Theoretical Analysis of the Bowing Factors in Electronic and Optical Properties in Cd$_{1-x}$Zn$_x$Te Alloys

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Abstract – *The electronic and optical properties of the ternary II–VI semiconductor alloys Cd$_{1-x}$Zn$_x$Te are calculated by the sp^{3}s* semi-empirical tight-binding theory. We found a nonlinear increase of the bandgap and a nonlinear decrease of the transverse effective charge and refractive index with increasing Zn composition x. For all these behaviours, the corresponding bowing factors are predicted and analysed. The results are compared with previous theoretical estimates and experiments.*

Résumé – *Les propriétés électroniques et optiques des alliages ternaires de la famille des semi-conducteurs II-VI, Cd$_{1-x}$Zn$_x$Te sont déterminées par la théorie des liaisons fortes semi-empirique avec la base des orbitales sp^{3}s*. Nous trouvons un accroissement non-linéaire de l'énergie du gap et un décroissement non-linéaire de la charge effective transversale et l'indice de réfraction avec l'accroissement de la composition x du Zn. Pour tous ces comportements, les facteurs de courbure correspondants sont prédits et analysés. Les résultats sont comparés avec ceux théoriques et expérimentales.*

Keywords: *Tight binding method – Electronic properties – Optical properties – Cd$_{1-x}$Zn$_x$Te alloys.*

1. INTRODUCTION

Ternary compounds of II–VI semiconductors are materials of considerable technological importance since they open the possibility for novel optoelectronic devices in the visible region. There has been particular interest in Cd$_{1-x}$Zn$_x$Te because of their large application in medical imagery, nuclear medicine, solar cells and other devices [1,2]. In order to gain a basic understanding of its properties, much effort has been recently devoted to study its parent elements (CdTe and ZnTe) and to calculating their electronic, structural [3], and thermodynamic properties [4] using first-principles as well as empirical theories [5]. Theoretical predictions such as alloy structural disorder due to the bond relaxation [6], have been confirmed by extended X-ray-absorption fine structure (EXAFS) measurements of nearest-neighbour distances for Cd$_{1-x}$Zn$_x$Te [7]. In our knowledge, there is no work which study the principle properties of this ternary alloys using tight binding approach.

Because of the importance of the electronic and optical properties in Cd$_{1-x}$Zn$_x$Te, we have intended in this paper to explore the electronic structure, the direct energy gap, the transverse effective charge and the refractive index of this alloyed system. Traditionally, because of simplicity, the virtual crystal approximation (VCA) is preferred for the treatment and study of properties in semiconductor alloys. By the means of this VCA, we are able to show how the physical properties of Cd$_{1-x}$Zn$_x$Te are related to those of its binary constituents CdTe and ZnTe, and how these change with the molar concentration x of Zn.

In this paper, we have used an sp^{3}s* semi-empirical TB method [14] to determine the TB parameters of the binary compounds CdTe and ZnTe. This sp^{3}s* basis is economic, for two essential reasons: (i) the introduction of excited state s* to the sp^3 basis is simpler than augmenting the basis with 5d orbitals in the aim of reproducing the first conduction band; (ii) the model employs only nearest-neighbour matrix elements. A systematic study of the fundamental energy gap, refractive index, polarity and transverse effective charge has been carried out. The calculated results are carefully analysed and compared with other theoretical predictions and experiments.

The paper is organized as follows. In Section 2, we briefly describe the computational method. The results corresponding to the various properties are presented and discussed in Section 3. The concluding remarks are given in Section 4.

2. THEORY

The TB method is a very useful tool to study the electronic structures because first-principle techniques based on the local-density approximation (LDA) usually underestimate the bandgaps of semiconductors [8]. We construct the empirical TB Hamiltonian, following the general form given by Kobayashi [9] :

$$H = \sum_{\vec{R},i} \left(|a,i,\vec{R}\rangle E_{i,a}\langle a,i,\vec{R}| + |c,i,\vec{R}+\vec{d}\rangle E_{i,c}\langle c,i,\vec{R}+\vec{d}| \right) + \sum_{\vec{R},\vec{R'},i,j} \left(|a,i,\vec{R}\rangle V_{i,j}(\vec{R}+\vec{R'}+\vec{d})\langle c,j,\vec{R'}+\vec{d}| \right) \quad (1)$$

where: $\vec{R}$ are the face-centred-cubic lattice positions of the anions, i and j are the basis orbitals s, p$_x$, p$_y$, p$_z$ and s*, a and c are the anion and cation, respectively, and $\vec{d}$ is the position of the cation relative to the anion in the

$\vec{R}$ th cell: $\vec{d}=\left(\dfrac{a_L}{4}\right)(1,1,1)$, with a_L being the lattice constant. The off-diagonal matrix elements V vanish unless $\vec{R}$ and $\vec{R'}+\vec{d}$ refer to nearest-neighbour atoms. We have neglected the spin–orbit interaction. We have used an sp^3s^* basis of five orbitals per atom; the excited s state s^* is introduced to properly locate in the energy the conduction band usually formed by d states in the II–VI zinc-blende semiconductor compounds [10].

To study the ternary semiconductor alloys $Cd_{1-x}Zn_xTe$, we construct the VCA Hamiltonian matrix in which the diagonal elements E_{ib}^{vca} (i = set of orbitals and b = a, c) are linearly interpolated as a function of x:

$$E_{ib}^{vca}=(1-x)E_{ib}^{CdTe}+xE_{ib}^{ZnTe} \tag{2}$$

while the first neighbour matrix elements V_{ij}^{vca} for different orbitals i and j are interpolated assuming that $V_{ij}^{vca}(d_{alloy})^2$ is a constant,

$$d_{alloy}^2V_{ij}^{vca}=(1-x)d_{CdTe}^2V_{ij}^{CdTe}+xd_{ZnTe}^2V_{ij}^{ZnTe} \tag{3}$$

Here, the several bond lengths are expressed according to the Cai and Thorpe formulae [11, 12] as:

$$d_{alloy}=d_{vca}+d_{relax} \tag{4}$$

in which the bond length from VCA (d_{vca}) and the d_{relax} which describes the cation–anion relaxation are given by:

$$d_{vca}=(1-x)d_{CdTe}^0+xd_{ZnTe}^0 \tag{5}$$

$$d_{relax}=x(1-x)(\xi_{CdTe:Zn}-\xi_{ZnTe:Cd})(d_{ZnTe}-d_{CdTe}) \tag{6}$$

and

$$d_{CdTe}(x)=d_{vca}-x\xi_{CdTe:Zn}(d_{CdTe}^0-d_{ZnTe}^0) \tag{7}$$

$$d_{ZnTe}(x)=d_{vca}-(1-x)\xi_{ZnTe:Cd}(d_{CdTe}^0-d_{ZnTe}^0) \tag{8}$$

where ξ are the dimensionless relaxation parameters, and d_{CdTe}^0 and d_{ZnTe}^0 are unrelaxed bond lengths of the pure semiconductors CdTe and ZnTe, respectively. The bond polarity of the compound can be obtained by:

$$\alpha_p=\dfrac{V_3}{(V_2^2+V_3^2)^{1/2}} \tag{9}$$

where V_2 is the hybrid covalent energy, which can be approximated in the following way:

$$V_2=-\eta_\sigma\dfrac{\hbar^2}{md_{alloy}^2} \tag{10}$$

and V_3 is the hybrid polar energy, which can be approximated in the following way:

$$V_3=\dfrac{1}{2}(E_{hc}^{alloy}-E_{ha}^{alloy}) \tag{11}$$

where E_{hb}^{alloy} ($b=a,c$) are the average values of the anion and cation hybrid energies of the compound. They are expressed in terms of on-site tight binding parameters respectively:

$$E_{hb}^{alloy}=\dfrac{1}{4}(E_{sb}^{alloy}+3E_{pb}^{alloy}) \tag{12}$$

The transverse effective charge can be expressed as :

$$e_T^*=4\alpha_p-\Delta Z+4\gamma\alpha_p(1-\alpha_p^2) \tag{13}$$

where $\Delta Z=2$ for II–VI compounds.

3. RESULTS

The energy bands of CdTe and ZnTe were obtained by fitting the TB eigenvalues to various energy values at Γ, X and L points of the Brillouin zone (BZ). Our adjusted TB parameters of CdTe and ZnTe are published elsewere [12]. However, we are able to accurately reproduce the electronic structures with a weaker number of parameters which allows easier calculation. The principle energies calculated at these high symmetry points in the band structures are tabulated in Table 1. The resulting band structures of CdTe and ZnTe are plotted in Figure 1. They give a coherent description with the pseudopotential calculation [9] and experimental data [13,14].

By employing the VCA with the relaxation effect described in Section 2, the bandgap versus Zn composition x of the $Cd_{1-x}Zn_xTe$ is calculated and given in Fig. 2. Our estimated values of ξ used in the calculation are 0.7012 and 0.6873 for CdTe and ZnTe, respectively.

Table 1: Comparison of the calculated energies at symmetry points Γ, X and L (in eV) with the empirical pseudopotential (EPM) and experimental results of CdTe and ZnTe

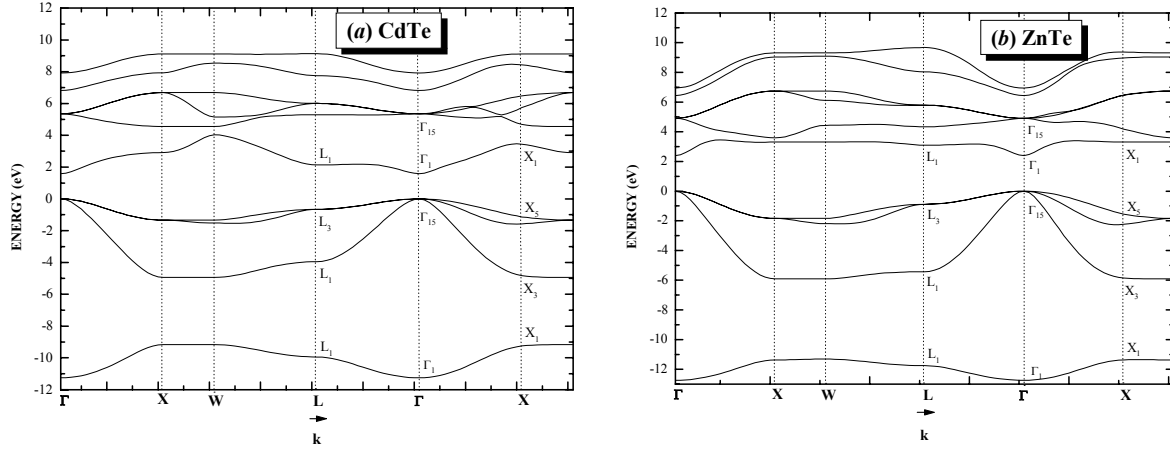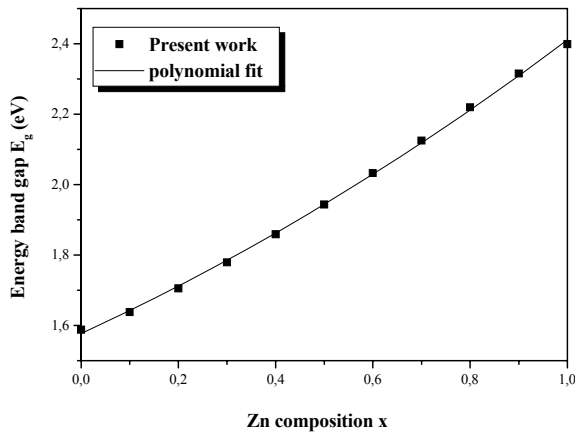| Symmetry point	CdTe		ZnTe	
	Present	EPM. [9]	Present	Expt. [13,14]
Γ_{1v}	-11.256	-11.07	-12.737	-12.6
Γ_{1c}	1.588	1.59	2.398	2.39
Γ_{15c}	5.349	5.36	4.902	-
X_{1c}	2.912	3.48	3.303	3.3
L_{1c}	2.134	2.47	3.095	3.1

Fig. 1: band structure of (*a*) CdTe and (*b*) ZnTe.

The curve exhibits a sublinearity yielding to the following quadratic form :

$$Eg\,(x) = 1.588 + 0.633x + 0.200x^2 \tag{14}$$

Fig. 2: Calculated direct band gap versus composition *x* for Cd$_{1-x}$Zn$_x$Te .
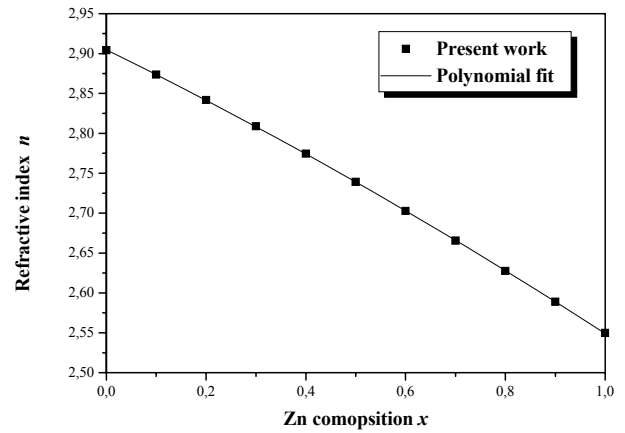
Fig. 3: Calculated refractive index versus composition *x* for Cd$_{1-x}$Zn$_x$Te .

The determination of the optical properties Cd$_{1-x}$Zn$_x$Te, whose energy gap is direct, regardless of alloy composition, is therefore an asset for the design and operation of devices based on this compound. A detailed description of the refractive index n   Cd$_{1-x}$Zn$_x$Te would be a useful complement to the determination of it pseudodielectric function. We have used the Hervé and Vandamme model [15] to calculate the variation of n with alloy composition. The results are displayed in Fig. 3. Our best fit of the curve yields :

$$n(x) = 2.90 - 0.307x - 0.049x^2 \tag{15}$$

As far as we know, many works have studied the polarities of CdTe and ZnTe, however all of these results are appreciably different. So the determination of polarity will be very important for the transverse effective charge. We have compared our results with the theoretical and experimental data [12]. It can be seen from Table 2 that our result polarity is qualitatively in good agreement with the experiments.

The results of CdTe, ZnTe and their Cd$_{1-x}$Zn$_x$Te alloys for the bond length *d* and the polarity α_p are shown in Table 2. It is clear that these properties exhibit an approximately linear decrease with increasing Zn composition

x and the decrease found is dominated by the change in polarity from CdTe to ZnTe. We estimate this change is about 7.47 %.

Table 2: Results for the bond length d (in Å), and the polarity α_p

	CdTe	ZnTe	Cd$_{1-x}$Zn$_x$Te	Ref.
d	2.81	2.64	2.81×(1-0.06x)	Present work
α_p	0.549	0.508	0.549×(1-0.0747x)	Present work
	0.77	0.73	0.77×(1-0.0519x)	XHTB
	0.82	0.77	0.82×(1-0.0609x)	Phillips
	0.58	0.57	0.58×(1-0.0172x)	Experiment

If we know that any property of the ternary alloys can be expressed in terms of the properties of the pure compounds, we can deduce the corresponding bowing factor of the Cd$_{1-x}$Zn$_x$Te alloys by fitting to the following expression:

$$P_{Cd_{1-x}Zn_xTe}(x)=(1-x)P_{CdTe}+xP_{ZnTe}-b_p x(1-x) \tag{16}$$

where b_p denotes the 'bowing' in the quantity P.

In Table 3, we summarize our results of the direct energy gap, refractive index and transverse effective charge for Cd$_{1-x}$Zn$_x$Te and its constituents CdTe and ZnTe. We can see that the calculated values of $e_T{}^*$ of the end point compounds agree well with the experimental results. Indeed, the deviations are about 0.718 % for the CdTe and 8.15 % for the ZnTe, while for the BOM results, they are about –37.9 % and –40.5 % for CdTe and ZnTe, respectively.

The study of the properties given in Table 2 with respect to the composition x yields to a sublinearity of their behaviours. The several corresponding bowing factors are predicted and given in the same table. this is clearly seen when we compare the obtained results with the experimental data and with the Bond-Orbital-Model values (BOM) [12].

Table 3: Calculated, theoretical and experimental values for the band gap
Eg (in eV), refractive index and transverse effective charge.

	CdTe	ZnTe	Cd$_{1-x}$Zn$_x$Te	Ref.
	P	P	b_p	
Eg	1.588	2.398	0.2	Present work
	0.82	1.22	0.02	Ab-initio PP
	1.59	2.39	0.25 (at 300 K)	Experiment
n	2.9	2.55	-0.049	Present work
	2.7		-	Experiment
$e_T{}^*$	2.367	2.163	-0.019	Present work
	1.46	1.19	-	BOM
	2.35	2.00	-	Experiment

4. CONCLUSION

Using a simple semi-empirical tight-binding method, which incorporates the lattice relaxation effect coupled with the bond orbital model, we have able to calculating the elastic properties of the ternary II–VI semiconductor alloys Cd$_{1-x}$Zn$_x$Te. The obtained results were found that these properties have a sublinearity of their behaviour as a function of the Zn composition x yielding to the prediction of several bowing factors. Comparing with previous theoretical estimates and experiments, we found that the polarity is in good agreement with the experiment. Also we have obtained an improvement in results for the elastic properties.

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