

# **$X$ -point deformation potentials of III-V semiconductors in a tight-binding approach**

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The hydrostatic  $E_1$  and shear  $E_2$  deformation potentials of the III-V semiconductor compounds are calculated within a nearest-neighbor tight-binding approach. In the  $sp^3s^*$  parametrization, analytical expressions for both  $E_1$  and  $E_2$  are derived. The scaling law of the  $s^*p$  interaction is modified in such a way that it provides deformation potentials at  $X$  in reasonable agreement with available experimental data. This phenomenological term takes into account the physical behavior of the actual excited states under strain and consequently, it allows us to describe accurately the dependence of the band-edge states under (001) biaxial strain.

Nowadays, high-quality strained-layer quantum wells and superlattices (SL's) can be grown from III-V semiconductors having a lattice mismatch of up to 7%.<sup>1-3</sup> In these systems, the constituent slabs are under biaxial tensile or compressive strain, which in addition to the band offset and layer thicknesses, determines their electronic structure. Consequently, any reliable theoretical calculation of the electronic properties of the heterostructure (HS) must rest on a realistic description of the strained bulk semiconductors. As is well known, the effect of strain on semiconductors is commonly described by deformation potentials. Therefore, the Hamiltonians used to model the bulk crystals must provide deformation potentials that agree with the experimental values. Among the theoretical approaches, the empirical tight-binding (ETB) model is particularly suitable to evaluate the HS's electronic properties, when mixing of the  $\Gamma$ - and  $X$ -like bulk states takes place: i.e., GaAs/GaP or InP/GaP short-period strained-layer SL's.<sup>4,5</sup> In this approach, reasonable deformation potentials at the  $\Gamma$  point have been previously obtained for all the III-V compounds.<sup>6-8</sup> The purpose of this paper is to calculate the hydrostatic and shear deformation potentials at the  $X_1$  minimum of the conduction band (CB) for the III-V binary semiconductor series. An ETB model with an  $sp^3s^*$  orbital basis and nearest-neighbor interaction will be used. For simplicity the spin-orbit interaction is neglected, since its inclusion does not alter the results.

In the ETB model the  $sp^3$  orbital basis provides a good description of the valence-band dispersion curves, although the CB is given inaccurately. Nevertheless, with the  $sp^3s^*$  parametrization, the lowest CB near  $X$  is well reproduced.<sup>9</sup> Hence, the deformation potentials at  $X$  are calculated with the  $sp^3s^*$  orbital basis. The excited  $s^*$  state avoids the inclusion of various excited states, i.e.,  $d$  orbitals. It models the average of the  $p$ - $d$  interactions although the precise behavior of the actual excited  $d$  states is not faithfully reproduced. The  $s^*$  orbital energy and the off-diagonal matrix element, which couples  $s^*$  and  $p$  orbital on adjacent sites, are the new ETB parameters as-

sociated with the  $s^*$  state. Biaxial strain produces atomic rearrangements, which change the bond angles and interatomic distances. In the  $sp^3s^*$  ETB model this results in modifications of the angular dependence of the structure factors and of the Hamiltonian parameters. The first effect can be taken into account exactly, while the second is usually approximated by scaling the off-diagonal parameters on the interatomic distance. The diagonal matrix elements, which are functions of the atomic orbital energies, change in a strain field as well. However, the common practice is to keep them fixed, since it is difficult to establish a general law for their strain dependence. The scaling rule of the nondiagonal parameters is of the form  $H_{\alpha\beta}(d) = H_{\alpha\beta}(d_0)(d/d_0)^{n_{\alpha\beta}}$ , where  $d_0/d$  is the unstrained or strained interatomic distance and the exponents  $n_{\alpha\beta}$ , which are adjustable parameters, depend on the pair of orbitals  $(\alpha, \beta)$  involved.<sup>10</sup>

Under the action of a biaxial strain in the (001) plane the  $X_1$  band edge of the III-V semiconductors shifts and splits. The  $X_z$  level splits with respect to the  $X_x$  and  $X_y$  levels and the center of gravity of the  $X_1$  levels moves. The shift and splitting are proportional to the  $E_1$  hydrostatic and  $E_2$  shear deformation potentials at  $X$ . Their magnitudes are given by  $E_1(2\epsilon_x + \epsilon_z)$  and  $E_2(\epsilon_x - \epsilon_z)$ , respectively, where  $\epsilon_i$  ( $i = x, y, z$ ) is the strain component in the  $i$  direction. Now, if the biaxial strain only modifies the off-diagonal terms according to the scaling law referred to above,  $E_1$  and  $E_2$  are given in terms of the matrix elements and the band energies at  $X$ .  $E_1$  can be written as

$$E_1 = 2[V_{sp}^2(E_{s^*} - X_1)n_{sp} + V_{s^*p}^2(E_s - X_1)n_{s^*p}] \times [3(X_1 - X'_1)(X_1 - X''_1)]^{-1}, \quad (1)$$

where the notation is that of Ref. 9, and the  $E_a, V_{\alpha\beta}$  parameters are those of the unstrained crystal. The  $s$  and  $s^*$  orbitals are centered at the anions and the  $p$  orbital at the cations. The energies of the  $X_1, X'_1$ , and  $X''_1$  levels are

the eigenvalues of the matrix

$$\begin{pmatrix} E_{s^*} & 0 & iV_{s^*p} \\ 0 & E_s & iV_{sp} \\ -iV_{s^*p} & -iV_{sp} & E_p \end{pmatrix}. \quad (2)$$

In the derivation of formula (1) the  $s$  symmetry of the excited  $s^*$  state is considered. The calculation of  $E_1$  is performed with the ETB parameters of Refs. 6 and 9 and Harrison's rule,<sup>10,11</sup> i.e.,  $n_{sp}=2$ . Then,  $n_{s^*p}$  is the only parameter which allows us to adjust  $E_1$ . Experimental values of the absolute hydrostatic deformation potential at the  $X$  minimum are scarce. Consequently,  $n_{s^*p}$  is chosen to fit the experimental variation of the indirect band gap,  $\Gamma$ - $X$ , with hydrostatic pressure.  $n_{s^*p}=3.3$  gives the best variation law valid for all the III-V compounds. The calculated deformation potentials  $E_1$  are shown in Table I. The agreement with the experimental data and other theoretical values obtained with more elaborate models is quite reasonable. A better agreement can be attained with an independent fit for each material, but our purpose is to derive a general law.

Similarly, the shear deformation potential  $E_2$  can be written as

$$E_2 = -2[V_{sp}^2(E_{s^*} - X_1) + V_{s^*p}^2(E_s - X_1)] \times [(X_1 - X'_1)(X_1 - X''_1)]^{-1}. \quad (3)$$

We would like to point out that in expression (3) there is no adjustable parameter. The calculated  $E_2$  are given in the first column of Table II. Their absolute values are very different from the experimental ones and they have the opposite sign. The incorrect sign of  $E_2$  has significant consequences on the relative energy position of the split  $X_i$  ( $i=x,y,z$ ) levels. The energies of the  $X_x$  ( $X_y$ ) and  $X_z$  levels are in the wrong order; i.e., under biaxial (001) tensile strain the degenerated  $X_x$  and  $X_y$  valleys must be above the  $X_z$ , while in the calculation they are at a lower energy. The opposite occurs for compressive strain. It is

TABLE I. Calculated and experimental values of the  $E_1$  hydrostatic deformation potential at the  $X$  point, given in eV.

	This work	Theory	Expt.
AlP	1.81	1.97 <sup>a</sup> 2.3 <sup>b</sup>	
AlAs	1.5	1.9 <sup>b</sup>	
AlSb	1.21	1.67 <sup>a</sup> 1.9 <sup>b</sup>	2.2 <sup>c</sup>
InP	1.85		2.2 <sup>c</sup>
InAs	1.59		
InSb	1.56		
GaP	1.93	1.5 <sup>a</sup> 2.3 <sup>b</sup>	1.6 <sup>c</sup>
GaAs	2.0	1.6 <sup>a</sup>	2.0 <sup>c</sup>
GaSb	1.99		

<sup>a</sup>Reference 12.

<sup>b</sup>Reference 13.

<sup>c</sup>Reference 14.

TABLE II. Calculated and experimental values of the  $E_2$  shear deformation potential at the  $X$  point, given in eV.

$E_2$	This work		Theory	Expt.
	$F=0$	$F=-0.63$		
AlP	-1.8	6.75		
AlAs	-1.26	6.11		5.1±0.7 <sup>a</sup>
AlSb	-0.94	6.0		5.4±0.3 <sup>b</sup>
InP	-2.3	3.3		
InAs	-1.92	3.7	4.5 <sup>c</sup>	
InSb	-1.4	4.53		
GaP	-2.03	5.65		6.5±0.5 <sup>b</sup> 6.3±0.9 <sup>b</sup>
GaAs	-1.92	6.0	8.6 <sup>c</sup>	6.5±1 <sup>d</sup>
GaSb	-1.57	6.46		

<sup>a</sup>Reference 15.

<sup>b</sup>Reference 14.

<sup>c</sup>Reference 12.

<sup>d</sup>Reference 16.

inferred from expression (3) that the shear deformation potential  $E_2$  does not depend on the scaling exponent. Then, any scaling rule would yield equal results. The only way to obtain  $E_2$  in agreement with the experimental findings is to alter the strain dependence of either the  $V_{sp}$  or the  $V_{s^*p}$  matrix elements. We propose to modify  $V_{s^*p}$ , since physical grounds justify the addition of an extra term to the usual scaling law of this parameter.

In the  $sp^3d^5$  parametrization the unstrained ETB Hamiltonian at the  $X$  point is an  $18 \times 18$  matrix which has a block structure. The  $X_1$  CB minimum, which has threefold degeneracy  $X_x = X_y = X_z$ , is an eigenvalue of the matrix

$$\begin{pmatrix} E_{d1} & iV_{dd} & 0 & -i2V_{pd\pi}/3 \\ -iV_{dd} & E_{d2} & -iV_{sd} & 0 \\ 0 & iV_{sd} & E_s & iV_{sp} \\ -i2V_{pd\pi}/3 & 0 & -iV_{sp} & E_p \end{pmatrix}, \quad (4)$$

where  $d1$  and  $d2$  stand for  $d$  orbitals with  $e_g$  and  $t_{2g}$  symmetry, respectively. The  $s$  and  $d1$  orbitals are centered at the anion and the  $p$  and  $d2$  at the cation sites. If the  $d$ - $d$  and  $s$ - $d$  interactions are neglected the resulting matrix is equivalent to that obtained for the  $sp^3s^*$  basis [matrix (2)] replacing  $E_{d1}$  by  $E_{s^*}$  and  $-2V_{pd\pi}/3$  by  $V_{s^*p}$ . For unstrained zinc-blende (ZB) crystals, the similarity between both matrices [(2) and (4)] explains why the  $sp^3s^*$  model describes reasonably the dispersion relation of the lowest CB along the [001] directions. Furthermore, we would like to emphasize that although two parameters are needed to describe the  $p$ - $d$  interaction  $V_{pd\pi}$  and  $V_{pd\sigma}$ , due to the ZB symmetry the energy of the  $X_1$  level depends only on one,  $V_{pd\pi}$ . Then, within the  $sp^3s^*$  model, the  $p$ - $d$  interaction at  $X_1$  for ZB crystals can be modeled with the  $V_{s^*p}$  parameter. On the other hand, a shear strain breaks the ZB cubic symmetry. Under biaxial strain in the (001) plane, the matrix elements between the  $d1$  and  $p_x$  or  $p_y$  orbitals are different from that of the  $p_z$  level. Particularly, the  $d1$ - $p$  interaction along the [001] direction has con-

tributions from both the  $V_{pd\pi}$  and  $V_{pd\sigma}$ ,

$$V(3z^2 - r^2, p_z) = -(d_0/d)^{n_{pd}+1} \times [2(1+\epsilon_z)V_{pd\pi}/3 + 2(\epsilon_z - \epsilon_x)V_{pd\sigma}/3\sqrt{3}] . \quad (5)$$

In the derivation of this formula only terms in first order in  $\epsilon_i$  are kept. Then, two parameters  $V_{pd\pi}$  and  $V_{pd\sigma}$  are needed to describe correctly the effect of biaxial strain in the  $d1-p_z$  interaction. Analogous expressions, involving both  $V_{pd\pi}$  and  $V_{pd\sigma}$ , are obtained for the  $d-p$  matrix elements along the [100] and [010] directions. However, in the  $sp^3s^*$  model only one parameter,  $V_{s^*p}$ , gives the  $s^*p$  interaction in the presence of a strain field. Therefore, to take into account the physical behavior of the actual  $d$  states under biaxial strain a new parameter, which models the  $V_{pd\sigma}$  interaction, is needed. We propose to modify the strain dependence of the  $s^*p$  interaction in the following way:

$$V_{s^*p_x}(d) = V_{s^*p_y}(d) = (d_0/d)^{n_{s^*p}+1} V_{s^*p}(d_0) [(1+\epsilon_x) - F(\epsilon_z - \epsilon_x)] , \quad (6)$$

$$V_{s^*p_z}(d) = (d_0/d)^{n_{s^*p}+1} V_{s^*p}(d_0) [(1+\epsilon_z) + 2F(\epsilon_z - \epsilon_x)] ,$$

where  $F$  is the new adjustable parameter and is given by  $F = V_{pd\sigma}/2\sqrt{3}V_{pd\pi}$ . In both expressions the first term arises from the usual scaling law, while the second is the added term, which allows us to describe correctly the strain dependence of the  $d-p$  interaction. Note that it becomes zero when the strain is hydrostatic.

Then, the shear deformation potential  $E_2$  is given by

$$E_2 = -2[V_{sp}^2(E_{s^*} - X_1) + V_{s^*p}^2(E_s - X_1) + F(E_s - X_1)V_{s^*p}^2]/[(X_1 - X_1')(X_1 - X_1'')] . \quad (7)$$

$F = -0.63$  gives the best general law for all the III-V compounds. The calculated  $E_2$  deformation potentials are given in Table II. The agreement with the available experimental data is reasonable. We would like to point out that Harrison's universal values for the TB  $pd\pi$  and  $pd\sigma$  interactions exactly yield  $F = -0.63$ .<sup>10</sup> The physical effect of the  $F$  term is better understood by inspection of Fig. 1, where the lowest CB of GaP under (001) biaxial tension is presented. The bulk dispersion curves are shown along the [100],[010] and [001] directions of the

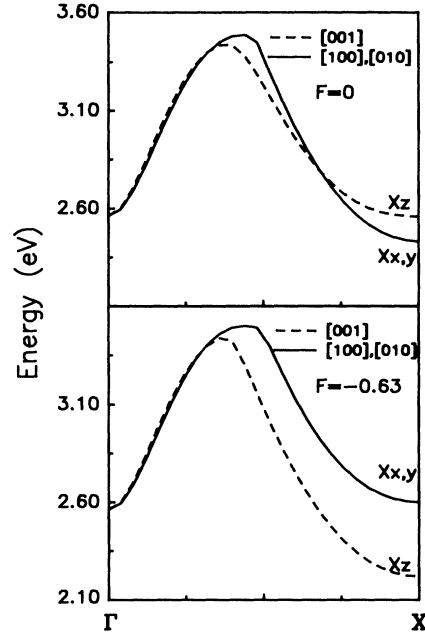


FIG. 1. Dispersion curve of the lowest conduction band of GaP lattice matched to (001) GaAs substrate, along the [001] and [100],[010] directions.

bulk Brillouin zone, and the GaP crystal is considered to be lattice matched to (001) GaAs. For  $F=0$  the CB minimum appears at the  $X_x, X_y$  valleys. However, for  $F = -0.63$  the minimum occurs at the  $X_z$  valley, as is expected for GaP under tensile strain. Thus, the reported modification of the scaling law for the  $s^*p$  interaction provides an accurate description of the  $X$  CB levels for the III-V semiconductors under biaxial and hydrostatic strain. Note that the modification does not alter the prediction of the band-edge deformation potentials at  $\Gamma$ . In summary, within the  $sp^3s^*$  parametrization a general law for the strain dependence of the ETB parameters has been derived. It provides a precise description of the band-edge states under strain for all the III-V semiconductor series. As explained above, this is essential to obtain a reliable picture of the electronic structure of strained heterostructures, not only to attain reasonable energies and localizations of their states, but also for accurate determination of band offsets.

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