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Electronic band structure of II-VI quaternary alloys in a tight-binding approach

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Based on a successful description of the band gap change with composition for the II-VI ternary alloys, we describe a method to set up tight-binding Hamiltonians for quaternary alloys. We use a formula that can be thought as a straightforward generalization of the virtual crystal approximation for this case. In this work we consider $\mathrm{Zn}_{1-y}\mathrm{Cd}_y\mathrm{Se}_{1-x}\mathrm{Te}_x$ and study the change of the band gap with composition obtained by direct diagonalization of the corresponding Hamiltonians. We next consider the technological interesting compound $\mathrm{Zn}_{1-y}\mathrm{Cd}_y\mathrm{S}_{1-x}\mathrm{Se}_x$. The agreement with the experimental data is remarkable.

Keywords: II-VI quaternary alloys; electronic band structure; tight-binding method

Con base en una descripción adecuada para el estudio del cambio de la banda de energía prohibida, en función de la concentración, de las aleaciones ternarias de compuestos II–VI, presentamos un método para el análisis de las propiedades electrónicas de las aleaciones cuaternarias. Aplicamos nuestro modelo al estudio de las aleaciones $\mathrm{Zn}_{1-y}\mathrm{Cd}_y\mathrm{Se}_{1-x}\mathrm{Te}_x$ y $\mathrm{Zn}_{1-y}\mathrm{Cd}_y\mathrm{S}_{1-x}\mathrm{Se}_x$. Mostramos que nuestros resultados se comparan aceptablemente bien con datos experimentales.

Descriptores: aleaciones cuaternarias II-VI, estructura electrónica de bandas, método de enlace fuerte.

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1. Introduction

Optical devices able to operate in the visible spectrum range have motivated a vigorous research in II-VI wide band gap semiconductor compounds. The main goal in these studies is to seek for the independent control of the fundamental parameters of the compound: the band gap value, the lattice constant and the valence band offset. The interest has been recently focused on the study of the ternary and quaternary alloys. In the quaternary alloys it is the simultaneous substitution of the anion and the cation that allows control of the band gap and the lattice constant values within certain limits. This procedure is very important in optoelectronic engineering. In fact, a binary/quaternary heterojunction with no stress at the interface and with a predetermined value for the band offset can be produced. Examples of basic and applied work can be found in Refs. 1–3. Brasil *et al.* [1] have reported photoconductivity and photoluminescence experiments on the $\mathrm{Zn}_{1-y}\mathrm{Cd}_y\mathrm{Se}_{1-x}\mathrm{Te}_x$ system, and they have fitted the measured band gap value to a quadratic function of the composition; Ichino *et al.* [3] have used the $\mathrm{Zn}_{.9}\mathrm{Cd}_{.1}\mathrm{S}_{.07}\mathrm{Se}_{.93}$ quaternary alloy as an active layer in a laser diode operating in the blue-green to the UV spectral region.

In previous work, we have described the composition dependence of the band gap value for the II-VI ternary alloys and compared our results with the existing experimental data [4]. To describe the ternary alloys we have used carefully studied tight-binding Hamiltonians for the binary compounds [5]. We took into account nearest neighbor interactions with an orthogonal basis of five atomic orbitals (sp^3s^*) per atom; in this approximation the s^*-state is included to better describe the lowest states in the conduction band. We have used the two-center integral approximation in the Slater-Koster language and we took into account the spin-orbit interaction [6]. The tight-binding method describes rather well the valence band region and gives correctly the band gap value [7]. To include composition we have used the virtual crystal approximation (VCA). We have found that the VCA can describe properly the behavior of the band gap, as a function of composition, if an empirical bowing parameter to calculate the mixed tight-binding parameters (TBPs) is introduced [4].

In this work, and as part of a series of applications to show the utility of our approach, we present the calculation of the band gap of the quaternary alloys $\mathrm{Zn}_{1-y}\mathrm{Cd}_y\mathrm{Se}_{1-x}\mathrm{Te}_x$ and $\mathrm{Zn}_{.9}\mathrm{Cd}_{.1}\mathrm{S}_{.07}\mathrm{Se}_{.93}$. We show that our calculations are in good agreement with the experimental data.

The rest of the paper is organized as follows. In Sect. 2 we describe briefly the method to be used; Sect. 3 contains our results and discussions, and finally in Sect. 4 we summarize our conclusions.

2. The method

In semiconductor compounds the band gap value, E_g, is given by the difference between the minimum of the conduction band (ϵ_c), and the maximum of the valence band (ϵ_v), $E_g = \epsilon_c - \epsilon_v$. In particular, for direct band gap semiconductor compounds, in the tight-binding approximation, ϵ_c and ϵ_v, at Γ, can be expressed as [8]

$$\epsilon_c = \frac{E_{sa} + E_{sc}}{2} + \sqrt{\left(\frac{E_{sa} - E_{sc}}{2}\right)^2 + V_{ss}^2}, \qquad (1)$$

and

$$\epsilon_v = \frac{E_{pa} + E_{pc} + \lambda_a + \lambda_c}{2} - \sqrt{\left(\frac{E_{pa} - E_{pc} + \lambda_a - \lambda_c}{2}\right)^2 + V_{xx}^2}, \quad (2)$$

where $E_{\alpha\nu}$ ($\alpha = s,\ p;\ \nu = a,\ c$) are the on-site TBP for the anion (a) or the cation (c), $V_{\alpha\alpha}$ are the nearest-neighbor interaction parameters, and λ_ν the spin-orbit ones.

Within the VCA model the TBPs of the alloy are given by the weighted averages of the corresponding end-point parameters. For a ternary alloy with an anion substitution $AB_{1-x}C_x$, for example, we have

$$E_{\alpha\alpha'}^{\mathrm{ABC}}(x) = (1-x)E_{\alpha\alpha'}^{\mathrm{AB}} + xE_{\alpha\alpha'}^{\mathrm{AC}}, \qquad (3)$$

where $E_{\alpha,\alpha'}^{j}$ is the corresponding TBPs for the j-compound (AB or AC), and α, α' denote the atomic orbitals (sp^3s^*). Hereafter our proposal is to use this expression for all the TBPs but the "s" on-site ones.

It is well known that in the ternary alloys the dependence of the band gap value is a non-linear function of composition. At the same time, as can be inferred from Eq. (1), the "s" on-site parameter is responsible for the correct energy position of the minimum of the conduction band at the Γ-point. From these facts and according with our previous analysis [4], where we found that the minimum of the conduction band shows bigger dispersion than the maximum of the valence band, as a function of the composition, we suggest to introduce an empirical bowing parameter in the VCA expression for the "s" on-site parameters. This empirical bowing parameter could be thought as an *ad hoc* introduction of the disorder effects [9]. With this scheme we avoid all the numerical complications from the CPA calculations, whereas the overall shift of the band gap value is still adequate, as we will show in the next section. Explicitly, we proceed in the following way, we introduce an empirical bowing parameter to calculate the "s" on-site TBP of the substituted ion, from Eq. (3) we have

$$E_{sa}(x)^{\mathrm{ABC}} = (1-x)E_{sa}^{\mathrm{AB}} + xE_{sa}^{\mathrm{AC}} + b_a x(1-x), \qquad (4)$$

where b_a is the appropriate empirical bowing parameter for the anion substitution. A cation-substituted compound can be handled in analogous way. With the idea to keep our approach the simplest possible and within the tight-binding language, we propose to calculate the empirical bowing parameter with an expression as

$$b_\nu = \pm k \frac{|E_{s\nu}^{\mathrm{AB}} - E_{s\nu}^{\mathrm{AC}}|^{\lambda}}{|V_{ss}^{\mathrm{AB}} - V_{ss}^{\mathrm{AC}}|}, \qquad \nu = a, c, \qquad (5)$$

where the TBPs involved ($E_{s\nu}$, V_{ss}) are the appropriate ones for each limit compound, and we use the sign $+(-)$ for a cation (anion) substitution. Here, λ is a free parameter used to adjust $E_g(x)$ in the ternary alloys. We have used $\lambda = 1.0$ 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_ν is given in eV. The numerical value used for k is 1/8, for all the alloys [4]. In this manner, our approach improves and our results are in good agreement with the experimental data. In Table I, we give our found values for the empirical bowing parameter for the different ternary compounds involve in this work. Notice that the $b-$anion parameters (b_a) have absolute values as high as in $b_{\mathrm{ZnSeTe}} = -6.964$ and the $b-$cation parameters (b_c) have smaller values. The biggest one, in Table I, is $b_{\mathrm{ZnCdSe}} = 1.349$.

TABLE I. Empirical bowing parameters obtained using the Eq. (5) and the tight-binding parameters given in the Refs. 5 and 11. All the parameters are in eV.

Compound	b_{anion}	b_{cation}
$ZnSe_{1-x}Te_x$	-6.964	
$CdSe_{1-x}Te_x$	-0.195	
$CdS_{1-x}Se_x$	-0.136	
$ZnS_{1-x}Se_x$	-2.833	
$Zn_{1-x}Cd_xSe$		0.037
$Zn_{1-x}Cd_xTe$		0.020
$Zn_{1-x}Cd_xS$		1.349

Now, we extend our formulation to quaternary alloys:

Let us consider the compound $A_{1-y}B_yC_{1-x}D_x$ which we assume as a zinc-blende compound constituted by a composed cation ($A_{1-y}B_y$) and a composed anion ($C_{1-x}D_x$) with a lattice constant given by the appropriate VCA expression. The TBPs are given, in terms of the corresponding TBPs of the final point binary compounds, for the expression

$$E_{\alpha,\alpha'}^{\mathrm{ABCD}}(x,y) = xyE_{\alpha\alpha'}^{\mathrm{BD}} + x(1-y)E_{\alpha\alpha'}^{\mathrm{AD}} + (1-x)yE_{\alpha\alpha'}^{\mathrm{BC}} + (1-x)(1-y)E_{\alpha\alpha'}^{\mathrm{AC}}, \quad (6)$$

here the definition of the TBPs, $E_{\alpha\alpha'}^{j}$, should be obvious. We will use again this formula for all but the "s" on-site parameter. For the "s" on-site parameter we will add a bowing parameter. We construct it from the corresponding bowing parameters of the ternary alloys. Hence, the calculations contain no additional adjustable parameters. For the anion "s" on-site parameter we use b_{ACD} ($AC_{1-x}D_x$) and b_{BCD} ($BC_{1-x}D_x$) from which we set $x(1-x)\left[(1-y)b_{\mathrm{ACD}} + yb_{\mathrm{BCD}}\right]$ as the appropriate anion bowing parameter to be used for the $A_{1-y}B_yC_{1-x}D_x$ alloy. Then, the full formula for the anion

TABLA II. Measured values for the band gap given in Ref. 1 for the $\mathrm{Zn}_{1-y}\mathrm{Cd}_y\mathrm{Se}_{1-x}\mathrm{Te}_x$ quaternary alloys are compared with our calculation. Band gap values given in eV.

x	y	E_g(PC)[a]	E_g(theo)[b]
0.015	0.10	2.610	2.642
0.020	0.23	–	2.453
0.050	0.22	2.443	2.427
0.070	0.34	2.244	2.256
0.080	0.28	2.362	2.316
0.038	0.32	2.024	2.002
0.039	0.11	2.224	2.194
1.000	0.31	2.049	2.099

[a] Values taken from photoconductivity measurements of Brasil *et al.* Ref. 1

[b] This work

"s" on-site parameter is

$$\begin{aligned} E_{sa}^{\mathrm{ABCD}}(x,y) &= xyE_{sa}^{\mathrm{BD}} + x(1-y)E_{sa}^{\mathrm{AD}} \\ &+ (1-x)yE_{sa}^{\mathrm{BC}} + (1-x)(1-y)E_{sa}^{\mathrm{AC}} \\ &+ x(1-x)\big[(1-y)b_{\mathrm{ACD}} + yb_{\mathrm{BCD}}\big]. \end{aligned} \tag{7}$$

It is trivial to set the corresponding formula for the cation "s" on-site parameter. We get

$$\begin{aligned} E_{sc}^{\mathrm{ABCD}}(x,y) &= xyE_{sc}^{\mathrm{BD}} + x(1-y)E_{sc}^{\mathrm{AD}} \\ &+ (1-x)yE_{sc}^{\mathrm{BC}} + (1-x)(1-y)E_{sc}^{\mathrm{AC}} \\ &+ y(1-y)\big[(1-x)b_{\mathrm{ABC}} + yb_{\mathrm{ABD}}\big]. \end{aligned} \tag{8}$$

Equations (6), (7) and (8) can be used for ternary alloys with the appropriate limit value for x and y.

3. Results and Discussion

Table II shows a comparison of our calculated band gap, as a function of composition, $E_g(x,y)$ and the photoconductivity measurements of Brasil *et al.* for $\mathrm{Zn}_{1-y}\mathrm{Cd}_y\mathrm{Se}_{1-x}\mathrm{Te}_x$ [1]. Our calculation agrees well with the measured values within 2% accuracy. The result is encouraging.

Figure 1 shows a 3-D graph for $E_g(x,y)$. The dots are the experimental data, the mesh is our calculation. The edges are the four ternary boundaries. As we have mentioned, our calculation reproduces properly the known bowing of E_g for all the range of compositions. In ternary alloys, the anion substitution produces a bowing in E_g that is more noticeable than in the cation substitution. This fact can be inferred from the figure if we take the projection of E_g onto the X-Z plane. Also notice the quasi-linear behavior of E_g for the cation substitution. It is worth mentioning again that the bowing parameter (in absolute value) for the anion substitution is bigger than for the cation one (see Table I).

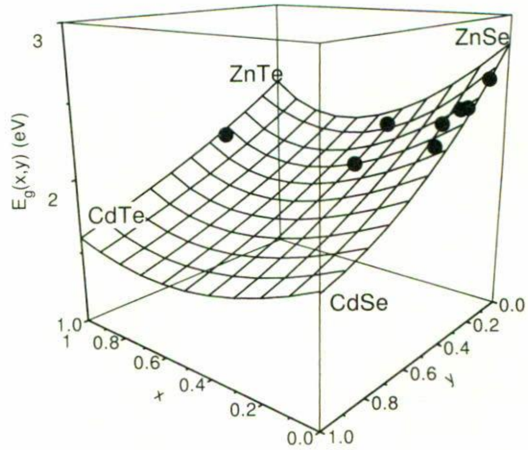

FIGURE 1. 3-D representation of the calculated band gap of the $\mathrm{Zn}_{1-y}\mathrm{Cd}_y\mathrm{Se}_{1-x}\mathrm{Te}_x$ quaternary alloy, as a function of the composition (x, y), using the tight-binding method and the virtual crystal approximation as is proposed in this work. The points are the experimental data of Brasil *et al.*[1]. It is noticeable that all the experimental points are just over our calculated surface.

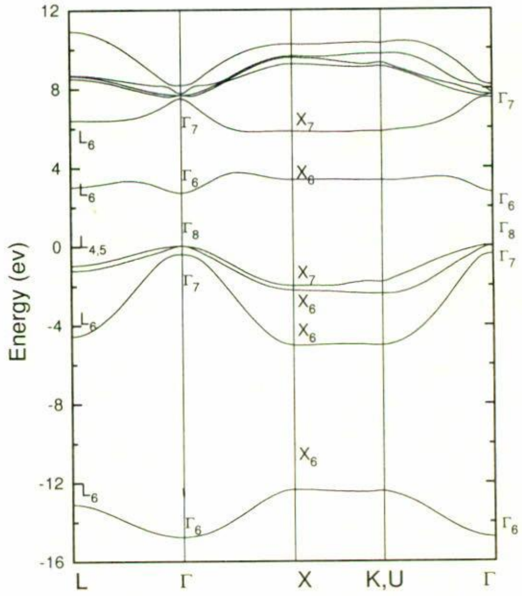

FIGURE 2. The electronic band structure of the $\mathrm{Zn}_{.9}\mathrm{Cd}_{.1}\mathrm{S}_{.07}\mathrm{Se}_{.93}$ quaternary alloy calculated using our tight-binding parametrization.

We have also used our method to calculate the electronic band structure for the $\mathrm{Zn}_{.9}\mathrm{Cd}_{.1}\mathrm{S}_{.07}\mathrm{Se}_{.93}$ quaternary alloy. Since Ichino *et al.* [3] have reported their experiment on it recently, our calculated band structure is of current interest. These authors propose the alloy as an active layer in a laser diode operating in the blue-green to ultraviolet spectral region. Figure 2 shows our result. The calculated electronic band structure is representative of a semiconductor compound with direct band gap. Our lowest conduction band shows less dispersion than that calculated, using the empirical pseudopotential method, by Feng *et al.* [10]. However, it is well known that this is one of the tight-binding features [7]. Our calculated band gap value for this alloy is 2.705 eV that is in good agreement with the experimental value of 2.73 eV at 4.2 K given by Ichino *et al.* [3], Feng *et al.* give 2.648 eV [10].

4. Conclusions

In conclusion, we have set up tight-binding Hamiltonians for quaternary II-VI zinc-blende alloys which are consistent with the corresponding ternary ones. All these Hamiltonians are based on the knowledge of the corresponding ones for the binary compounds.

We have calculated the changes in the band gap value as a function of composition for the zinc-blende quaternary alloy $Zn_{1-y}Cd_ySe_{1-x}Te_x$, our calculated values are in good agreement with the experimental data. We have further calculated the electronic band structure of $Zn_{.9}Cd_{.1}S_{.07}Se_{.93}$, which is a technologically important compound of current interest. We get a band gap value closer to experiment than a pseudopotential calculation. Tight-binding Hamiltonians for quaternary alloys can help establishing the importance of different factors in the physics of complicated systems. They can be used as a basis to study the effect of pressure, reconstruction, interface states, etc., in the electronic band structure of complex heterojuntions.

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