The band gap of II-VI ternary alloys in a tight-binding description

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We present tight-binding calculations for the band gap of II-VI pseudobinary ternary alloys. We use an $sp^3s^*$ tight-binding Hamiltonian which include spin-orbit coupling. The band gap composition dependence is calculated using an extended version of the virtual crystal approximation, which introduce an empirical correction factor that takes into account the non-linear dependence of the band gap with the composition. The results compare quite well with the experimental data, both for the ternary alloys with wide band gap and for the narrow band gap ones.

Keywords: II-VI semiconductor alloys, tight-binding calculations

Presentamos el cálculo de la banda de energía prohibida de aleaciones ternarias de compuestos II-VI. El cálculo, que incluye interacción espín-orbita, se hace con el método de enlace fuerte, utilizando una base ortogonal de cinco orbitales atómicos por átomo ($sp^3s^*$), en conjunto con la aproximación del cristal virtual. En la aproximación del cristal virtual, incluimos un factor de corrección que toma en cuenta la no linealidad de la banda de energía prohibida como función de la concentración. Con esta corrección nuestros resultados reproducen aceptablemente los datos experimentales hallados en la literatura.

Descriptores: Aleaciones ternarias de compuestos II-VI, método de enlace fuerte

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1. Introduction

The technological interest in optical devices that can operate in the whole spectrum, has given origin to the study of the semiconductor compounds with both the wide band gap and the narrow band gap value. This research has lead the investigation from the binary compounds to the ternary and quaternary alloys. In particular, in the last 10-15 years the study on II-VI alloys has been very intensive. Due to the fact that the band gap of these alloys is direct and tunable in the whole range of the visible spectrum, they have potential application in the design and fabrication of a wide kind of semiconductor devices [1-7].

In semiconductor alloys the band gap value and the lattice parameter are among the most important physical parameters, since these parameters control the band offset and the mismatching in the different devices. The theoretical prediction for these parameters gives good agreement for the lattice parameter, through the known Vegard's law, but not for the band gap value.

In this work we present on the study of the band gap value for II-VI pseudobinary ternary alloys using the tight-binding method (TBM) and the virtual crystal approximation (VCA). We assume that the alloy crystallizes in the zinc-blende crystal structure, so that we can use the same tight-binding Hamiltonians used for the binary compounds. We introduce an empirical correction factor in the VCA in order to take into account the non-linear dependence of the band gap value with the concentration. This parametrization shows its applicability in the calculation of surface electronic properties of II-VI ternary alloys [8], and the band gap calculation of the II-VI pseudomorphic quaternary alloys (as we will show in a work parallel to this one) [9].

The paper is organized as follows: in Sect. 2 we comment some generalities used in the study of the band gap of the ternary alloys found in the present literature. Section 3 presents our method of calculation and the modifications to the VCA. In Sect. 4 we present our results and the comparison with available experimental data, Sect. 5 presents our conclusions, and finally in the Appendix we present the tight-binding parameters used in our calculations.

2. The approach

2.1. The phenomenology

We find in a phenomenological approach that the physical properties of an alloy $A_xB_{1-x}C$ can be obtained, in good approximation, by a linear relation between the physical property $F(A_xB_{1-x}C)$ and the composition $x$, by taking the weighted average of the corresponding physical properties $F_{AC}$ and $F_{BC}$ of the end-point compounds

$$F(x) = xF_{AC} + (1 - x)F_{BC},$$

and, in a more general expression by a quadratic relationship

$$F(x, k) = F(x) + kx(1 - x),$$

where \( k \), known as the bowing parameter, is approximately composition independent [10, 11]. As an example we mention the lattice parameter: we have from X-ray diffraction experiments that the lattice parameter, \( a(x) \), follows the relation (1). That is, we find that the bowing parameter \( k_a \approx 0 \) and we have
\[
a(x) = xa_{AC} + (1 - x)a_{BC},
\]
a linear dependence in \( x \), known as Vegard’s law.

On the other hand, the experimental data shows that the band gap \( E_g \) of the alloys is not linear with the composition \( x \). In most of the cases we have a quadratic dependence of the band gap value in \( x \), i.e.,
\[
\overline{E}_g(x, b) = \overline{E}_g(x) + bx(1 - x),
\]
where \( \overline{E}_g(x) \) is the average value of the band gap and \( b \) is the optical bowing parameter. The most important evidence, for example, is observed in the anion substitution of the II-VI ternary alloys [4, 11-13].

2.2. The approximation to the band gap value and the disorder effects

The experimental interest in the alloys has given origin to an extensive theoretical study of the more relevant parameters, the lattice parameter \( a(x) \) and the band gap value \( E_g(x) \), in terms of simple relationships. However, there is only good agreement for the lattice parameter. For the band gap value, the theoretical work has made use of several methods to calculate its composition dependence. For example, we have the dielectric model [14, 15], the pseudopotential method [11, 16-18], the coherent potential approximation [19-21], the empirical tight-binding method [22-25] (see Ref. 10 for a detailed discussion). In some cases these models are successfully applied to a whole family of compounds, in other cases the approach is only applied to a few compounds.

Several authors [14, 24-26] have proposed that the non-monotonic behavior of \( E_g \) on \( x \) is due to disorder effects. Disorder effects of short as long range. However, the arguments are not definitive. The theoretical studies continue looking for a simple relationship between the band gap value and the alloy composition.

The main phenomenological parameter, in the description of the band gap value of the alloys, is the bowing parameter and their prediction takes lot of work. There are arguments for a bowing parameter as having intrinsic component due to linear variations in the homopolar and ionic energy gap and having extrinsic component as a potential due to charge fluctuations arising from the random positioning of the ions in the alloy [14]; other approximations take the difference of the lattice parameters of the compounds in the alloy [17], the difference between the band gaps or the electronegativity differences [10].

The most simple approximation to the alloy problem is the virtual crystal approximation. In this approximation we take the average values of the quantities of interest, and then the average values are substituted in the model as the new value of the system. However, in the VCA the description of the quadratic behavior of the band gap value, \( E_g(x) \), is deficient due to the fact that in this approximation the disorder effects are not included in an explicit way [14, 24].

Usually, the CPA calculations, in conjunction with empirical methods, are preferred to study the ternary alloys (see for example Refs. 24 and 25). However, in general the CPA calculations implies complicate numerical algorithms [21]. Thus, looking for an alternative approach, we have found that it is possible to obtain an acceptable description of \( E_g(x) \) using the TBM an appropriate reformulated VCA, as we discuss below.

3. Method

To calculate the band gap value, and the electronic band structure, of the semiconductor compounds we use the empirical TBM in a nearest neighbors description [27] with an orthogonal basis of five atomic orbitals per atom (\( sp^3s^* \)). Where, the \( s^* \) virtual orbital is added in order to improve the description of the conduction bands [28]. In our description we include the spin-orbit coupling, since it is important in Te-based compounds [19, 22].

For the semiconductor compounds the band gap is given by
\[
E_g = E_C - E_v,
\]
where \( E_c \) and \( E_v \) are the minimum of the conduction band (cb) and the maximum of the valence band (vb), respectively. In the \( \Gamma \)-point \( E_c \) and \( E_v \) have the next tight binding expressions [30, 31]
\[
E_c = \frac{E_{sa} + E_{sc}}{2} + \sqrt{\left(\frac{E_{sa} - E_{sc}}{2}\right)^2 + V_{sz}^2},
\]
\[
E_v = \frac{E_{pa} + E_{pc} + \lambda_a + \lambda_c}{2} + \sqrt{\left(\frac{E_{pa} - E_{pc} + \lambda_a - \lambda_c}{2}\right)^2 + V_{sz}^2},
\]
where \( E_{\mu\nu} (\mu = s, p; \nu = a, c) \) are the on-site tight-binding parameters (TBPs) for the anion (\( \nu = a \)) [cation (\( \nu = c \)), \( V_{\mu\nu} \) are the nearest neighbors interaction TBPs, and \( \lambda \) the spin-orbit ones.

As is well accepted, the TBM describes quite well the dispersion of the valence bands, as well as the lower conduction band in the high symmetry points (after the inclusion of the \( s^* \)-states), of the binary semiconductor compounds [28, 29]. In this manner, our main hypothesis will be assume that the TBM in conjunction with the VCA describes the valence bands of the ternary alloys as well as in the binary compounds. Then our aim is to look for some corrections in the model that could help us to improve the description of the
lower conduction band. With this approach we want to keep the simplicity and transparency of the TBM, characteristics that are among the more attractive features of the model.

In the VCA the TBPs, of a ternary alloy $A_xB_{1-x}C$, are given by the weighted averages of the corresponding end-point parameters

$$
E_{\mu\nu}(x) = xE_{\mu\nu}^{AC} + (1-x)E_{\mu\nu}^{BC},
$$

where $E_{\mu\nu}^j (\mu, \nu = s, p^s, s^*)$ are the TBPs of the $j$-compound ($j = AC, BC$).

At this point we will take advantage of the fact that in ternary alloys the lower conduction band shows bigger shift than the top of the valence bands, as a function of the composition, as it is shown in ab initio calculations for ZnM$_{1-x}$N$_x$ (M,N = S, Se, Te) ternary alloys by Bernard and Zunger [32].

Then, assuming that the non-linear behavior of $E_g(x)$ comes from the biggest shift of the conduction band edge, compared with the corresponding valence band edge, and from the fact that the $s$-on-site tight-binding parameters locate in energy the conduction band minimum at $\Gamma$ [Eq. (6)], we suggest to correct the VCA expression for the $s$-on-site TBP of the substituted ion. In a second order perturbation theory approach in $x$, and in close analogy with the experimental bowing parameter used for $E_g(x)$, we substitute the VCA expression for the $s$-on-site parameter with an expression that include an empirical bowing parameter. That is, we use the expression

$$
E_{sv}(x, b) = \bar{E}_{sv}(x) + b_x(1-x), \quad \nu = a, c,
$$

for the $s$-on-site parameter of the substituted ion. Where $\bar{E}_{sv}$ is the corresponding VCA average of the $s$-on-site tight-binding parameters [Eq. (8)], and $b_x$ the empirical bowing parameter. Following these ideas and trying to keep our approach within the tight-binding language, we use an empirical bowing parameter proportional to a power of the absolute value of the difference between the $s$-on-site tight-binding parameters of the substituted ions and inversely proportional to the absolute value of the difference of the $V_{ss}$ nearest neighbors interaction tight-binding parameters. Consequently, the bowing parameter is given as

$$
b_x = \pm k \frac{|E_{sv}^{AB} - E_{sv}^{BC}|^\lambda}{|V_{sv}^{AB} - V_{sv}^{BC}|}, \quad \nu = a, c.
$$

Here we use the sign $+$ (−) for the cation (anion) substitution. $\lambda$ is as a free parameter used to fit $E_g(x)$. We use $\lambda = 1.0$ for the sulphur-based alloys, and $\lambda = 1.75$ for all the other alloys. Thus, in the proportionality constant $k$ we include the appropriate dimensions, so that $b_x$ is given in eV. The numerical value used for $k$ is $1/8$, for all the alloys. In Table I we list the empirical bowing parameter obtained by using the Eq. (10) and the TBP given in the Appendix.

### 4. Results and discussion

In this section we present our calculation of $E_g(x)$ for the II-VI semiconductor alloys studied in this work. The results for the ternary alloys are graphically showed in Figs. 1-4. In the figures the experimental data, obtained after the empirical expressions given in the experimental reports, are showed by symbols and the continuous line represents our calculation. Figures 1 and 2 show $E_g(x)$ for the anion substitution, and Figs. 3 and 4 show $E_g(x)$ for the cation case. In Table II we compare our calculated optical bowing parameter, the second order coefficient in a polynomial fit to $E_g(x)$, with the experimental one. We can appreciate good agreement between our calculation and the experimental results for all the studied alloys. We will discuss first our results for the anion substitution and after the cation case.

#### 4.1. Anion substitution

In the anion substitution case $E_g$ shows a noticeable non linear dependence on $x$, modeled through a quadratic relationship on the composition, where the optical bowing parameter has values as high as in $b_{zTeS} = 3.0$ [16], whereas the cation optical bowing parameter has smaller values (see Table II). In our model we can obtain a similar effect after the inclusion of our empirical bowing parameter. We find that the absolute value of the anion empirical bowing parameter is bigger than

<table>
<thead>
<tr>
<th>Compound</th>
<th>$b_a$</th>
<th>$b_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTe$_{1-x}$S$_x$</td>
<td>−3.530</td>
<td></td>
</tr>
<tr>
<td>ZnTe$_{1-x}$Se$_x$</td>
<td>−6.964</td>
<td></td>
</tr>
<tr>
<td>CdTe$_{1-x}$Se$_x$</td>
<td>−0.195</td>
<td></td>
</tr>
<tr>
<td>Cd$_{1-x}$Zn$_x$Te</td>
<td>0.0200</td>
<td></td>
</tr>
<tr>
<td>Cd$_{1-x}$Zn$_x$Se</td>
<td>0.0370</td>
<td></td>
</tr>
<tr>
<td>Hg$_{1-x}$Zn$_x$Te</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>Hg$_{1-x}$Cd$_x$Te</td>
<td>0.0180</td>
<td></td>
</tr>
</tbody>
</table>

#### Table II. Experimental and calculated optical bowing parameter.

The calculated optical bowing parameter is obtained after adjusting our $E_g(x)$ results to a second order polynomial. The parameters are given in eV.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experiment</th>
<th>Ref.</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTe$_{1-x}$S$_x$</td>
<td>3.0 ± 0.1</td>
<td>16</td>
<td>2.90</td>
</tr>
<tr>
<td>ZnTe$_{1-x}$Se$_x$</td>
<td>1.507 ± 0.10</td>
<td>4</td>
<td>1.51</td>
</tr>
<tr>
<td>CdTe$_{1-x}$Se$_x$</td>
<td>0.755</td>
<td>5</td>
<td>0.756</td>
</tr>
<tr>
<td>Cd$_{1-x}$Zn$_x$Te</td>
<td>0.166 ± 0.010</td>
<td>2</td>
<td>0.215</td>
</tr>
<tr>
<td>Cd$_{1-x}$Zn$_x$Se</td>
<td>0.26</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Hg$_{1-x}$Zn$_x$Te</td>
<td>0.35</td>
<td>38</td>
<td>0.597</td>
</tr>
<tr>
<td>Hg$_{1-x}$Cd$_x$Te</td>
<td>0.654</td>
<td>39</td>
<td>0.587</td>
</tr>
<tr>
<td>Hg$_{1-x}$Cd$_x$Te</td>
<td>0.132</td>
<td>42</td>
<td>0.222</td>
</tr>
</tbody>
</table>
The band gap value shows an important non-linear behavior with the composition [16, 33]. From the figure it is evident that we have obtained a fairly description in this system. We obtain that $E_g(x)$ has a minimum at $x_{\text{min}}^\text{theo} = 0.74$, so nearly to the experimental value, $x_{\text{min}}^\text{exp} = 0.73$. From Table II we can see that the calculated optical bowing parameter shows good agreement with the experimental one.

Figure 2a shows our calculation for the ZnTe$_{1-x}$Se$_x$ system. The calculation shows good agreement with the experiment [4] in the high Se-concentration limit, although around the minimum of the curve we observe some differences. However, the calculated concentration for the minimum of $E_g(x)_{\text{theo}} = 0.30$ is very close to the experimental value $x_{\text{min}}^\text{exp} = 0.35$. At this $x$-value we have found that $E_g(x)$ is underestimated about 0.08 eV; value that, in the most of the cases, is within the experimental accuracy. Table II shows that our calculated optical bowing parameter is in good agreement with the experimental one.

In Fig. 2b we show our calculation of $E_g(x)$ for the CdTe$_{1-x}$Se$_x$ system, we appreciate good agreement with the experimental data. For this system we have used the experimental expression cited in Ref. 5. This system crystallizes in the zinc-blende crystal structure for low Se-concentration, and adopts the wurtzite structure for high Se-concentration. Hereafter we assume the cubic structure, so that we have extrapolated our results for all values of $x$ for this structure. From the Table II we can see that our calculated optical bowing parameter, $b_{\text{theo}} = 0.756$, compares well with the experimental one, $b_{\text{exp}} = 0.755$, measured at low temperature [34], in contrast with room temperature measurements that give $b_{\text{exp}} = 0.88$ [35].
4.2. Cation substitution

In the cation substitution case we have that the band gap composition change shows more linear behavior than in the anion substitution. Additionally, the alloys with narrow band gap value, such as those constituted by Hg, represent a challenge from the theoretical point of view. Alloys like HgZnTe go from a quasi-metallic compound HgTe with negative band gap to a semiconductor compound ZnTe with band gap higher than 2.0 eV. We show that our approach goes for these compounds as well.

Figure 3a shows our calculation for \( E_g(y) \) for the Cd\(_{1-y}\)Zn\(_y\)Te alloy. We use for comparison the work of Olego et al. [2] (full points) and Li et al. [37] (void squares). As we can appreciate we have obtained a qualitatively good agreement with both experimental reports. However, our calculated optical bowing parameter has better agreement with that cited by Li et al. [37] than for that from Olego et al. [2]. Our calculations under-estimate the optical bowing parameter by 20% in the former case.

Figure 3b shows our band gap calculation for the Cd\(_{1-y}\)Zn\(_y\)Se system. We compare our results with the experimental report of Areshkin et al. [38]. The figure shows some differences between the calculation and the experimental data. Our calculation does not show the fully linear behavior of the band gap value, which is the characteristic of the cation substitution. However, we found numerically that between our calculation and the experimental data there is an energy difference lesser than 0.06 eV, which is within the experimental accuracy, in the most of the cases.

Figure 4a shows our calculation for the Hg\(_{1-y}\)Cd\(_y\)Te system. The experimental fit corresponds to measurements in the low temperature regime from Ravid et al. [39] (full points).

Our fit to the optical bowing parameter give us the value \( b_{\text{theo}} = 0.587 \) eV, which is in good agreement with the experimental value \( b_{\text{exp}} = 0.654 \) eV. Furthermore, for Hg-based alloys it is usual to find experimental reports where the given expression for \( E_g(x) \) is represented by high order polynomials, such as third order terms or expressions proportional to \( x^{1/2} \) [40, 41], we have found that our approach reproduce also these fits. We can appreciate in Fig. 4a that an experimental expression including a \( x^3 \) plus a \( x^{1/2} \) terms, after Toulouse et al. [40] (void squares), is well reproduced in our calculations.

Figure 4b shows our calculation for the Hg\(_{1-y}\)Cd\(_y\)Te system. In the figure we compare our results with the quadratic fit of Laurenti et al. [42] (full points), the cubic fit used by Hansen et al. [43] (void triangles), and that from Tong and Ravindra [44] (void squares). Graphically we have obtained good agreement with the experimental reports, as we appreciate in the figure. However, due to the different polynomial fits used in the experiments, we compare our calculated optical bowing parameter only with the reported by Laurenti et al. [42], see Table II. From the table we can see that the optical bowing parameter is over-estimated in our calculations. However, from the numerical values for \( E_g(x) \) we do not found significant deviations, as is evident from the Fig. 4b.

5. Conclusions

We have calculated the band gap value of the II-VI pseudobinary ternary alloys using the tight-binding method and the virtual crystal approximation. In order to properly describe the change of the band gap value, as a function of the concentration, we have introduced an empirical bowing parameter in the VCA expression for the s-on site tight-binding param-
Figure 4. Band gap change for the cation substitution in (a) the Hg$_{1-x}$Zn$_x$Te system and (b) the Hg$_{1-y}$Cd$_y$Te system. The experimental expression are of (a) Ravid et al. [39] (full points), and Toulouse et al. [40] (void squares), (b) Laurens et al. [42] (full points), Hansen et al. [43] (void triangles), Tong et al. [44] (void squares), and the continuous line is our calculation.

6. Appendix

Table III. Tight-binding parameters used in this work, the values are given in eV. We use the notation of Kobayashi et al. [30].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ZnS$^{(a)}$</th>
<th>ZnSe$^{(a)}$</th>
<th>ZnTe$^{(a)}$</th>
<th>CdSe$^{(b)}$</th>
<th>CdTe$^{(c)}$</th>
<th>HgTe$^{(d)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_p$</td>
<td>2.07151</td>
<td>1.78236</td>
<td>0.62682</td>
<td>1.03400</td>
<td>0.32790</td>
<td>0.15500</td>
</tr>
<tr>
<td>$E_x$</td>
<td>0.72842</td>
<td>0.04728</td>
<td>-1.42000</td>
<td>1.07977</td>
<td>-0.85000</td>
<td>-1.40400</td>
</tr>
<tr>
<td>$V_{x}$</td>
<td>-6.58933</td>
<td>-6.50203</td>
<td>-6.64227</td>
<td>-2.89240</td>
<td>-5.00000</td>
<td>-3.26700</td>
</tr>
<tr>
<td>$V_{zp}$</td>
<td>3.63229</td>
<td>3.30661</td>
<td>1.94039</td>
<td>3.01320</td>
<td>2.14000</td>
<td>1.44300</td>
</tr>
<tr>
<td>$V_{zp'}$</td>
<td>6.34679</td>
<td>5.41204</td>
<td>4.07748</td>
<td>5.73040</td>
<td>5.28170</td>
<td>3.63900</td>
</tr>
<tr>
<td>$V_{zp''}$</td>
<td>5.19403</td>
<td>1.13681</td>
<td>5.92472</td>
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<td>2.42100</td>
</tr>
<tr>
<td>$V_{zp''}$</td>
<td>5.87772</td>
<td>5.80232</td>
<td>4.67265</td>
<td>5.65560</td>
<td>3.63824</td>
<td>3.24300</td>
</tr>
<tr>
<td>$E_{s,Zn}$</td>
<td>8.69781</td>
<td>7.84986</td>
<td>6.22682</td>
<td>6.02650</td>
<td>10.44540</td>
<td>6.00000</td>
</tr>
<tr>
<td>$E_{s,Cd}$</td>
<td>9.27886</td>
<td>8.52031</td>
<td>6.77952</td>
<td>3.96150</td>
<td>6.02690</td>
<td>5.05000</td>
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<tr>
<td>$V_{s,Cd}$</td>
<td>5.46999</td>
<td>3.26633</td>
<td>2.96202</td>
<td>2.11640</td>
<td>2.52468</td>
<td>3.52000</td>
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<td>2.21680</td>
<td>2.94540</td>
<td>0.32300</td>
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<tr>
<td>$\lambda_{s}$</td>
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<td>0.36226</td>
<td>0.14300</td>
<td>0.32267</td>
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<tr>
<td>$\lambda_{p}$</td>
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<td>0.02717</td>
<td>0.06700</td>
<td>0.07567</td>
<td>0.28600</td>
</tr>
</tbody>
</table>

(a) Ref. 45, (b) Ref. 46, (c) Ref. 47, (d) Ref. 30

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32. See in particular the discussion related with Figs. 12–14 in Ref. 10.