ELECTRONIC BAND STRUCTURE OF THE ORDERED $Zn_{0.5}Cd_{0.5}Se$ ALLOY CALCULATED BY THE SEMI-EMPIRICAL TIGHT-BINDING METHOD CONSIDERING SECOND-NEAREST NEIGHBOR

ESTRUCTURA ELECTRÓNICA DE BANDAS DE LA ALEACIÓN ORDENADA DE $Zn_{0.5}Cd_{0.5}Se$ CALCULADA POR EL MÉTODO SEMI-EMPÍRICO DE ENLACE FUERTE TENIENDO EN CUENTA INTERACCIÓN A SEGUNDOS VECINOS

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Abstract

Usually, semiconductor ternary alloys are studied via a pseudo-binary approach in which the semiconductor is described like a crystalline array were the cation/anion sub-lattice consist of a random distribution of the cationic/anionic atoms. However, in the case of reported III-V and II-VI artificial structures, in which an ordering of either the cations or the anions of the respective fcc sub-lattice is involved, a pseudo-binary approach can no longer be employed, an atomistic point of view, which takes into account the local structure, must be used to study the electronic and optical properties of these artificial semiconductor alloys. In particular, the ordered $Zn_{0.5}Cd_{0.5}Se$ alloy has to be described as a crystal with the simple-tetragonal Bravais lattice with a composition equal to the zincblende random ternary alloy. The change of symmetry properties of the tetragonal alloy, in relation to the cubic alloy, results mainly in two effects: i) reduction of the banned gap, and ii) crystal field cleavage of the valence band maximum. In this work, the electronic band structure of the ordered $Zn_{0.5}Cd_{0.5}Se$ alloy is calculated using a second nearest neighbor semi-empirical tight binding method. Also, it is compared with the electronic band structure obtained by FP-LAPW (full-potential linearized augmented-plane wave) method.

Key words: band gap narrowing; electronic band structure; ordered alloys; Semi-empirical thigh binding method; ZnCdSe alloy.

Resumen

Aunque la descripción de las aleaciones ternarias semiconductoras se hace tradicionalmente asumiendo la aproximación de compuesto pseudo-binario. Para el caso de aleaciones artificiales de compuestos II-VI y III-V, en las cuales se ha reportado un ordenamiento inducido por el crecimiento, una aproximación de este tipo no es aplicable, de modo que, con el fin de hacer una descripción adecuada de las propiedades ópticas y electrónicas de dichas aleaciones artificiales, se debe asumir una descripción atomística que tenga en cuenta la estructura local. En particular, para la aleación ordenada de $Zn_{0.5}Cd_{0.5}Se$, el cambio de simetría implica que se debe usar una estructura tetragonal simple, dando lugar, principalmente, a dos efectos: i) disminución de la brecha prohibida del material y ii) un desdoblamiento en el máximo de la banda de valencia. En este trabajo se calcula la estructura de bandas de la aleación ordenada de $Zn_{0.5}Cd_{0.5}Se$ usando la aproximación semi-empírica de enlace fuerte teniendo en cuenta interacción a segundos vecinos y se compara con la estructura de bandas obtenida por el método FP-LAPW (full-potential linearized augmented-plane wave). Se obtiene una buena concordancia de las principales características entre las estructuras de bandas calculadas por el método *semi-empírico* y el método *ab initio*.
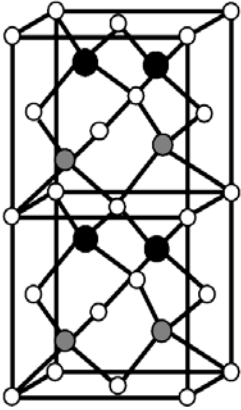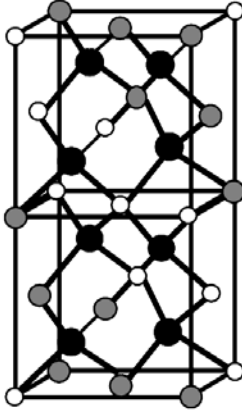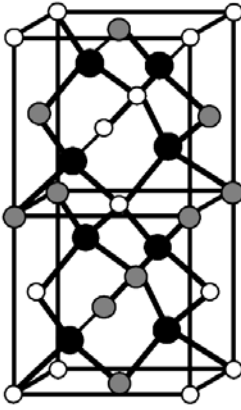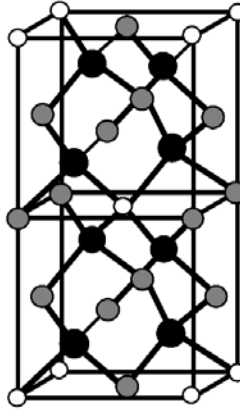
Palabras clave: aleaciones ordenadas; aleaciones de ZnCdSe; Disminución de la brecha de energía; Estructura electrónica de bandas; Modelo de enlace fuerte.

INTRODUCTION

From the traditional point of view, when two zincblende binary compounds AC and BC are mixed homogeneously obtaining a random ternary alloy $A_{1-x}B_xC$, the ternary II-VI and III-V semiconductors alloys are treated as pseudo-binary compounds (Bernard and Zunger, 1987), in which, traveling along the [001] direction, a sequence of cation-anion planes can be found. The A and B cations, in a pseudo-binary alloy, are randomly distributed in each cation plane. In particular, for the II-VI pseudo-binary zincblende $Zn_{0.5}Cd_{0.5}Se$ alloy, the Se layers are alternating with $Zn_{0.5}Cd_{0.5}$ layers with a random distribution in average of the same amount of Cd and Zn atoms. However, ordering of isovalent $A_{0.5}B_{0.5}C$ semiconductors alloys has been widely observed and studied (Kuan *et al.*, 1985; Su *et al.*, 1994; Lu *et al.*, 1987; Wei and Zunger, 1991). That is how, at least four ordered structures related to the zincblende structure have been found to date (see Table 1): CuPt (Gomyo *et al.*, 1987), CuAu (Mowgray *et al.*, 1992), femetinite (Wang, 1989), and chalcopyrite (Jen *et al.*, 1986).

In particular, in the CuAu ordered structure, a sequence of A-C-B-C-A-C-… planes along the [001] azimuth is found. Sometimes, this structure is described as an $(AC)_1(BC)_1$ superlattice. However, it is not a true superlattice. It is a crystal with the simple tetragonal Bravais lattice and the same $A_{0.5}B_{0.5}C$ composition of a zincblende random ternary alloy. Due to changes in symmetry, local ordering, and, in particular, to the change from zincblende unit cell -with space group T_d^2 - to simple tetragonal primitive cell -with space group D_{2d}^5 - predicted and observed changes in material properties such as band gap reduction, valence band splitting, polarization dependence of optical transitions, vibrational spectrum, and others may be expected (Salcedo-Reyes and Hernández-Calderón, 2005). In the case of a pseudo-binary alloy most of the optical, structural and electronic properties are correctly described by the virtual crystal approximation (VCA). However, it is evident that in the case of an ordered alloy, with x=0.5, the VCA approach can no longer be employed to explain the physical properties and a more suitable crystalline structure must be considered.

TABLE 1. Different ordered structures related to the zincblende structure, that have been found to date. The related compounds, the growth method (MOCVD, Metal-Organic Chemical Vapor Deposition, MBE, Molecular Beam Epitaxy, and/or LPE, Liquid Phase Epitaxy), and a example of the semiconductor allow obtained as shown.

CuAu	CuPt	Chalcopyrite	Femetinite
ABC_2	ABC_2	ABC_2	A_3BC_4
● A ○ C ◐ B	● C ○ A ◐ B	● C ○ A ◐ B	● C ○ B ◐ A
MOCVD-MBE	MOCVD	MOCVD	MBE
$Al_{0.5}Ga_{0.5}As$	$In_{0.5}Ga_{0.5}P$	$Ga_{0.5}As_{0.5}Sb$	$In_{0.5}Ga_{0.5}As$

On the other hand, the Semiempirical Tight-Binding (STB) is one example of the so- called *simplified quantum mechanical methods*, in which a compromise between the computational efficiency and the physical correctness of the approximation is used. The usefulness of these *approximated* methods comes from the balance between theoretical rigor and pragmatism, speed, and accuracy. That is, despite the generality and transferability of the method is limited, the heavy computational effort of first-principles calculations is avoided by replacing difficult integrals, *i.e.* the so called two centers (Coulombic) integrals, by empirical parameters to fit experimental results. In general terms, in the STB method the solution to the time-independent single electron Schrödinger equation is assumed as a linear combination of atomic orbitals centered at each lattice point. The atomic orbitals are assumed to be very small at distances exceeding the lattice constant (this is what is meant by tight-binding), and, therefore, practically all matrix elements are approached by analytical functions of the inter-atomic separation and of the atomic environment. In section 2, the STB method, taking into account all first and second nearest-neighbor interaction, is applied in order to obtain the tight binding parameters (TBP) of the binary compounds ZnSe and CdSe. In section 3, the tetragonal STB Hamiltonian is deduced and, in addition to those second nearest neighbor TBP, the electronic band structure of the ordered ZnCdSe alloy is obtained, and then, in section 4 it is compared with the band structure obtained by FP-LAPW.

TIGHT BINDING METHOD FOR ZINCBLENDE ZnSe AND CdSe BINARY COMPOUNDS

In the STB method the basis of the system is assumed as a lineal combination of quasi-atomic functions centered in each lattice point. That is, the tight binding basis is written as

$$|nb\mathbf{k}\rangle = N^{-1/2} \sum_{i,b} exp(i\mathbf{k} \cdot \mathbf{R}_i)|nb\mathbf{R}_i\rangle, \qquad (1)$$

where the numbers n runs over the atomic orbitals, the N wavevectors $\mathbf{k}$ lie in the first Brillouin zone (FBZ), the site index, b, is either a for anions or c for cations, and the anion/cation positions are $\mathbf{R}_i$. The Schrödinger equation for the Bloch function $|k\lambda\rangle$, written in terms of the tight binding basis, is

$$\sum_{m,b}\left\{\langle nb\mathbf{k}|H|mb'\mathbf{k}\rangle - \varepsilon(k\lambda)\delta_{nm}\delta_{bb'}\langle mb'\mathbf{k}|k\lambda\rangle\right\}= 0 \quad, \quad (2)$$

where λ is the band index. In this work one s and three p orbitals (p_x, p_y, and p_z) are used per every atom, that is a sp^3 basis, and all first and second nearest neighbor interaction is taken into account. As every atom in a zincblende structure is tetrahedrally coordinated, each atom (anion/cation) has four first nearest neighbor of the other specie (cation/anion) to $d = \frac{a\sqrt{3}}{4}$, and twelve second neighbor of the same specie (anion/cation) to $d = \frac{a}{\sqrt{2}}$, where d is the inter-atomic distance. The resulting *8x8* tight binding Hamiltonian matrix is shown in appendix 1, were the site index $b(b')$, is either a for anions and c for cations, and $\alpha = ak_x/4$, $\beta = ak_y/4$, $\gamma = ak_z/4$, $\alpha' = ak_x/2$, $\beta' = ak_y/2$, $\gamma' = ak_z/2$, being a the lattice constant. The E^b_n's are the on-site parameters, the $E^{bb'}_{mnn}$'s are the first-nearest-neighbor parameters, and the $V^{bb'}_{mnn}$'s are the parameters that represent the second-nearest-neighbor interaction. The nineteen tight binding parameters (TBP) to be determined by fitting band structure data have the same sense of those described by Slater-Koster (Slater and Koster, 1954).

In order to calculate the TBP, symmetry properties of the zincblende structure are used. From the irreducible representation (IR) of the wave vector group, $g_0(\mathbf{k})$, at each high symmetry point at the FBZ, dependence of the energy on the TBP can be described by the relation

$$E(\mathbf{k}) = \frac{1}{2}\left\{(\alpha + \beta) \pm \sqrt{(\alpha - \beta)^2 + 4\gamma^2}\right\}, \qquad (3)$$

where the plus sign corresponds to the energy of the conduction band, in each $\mathbf{k}$-value, and the minus sign to the valence band. For the Γ point ($\mathbf{k}$=(0,0,0) and $g_0(\mathbf{k}) = T_d$) two IR can be found: One three-fold degenerate, Γ_4, in which $\alpha = E^c_p + 2V^c_{xx} + V'^c_{xx}$, $\beta = E^a_p + 2V^a_{xx} + V'^a_{xx}$, and $\gamma = E^{ac}_{xx}$, and one one-fold degenerate, Γ_1, in which $\alpha = E^c_s + 3V^c_{ss}$, $\beta = E^a_s + 3V^a_{ss}$, and $\gamma = E^{ac}_{ss}$. For the X point ($\mathbf{k}$=(2π/a,0,0) and $g_0(\mathbf{k}) = D_{2d}$) three IR can be found: One two-fold degenerate, X_5, in which $\alpha = E^c_p - V^c_{xx}$, $\beta = E^a_p - V^a_{xx}$, and $\gamma = E^{ac}_{xy}$, one one-fold degenerate, X_1, with $\alpha = E^c_s - V^c_{ss}$, $\beta = E^a_p - 2V^a_{xx} + V'^a_{xx}$, and $\gamma = E^{ac}_{sp}$, and one one-fold degenerate, X_3, in which $\alpha = E^a_s - V^a_{ss}$, $\beta = E^c_p - 2V^c_{xx} + V'^c_{xx}$, and $\gamma = E^{ac}_{ps}$. For the L point (κ=(π/a, π/a, π/a) and $g_0(\mathbf{k}) = C_{2v}$) the relationships $\alpha = E^a_p - V^a_{xx}$, $\beta = E^c_p - V^c_{xx}$, and $\gamma = \{E^{ac}_{xx} + E^{ac}_{xy}\}/2$ can be found to the two-fold degenerate L_3 IR. Since in this work the spin-orbit interaction is not included, the single group notation of the IR's of Parmenter (1955) is used to label the energy bands at the points and axes of symmetry.

A group of twelve equations and seventeen unknown quantities, then, have to be solved. The parameters E^c_{sp} and E^a_{sp} are used to fit the light hole (*lh*) and heavy hole (*hh*) mass effective of each compound. The energy eigenvalues, obtained from the calculated TBP shown in Table 2, are compared with other –experimental and theoretical– values in Table 3 and the resulting band structures for ZnSe and CdSe are shown in Figure 1.

TABLE 2. TBP (in eV) for ZnSe and CdSe. The E_s represent the on-site parameters, the $E_{nn'}$ parameters represent the first-nearest-neighbor interaction, and the $V_{nn'}$ the second-nearest-neighbor interaction

ZnSe		CdSe	
E^c_s	2.498	E^c_s	3.317
E^a_s	-10.55	E^a_s	-10.40
E^c_p	7.110	E^c_p	7.270
E^a_p	-0.681	E^a_p	-1.016
E^{ac}_{ss}	-6.040	E^{ac}_{ss}	-0.238
E^{ac}_{sxx}	2.427	E^{ac}_{sxx}	0.029
E^{ac}_{sxy}	5.465	E^{ac}_{sxy}	4.659
E^{ac}_{sp}	2.767	E^{ac}_{sp}	0.213
E^{ac}_{sps}	6.637	E^{ac}_{sps}	3.812
V^c_{ss}	-0.668	V^c_{ss}	-0.517
V^a_{ss}	-0.773	V^a_{ss}	-0.366
V^c_{sxx}	1.171	V^c_{sxx}	0.892
V'^c_{xx}	-1.054	V'^c_{xx}	-1.453
V^a_{xx}	1.277	V^a_{xx}	0.999
V'^a_{sxx}	-1.171	V'^a_{sxx}	-0.981
V^c_{sxy}	-1.221	V^c_{sxy}	-3.249
V^a_{sxy}	-1.349	V^a_{sxy}	-0.597

TABLE 3. Comparison of the energy eigenvalues (in eV) of ZnSe at some symmetry points in the FBZ. The references are: GW (PP-LDA) in Zakharov *et al.* (1994), FLAPW (all-electron full-potential linear-augmented-plane-wave) in Contineza *et al.* (1994), PVMB (all-electron mixed-basis approach to the density-functional formalism) in Bernard and Zunger (1987), PP-LDA (ab initio pseudopotential total-energy calculations) in Lee *et al.* (1995), XPS (x-ray photoemission spectroscopy) in Ley *et al.* (1974), and (AR)-PE (Angle-resolved photoemission) in Fleszar *et al.* (2004). X_6, X_7, and L_6 correspond to double group notation.

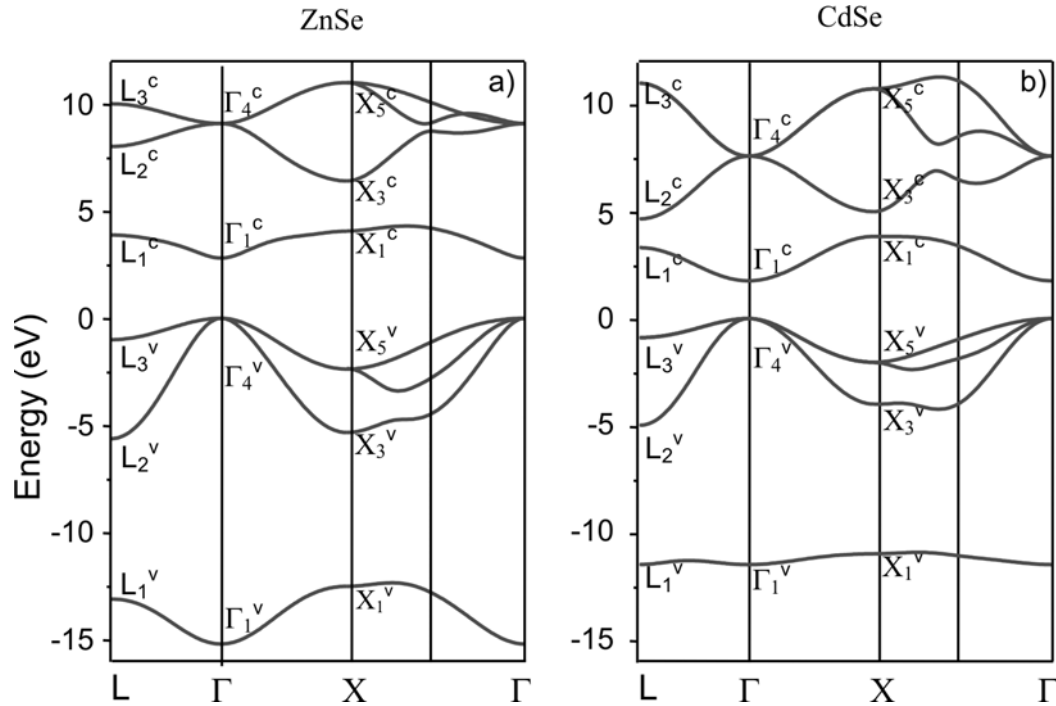|	Therein	GW	FLAPW	PVMB	PP-LDA	XPS	(AR)-PE
G^v_1	-15.2	-13.49	-13.43	-12.86	-12.06	-15.2(6)	-
G^v_4	0.0	0.0	0.0	0.0	0.0	-	-
G^c_1	2.82	2.84	1.10	1.45	2.29	-	-
G^c_4	9.1	7.67	5.69	5.77	6.23	-	-
X^v_1	-12.5	-12.07	-12.33	-11.79	-10.76	-12.5(4)	-
X^v_3	-5.31	-5.03	-4.92	-4.82	-4.28	-5.6(3)	$X^v_6 = -5.10$
X^v_5	-2.35	-2.08	-2.27	-2.20	-1.57	-2.1(3)	$X^v_6 = -2.36$, $X^v_7 = -2.54$
X^c_1	4.07	4.41	2.79	2.88	3.07	-	-
X^c_3	6.43	5.01	3.33	3.47	3.62	-	-
X^c_5	11.0	-	-	-	-	-	-
L^v_1	-13.09	-12.44	-12.61	-12.06	-11.10	-13.1(3)	-
L^v_2	-5.61	-5.23	-5.41	-5.21	-4.44	-5.6(3)	$L^v_6 = -5.55$
L^v_3	-1.0	-0.81	-0.31	-0.87	-0.56	-1.3(3)	-
L^c_1	3.91	4.14	2.38	2.63	3.20	-	-
L^c_2	8.02	-	6.32	-	-	-	-
L^c_3	10.0	8.18	8.43	6.36	-	-	-

FIGURE 1. Second-nearest neighbor Tight Binding band structure for ZnSe (a) and CdSe (b). The simple group notation of Parmenter (1955) is used.

TABLE 4. Comparison of the energy eigenvalues (in eV) of b-CdSe at some symmetry points in the FBZ. The references are: GW (PP-LDA) in Zakharov *et al.* (1994), TB in Pantelides and Harrison (1975), OPW (modified or thogonalized plane wave method) in Kurganski *et al.* (1980), AR-PE (Angle-resolved photoelectron spectroscopy) in Magnusson *et al.* (1998), and Extrap. (sp^3 tight-binding model) in Wang and Duke (1988). X_6, X_7, and L_6 correspond to double group notation.

	Therein	GW	TB	OPW	AR-PE	Extrap.
Γ_1^v	-11.5	-12.71	-11.5	-13.6	-	-11.5
Γ_4^v	0.0	0.0	0.0	0.0	-	
Γ_1^c	1.77	2.01	-	-	-	1.9
Γ_4^c	7.6	7.60	-	-	-	6.25
X_1^v	-11.0	-11.65	-11.0	-13.4	-	
X_3^v	-4.0	-4.22	-3.9	-3.6	$X_6^v = -4.0$	-5.1
X_5^v	-2.05	-1.78	-1.6	-1.6	$X_6^v = -1.95$, $X_7^v = -2.15$	-2.45
X_1^c	3.84	4.37	-	-	-	3.81
X_3^c	5.0	5.20	-	-	-	
X_5^c	10.73	-	-	-	-	
L_1^v	-11.49	-11.91	-11.1	-13.5	-	
L_2^v	-4.99	-4.42	-3.7	-3.6	$L_6^v = -5.55$	
L_3^v	-0.9	-0.71	-0.8	-0.8	-	-1.20
L_1^c	3.31	3.87	-	-	-	3.36
L_2^c	4.64	-	-	-	-	
L_3^c	11.0	8.04	-	-	-	

TIGHT BINDING METHOD FOR THE ORDERED $Zn_{0.5}Cd_{0.5}Se$

In order to calculate the electronic band structure of the tetragonal $Zn_{0.5}Cd_{0.5}Se$ alloy, their crystal structure has to be taken into account. In this case each cation (Cd, for example) has four anions (Se) first-nearest neighbors, to , and eight cations of the same specie (Cd) and four cations of the other specie (Zn) as second-nearest neighbors, to , as is shown in Figure. 2.
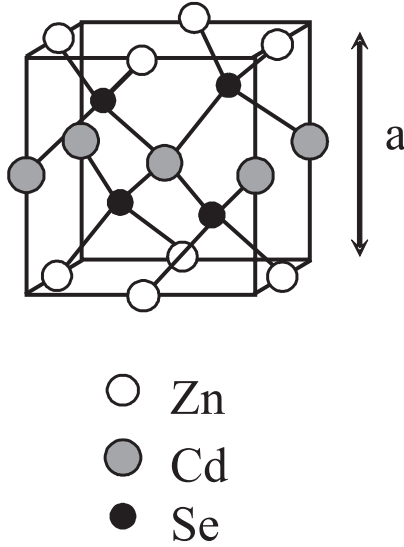

○ Zn
◉ Cd
● Se

FIGURE 2. Crystal structure (not the unit cell) used to calculate the electronic band structure of the tetragonal $Zn_{0.5}Cd_{0.5}Se$ alloy.

It is very important to note that the Hamiltonian matrix has to be invariant under the chosen origin. That is, it has the same form when the origin coincides with one cation or when it coincides with one anion.

In this work, the ZnSe and CdSe first and second nearest neighbor TBP's are used to *simulate* the parameters of the ordered alloy. The *16x16* ordered STB-Hamiltonian matrix, in the sp^3 basis, is

$$H = \begin{pmatrix} h_{Zn-Zn} & h_{Zn-Se} & h_{Zn-Cd} & h_{Zn-Se} \\ h_{Zn-Se}^* & h_{Se-Se} & h_{Cd-Se} & h_{Se-Se} \\ h_{Zn-Cd}^* & h_{Cd-Se}^* & h_{Cd-Cd} & h_{Cd-Se} \\ h_{Zn-Se}^* & h_{Se-Se}^* & h_{Cd-Se}^* & h_{Se-Se} \end{pmatrix}. \qquad (5)$$

The matrixes on the diagonal are

$$h_{Zn-Zn} = \begin{pmatrix} E_s^c(ZnSe)+V_{ss}^c(ZnSe)g_1 & V_{sp}^c(ZnSe)g_2 & V_{sp}^c(ZnSe)g_3 & 0 \\ V_{sp}^c(ZnSe)g_2^* & E_p^c(ZnSe)+V_{xx}^c(ZnSe)g_1 & V_{xy}^c(ZnSe)g_4 & 0 \\ V_{sp}^c(ZnSe)g_3^* & V_{xy}^c(ZnSe)g_4^* & E_p^c(ZnSe)+V_{xx}^c(ZnSe)g_1 & 0 \\ 0 & 0 & 0 & E_p^c(ZnSe)+V_{xx}^c(ZnSe) \end{pmatrix}$$

$$h_{Cd-Cd} = \begin{pmatrix} E_s^c(CdSe)+V_{ss}^c(CdSe)g_1 & V_{sp}^c(CdSe)g_2 & V_{sp}^c(CdSe)g_3 & 0 \\ V_{sp}^c(CdSe)g_2^* & E_p^c(CdSe)+V_{xx}^c(CdSe)g_1 & V_{xy}^c(CdSe)g_4 & 0 \\ V_{sp}^c(CdSe)g_3^* & V_{xy}^c(CdSe)g_4^* & E_p^c(CdSe)+V_{xx}^c(CdSe)g_1 & 0 \\ 0 & 0 & 0 & E_p^c(CdSe)+V_{xx}^c(CdS) \end{pmatrix}$$

and

$$h_{Se-Se} = \begin{pmatrix} E_s^a(ZnCd)+V_{ss}^a(ZnCd)g_1 & V_{sp}^a(ZnCd)g_2 & V_{sp}^a(ZnCd)g_3 & 0 \\ V_{sp}^a(ZnCd)g_2^* & E_p^a(ZnCd)+V_{xx}^a(ZnCd)g_1 & V_{xy}^a(ZnCd)g_4 & 0 \\ V_{sp}^a(ZnCd)g_3^* & V_{xy}^a(ZnCd)g_4^* & E_p^a(ZnCd)+V_{xx}^a(ZnCd)g_1 & 0 \\ 0 & 0 & 0 & E_p^a(ZnCd)+V_{xx}^a(\end{pmatrix}$$

The functions g_1, g_2, g_3, and g_4 are given by

$$g_1 = \cos\alpha'\cos\beta',$$

$$g_2 = i\sin\alpha'\cos\beta',$$

$$g_3 = i\cos\alpha'\sin\beta',$$

and

$$g_4 = \sin a'\sin b'.$$

The off-diagonal matrixes are

$$h_{Cd-Se} = \begin{pmatrix} E_{ss}^{ac}(CdSe)g_{51} & E_{sp}^{ac}(CdSe)g_6 & E_{sp}^{ac}(CdSe)g_6 & E_{sp}^{ac}(CdSe)g_6 \\ E_{sp}^{ac}(CdSe)g_6^* & E_{xx}^{ac}(CdSe)g_5 & E_{xy}^{ac}(CdSe)g_5 & E_{xy}^{ac}(CdSe)g_6 \\ E_{sp}^{ac}(CdSe)g_6^* & E_{xy}^{ac}(CdSe)g_5 & E_{xx}^{ac}(CdSe)g_5 & E_{xy}^{ac}(CdSe)g_6 \\ E_{sp}^{ac}(CdSe)g_6^* & E_{xy}^{ac}(CdSe)g_6^* & E_{xy}^{ac}(CdSe)g_6^* & E_{xx}^{ac}(CdSe)g_5 \end{pmatrix},$$

$$h_{Zn-Se} = \begin{pmatrix} E_{ss}^{ac}(ZnSe)g_5 & E_{sp}^{ac}(ZnSe)g_6 & E_{sp}^{ac}(ZnSe)g_6 & E_{sp}^{ac}(ZnSe)g_6 \\ E_{sp}^{ac}(ZnSe)g_6^* & E_{xx}^{ac}(ZnSe)g_5 & E_{xy}^{ac}(ZnSe)g_5 & E_{xy}^{ac}(ZnSe)g_6 \\ E_{sp}^{ac}(ZnSe)g_6^* & E_{xy}^{ac}(ZnSe)g_5^* & E_{xx}^{ac}(ZnSe)g_5 & E_{xy}^{ac}(ZnSe)g_6 \\ E_{sp}^{ac}(ZnSe)g_6^* & E_{xy}^{ac}(ZnSe)g_6^* & E_{xy}^{ac}(ZnSe)g_6^* & E_{xx}^{ac}(ZnSe)g_5 \end{pmatrix},$$

where

$$g_5 = \{\cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\beta\sin\gamma\} + i\{\cos\alpha\cos\beta\sin\gamma - \sin\alpha\sin\beta\sin\gamma\},$$

and

$$g_6 = \{-\sin\alpha\cos\beta\sin\gamma - \cos\alpha\sin\beta\cos\gamma\} + i\{\cos\alpha\sin\beta\cos\gamma - \sin\alpha\cos\beta\cos\gamma\}.$$

Also

$$h_{Zn-Cd} = \begin{pmatrix} V_{ss}^c(ZnCd)g_7 & V_{sp}^c(ZnCd)g_8 & V_{sp}^c(ZnCd)g_9 & V_{sp}^c(ZnCd)g_{10} \\ -V_{sp}^c(ZnCd)g_8 & V_{xx}^c(ZnCd)g_{11}+V_{xx}^{'c}(ZnCd)g_{12} & 0 & V_{xy}^c(ZnCd)g_{13} \\ -V_{sp}^c(ZnCd)g_9 & 0 & V_{xx}^c(ZnCd)g_{12}+V_{xx}^{'c}(ZnCd)g_{11} & V_{xy}^c(ZnCd)g_{14} \\ -V_{sp}^c(ZnCd)g_{10} & V_{xy}^c(ZnCd)g_{13}^* & V_{xy}^c(ZnCd)g_{14}^* & V_{xx}^c(ZnCd)g_7 \end{pmatrix}$$

and

$$h_{Se-Se} = \begin{pmatrix} V_{ss}^a(ZnCd)g_7 & V_{sp}^a(ZnCd)g_8 & V_{sp}^a(ZnCd)g_9 & V_{sp}^a(ZnCd)g_{10} \\ -V_{sp}^a(ZnCd)g_8 & V_{xx}^a(ZnCd)g_{11}+V_{xx}^{'a}(ZnCd)g_{12} & 0 & V_{xy}^a(ZnCd)g_{13} \\ -V_{sp}^a(ZnCd)g_9 & 0 & V_{xx}^a(ZnCd)g_{12}+V_{xx}^{'a}(ZnCd)g_{11} & V_{xy}^a(ZnCd)g_{14} \\ -V_{sp}^a(ZnCd)g_{10} & V_{xy}^a(ZnCd)g_{13}^* & V_{xy}^a(ZnCd)g_{14}^* & V_{xx}^a(ZnCd)g_7 \end{pmatrix}$$

with

$$g_7 = \cos\gamma'\{\cos\alpha' + \cos\beta'\},$$

$$g_8 = i\,\sin\alpha'\cos\gamma',$$

$$g_9 = i\,\sin\beta'\cos\gamma',$$

$$g_{10} = i\,\sin'\{\cos\alpha' + \cos b'\},$$

$$g_{11} = \cos\alpha'\cos\gamma',$$

$$g_{12} = \cos\beta'\cos\gamma',$$

$$g_{13} = \sin\alpha'\sin\gamma',$$

and

$$g_{14} = \sin\beta'\sin\gamma'.$$

In all cases, the ZnCd parameters are the average between the corresponding ZnSe-CdSe parameters, α, β, γ, α', β', γ' are like in the zincblende case, and *a* the lattice constant calculated from the Vegard's law.

RESULTS

Since there is no experimental information on optical transitions of the ordered $Zn_{0.5}Cd_{0.5}Se$ alloy, the band structure obtained by STB is compared to the electronic band structure obtained by the FP-LAPW method (that do not include spin-orbit interaction), as it is implemented in the Wien97 code (Blaha *et al.*, 1997), in the Fig 3, along the [100] direction of the FBZ of the simple tetragonal lattice, and in the Fig. 4, along the [110] direction. It is remarkable the good qualitative agreement between both methods.

SUMMARY

An improved STB calculation of the band structure of the $Zn_{0.5}Cd_{0.5}Se$ ordered alloy, employing a sp^3 basis that takes into account second nearest neighbor interaction, necessary to describe the alloy ordering, was made. A complete description of the electronic band structure of the tetragonal alloy employing both, the STB and FP-LAPW methods, was done obtaining numerical values for crystal field
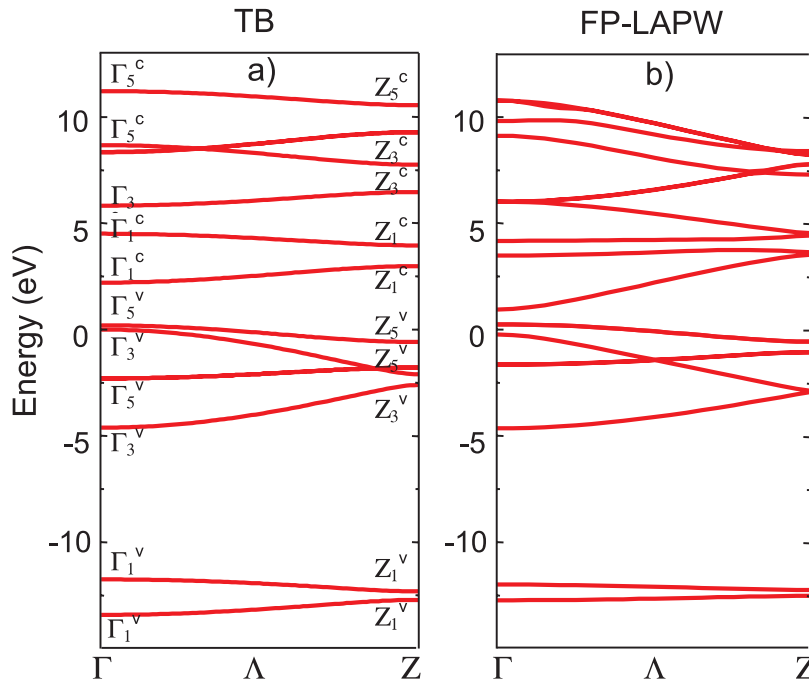

FIGURE 3. Calculated electronic band structure of the $Zn_{0.5}Cd_{0.5}Se$ ordered alloy along the [100] direction (Λ axis). (a) Band structure from an ETB calculation. (b) Band structure from FP-LAPW method.
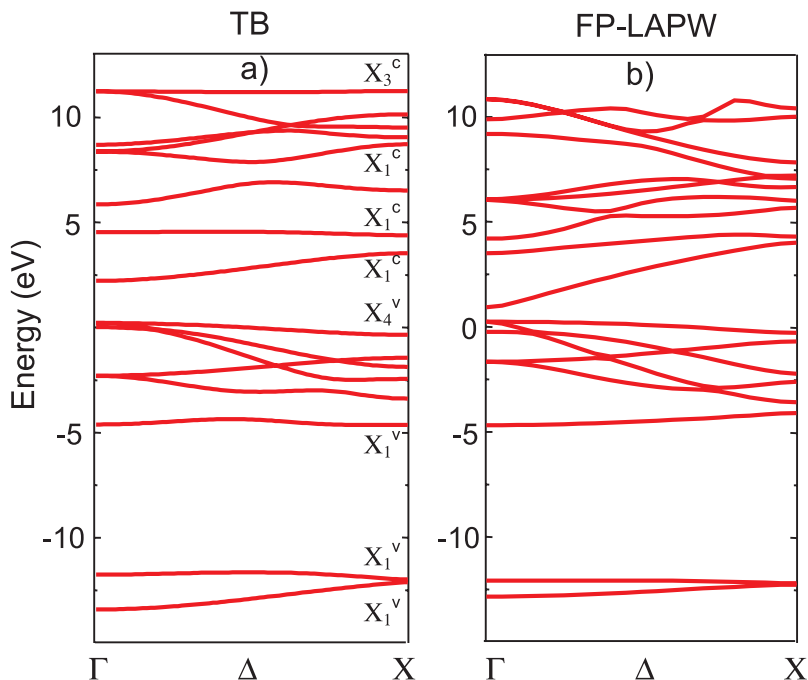
FIGURE 4. Calculated electronic band structure of the $Zn_{0.5}Cd_{0.5}Se$ ordered alloy along the [110] direction (Λ axis). (a) Band structure from an ETB calculation. (b) Band structure from FP-LAPW method.

splitting of the valence band maximum and for the band gap reduction in relation to the band gap of the disordered alloy. A good qualitative agreement is observed between the obtained STB band structure (do not include spin-orbit interaction) and the band structure calculated by FP-LAPW.

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APPENDIX 1

$$\begin{pmatrix}
\langle sa|sa\rangle & \langle sa|xa\rangle & \langle sa|ya\rangle & \langle sa|za\rangle & \vdots & \langle sa|sc\rangle & \langle sa|xc\rangle & \langle sa|yc\rangle & \langle sa|zc\rangle \\
\langle xa|sa\rangle & \langle xa|xa\rangle & \langle xa|ya\rangle & \langle xa|za\rangle & \vdots & \langle xa|sc\rangle & \langle xa|xc\rangle & \langle xa|yc\rangle & \langle xa|zc\rangle \\
\langle ya|sa\rangle & \langle ya|xa\rangle & \langle ya|ya\rangle & \langle ya|za\rangle & \vdots & \langle ya|sc\rangle & \langle ya|xc\rangle & \langle ya|yc\rangle & \langle ya|zc\rangle \\
\langle za|sa\rangle & \langle za|xa\rangle & \langle za|ya\rangle & \langle za|za\rangle & \vdots & \langle za|sc\rangle & \langle za|xc\rangle & \langle za|yc\rangle & \langle za|zc\rangle \\
\hdashline
\langle sc|sa\rangle & \langle sc|xa\rangle & \langle sc|ya\rangle & \langle sc|za\rangle & \vdots & \langle sc|sc\rangle & \langle sc|xc\rangle & \langle sc|yc\rangle & \langle sc|zc\rangle \\
\langle xc|sa\rangle & \langle xc|xa\rangle & \langle xc|ya\rangle & \langle xc|za\rangle & \vdots & \langle xc|sc\rangle & \langle xc|xc\rangle & \langle xc|yc\rangle & \langle xc|zc\rangle \\
\langle yc|sa\rangle & \langle yc|xa\rangle & \langle yc|ya\rangle & \langle yc|za\rangle & \vdots & \langle yc|sc\rangle & \langle yc|xc\rangle & \langle yc|yc\rangle & \langle yc|zc\rangle \\
\langle zc|sa\rangle & \langle zc|xa\rangle & \langle zc|ya\rangle & \langle zc|za\rangle & \vdots & \langle zc|sc\rangle & \langle zc|xc\rangle & \langle zc|yc\rangle & \langle zc|zc\rangle
\end{pmatrix}$$

where:

$$\langle sb|sb\rangle = E_s^b + V_{ss}^{\,b}\{\cos\alpha'\cos\beta' + \cos\alpha'\cos\gamma + \cos\beta'\cos\gamma\}$$

$$\langle sb|xb\rangle = \langle xb|sb\rangle^* = i\,V_{sp}^b\sin\alpha'\{\cos\beta' + \cos\gamma\}$$

$$\langle sb|yb\rangle = \langle yb|sb\rangle^* = i\,V_{sp}^b\sin\beta'\{\cos\alpha' + \cos\gamma\}$$

$$\langle sb|zb\rangle = \langle zb|sb\rangle^* = i\,V_{sp}^b\sin\gamma\{\cos\alpha' + \cos\beta'\}$$

$$\langle xb|xb\rangle = E_p^{\,b} + V_{xx}^b\cos\alpha'\{\cos\beta' + \cos\gamma\} + V'^{\,b}_{xx}\cos\beta'\cos\gamma$$

$$\langle xb|yb\rangle = \langle yb|xb\rangle^* = V_{xy}^b\sin\alpha'\sin\beta'$$

$$\langle xb|zb\rangle = \langle zb|xb\rangle^* = V_{xy}^b\sin\alpha'\sin\gamma$$

$$\langle yb|yb\rangle = E_p^b + V_{xx}^b\cos\beta'\{\cos\alpha' + \cos\gamma\} + V'^{\,b}_{xx}\cos\alpha'\cos\gamma$$

$$\langle yb|zb\rangle = \langle zb|yb\rangle^* = V_{xy}^b\sin\beta'\sin\gamma$$

$$\langle zb|zb\rangle = E_p^b + V_{xx}^b\cos\gamma\{\cos\alpha' + \cos\beta'\} + V'^{\,b}_{xx}\cos\alpha'\cos\beta'$$

$$\langle sb|sb\text{'}\rangle = E_{ss}^{bb'}\{\cos\alpha\cos\beta\cos\gamma - i\sin\alpha\sin\beta\sin\gamma\}$$

$$\langle sb|xb\text{'}\rangle = \langle xb\text{'}|sb\rangle^* = E_{sp}^{bb'}\{-\cos\alpha\sin\beta\sin\gamma + i\sin\alpha\cos\beta\cos\gamma\}$$

$$\langle sb|yb\text{'}\rangle = \langle yb\text{'}|sb\rangle^* = E_{sp}^{bb'}\{-\sin\alpha\cos\beta\sin\gamma + i\cos\alpha\sin\beta\cos\gamma\}$$

$$\langle sb|zb\text{'}\rangle = \langle zb\text{'}|sb\rangle^* = E_{sp}^{bb'}\{-\sin\alpha\sin\beta\cos\gamma + i\cos\alpha\cos\beta\sin\gamma\}$$

$$\langle xb|xb\text{'}\rangle = E_{xx}^{bb'}\{\cos\alpha\cos\beta\cos\gamma - i\sin\alpha\sin\beta\sin\gamma\}$$

$$\langle xb|yb\text{'}\rangle = \langle yb\text{'}|xb\rangle^* = \langle yb|xb\text{'}\rangle = E_{xy}^{bb'}\{-\sin\alpha\sin\beta\cos\gamma + i\cos\alpha\cos\beta\sin\gamma\}$$

$$\langle xb|zb\text{'}\rangle = \langle zb\text{'}|xb\rangle^* = \langle zb|xb\text{'}\rangle = E_{xy}^{bb'}\{-\sin\alpha\cos\beta\sin\gamma + i\cos\alpha\sin\beta\cos\gamma\}$$

$$\langle yb|yb\text{'}\rangle = E_{xx}^{bb'}\{\cos\alpha\cos\beta\cos\gamma - i\sin\alpha\sin\beta\sin\gamma\}$$

$$\langle yb|zb\text{'}\rangle = \langle zb\text{'}|yb\rangle^* = \langle zb|yb\text{'}\rangle = E_{xy}^{bb'}\{-\cos\alpha\sin\beta\sin\gamma + i\sin\alpha\cos\beta\cos\gamma\}$$

$$\langle zb|zb\text{'}\rangle = E_{xx}^{bb'}\{\cos\alpha\cos\beta\cos\gamma - i\sin\alpha\sin\beta\sin\gamma\}$$

$$\langle xb|sb\text{'}\rangle = \langle sb\text{'}|xb\rangle^* = E_{ps}^{bb'}\{-\cos\alpha\sin\beta\sin\gamma + i\sin\alpha\cos\beta\cos\gamma\}$$

$$\langle yb|sb\text{'}\rangle = \langle sb\text{'}|yb\rangle^* = E_{ps}^{bb'}\{-\sin\alpha\cos\beta\sin\gamma + i\cos\alpha\sin\beta\cos\gamma\}.$$