Abstract

In a previous paper [Phys. Rev. 50, 1980 (1994)] we gave account of the nondispersive band first found experimentally at –4.4 eV for CdTe(001) by Niles and Höchst. We have characterized this band as a surface–induced bulk state. In a second paper we showed that a similar state does exist in II–VI and III–V zincblende semiconductor compounds. In this paper we show that there are more such states within the valence band energy interval. We use tight-binding hamiltonians and the surface Green’s function matching method to calculate the surface and surface–induced bulk states in the wide band gap zincblende semiconductors CdTe, CdSe, ZnTe and ZnSe. We find a distinctive surface state for the cation and two for the anion termination of the (001)–surface and three (001)–surface–induced bulk states with energies that correspond to the value of the heavy hole, light hole and spin–orbit bands at X.

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I. INTRODUCTION

The study of the physics of surfaces, interfaces, quantum wells and superlattices of semiconductors has call interest in the last few years. [1–9] The interest is not only for binary compounds but also, more recently, for ternary and quaternary compounds.

The starting point is an accurate description of the electronic band structure of the binary compound by a method which serves as a sound basis to a clear and simple description of the more complicated compounds and systems.

In previous work [10,11] we have used the tight-binding formulation to calculate the total density of states (DOS) and, in conjunction with the known surface Green’s function matching method (SGFM), [12] to derive the surface and the interface DOS. In this paper we want to use the same method to calculate the surface and surface–induced bulk states. The method can be also applied to superlattices [9,13] and phonons. [14] These band structures can be also used to calculate transport properties in heterostructures as quantum wells, for example, by making use of the well known many–body formulation by Keldysh. [15]

In this paper, we consider the band structure of the II-VI wide band gap semiconductors CdTe, ZnTe, CdSe and ZnSe. We have first obtained the bulk bands (infinite medium) from the direct diagonalization of the tight–binding Hamiltonians and from the poles of the real part of the corresponding Green’s function which is totaly equivalent. These very same results were obtained using the SGFM method, from the (001)–bulk–projected Green’s function. This is actually a proof of consistency which gives us confidence in the new results.

Our calculation shows the existence of three surface–induced bulk states which have no dispersion from Γ to X and which do not change in energy with different atom termination of the sample. These states were first found experimentally by Niles and Höchst [3] in CdTe(001). There is also a distinct surface state for each the anion and the cation termination of the surface. They do differ noticely in energy. A general pattern develops for the location of the different bands in II-VI wide band gap zincblende semiconductors within the range of their valence band energy.
The rest of the paper is organized as follows. In Section II, to make the paper self–contented, we briefly describe the main highlights of the method and present the formulae that we have used. In Section III, we first introduce the general characteristics of the valence band and the location in energy of the surface and surface–induced bulk states. Next, we discuss the results for each system studied. In a final section, we present our conclusions. We have included an appendix where we quote all the tight–binding parameters of interest for this calculation.

II. METHOD

We make use of tight–binding Hamiltonians. Since the Green’s function matching method takes into account the perturbation caused by the surface exactly, at least in principle, we can use the tight–binding parameters (TBP) for the bulk. \[10,11,16\] This does not mean that we are using the same TBP for the surface and the bulk. Their difference is taken into account through the matching of the Green’s functions. We use the method in the form cast by García–Moliner and Velasco. \[12\] They make use of the transfer matrix approach first introduced by Falicov and Yndurain. \[17\] This approach became very useful due to the quickly converging algorithms of López–Sancho et al. \[18\] Following the suggestions of these authors, the algorithms for all transfer matrices needed to deal with these systems can be found in a straightforward way. \[19\] This method has been employed successfully for the description of surfaces, \[5,10,16\] interfaces, \[11,20\] and superlattices. \[9,13\]

A. The formalism

We have first, calculated the bulk (infinite medium) band structure of the compounds by the tight–binding method (TB) in the Slater–Koster language \[21\] using an orthogonal basis of five orbitals, \(sp^3s^*\). The \(s^*\) state is introduced to properly locate in energy the conduction band usually formed by \(d\) states in the II–VI zincblende (ZB) semiconductor compounds. \[22,23\] In our calculation, we have included the effect of the spin–orbit (SO) interaction. \[24\]
The TBP that we have used in our calculation are listed in the appendix. They reproduce
the known bulk bands quite well. \cite{23,26} We assumed ideal truncation.

We obtain the Green’s function from

$$ (\omega - H)G = I $$

where $\omega$ is the energy eigenvalue, $H$ the tight–binding Hamiltonian and $I$ is the unit matrix.

We adopt the customary description in terms of principal layers. We label them with positive
numbers and zero for the surface principal layer. Atomic layers are labelled with negative
numbers and zero for the atomic surface layer. Let $| n \rangle$ be the principal wave function
describing the $n^{th}$ principal layer. It is a LCAO wave function with one $s$–like, three $p$–like,
and one $s^*$–like atomic functions per spin on each atom in the unit cell (there are two different
atoms in the cell, and two atomic layers per principal layer, i. e., it is a 20–dimensional
vector). If we take matrix elements of eq. (2.1) in the Hilbert space generated by the
complete set of the wave functions $| n \rangle$, we get

$$ \langle n | (\omega - H) | m \rangle = \delta_{mn}. $$

Since there is only nearest–neighbors interactions between principal layers, the identity
operator for the $n^{th}$ principal layer is

$$ I = | n - 1 \rangle \langle n - 1 | + | n \rangle \langle n | + | n + 1 \rangle \langle n + 1 | $$

and therefore $H_{m,m+i} \equiv 0$ for $i \geq 2$. By inserting eq. (2.3) into eq. (2.2) we get

$$ (\omega - H_{nn})G_{nm} - H_{nn-1}G_{n-1m} - H_{nn+1}G_{n+1m} = \delta_{mn} $$

The matrix elements of the Hamiltonian, $H_{nn}$, that appear in this formula are $2 \times 2$ super-
matrices (each principal layer contain two atomic layers) each of whose elements is a $10 \times 10$
matrix (since we are using a $5$–wave functions basis by spin per atom). For example, for the
surface

$$ H_{00} = \begin{pmatrix} h_{00} & h_{0-1} \\ h_{-10} & h_{-1-1} \end{pmatrix}, $$

(2.5a)
\[ H_{01} = \begin{pmatrix} h_{0-2} & h_{0-3} \\ h_{-1-2} & h_{-1-3} \end{pmatrix}. \]  

(2.5b)

Notice that rows are labeled with the index of the surface principal layer zero (containing atomic layers 0 and −1) while the columns are indexed with the first principal and second principal layer (atomic layers 0 and −1 and atomic layers −2 and −3), respectively. We shall adopt the hypothesis of an ideal, non reconstructed surface. Then, for the (001)–surface, for example, we have one atomic layer of anions and one of cations per principal layer. Therefore in this case \( h_{00} \neq h_{-1-1}, h_{0-1} = h_{-10}^\dagger \). Thus, to calculate \( H_{00} \) and \( H_{01} \) we need to know \( h_{00}, h_{-1-1}, h_{0-1}, \) and \( h_{-1-2} \). These matrices are readily written in a tight–binding language and can be calculate with the bulk parameters as mentioned above. They depend on the wave vector \( \mathbf{k} \).

Using eq. (2.4) for \( n = m, \) and \( m = 0 \) for the surface, it is straightforward to get the surface Green’s function \[ G_s^{-1} = (\omega I - H_{00}) - H_{01}T \]  

(2.6)

and the principal layer projected bulk Green’s function \[ G_b^{-1} = G_s^{-1} - H_{10}\tilde{T} \]  

(2.7)

It is customary to define the transfer matrices as

\[ G_{k+1p} = TG_{kp}, \quad G_{k+1p} = G_{kp}S, \quad k \geq p \geq 0 \]  

(2.8a)

\[ G_{ij+1} = \tilde{T}G_{ij}, \quad G_{ij+1} = G_{ij}\tilde{S}, \quad j \geq i \geq 0. \]  

(2.8b)

These matrices can be calculated by the quick algorithm of López–Sancho et al. \[18\], recalculated later by Baquero \[19\] (see Refs. \[10,11\] for a compilation of all the formulae).

From the knowledge of the Green’s function, the surface states and the surface–induced bulk states can be calculated from the poles of the real part of the corresponding Green’s function. We have applied previously this formalism to other surfaces \[3,10,16,27\]. We will now present our results.
III. RESULTS

The general characteristics of the zincblende II–VI wide band gap semiconductor valence band as we have obtained from our calculations is as follows. The heavy–hole (hh) and light–hole (lh) bands follow each other closely in energy. The corresponding wave functions are mainly \((p_x, p_y)\) in character. The hh band disperses from \(\Gamma\) to \(X\) about 2.0 eV and the lh one about 2.4 eV. The spin–orbit splitting is around 1 eV in the Te–compounds and around 0.5 in the Se–ones. This band reaches \(X\) at about 5.0 eV. This is the band with the most dispersion and is composed essentially of \(p_z\) states only. Finally, a very deep bulk band of mostly \(s\)–character appears below −10 eV. It disperses about 2 eV from \(\Gamma − X\). We will call this band \(b_{10}\).

From the (001)–bulk–projected Green’s function we get also the energy of the (001)–surface–induced bulk states. Three such states appear, \(B_h\), \(B_l\) and \(B_s\). These surface–induced bulk bands show no dispersion \([3, 28, 29]\). \(B_s\) was first found experimentally by Niles and Höchst \([3]\) and confirmed later by Gawlik et al. \([4]\) for CdTe(001). \(B_h\) mixes with the hh band at \(X\) and is located at the same energy (in \(\Gamma\)) than the surface state, \(S_{c}\), see below) of the cation terminated (001)–surface. \(B_l\) mixes with the lh band at \(X\). The composition of both \(B_h\) and \(B_l\) is mainly of \((p_x, p_y)\), while the one of \(B_s\) which mixes with the spin–orbit band at \(X\) is \((s, p_z)\). The three states appear at the same position in energy irrespective of the cation or anion termination of the surface as one expects for surface–induced bulk states which only depend on the surface through the boundary condition (the wave function has to be zero at the surface).

The (001)–surface valence band is rich \([3, 28]\) in other features. In particular, three characteristic surface states do exist in this range of energy. Two correspond to the anion \((S_{a1}, S_{a2})\) and the other to the cation \((S_{c})\) termination of the (001)–surface. In all the systems considered, the anion terminated surface higher band \((S_{a1})\) follows roughly the dispersion of the hh bulk band but it is at slightly higher energy. The cation terminated surface band \((S_{c})\) starts roughly around 2–3 eV from the top of the valence band in \(\Gamma\) and
has a varying amount of dispersion. The two states appear at very different energy values and are distinctive of the termination of the surface for the four systems under consideration. One could speculate on the use of these two states to characterize the termination of the surface. A second (001)–surface anion state \( S_{a2} \) appears at much lower energies, for all the compounds considered, near the lowest bulk band \( b_{10} \). This surface state has very little dispersion and its wave function is mostly \( s \)–character.

There is only one set of experimental results available at this moment to compare our results with, namely the already cited CdTe(001).\[3,4\] We have studied this state and found that this is a surface–induced bulk one. Such bulk states appears as a consequence of the breaking of the symmetry implied by the creation of the (001)–surface in the infinite medium. To support our argument, we showed \[5\] specifically that a pole in the real part of the (001)–bulk-projected Green’s function appears at \(-4.4\) eV from \( \Gamma \) to \( X \), and does not appear neither in the real part of the (001)–surface–projected Green’s function nor in the real part of the bulk Green’s function for any termination (anion or cation) of the sample. In other words, this is neither a solution of the Shrodinger’s equation for an infinite medium nor a solution for a semi–infinite one that is localized at the surface. It is a bulk state existing as a consequence of the creation of the surface for which the crystal momentum is not a good quantum number anymore due to the new boundary condition. It has no \( \epsilon(k) \)–dispersion as a consequence. This is a surface–induced bulk state, as we already stated above.

In the rest of this paper, we want to describe in detail these (001)–surface and (001)–surface–induced bulk states for the four systems under consideration as well as the bulk bands obtained from our calculation. We will use our Hamiltonians to describe interfaces, superlattices and quantum wells of these compounds in future work.

We summarize our results in Tables I–IV. In Table I, we give the characteristics of the bulk bands according to our obtained values. We give the gap and the spin–orbit coupling for each element and the value for the bands in \( \Gamma \) and at \( X \). In Table II, we give the energy of the three surface–induced bulk states, then, in Table III, we give the energy of the surface states and, finally, in Table IV, the composition of all the bands involved in our work.
A. CdTe(001)

Fig. 1 shows the full valence band for this system. The bulk states appear as the dotted curves in the figure. Our tight-binding description reproduces correctly the band–gap value (1.6 eV) and the spin–orbit splitting (0.9 eV). Our tight–binding parameters were adjusted to give energy values at the $X$–high symmetry point of the Brillouin zone that reproduce the experimental values for CdTe very closely. The heavy hole and light hole bands have a width of 1.8 eV and 2.2 for this interval of the Brillouin zone, respectively. The wave functions are constituted mainly by an admixture of $p_x$ and $p_y$ states. See Tables I and IV.

The surface states existing in this energy interval are identified as $S_{a1}$, $S_{a2}$ and $S_c$. The band $S_{a1}$ corresponds to the anion termination of the surface (black triangles), its width ($\Gamma - X$) is about 1 eV. The wave functions are constituted mainly by an admixture of $s$ and $p_z$ cation orbitals. The $S_c$ surface state (white triangles) corresponds to the cation terminated (001)–surface. This band develops from about 2.2 eV below the top of the valence band in $\Gamma$ to about –3.5 eV at $X$. Its width is therefore about 1.3 eV and is mainly of $s$–character. This band mixtures with a surface-induced bulk band, ($B_l$), for about half of the wave-vector interval $\Gamma - X$ (see below). The $S_{a2}$ surface state shows a small dispersion and is located at –8.5 eV. Its wave function is of $s$–character. These surface states were described before.

Three surface–induced bulk states exist in this range of energy according to our findings. They are denoted by $B_h$, $B_l$ and $B_s$.

The states $B_h$ and $B_l$ are newly found surface–induced bulk states. $B_h$ is located at –1.8 eV and has no dispersion as is characteristic of these surface–induced bulk bands. $B_h$ seems to mix with the hh band at X. $B_l$ appears at –2.2 eV and mixes with the lh band at $X$. $B_l$ could present branches with slightly different energy and be actually a group of states differing slightly in energy. This states are mainly ($p_x$, $p_y$). $B_l$ starts at $\Gamma$ at the same energy as the surface state $S_c$. Their energy difference is very small for about half the interval $\Gamma - X$ when the surface state begins to have an important dispersion while the bulk
one has none. We have obtained each state from the corresponding Green’s function. The
$B_s$ state has a $(s, \ p_z)$–composition.

In conclusion, CdTe(001) presents in the range of energy covered by its valence band,
as it is shown in Fig. 1, in addition to the known bulk bands distinct surface states for
each the anion ($S_{a1}$, $S_{a2}$) and the cation ($S_c$) terminated (001)–surfaces and a total of three
surface–induced bulk states, $B_h$, $B_l$, and $B_s$. $B_s$ is the recently established surface–induced
bulk state at $-4.4$ eV. [3–5] None of them presents dispersion and they appear at the same
energy irrespective of the termination of the (001)–surface.

B. CdSe(001)

In general, CdSe is grown in an hexagonal structure. Nevertheless, recent experiments
[31] have shown that it is possible to grow this material in a cubic phase and that it is stable.
Our calculation has been done assuming the zincblende structure. Our bands do not apply
for the hexagonal structure.

We can see in Fig. 2 the general characteristic of the II–VI zincblende wide band gap
semiconductor valence band already described above. The hh and lh bands follow each other
closely in energy and are both composed by $(p_x, \ p_y)$. The hh band disperses from $\Gamma$ to $X$
2.2 eV and the lh one 2.4 eV. The spin–orbit splitting is 0.43 eV and the band $(p_z)$ ends at
$-5.0$ eV at $X$ and has therefore a width of about 4.6 eV. The $b_{10}$ band appears at $-11.0$ eV
in $\Gamma$ and has little dispersion towards $X$.

For the anion terminated (001)–surface, there is one surface state ($S_{a1}$) of $(s, \ p_z)$–
composition which develops right from the top of the valence band in $\Gamma$ to $X$ with a quite
less dispersion than the hh band. At $X$ it takes the value 1.0 eV. The cation terminated
(001)–surface shows a surface state ($S_c$) of $s$–character at a lower energy in $\Gamma$ ($-2.2$ eV) that
disperses very little up to half the $\Gamma – X$ interval but then disperses strongly and ends at
$-4.0$ eV at $X$. Its width in the interval is 1.8 eV. The $S_{a2}$ band appears again very closely to
the $b_{10}$ bulk one and shows very little dispersion as it is the general behavior for this surface
The three (001)–surface–induced bulk states ($B_h$, $B_l$ and $B_s$) appear at –2.2 eV ($p_x$, $p_y$), –2.45 eV ($p_x$, $p_y$) and –5.0 eV ($s$, $p_z$) irrespective of the cation or anion termination of the surface. The first two mix with the hh and lh bands at $X$, respectively, and the third one mixes with the spin–orbit band at $X$. None of them presents dispersion.

As we can conclude from the previous description, CdSe(001) follows very closely the general picture described above for the number, composition and relative location of the surface and surface–induced bulk states within the valence band energy interval. We will now show that the last two compounds studied follow the same pattern.

C. ZnTe(001)

The full valence band for ZnTe(001) is presented in Fig. 3. It is clear that the general pattern is followed. $S_{a1}$ is the highest band in energy. It starts at $\Gamma$ and disperses 1.0 eV as it reaches $X$. It is of ($s$, $p_z$) character. The hh and lh bands (both ($p_x$, $p_y$)) follow each other and disperse 2.0 and 2.3 eV, respectively. $B_h$ and $B_l$ both mix with the hh and lh band, respectively, at $X$ and have the same composition. The $S_c$ state disperses 2.0 eV and mixes with the $B_h$ band at $\Gamma$. It is $s$–like character following the general rule. Finally, the $B_s$ state is located at –5.3 eV from the top of the valence band and is of ($s$, $p_z$)–character. This state seems to be composed of two very nearly lying in energy states. The surface–induced bulk states present no dispersion and are found at the same energy irrespective of the surface termination. [28] There is no experimental evidence known to us for this findings. The two surface states were described before. [27]

D. ZnSe(001)

We present our results for this compound in Fig. 4. In all respects ZnSe(001) follow the general picture for the states in the valence band energy interval. The hh, lh and spin–orbit bands have the usual composition and behavior. Three different surface states
appear, two for the anion–surface ($S_{a1}$, $S_{a2}$) and one for the cation–surface ($S_c$), and three surface–induced bulk states with the same usual characteristics. The surface states have been studied previously. [30] We have summarize the details in Tables I–IV.

### IV. CONCLUSIONS

In conclusion, we have studied the (001)–surface and surface–induced bulk states that appear in the range of the valence band energy for the II–VI wide band gap zincblende semiconductors. We found that a general pattern applies to the states and relative energy of these states with respect to the bulk bands. First, near the top of the valence band a surface state develops with little dispersion from Γ to X for the anion–terminated surface. A surface state also exists for the cation terminated surface but it appears at a quite lower energy. A second anion–surface state appears in the range of energies of the bottom of the valence band. Simultaneously three (001)–surface induced bulk states appear which show no dispersion and appear at the same energy irrespective of the surface termination. These states mix with the hh, lh and spin–orbit bands at X, respectively.

It would be interesting to study other directions of the surface as well as interfaces, superlattices and quantum wells in different high–symmetry directions to characterize the different states that this break of symmetry due to the creation of a border might induce.
REFERENCES

[1] G. W. Bryant, Phys. Rev. Lett. 55, 1786 (1985)

[2] J. E. Lowther, J. Phys. C: Solid St. Phys. 19, 1863 (1986)

[3] D. Niles and H. Höchst, Phys. Rev. 43, 1492 (1991)

[4] K. –U. Gawlik, J. Brügmann, S. Harm, C. Janowitz, R. Manzke, M. Skibowski, C. –H. Solterbeck, W. Schattke, and B. A. Orlowski, Acta. Physica Polonica A 82, 355 (1992)

[5] D. Olguín and R. Baquero, Phys. Rev. B 50, 1980 (1994)

[6] W. Bala, M. Drozdowski, and M. Kozielski, Acta Physica Polonica A 80, 723 (1991)

[7] D. G. Kilday, G. Maragaritondo, T. F. Ciszek, and S. K. Deb, J. Vac. Sci. Technol. B 6, 1364 (1988)

[8] T. M. Duc, C. Hsu, and J. P. Faurie, Phys. Rev. Lett. 58, 1127 (1987)

[9] J. Arriaga and V. R. Velasco, Phys. Scripta 46, 83 (1992)

[10] R. Baquero and A. Noguera, Rev. Mexicana de Física 35, 638 (1989)

[11] C. Quintanar, R. Baquero, V. R. Velasco, and F. García–Moliner, Rev. Mexicana de Física 37, 503 (1991)

[12] F. García–Moliner and V. R. Velasco, Prog. Surf. Scie. 21, 93 (1986)

[13] V. R. Velasco, R. Baquero, R. A. Brito-Orta, and F. García–Moliner, Condens. Matter 1, 6413 (1989)

[14] R. A. Brito–Orta, V. R. Velasco, and F. García–Moliner, Phys. Scripta 37, 131 (1988); Phys. Rev. 38, 9631 (1988)

[15] L. V. Keldysh, Sov. Phys. Jetp 20, 1018 (1965)

[16] R. Baquero, V. R. Velasco, and F. García–Moliner, Physica Scripta 38, 742 (1988)
[17] L. Falicov and F. Yndurain, J. Phys. C: Solid St. Phys. 8, 147 (1975)

[18] M. P. López–Sancho, J. M. López–Sancho, and J. Rubio, J. Phys. C: Metal Phys. 14, 1205 (1984); 15, 855 (185)

[19] R. Baquero, ICTP-report

[20] R. Baquero, A. Noguera, A. Camacho, and L. Quiroga, Phys. Rev. B 42, 7006 (1990)

[21] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954)

[22] P. Volg, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids 14, 365 (1983)

[23] W. A. Harrison, Phys. Rev. 24, 5835 (1981)

[24] J. N. Chadi, Phys. Rev. 16, 790 (1977)

[25] D. Bertho, D. Boiron, A. Simon, C. Jouanin, and C. Priester, Phys. Rev. 44, 6118 (1991)

[26] A. Camacho, private communication.

[27] F. Rodríguez, A. Camacho, L. Quiroga, and R. Baquero, Phys. Status Solidi B 160, 127 (1990)

[28] D. Olguín, R. de Coss, and R. Baquero, to be published

[29] D. Olguín, M. Sc. Thesis, CINVESTAV-IPN, México 1994.

[30] J. Pollmann and S. T. Pantelides, Phys. Rev. 18, 5524 (1978)

[31] K. Ichino, K. Iwami, Y. Kawakami, S. Z. Fujita, and S. G. Fujita, J. Electronic Matt. 22, 445 (1993)
APPENDIX:

We present in this appendix the tight-binding parameters that we used for the systems studied in this work.

Tight–binding parameters used in our calculation. We used the notation of Bertho et al.

| Parameter | CdTe<sup>a</sup> | ZnTe<sup>b</sup> | ZnSe<sup>b</sup> | CdSe<sup>c</sup> |
|-----------|-----------------|-----------------|-----------------|-----------------|
| $E_s^a$   | -8.19210        | -9.19000        | -12.42728       | -10.16740       |
| $E_p^a$   | 0.32790         | 0.62682         | 1.78236         | 1.03400         |
| $E_s^c$   | -0.95000        | -1.42000        | 0.04728         | 1.07977         |
| $E_p^c$   | 6.93790         | 3.77952         | 5.52031         | 7.64650         |
| $V_{ss}$  | -5.00000        | -6.64227        | -6.50203        | -2.89240        |
| $V_{xx}$  | 2.13600         | 1.94039         | 3.30861         | 3.01320         |
| $V_{xy}$  | 4.52817         | 4.07748         | 5.41204         | 5.73040         |
| $V_{ac}^p$| 3.31200         | 5.92472         | 1.13681         | 2.16040         |
| $V_{sp}^c$| 3.63824         | 4.67265         | 5.80232         | 5.65560         |
| $V_{as^*s^*}^a$| 10.44540 | 6.22682         | 7.84986         | 6.02650         |
| $V_{as^*s^*}^c$| 6.62960 | 6.77952         | 8.52011         | 3.96150         |
| $V_{ac}^{sp}$ | 2.52468 | 2.96202         | 3.26633         | 2.11640         |
| $V_{ca}^{sp}$ | 2.94540 | 3.82679         | 1.86997         | 2.21680         |
| $\lambda_a$ | 0.32267 | 0.36226         | 0.19373         | 0.14300         |
| $\lambda_c$ | 0.07567 | 0.02717         | 0.01937         | 0.06700         |

<sup>a</sup> Ref. 3
<sup>b</sup> Ref. 25
<sup>c</sup> Ref. 26
FIGURES

FIG. 1. The full electronic valence band structure for CdTe(001) in the Γ – X direction. The dot lines are the bulk band structure from direct diagonalization of the tight–binding Hamiltonian using the tight–binding parameters that appear in the Appendix. The two surface states for the anion terminated (001)–surface are denoted by full triangles, $S_{a1}$ and $S_{a2}$. The empty triangles are the surface state for the cation terminated surface, $S_c$. The (001)–surface–induced bulk states, $B_h$, $B_l$ and $B_s$ are the full dots (the dashed lines are keep up only for eye guide). Their occurrence is explained in the text. $B_s$ was first found experimentally by Niles and Höchst.[3]

FIG. 2. Electronic structure of the CdSe(001) valence band in the Γ – X direction. The conventions are the same as in Fig. 1 (See figure caption). The (001)–surface–induced bulk states, $B_h$, $B_l$ and $B_s$ mix at X with the hh, lh and spin–orbit bands respectively as a general rule. The pattern presented by the surface and surface–induced bulk states as they appear in this figure is the general one found also in the rest of the systems studied.

FIG. 3. Electronic structure of the ZnTe(001) valence band in the Γ – X direction. See figure captions 1 and 2 for details.

FIG. 4. Electronic structure of the ZnSe(001) valence band in the Γ – X direction. See figure captions 1 and 2 for details.
TABLE I. Characteristics of the band structure. $E_g$ is the gap and $E_{so}$ is the spin–orbit splitting. The last three columns are the values at the $X$–point of the Brillouin zone of the energy of the heavy hole band ($E_{hh}$), the light hole band ($E_{lh}$), and the spin orbit ($E_{so}$). All the values are in eV.

|       | $E_g$   | $E_{so}$ | $E_{hh}$ | $E_{lh}$ | $E_{so}$ |
|-------|---------|----------|----------|----------|----------|
| CdTe  | 1.602   | -0.9     | -1.7     | -2.2     | -4.4     |
| CdSe  | 1.78    | -0.4     | -2.18    | -2.36    | -4.89    |
| ZnTe  | 2.39    | -0.91    | -1.93    | -2.40    | -5.50    |
| ZnSe  | 2.82    | -0.45    | -1.95    | -2.19    | -5.30    |

TABLE II. The energy position of the (001)–surface–induced bulk states. All the values are in eV.

|       | CdTe | CdSe | ZnTe | ZnSe |
|-------|------|------|------|------|
| $B_h$ | -1.8 | -2.2 | -2.0 | -2.0 |
| $B_l$ | -2.2 | -2.45| -2.5 | -2.3 |
| $B_s$ | -4.4 | -5.0 | -5.5 | -5.3 |
TABLE III. The energy position of the (001)–surface states. All the values are in eV.

|          | Γ-point |          | X–point |          |
|----------|---------|----------|---------|----------|
|          | $S_{a1}$ | $S_{a2}$ | $S_c$   | $S_{a1}$ | $S_{a2}$ | $S_c$   |
| CdTe     | 0.0     | –8.5     | –2.2    | –1.0     | –8.5     | –3.6    |
| CdSe     | 0.0     | –10.4    | –2.2    | –0.9     | –10.4    | –3.9    |
| ZnTe     | 0.0     | –11.6    | –2.0    | –0.9     | –11.7    | –4.4    |
| ZnSe     | 0.0     | –12.5    | –2.0    | –0.7     | –12.4    | –4.2    |

TABLE IV. The wave function decomposition for all the states that appear in this study.

| State | Composition |
|-------|-------------|
| hh    | $(p_x, p_y)$ |
| lh    | $(p_x, p_y)$ |
| so    | $(p_z)$     |
| $S_{a1}$ | $(s, p_z)$ |
| $S_{a2}$ | $(s)$      |
| $S_c$  | $(s)$       |
| $B_h$  | $(p_x, p_y)$ |
| $B_l$  | $(p_x, p_y)$ |
| $B_s$  | $(s, p_z)$  |