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Band Structure of GaAs, GaP, InP and AlSb: the *k.p* Method*

F. H. POLLAK, C. W. HIGGINBOTHAM and M. CARDONA

Physics Department, Brown University
Providence, Rhode Island, U.S.A.

The energy bands of Si, Ge and α-Sn, throughout the entire Brillouin zone, have been obtained by diagonalizing a 15×15 ***k.p*** Hamiltonian referred to basis states at $k=0$. The effects of the spin-orbit interaction have been determined by using only two adjustable parameters. The band structures of several III-V materials have then been calculated by adding 6 independent matrix elements of an antisymmetric potential V^- to the ***k.p*** Hamiltonian of the appropriate group IV element. Spin-orbit splittings are included by using only one additional adjustable parameter.

§ 1. The Basis Hamiltonian

The results of an entire zone ***k.p*** calculation for Si, Ge and α-Sn have been published elsewhere.[1,2] The basis states of the ***k.p*** Hamiltonian correspond to plane-wave states of wave vector (in units of $2\pi/a$) [000], [111] and [200]. These states are labelled Γ_1^l, $\Gamma_{25'}^l$, $\Gamma_{2'}^l$, Γ_{15}, Γ_1^u, $\Gamma_{12'}$, $\Gamma_{25'}^u$ and $\Gamma_{2'}^u$. For matrix elements and energy gaps of the ***k.p*** Hamiltonian we have used, when available, experimental data from cyclotron resonance, optical measurements, etc. The energies of the basis states not available from experimental data can be obtained from O. P. W. calculations or by solving 2×2 pseudopotential matrices. The matrix elements of the momentum not experimentally available have been adjusted until the calculated bands agree with data taken from ultraviolet reflection or electroreflectance experiments. Listed in Table I are the energy eigenvalues and matrix elements of the linear momentum ***p*** between the basis states of the ***k.p*** Hamiltonian used to obtain the orbital energy bands of Si, Ge and α-Sn.

The eigenvectors of the ***k.p*** Hamiltonian have been used to determine the effects of the spin-orbit interaction on the energy bands of the above materials using only two matrix elements of the spin-orbit Hamiltonian $\mathscr{H}_{s0}$:

$$\Delta_{25'}=(3\,i/c^2)<X(\Gamma_{25'}^l)\uparrow|\mathscr{H}_{s0}|Y(\Gamma_{25'}^l)\uparrow> ,$$
$$\Delta_{15}=(3\,i/c^2)<x(\Gamma_{15})\uparrow|\mathscr{H}_{s0}|y(\Gamma_{15})\uparrow> ,$$

where the notation is that of ref. 1). The values of $\Delta_{25'}$ and Δ_{15} listed in Table I were determined from the experimentally observed spin-orbit splitting at $\Gamma_{25'}^l$ (Si and Ge) or Λ_3 (α-Sn) and the degeneracy imposed by symmetry at the X_4 valence band state.

Having thus established a basis Hamiltonian it is possible to calculate the band structure, including the influence of the spin-orbit interaction, of a number of zincblende-type materials.

§ 2. Hamiltonian for Zincblende-Type Materials

It is possible to obtain the crystal potential of a zincblende-type compound from that of the appropriate group IV element by the application of a potential V^-, antisymmetric to the permutation of the two kinds of atoms in the zincblende structure.[3,4] The orbital energy bands of a III-V material can then be calculated by adding 6 independent matrix elements of V^- (see Table II) to the 15×15 ***k.p*** Hamiltonian of the appropriate diamond-type material. The values of these matrix elements are then adjusted until the calculated bands agree with experimental data.

The antisymmetric potential V^- introduces an antisymmetric term, Δ^-, into the spin-orbit Hamiltonian, where

$$\Delta^-=(3\,i/c^2)<X(\Gamma_{25'}^l)\uparrow|\mathscr{H}_{s0}|y(\Gamma_{15})\uparrow> .$$

Spin-orbit effects on the valence bands and lowest conduction bands of these materials can then be determined from the eigenvectors of the above Hamiltonian, the appropriate $\Delta_{25'}$ and Δ_{15}, and by adjusting Δ^- so that the calculated energy bands agree with one of the experimentally observed spin-orbit splittings.[5]

§ 3. Choice of Parameters

For GaAs the Ge ***k.p*** Hamiltonian was used as a basis since they both occur in the same row of the periodic table. Germanium was also

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Table I. Energy eigenvalues (in rydbergs) as measured from the top of the valence band ($\Gamma^l_{25'}$), and matrix elements of the linear momentum $\boldsymbol{p}$ (in atomic units) used in the $\boldsymbol{k.p}$ Hamiltonian for Si, Ge and α-Sn. Also listed are the spin-orbit splitting parameters (in rydbergs) $\Delta_{25'}$ and Δ_{15}.

	Si	Ge	α-Sn
$\Gamma^l_{2'}$	0.265	0.0728	0.0022
Γ_{15}	0.252	0.232	0.232
Γ^u_1	0.520	0.571	0.400
$\Gamma_{12'}$	0.710	0.771	0.494
$\Gamma^u_{25'}$	0.940	1.25	0.726
$\Gamma^u_{2'}$	0.990	1.35	0.765
Γ^l_1	−0.950	−0.966	−0.8455
$2i<\Gamma^l_{25'}\|\boldsymbol{p}\|\Gamma^l_{2'}>$	1.200	1.360	1.120
$2i<\Gamma^l_{25'}\|\boldsymbol{p}\|\Gamma_{15}>$	1.050	1.070	1.002
$2i<\Gamma^l_{25'}\|\boldsymbol{p}\|\Gamma_{12'}>$	0.830	0.8049	0.6411
$2i<\Gamma^l_{25'}\|\boldsymbol{p}\|\Gamma^u_{2'}>$	0.100	0.100	0.0380
$2i<\Gamma^u_{25'}\|\boldsymbol{p}\|\Gamma^l_{2'}>$	−0.090	0.1715	0.5574
$2i<\Gamma^u_{25'}\|\boldsymbol{p}\|\Gamma_{15}>$	−0.807	−0.752	−0.3891
$2i<\Gamma^u_{25'}\|\boldsymbol{p}\|\Gamma_{12'}>$	1.210	1.436	1.272
$2i<\Gamma^u_{25'}\|\boldsymbol{p}\|\Gamma^u_{2'}>$	1.320	1.623	1.079
$2i<\Gamma^u_1\|\boldsymbol{p}\|\Gamma_{15}>$	1.080	1.200	0.952
$2i<\Gamma^l_1\|\boldsymbol{p}\|\Gamma_{15}>$	0.206	0.5323	0.3560
Δ'_{25}	0.0032	0.0213	0.0516
Δ_{15}	0.0036	0.0265	0.0776

Table II. Matrix elements of V^- (in rydbergs) and the spin-orbit splitting parameter Δ^- (in rydbergs) for GaAs, GaP, InP and AlSb.

	GaAs	GaP	InP	AlSb
$V_1^-(<\Gamma_{15}\|V^-\|\Gamma^l_{25'}>)$	0.12652	0.14924	0.13973	0.10650
$V_2^-(<\Gamma^l_{2'}\|V^-\|\Gamma^u_1>)$	−0.24791	−0.26885	−0.22161	−0.06582
$V_3^-(<\Gamma^l_{2'}\|V^-\|\Gamma^l_1>)$	0.38210	0.45687	0.26413	0.14013
$V_4^-(<\Gamma_{15}\|V^-\|\Gamma^u_{25'}>)$	0.12297	0.21044	0.15348	0.12500
$V_5^-(<\Gamma^u_{2'}\|V^-\|\Gamma^u_1>)$	−0.34820	−0.33021	−0.28018	−0.09599
$V_6^-(<\Gamma^u_{2'}\|V^-\|\Gamma^l_1>)$	0.0	0.0	0.0	0.0
Δ^-	0.00507	−0.00485	−0.02922	0.0329

used as a basis for InP because the lattice constants are similar and the energy gaps of InP are close to those of GaAs. The average ***k.p*** parameters of Si and Ge are used for GaP while for AlSb the average parameters of Si and α-Sn are used since the lattice constant and energy gaps of this material are about midway between those of Si and α-Sn.

It is found that the calculated orbital bands are not very sensitive to V_6^-. Since it corresponds to interactions between very distant atomic orbitals (see Table II) we assume $V_6^-=0$. The values of V_1^- and V_4^- listed in Table II are obtained by adjusting the L_3-L_3 and $\Gamma_{15}-\Gamma_{15}$ gaps to agree with reflection[6] or electroreflectance[7] data (in the determinations of V_i^- the spin-orbit splittings have been removed from the experimental data) while V_2^-, V_3^- and V_5^- were obtained by fitting the experimental values of the energy gaps listed below:

GaAs[7]: $\Gamma_{15}-\Gamma_1$, X_5-X_3, $\Lambda_3-\Lambda_1$
GaP[7,8]: $\Gamma_{15}-\Gamma_1$, X_5-X_3, $\Gamma_{15}-\Delta_1$
InP[7] : $\Gamma_{15}-\Gamma_1$, X_5-X_3, X_5-X_1 .
AlSb[7] : $\Gamma_{15}-\Gamma_1$, X_5-X_3, X_5-X_1

The values of Δ^- listed in Table II were obtained by adjusting the bands to agree with the experimentally observed spin-orbit splitting of the Γ_{15} valence band (Δ_0).[7,9] For GaAs, GaP and AlSb the spin-orbit parameters were those of the ***k.p*** basis. However, for InP it was found that better agreement with experimental results is achieved if the average $\Delta_{25'}$ and Δ_{15} of Si and α-Sn are used rather than the parameters of Ge.

§ 4. Results

Shown in Figs. 1 and 2 are the calculated energy bands, including spin-orbit splittings, of GaAs and GaP, respectively. In Fig. 1 both the single and the double group notation are indicated. Because of the small spin-orbit splittings of GaP the splittings of the Λ_3 (valence band), Λ_3 (conduction band), and Δ_3, Δ_4 (valence bands) are given in detail in Fig. 3. The band structures of InP and AlSb are given in Figs. 4 and 5, respectively. Using the eigenvectors of the Hamiltonian we have calculated mass parameters at a number of points in the Brillouin zone. These are listed in Table III.

Table III. Calculated and experimental values of the band parameters at Γ_{15} (valence), Γ_1, L_1 and $X_1(\Delta_1)$ for GaAs, GaP, InP and AlSb. The effective masses are given in units of the free electron mass.

		GaAs	GaP	InP	AlSb
A	calc.	−7.39	−4.72	−8.13	−5.51[e]
B	calc.	−4.93	−2.52	−5.81	−2.84[e]
C^2	calc.	25.65	7.32	26.13	12.60[e]
$m^*(\Gamma_1)$	calc. exp.	0.0651 0.065[a]	0.135	0.0545	0.121
$m^*_{\|\|}(L_1)$	calc.	0.970	1.184	1.208	1.357
$m^*_{\perp}(L_1)$	calc.	0.116	0.150	0.112	0.123
$m^*_{\|\|}(X_1, \Delta_1)$	calc.	—[b]	1.51(Δ_1)[c]	3.71(Δ_1)[c]	0.95(Δ_1)[c]
$m^*_{\perp}(X_1, \Delta_1)$	calc. exp.	0.23(X_1)	0.28(Δ_1)[c] 0.22[d]	0.24(Δ_1)[c]	0.25(Δ_1)[c] 0.25[d]

a) W. M. DeMeis and W. Paul: private communication, see also H. Piller: *Proc. Int. Conf. Semiconductor Physics*, Kyoto (1966) p. 206.
b) The calculated value of the mass at X_1 is negative. It is very sensitive to the value of the X_1-X_3 gap and small changes in this gap may be sufficient to change the sign.
c) Calculated at the minimum in the conduction band in the [100] direction, which occurs at a value of ***k*** somewhat less than the zone edge.
d) Reference 6.
e) Some recent experimental results [R. J. Stirn and W. M. Becker: Bull. Amer. Phys. Soc. **11** (1966) 439.] are in good agreement with these values.

A. GaAs

The calculated bands show critical points in the [100] direction ($E_0'=4.42$ eV, $E_0'+\Delta_0'=4.60$ eV) which have been identified with the structure seen in electroreflectance at 4.44 and 4.63 eV.⁷⁾ The calculated value of Δ_1 (0.22 eV) also is in good agreement with the experimental value (0.24 eV).⁷⁾ The X_1 point is 0.25 eV above the Γ_1 conduction band minimum, as indicated by certain experiments.⁸⁾ The value of E_2 (4.36 eV) shown in Fig. 1 is about 0.6 eV lower than the peaks in the reflectance (5.12 eV)⁶⁾ and electroreflectance (4.99 eV)⁷⁾ spectrum usually assigned to this transition. Cohen and Bergstresser have found similar results.⁴⁾ Our calculations show that the saddle point in the [110] direction ($\Sigma_2-\Sigma_1$) corresponds to an energy of 5.0 eV and may be responsible for the structure seen at 5 eV while the E_2 and E_0' gaps are degenerate and cause the structure observed at 4.5 eV. Piezo-electroreflectance studies¹⁰⁾ are presently being performed in order to clarify this point.

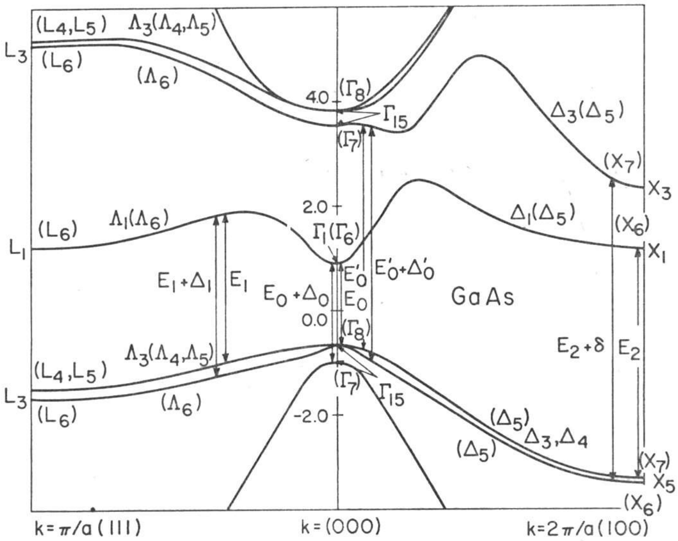

Fig. 1. Energy bands of GaAs, including spin-orbit splittings, in the [100] and [111] directions. The double group notation is indicated in parentheses.

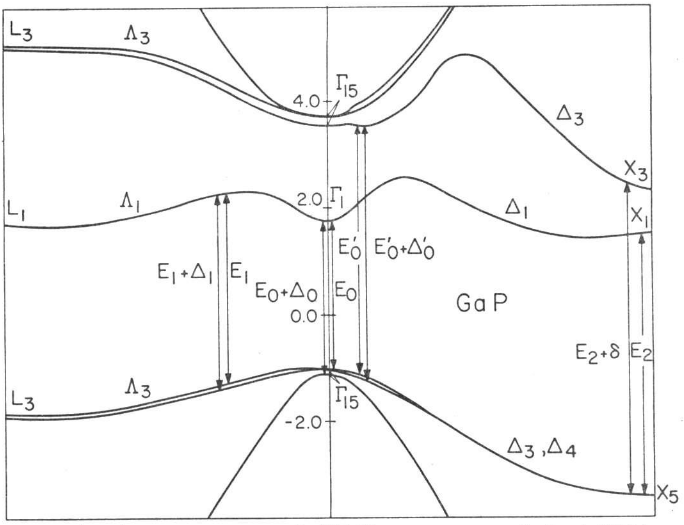

Fig. 2. Energy bands of GaP, including spin-orbit splittings, in the [100] and [111] directions.

B. GaP

The calculated values of E_1 (3.59 eV), Δ_1 (0.072 eV), E_0' (4.72 eV) and Δ_0' (0.051 eV) are in good agreement with experiment.[7,11] As in GaAs the E_2 gap (4.92 eV) shown in Fig. 2 is somewhat lower in energy than the structure in the optical spectrum[6,7] assigned to this transition. Also in this material the energy of the $\Sigma_2-\Sigma_1$ saddle point (5.40 eV) corresponds more closely to the structure in the optical spectrum (5.3 eV) while the E_0' and E_2 transitions are almost degenerate at about 4.8 eV.

C. InP

In general the bands shown in Fig. 4 agree with experimental data. The E_0' gap (4.42 eV) is somewhat lower than energy of the structure in electroreflectance associated with this transition. This is caused by the large spin-orbit splitting of the Γ_{15} (conduction band) and can be corrected by increasing the $\Gamma_{15}-\Gamma_{15}$ gap in

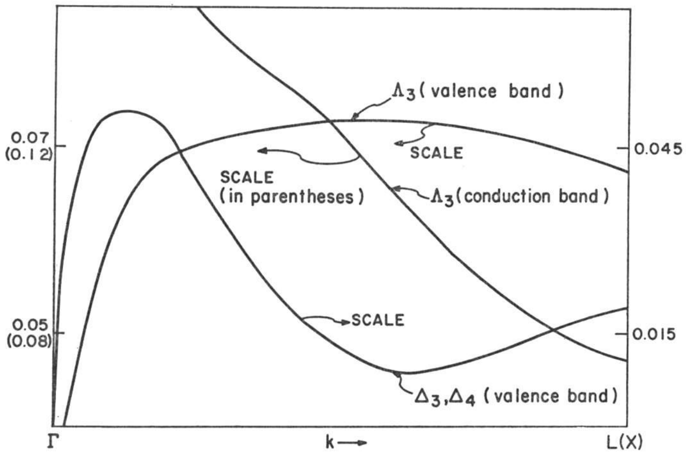

Fig. 3. Spin-orbit splittings (in eV) for GaP of the Λ_3 (valence band), Λ_3 (conduction band), and Δ_3, Δ_4 (valence band) across the Brillouin zone. The energy scale for Λ_3 (conduction band) is indicated on the left in parentheses.

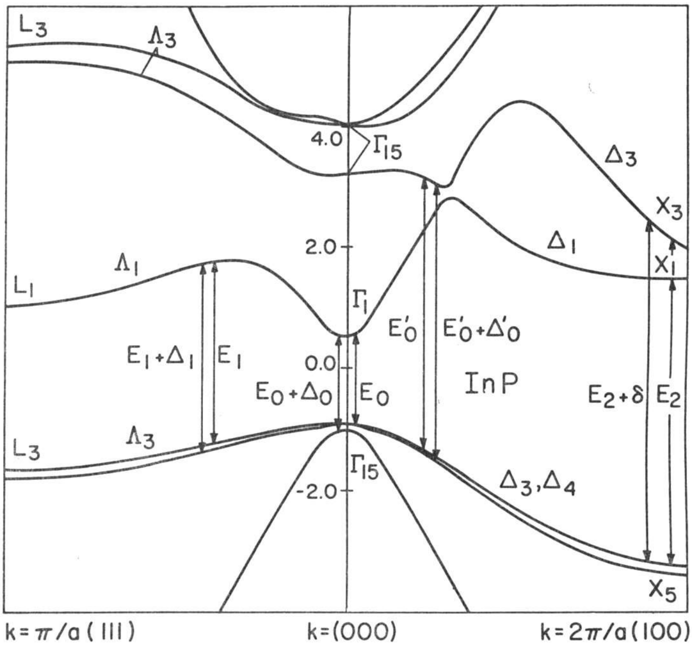

Fig. 4. Energy bands of InP, including spin-orbit splittings, in the [100] and [111] directions.

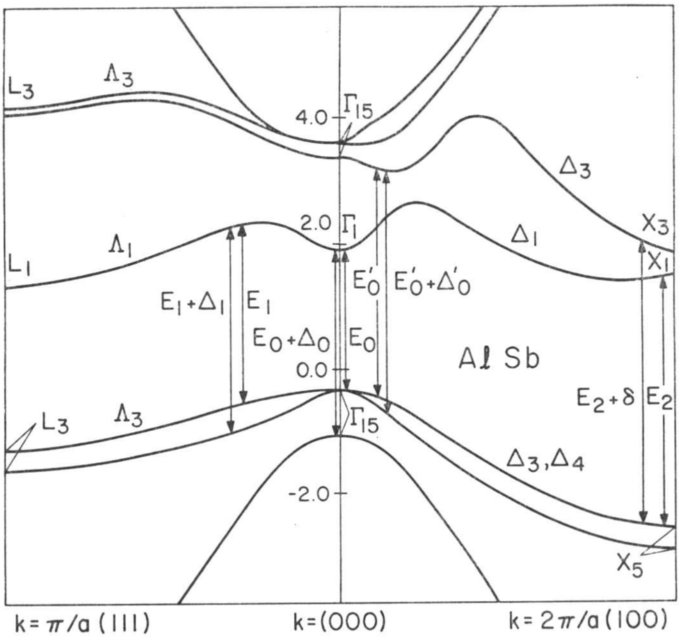

Fig. 5. Energy bands of AlSb, including spin-orbit splittings, in the [100] and [111] directions.

the determination of V_1^- and V_4^-. The $\Sigma_2-\Sigma_1$ saddle point energy (5.13 eV) is quite close to the energy of the E_2 gaps. The calculated Δ_1 splitting (0.11 eV) is somewhat smaller than the experimental value (0.16 eV) but is larger than Δ_0 (0.10 eV) as is the case in materials where there is a large difference between the cation and anion splittings. Because of the large amount of compensation (note the large negative value of Δ^- in Table II) it may be necessary to include the effects of higher bands in the spin-orbit Hamiltonian.

D. AlSb

As shown in Fig. 5 the values of the energy gaps E_1 (2.86 eV), Δ_1 (0.42 eV), E_0' (3.79 eV), Δ_0' (0.29 eV), etc., correspond almost exactly to the structure in the optical spectrum[7] assigned to these transitions. The $\Sigma_2-\Sigma_1$ saddle point (4.37 eV) is degenerate with the E_2 transitions.

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DISCUSSION

Herman, F.: My colleague, Dr. Narcinda R. Lerner, has recently succeeded in finding a set of empirical ***k.p*** matrix elements which leads to a ***k.p*** band structure which closely approximates our *E*(PERT) band structure (cf. paper I-2). Here empirical parameters are similar to yours, though some differences exist. In effect, the difference between your germanium band structure and ours is produced by relatively small changes in the empirical ***k.p*** parameters.

Cardona, M.: Yes, in fact, E_0' is an adjustable parameter in our calculation and we encounter no difficulty in changing it from Cohen's values to your values. In gray tin the E_0' structure is affected very strongly by spin-orbit interaction so that any purely orbital calculation gives erroneous energies for the E_0' critical point. In order to fit the E_0' structure observed in electroreflectance we actually need orbital $\Gamma_{25'}-\Gamma_{15}$ gaps smaller than those of Cohen and Bergstresser and close to yours.