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Energy bands of ternary alloy semiconductors: Coherent-potential-approximation calculations

M. Bugajski and A. M. Kontkiewicz
Institute of Electron Technology, Aleja Lotników 32/46, PL-02-668 Warsaw, Poland

H. Mariette
Laboratoire de Physique des Solides, Centre National de la Recherche Scientifique, 1 place Aristide Briand, F-92190 Meudon-Bellevue, France

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A method for calculating compositional variations of energy bands of ternary alloy semiconductors based on the coherent-potential approximation is presented. A generalized, Soven-type equation in a matrix form is derived and then solved by subsequent iterations. Zeroth-order approximation for band-gap energies is taken from the virtual-crystal approximation. The nonlinear dependence of the energy upon the alloy composition at various symmetry points within the first Brillouin zone is calculated for $GaAs_{1-x}P_x$ and $Ga_xIn_{1-x}P$ crystals. Significant band bowing has been found in both cases. The theoretical results are compared with experimental data available for these systems.

I. INTRODUCTION

Extensive experimental investigations of the electronic structure of compound semiconductors have been carried out because of their importance in optoelectronic device technology. Consequently, a quantitative understanding of important apsects of the band structure such as variations of band gaps in different symmetry points of the Brillouin zone has been gained.

However, the theory of substitutional alloys in quite unsatisfactory. The fundamental difficulty in such analysis is that no exact solution of the Schrödinger equation for the disordered system is obtainable. This motivated an interest in approximate theories.

The models which have been frequently used to describe the electronic structure of semiconductor alloys are the virtual-crystal approximation[1] (VCA) and semiempirical dielectric model (DM) of Van Vechten and Bergstresser.[2] None of them, however, can account for the full range of important band properties that are known from experiment.

The theories which can provide this are the ones derived from the multiple-scattering description of disordered systems.[3] Such procedure is appropriate if the disordered potential of the alloy can be decomposed into a sum of contributions due to the individual atomic scatters. The propagation of an electron through such system can therefore be treated as a succession of elementary scatterings from these randomly distribution atomic potentials.

Most of the works have used a single-site approximation in which scattering of the electron wave from one site is taken into account exactly, while the remainder of the crystal is treated at best as a mean environment. Crucial for these theories is a choice of the so-called effective medium in which individual scatters are embedded. If the effective medium is determined by requiring that it reproduce the average scattering at each site, we deal with the average—*t*-matrix approximation (ATA).[4–6] The next development was the coherent-potential approximation (CPA) of Soven.[7] The CPA adds to the ATA the idea of self-consistency. Stroud and Ehrenreich[8] first applied the CPA method to semiconductor alloys. Their calculations, however, involved complicated Brillouin-zone integrations. Furthermore, their results, due to a small difference between Si and Ge potentials, were not so different from VCA results. The considerable progress has been made in recent years. CPA calculations, based on the method of linear combination of bond orbitals, have been applied to the number of III-V alloys.[9–13] On the other hand, Mariette *et al.*[14] instead of using a tight-binding approximation have adopted for their calculations a semielliptic density of states suggested by Hubbard.[15] Their calculations for the $GaAs_{1-x}P_x$ alloys have shown the ability of this method to account for not only the compositional dependence of band gaps, but also, with cluster-type extension,[16] to incorporate the local environment effect on the nitrogen bound-exciton state.

This paper is concerned with detailed calculations of energy bands of ternary alloy semiconductors: $GaAs_{1-x}P_x$ and $Ga_xIn_{1-x}P$. The calculations are based on the formulation of Mariette *et al.*[14] of the CPA method, however, certain extensions of their treatment are introduced. This paper presents a systematic derivation of generalized, multiband Soven-type equation in a matrix form. This form of the CPA equation is particularly suited for iterative numerical calculations. The preliminary results of these calculations have been published elsewhere.[17]

II. CPA CALCULATIONS FOR TERNARY ALLOY SEMICONDUCTORS

This section develops the formalism underlying the single-site approximation and derives a generalized

Soven-type CPA equation for ternary alloy semiconductors. The single-particle properties of the system are described by the resolvent operator $G(z)$,

$$G(z)=(z-H)^{-1}\ , \tag{2.1}$$

where H is the configuration-dependent one-electron Hamiltonian. The macroscopic properties of the crystal depend on an average taken over all configurations and can be determined from an average resolvent operator $\langle G(z)\rangle$

$$\langle G(z)\rangle=\langle (z-H)^{-1}\rangle\ . \tag{2.2}$$

The CPA method is based on the assumption that an effective Hamiltonian can be defined by the relation

$$\langle G(z)\rangle=(z-H_{\text{eff}})^{-1}\ . \tag{2.3}$$

H_{eff} is configuration independent and possesses full crystal symmetry, although it is energy dependent and non-Hermitian, which results in finite lifetime of electron states. When employed, the effective Hamiltonian does not produce further scattering from the individual states on the average. It incorporates such a potential that an electron wave propagates coherently through the material. Once the function $G(z)$ is known, the density of states per atom can be calculated from the standard formula

$$\rho(E)=-\frac{1}{\pi N}\text{Im}\,\text{Tr}G(z)\ . \tag{2.4}$$

In the case of an alloy, relation (2.4) takes the form

$$\rho(E)=-\frac{1}{\pi N}\text{Im}\,\text{Tr}\langle G(z)\rangle=-\frac{1}{\pi}\text{Im}F(z)\ , \tag{2.5}$$

where the diagonal element of the averaged Green's function $\langle G(z)\rangle$ is denoted by $F(z)$

$$F(z)=\langle 0\,|\,\langle G(z)\rangle\,|\,0\rangle=\frac{1}{N}\text{Tr}\langle G(z)\rangle\ . \tag{2.6}$$

In a simplest approximation to CPA, i.e., a single-site approximation,[18] the mixed crystal is replaced by an effective medium created by placing on every lattice site the energy-dependent complex potential σ, the so-called self-energy. The self-energy σ is chosen in such a way that the average scattering on the ith site on which σ is replaced by the actual potential (V^A or V^B) is the same as if there was potential σ. That means there is no scattering at all, since σ is the same as the potential assumed for all other sites; that is, the averaged t matrix for the scattering should vanish. The ternary alloy semiconductor can be treated as a pseudobinary compound of A_xB_{1-x} type. Using this notation, we have the following equivalences:

$$\text{GaAs}_{1-x}\text{P}_x \leftrightarrow (\text{GaP})_x(\text{GaAs})_{1-x} \leftrightarrow A_xB_{1-x}\ ,$$

$$\text{Ga}_x\text{In}_{1-x}\text{P} \leftrightarrow (\text{GaP})_x(\text{InP})_{1-x} \leftrightarrow A_xB_{1-x}\ .$$

The configurational average of the scattering t matrix is simply the weighted average

$$\langle t\rangle=xt^A+(1-x)t^B\ , \tag{2.7}$$

where the t matrices associated with the individual sites are given by[18,19]

$$t^{A,B}=\frac{V^{A,B}-\sigma(z)}{1-F(z)[V^{A,B}-\sigma(z)]}\ . \tag{2.8}$$

The $V^{A,B}$ represent in a single-site approximation the one-electron energies for the particular site of an alloy described by the tight-binding Hamiltonian

$$H=\sum_{n}|\,n\,\rangle V_n\langle\, n\,|+\sum_{\substack{n,m\\ n\neq m}}|\,n\,\rangle h_{nm}\langle\, m\,|\ . \tag{2.9}$$

As has been pointed out by Mariette *et al.*,[14] in a semiconductor alloy it is necessary to account for three subbands of a conduction band, i.e., to introduce three self-energies σ_α $(\alpha=\Gamma,X,L)$ as well as to express the total Green's function for the alloy in the form of a sum over subbands

$$F=\sum_{\alpha=\Gamma,X,L}F_\alpha\ . \tag{2.10}$$

By substituting (2.10) and (2.8) into (2.7), and imposing the condition of vanishing of the average t matrix, the CPA equation for the substitutional ternary alloy can be written as

$$\frac{x(V_\alpha^A-\sigma_\alpha)}{1-\Delta V^AF}+\frac{(1-x)(V_\alpha^B-\sigma_\alpha)}{1-\Delta V^BF}=0\ , \tag{2.11}$$

where

$$\Delta V^{A,B}F=\sum_{\alpha=\Gamma,X,L}(V_\alpha^{A,B}-\sigma_\alpha)F_\alpha\ . \tag{2.12}$$

The equation (2.11) is to be solved self-consistently. Taking into account (2.12), it can be rewritten in the form

$$x(V_\alpha^A-\sigma_\alpha)\left[1-\sum_{\alpha}(V_\alpha^B-\sigma_\alpha)F_\alpha\right]+(1-x)(V_\alpha^B-\sigma_\alpha)\left[1-\sum_{\alpha}(V_\alpha^B-\sigma_\alpha)F_\alpha\right]=0\ . \tag{2.13}$$

Setting $\alpha=\Gamma$, one can obtain

$$\begin{aligned}&x(V_\Gamma^A-\sigma_\Gamma)\left[1-\left[(V_\Gamma^B-\sigma_\Gamma)F_\Gamma+\sum_{\alpha\,(\neq\Gamma)}(V_\alpha^B-\sigma_\alpha)F_\alpha\right]\right]\\ &\qquad+(1-x)(V_\Gamma^B-\sigma_\Gamma)\left[1-\left[(V_\Gamma^A-\sigma_\Gamma)F_\Gamma+\sum_{\alpha\,(\neq\Gamma)}(V_\alpha^A-\sigma_\alpha)F_\alpha\right]\right]=0\ ,\end{aligned} \tag{2.14}$$

and furthermore,

$$xV_\Gamma^A+(1-x)V_\Gamma^B-(V_\Gamma^A-\sigma_\Gamma)F_\Gamma(V_\Gamma^B-\sigma_\Gamma)-\sigma_\Gamma -x(V_\Gamma^A-\sigma_\Gamma)\sum_{\alpha\,(\neq\Gamma)}(V_\alpha^B-\sigma_\alpha)F_\alpha-(1-x)(V_\Gamma^B-\sigma_\Gamma)\sum_{\alpha\,(\neq\Gamma)}(V_\alpha^A-\sigma_\alpha)F_\alpha=0\ . \tag{2.15}$$

The expression $xV_\Gamma^A+(1-x)V_\Gamma^B=V_\Gamma$ is a linearly interpolated potential value between binary constitutent, i.e., V_Γ is the VCA potential. Therefore, the self-energy σ_Γ can be finally expressed in a form convenient for iterative calculations:

$$\sigma_\Gamma=V_\Gamma-(V_\Gamma^A-\sigma_\Gamma)F_\Gamma(V_\Gamma^B-\sigma_\Gamma)-x(V_\Gamma^A-\sigma_\Gamma)F_X(V_X^B-\sigma_X)-(1-x)(V_\Gamma^B-\sigma_\Gamma)F_X(V_X^A-\sigma_X) -x(V_\Gamma^A-\sigma_\Gamma)F_L(V_L^B-\sigma_L)-(1-x)(V_\Gamma^B-\sigma_\Gamma)F_L(V_L^A-\sigma_L)\ . \tag{2.16}$$

The expressions for σ_X and σ_L can be derived in exactly the same way by setting in (2.13) $\alpha=X$ and $\alpha=L$, respectively. It can be easily noticed that each of the expressions for σ_α has the following form

$$\sigma_\alpha=V_\alpha-(V_\alpha^A-\sigma_\alpha)F_\alpha(V_\alpha^B-\sigma_\alpha)-\cdots\ , \tag{2.17}$$

where the ellipsis stands for the remaining terms. The part $V_\alpha-(V_\alpha^A-\sigma_\alpha)F_\alpha(V_\alpha^B-\sigma_\alpha)$ is exactly the result obtained by Soven[7] in the case of one-band model. It describes the contribution to the self-energy coming from a substitutional A-B disorder within the particular subband. The remaining four terms are the compositionally weighted contributions due to off-diagonal interactions of a given subband with the remaining two ones. The original Soven equation has a scalar form and appears to be a special case of generalized matrix equation referring to our case, which reads as follows:

$$\begin{bmatrix}\sigma_\Gamma\\ \sigma_X\\ \sigma_L\end{bmatrix}=\begin{bmatrix}V_\Gamma\\ V_X\\ V_L\end{bmatrix}-\underline{S}\begin{bmatrix}F_\Gamma\\ F_X\\ F_L\end{bmatrix}\ , \tag{2.18}$$

or using a closed-form notation,

$$\sigma_\alpha=V_\alpha-S_{\alpha\beta}F^\beta\ . \tag{2.19}$$

The complete $\underline{S}$ matrix is given in Table I.

The valence band is treated here within a framework of a simple, single-band model. The appropriate self-energy is derived from the equation

$$\sigma_{v\Gamma}=V_{v\Gamma}-(V_{v\Gamma}^A-\sigma_{v\Gamma})F_{v\Gamma}(V_{v\Gamma}^B-\sigma_{v\Gamma})\ , \tag{2.20}$$

where

$$V_{v\Gamma}=xV_{v\Gamma}^A+(1-x)V_{v\Gamma}^B \tag{2.21}$$

and $F_{v\Gamma}$ is an alloy Green's function for the valence band.

TABLE I. Elements of S matrix.

$S_{11}=(V_\Gamma^A-\sigma_\Gamma)(V_\Gamma^B-\sigma_\Gamma)$

$S_{12}=x(V_\Gamma^A-\sigma_\Gamma)(V_X^B-\sigma_X)+(1-x)(V_\Gamma^B-\sigma_\Gamma)(V_X^A-\sigma_X)$

$S_{13}=x(V_\Gamma^A-\sigma_\Gamma)(V_L^B-\sigma_L)+(1-x)(V_\Gamma^B-\sigma_\Gamma)(V_L^A-\sigma_L)$

$S_{21}=x(V_X^A-\sigma_X)(V_\Gamma^B-\sigma_\Gamma)+(1-x)(V_X^B-\sigma_X)(V_\Gamma^A-\sigma_\Gamma)$

$S_{22}=(V_X^A-\sigma_X)(V_X^B-\sigma_X)$

$S_{23}=x(V_X^A-\sigma_X)(V_L^B-\sigma_L)+(1-x)(V_X^B-\sigma_X)(V_L^A-\sigma_L)$

$S_{31}=x(V_L^A-\sigma_L)(V_\Gamma^B-\sigma_\Gamma)+(1-x)(V_L^B-\sigma_L)(V_\Gamma^A-\sigma_\Gamma)$

$S_{32}=x(V_L^A-\sigma_L)(V_X^B-\sigma_X)+(1-x)(V_L^B-\sigma_L)(V_X^A-\sigma_X)$

$S_{33}=(V_L^A-\sigma_L)(V_L^B-\sigma_L)$

In order to calculate the compositional variations of energy bands in the alloy it is necessary to specify some unperturbed densities of states. The simplest approximation is the semielliptic partial density of states[14,15]

$$\rho_\alpha^0(E)=\begin{cases}\dfrac{2P_\alpha}{\pi W_\alpha}[W_\alpha^2-(E-V_\alpha)^2]^{1/2} & \text{for } |E-V_\alpha|\le W_\alpha\\ 0 \ \text{ for } |E-V_\alpha|>W_\alpha\ . & \end{cases} \tag{2.22}$$

This approximation is well justified for binary limits even sufficiently far from the band edges: This can be checked with the use of the band structure as obtained from pseudopotential calculations.[20] It still holds, although with limited accuracy, for ternary compounds. The density-of-states model that is used is acceptable for Γ as well as for X and L regions of the conduction band; the model has been recently proved by its ability to fit spectral dependence of the optical cross sections for the transitions between a localized level and the conduction band.[21] On the other hand, using a more realistic density-of-states model, one needs to adjust more parameters to describe it.

The P_α is a partition function satisfying the normalization condition

$$\int_{-\infty}^{\infty}\rho_\alpha^0(E)dE=P_\alpha\ . \tag{2.23}$$

It can be calculated by purely geometrical considerations applied to the first Brillouin zone of the crystal.[14] The total unperturbed density of the states for the alloy is given by

$$\rho^0(E)=\sum_{\alpha=\Gamma,X,L}\rho_\alpha^0(E)\ , \tag{2.24}$$

whereas $\rho_\alpha^0(E)$ is the contribution to the total density of states from the subband α centered at V_α and having the halfwidth W_α.

The density of states in the alloy is related to the one-particle Green's function by the equation (2.5). Taking into account three subbands of the conduction band, one can obtain the following expression for the partial density of states $\rho_\alpha^0(E)$:

$$\rho_\alpha^0(E)=-\frac{1}{\pi}\mathrm{Im}F_\alpha^0(z)\ . \tag{2.25}$$

Making use of the Hilbert transform,[22] we find the following explicit expression can be written for the alloy Green's function:

TABLE II. Band-structure parameters for binary GaAs, InP, and GaP compounds (all energies refer to 0 K).

	GaAs				InP				GaP			
	m_α (m_e)	E_G (eV)	E_α (eV)	V_α^B (eV)	m_α (m_e)	E_G (eV)	E_α (eV)	V_α^B (eV)	m_α (m_e)	E_G (eV)	E_α (eV)	V_α^A (eV)
Γ_{15v}	0.61[a]		−5.6[b]	−7.584	0.87[a]		−5.7[b]	−7.051	0.83[a]		−5.7	−7.342
Γ_{1c}	0.067[c]	1.519[d]	−4.081	−1.903	0.077	1.418	−4.282	−2.523	0.135	2.884[d]	−2.816	−1.653
X_{1c}	0.850[c]	1.981[d]	−3.619	−2.703	0.88[e]	2.369	−3.331	−2.51	0.820	2.350[f]	−3.35	−2.328
L_{1c}	0.560[c]	1.815	−3.785	−2.387	1.01	1.910	−3.79	−3.071	1.01	2.745	−2.955	−2.121

[a] Reference 27.
[b] Reference 9.
[c] Reference 23.
[d] Reference 25.
[e] Reference 24.
[f] Reference 26.

$$F_\alpha^0(z)=\int_{-\infty}^{\infty}\frac{\rho_\alpha^0(E)}{z-\sigma_\alpha(z)-E}dE\ . \tag{2.26}$$

The above integral has been evaluated using the unperturbed density of states given by (2.22),

$$F_\alpha(z)=\frac{2P_\alpha}{W_\alpha^2}\{z-\sigma_\alpha+[(z-\sigma_\alpha)^2+W_\alpha^2]^{1/2}\}\ . \tag{2.27}$$

The halfwidth of the semielliptic bands can be simply expressed as a function of a lattice constant denoted by a and the effective mass m_α

$$W_\alpha=\frac{(4\pi P_\alpha)^{2/3}\hbar^2}{a^2 m_\alpha}\ . \tag{2.28}$$

It has been assumed for the calculations that V_α and W_α vary linearly with composition.

III. NUMERICAL CALCULATIONS

The theory formulated in the preceding section has been used to calculate the band structure of selected ternary alloys. Both the absolute energy variations at main symmetry points of the Brillouin zone as well as the energy gaps at these points have been calculated. The materials chosen are $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ and $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ for their technological importance and the availability of experimental data. With these materials we could compare numerous experimental results from different laboratories. Moreover, the case of $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ is also challenging since there is still an unresolved question about location and the nature of direct-indirect crossover in this material.

The numerical values of band-structure parameters for binary limits of considered ternary alloys are listed in Table II. Conduction-band effective masses for GaAs and GaP are well established from various experiments, whereas for InP there are some discrepancies in the values listed in the literature. Particularly, the effective mass at L minimum is uncertain. For the calculations we have adopted the value $1.01m_0$, which is the same as m_L in GaP and produces correct downward bowing of the L subband in mixed crystal.

The valence-band masses listed in Table II, due to the lack of reliable experimental data, have been calculated as the density-of-states effective masses with the use of theoretical heavy-hole and light-hole effective masses given by Lawaetz.[27] The contribution from a spin-orbit split-off band has been neglected.

The only absolute energies that enter calculations are E_α's at Γ_{15v}, i.e., the top of valence band in III-V compounds. They have been taken from photoelectric thresholds obtained by fitting the x-ray photoemission spectra.[28] The values of E_α for the conduction-band subbands (Γ,X,L) are computed using appropriate values of energy gaps Γ_{1c}-Γ_{15v}, X_{1c}-Γ_{15v}, and L_{1c}-Γ_{15v}, which are known from the experiment.

The energetic positions of the centers of each semielliptic band have been calculated from the relation (2.28). For the calculations of partitioning of Brillouin zone we have adopted the scheme proposed by Mariette *et al.*,[14] which gives the following values of P_α's for III-V compounds with zinc-blende structure:

$$P_\Gamma = 0.0379\ ,$$

$$P_X = 0.4792\ ,$$

$$P_L = 0.4829\ .$$

The lattice constants required to calculate the halfwidths of the semielliptic bands in binary compounds are listed below[29]:

$$a_{\mathrm{GaAs}} = 5.653\ ,$$

$$a_{\mathrm{InP}} = 5.869\ ,$$

$$a_{\mathrm{GaP}} = 5.451\ ,$$

in units of Å.

For a given composition of a mixed crystal, $V_\alpha(x)$ and $W_\alpha(x)$ are calculated by a linear interpolation between the binary limits. Then the equation (2.27) is used to calculate the alloy Green's function $F_\alpha(z)$. As a first approximation for the self-energy we set the VCA result $\sigma_\alpha(z) = V_\alpha(x)$, which is actually energy independent. The starting energy, denoted here by z variable, is chosen well below the unperturbed band edge, which results in real $F_\alpha(z)$. This greatly simplifies further calculations. At the same time a complete $\underline{S}$ matrix is computed and a new self-energy $\sigma(z)$ is obtained from the matrix equation (2.18). The new $\sigma(z)$ is used to compute a new $F(z)$ and a new $\underline{S}$ matrix, and the whole procedure is repeated until a self-consistent value of $\sigma_\alpha(z)$ is attained. Sufficient convergence is accomplished by iterating several times. For this $\sigma_\alpha(z)$ we check the imaginary part of $F_\alpha(z)$, and if it is equal to zero, then the z variable is incremented and new self-consistent $\sigma_\alpha(z+\Delta z)$ and $F_\alpha(z+\Delta z)$ are calculated. At the moment when for some $F_\alpha(z+n\,\Delta z)$ we get $\mathrm{Im}F>0$, the precise location of the band edge is tracked by bisection procedure applied to the z range $[z+n\,\Delta z, z+(n-1)\Delta z]$. Such numerical procedure is very efficient, and combined with rapidly convergent σ_α, it results in reasonable computing times.

IV. RESULTS AND DISCUSSION

The results of calculation of energy at the main symmetry points versus the alloy composition for $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ and $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ at the absolute-zero temperature are shown in Figs. 1 and 2. Zero of energy corresponds to the vacuum level. The energy variations are characterized by the so-called bowing parameter defined as 4 times the energy deviation from straight-line interpolation at $x=0.5$.[2] One can notice that both the conduction and valence bands contribute to the total bowing of the band gap. Furthermore, the amount of bowing is different for different subbands of the conduction band. This result supports the earlier claim that the effect of disorder is different at different points of the Brillouin zone. Altarelli[30] has argued that this variations can be explained by the difference in the ionic pseudopotentials of the alloyed elements. On the other hand, a definite correlation between the bowing parameters for several ternary alloys and the lattice constant differences between the two end-point binary compounds has been found.[31] While there is some scatter in the experimental data, there does appear to be a trend toward larger bowing parameters with larger lattice constant differences. Both these facts are inherent to our theoretical treatment. The main equations of CPA theory, i.e., (2.11) and (2.12), involve $V^{A,B}$—the one-electron energies for the particular site of an alloy described by the tight-binding Hamiltonian (2.9). In the case of our model, where the density of states has semielliptic form suggested by Hubbard, these energies refer to the centers of each band. They are calculated from the known positions of band edges and the halfwidths W_α of the band in question. The latter depends on the lattice constant, effective mass, and, throughout the partition function P_α, the geometry of the Brillouin zone.

The inspection of Figs. 1 and 2 shows that there is no correlation between the bowing parameter and the energy differences between the binary end-point compounds. This is particularly striking when comparing bowing at Γ and L minima of the conduction band in $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$. However, if we plot the linearly interpolated positions of the centers of each band versus the composition of the alloy (as has been done in Fig. 3), one can observe that they do not follow the variations of band edges, which are represented here by straight-line interpolation. Figure 3

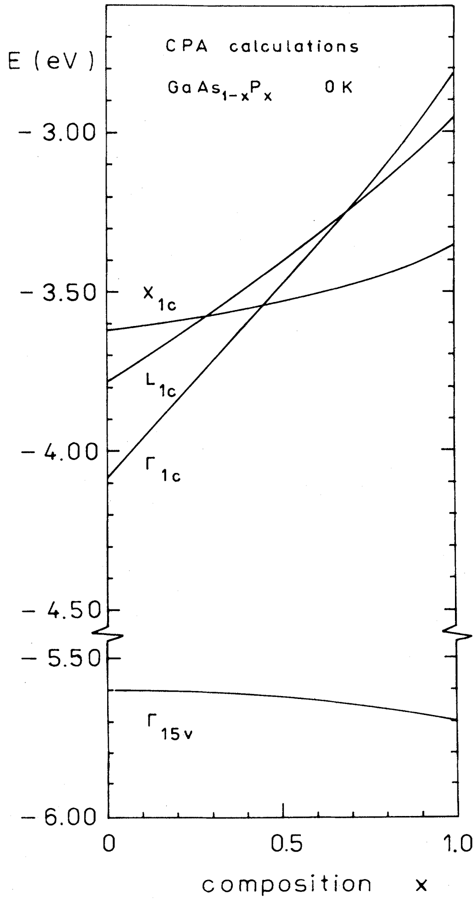

FIG. 1. Calculated energies at the main symmetry points of Brillouin zone versus alloy composition for $\mathrm{GaAs}_{1-x}\mathrm{P}_x$.

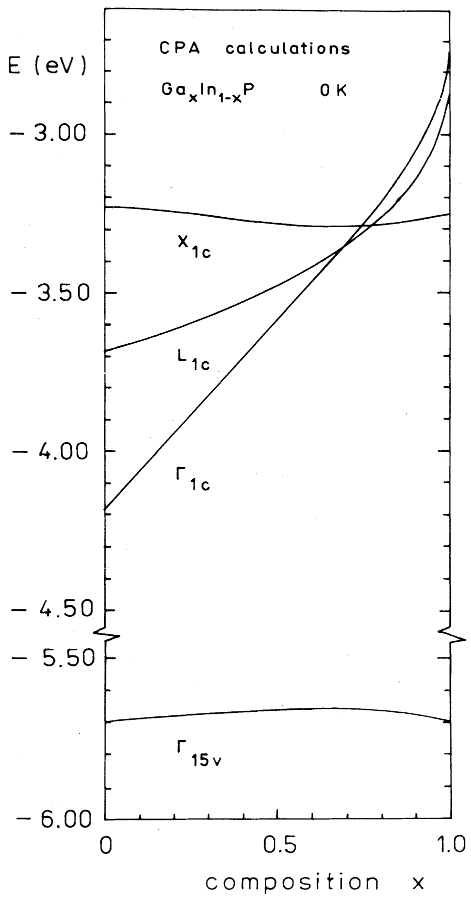

FIG. 2. Calculated energies at the main symmetry points of Brillouin zone vs alloy composition for $Ga_xIn_{1-x}P$.

reveals a clear trend: The higher the energy difference between the centers of a given band, the greater is the value of bowing parameter for this band. This is illustrated in Fig. 4. The straight line drawn in Fig. 4, fitted by the least-squares method, gives an approximate relationship between the absolute value of the energy different $|\Delta V_\alpha|$ and the bowing parameter b_α,

$$b_\alpha = 0.67\,|\Delta V_\alpha| \; . \tag{4.1}$$

The equation (4.1) can be used for quick, rough estimation of an unknown bowing parameter without the necessity of performing complicated numerical calculations.

The parameter that can be easily referred to the experimental results is the band gap. Therefore we plot in Figs. 5 and 6 the compositional variations of the band gaps at the main symmetry points both for $GaAs_{1-x}P_x$ and $Ga_xIn_{1-x}P$ alloys. The solid lines are derived from our work, whereas dashed lines are from the work of Chen and Sher.[32] We have chosen to compare our results with those of Chen and Sher since their work presents so far the most rigorous calculations of electronic structure of ternary alloys. However, the input of their calculations includes the scaled virtual crystal approximation (SVCA) densities of states as well as the bonding and antibonding energies for the binary end compounds. The calculation of these quantities requires complicated numerical integrations over the entire Brillouin zone of the crystal. Moreover, such calculations are sensitively dependent on the large number of adjustable parameters needed to generate parametrized band structure of binary compounds. On the other hand, our calculations, despite the use of greatly simplified band structure, provide by far the most efficient way of obtaining compositional variations of ternary alloy energy band edges. For $GaAs_{1-x}P_x$ we get practi-

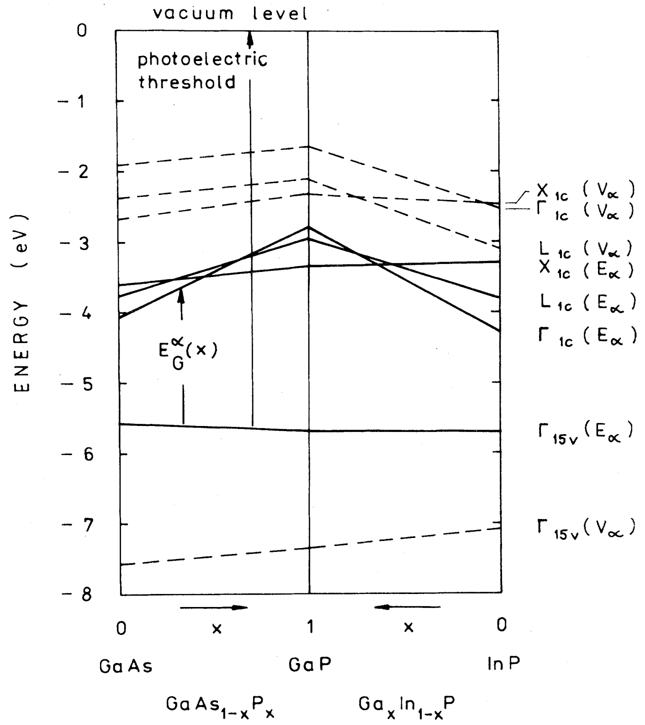

FIG. 3. Linearly interpolated positions of the centers of each semielliptic band vs alloy composition for $GaAs_{1-x}P_x$ and $Ga_xIn_{1-x}P$.

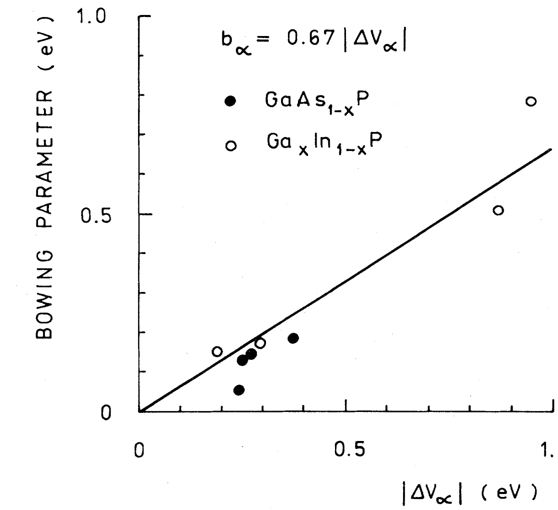

FIG. 4. Calculated bowing parameter vs the energy difference between the centers of semielliptic bands in binary endpoint compounds.

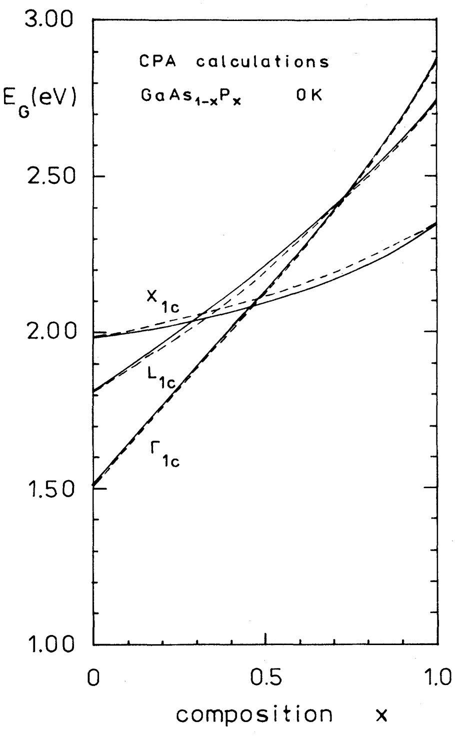

FIG. 5. Calculated band gaps vs alloy composition fo $GaAs_{1-x}P_x$ at 0 K (solid line, this work; dashed line, Ref. 32).

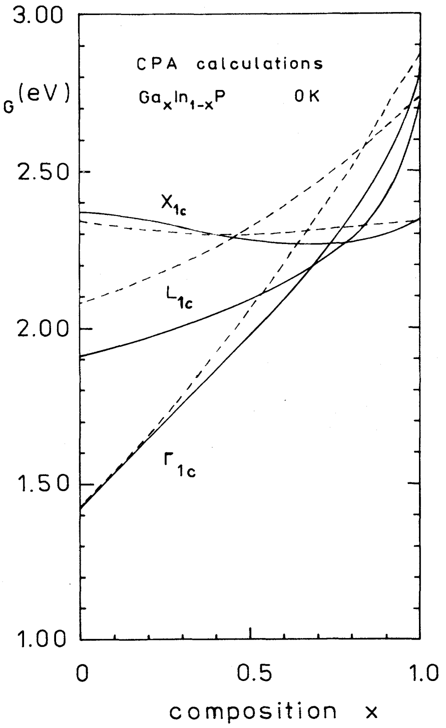

FIG. 6. Calculated band gaps vs alloy composition for $Ga_xIn_{1-x}P$ at 0 K (solid line, this work; dashed line, Ref. 32).

cally identical results as those of Chen and Sher, whereas for $Ga_xIn_{1-x}P$ there is the essential difference concerning the location and precise nature of direct-indirect crossover.

To check the validity of our calculations we have compared the bowing parameters obtained in this work with those quoted in literature. In the case of the band gap the total bowing parameter is a sum of the contributions from the conduction and valence bands. Tables III and IV list the results of extensive search in the literature published in recent years. They contain both experimental results as well as theoretical estimates obtained by such methods as: dielectric model[2] (DM), empirical-pseudopotential-method band-structure calculation[42] (EPM BS), first-principle CPA calculations based on linear combination of bond-orbitals method[13] (LCBO CPA) and VCA effective-pseudopotential method[43] (VCA EPM).

First we shall discuss the $GaAs_{1-x}P_x$ alloy. We have obtained a perfect agreement with the numerous experimental data available for this alloy. As far as comparison with other theories is concerned, the general tendency pointed out by Altarelli,[30] that in the case when a group-V element is alloyed, the X-band bowing should be as large or larger than those of Γ and L bands, is reproduced in this theory, while other theories generally do not reproduce this feature. The dielectric model (DM) as well as EPM BS and VCA EPM give too small X-band bowing and too large Γ-band bowing when compared to the experimental results.

In the case of $Ga_xIn_{1-x}P$ we deal with an opposite situation. The conduction-band X_1 state corresponds to a charge distribution, attaining its maximum at the group-V site and vanishing at the group-III site. Therefore, it is

TABLE III. Survey of experimental and theoretical values of the bowing parameters for $GaAs_{1-x}P_x$.

Bowing parameter b_α (eV)			
Γ	X	L	Reference
		Experiment	
0.21	0.03	0.25	33
0.21		0.23	35
0.174	0.202	0.16	23
0.2	0.2		25
	0.280		36
0.210	0.211		37
0.210			38
0.210	0.27		39
0.186	0.211		40
0.210	0.221	0.160	41
		Theory	
0.148	0.208	0.160	This work
0.26	0.22	0.45	32
0.30	0.11	0.19	2,34
0.21	0.21	0.25	31
0.23		0.23	35
0.38		0.22	42
0.17	0.08	0.21	13
0.30	0.10		39
0.22	0.13	0.18	43

TABLE IV. Survey of experimental and theoretical values of the bowing parameters for $Ga_xIn_{1-x}P$.

Bowing parameters b_α (eV) Γ	X	L	Reference
	Experiment		
0.684	0.147		44
0.76	0.15	0.68	45
0.758	0.203		46
0.50		0.86	47,48
0.758			49
0.40–0.88		0.34	35
	Theory		
0.508	0.148	0.790	This work
0.40	0.17	0.41	32
0.70	0.40	0.50	2,34
0.758	0.15	0.68	31
0.43		0.43	35
1.36		0.27	42
0.39	0.16	0.23	43

expected that the effect of disorder on the X_1 conduction-band edge in the case when the group-III element is alloyed should be small in comparison with the effects at the Γ and L points. This is indeed the case we have obtained from our calculations. As can be seen from Table IV, the values of the band-gap bowing at the Γ, X, and L points are in satisfactory agreement with experiment, whereas the DM model predicts generally too large X-band bowing.

Another important characteristic of a ternary alloy is the composition at which the smallest direct and indirect gaps become equal and where the luminescence properties change drastically. As before we have listed available experimental and theoretical crossover compositions for $GaAs_{1-x}P_x$ (Table V) and for $Ga_xIn_{1-x}P$ (Table VI). For $GaAs_{1-x}P$ our calculations predict $x=0.46$, which is in agreement with both experimental and theoretical results quoted in literature. In the case of $Ga_xIn_{1-x}P$ alloys the situation is a little more complicated. The available experimental results fall into two distinct categories. One predicts Γ-X crossover close to either $x_c=0.63$ or $x_c=0.74$; the other argues in favor of two crossover compositions. The latter situation is attributed to the behavior of the L-band edge. The first crossover refers to the Γ-L transition, the second one at higher composition to the L-X transition. The results of our calculations support clearly the second view advanced by Pitt *et al.*[61] and Merle *et al.*[44] This result is consistent with their high-pressure electrical measurements[61] and with a detailed piezoreflectance study[44] of the $Ga_xIn_{1-x}P$ system. Both methods are in this particular case more reliable than optical luminescence measurements, since they allow one to follow the positions of three conduction-band minima across the whole composition range. Therefore, they can be understood as giving strong support to our calculations. For a further test of reliability of our calculations we have replotted Fig. 10 of the paper by Chen and Sher[32] (see Fig. 7), including our results. It can be seen that our calculations agree very well with a larger number of the experimental data quoted from Refs. 44, 45, 48, and 59.

TABLE V. Experimental and theoretical values of the crossover composition for $GaAs_{1-x}P_x$.

x_c	Reference
	Experiment
0.45	40,50,51
0.46	25,37,39,52
	Theory
0.46	This work, 14,53
0.47	2,30,43
0.48	32
0.25	54

TABLE VI. Experimental and theoretical values of the crossover compositions for $Ga_xIn_{1-x}P$.

One crossover	Two crossovers		
$x_{c,\Gamma\text{-}X}$	$x_{c1,\Gamma\text{-}L}$	$x_{c2,L\text{-}X}$	Reference
	Experiment		
0.63			47,48,55,56
0.65			57,58
0.69			48
0.72			46
0.74			45,59,60
	0.68	0.77	44
	0.63	0.74	61
	Theory		
	0.68	0.77	This work
0.66			32
	0.65	0.80	53
0.68			2,43
0.74			30

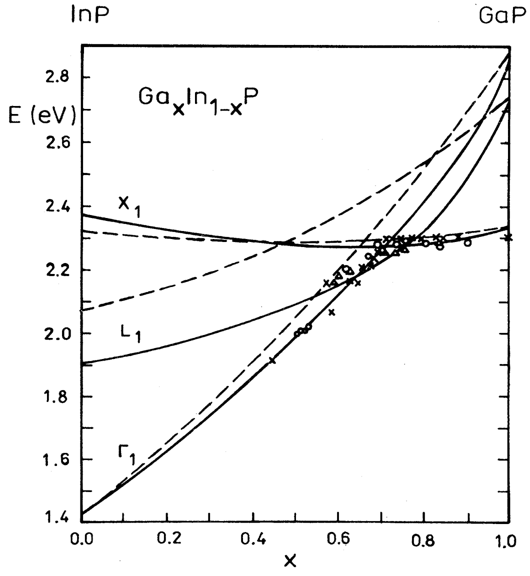

FIG. 7. Comparison of theoretical and experimental band gaps for $Ga_xIn_{1-x}P$ alloy (solid line, this work; dashed line, Ref. 32; circles, Ref. 48; crosses, Ref. 45; triangles, Ref. 59).

V. CONCLUSIONS

The CPA method has been used for evaluating the effect of substitutional disorder on the band bowing in ternary alloys. The closed form, matrix equation, an analog of Soven's equation has been derived. This form of CPA equation is particularly convenient for iterative numerical calculations. The results of calculations for $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ and $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ have been compared with available experimental data. It has been shown that the CPA theory reproduces correctly both the compositional variations of band gaps as well as the crossover compositions, while the other models give only a rough estimation of bowing at various symmetry points. For $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$, where a considerable controversy exists about the location and the nature of the direct-indirect transition, our results support the recent hypothesis of two crossover compositions attributed to the behavior of the L-band edge. Finally, we have found that the amount of band bowing for a particular symmetry point of the Brillouin zone is proportional to the absolute value of the difference between the potentials referring to the centers of the bands in question in binary limits. Although the band structure of binary consituents is treated only approximately in our calculations (semielliptic density of states is assumed), the experimental features of ternary alloy band structure are reproduced surprisingly well. This result proves the essential role of substitutional disorder, which is treated by CPA theory exactly, in producing the nonlinear variations of the band gaps in the semiconductor alloys.

The ability to calculate the band structure of compound semiconductors is an important prerequisite for any analysis of the phenomena occurring in these alloys as well as in the devices based on these materials. The relevance of CPA methods for such calculations has been demonstrated. The certain simplifications introduced in the model to make the calculation tractable, i.e., the assumption of semielliptic density of states are justified, since the principal interactions affecting the alloy properties are incorporated in the present calculations.

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