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Frontier induced semi-infinite-medium (FISIM) states at semiconductor surfaces and interfaces

D. Olguín[1], J.A. Rodríguez[2], and R. Baquero[1,a]

[1] Departamento de Física, CINVESTAV, Apartado Postal 14-470, 07000 México D.F.
[2] Departamento de Física, Universidad Nacional de Colombia, Bogotá, Colombia

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Abstract. In a previous work we have discussed the valence band electronic structure of *a* (001) oriented surface (semi-infinite medium) of some II-VI wide band gap zinc-blende semiconductor compounds. For these systems, we have found three characteristic surface resonances, besides the known bulk bands (hh, lh and spin-orbit bands). Two of these resonances correspond to the anion terminated surface and the third one to the cation terminated one. We have shown, specifically, that three non dispersive (001)-surface-induced bulk states, in the $\Gamma - X$ direction of the 2D Brillouin zone, do exist and are characteristic of these systems. The existence of these states has been confirmed, independently, by two experimental groups and further evidence of our predictions has been more recently found. In order to continue with the description of these states, in this work, we briefly review the main characteristics of the electronic structure of the (001)-surfaces to up-date their analysis and we present new results concerning the existence of the same kind of states in Cu-based calcopyrites and at interfaces. This shows that, in general, the non-dispersive states occur in several, if not all, crystal surfaces, and, on general grounds, as the consequence of introducing to an infinite medium a frontier of any kind (not only with the vacuum). For that reason we propose here, to name them, more appropriately as Frontier Induced Semi-Infinite Medium (FISIM) states. We present in this paper two new interesting cases where the non-dispersive states appear. First, the (112)-oriented $\mathrm{CuInSe_2}$ calcopyrite surface and, secondly, the interface $\mathrm{CdTe/CdSe}_x\mathrm{Te}_{1-x}$ ($x = 0.15$) which, essentially, does not introduce the additional effects due to lattice mismatch so that the FISIM states are clearly seen. We have calculated them for a broader range of x and for other II-VI and III-V semiconductor compounds to check that the result is general. The surface and the interface that we present here, allow us to discuss the characteristics of these newly found states, in a more general way.

PACS. 71.15.Ap Basis sets (LCAO, plane-wave, APW, etc.) and related methodology (scattering methods, ASA, linearized methods, etc.) – 73.20.At Surface states, band structure, electron density of states

1 Introduction

The electronic band structure of the valence-band of the II-VI wide band gap semiconductors CdTe, ZnTe, CdSe and ZnSe semi-infinite crystals terminated by a (001)-surface has been discussed in references [1,2]. The general characteristics of the electronic band structure, obtained from these previous calculations are sketched in Figure 1, where we have taken the CdTe case as an example. The dispersion of the heavy hole (hh) and light hole (lh) bands (solid line), in the Δ-direction, follow each other closely in energy. In the different compounds, the hh band widths from Γ to X is around $1.7-2.2$ eV and the lh band widths about $2.2-2.4$ eV. The spin-orbit splitting is about 1.0 eV in the Te-based compounds and about 0.5 eV in the Se-based compounds. The spin-orbit band (*so*) widths are about $3.5-4.5$ eV. The wave function decomposition for the hh, lh indicates that mainly the p_x and p_y orbitals of both anion and cation contribute to these bands, while the spin-orbit band has a p_z character. Table 1 shows the orbitals which contribute to the different states shown in Figure 1. The lower band, around -8.5 to -10.8 eV, has only s-orbital contributions for all II-VI zinc-blende compounds as it is in our CdTe example.

The electronic band structure of the valence band of the (001)-surface is very rich in several other features. In particular, three characteristic surface-resonances appear in the energy range studied (solid and empty triangles in Fig. 1). Two correspond to the anion-terminated surface ($S_{a1},\ S_{a2}$) and the third one to the cation terminated one (S_c). In all the systems considered, the anion-terminated surface resonance (S_{a1}) follows roughly the dispersion of the heavy hole bulk band, but at a slightly higher energy (see Fig. 1). The S_{a2} surface resonance state does not show dispersion and, approximately, coincidences at K with the lower bulk band of s-character. We use the surface

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[a] e-mail: `rbaquero@fis.cinvestav.mx`

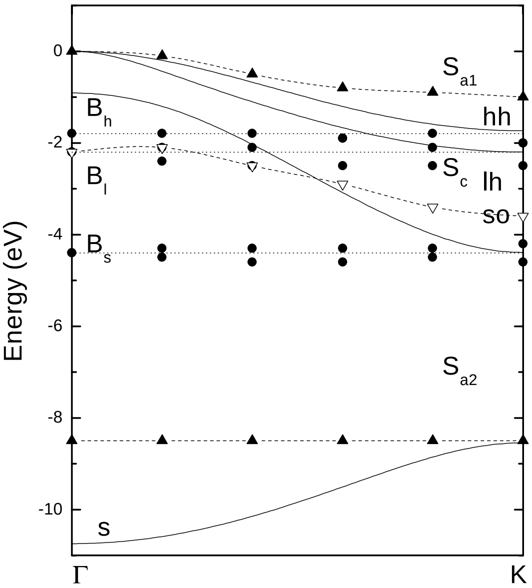

Fig. 1. Electronic band structure of (001)-CdTe in the valence band range. We show the heavy hole (hh), light hole (lh), spin-orbit (*so*), and the lower *s*-cation character bulk bands with solid lines. We also show the FISIM states B_h, B_l, and B_s (solid points), and the surface resonances S_{a1}, S_{a2} (solid triangles), and S_c (open triangles), the broken lines are a guide to the eye. The first two surface resonances appear only for an anion-terminated surface, and the last resonance for a cation-terminated surface.

Table 1. LCAO composition of the wave function for the states existing at the (001)-surface considered in this work.

State	Composition
hh	(p_x, p_y)
lh	(p_x, p_y)
so	(p_z)
B_h	(p_x, p_y)
B_l	(p_x, p_y)
B_s	(s, p_z)

notation in Figure 1, that is to say, in the bulk bands X should be used instead of K. The cation-terminated surface resonance (S_c) starts roughly around 2−3 eV from the top of the valence band in Γ and has a varying amount of dispersion, depending on the compound. These surface resonances are characteristic of the kind of atomic species standing on the surface.

On the other hand, by looking at the poles of the real part of the (001)-bulk-projected Green's function we obtain the eigenvalues of the (001)-surface-induced bulk states. Three such states appear (B_h, B_l, and B_s) in this range of energy. These surface-induced bulk bands do not show dispersion from Γ to X. We found that the energy of these states can be associated with the energy of the hh, the lh, and spin-orbit bulk band at the X-high-symmetry point [1,2]. Thus, at X, B_h mixes mainly with the hh bulk band and B_l with the lh bulk band, both states are mainly of (p_x, p_y)-character. B_s mixes with the spin-orbit band and is mainly of (s, p_z)-composition (see Tab. 1). The three states appear at the same position in energy irrespective of the cation or anion termination of the surface, as can be expected for surface-induced *bulk* states, since they must depend on the surface through only the boundary condition (the wave function must be zero at the surface).

We have further found that the surface-induced bulk states do exist also in the calcopyrite structure and at the (001)-interfaces as well. We give below the details of these new results. So, the existence of these states seems quite general. It is for this reason that we propose to introduce the idea that these states are semi−infinite medium states as opposed to bulk (infinite medium) or surface (local) states, and that their appearance is the result of the introduction of any kind of frontier (not only the vacuum). We propose the generic denomination of Frontier-Induced Semi-Infinite Medium (FISIM) states. Independent experimental evidence for the FISIM states has been found on the (001)-CdTe oriented semi-infinite crystals [3,4], and, more recently, on the (001)-ZnSe with a monolayer of Na grown on top of the surface [5–7]. In this work, we extend the discussion on the FISIM states to surfaces of calcopyrites and to interfaces. In the following section, we briefly describe the method that we have used, for completeness. Section 3 is devoted to the discussion of the FISIM states themselves and constitutes the main part of this paper. We summarize our conclusions in a final Section 4.

2 The method

The Schrödinger equation, with the appropriate Hamiltonian describing an infinite periodic system gives Bloch wave functions and energy eigenvalues. The Bloch wave functions fulfil the periodic boundary conditions. When a surface is introduced, and thus the system becomes semi-infinite, the boundary conditions require that the wave function vanishes at the surface. These new boundary conditions modify the energy spectrum and cause the occurrence of new states. These new states exist only in the few atomic layers close to the surface atomic layer. The wave function of these states decays exponentially from the surface into the bulk. On the other hand, there are other states that do not decay exponentially from the surface, and can exist in layers inside the semi-infinite medium, but have a 2D character and therefore can only be detected by photoemission of an oriented crystal. All these effects, that are a consequence of the introduction of a surface into an infinite periodic medium, can be better described within the Green's function formalism. The infinite periodic medium Green's function is

$$G(E, \mathbf{k}) = (E - H(\mathbf{k}))^{-1}, \tag{1}$$

where $\mathbf{k}$ is the crystal momentum, E is the quasiparticle energy and H the Hamiltonian for the infinite periodic system with translational symmetry. Periodic boundary conditions are assumed. For a semi-infinite medium we have to introduce the following Green's function [8]:

$$G_s = G - G\mathcal{G}_B^{-1}G + G\mathcal{G}_B^{-1}\mathcal{G}_S^{-1}\mathcal{G}_B^{-1}G, \tag{2}$$

where the first term on the right hand side is just the Green's function for the infinite medium. The second and third terms describe the total effect of introducing a surface to an infinite medium. The second term describes the hard wall effect, in close analogy to the hard core term in scattering theory. The third term describes the new states, the new solutions due to the matching conditions, and gives rise to surface states that decay a few atomic layers away from the surface.

In order to compute the bulk (infinite medium) band structure of the II-VI semiconductor compounds we have used the empirical tight-binding (TB) method in the Slater-Koster formalism [9,10]. We have used an orthogonal basis set of five atomic orbitals per atom in the unit cell, ($s\ p^3\ s^*$), and we have included the effect of the spin-orbit interaction [11]. It is widely accepted that this representation provides an accurate enough description of the electronic band structure of semiconductor compounds [10,12,13].

To study the (001) surfaces we use the Surface Green's Function Matching Method (SGFM) in the appropriate tight-binding representation [8,14,15]. This method uses as input the bulk tight-binding parameters (TBP). The difference between the bulk TBP and the surface ones is taken into account through the matching in the SGFM method [8]. We have calculated the (001)-bulk-projected ($\mathcal{G}_B$) and the (001)-surface-projected ($\mathcal{G}_S$) Green's functions, given in equation (2). From $\mathcal{G}_B$ we can obtain the effects on the band structure derived from the hard wall effect (second term contribution above) and from $\mathcal{G}_S$ we obtain the surface band structure (third term contribution). To calculate these Green functions we use the known formulae [14,15]:

$$\mathcal{G}_S^{-1} = (E - H_{00}) - H_{01}T, \tag{3}$$

$$\mathcal{G}_B^{-1} = \mathcal{G}_S^{-1} - H_{10}\widetilde{T}. \tag{4}$$

The way in which the Hamiltonian matrices are related to the TB Hamiltonians is described in detail in references [14,15], so we will omit further details here. The use of these formulae for calcopyrites is described in reference [17]. T and $\widetilde{T}$ are transfer matrices depending only on H_{00}, H_{01} and H_{10}, the principal-layer-projected Hamiltonian matrices [16]. Quickly converging algorithms to calculate the transfer matrices were first obtained by López Sancho *et al.* [18].

The SGFM Green's function for the interface is given by [8,15],

$$G_I^{-1} = G_{s(A)}^{-1} + G_{s(B)}^{-1} - I_B H^i I_A - I_A H^i I_B, \tag{5}$$

where $G_{s(A)}$ and $G_{s(B)}$ are the surface Green's function of medium A and B, respectively. $-\mathcal{I}_A H^i \mathcal{I}_B$ and $-\mathcal{I}_B H^i \mathcal{I}_A$ are the Hamiltonian matrices that describe the interaction between the two media.

Table 2. Empirical Bowing parameters for the anion- (b_a) and for the cation-substitution (b_c) in eV.

Compound	b_a	b_c
$ZnTe_{1-x}S_x$	−3.530	
$ZnTe_{1-x}Se_x$	−6.964	
$CdTe_{1-x}Se_x$	−0.195	
$Cd_{1-y}Zn_yTe$		0.0200
$Cd_{1-y}Zn_ySe$		0.0370
$Hg_{1-y}Zn_yTe$		0.0003
$Hg_{1-y}Cd_yTe$		0.0180

The tight-binding Hamiltonians for the II-VI ternary alloys are described in detail in reference [27]. Briefly speaking, we have used the tight-binding method and, with certain conditions, the virtual crystal approximation to study the ternary alloys. We have included an empirical bowing parameter in the s-on site TBP of the substituted ion. This procedure gave us the correct behaviour of the band gap value with composition [27]. More exactly for the TBP of the ternary alloy, we take

$$\overline{E}_{\alpha,\alpha'}(x) = xE_{\alpha,\alpha'}^{(1)} + (1-x)E_{\alpha,\alpha'}^{(2)}, \qquad \alpha,\ \alpha' = s,\ p^3,\ s^* \tag{6}$$

for all but the s-on site TBP of the substituted ion. In equation (6) $E_{\alpha,\alpha'}^{(1,2)}$ are the TBP for the compound 1 (2); $\alpha,\ \alpha'$ are the atomic orbitals used in the basis set.

For the s-on site TBP of the substituted ion we use the following expression

$$\overline{E}_{s,\nu}(x, b_\nu) = \overline{E}_{s,\nu}(x) + x(1-x)b_\nu, \qquad \nu = a,\ c \tag{7}$$

where $\overline{E}_{s,\nu}(x)$ is given by equation (6) and b_ν is the empirical bowing parameter for each different substitution (anion-substitution (a) or cation-one (c)). In Table 2 we show the empirical bowing parameters used in this work. We do not introduce any further parameter [27].

From the knowledge of the Green's function, the local density of states can be calculated from its imaginary part by integrating over the two−dimensional first Brillouin zone, the dispersion relations can be obtained from the poles of the real part. We have applied previously this formalism to surfaces [1,2,28,29], interfaces [30–32] and superlattices [33].

3 The FISIM states

3.1 Experiment

3.1.1 (001)-CdTe

Optical spectroscopy techniques provide most of the information needed to understand the valence band electronic structure of semiconductors. Based on the critical-point energies determined through measurements on semiconductor compounds, theoretical schemes were developed to calculate electronic band dispersions throughout the entire Brillouin zone. Among the various theoretical methods employed, the relativistic linear augmented plane wave method (LAPW) and empirical pseudopotential techniques are the most realistic in predicting characteristic valence- and/or conduction-band features, as well as the optical properties of many representative semiconducting materials [19,20]. Optical spectroscopy, however, cannot provide information on the band dispersion. One of the most capable techniques to determine absolute critical point energies and energy dispersion is angle resolved photoelectron spectroscopy (ARPES).

From the ARPES data for CdTe(001), obtained by Niles and Höchst [3], the measured spin-orbit splitting $\Delta E_{SO} = 0.95$ eV agrees well with earlier electroreflectance and photoluminescence measurements [21,22]. The experimentally determined dispersion of the heavy- and light-hole valence bands agrees well with predictions based on nonlocal pseudopotential calculations [20]. For the width and dispersion of the split-off valence band, however, Niles and Höchst found a small but noticeable discrepancy with theoretical predictions [20,23]. Their data imply a width of 4.4 eV, whereas nonlocal pseudopotential calculations predict 5.05 eV. Furthermore, in their ARPES report, Niles and Höchst notice the persistence of photon momentum independent emission at 4.4 eV. In Figure 6 of reference [3], they report a non-dispersive (k-independent) band measured up to about half the way from $\Gamma - X$. They attribute this state to indirect transitions from a high-density-of-states region around the critical valence band point X_6.

Later on, Gawlik *et al.* [4] investigated an unreconstructed CdTe(001) surface prepared by ion bombardment and annealed using angle resolved photoemission. To separate surface and bulk related spectral features they used different criteria. They found, at 4.6 eV binding energy, a weakly dispersing band which has, according to them, mixed surface and bulk character. The high density of bulk states associated with this edge of the heteropolar gap, they add further, is also expected to contribute to this feature.

3.1.2 (001)-ZnSe

In more recent work, Lopinski *et al.* [5], Zhang *et al.* [6], and Chen *et al.* [7] have reported experimental results on the (001)-ZnSe system. These new results give further support to our predictions for the anion-type resonances and also for our FISIM states. On the other hand, the upper anion valence band surface resonance has been also predicted in *ab initio* calculations by Park and Chadi [24], and their results are in agreement with the experimental measurements. Our predicted dispersion for this surface resonance is found to agree with both the theoretical and experimental results (see Tab. 1 of Ref. [6]). Furthermore, Zhang *et al.* discuss the possibility that some of the structures they measure could be related with our lower anion-type surface resonance and with our B_l and B_s FISIM states, although they consider the alternative explanation for two of the states as bulk umklapp transitions.

Even more recently, Chen *et al.* [7], in a photoemission study of the Na/ZnSe(001) system, have identified the band structure they measure with our predicted FISIM states (B_h, B_l, B_s). They consider a ZnSe (100)c(2×2) surface (cation terminated surface). Their structures are located at 0.6, 1.6, 2.7, and 5.0 eV from the top of the valence band, they labeled them A, B, C, and D, respectively. The experimental peaks B, C and D can be related to our B_h, B_l, and B_s states, located at 2.0, 2.3 and 5.3 eV from the top of the valence band [2], respectively. Notice that the deviation from our predictions is small in spite of the fact that they report that their measurements have been done with deficient angle resolved precision. So, we can conclude that there is enough experimental evidence on the real existence of the FISIM states.We will now review, for completeness, our theoretical findings on the FISIM states in surfaces of II-VI semiconductor compounds and extend them to the surfaces of calcopyrites and interfaces to point out that these states might appear, in general, whenever a medium is limited by a frontier.

3.2 Theory

We think that, although at slightly different energies, the experimental results of Niles and Höchst and Gawlik *et al.* report both the same non-dispersive state at ~4.4 eV. Niles and Höchst attribute their signal to indirect transitions from a high-density-of-states region around the X_6 valence band critical point. Gawlik *et al.* assign to this state a mixed surface and bulk character, although they found plausible the explanation given by Niles and Höchst. We will look now at the indications given by our calculations. First, let us point out that we have calculated the bulk bands with an emphasis on the agreement with experimental results.They also agree with *ab initio* calculations [1,2] which also agree with experiment.

We obtain the non-dispersive state as a solution (one of the poles) of the 2D-projected bulk Green's function at the energy of 4.4 eV for the whole $\Gamma - X$ interval. The state appears to have a very slight dispersion. In contrast to this, when we look at the surface Green's function we do not see traces of this state (this point is dealt with in detail in Ref. [1]), therefore we conclude that the state is of bulk character but induced by the surface (semi-infinite medium). This is our definition of a surface induced bulk state.

It is important to see the bulk character of these states. To show it explicitly, we have calculated the bulk (001)-projected density of states, $N(\omega)$, from the corresponding Green's function of the (001)-CdTe semi-infinite medium with an unreconstructed surface. We projected it onto the first 11 atomic layers from the surface into the bulk. $N(\omega)$ is proportional to $|\Psi|^2$, where Ψ is the semi-infinite

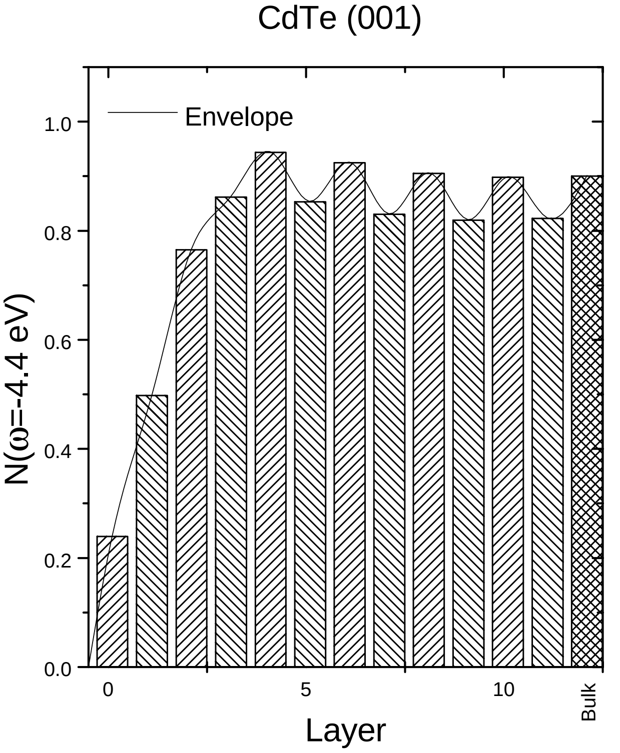

Fig. 2. 2D density of states $N(\omega)$, for the unreconstructed CdTe (001)−surface projected onto the first 11 atomic layers. $N(\omega)$ is calculated at the energy eigenvalue of −4.4 eV, corresponding to the B_s state in Figure 1, and integrated over the 2D Brillouin zone. $N(\omega)$ does decay towards the surface but into the bulk it takes a constant value, showing that the B_s state is of semi−infinite character.

medium wave function for this state with energy eigenvalue −4.4 eV. The projected density of states is obtained from the imaginary part of the 2D-projected bulk Green's function by integration in the 2D first Brillouin zone (BZ) using the method of Cunningham [25]. Here we have used a set of 9 special k-points in the 2D-BZ. For numerical convergence, a small imaginary part of 0.001 eV was added to the real energy variable. Our result is shown in Figure 2. From the figure it is clear that $N(\omega = -4.4\text{ eV})$ does decay from the bulk towards the surface, while from the 5th atomic layer on, inside the bulk, it takes a constant value (as one expects for a bulk state), although different for cation and anion atomic planes. We do not find any surface character attributable to this state. We stress that there is no exponential decay of the amplitude as one enters the bulk as it would be expected for a surface state. This state is, strictly speaking, neither of bulk (Bloch) character nor of surface character; for this reason we found it convenient to call it a FISIM state.

A question remains to be addressed: where do these states come from? Do these states come from an accumulation of density at the X-high symmetry point? To answer this question, we have checked that the conservation law for the number of states within a band at constant **k** does hold. That is to say, if we integrate the 2D density of states over all the energy range at constant **k**, we obtain the same number of states per unit lattice in the bulk (Bloch−states) as the system having a boundary surface. This can be written as

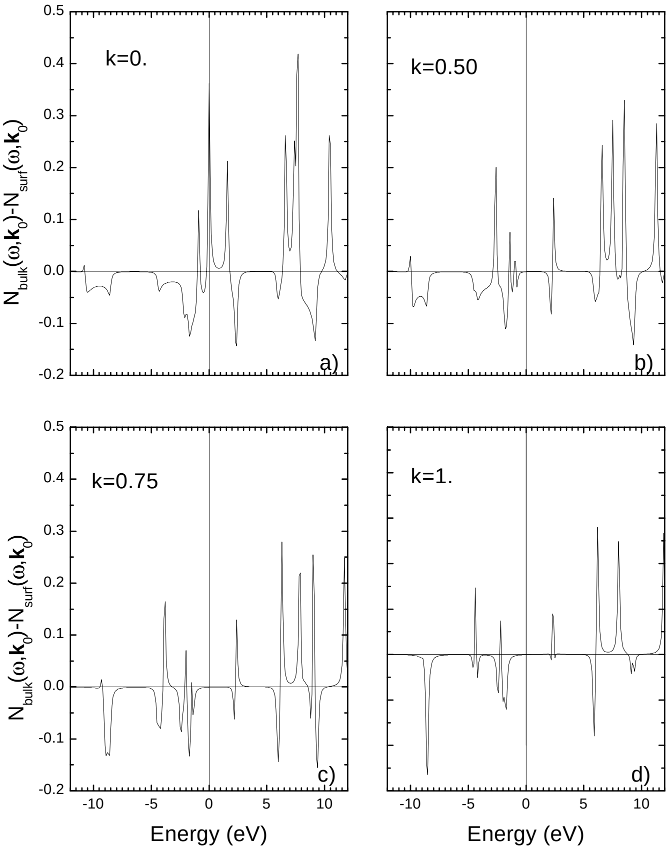

Fig. 3. The difference of the density of states, $N_{\text{bulk}}(\omega, \mathbf{k}_0) - N_{\text{surface}}(\omega, \mathbf{k}_0)$, for a fixed **k**-value. N_{bulk} is the bulk density of states for an infinite medium, and N_{surf} is the bulk density of states for a semi−infinite system projected onto the (001)-surface. This result shows that the existence of a surface shifts spectral weight from one energy state to another at the same **k**. The integral over the energy is zero, showing that the number of states at the same **k** is conserved. Here the calculation is for the Γ-point (a)), $\mathbf{k} = \frac{2\pi}{a}(0.5, 0)$ (b)), $\mathbf{k} = \frac{2\pi}{a}(0.75, 0)$ (c)), and for the X−point (d)).

$$\int [N_{\text{bulk}}(\omega, \mathbf{k}) - N_{\text{surface}}(\omega, \mathbf{k})]\mathrm{d}\omega = 0.$$

Here, N_{bulk} is the (001)-projected bulk density of states for an infinite medium, and N_{surface} the bulk density of states for a semi-infinite system projected onto the (001)-surface. This means that, any spectral weight for any new state that appears due to a change in the boundary condition is removed from a bulk state with the same **k**. Figure 3 shows the difference of the density of states, $N_{\text{bulk}}(\omega, \mathbf{k}) - N_{\text{surface}}(\omega, \mathbf{k})$, for different **k**-values. This result shows indeed that the creation of a surface removes spectral weight from one energy-state to another at the same **k**. Thus, the new state is an LCAO combination of eigenfunctions of different energy but same quantum number **k**. This conservation law is a manifestation of the

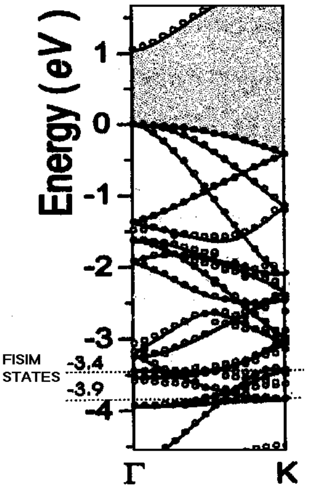

Fig. 4. Electronic band structure of the valence band of the calcopyrite $CuInSe_2$. Some of the states were omitted for the sake of clarity. The full band structure can be found in reference [17]. The two FISIM states that we have identified are shown at energies −3.4 and −3.9 eV below the top of the valence band.

so-called Levinson's theorem [8,26]. Our calculation therefore is not consistent with a spectral weight displacement from X_6 to other values of **k**, a displacement that would violate Levinson's theorem. Do surfaces with other crystal structures produce the FISIM states?

3.3 The FISIM states at a calcopyrite surface

To explore a new possibility we will now show that a surface of technological interest like the (112)-$CuInSe_2$ does present the FISIM states as well. This result might be of interest to fully understand the detailed behavior of some solar cells or lasers.

Rodríguez *et al.* [17] have discussed the electronic band structure of bulk $CuInSe_2$ and of the (112)-$CuInSe_2$ surface. In the case of a metallic termination of the surface (Cu-In), three states appear. The first one stays near to the conduction band within the energy gap region, so it is a surface state. A second one, higher in energy enters the conduction band at Γ where it becomes a resonance state. A third state, remains always at the border of the conduction band. The spectral weight that these states have is removed from the valence band region in the three cases (see Fig. 2 of Ref. [17]).

Again, in analogy to the (001)-CdTe projected bulk bands, we find in the (112)-$CuInSe_2$ bulk projected bands two non-dispersive states,which are two FISIM states. These are illustrated in Figure 4. As we can see, at −3.4 eV and at −3.9 eV the non-dispersive states occur. Their approximate composition is as follows:

E = −3.4 eV: p-Cu(10%), d-Cu (5%), p-In (18%), and p-Se (60%),

E = −3.9 eV: p-Cu (5%), d-Cu (3%), p-In (25%), and p-Se (62%).

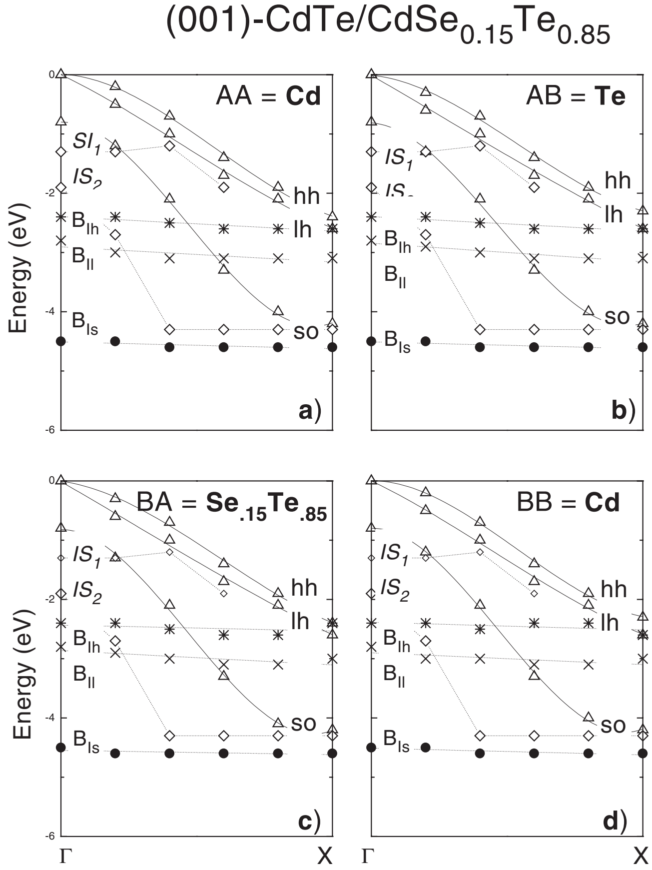

Fig. 5. Electronic band structure of the valence band projected on each atomic layer of the (001)-$CdTe/CdSe_{0.15}Te_{0.85}$ interface. The dispersion relations are obtained from the poles (triangles) of the real part of the interface Green's function. The solid lines are a guide to the eye. B_{Ih}, B_{Il} and B_{Is} are the calculated FISIM states (the dotted lines, intended to show the dispersion of the bands, are a guide to the eye). We show the interface states IS_1 and IS_2.

It is very interesting that the FISIM states do appear in surfaces of simple crystallographic structures such as the zinc-blende one and also at more complicated ones such as the calcopyrites. Nevertheless, a further question −central to this paper− remains to be answered. Does any frontier give rise to FISIM states? In answering this question, we will show that the states appear at interfaces as well.

3.4 The FISIM states at an interface

In Figure 5, we show the electronic band structure of the valence band for the interface (001)-$CdTe/CdTe_{0.85}Se_{0.15}$. Notice the bulk band results at the top of the valence band. We get the heavy hole band and the light hole bands both at the top, indicating that the crystal field splitting was taken to be zero on both sides. We show the top of the valence band up to energies −6 eV. The spin-orbit band is also shown. For this amount of impurities, and neglecting the small lattice parameter difference, there is a small difference as well in the bulk bands on both sides. Selecting this case is important for the purpose of the paper as we will comment on it further.

We present now our study of the valence band of the (001)-CdTe/CdSe$_{0.15}$Te$_{0.85}$ interface concentrating, in particular, on the FISIM states.

The (001)-CdTe/CdSe$_{0.15}$Te$_{0.85}$ interface has been chosen to eliminate the effect of stress, reconstruction and relaxation. We want to establish that the FISIM states do exist as an effect of the frontier alone. The real induced stress is small, about 1%. This magnitude of the induced stress allows us to ignore its effect in our calculation. The real bulk bands as well as the FISIM states, should lie very close to our calculated ideal case. We have taken the interface domain to be composed of four atomic planes, two belonging to each medium.

To distinguish between the different atomic layers we will label each atomic layer by two letters, the first one indicates the medium it belongs to, and the second one the medium its interface-neighbor belongs to. The atomic layer AA will be the second from the interface into medium A. AB will be the last atomic layer belonging to medium A and facing the first atomic layer of medium B and so on. So the four atomic layers that constitute the interface domain will be labeled AA, AB, BA, and BB.

For the interfaces aligned along the (001) direction the two media are facing each other either through its anion or cation atomic layer. In the alloy case, we consider a pseudobinary compound so that the concept of anion and cation atomic layers remains meaningful. We will project the interface electronic band structure on each atomic layer and we will look at the different states that we find.

It is known that the common anion interfaces have a small valence band-offset and the common cation ones have a small conduction band-offset, both are of the order of few meV [34–36]. So, since we will present here our results for the common cation interface, it is accurate enough for our purpose to use the boundary condition that the top of the valence bands at the interface are aligned. We choose this energy as our zero. Accordingly, the conduction band offset will be equal to the difference in the band gaps. The actual theoretical calculation of the band offset is still an open question that we do not want to address in this work [37].

On the other hand, the existence of a frontier breaks the symmetry of the infinite medium. FISIM states are bulk states and are neither Bloch states nor surface states. They do exist in the semi-infinite medium space but they do not follow the infinite-medium symmetry of the crystal.

Notice that the boundary condition is different for a surface and the interface. For an interface, the wave function must not be zero, it has to be continuous together with its derivative. The boundary condition therefore will depend on **k**. This is because the Hamiltonian that describes the infinite system, that is, medium A, medium B and the interaction at the interface does depend on it. So what we have is, actually, a matching problem (the wave function value and its derivative at the interface) for each **k** value. It is then natural to expect, on general grounds, a **k**-dependence of the energy eigenvalues of the FISIM states, for the case of an interface. For a surface the boundary condition is always zero and, on the contrary, we do not expect a **k**-dependence.

In this work, we have chosen a ternary alloy, on one side of the interface, with the same lattice constant as the binary one on the other side of the interface so as to show that the FISIM states do occur at it in a clean way. We leave aside the **k**-dependence of the FISIM state that comes purely from the boundary condition since in our chosen case it is, as expected, minimal. Notice that stress (lattice mismatch) could enhance substantially the **k**-dependence of the FISIM states. Therefore, FISIM states are a consequence of the existence of a frontier and their **k**-dependence is a result of the physical parameters at the frontier.

Let us now concentrate in Figure 5. Specially, the interface occurs as AA (Cd), AB (Te) on one side of the interface and BA (Te$_{0.85}$Se$_{0.25}$) and BB(Cd) on the other side. The two media interact directly through the Te atomic plane on one side and the Te$_{0.85}$Se$_{0.25}$ one on the other.

The dispersion relation is found from the poles (triangles in the figures) of the real part of the interface Green's function. The solid-lines are a guide to the eye. These are to be compared with the dispersion curves found for the bulk (infinite medium) case.

Let us point out, first, that we have obtained from this calculation two interface states in the valence band region. This seems to be actually a general feature of the CdTe-based interfaces according to the results of several of our calculations that will be presented elsewhere. The interface states do exist on the four atomic layers constituting the interface and disappear as one enters the bulk on either of the two sides of the interface. These are truly interface states. We have labelled them IS_1 and IS_2.

The calculated energy eigenvalues for the FISIM states are denoted by stars, crosses and points; the dotted lines are intended only as a guide to the eye. We label the FISIM states as B_{Ih}, B_{Il}, and B_{Is}. This convention follows the previous free (001)-surfaces study (see Refs. [1,2]). The three states appear at energies around −2.45, −2.83, and −4.49 eV for all the atomic layers considered. This seems to be a characteristic feature and the small dispersion they show, makes them easier to detect. We conclude that an interface gives rise to the FISIM states as well.

4 Conclusions

In conclusion, we have shown that in the II-VI direct band gap semiconductor compounds there is a new type of state that we have called the FISIM states. They are of semi-infinite medium character as opposed to surface character. We have shown that the density of states, projected onto the first eleven atomic layers of the (001)-semi-infinite perfect crystal, for the energy eigenvalue of −4.4 eV, remains constant within the bulk and decays towards the surface. To better characterize the FISIM-states, we have calculated the difference between the bulk density of states for an infinite and a semi-infinite system. We have found that the FISIM-states appearing only in the semi-infinite systems are built up from states of different energy by a LCAO but with the same **k**. They do follow Levinson's theorem. The new result that we report in this paper is the existence of these states also at surfaces of other crystallographic structures and at interfaces.

To further study their character, we have chosen the (112)-CuInSe$_2$ calcopyrite which is a surface of technological interest and the (001) oriented interface CdTe/CdSe$_{0.15}$Te$_{0.85}$ where stress at the interface is avoided explicitly since the lattice mismatch is almost zero.

In the first example, the (112)-CuInSe$_2$ calcopyrite surface presents two FISIM states. This result might be of interest to give full account of the working efficiencies of solar cells and lasers.

On the other hand, we pointed out that interfaces do follow a different boundary condition than surfaces. On surfaces a zero boundary condition has to be imposed. At interfaces the wave function and its derivative have to be continuous. These boundary conditions do depend on **k** (see text) and, as a consequence, the FISIM states eigenvalues depend on **k** as well.

The general conclusion that results from this work is that FISIM states *per se* are the result of the existence of a frontier but the dispersive character of their eigenvalues comes from the specificities of the frontier. These states add a new feature to the solution of the Schrödinger equations in solids that might be general. In addition to Bloch states, surface states and interface states, in solids there exists the FISIM states.

A last word should be said concerning the precision of our predictions due to the use of the tight-binding method. We have performed an *ab initio* calculation of the electronic band structure of the (100)-CdTe surface using the Wien-97 code in the latest 2K version [19]. *Ab initio* calculations sometimes do not give the right result for the gap in semiconductor systems (a well known fact) but describe well the valence band. Our *ab initio* results show the existence of the same FISIM states as we have described them here. The calculation consumes much more computer-time though. So, we can also conclude, that the careful use of the tight binding method gives sensible predictions as far as this problem is concerned.

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