ABSTRACT

We set an analytical expression for the gap as a function of hydrostatic deformation, $E_g(\epsilon)$, by diagonalizing in $\Gamma$ the corresponding Empirical Tight-binding Hamiltonian (ETBH). In our ETBH we use the well known $d^2$ Harrison Scaling Law (HSL) to adjust the TB parameters (TBP) to the changes in interatomic distances. We do not consider cation-anion charge transfer.

We calculate $E_g(\epsilon)$ for wide band gap II-VI semiconductors with zincblende crystal structure for deformations under pressure up to -5%. Our results are in quite good agreement with experiment for the compounds of lower ionicity but deviate as the ionicity of the compound increases. This is due to the neglect of charge transfer which should be included self-consistently as done, for example, by Bertho et al. starting from an Empirical Tight-binding description of the bands similar as the one presented here. They sometimes get nevertheless a negative second derivative of $E_g(\epsilon)$ with respect to $\epsilon$ which is never gotten in the experiments. Within our approximation we always find a positive sign independently of the material. It seems that the procedure in which self consistency is achieved is the source of this wrong sign. Furthermore, the inclusion of deviations from HSL appear to be unimportant to this problem.
1 Introduction

As it is very well known, II-VI semiconductors are formed from one element in the IIIb row of the Periodic Table (Zn, Cd, Hg) and another from the VIA one (O, S, Se, Te). The compounds with Hg are narrow gap semiconductors. ZnTe, ZnSe, ZnS and CdTe are wide gap and grow usually in the zincblende structure. ZnO, CdS and CdSe are wurtzites and CdO has the NaCl crystal structure [1]. Multilayer materials built up from wide and narrow gap semiconductors emit in the visible region of the optical spectrum and are potential candidates for electro-optical applications.

These materials build stress at the interface due to their lattice constant difference [2]. The calculation of deformation potentials as a function of hydrostatic and uniaxial deformation for II-VI semiconducting compounds with zincblende structure [3,4] to describe properly these interfaces is of actual interest. Stress has important effects in the electronic band structure and therefore in the optical properties of these materials which are basically determined by the value and character of the band gap. Its dependence under hydrostatic deformation is the subject of this work.

2 Analysis of previous work

Calculations of the gap $E_g(c)$ as a function of hydrostatic deformation, $c$, have been done in the past using different methods [5]. The agreement with experiment varies broadly from one method to another. Bertho et al. [5] have compared recently different methods for II-VI semiconductors based on Zn. First principle calculations do well at high pressure while semi-empirical methods adjust better to experimental results at low pressure. The self-consistent tight-binding method (SCTBM) of Priester, Allam and Lauoo [6] produces results for the deformation potentials and band offsets that compare quite well with experiment [6,7]. The precision of the method is claimed to be 10 meV.

It is convenient to briefly describe the SCTBM in order to formulate precisely the contribution of this work. The SCTBM [7] starts with an ETF description of the non-stressed compound (NSC). The bandstructure matrix elements (HME) are adjusted to fit experimental results for the NSC. These HME are representative of the interactions taking place between ions at the equilibrium positions of the lattice. Hydrostatic pressure changes the distance between them and therefore their mutual interaction. This modifies the HME.

For the non-diagonal HME, this is taken into account in this method through the following formula:

$$V_{ac}(d) = \left( \frac{d}{\eta} \right) V_{ac}(\infty).$$

where $V_{ac}(d)$ represents the interaction between atomic orbitals $\alpha$ centered at the anion site and $\gamma$ at the cation site as a function of their mutual distance $d$, $d_0$ is the corresponding distance for the NSC. Provenz and Harrison [8] have obtained $\eta = 2$, the known $\eta^2$ Harrison Scaling Law (HSL). Priester et al. [9] have proposed different values for $\eta$ depending on the orbitals involved and of the type of compound (III-V or II-VI).

These can differ quite substantially from $\eta = 2$:

For III-V:

$$n_{ppt} = 3.76, \quad n_{ppt} = 1.98, \quad n_{ppt} = 2.16.$$  

For II-VI:

$$n_{ppt} = 3.0, \quad n_{ppt} = n_{ppt} = 1.78.$$  

These values were obtained from the best fit to experimental data within a family of compounds.

For the diagonal HME the energy levels for the free atom are shifted by the potential energy due to charge transfer between anions and cations. As stress is introduced, the interatomic distances change and charge transfer occurs further. This changes the value for the potential energy correction and the diagonal elements have to be recalculated. This is done self-consistently until charge converges within 0.001 eV. The model assumes point charges and reproduces the dielectric constant, $\varepsilon_r$ [5,6,7].

The SCTBM leads to quite satisfactory results. Few questions nevertheless remain unanswered. The method introduces both, self-consistency and a different variation of the TBP than HSL. Are these independent? In other words, could one get a reasonable result keeping the HSL and treating the problem self-consistently? Is there a regime where self-consistency is not necessary? And if it exists, does HSL leads to reasonable results?

On the other hand, there is some concern [5] about the sign of the second derivative of $E_g(c)$ with respect to $c$ which differs in different calculations. Is this a regime universal?

In this work, we try to answer to these questions. For this purpose we will use ETBH and will not repeat the self-consistent calculation since we know the result from the work of Bertho et al. [5].

We will also show some general trends of the gap as a function of hydrostatic pressure in terms of properties that reflect the characteristics of the chemical bond in these compounds. We will consider the family of compounds ZnTe, ZnSe, ZnS and CdTe.

3 Our analytic expression for $E_g(c)$

To calculate the electronic band structure we use the ETBH with an orthogonal $s, p, s^*$ atomic basis and keep the interaction up to first nearest neighbors. We take into account the spin-orbit interaction. Our notation follows the work of Kobayashi et al. [10].

ZnTe, ZnSe, ZnS and CdTe are zincblende-direct gap semiconductors. When evaluated in $V$ the TBP takes a block structure and some HME are zero. This makes possible the direct diagonalization of the TBP and to obtain an expression for the gap $E_g$ as a function of some of the TBP. From Kobayashi et al. [10], the conduction and valence band energies at $\Gamma$ are given by:

$$E_c = E_{x\alpha} + E_{\alpha \gamma} + \lambda + \lambda = \left( \frac{E_{\alpha \alpha} - E_{\gamma \gamma}}{2} \right) + V_{\alpha \gamma}$$  

$$E_v = E_{x\gamma} + E_{\gamma \alpha} + \lambda + \lambda = \left( \frac{E_{\alpha \alpha} - E_{\gamma \gamma}}{2} \right) + V_{\alpha \gamma}$$

where $E_{x\alpha}$ and $E_{x\gamma}$ are the anion and cation $s$-band energies at $\Gamma$ and $V_{\alpha \gamma}$ their mutual first nearest neighbors interaction. $E_{x\gamma}$, $E_{\gamma \alpha}$ and $V_{\alpha \gamma}$ are their analog for the $p$-band. $\lambda_c$ and $\lambda_v$ are the spin-orbit shift for the cation and anion respectively.
In $I$, $E_c$ is twofold degenerate and $E_v$ fourfold. Hydrostatic pressure does not split the degenerated states since the cubic symmetry is not broken in this case. This fact allows us to use (3) to calculate $E_g$ as a function of hydrostatic pressure by scaling $V_{\text{un}}$ and $V_{\text{ex}}$ with interatomic distance. This expression can be used to calculate the volume dependence of physical quantities. We will study deformations up to -5% and we will assume that HSL holds.

We take hydrostatic pressure to be $\epsilon = \frac{P}{P}$, where $P$ is the lattice parameter for the uncompressed sample and get:

$$V_{\text{ex}} = \frac{V_{\text{un}}}{(1 + \epsilon)^3}, \quad V_{\text{ex}} = \frac{V_{\text{un}}}{(1 + \epsilon)^3},$$

(4)

which we can substitute in (3) and use:

$$E_g(\epsilon) = E_g(0) - \epsilon - 3\frac{\alpha}{J} \epsilon^2,$$

(5)

to calculate $E_g(\epsilon)$ as a function of the TBP for the compound at equilibrium for deformations not higher than about -5%. The TBP for most of the compounds of interest here are available from the literature [5,10.11].

In previous work, $E_g(\epsilon)$ was always obtained numerically and the result is adjusted to an expression of the type:

$$E_g(\epsilon) = E_g(0) + \alpha \epsilon + \beta \epsilon^2,$$

(6)

and the values for the coefficients $\alpha$ and $\beta$ are compared to the ones obtained from experiment fit to a similar expression. Berlinsky et al. [5] use the question about the sign of $\beta$ in eq. (6), since different methods yield different signs. Experiments give always a non-negative sign for $\beta$. A power series expansion of (5) using (4) gives the following expressions for $\alpha$ and $\beta$:

$$\alpha = -2 \left( \frac{b^2}{(a^2 + b^2)} + \frac{a^2 b}{(a^2 + b^2)} \right),$$

(7)

$$\beta = \frac{a^3 b + 3a b^3}{(a^2 + b^2)^2} + \frac{3a b^4}{(a^2 + b^2)^2},$$

(8)

where $a$, $b$, $c$ and $d$ are given by:

$$a = \frac{E_{\text{un}} - E_{\text{ex}}}{2}, \quad b = V_{\text{ex}},$$

$$c = \frac{E_{\text{un}} - E_{\text{ex}} + \lambda_e - \lambda_v}{2} \quad \text{and} \quad d = V_{\text{ex}}.$$

Equation (8) shows a very interesting result. Within our approximation the sign for $\beta$ is always positive for any zincblende semiconductor independently of the details of the material. From our result the positive sign is therefore universal. This agrees qualitatively with experiment. Nevertheless, the absolute value for $\beta$ from expression (8) in certain cases can be much higher in magnitude than the experimental one. Obviously charge transfer has to be included. We care how that modification whatsoever from HSL could change this sign.

Finally, from the change in energy $\Delta E$, of the band energy $E$, which is proportional to the relative variation of the volume of the unitary cell $\Delta V$:

$$\Delta E = \frac{\partial E}{\partial V} \Delta V,$$

(9)

where $q_0$ is the deformation potential associated with the energy band $E$, we get, to first order in $\epsilon$, using (6):

$$q_0 = \frac{\alpha}{3} \frac{\Delta E}{\Delta V},$$

(10)

4 Application to the II-VI Compounds

In this section we use eq. (5) to calculate for some wide band gap semiconductors with zincblende structure the variation of $E_g$ with deformations ranging from 0% to -5%. From eqs. (7)-(10) we get the values for $q_0$, $\alpha$ and $\beta$, that we show in Table I. For ZnTe, ZnS and ZnSe we use the TBP from reference [5] and for CdTe from [11].

<table>
<thead>
<tr>
<th>Reference</th>
<th>$E_g(\text{eV})$</th>
<th>$q_0(\text{eV})$</th>
<th>$\alpha(\text{eV})$</th>
<th>$\beta(\text{eV})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTe</td>
<td>2.27</td>
<td>-5.30</td>
<td>-16.26</td>
<td>0.0</td>
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<tr>
<td>D. Berlinsky et al.</td>
<td>2.30</td>
<td>-5.43</td>
<td>-16.66</td>
<td>-24</td>
</tr>
<tr>
<td>This work</td>
<td>2.39</td>
<td>-5.46</td>
<td>-16.46</td>
<td>23.91</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.72</td>
<td>-5.96</td>
<td>-20.12</td>
<td>-29.21</td>
</tr>
<tr>
<td>D. Berlinsky et al.</td>
<td>3.78</td>
<td>-5.11</td>
<td>-16.31</td>
<td>30.29</td>
</tr>
<tr>
<td>This work</td>
<td>3.78</td>
<td>-5.11</td>
<td>-16.31</td>
<td>30.29</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.685</td>
<td>-5.43</td>
<td>-17.42</td>
<td>-32</td>
</tr>
<tr>
<td>D. Berlinsky et al.</td>
<td>2.82</td>
<td>-5.71</td>
<td>-15.21</td>
<td>28.61</td>
</tr>
<tr>
<td>This work</td>
<td>2.82</td>
<td>-5.71</td>
<td>-15.21</td>
<td>28.61</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.6</td>
<td>-2.71</td>
<td>-2.22</td>
<td>-2.22</td>
</tr>
<tr>
<td>D.J. Gunston et al.</td>
<td>1.6</td>
<td>-2.71</td>
<td>-2.22</td>
<td>-2.22</td>
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<tr>
<td>This work</td>
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<td>-2.71</td>
<td>-2.22</td>
<td>-2.22</td>
</tr>
</tbody>
</table>

Table I: Our calculated values for the gap $E_g$, the deformation potential $q_0$, and the coefficients $\alpha$ and $\beta$.

In Figs 1-4 we present our result for $E_g(\epsilon)$ for ZnTe, ZnS, ZnSe and CdTe respectively, and compare them with the available experimental results (full line) and with the SCETB calculations (dotted line). To make the comparison easier we assume the same value for the gap at zero pressure in all three cases and we put it equal to zero.

Let us first deal with ZnTe. In Table I, we can see that our value for the gap in the NSC coincides with the calculation of Berlinsky et al. [5]. It compares well with experiment [12] whose result is 0.12 eV lower. The absolute value of the deformation potential associated to $E_g$, $q_0$, we get a 0.44 eV lower value than the experiment whereas in [5] they get a value 0.23 eV higher. For the coefficient $\alpha$ in (6) they get a slightly better agreement with experiment than we do. The experimental curve for $E_g(\epsilon)$ has been fitted to a straight line and therefore $\beta=0$. The magnitude of this coefficient in the calculation of
Bertho et al. [5] and in ours differs very little in absolute value but has the opposite sign. We get, as stated before, always a positive sign in agreement with experiment.

Let us examine Fig. 1. We can see that the difference in the sign does not seem to be as important in the overall for the studied range of deformations. If we look in more detail, nevertheless, we see that the results of ref. [5] compared very well with experiment only up to about 3% and then it deviates considerably more than the non self-consistent one. Since our result is the starting point for self-consistency (SC), we see that while for low deformations SC corrects very well the ETB calculation, for higher deformations it enhances the disagreement. If we just change the sign of beta in the SCETB calculation [5], the agreement deteriorates noticeably.

For ZnS there are no experimental results known to us. The same analysis can be done based on Table I. The most important difference is the sign of $\beta$. In Fig. 2, we compare our result to the SCETB one by Bertho et al. [5] (dotted curve). The two curves essentially agree for deformations less than 3.5% but for higher deformations the disagreement begins to be important. Notice again that we get a different curvature (we get always $\beta > 0$).

Next we show in Fig. 3, our results for ZnSe. On the overall, both our results and the one of ref. [5] (dotted curve) are in fair agreement with experiment (full curve) [13]. It is worth noticing that none of them can be said to be in real better agreement with experiment. Notice again the different curvature of the two curves. For deformations higher than 3% our disagreement with the experimental results increases. It is worth noticing here that the overall disagreement of the non SC result with SCETB one of Bertho et al. [5] is only important for deformations higher than 3.5%.

We can conclude that for the zinc-blende, wide band gap, II-VI semiconductor compounds based on ZnS the inclusion of self-consistency brings on the overall an slightly better agreement with experiment together with a wrong sign for the curvature of $E_g(\beta)$.

Fig. 1 shows a very important different result. The non inclusion of SC for CdTe gives a result where the disagreement with experiment [14] is important even for low deformations and the SCETB calculation gives a good agreement with experiment. But again, the curvature of $E_g(\beta)$ is wrong.

At this point one can answer some of the questions we raised before. First, the deviations from HSL are unimportant to the problem. We have reduced the calculation using (2) and found no essential difference in our results. It is probable that HSL together with SC will give essentially the same result. Furthermore, it is clear from our analysis that SC is not always necessary. We will show now that the disagreement due to the non inclusion of self-consistency aligns directly with the ionicity of the material. This is shown in Table II.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ionocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTe</td>
<td>0.609</td>
</tr>
<tr>
<td>ZnS</td>
<td>0.623</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.630</td>
</tr>
<tr>
<td>CdS</td>
<td>0.665</td>
</tr>
<tr>
<td>CdSe</td>
<td>0.769</td>
</tr>
</tbody>
</table>

Table II: Ionocity for II-VI wide band gap semiconductors [15]

In Table II we list the ionocity of the compounds we studied here. The correlation between ionocity and the disagreement from ETB calculations without SC is evident. The more ionic the compound, the bigger the deviation from experiment. We argue that ionocity and charge transfer go along and therefore the result in this shows, indicates that the most important correction to ETB is the inclusion of self-consistency and not the corrections to HSL. The SC correction is important for the more ionic compounds. For compounds of lower ionocity, we get a similar result using the HSL and an ETB as the SCETBM calculation using (2). We even get a clearer result to experiment by not including SC as shown below in the case of ZnTe for the low deformations. In this case SC can be safely neglected and therefore these results show as well that the use of a different scaling law is important to the problem since we do not get any substantial difference using (2) or the HSL, as we stated before. Actually the ETBM together with (2) and neglecting SC, gives very similar result to the one in ref. [5], as we also stated above.

A last point is worth dealing with. SC is a necessary correction. But, since Bertho et al. introduces SC to an ETB calculation essentially identical to ours, the negative sign in $\beta$ that they obtained for all cases dealt with here, is due to the method in which SC is introduced. Experiments give always $\beta > 0$. From our analytic expression we can see that this sign is universal. It is probable that the process of SC is to be refined imposing an extra condition so that $\beta$ is always positive. Such a condition is the subject of a future work.

5 Conclusions

We have considered the variation of the gap, $E_g$, in the zinc-blende, wide band gap, II-VI semiconductor compounds under hydrostatic pressure using the empirical tight-binding method and neglecting charge transfer. We found a parabolic expression for the gap as a function of deformation $e \equiv \Delta 1$ with a quadratic coefficient $\beta$ that is always non-negative independently of the material. The universality of this sign is consistent with experiment. We compare our results with the self-consistent empirical tight-binding calculation of Bertho et al. [5] and with the available experimental results. We find that for compounds of high ionocity it is necessary to include charge transfer while it can be neglected in compounds of low ionocity such as ZnTe. As ionocity gets higher, charge transfer can be only neglected for deformations less than about 3% in absolute value as in the case of ZnSe and ZnTe. For CdTe, a compound of high ionocity charge transfer has to be included. It is worth noticing that Bertho et al. [5] get in all these cases a negative sign for $\beta$ which disagrees with experimental results. Since they include charge transfer by introducing a self-consistent process to an empirical tight-binding calculation similar to the one presented here, the way in which self-consistency is introduced is to be blamed for the apparently wrong sign. This process should be refined.

6 Acknowledgements

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References


FIGURE CAPTIONS

Fig. 1- Experiment (full line), the result of Bertho et al. [5] (dots) and our result for ZnTe are compared. The gap for the un-stressed compound has been set to 0.0 to facilitate the comparison of the description of the effect of deformation ($\Delta E_g$) in the three cases. The curves are calculated from formula (6) using the input parameters of Table 1. Notice how the self-consistent calculation corrects properly at low deformations but deviates more and more from experiment for higher values. Notice also the curvature of the dotted curve.

Fig. 2- Same comparison as before for ZnS. There are no experimental results known to us for this case. The deviations from both descriptions is due mainly to the sign of $\beta$. The dotted curve is the result of Bertho et al. [5].

Fig. 3- Results for ZnSe. The inclusion of self-consistency (dotted curve) present on the overall the same degree of disagreement with experiment (full curve) than our result. For lower deformations our result agrees better with experiment. Again the curvatures are different.

Fig. 4- The CdTe case is actually the only case where the inclusion of self-consistency gives a clearly better agreement with experiment. This is due to the high ionicity of CdTe (See Table II).
Fig. 1

Fig. 2
Fig. 3 ZnSe

Non SC calculation

SC calculation

Experiment

Fig. 4 CdTe

Non SC calculation

SC calc.

Experiment

Deformation (-da/a)\%

Fig. 3

Fig. 4