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Electronic structure of III–V ternary semiconductors

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Abstract. Electronic band structures of the ternary alloys $Ga_xIn_{1-x}P$, $GaAs_{1-x}P_x$, $Ga_xIn_{1-x}As$ and $InAs_{1-x}P_x$ are calculated in the coherent-potential approximation (CPA) using the tight-binding Hamiltonian. The CPA energy bands are reported for the first time for the $Ga_xIn_{1-x}As$ and $InAs_{1-x}P_x$ systems. The calculated variation of important direct and indirect energy gaps with composition x and their bowing is compared with the available experimental data, and good agreement is found for all the four ternary alloys studied.

1. Introduction

Considerable interest has been generated in the study of electronic and optical properties of III–V compound semiconductors and their alloys due to their many applications in semiconductor devices (Kressel and Butler 1977, Casey and Ponish 1978). Experimental measurements of photoluminescence, cathodoluminescence and absorption yield information on band parameters like direct and indirect energy gaps and electron and hole mobilities.

In the literature there are predominantly two schemes for the band-structure calculations of the III–V binary semiconductors, i.e. the pseudopotential method of Chelikowsky and Cohen (1976) and the tight-binding method initially formulated by Harrison (1980). The fundamental concept involved in a pseudopotential calculation is that the ion core can be omitted and a simple plane-wave basis yields rapid convergence. The empirical pseudopotential parameters are determined by detailed comparison with experimental data, and the energy band structures are obtained (Chelikowsky and Cohen 1976). Recently, Chen and Sher (1980) have used a set of orthogonalised Gaussian orbitals and empirical pseudopotential parameters for band-structure calculations of some of the III–V binary semiconductors. They find that band structures obtained within a few electronvolts on either side of the band gap are excellent fits to those obtained from more elaborate calculations (Chelikowsky and Cohen 1976), whereas well away from the gap there are differences. However, Chen and Sher (1980) have used the same band energies as obtained by Chelikowsky and Cohen (1976) for fixing the parameters used for their band-structure calculations.

The tight-binding method for band-structure calculations uses atomic energy parameters and the expansion of the electron wavefunction in terms of a linear combination of atomic orbitals (LCAO). Harrison's (1980) treatment considers only the first-neighbour interaction and therefore does not reproduce the conduction bands well. Talwar and Ting (1982) have computed the band structure of III–V binary semiconductors using

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the tight-binding approach and have incorporated interaction terms beyond the first-neighbour interaction. Their calculation is similar in spirit to that of Dresselhaus and Dresselhaus (1967) and Koster and Slater (1954) for the diamond-structure semiconductors silicon and germanium, and the results are in good agreement with the pseudopotential calculations.

Ternary III–V semiconductor alloys are characterised by structural and chemical disorder, which makes the task of formulating an exact Hamiltonian for the system difficult. However, there are various mean-field approximations available (Economou 1979, Ziman 1979), the simplest of these being the virtual-crystal approximation (VCA), which is a simple interpolation between the constituent binaries and does not take account of the disorder. Another effective-medium approach, the coherent-potential approximation (CPA), consists of defining a self-consistently determined effective medium which contains effective atoms characterised by a site-independent complex effective energy (E) so that the average electron scattering is zero. The CPA formulation is recognised as the best single-site approximation for determining the spectral properties of a disordered system, and has been applied mainly within the framework of a tight-binding Hamiltonian.

Band-structure calculations, within CPA, have been reported for the III–V ternary semiconductors $GaAs_{1-x}P_x$ (Sakai and Sugano 1979, Chen and Sher 1981, Bugajski *et al* 1983, Shen and Myles 1987), $Ga_xIn_{1-x}P$ (Chen and Sher 1981, Bugajski *et al* 1983, Shen and Myles 1987), $Ga_xIn_{1-x}As$ (Shen and Myles 1987) and $Al_xGa_{1-x}As$ (Chen and Sher 1981, Shen and Myles 1987). Sakai and Sugano (1979) have constructed the Hamiltonian matrix for the ternary alloy in terms of a linear combination of bond orbitals (LCBO) and consider only the first-neighbour interaction. The LCBO method, while giving a good description of valence bands, is not found to be a good approximation for the conduction bands. Chen and Sher (1981), on the other hand, use a set of Gaussian wavefunctions as basis set, the same approach as they had used for the binaries. In another CPA calculation of the electronic band structure of $GaAs_{1-x}P_x$ and $Ga_xIn_{1-x}P$, Bugajsky *et al* (1983) have used a semielliptic form for the electron density of states (DOS) at high symmetry points of the Brillouin zone (BZ), while the other band-structure calculations involve the DOS covering the whole BZ. Shen and Myles (1987) utilised the sp^3s band structures as input into Chen and Sher's CPA formalism to calculate CPA self-energies of III–V alloys. The complex energy band structure of II–VI ternary alloy $Hg_xCd_{1-x}Te$ has also been calculated recently by Hass *et al* (1983) using the tight-binding Hamiltonian. Using the all-electron mixed-basis approach to density-functional formalism for crystals, Bernard and Zunger (1987) calculated the electronic structure of zincblende ZnS, ZnSe and ZnTe and that of their pseudo-binary alloys. A recent calculation by Lempert *et al* (1987) considers the effects of both random chemical and random bond-length variations.

This paper presents a tight-binding calculation of energy bands of III–V ternary alloys $GaAs_{1-x}P_x$, $Ga_xIn_{1-x}P$, $Ga_xIn_{1-x}As$ and $InAs_{1-x}P_x$ in the CPA including the second-neighbour interaction terms. Detailed band-structure calculations are reported for the first time for the last two ternary alloy systems. The input tight-binding parameters of the constituent binary systems reproduce the values of important energy gaps of the binary semiconductors obtained from room-temperature experiments. Therefore, the present CPA calculations yield room-temperature energy bands for these ternary alloys. These computations involve a three-dimensional numerical evaluation of the partial density of states (DOS) and takes account of the random anion or cation substitution (Hass *et al* 1983). The variations of energies of the seven bands Γ_{15v}, Γ_{1c}, X_{5v}, I_{1c}, X_{3c}, L_{3v}

and L_{1c} together with their bowing are studied, and the important direct and indirect energy gaps, obtained from the present calculations, are found to agree rather well with the experimentally determined values, for all the four ternary alloys considered here. Section 2 presents details of the calculational procedure, while the results of these computations are discussed in § 3 and the concluding remarks are made in § 4.

2. Calculational procedure

The electronic band structures of III–V ternaries have been calculated in the CPA within the tight-binding framework of Koster and Slater (1954) neglecting spin–orbit interaction. The Hamiltonian matrix $[H_{\alpha\beta}]$ describing the alloy system A_xB_{1-x} may be written as:

$$[H_{\alpha\beta}] = [H_{\alpha\beta}^{\mathrm{VCA}}] + [H_{\alpha\beta}^{\mathrm{disorder}}] \tag{1}$$

with

$$H_{\alpha\beta}^{\mathrm{VCA}} = xH_{\alpha\beta}^{\mathrm{A}} + (1-x)H_{\alpha\beta}^{\mathrm{B}} \tag{2}$$

where $H_{\alpha\beta}^{\mathrm{A}}$ and $H_{\alpha\beta}^{\mathrm{B}}$ are the tight-binding parameters of the constituent binaries, respectively, and α and β refer to the s or p states of the cation or the anion. The term H^{disorder} describes both the diagonal as well as the off-diagonal components of the alloy disorder. For the substitutional alloys under consideration here, diagonal disorder refers to the difference $\Delta_\alpha = E_\alpha^{\mathrm{A}} - E_\alpha^{\mathrm{B}}$ in the atomic term values, $E^{\mathrm{A,B}}$, while the off-diagonal disorder pertains to the differences in various inter-atomic terms. In most of the CPA band-structure calculations (Sakai and Sugano 1979, Chen and Sher 1981, Bugajski *et al* 1983, Hass *et al* 1983), it is the diagonal part which has been considered. Hass *et al* (1983) and later on a detailed study by Lempert *et al* (1987) have included the off-diagonal part of the disorder, H^{disorder}, in the framework of molecular CPA (MCPA) of Ducastelle (1974). For $Ga_xIn_{1-x}As$, their MCPA calculations predict a smaller bowing for the direct band gap compared to the CPA calculations (see figure 4 of Hass *et al* 1983). They attribute this effect to a destructive interference between chemically and structurally induced scattering, which is discussed in the following sections.

In the present treatment, we neglect the off-diagonal component of the alloy disorder and calculate the CPA self-energies Σ in the single-site approximation. The average Green function for complex energy ζ is defined as

$$G(\zeta) = (\zeta - H)^{-1} = (\zeta - H_{\mathrm{eff}})^{-1} \tag{3}$$

where the effective Hamiltonian

$$H_{\mathrm{eff}} = H^{\mathrm{VCA}} + \Sigma \tag{4}$$

has the periodicity of the crystal lattice. The effective-medium energy Σ is determined self-consistently in such a manner that the average electron scattering from the disordered arrangement of A and B atoms or molecules is zero. This condition for self-consistency yields a system of coupled equations for Σ. They are (Ehrenreich and Hass 1982)

$$\Sigma_\alpha = (x\Delta_\alpha + \Sigma_\alpha)\, F_\alpha((1-x)\Delta_\alpha - \Sigma_\alpha) \tag{5}$$

with

$$F_\alpha(\zeta) = \int_{-\infty}^{\infty} \mathrm{d}E \frac{g_\alpha(E)}{(\zeta - \Sigma_\alpha - E)} \tag{6}$$

where Δ_α is the alloy scattering parameter associated with the cation or the anion

site-diagonal disorder. The function $g_\alpha(E)$ is the partial energy density of state (DOS) calculated from the VCA alloy band structure as

$$g_\alpha(E) = \langle\alpha|\delta(E - H^{\mathrm{VCA}})|\alpha\rangle = \sum_{n,k} |\langle\alpha|nk\rangle|^2\, \delta(E - E_{nk}^{\mathrm{VCA}}). \qquad (7)$$

A sampling procedure has been used to compute cation and anion s as well as p partial DOS. For the three-dimensional BZ integration the reduced BZ is divided into three tetrahedra, each of which is subdivided into 343 tetrahedra, and the VCA Hamiltonian is diagonalised at the centre, corners and four intermediate points of each of the small tetrahedra. In equation (7) $\langle\alpha|$ and $|nk\rangle$ refer to the localised and Bloch wavefunction, respectively.

Equation (6) is similar in spirit to equation (14) of Chen and Sher (1981) and is different from equation (16) of Hass *et al* (1983) since the present procedure avoids the calculation of CPA electron DOS in each step of iteration by using partial VCA DOS and performing the iteration for Σ between equations (5) and (6). This is a reasonable approach, since it is not the intention of the present work to calculate CPA DOS, and furthermore the numerical calculations for Σ are simplified significantly. About four or five iterations are required to obtain convergence for the four ternary systems studied here. When the self-energies are not too large, which is presently the case, then the spectral density function

$$A(\boldsymbol{k}, E) = \mathrm{Im}\{[E - E_{nk}^{\mathrm{VCA}} - \Sigma(\boldsymbol{k}, E)]^{-1}\} \qquad (8)$$

will have sharp peaks at values such that

$$E - E_{nk}^{\mathrm{VCA}} - \Sigma_{\mathrm{R}}(\boldsymbol{k}, E) = 0 \qquad (9)$$

where $\Sigma(\boldsymbol{k}, E) = \Sigma_{\mathrm{R}}(\boldsymbol{k}, E) - \mathrm{i}\Sigma_{\mathrm{I}}(\boldsymbol{k}, E)$. The complex self-energy correction to the VCA electron band structure is then obtained as

$$\Sigma(\boldsymbol{k}, E) = \langle\boldsymbol{k}|\Sigma(E)|\boldsymbol{k}\rangle = \sum_{\alpha} |\langle\boldsymbol{k}|\alpha\rangle|^2\, \Sigma_\alpha(E). \qquad (10)$$

The CPA alloy band structure is sensitively dependent on the input band structure of the constituent binaries, and their selection requires special care. The band structures of semiconductors GaP, GaAs, InP and InAs have been calculated in the tight-binding formalism by Talwar and Ting (1982) and their results are in agreement with the pseudopotential calculations of Chelikowsky and Cohen (1976). However, both these calculations (for band structure at 0 K) predict the lowest Γ–X band gap in GaP to be $E_g(X)(\mathrm{GaP}) = 2.16$ eV whereas the experimentally determined value is 2.368 eV (Thurmond 1975). Porod *et al* (1982) have given their tight-binding parameters for these four binary systems when they describe a model for the relationship between clustering of like ions and band-gap bowing. These tight-binding parameters generate room-temperature band structures for these semiconductors, and the important energy gaps, including the X indirect gap in GaP, are predicted correctly. Therefore, these tight-binding parameters have been used in the present CPA band-structure calculation of the four ternaries $GaAs_{1-x}P_x$, $InAs_{1-x}P_x$, $Ga_xIn_{1-x}P$ and $Ga_xIn_{1-x}As$. Hence the band structures discussed in this paper are all at room temperature. The input values of the alloy scattering parameters Δ_α for the four ternary alloy series are given in table 1.

The VCA energy band structures for the four ternaries, calculated from these parameters, are used to compute the partial DOS. The anion-projected s- and p-like DOS have been calculated for the ternaries $GaAs_{1-x}P_x$ and $InAs_{1-x}P_x$ (figure 1) while the cation-projected DOS have been enumerated for the other ternaries $Ga_xIn_{1-x}P$ and

Table 1. Alloy scattering parameters Δ_α for the ternary alloys.

	$GaAs_{1-x}P_x$ $InAs_{1-x}P_x$	$Ga_xIn_{1-x}P$ $Ga_xIn_{1-x}As$
Δ_s (eV)	$E_s^{As} - E_s^{P} = 0.263$	$E_s^{In} - E_s^{Ga} = 1.043$
Δ_p (eV)	$E_p^{As} - E_p^{P} = 0.3$	$E_p^{In} - E_p^{Ga} = 0.12$

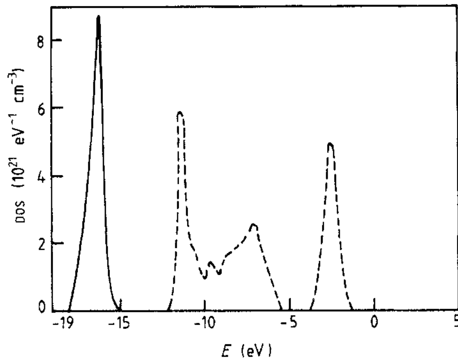

Figure 1. Representative partial s-like (——) and p-like (- - - -) VCA electron density of states for the anion-substituted alloys $GaAs_{1-x}P_x$ and $InAs_{1-x}P_x$.

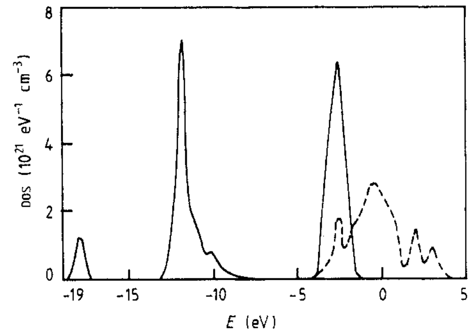

Figure 2. Representative partial s-like (——) and p-like (- - - -) VCA electron density of states for the cation-substituted alloys $Ga_xIn_{1-x}P$ and $Ga_xIn_{1-x}As$.

$Ga_xIn_{1-x}As$ (figure 2). Partial densities of states are calculated since the present treatment considers only the effect of disorder arising from the random anion or cation substitution, which is measured in terms of differences in the atomic term values. In this respect the present procedure is similar to that of Hass and co-workers (1981) (Hass *et al* 1983, Ehrenreich and Hass 1982) and different from that of Chen and Sher (1981), where the latter define the differences in bonding (antibonding) energies as alloy scattering parameters and employ the corresponding DOS for their calculations. Moreover, they have used the SVCA ternary alloy band structure as input to their CPA calculations where the parameters of the binary systems have been scaled by the average lattice constant of the ternary semiconductor. On the other hand, no such scaling of the binary tight-binding parameters has been performed in the present calculation. This is consistent with the recent extended x-ray absorption fine-structure (EXAFS) studies of mixed III–V semiconductors, where is has been shown that the change of bond lengths with composition is linear but far slower than the change in the alloy lattice constant. Consequently, the concept of covalent radii being conserved is a better approximation than VCA (Mikkelsen and Boyce 1984).

3. Results and discussions

Partial densities of states, and consequently the CPA self-energies and the complex band structures, have been calculated for the four ternary alloys $GaAs_{1-x}P_x$, $InAs_{1-x}P_x$, $Ga_xIn_{1-x}P$ and $Ga_xIn_{1-x}As$ at $x = 0.1$, 0.3, 0.5, 0.7 and 0.9. A representative curve for the anion-projected density of states DOS for the two anion-substituted ternaries $GaAs_{1-x}P_x$ and $InAs_{1-x}P_x$ is given in figure 1. No qualitative difference in the partial

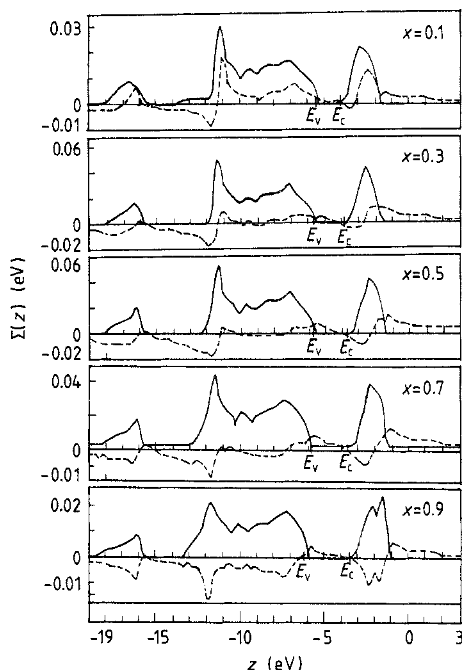

Figure 3. Real (- - - -) and imaginary (——) parts of CPA self-energy $\Sigma(E)$ of the ternary alloy $GaAs_{1-x}P_x$.

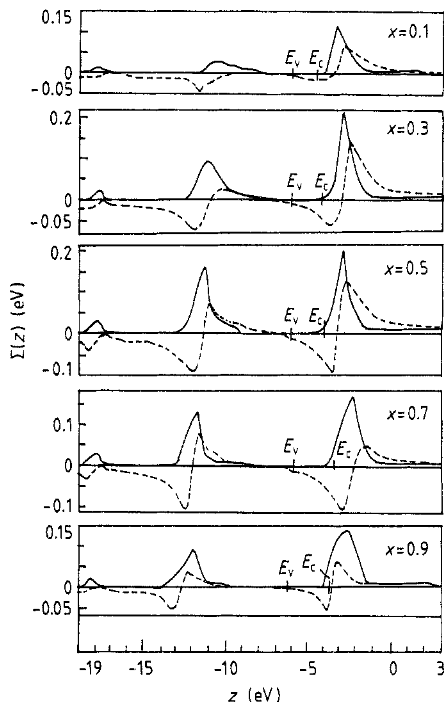

Figure 4. Real (- - - -) and imaginary (——) parts of the CPA self-energy $\Sigma(E)$ of the ternary alloy $Ga_xIn_{1-x}P$.

density of states has been seen for different values of x or for the alloy series, and it is found that the anion-projected DOS is dominated by p-like states in the region of top of valence band and bottom of conduction band (−6 to −4 eV). This is in contrast with the cation-projected DOS for the two ternaries $Ga_xIn_{1-x}P$ and $Ga_xIn_{1-x}As$, a representative curve of which is presented in figure 2, and is seen to be dominated by s-like states in the region of interest (−6 to −4 eV). Here again the partial DOS for the two cation-substituted alloy series are similar in nature.

These anion- and cation-projected DOS have been used to calculate the s-like, Σ_s, and p-like, Σ_p, CPA self-energies for the ternary alloy series†. For clarity, total self-energy $\Sigma = (\Sigma_s + 3\Sigma_p)/4$ for the anion-substituted and cation-substituted alloys is shown in figures 3 and 4, where the positions of the valence band maximum E_v, and conduction band minimum E_c, are also indicated. One notices from figure 3‡ that for both the anion-substituted ternary alloys the CPA self-energy correction Σ_R is relatively small at E_c and E_v, it being greater at E_v and opposite in sign to that at E_c. The imaginary part of the self-energy, Σ_I, at the CPA band energies provides a measure for the alloy scattering lifetimes. It is seen from figure 3 that the CPA lifetime effects are small at E_c and E_v for these two ternary alloys. However, these effects are expected to be larger for the

† In general a convergent value of self-energy Σ is obtained in four or five iterations. However, no convergence could be obtained for Σ_s for the cation-substituted ternaries in the narrow range of ~1 eV around $E = -3.0$ eV. This could be due to the peaking of s-like DOS in this region coupled with a large value of alloy scattering parameter Δ_s for these alloy semiconductors. The values of Σ_s were obtained in this region by polynomial extrapolation.

‡ The self-energy of $GaAs_{1-x}P_x$ alloy is shown in figure 3. The self-energy curve for $InAs_{1-x}P_x$ is found to be similar to that of $GaAs_{1-x}P_x$.

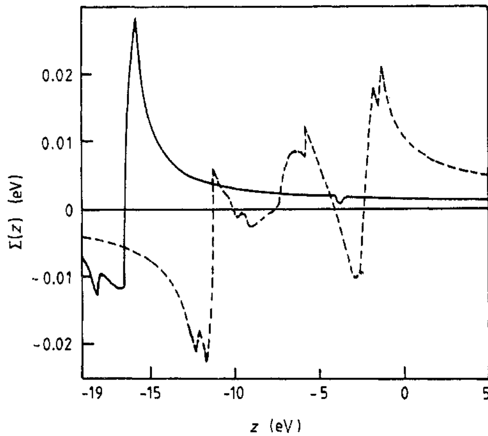

Figure 5. Representative s-like (——) and p-like (- - - -) CPA self-energies for the anion-substituted alloys $GaAs_{1-x}P_x$ and $InAs_{1-x}P_x$.

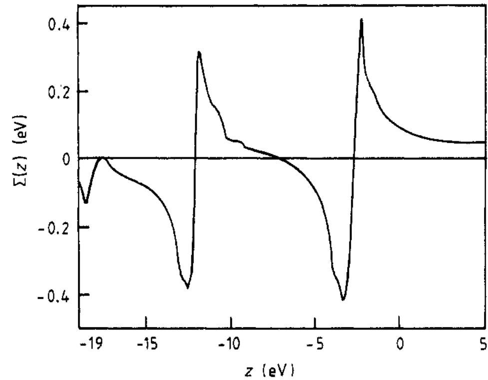

Figure 6. Representative s-like (——) CPA self-energies for the cation-substituted alloys $Ga_xIn_{1-x}P$ and $Ga_xIn_{1-x}As$. The p-like self-energies for these alloys are nearly zero.

higher-lying conduction band and the lower-lying valence bands, e.g. the valence band maximum at X or L points of the BZ.

The representative curve for the CPA self-energy of cation-substituted ternary alloys $Ga_xIn_{1-x}P$ and $Ga_xIn_{1-x}As$ is presented in figure 4. It is noticed that the self-energies associated with the cation-substituted alloys are larger (by more than a factor of 2) than those associated with the anion-substituted ternary systems. This difference of effect of disorder in these anion-substituted and cation-substituted ternary systems is understood to arise from the differences in the alloy scattering parameters Δ_α in the two cases, which are $\Delta_s = 1.043$ eV and $\Delta_p = -0.12$ eV for the cation-substituted alloy system and $\Delta_s = 0.263$ eV and $\Delta_p = 0.3$ eV for the anion-substituted system. This also explains the dominance of Σ_s over Σ_p, observed in the cation-substituted ternary alloys, while for the anion-substituted ternary alloys Σ_s and Σ_p are comparable in magnitude. However, for $GaAs_{1-x}P_x$ and $InAs_{1-x}P_x$, Σ_s is found to be negligible in the entire region $E > -16$ eV as is also to be expected since the anion-projected DOS for these ternary alloys is dominated by p-like states in this energy region (figure 1). Representative curves for the real components of Σ_s and Σ_p for the two cases are given in figures 5 and 6. The imaginary parts of Σ_s and Σ_p closely resemble the respective DOS curves. The calculations, their results and discussions of individual ternary alloys will be taken up below one by one.

3.1. $GaAs_{1-x}P_x$

This ternary alloy has been well studied both theoretically (Sakai and Sugano 1979, Chen and Sher 1981, Bugajski *et al* 1983) as well as experimentally (Kressel and Butler 1977), especially in the composition range $0 < x < 0.5$ where the direct gap is the lowest energy gap. Figure 7 presents the variation of the seven energy levels (Γ_{15v}, Γ_{1c}, X_{5v}, X_{1c}, X_{3c}, L_{3v} and L_{1c}) as a function of composition x of phosphorus in $GaAs_{1-x}P_x$. In general, the x-dependence of the energy levels may be written as

$$E_i(x) = A_i + B_i + C_i x^2$$

where C_i designates the bowing of the ith energy level. Table 2 gives the bowing of these energy states, calculated in the CPA, together with the band-gap bowing for the lowest

Table 2. Bowing parameters (eV) for the seven energy states at Γ, X and L and the three energy gaps $E_g(\Gamma) = \Gamma_{1c} - \Gamma_{15v}$, $E_g(X) = X_{1c} - \Gamma_{15v}$ and $E_g(L) = L_{1c} - \Gamma_{15v}$ at the various values of x calculated in CPA as well as in VCA (given in parentheses) for the alloy $GaAs_{1-x}P_x$. Also listed is the average bowing for the three gaps.

	$x = 0.1$	0.3	0.5	0.7	0.9	Average bowing
Γ_{15v}	−0.182 (−0.149)	−0.172 (−0.144)	−0.202 (−0.14)	−0.166 (−0.1324)	−0.151 (−0.129)	
Γ_{1c}	0.0133 (0.0155)	0.0095 (0.01)	0.0072 (0.008)	0.0081 (0.0086)	0.0056 (0.0067)	
X_{5v}	−0.036 (−0.002)	−0.0024 (−0.00285)	0.004 (−0.004)	0.0124 (−0.0019)	0.047 (0.002)	
X_{1c}	0.0144 (0.015)	0.0148 (0.015)	0.0112 (0.012)	0.0129 (0.013)	0.0167 (0.017)	
X_{3c}	−0.074 (0.003)	−0.043 (0.0043)	−0.03 (0.0068)	−0.014 (0.0052)	−0.048 (0.007)	
L_{3v}	−0.10 (−0.033)	−0.067 (−0.038)	−0.052 (−0.036)	−0.033 (−0.033)	0.033 (−0.033)	
L_{1c}	0.0122 (0.01)	0.0114 (0.008)	0.0088 (0.006)	0.0081 (0.0062)	0.0018 (0.001)	
$E_g(\Gamma)$	0.196 (0.164)	0.182 (0.154)	0.177 (0.148)	0.174 (0.141)	0.157 (0.135)	0.1772 (0.148)
$E_g(X)$	0.198 (0.165)	0.189 (0.1604)	0.183 (0.154)	0.182 (0.149)	0.178 (0.156)	0.186 (0.157)
$E_g(L)$	0.194 (0.159)	0.184 (0.152)	0.1784 (0.146)	0.174 (0.1386)	0.153 (0.13)	0.177 (0.145)

Table 3. Bowing parameters (eV) for the seven energy states and the energy gaps $E_g(\Gamma)$, $E_g(X)$ and $E_g(L)$ calculated in CPA as well as in VCA (given in parentheses) of ternary alloy $InAs_{1-x}P_x$.

	$x = 0.1$	0.3	0.5	0.7	0.9	Average bowing
Γ_{15v}	−0.032 (−0.0167)	−0.036 (−0.021)	−0.039 (−0.022)	−0.041 (−0.021)	−0.0033 (−0.0167)	
Γ_{1c}	−0.005 (−0.003)	0.0 (0.0)	−0.003 (−0.002)	0.002 (0.0)	0.001 (0.003)	
X_{5v}	−0.038 (−0.004)	0.004 (−0.006)	0.014 (−0.008)	0.025 (−0.001)	0.06 (−0.0067)	
X_{1c}	0.23 (0.23)	0.22 (0.22)	0.22 (0.22)	0.216 (0.217)	0.211 (0.213)	
X_{3c}	0.0 (0.0)	−0.065 (0.0)	−0.063 (0.0)	−0.047 (0.0)	0.0811 (0.0)	
L_{3v}	−0.082 (0.0)	−0.0457 (−0.0048)	−0.0223 (−0.004)	−0.0026 (−0.0048)	0.0693 (−0.0111)	
L_{1c}	−0.0174 (−0.017)	−0.009 (−0.0119)	−0.0105 (−0.014)	0.015 (0.0119)	−0.0033 (−0.0056)	
$E_g(\Gamma)$	0.029 (0.0133)	0.035 (0.022)	0.0356 (0.02)	0.039 (0.021)	0.036 (0.02)	0.0345 (0.019)
$E_g(X)$	0.262 (0.259)	0.261 (0.247)	0.258 (0.242)	0.257 (0.239)	0.24 (0.23)	0.255 (0.243)
$E_g(L)$	0.0148 (0.0)	0.0268 (0.0095)	0.0287 (0.008)	0.0559 (0.0333)	0.03 (0.0111)	0.0312 (0.0124)

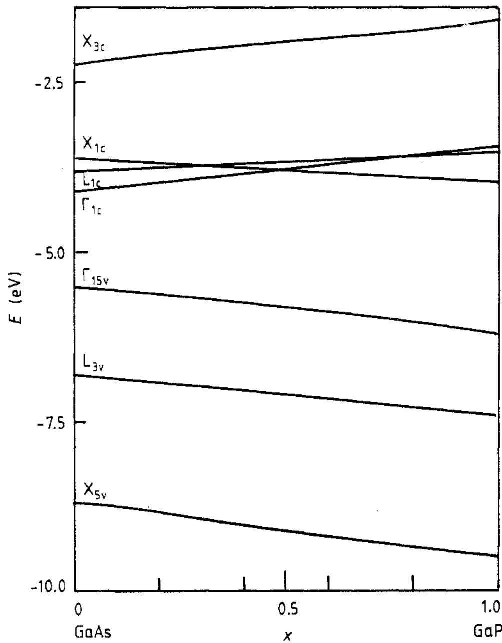

Figure 7. Variation of the indicated symmetry-point energies with concentration x for the alloy $GaAs_{1-x}P_x$.

direct as well as the indirect Γ–X and Γ–L gaps. These CPA bowing parameters should be studied in context with the VCA energy level bowings, which are also listed in table 2. It is seen that the total bowing (~ -0.17 eV) and its VCA contribution (-0.14) are largest for the state Γ_{15v}. This is in contrast to the results of Chen and Sher (1981) who calculate a very small bowing (~ 0.03 eV) for this state. Also, from a comparison of the CPA bowing parameters and their VCA contributions, the effect of alloy disorder is seen to be large for p-like valence states Γ_{15v} (~ 0.03 eV), L_{3v} (~ 0.06 eV) and X_{5v} and the conduction band state X_{3c}, while the CPA modification is seen to be negligible for the other three energy levels which are s-like in nature.

The average bowing of the direct gap is calculated to be $C = 0.1772$ eV when averaged all over x, and $C = 0.185$ eV when averaged for $x \leq 0.5$ when the ternary alloy is a direct-gap semiconductor. This is in close agreement with the experimentally measured values of 0.186 eV (Nelson *et al* 1974) and 0.21 eV (Craford *et al* 1972). The average bowing for the indirect gap $E_g(x)$ is calculated to be 0.186 eV and is in agreement with the experimentally determined value of 0.21 (Craford *et al* 1972). Onton and Foster (1972), on the other hand, have reported a value of 0.26 eV, which is quite large compared to the calculated value. The energy-gap bowing at L is calculated to be 0.177 eV and agrees well with the previously quoted values of 0.16 eV (Aspnes 1976) and 0.25 eV (Hill 1974). The corresponding value of bowing calculated by Chen and Sher (1981) is quite large (0.45 eV).

The variation of these three energy gaps with composition x is presented in figure 8. These calculated energy gaps are found to be in close agreement with those of Chen and Sher (1981). The compositional dependence of the direct gap is seen to match well with the room-temperature electro-reflectance data of Thompson *et al* (1966) and those of Craford *et al* (1972) for $x < 0.5$. For $x > 0.5$ this alloy becomes an indirect-gap semiconductor with Γ_v–X_c as the lowest energy gap. The calculated values of this gap are also compared with the optical absorption data of Craford *et al* (1972) and a good agreement is obtained. Figure 8 also presents the values of $E_g(x)$ obtained by Onton and

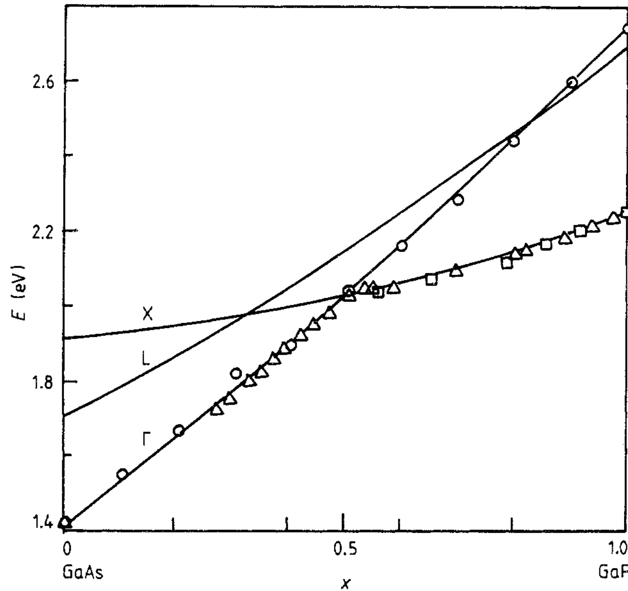

Figure 8. The present theoretical band gaps between the states Γ_{1c}, X_{1c} and L_{1c} and the states Γ_{15v} (——) with composition x of phosphorus in $GaAs_{1-x}P_x$. The experimental measurements are from the following: ○, Thompson *et al* (1966); △, Craford *et al* (1972); and □, Onton and Foster (1972).

Foster (1972), where their experimental results have been reduced to room-temperature values† and a fairly good agreement between present theory and experiment is obtained. The crossover between the direct and the indirect X gap is obtained at $x_c = 0.5$ with $E_c = 2.038$ eV. This is in close agreement with the value of $x_c = 0.49$ (at room temperature) determined by Craford *et al* (1972) and $x_c = 0.51$ determined by Marciniak and Wittry (1975).

3.2. $InAs_{1-x}P_x$

In contrast to $GaAs_{1-x}P_x$, the other anion-substituted ternary alloy under consideration, $InAs_{1-x}P_x$, is a very scantily studied system, both experimentally as well as theoretically. There is as yet no CPA band-structure calculation available in the literature and only one optical study of this ternary system has been reported (Antypas and Yep 1971). Figure 9 shows the variation of the seven energy states of $InAs_{1-x}P_x$ with composition x. No crossing of bands is observed for this ternary alloy. The CPA as well as VCA bowing parameters for these energy levels are presented in table 3, and the qualitative trend is seen to be similar to that of $GaAs_{1-x}P_x$. Table 3 also presents the bowing of the three lowest energy gaps $E_g(\Gamma)$, $E_g(X)$ and $E_g(L)$ for various concentrations, and the average bowings for these energy gaps are calculated to be 0.035, 0.243 and 0.048 eV respectively.

† Room-temperature values of the gaps are calculated by interpolating between the temperature variations of GaP and GaAs. Roessler and Swets (1978) gives these values as

$$E_g^{GaP}(0) - E_g^{GaP}(T) = 6.55 \times 10^{-4}\, T^2/(T + 460)\ \text{eV}$$

and

$$E_g^{GaAs}(0) - E_g^{GaAs}(T) = 7 \times 10^{-4} T^2/(T + 350)\ \text{eV}.$$

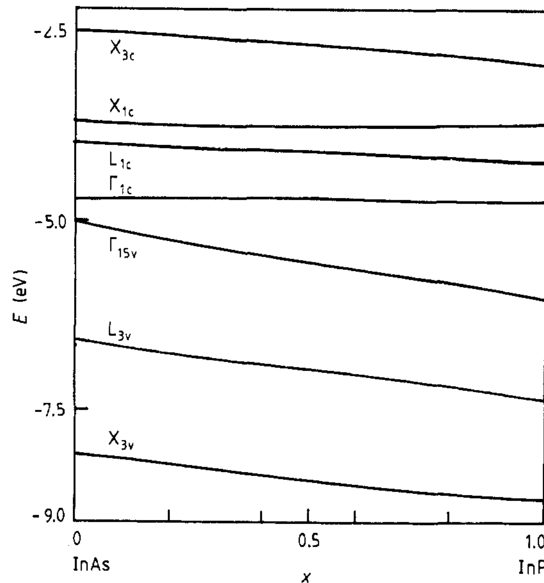

Figure 9. Variation of the indicated symmetry-point energies with concentration x of phosphorus in $InAs_{1-x}P_x$.

Only the direct gap of this semiconductor alloy has been studied experimentally by Antypas and Yep (1971). The bowing measured by them is 0.101 eV, which is larger than the presently estimated value. Their experimentally measured energy gaps are compared with the results of the present calculation in figure 10.

3.3. $Ga_xIn_{1-x}P$

This ternary alloy, like $GaAs_{1-x}P_x$, has also been well studied both theoretically (Chen and Sher 1981, Bugajski *et al* 1983) as well as experimentally (Kressel and Butler 1977) in the whole composition range. Figure 11 presents the variation of the seven energy levels with composition x of gallium in $Ga_xIn_{1-x}P$. The CPA and the VCA bowing parameters for these seven energy states as well as for the direct and indirect Γ–X and Γ–L energy gaps are listed in table 4. It is seen that the bowing is very small for the three valence bands Γ_{15v}, L_{3v} and X_{5v} and the conduction band state X_{1c}, all these states being predominantly p-like. On the other hand, for the s-like conduction band states Γ_{1c}, X_{3c} and L_{1c}, the CPA self-energy correction to the VCA bowing is large. This is due to the fact that, as mentioned previously, the alloy scattering parameter Δ_s for the s-like states is large compared to Δ_p for the cation-substituted ternary alloys under consideration. Also, it may be noticed that the bowing of the X_{3c} conduction state is negative. The present results for the bowing of these energy states are at variance with those of Chen and Sher (1981), who find for example that, for $Ga_xIn_{1-x}P$, the effect of disorder is greater for the valence state Γ_{15v} than for the conduction state Γ_{1c}.

The CPA (and the VCA) bowings of the direct and the two indirect energy gaps are also listed in table 4. The average CPA bowing for the direct gap is calculated to be $C = 0.7$ eV, which lies between the experimentally determined values of 0.758 eV (Onton *et al* 1971) to 0.786 eV (Nelson and Holonyak 1976) and 0.5 eV (Alibert *et al* 1972). The corresponding values of the bowing calculated by Chen and Sher (1981) (0.4 eV) and Bugajski *et al* (1983) (0.508 eV) are on the lower side. Present calculations yield the

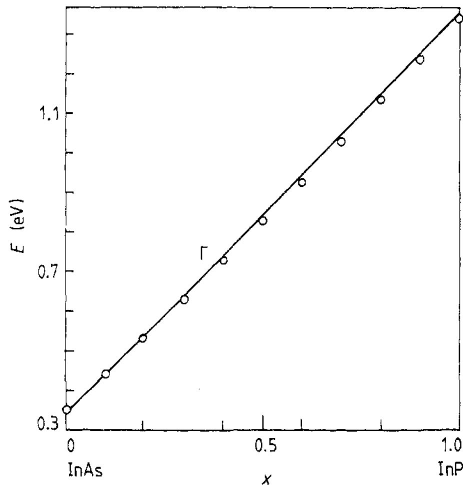

Figure 10. The present theoretical band gap between the states Γ_{1c} and Γ_{15v} (——) with composition x of phosphorus in $InAs_{1-x}P_x$ compared with the experimental measurements (○) of Antypas and Yep (1971).

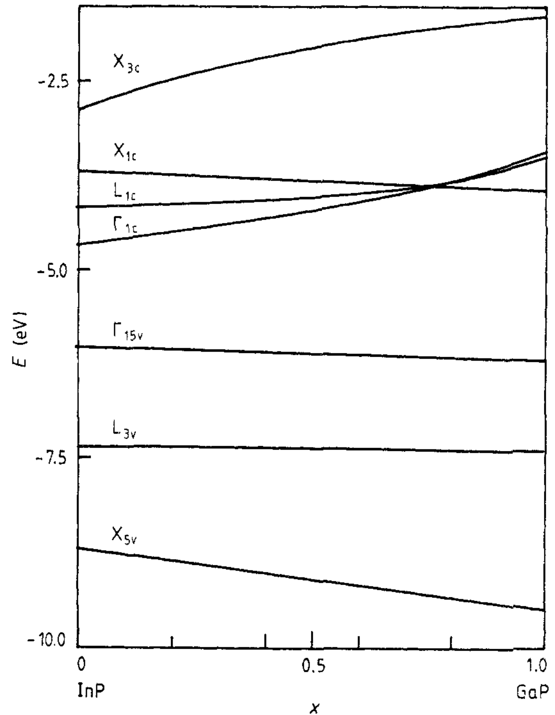

Figure 11. Variation of the indicated symmetry-point energies with concentration x of gallium in $Ga_xIn_{1-x}P$.

average bowing for the lowest L indirect gap as 0.79 eV, which lies between the experimentally measured values of 0.86 eV (Alibert *et al* 1972) and 0.68 eV (Onton and Chikotka 1971). Again, the corresponding value of bowing calculated by Chen and Sher (1981) (0.41 eV) is considerably lower. For the lowest X indirect gap, the present calculations predict a very small bowing of 0.053 eV, which is consistent with the observation of linear variation of this gap by Joullie and Alibert (1974) and Onton and Chikotka (1971). Nelson and Holonyak (1976) have, on the other hand, measured a large bowing for this indirect gap (0.21 eV).

The variation of these three energy gaps with composition x is shown in figure 12, where the ternary alloy $Ga_xIn_{1-x}P$ is seen to be a direct-gap semiconductor for $x < 0.77$, and for $x > 0.77$ the Γ_v–Γ_c energy gap is seen to be the lowest one. In the direct-gap region, the present theoretical results for the direct gap are compared with the absorption data of Nelson and Holonyak (1976), the cathodoluminescence data of Onton *et al* (1971) and the electro-reflectance measurements of Alibert *et al* (1972) in the whole of the composition range x, all these measurements being at room temperature. It is observed that the present calculations agree very well with the experimental results of Onton *et al* (1971) and Nelson and Holonyak (1976) and not so well with those of Alibert *et al* (1972), who obtain a fairly low bowing of 0.5 eV. In the indirect-gap region $x > 0.77$, the values of the X gap are compared with the experimental results of Onton *et al* (1971) and Nelson and Holonyak (1976) and a good agreement with the former is obtained. As mentioned earlier, Nelson and Holonyak estimate a large bowing of 0.2 eV for this indirect gap, which is at variance with the conclusions reached from other experiments (Onton and Chikotka 1971, Joullie and Alibert 1974).

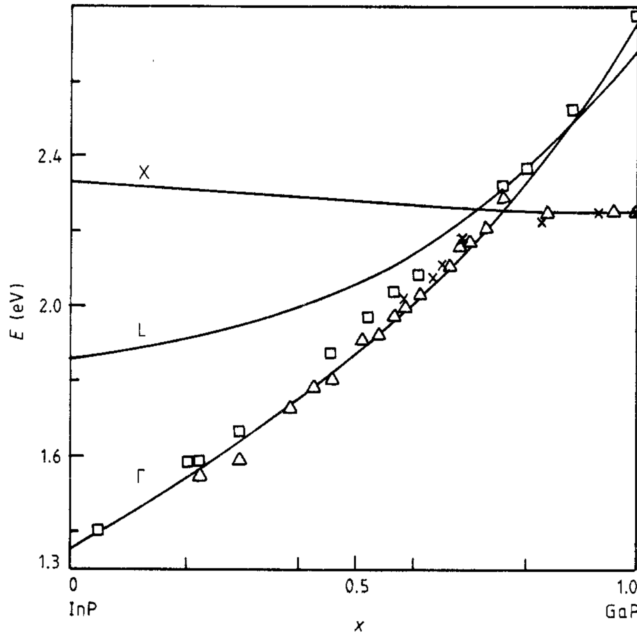

Figure 12. The present theoretical band gaps between the states Γ_{1c}, X_{1c} and L_{1c} and the states Γ_{15v} (——) with composition x of gallium in $Ga_xIn_{1-x}P$. The experimental measurements are from the following: ×, Nelson and Holonyak (1976); △, Onton *et al* (1971); and □, Alibert *et al* (1972).

The present calculation predicts a single crossover between the lowest direct and the indirect Γ–X gaps at $x_c = 0.77$ which is close to the experimentally determined value of 0.74 (Onton and Chikotka 1971, Macksey *et al* 1973, Lee *et al* 1974). Various experimental measurements (Alibert *et al* 1972, Hakki *et al* 1970, Williams *et al* 1970) yield the value of x_c ranging from 0.63 to 0.74. The results of the present CPA calculation, like those of Chen and Sher (1981), are found to disagree with the hypothesis of two crossovers between the direct and indirect gaps for this ternary alloy, proposed by Merle *et al* (1977) and Pitt *et al* (1974) and supported by the semielliptic DOS model of Bugajski *et al* (1983).

3.4. $Ga_xIn_{1-x}As$

Valence band energies in CPA for this ternary alloy have been calculated previously by Chen and Sher (1978) using the bond orbital model. Figure 13 presents the variation of the usual seven energy states with composition x of gallium in the ternary alloy $Ga_xIn_{1-x}As$, obtained from the present calculations, and the bowing parameters of these energy levels are listed in table 5. It is seen that the pattern of the effect of disorder on various states and the bowing parameters is similar to that of $Ga_xIn_{1-x}P$. However, in this case the VCA contribution to the bowing of the conduction states X_{1c} is comparatively larger. Like $InAs_{1-x}P_x$, no crossing of bands is observed for this alloy also. Table 5 also shows the bowings of the lowest direct and the two indirect Γ–X and Γ–L energy gaps, their average values being 0.8, 0.34 and 0.6 eV, respectively. The variation of the direct energy gap with x is presented in figure 14, where the results of the present calculation are compared with the molecular CPA (MCPA) calculation of Hass *et al* (1983) and the

Table 4. Bowing parameters (eV) for the seven energy states, the energy gaps $E_g(\Gamma)$, $E_g(X)$ and $E_g(L)$ calculated in CPA and VCA (in parentheses) for the ternary alloy $Ga_xIn_{1-x}P$.

	$x = 0.1$	0.3	0.5	0.7	0.9	Average bowing
Γ_{15v}	−0.0289 (−0.033)	−0.032 (−0.0333)	−0.028 (−0.032)	−0.0329 (−0.0333)	−0.028 (−0.0333)	
Γ_{1c}	0.421 (−0.0011)	0.578 (−0.0048)	0.738 (0.002)	0.9 (0.0014)	0.69 (0.0011)	
X_{5v}	−0.0311 (−0.032)	−0.0262 (−0.0271)	−0.0212 (−0.022)	−0.0195 (−0.0205)	−0.022 (−0.0233)	
X_{1c}	0.033 (0.019)	0.027 (0.0148)	0.0168 (0.014)	0.0181 (0.0138)	0.0189 (0.0144)	
X_{3c}	−1.225 (0.049)	−1.084 (0.043)	−0.664 (0.04)	−0.438 (0.037)	−0.321 (0.04)	
L_{3v}	−0.0633 (−0.064)	−0.0581 (−0.059)	−0.0552 (−0.056)	−0.0543 (−0.055)	−0.056 (−0.058)	
L_{1c}	0.459 (0.114)	0.658 (0.104)	0.822 (0.098)	0.867 (0.091)	0.987 (0.0856)	
$E_g(\Gamma)$	0.454 (0.0322)	0.621 (0.037)	0.766 (0.034)	0.934 (0.0348)	0.723 (0.0344)	0.7 (0.0345)
$E_g(X)$	0.0633 (0.052)	0.0576 (0.0481)	0.046 (0.046)	0.051 (0.047)	0.048 (0.048)	0.0532 (0.0482)
$E_g(L)$	0.492 (0.148)	0.69 (0.138)	0.85 (0.13)	0.9 (0.124)	1.014 (0.119)	0.79 (0.132)

Table 5. Bowing parameters (eV) for the seven energy states and the three energy gaps calculated in CPA and VCA (in parentheses) for the alloy $Ga_xIn_{1-x}As$.

	$x = 0.1$	0.3	0.5	0.7	0.9	Average bowing
Γ_{15v}	−0.1 (−0.101)	−0.111 (−0.110)	−0.114 (−0.114)	−0.117 (−0.118)	−0.121 (−0.121)	
Γ_{1c}	0.297 (0.024)	0.392 (0.022)	0.588 (0.024)	0.866 (0.0257)	1.269 (0.031)	
X_{5v}	−0.022 (−0.023)	−0.024 (−0.025)	−0.025 (−0.026)	−0.026 (−0.027)	−0.02 (−0.0211)	
X_{1c}	0.228 (0.223)	0.229 (0.225)	0.228 (0.222)	0.222 (0.218)	0.216 (0.21)	
X_{3c}	−0.412 (0.0122)	−0.359 (0.011)	−0.33 (0.01)	−0.544 (0.013)	−0.378 (0.01)	
L_{3v}	−0.0074 (−0.009)	−0.0105 (−0.0114)	−0.0112 (−0.012)	−0.0114 (−0.0124)	−0.0119 (−0.0133)	
L_{1c}	0.394 (0.121)	0.608 (0.118)	0.758 (0.114)	0.903 (0.111)	0.954 (0.112)	
$E_g(\Gamma)$	0.397 (0.126)	0.502 (0.133)	0.702 (0.258)	0.981 (0.143)	1.39 (0.152)	0.7944 (0.1624)
$E_g(X)$	0.328 (0.324)	0.34 (0.336)	0.341 (0.336)	0.34 (0.335)	0.337 (0.331)	0.3372 (0.3324)
$E_g(L)$	0.495 (0.222)	0.719 (0.229)	0.872 (0.228)	1.02 (0.229)	1.075 (0.233)	0.836 (0.228)

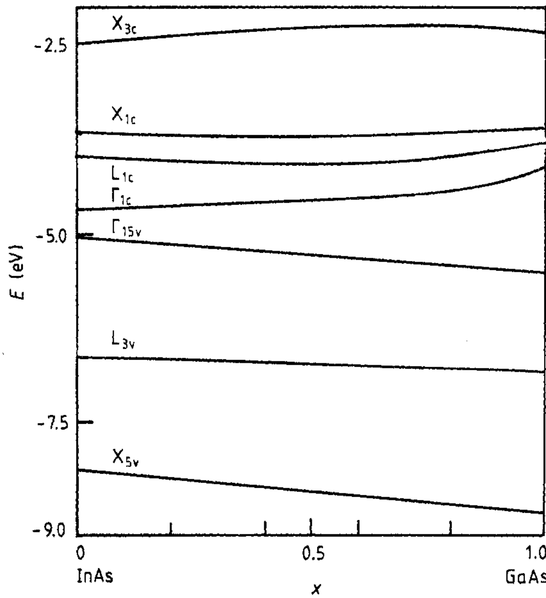

Figure 13. Variation of the indicated symmetry-point energies with concentration x of gallium in $Ga_xIn_{1-x}As$.

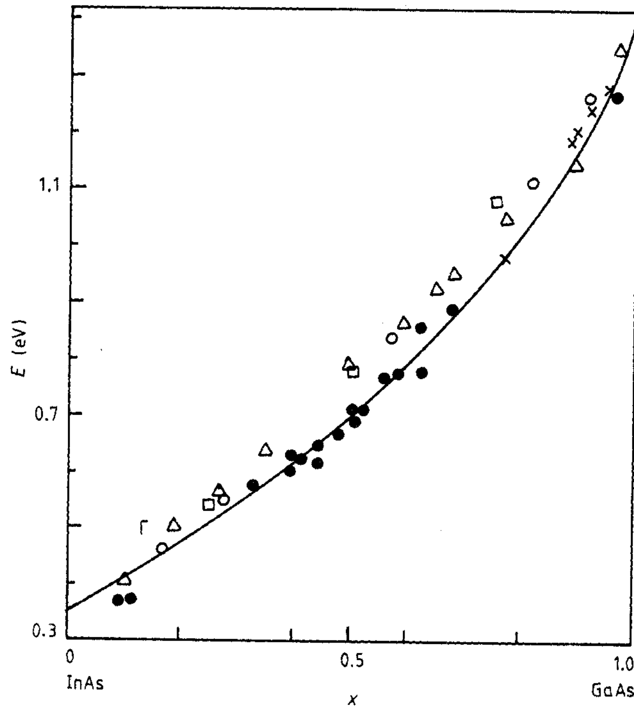

Figure 14. The present theoretical band gap between the states Γ_{1c} and Γ_{15v} (——) with composition x of gallium in $Ga_xIn_{1-x}As$. The experimental measurements are from the following: ○, Wu and Pearson (1972); △, Woolley *et al* (1961); ●, Hockings *et al* (1966); and ×, Antypas (1970). Also shown is the molecular CPA calculation (□) of Hass *et al* (1983).

experimental data of Hockings *et al* (1966), Antypas (1971), Wu and Pearson (1972) and Woolley *et al* (1961). It is seen that the present calculations agree with the experimental findings of Hockings *et al* (1966) and Antypas (1971), who measure a larger bowing for the direct gap than the other two. Hass *et al* (1983) have calculated the CPA and MCPA bowings only at $x = 0.25$, 0.5 and 0.75 and find that MCPA predicts a smaller bowing compared to CPA. Their MCPA results seem to agree with the experiments of Woolley *et al* (1961) and Wu and Pearson (1972).

4. Conclusions

The results of band-structure calculations in the CPA have been presented for the mixed III–V semiconductors $GaAs_{1-x}P_x$, $Ga_xIn_{1-x}P$, $Ga_xIn_{1-x}As$ and $InAs_{1-x}P_x$. In particular, detailed energy bands have been calculated and discussed for the first time for the last two alloy systems. These room-temperature band structures were obtained in the tight-binding framework, neglecting spin–orbit interaction. This interaction term can play an important role in determining the band structure of semiconductors, especially for InAs where the spin–orbit splitting at Γ is of the order of the band gap. However, the value of direct energy gap in InAs, presently obtained from the tight-binding parameters of Porod *et al* (1982), is in agreement with the experimental value (Kressel and Butler 1977). Moreover, the electron band structure, including the major energy gaps and the DOS, calculated by Talwar and Ting (1982) match very well with those of Chelikowsky and Cohen (1976), where the latter include the spin–orbit term, while the former do not. For InAs, in particular, the two calculations yield almost the same DOS curves with only a slight mismatch at 1–2 eV below the top of the valence band. In the present calculations, the VCA DOS is used in equation (6) so that no mixing of states takes place during interaction. Therefore, neglect of spin–orbit interaction is not expected to affect a discussion of the band gaps in $Ga_xIn_{1-x}As$ and $InAs_{1-x}P_x$ in the present case.

It is seen that the calculated values of energy-gap variation and bowing are in good agreement with the experimental data for all the four ternary alloys studied here. Also, the present calculations predict a crossover between direct and indirect energy gaps in $GaAs_{1-x}P_x$ and $Ga_xIn_{1-x}P$ correctly. A controversy exists in $Ga_xIn_{1-x}P$ regarding the nature and location of this crossover, and the present calculations support the hypothesis of a single crossover between the Γ and X bands.

The present calculations indicate that the CPA self-energy effects are larger for the cation-substituted alloys $Ga_xIn_{1-x}P$ and $Ga_xIn_{1-x}As$, primarily because of the large alloy scattering parameter Δ_s for the s-like states. This explains qualitatively the large bowing observed for the direct as well as the indirect L energy gap (~0.7 eV) observed experimentally. The comparatively smaller bowing observed for the X indirect gap may also be understood within this framework, since the lowest conduction state at X in these alloys is primarily p-like.

Our results for the seven energy bands for $GaAs_{1-x}P_x$ and $Ga_xIn_{1-x}P$ differ qualitatively from those of Chen and Sher (1981). For example, they predict a large CPA self-energy correction for the conduction band Γ_{1c} compared to that of valence band Γ_{15v} in $GaAs_{1-x}P_x$, and vice versa for $Ga_xIn_{1-x}P$. The present calculations, on the other hand, show just the reverse trend. This may be attributed partly to the difference in the definition of the alloy scattering parameters, which are measured in terms of atomic values in the present case and in terms of bonding and antibonding energies by Chen and Sher. Our calculations predict a negative bowing for the conduction state X_{3c} in the

cation-substituted alloys $Ga_xIn_{1-x}P$ and $Ga_xIn_{1-x}As$, even though both the present calculations as well as those of Chen and Sher obtain a positive bowing for the conduction states and a negative bowing for the valence states in general.

The present CPA calculation of the energy band structure of III–V semiconductors takes account of only the diagonal component of the alloy disorder. The effect of off-diagonal disorder on band-gap bowing has been calculated for the ternary alloy $Ga_xIn_{1-x}As$ (Hass *et al* 1983, Krishnamurthy 1987), and both these calculations show that the bowing is reduced by ~20% when full disorder is considered instead of only its diagonal component. However, a good match between theory and experiment is obtained for all the four ternary alloys studied here, including $Ga_xIn_{1-x}As$. Therefore, it appears that the off-diagonal disorder term does not play an important role in determining the band structure of these ternary alloys.

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