 7.38 |
| CuGaSe$_2$  | 5.55    | 5.55   | 5.55 | 5.70    | 5.70 | 5.70 | 6.87 | 6.87 | 6.87 |
| CuGaTe$_2$  | 4.89    | 4.91   | 4.91 | 5.02    | 5.06 | 5.06 | 6.10 | 6.11 | 6.11 |
| CuInS$_2$   | 4.32    | 3.49   | 3.49 | 4.86    | 4.53 | 4.53 | 6.72 | 6.66 | 6.66 |
| CuInSe$_2$  | 5.28    | 5.07   | 5.07 | 5.28    | 5.16 | 5.16 | 6.30 | 6.27 | 6.27 |
| CuInTe$_2$  | 4.80    | 4.80   | 4.80 | 4.94    | 4.92 | 4.92 | 5.91 | 5.91 | 5.91 |

Table III- The same as Table I for the three states that appear in gap region in the conduction band.

In the series $CuAlC^{VI}$ the state $E_5$ lies in the CB for the whole interval $X - \Gamma - M$ for $C^{VI} = S$ but emerges from the bulk band energies for $C^{VI} = Se$ and is neatly detached
from the CB for \( C^{VI} = Te \). \( E_6 \) is a resonance around \( \Gamma \) but emerges as a pure surface state around \( X \) and \( M \) for the first element of this sub-series but is a pure surface state for the other two. \( E_7 \) remains as a pure surface state in the whole branch of the 2D-FBZ reported here for the three elements.

In the series \( CuGaC^{VI} \) the behavior of the three surface states \( E_5, E_6, \) and \( E_7 \) is approximately the same as for the \( CuAlC^{VI} \) one.

The series \( CuInC^{VI} \) presents a different behavior. The state \( E_5 \) lies in the upper border of a lens that develops in the second inner gap in the CB and it is therefore to be consider as a resonance for \( C^{VI} = S \). For \( C^{VI} = Se \), \( E_5 \) gets through the gap towards higher energies and enters the CB. But for \( C^{VI} = Te \), \( E_6 \) is a pure surface state for the whole interval \( X - \Gamma - M \).

Also the state \( E_6 \) behaves specially. In \( X - \Gamma - M \), it is a resonance in almost the whole interval (see Fig. 3 for details) for \( C^{VI} = S, Se \). But for \( C^{VI} = Te \) it emerges as a surface state in the whole interval presented here. \( E_7 \) remains essentially as a pure surface state in \( X - \Gamma - M \) for the whole series. The three \( E_5, E_6, \) and \( E_7 \) states are of almost exclusively of p-character.

Finally, two more surface states emerge in the energy region under study (less than 10 eV) since as a consequence of the displacement towards lower energies of the bulk bands (shadowed areas in the figures 1-3) as the mass of the \( B^{III} \) cation and of the anion gets heavier, a new third gap appears in the CB below 10 eV. This is apparent in \( CuAlTe_2 \) in Fig.1. \( Te \) is the heavier anion of the sub-series \( CuAl \). In the second series \( CuGa \) in Fig.2, the third gap in the CB is seen for the anion \( Se \) at around 10 eV and appears around 9 eV for the anion \( Te \) and moves towards 8 eV for \( CuInTe_2 \). The energy at \( \Gamma \) for some of these states is presented in the next Table IV. The composition at \( \Gamma \) of both states that appear at this energy is almost exclusively of p-orbitals, with a very minor contribution from s-orbitals and a tiny one from d-orbitals.

|     | \( E_8 \) | \( E_9 \) |
|-----|---------|---------|
| CuInS_2 | 9.48   | 9.83   |
| CuInSe_2 | 9.12   | 9.48   |
| CuInTe_2 | 8.34   | 8.78   |

Table IV. The surface states at higher energies in the conduction bands.
Just for completeness, we mention that some surface state appear in the range of energy studied here in some of the lenses in the valence band region that are apparent from Figs. 1-3.

IV. THE (001) IDEAL SURFACE LOCAL DENSITY OF STATES FOR THE SERIES OF CHALCOPYRITES $CuB^{III}C^{VI}$ ($B = Al, Ga, In; C = S, Se, Te$).

In Fig. 4 we present the (001) surface local density of states (LDOS) for the series of chalcopyrites studied here. The points indicate the optical gap. The peaks in the optical gap indicate the spectral weight of the surface states in the optical gap energy region, namely $E_1$, $E_2$, $E_3$, and $E_4$.

The CB present two minima associated with the two inner gaps that we have presented above. Also its evolution with the anion and $B^{III}$ cation masses is apparent. The shrinking of the optical gap as the anion mass, on one hand, and the cation one, on the other, increases is clearly seen in this figure as well. Between -6 and -8 eV the LDOS has the highest spectral weight, a common feature to all the nine Cu-based chalcopyrites due to the contribution of $d - Cu$ orbitals. Notice that this peak becomes thinner and higher as the mass of the $B^{III}$ cation enhances. The LDOS at this energy presents two peaks for $C^{VI} = S, Se$ and only one for $C^{VI} = Te$.

V. FISIM STATES

Non dispersive states have been experimentally found in (100) CdTe [47]. These states were described as bulk states induced by the presence of a surface [48]. It was found that these states are more general and predicted to exist at interfaces as well [49]. The states were consequently suggested to be named Frontier Induced Semi-Infinite Medium (FISIM) states [51]. In these papers, the FISIM states are shown to be built from spectral weight that accumulates at a certain fixed energy from states with the same crystal momentum $k$ and therefore their occurrence does not violate the conservation of the number of states when integrating in the energy interval of the whole valence band at constant $k$. A detailed study of the valence-band electronic structure for ZnSe(001) is presented in reference [50]. The non-dispersive states are found. It seems that this work is consistent with these states.
being bulk states (existing not only in the surface region) but induced by the particular surface in the direction studied, that is to say FISIM states. Nevertheless whether their detailed interpretation does violate or not the conservation theorem quoted above has not been studied in detail. We will examine further this point somewhere else. In the energy interval studied here we did not find FISIM states for the (001) direction as it was found in the (112) surface electronic band structure for \( \text{CuInSe}_2 \) [51].

VI. CONCLUSIONS

We have used the SGFM method and a tight-binding hamiltonian to calculate the ideal (001)-surface electronic band structure and the Local Density of States (LDOS) for the series of Cu-based chalcopyrites \( \text{CuB}^{III} \text{C}^{VII} \) (\( B = \text{Al, Ga, In}; C = \text{S, Se, Te} \)). The general characteristics are similar although important differences occur in the bands as in the LDOS. Within the optical gap energy region we find four surface states of mainly s-p character and in the CB region we find three surface states of predominantly p-character. The bulk projected electronic bands evolve in the series as the mass of the anion, on one side, and the one of the \( B^{III} \) cation on the other, gets heavier, moving the conduction band (CB) as a whole towards lower energies. We found two consequences of this fact. First, the optical gap shrinks and second a third inner gap appears in the higher energy region of the CB. Two new surface states of predominantly p-character exists in this new gap for the chalcopyrites that do show this third inner gap within 10 eV from the origin. Presumably the gap is a common fact to the whole series but lies at higher energies in the rest of the members of the series. Finally, we did not find FISIM states for the (001) surface band structure as it was found for the (112) one previously for \( \text{CuInSe}_2 \) [51].

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FIGURE CAPTIONS
FIG. 1 The electronic band structure for the sub-series $CuAlC^{VI}$. The surface states are indicated as dotted lines.

FIG. 2 We present in this figure the electronic band structure for the sub-series $CuGaC^{VI}$. The conventions are the same as in Fig. 1.

FIG. 3 The electronic band structure for the sub-series $CuInC^{VI}$.

FIG. 4 The Local Density of States (LDOS) at the (001) surface layer for the whole series of Cu-based chalcopryiyes.
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