Electronic structure and band gap composition–dependence of the II–VI quaternary alloys

A. E. García, A. Zepeda–Navratil, A. Camacho, D. Olguín, and R. Baquero

Departamento de Física, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, AP. 14-740, México, D.F., Mexico 07000

Departamento de Física, Universidad de los Andes, A. P. 4976, Santa Fé de Bogotá, Colombia.

Abstract

Based on a successful description of II–VI ternary alloys, which introduces an empirical bowing parameter to the widely used virtual crystal approximation, we set up a tight–binding Hamiltonian to describe the Zn$_{1−y}$Cd$_y$Se$_{1−x}$Te$_x$ and Zn$_9$Cd$_1$S$_{0.07}$Se$_{0.93}$ quaternary alloys. We just use a formula that can be thought as a straightforward generalization of the virtual crystal approximation for this case. Our Hamiltonians reproduce very well the change in the band gap value with the composition observed in recent experimental reports. PACS: 71.15.Fv, 71.55.Gs, 73.10.-r
Interest in optical devices that can operate in the visible spectrum range has 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, 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 the manufacture of a compound with band gap and the lattice constant values within certain limits. This procedure is very important in optoelectronic engineering. In fact, it could be produced a binary/quaternary heterojunction with no stress at the interface and with a predetermined value for the band offset [1–3].

Recently, Brasil et al. [1] have reported photoconductivity and photoluminiscence experiments on the Zn$_{1-y}$Cd$_y$Se$_{1-x}$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 Zn$_{0.9}$Cd$_{1.1}$S$_{0.07}$Se$_{0.93}$ quaternary alloy as an active layer in a laser diode operating in the blue–green to the UV spectral region.

In a previous work, we have described the change of the band gap value for the ternary alloys and compared the 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 neighbors interactions with an orthogonal basis of five atomic orbitals (sp$^3$s$^*$) per atom; in this approximation the s$^*$–state is included to better describe the lower states in the conduction band. We have used the two center integrals approximation in the Slater–Koster language and we took into account the spin–orbit interaction [6,7]. The tight–binding method describes rather well the valence band region and gives correctly the band gap value [8]. To include composition we have generalized the virtual crystal approximation (VCA) by introducing an empirical bowing parameter. As we have found, the VCA model can describe properly the behavior of the band gap if we introduce an empirical bowing parameter to calculate the “s” on–site tight–binding parameter of the substituted ion [4].
In the semiconductor compounds the band gap, \( E_g \), is given by the difference between the minimum of the conduction band, \( E_c \), and the maximum of the valence band, \( E_v \),

\[
E_g = E_c - E_v
\]  

In particular, for the compounds with direct transition the expressions for \( E_c \) and \( E_v \) at \( \Gamma \), in the tight–binding method, are: \[7\]

\[
E_c = \frac{E_{sa} + E_{sc}}{2} + \sqrt{\left(\frac{E_{sa} - E_{sc}}{2}\right)^2 + V_{ss}^2}
\]  

and

\[
E_v = \frac{E_{pa} + E_{pc} + \lambda_a + \lambda_c}{2} - \sqrt{\left(\frac{E_{pa} - E_{pc} + \lambda_a - \lambda_c}{2}\right)^2 + V_{xx}^2}
\]

where \( E_{\alpha\nu} \) (\( \alpha = s, p; \ \nu = a, c \)) are the on–site tight–binding parameters with \( s \) or \( p \) character for the anion \( (a) \) and the cation \( (c) \), \( V_{\alpha\alpha} \) are the nearest neighbor interaction parameters, and \( \lambda_{\nu} \) the spin–orbit parameters.

To describe the alloy we have used the VCA model, as we stated above. In this approximation the tight–binding parameters are given by the weighted averages of the corresponding end–point parameters. For a ternary alloy \( \text{AB}_{1-x}\text{C}_x \), for example, we have:

\[
E_{\alpha\alpha'}(x) = x E_{\alpha\alpha'}^{AC} + (1 - x) E_{\alpha\alpha'}^{AB}
\]

where \( E^J \) is the corresponding tight–binding parameter of the different binary compounds and \( \alpha, \alpha' \) denote the atomic orbitals (\( sp^3s^* \)). We will use this expression for all the tight–binding parameter but the “s” on–site ones.

As it is well known, the VCA model by itself does not describe correctly the non–linear behavior of the band gap value in the alloy. Therefore, to take into account the non–linear behavior of the band gap in the ternary description, we have included an empirical bowing parameter in the “s” on–site tight–binding parameter of the substituted ion. This is because the “s” on–site tight–binding parameter is responsible for the correct energy position of the conduction band in the \( \Gamma \)–point \[3\], as can be inferred from eq. (2). In an explicit way,
when we have an anion substitution we introduce an empirical bowing parameter in the “s” on-site anion-VCA expression, and the same for the cation case. We use the next VCA expression for the “s” on-site tight-binding parameter

$$E_{sv}'(x, b_\nu) = E_{sv}(x) + b_\nu x(1 - x), \quad \nu = a, c$$

(5)

where $E_{sv}(x)$ is given by eq. (4), and $b_\nu$ is the empirical bowing parameter appropriate to each substitution. We define the empirical bowing parameter as

$$b_\nu = \pm k \frac{|E_{sv}^{1} - E_{sv}^{2}|^\lambda}{|V_{ss}^{1} - V_{ss}^{2}|},$$

(6)

where $E_{sv}^{1(2)}$ is the “s” on-site tight-binding parameter for the compound 1 (2), $V_{ss}^{1(2)}$ the corresponding nearest neighbour $s-s$ interaction parameter for the compound 1 (2), and we use the sign $+(-)$ for cation (anion) substitution, the proportionality constant is taken as $k = 1/8$, and we take $\lambda$ as our free parameter in order to obtain the best fit to the experimental data. For the most of the alloys we have used $\lambda = 1.75$, and for the S–based alloys we have used $\lambda = 1.0$. We will show that these values for $\lambda$ give us good agreement with experiment. The values for the empirical bowing parameter, given in Table I, are the same that we have used in the ternary description (see Ref. [4]). With this Hamiltonians we can calculate the band gap for any composition in a straightforward way. However, before to do that we should to extend our approximation in order to incorporate properly the quaternary alloys.

In the quaternary alloy $A_{1-y}B_yC_{1-x}D_x$ the VCA expression for the tight-binding parameters, that is the appropriate extension of eq. (4), is

$$E_{aa'}(x, y) = xyE_{aa'}^{BD} + x(1 - y)E_{aa'}^{AD} + (1 - x)yE_{aa'}^{BC} + (1 - x)(1 - y)E_{aa'}^{AC},$$

(7)

where the $E^{ij}$’s are defined in eq. (4). In these alloys we have both substitutions, anion– as well as cation–substitution. For that reason we have found natural to extend (in the spirit of the VCA) our formula, for the “s” on-site parameters, of the ternary alloys as follows: For the anion substitution,
\[ E_{sa}(x, y, b_a) = E_{sa}(x, y) + x(1-x)(yb_a^B + (1-y)b_a^A), \]  
\[ E_{sc}(x, y, b_c) = E_{sc}(x, y) + y(1-y)(xb_c^D + (1-x)b_c^C), \]

where \( E_{sa}(x, y) \) is given by eq. (7), \( b_a^B \) and \( b_a^A \) are the empirical bowing parameters for the anion substitution in the \( BC_{1-x}D_x \) and \( AC_{1-x}D_x \) systems, respectively.

For the cation substitution,

\[ E_{sc}(x, y, b_c) = E_{sc}(x, y) + y(1-y)(xb_c^D + (1-x)b_c^C), \]

where \( E_{sc}(x, y) \) is given by eq. (7), \( b_c^D \) and \( b_c^C \) are the empirical bowing parameters for the cation substitution in the \( A_{1-y}B_yD \) and \( A_{1-y}B_yC \) systems, respectively. Note that in the end–values of the compositional variable \( y \) in eq. (8) (or \( x \) in eq. (9)) we obtain the appropriate expression for the ternary case, eq. (5). Using these expressions, for the “s” on–site tight–binding parameters, we can calculate the band gap value and the electronic structure for any composition of the quaternary alloys.

Table II shows a comparison of our calculation of \( E_g(x, y) \) and the photoconductivity measurements of Brasil et al. for \( \text{Zn}_1-\gamma \text{Cd}_\gamma \text{Se}_{1-x} \text{Te}_x \) \([1]\). As can be judged through the study of the table our calculation agrees well with the measured values. In general, we reproduce the experimental values within 2% accuracy.

Fig. 1 shows a 3–D graph for \( E_g(x, y) \). The dots are the experimental data, the mesh is our calculation. Note that all the experimental data are just over the calculate surface. The edges are the four ternary boundaries. As we have noticed, our calculation reproduces well the known bowing of \( E_g \), both in the anion substitution as in the cation case. In the anion substitution the bowing of \( E_g \) is more noticeably than in the cation one. This fact can be inferred from the figure if we take the projection of \( E_g \) on the \( X - Z \) plane. In the same way, we also appreciate the quasi–linear behavior of \( E_g \) in the cation substitution case. We can see this facts from the Table I as well. Notice that, in absolute value, the bowing parameter for the anion substitution is greater than the cation one. Although our empirical bowing parameter is not given by the experiment it can be shown, through the tight–binding equations, that a great empirical bowing parameter, in absolute value, gives
great optical bowing parameter; and the optical bowing parameter is the measured value in the experiment (see Ref. [4] for details in this fact).

We have calculated the electronic structure for the Zn_{9.9}Cd_{1.1}S_{0.7}Se_{9.3} quaternary alloy, as well. The particular interest for this quaternary alloy is the experimental report of Ichino et al. [3] These authors propose the alloy as an active layer in laser diode operating in the blue–green to ultraviolet spectral region. Fig. 2 shows our calculated electronic structure. This electronic structure is representative of a semiconductor compound with direct band gap. From the figure we appreciate that the lowest conduction band shows lesser dispersion than the calculated one, using the empirical pseudopotential method (EPM), by Feng et al. [9]. However, the general pattern obtained for the valence band is the expected one from tight–binding calculations. The calculated band gap 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], and better than the value of 2.648 eV calculated by Feng et al. [9] using the EPM.

It is noteworthy that: This work is based on a correct description for the ternary systems. We believe that this fact gives an important support to our method in general and to the potential use of this Hamiltonians in further calculations for surfaces, interfaces, quantum wells and superlattices of II–VI compound systems [10].

In conclusion, we have calculated the changes in the band gap value of the Zn_{1−y}Cd_{y}Se_{1−x}Te_{x} and Zn_{9.9}Cd_{1.1}S_{0.7}Se_{9.3} quaternary alloys within a tight–binding description. For the pure binary compounds, we have used the tight–binding parameters which describe well the known band structures. To describe the alloys, we have used the virtual crystal approximation reformulated according to reproduce the observed nonlinear behavior of the band gap with the composition. We have introduced an empirical bowing parameter in the tight–binding parameters of the “s” atomic orbitals which are known to be responsible for the correct energy position of the conduction band in the Γ–point. Our results agree well with experimental results. Our Hamiltonians can be used as a basis for other calculations that include this kind of pseudobinary compounds.
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TABLES

TABLE I. Empirical bowing parameters obtained using the eq. (6) and the tight–binding parameters given in the Refs. [5,11]

| Compound                | $b_a$   | $b_c$ |
|-------------------------|---------|-------|
| 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$_x$Se      | -       | 0.037 |
| Zn$_{1-x}$Cd$_x$Te      | -       | 0.020 |
| Zn$_{1-x}$Cd$_x$Se      | -       | 1.349 |

TABLE II. Measured values for the band gap given in Ref. [1] for the Zn$_{1-y}$Cd$_y$Se$_{1-x}$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
FIGURES

FIG. 1. 3–D representation for the calculated band gap of the Zn$_{1-y}$Cd$_y$Se$_{1-x}$Te$_x$ quaternary alloy, as 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].

FIG. 2. Electronic structure for the Zn$_{0.9}$Cd$_{1.07}$S$_{0.93}$ quaternary alloy calculated using our tight–binding parametrization.