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Band structure calculations in N-ary alloys

A. A. Mbaye

Laboratoire de Physique du Solide et Energie Solaire, C.N.R.S. Sophia Antipolis, rue Bernard Grégory,
 06560 Valbonne, France

and F. Aymerich

Istituto di Fisica dell'Universita di Cagliari, Cagliari and Gruppo Nazionale di Struttura della materia del Consiglio Nazionale della Ricerche, Cagliari, Italy

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Résumé. — Une méthode simple pour les calculs des structures électroniques et d'alliages complexes est présentée. Cette méthode comporte deux étapes : dans l'approximation du cristal virtuel (VCA) nous avons établi un schéma général d'interpolation des propriétés physiques de l'alliage en fonction de celles de ses constituants purs et des effets de non-linéarité intrinsèque dans leurs alliages les plus simples (pseudobinaires). Dans la seconde étape les effets de non-linéarité liés au désordre dans l'alliage sont pris en compte par une paramétrisation dépendant de \mathbf{k} . Cette méthode est appliquée aux alliages isovalents ternaires et quaternaires de composés III-V, établissant des expressions générales de leurs paramètres cristallins et des transitions optiques aux points de plus haute symétrie de la zone de Brillouin.

Abstract. — A method for simple calculations of the electronic structure of complex crystalline alloys is presented. This method is twostepwise : within the virtual crystal approximation (VCA) a general interpolation scheme is achieved for the determination of the physical properties of the alloy in terms of those of its pure constituents and the intrinsic (VCA) bowing effects of their related simplest (pseudo binary) alloys. The second step of this method is an extension of the Dielectric Method to account for disorder effects in the general alloy, including a \mathbf{k} dependent parameterization of the extrinsic bowing effects. Applied to the III-V compound-based materials, the general expressions of lattice parameter and higher symmetry points optical transitions as functions of compositions are derived for these isovalent ternary and quaternary alloys.

1. Introduction.

The III-V compounds based isovalent alloys play a central rôle in semiconductor physics. The interest devoted to these materials is due to the wide range of their applications to opto-electronic devices. Among them, the quaternary alloys are of great technical interest due to their flexibility for the realization of high quality material required for these devices. Such requirements are fulfilled by an epitaxial growth yielding lattice matched to the substrate for crystal layers and high quality interfaces in heterostructures. Yet, in the ternary $A_{1-x}B_xC$ alloys the electronic structure (optical gap E_g) and the lattice parameter (a) are functions of the composition and hence are related by a unique relation $E_g(a)$. The dual requirements of independent variations of E_g and a require an addi-

tional degree of freedom for adjusting the alloy composition, i.e. the use of a quaternary alloy. Such flexible behaviour makes quaternary alloys good candidates for various applications : $Ga_{1-x}In_xAs_{1-y}P_y$ to detectors [1] and emitters for optic fibre [2] systems, and solar cells [3], $Ga_{1-x}Al_xAs_{1-y}Sb_y$ to DH laser [4], infrared emitting and photo-diodes [5], CCD's [6].

A general theory of the electronic structure of these material is still needed. Yet, for such complex systems, direct and simple methods, for the estimation of important physical properties, may be a useful tool for the prediction and the realization of required properties for specific applications [7]. The Dielectric Method [8] (DM) has been proved to satisfy these constraints in the case of ternary alloys. However, for III-V or II-VI quaternary or more complex alloys, no such definite method exists. In fact, various schemes

have been used to evaluate alloys properties [9-11, 12]. However most of these methods are based on a purely geometrical view of the alloy problem hiding some of the physical assumptions they involve [9-11]. Recently, pseudopotential band structure calculations have been performed for the optical gaps of $Al_{1-x-y}Ga_xIn_yAs$ alloys [12] with a pseudo Hamiltonian constructed within an extended VCA framework. The purpose of the present paper is to formulate a method based on the DM idea for the calculation of electronic properties of general alloys. To this end, an interpolation scheme is given which allows the determination of the physical properties of general alloys from those of their pure constituent compounds and of their related simplest (pseudo binary) alloys. The disorder effects arising from the statistical nature of the alloying process are treated using a second order approximation. When the only disorder-produced intraband interaction is considered the present approach can be reduced to a parameterized theory of these effects analog to the DM [8].

The paper is organized as follows : in section 2, the notation is clarified (subsection 2.1), and the VCA alloy (2.2) and disorder effects (2.3) are studied. The formal theory description in this latter section is then applied to III-V compound based ternary or quaternary alloys. Discussions and conclusions may be found in the last section.

2. Formal theory.

2.1 NOTATION AND ALLOY REPRESENTATION. — In this section, we consider a general alloy with an arbitrary number of sublattices and substituents on each sublattice. This alloy is, thus, based on multinary compounds, denoted (MC) = $(A^{(1)} \dots A^{(i)} \dots A^{(s)})$, s being the number of sublattices. On each sublattice (i), a given site may be occupied by one of the substituents $A_k^{(i)}$; $k = 1, K^{(i)}$. $K^{(i)}$ is the number of substituents on the i th sublattice. The atomic distribution, on each sublattice, is given by the type of solid solution dealt with. Let $x_k^{(i)}$ be the macroscopic composition of the alloy associated with the $A_k^{(i)}$ species.

In the present work, we shall represent the disorder state in the alloy by the ensemble of all possible values of the fluctuating composition within cells of *a priori* size paving the actual crystal.

The local concentration of the substituents $A_k^{(i)}$, say, $C_k^{(i)}$ is, in general, different from its macroscopically observed concentration denoted by $x_k^{(i)}$. The crystal potential in this cell is, then, approximated by a linearly averaged one where the respective weights of atomic potentials $V_k^{(i)}$ associated to the substituents $A_k^{(i)}$ are $C_k^{(i)}$. Such a potential is equivalent to the potential one should obtain in a macroscopic mixed crystal in which the concentration of $A_k^{(i)}$ is $C_k^{(i)}$, and which is treated in the virtual crystal approximation. This latter macroscopic crystal will be referred to as a subcrystal and is defined by the fluctuating compo-

sition matrix $[C_k^{(i)}]$. The crystal potential in a given subcrystal is, hence, given by

$$H_c = -\frac{\hbar^2}{2m} \nabla^2 + \sum_{i,k,l} C_k^{(i)} V_k^{(i)}(r - R_l - \tau_i) \quad (2.1)$$

where l runs on all sites and τ_i is the displacement of the i th lattice with respect to the chosen origin.

H_c may be rewritten as

$$H_c = H_0 + V$$

where

$$H_0 = -\frac{\hbar^2}{2m} \Delta + \sum_{i,k,l} x_k^{(i)} V_k^{(i)}(r - R_l - \tau_i) \quad (2.2a)$$

and

$$V = \sum_i \sum_{k \neq \mu^i} \xi_k^{(i)} \Delta_k^{(i)}(r) \quad (2.2b)$$

with

$$\begin{aligned} \xi_k^{(i)} &= C_k^{(i)} - x_k^{(i)} \\ \Delta_k^{(i)} &= \sum_l V_k^{(i)}(r - R_l - \tau_i) - V_{\mu^i}^{(i)}(r - R_l - \tau_i). \end{aligned} \quad (2.3)$$

Here $A_{\mu^i}^{(i)}$ denotes a chosen substituted element on the i th sublattice associated with the composition given by

$$x_{\mu^i}^{(i)} = 1 - \sum_{k \neq \mu^i} x_k^{(i)}. \quad (2.4)$$

H_0 denotes the ordered macroscopic virtual crystal approximation of the Hamiltonian, while V depends on the subcrystal and characterizes the disorder state in the alloy. These contributions of H_0 , and V will be treated separately in order to clarify the physical assumptions involved in both treatments.

2.2 GENERAL INTERPOLATION SCHEME IN THE VCA FRAMEWORK : INTRINSIC BOWING EFFECTS. — Our purpose in this subsection is to express in the VCA framework the intrinsic bowing effects (δ^1) [8] on the physical properties (here, electronic) of the general alloy defined in A, as combinations of those of the simplest alloys based on the same group of pure compounds ((MC)).

It must be first noted that the parameters used in parameterized electronic structure calculation methods are generally characteristic of the compounds rather than atomic species. Therefore, it is more useful to interpolate alloy internal parameters (Q) between those of its pure constituents rather than those of atomic species as suggested by equation 2.2a. Therefore a given parameter Q of the alloy may be written as

$$Q = \sum_{(MC)} P((MC)) \cdot Q((MC)) \quad (2.5)$$

where $Q((MC))$ is the value of the corresponding parameter in any pure multinary compound (MC) involved in the alloy formation, $P((MC))$ is its sta-

tistical weight. This weight is, of course, related to the concentration $x_k^{(i)}$ in the alloy of the respective atomic species $A_k^{(i)}$ forming the multinary compound (MC). It can be easily found that

$$P((MC)) = \prod_i x_k^{(i)} \quad (2.6)$$

$$A_k^{(i)} \in (MC).$$

This decomposition (Eqs. 2.5-6) is sufficient for interpolating the linear alloy parameters such as the lattice parameter (Vegard Law). For optical transitions (E), a higher (second) order approximation is needed. To achieve this, we shall assume that, under the VCA, the general alloy is a *superposition* of the simplest alloys based on the same group of multinary

compounds (MC). Let $\{(MC)_i\}$ be the ensemble of pure (MC) where all species on the sublattices other than the i th are fixed and where the i th sublattice is occupied by any one of the substituents $A_k^{(i)}$. Secondly, let $((MC)_i, A_m^{(i)})$ be any pure multinary compound formed from any one of the $(MC)_i$'s and where the i th sublattice is occupied by the only $A_m^{(i)}$ substituent. Therefore $((MC)_i, A_k^{(i)}, A_m^{(i)})$ may be thought of as any pseudo-binary alloy where alloying effects occur on the only i th sublattice using two of the possible substituents. It is obvious that these pseudo-binary alloys are the simplest alloys based on the same (MC)'s as the general alloy. Hence this latter alloy will be decomposed as a superposition of such pseudo-binaries. Any parameter Q , thus may be rewritten as

$$Q = \sum_i \sum_{(MC)_i} P((MC)_i) \sum'_{k,m} Q_{k,m}((MC)_i) \quad (2.7)$$

where

$$Q_{k,m}((MC)_i) = x_k^{(i)} Q((MC)_i, A_k^{(i)}) + x_m^{(i)} Q((MC)_i, A_m^{(i)}).$$

The prime means that each (k, m) pair must be encountered only once. $Q_{k,m}((MC)_i)$ is the linearly interpolated value of Q in the pseudo-binary $((MC)_i, A_k^{(i)}, A_m^{(i)})$.

An optical transition (E) of this pseudo binary alloy displays an intrinsic non linear behaviour δ^I as given by

$$E(Q_{k,m}((MC)_i)) = E^L(Q_{k,m}((MC)_i)) + \delta_{k,m}^I((MC)_i) \quad (2.8)$$

and

$$E^L(Q_{k,m}((MC)_i)) = x_k^{(i)} \cdot E((MC)_i, A_k^{(i)}) + x_m^{(i)} \cdot E((MC)_i, A_m^{(i)})$$

$\delta_{k,m}^I((MC)_i)$ being the deviation from linearity of E in the considered binary alloy. Therefore, using the decomposition (Eqs. 2.5-6), we obtain the VCA value E in the general alloy

$$E = \sum_i \sum_{(MC)_i} P((MC)_i) \sum'_{k,m} E(Q_{k,m}((MC)_i)). \quad (2.9)$$

From equations 2.8, equation 2.9 may be decomposed into a linear part given by

$$E^L = \sum_i \sum_{(MC)_i} P((MC)_i) \sum'_{k,m} E^L(Q_{k,m}((MC)_i))$$

$$= \sum_{(MC)} P((MC)) \cdot E((MC)) \quad (2.10a)$$

and an intrinsic deviation δ^I from linearity

$$\delta^I = \sum_i \sum_{(MC)_i} \sum'_{k,m} \delta_{k,m}^I((MC)_i) \cdot P((MC)_i) \quad (2.10b)$$

$P((MC)_i)$ is given by (2.6) where $x_k^{(i)} = 1$.

Equation 2.10a yields, as expected, a linear interpolation between the pure constituents. While, (2.10b) describes the intrinsic bowing effects in the general alloy in terms of those in the pseudo binaries. It must be emphasized that the assumption of the decomposition (Eqs. 2.5-6) is consistent with the VCA. However, no such decomposition is justified when dealing with disorder effects. We shall come back on this point later. Before closing this subsection let us express δ^I as function of the compositions. To this end, we recall the parabolic behaviour of δ^I in the pseudo binaries :

$$\delta_{k,m}^I((MC)_i) = - C^I((MC)_i, A_k^{(i)}, A_m^{(i)}) \cdot x_k^{(i)} \cdot x_m^{(i)} \quad (2.11a)$$

where $C^I((MC)_i, A_k^{(i)}, A_m^{(i)})$ is the so-called intrinsic bowing parameter [8] associated to the pseudo binary alloy $((MC)_i, A_k^{(i)}, A_m^{(i)})$. Then δ^I may be rewritten as

$$\delta^I = - \sum_i \sum_{(MC)_i} P((MC)_i) \sum_{k,m} C^I((MC)_i, A_k^{(i)}, A_m^{(i)}) \cdot x_k^{(i)} \cdot x_m^{(i)}. \quad (2.11b)$$

This, completely, describes the VCA alloy, at least, within a second order approximation. Let us now turn to the disorder effects problem.

2.3 DISORDER EFFECTS : A GENERAL DIELECTRIC METHOD FOR EXTRINSIC BOWING ESTIMATION. — In addition to the intrinsic bowing effects a further deviation from linearity for the physical properties (electronic structure) of alloys as functions of composition must be considered. This arises from the statistical disorder state in the alloy. It is generally referred to as extrinsic bowing effects. For ternary (pseudo binary) III-V or II-IV alloys, the dielectric method (DM) of Van Vechten and Bergtresser [8] has been proved to be a useful tool for estimating the optical band extrinsic bowing. Note, however, that the physical information embodied in the bandwidth parameter in this latter theory was not clearly analysed. This method can be easily extended to the case of quaternary alloys. This latter approach (Ref. 8) assumes a short ranged fluctuating potential. In the present section we shall derive an analog but somewhat different method for complex mixed crystals. The disorder effects to be studied have been experimentally proved to be very small compared to the pure crystals bandwidths [8]. Therefore using a self-energy formalism these effects may be accounted for by the second order term in the self-energy expansion as a function the perturbing potential V defined in equations 2.2-2.3. The disorder effects are, then, given by the self energy $\Sigma(E)$ as [13].

$$\Sigma(E) = \langle VG^0(E)V \rangle \quad (2.12)$$

where $G^0(E)$ stands for the VCA green function and $\langle \rangle$ for the averaging operator upon the ensemble of subcrystals representing the disorder state in the alloy. From equations 2.2 and recalling that the only subcrystal (disorder) dependent quantities in V are the $\xi_k^{(i)}$'s we have

$$\Sigma(E) = \sum_{\substack{i,j \\ l \neq \mu^i \\ m \neq \mu^j}} \langle \xi_l^{(i)} \cdot \xi_m^{(j)} \rangle A_l^{(i)} G^0(E) A_m^{(j)}. \quad (2.13)$$

Now let $|ck\rangle$ and $|vk\rangle$ be the conduction and valence band states associated to the VCA eigen values $E_c(\mathbf{k})$ and $E_v(\mathbf{k})$ respectively. $|c_0\mathbf{k}\rangle$ and $|v_0\mathbf{k}\rangle$ denote the lower conduction and the upper valence bands at the same \mathbf{k} point of the Brillouin zone. In the following, we assume, as in the usual DM a short range potential difference between substituted atoms [8]. We also assume that disorder induced s-p mixing between valence and conduction is negligible compared to the

intraband mixing which mainly controls the gap downward bowing in III-V alloys [14]. The respective displacements of band extrema $|c_0\mathbf{k}\rangle$ and $|v_0\mathbf{k}\rangle$ are, thus, given by

$$\Sigma_{c_0}(\mathbf{k}) = - \sum_{\substack{i,j \\ l \neq \mu^i \\ m \neq \mu^j}} \langle \xi_l^{(i)} \cdot \xi_m^{(j)} \rangle \frac{\Gamma_l^{(i)} \cdot \Gamma_m^{(j)}}{|\Delta E_c(\mathbf{k})|} \quad (2.14a)$$

$$\Sigma_{v_0}(\mathbf{k}) = \sum_{\substack{i,j \\ l \neq \mu^i \\ m \neq \mu^j}} \langle \xi_l^{(i)} \cdot \xi_m^{(j)} \rangle \frac{\Gamma_l^{(i)} \cdot \Gamma_m^{(j)}}{\Delta E_v(\mathbf{k})} \quad (2.14b)$$

$\Gamma_l^{(i)}$ is the core potential difference between $A_l^{(i)}$ and $A_\mu^{(i)}$. $\Delta E_v(\mathbf{k})$ and $\Delta E_c(\mathbf{k})$ are given by similar formulas. We have

$$\Delta E_c(\mathbf{k}) = - |\Delta E_c(\mathbf{k})| = \sum_{c \neq c_0} \frac{|\alpha_{cc_0}(\mathbf{k})|^2}{E_{c_0}(\mathbf{k}) - E_c(\mathbf{k})} \quad (2.14c)$$

where

$$\alpha_{cc_0}(\mathbf{k}) = \frac{1}{\Omega} \sum_{\mathbf{G}} B_G^c(\mathbf{k})^* B_G^{c_0}(\mathbf{k}). \quad (2.14d)$$

The $B_G^n(\mathbf{k})$'s are momentum eigenfunctions associated with the n th band and the reciprocal vector \mathbf{G} at the \mathbf{k} point. Ω is the unit cell volume. Note that from (2.14c-d) $\Delta E_c(\mathbf{k})$ is negative, yielding a lowering of the conduction band minimum. Similar equations for $\Delta E_v(\mathbf{k})$ should show that the valence band maximum is raised. This, finally, give a shrinkage of the band gap. The disorder induced band gap variation is given by

$$\delta^E(\mathbf{k}) = \Sigma_{c_0}(\mathbf{k}) - \Sigma_{v_0}(\mathbf{k}) \quad (2.15a)$$

$$= - \sum_{\substack{i,j \\ l \neq \mu^i \\ m \neq \mu^j}} 2 \cdot \langle \xi_l^{(i)} \cdot \xi_m^{(j)} \rangle \frac{\Gamma_l^{(i)} \Gamma_m^{(j)}}{\Delta E(\mathbf{k})} \quad (2.15b)$$

where the geometric average band width of valence and conduction bands $\Delta E(\mathbf{k})$ is given by

$$\frac{2}{\Delta E(\mathbf{k})} = \frac{1}{\Delta_v E(\mathbf{k})} + \frac{1}{\Delta_c E(\mathbf{k})}, \quad (2.15c)$$

for the direct gap semiconductor.

In order to have an explicit expression for δ^E as a function of composition, some further approximations must be made : the virtual lattice hypothesis [8] is

assumed. *i.e.*, all sublattices are undistorted. In such cases, it is reasonable to assume (although not necessary) that these sublattices are statistically uncorrelated. *i.e.*, the composition fluctuations on different sublattices are uncorrelated. We, therefore, have

$$\langle \xi_l^{(i)} \cdot \xi_m^{(j)} \rangle = \delta_{ij} \langle \xi_l^{(i)} \cdot \xi_m^{(i)} \rangle. \quad (2.16)$$

Furthermore, in an ideal solid solution equation 2.16 may be explicitly calculated (see Appendix) yielding

$$\langle \xi_l^{(i)} \cdot \xi_m^{(i)} \rangle^{\text{ideal}} = x_l^{(i)}(1 - x_l^{(i)}) \delta_{lm} + 2 x_l^{(i)} x_m^{(i)} (\delta_{lm} - 1). \quad (2.17)$$

Yet, when no assumption about the solid solution type is made, these statistical factors $\langle \xi_l^{(i)} \cdot \xi_m^{(i)} \rangle$ may be taken as disorder characteristic parameters [13]. In the present work, we introduce such parameterization as follows :

$$\langle \xi_l^{(i)} \cdot \xi_m^{(i)} \rangle = \alpha_{lm}^{(i)} (x_l^{(i)}(1 - x_l^{(i)}) \delta_{lm} + 2 x_l^{(i)} x_m^{(i)} (\delta_{lm} - 1)). \quad (2.18)$$

Such that $\alpha_{ll}^{(i)} = 1$ for ideal solutions and $(\alpha_{ll}^{(i)} - 1)$ stands for the deviation from random disorder and may be thought of as a *disorder measure*. Therefore, for any direct transition δ^E becomes

$$\delta^E(\mathbf{k}) = - \sum_{i,l \neq \mu^i} \frac{\Gamma_l^{(i)2}}{B_{ll}^{(i)}(\mathbf{k})} x_l^{(i)}(1 - x_l^{(i)}) - \sum_{l,m \neq \mu^i} 2 \frac{\Gamma_l^{(i)} \Gamma_m^{(i)}}{B_{lm}^{(i)}(\mathbf{k})} \cdot x_l^{(i)} \cdot x_m^{(i)} \quad (2.19)$$

where

$$B_{lm}^{(i)}(\mathbf{k}) = \frac{\Delta E(\mathbf{k})}{2 \alpha_{lm}^{(i)}}$$

are adjustable bandwidth parameters.

These parameters may be chosen such that they only depend on the substituted atomic species (*l, m*) for each gap transition (Table I). When the $B_{lm}^{(i)}(\mathbf{k})$'s are assumed to be independent of atomic species and of the \mathbf{k} point (*i.e.*, $B_{lm}^{(i)}(\mathbf{k}) = B = 0.98$ eV) equation 2.19 reduces for III-V or II-VI alloys to a simple extension of the dielectric method for the general alloy based on these compounds. However, in the present work, we shall fit the $B_{lm}^{(i)}(\mathbf{k})$ to experiments to include the variation of disorder effects as function of \mathbf{k} .

Table I. — Bandwidth parameters (eV) associated to each substituent pair for higher symmetry points in the Brillouin zone (Γ, L, X).

B (eV)	Γ	L	X
—	—	—	—
Ga-In	0.679	0.585	1.065
Ga-Al	0.096	0.055	1.183
P-As	0.632	0.371	1.0
As-Sb	0.700	0.867	1.0

The above described theory will be only applied to III-V alloys, although it is obvious that all equations in this section 2 are valid for alloys based on any type of crystalline multinary compounds.

3. Applications to III-V alloys.

3.1 TERNARY (PSEUDO)BINARY ALLOYS : $A_{1-x}B_xC$. — The III-V compounds form one of the simplest group of multinary compounds. They possess only two sublattices (metallic, and metalloid). The simplest alloys based on them are generally referred to as ternary alloys though they may be taken as pseudo binary alloys. These alloys have been previously

Table II. — The intrinsic bowing parameters (C_i^I) are calculated from ref. 14 and the extrinsic bowing (C_i^E) is obtained from the present theory. The total bowing to be compared with experimental data (C_i^{Exp}) is given by $C_i = C_i^I + C_i^E$.

	C_0^I	C_0^E	C_0^{Exp}	C_1^E	C_1^E	C_1^{Exp}	C_2^I	C_2^E	C_2^{Exp}
(Al, Ga)P	0.00	0.302	—	0.00	0.527	—	0.00	0.025	—
(Al, Ga)As	0.00	0.28	0.26 ^(a)	0.00	0.49	0.45 ^(a)	0.00	0.023	0.02 ^(a)
(Al, Ga)Sb	0.160	0.207	0.37 ^(d) 0.4 ^(e)	0.100	0.362	0.33 ^(f) 0.50 ^(g)	0.054	0.017	0.08 ^(h)
(Ga, In)P	0.389	0.352	0.70 ^(d) 0.76 ^(f)	0.185	0.409	0.68 ^(e)	0.092	0.224	0.15 ^(e)
(Ga, In)As	0.286	0.333	0.60 ^(g)	0.133	0.386	0.50 ^(h)	0.065	0.212	0.27 ^(h)
(Ga, In)Sb	0.128	0.246	0.43 ^(h)	0.076	0.285	0.33 ^(h)	0.063	0.156	0.24 ^(h)
Al(P, As)	0.354	0.136	—	0.155	0.232	—	0.021	0.086	—
Ga(P, As)	0.207	0.116	0.21 ^(h)	0.096	0.197	0.25 ^(h) 0.28 ⁽ⁱ⁾	0.020	0.073	0.03 ^(h)
In(P, As)	0.153	0.084	0.27 ^(h)	0.071	0.143	0.26 ^(h)	0.020	0.053	0.27 ^(h)
Al(As, Sb)	0.169	1.048	—	0.103	0.847	—	0.115	0.734	—
Ga(As, Sb)	0.160	0.899	1.21 ^(j)	0.086	0.725	—	0.081	0.629	—
In(As, Sb)	0.037	0.651	0.68 ^(h)	0.024	0.526	0.55 ^(h)	0.049	0.456	0.60 ^(h)

(^a) : Ref. 16; (^b) : Ref. 18; (^d) : Ref. 19; (^e) : Ref. 20
 (^f) : Ref. 21; (^g) : Ref. 22; (^h) : Ref. 23; (ⁱ) : Ref. 24
 (^j) : Ref. 25; (^k) : Ref. 26.
 (^l) : Ref. 25; (^m) : Ref. 26.

studied using the dielectric method of Van Vechten and Bergerstresser [8]. This method has been proved to be a useful tool for determining band gap variation as a function of composition though the parameterized scheme used in it might use some improvements as described in section 2. From the general results in this latter section the variation of a direct transition $E_{g,i}$ is given from equations 2.10, 2.19 by

$$E_{g,i}(x) = E_{g,i}^L + \delta_i^I + \delta_i^E \quad i = 0, 1, 2 \quad (3.1a)$$

$$E_{g,i}^L = (1-x) E_{g,i}(AC) + x E_{g,i}(BC) \quad (3.1b)$$

$$\delta_i^I = -C_i^I(ABC) \times (1-x) \quad (3.1c)$$

$$\delta_i^E = -\frac{|\Gamma_B^{(A)}|^2}{B_{B,i}^A} \times (1-x) = -C_i^E(ABC) \times (1-x). \quad (3.1d)$$

Here i refers to Γ , L , X respectively. The $B_{B,i}^{(A)}$ are adjustable bandwidth parameters as defined in section 2. For the sake of transferability from one ternary to another, they are chosen to characterize the average statistical and optical effects of the substitution (A, B) for each transition $E_{g,i}$. Therefore these parameters depend only on the pair (A, B) for a given transition. In what follows, we use the theory established in reference 14 to determine the optical transitions of pure constituents and the associate intrinsic bowing parameter $C^I(ABC)$ in the related alloys. The parameter used in this calculation are taken from reference 8. The fluctuating potential rms $\Gamma_B^{(A)}$ are calculated using the DM formula :

$$\Gamma_B^{(A)} = b e^2 \left(\frac{Z_B}{r_B} - \frac{Z_A}{r_A} \right) e^{-k_s R} \quad (3.2)$$

where $b = 1.5$ and Z_A, r_A are the valence charge and covalent radius associated with the atomic species A respectively. k_s is the Thomas Fermi wave vector, and R is the average covalent radius. The $B_{B,i}^{(A)}$ have been determined from existing data for each pair (A, B), and are in table I. Some of these parameters need to

be recalculated when more extensive experimental data is available. From this, the intrinsic and extrinsic bowing parameters for ternary alloys are fully determined (Table II) and compared with existing experimental data. It must be emphasized that instead of determining the $B_{B,i}^{(A)}$ one could attempt to fit the disorder characteristic parameter $\alpha_B^{(A)}$. However, the present accuracy of bowing experimental determination does not reasonably allow this. Therefore, the DM view has been adopted and extended to include the extrinsic bowing variation as function of \mathbf{k} . This \mathbf{k} dependence is analog to the one obtained from single site CPA calculation which results from the dependence of $E^0(\mathbf{k})$ [15]. Other physical quantities are generally needed to study semiconductor alloys. These are the distance between the top of the valence band and the bottom of the conduction band *i.e.*, E_X, E_L . The bowing parameters of these gaps are intimately related to those of the direct transitions E_0, E_1, E_2 . The bowing parameters of E_X and E_L are respectively given by the half sums of E_0 and E_2 , and E_0 and E_1 . Hence they may be calculated using table II.

3.2 QUATERNARY ALLOYS. — The quaternary III-V compound based alloys are being widely studied, due to the flexibility they offer for technical applications to opto-electronic devices. In fact, in these materials both electronic structure and lattice parameter can be separately optimized yielding the lattice matching and the opto-electronic properties required for specific applications such as multispectral (tandem) solar cells. These alloys are of two forms : the trimetallic or trimetalloid ($A_{1-x-y}B_xC_yD$ or $DA_{1-x-y}B_xC_y$) and the dimetallic-dimetalloid $A_{1-x}B_xC_{1-y}D_y$. These two cases present some difference mainly, when disorder effects are dealt with.

3.2.1 $A_{1-x}B_xC_{1-y}D_y$ alloys. — The most widely studied quaternary alloy $Ga_{1-x}In_xAs_{1-y}P_y$ belong to this class. The direct transitions $E_{g,i}$ in these alloys are always given by (3.1a) where using (2.10) and (2.19) we obtain

$$E_{g,i}^L = (1-x)(1-y) E_{g,i}(AC) + (1-x)y E_{g,i}(AD) + x(1-y) E_{g,i}(BC) + xy E_{g,i}(BD)$$

$$\delta_i^I = - (C_i^I(ACD)(1-x)y(1-y) + C_i^I(BCD)xy(1-y) + C_i^I(ABC)(1-y) \times (1-x) + C_i^I(ABD)xy(1-x))$$

$$\delta_i^E = - \left(\frac{|\Gamma_B^{(A)}|^2}{B_{B,i}^{(A)}} x(1-x) + \frac{|\Gamma_D^{(C)}|^2}{B_{B,i}^{(C)}} y(1-y) \right). \quad (3.3)$$

Two things are worth mentioning. First, due to the statistical decoupling of the two sublattices which results from the virtual lattice hypothesis, the statistical disorder effects becomes additive with respect to sublattices. Therefore, the total bowing effects in these quaternaries are completely determined once the rms of the fluctuating potentials in this alloy are determined. That is only two calculations using equation 3.2 are required to extend the results obtained for the ternary to the quaternary alloys of the present type. On the other hand, in these quaternary alloys, there exists no physical justification to assume that the disorder induced bowing parameters

Table III. — General expansion of optical gaps (E) as a function of the composition in $A_{1-x}B_xC_{1-y}D_y$. The $\gamma(1 - m)$ parameter for each sublattice are obtained from (2.19) : $\gamma(1 - m) = \frac{|\Gamma_l^{(m)}|^2}{B_{lm}}$. The last row corresponds to the lattice parameter expansion.

E	$(1-x)(1-y)$ $E(AC)$	$(1-x)y$ $E(AD)$	$x(1-y)$ $E(BC)$	xy $E(BD)$	$-\frac{1}{2}(1-x)y(1-y)$ $C_l^i(ACD)$	$-\frac{1}{2}xy(1-y)$ $C_l^i(BCD)$	$-\frac{1}{2}(1-y)x(1-x)$ $C_l^i(ABC)$	$-\frac{1}{2}xy(1-x)$ $C_l^i(ABD)$	$-\frac{1}{2}x(1-x)$ $\gamma(A-B)$	$-\frac{1}{2}y(1-y)$ $\gamma(C-D)$
	$Ga_{1-x}In_xAs_{1-y}P_y$									
E_0 (eV)	1.551	2.770	0.583	1.392	0.207	0.153	0.286	0.389	0.415	0.147 6
E_1 (eV)	3.112	3.851	2.510	3.150	0.091	0.071	0.133	0.185	0.481	0.251
E_2 (eV)	5.013	5.549	4.420	5.014	0.020	0.020	0.065	0.092	0.264	0.093
a (Å)	5.653 4	5.450 5	6.058 5	5.868 8	0.0	0.0	0.0	0.0	0.0	0.0

for the pair of substituents (A, B) is a linear average of the bowing parameter in the ternary alloy $A_{1-x}B_xC$ and $A_{1-x}B_xD$ with respective weights $(1 - y)$ and y . The same is true for the pair (C, D). This linear interpolation for disorder effects is, in fact, incompatible with the general disorder effect behaviours. All coefficients of the composition products in equation 3.3 are determined for the test material $Ga_{1-x}In_xAs_{1-y}P_y$ (see Table III). In figure 1, are shown the 0.94 eV-isogap contour in the (x, y) plane (curve a) together with the $y(x)$ relation for a perfect lattice matching of $Ga_{1-x}In_xAs_{1-y}P_y$ on InP (curve b) and GaAs (curve c) substrates.

3.3 $A_{1-x-y}B_xC_yD$ (OR $DA_{1-x-y}B_xC_y$) ALLOYS. — To this class belongs $Al_{1-x-y}Ga_xIn_yAs$ which potentially is of great importance for optical communication devices [12]. From equations 3.1a, 2.10, 2.19 we have for each direct transition $E_{g,i}$

$$E_{g,i}^L = (1 - x - y) E_{g,i}(AD) + xE_{g,i}(BD) + yE_{g,i}(CD)$$

$$\delta_i^L = - (C_l^i(ABD) x(1 - x - y) + C_l^i(ACD)(1 - x - y) y + C_l^i(BCD) xy) \quad (3.4)$$

$$\delta_i^E = - \left(\frac{|\Gamma_B^{(A)}|^2}{B_{B,i}^{(A)}} x(1 - x) + \frac{|\Gamma_C^{(A)}|^2}{B_{B,i}^{(A)}} y(1 - y) - 2 \frac{\Gamma_B^{(A)} \Gamma_C^{(A)}}{B_{C,i}^{(B)}} xy \right).$$

Once gain, equation 3.4 is different from the corresponding one in reference 11. Where the intercorrelation between the fluctuations of the substituents B and C is not statistically coherent with the assumptions underlying the DM type calculations. As in the preceding subsection the determination of rms of fluctuating potential yields the coefficients of the composition in (3.4) (see Table IV). In figure 2, are drawn the 0.94 eV-isogap contour in the (x, y) plane (curve a) together with the $y(x)$ relation for a perfect lattice matching of $Al_{1-x-y}Ga_xIn_yAs$ on InP (curve b).

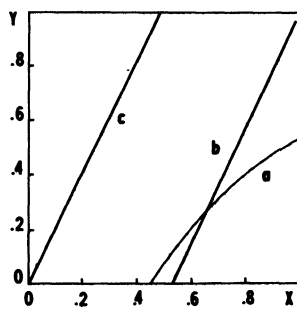


Fig. 1. — $Ga_{1-x}In_xAs_{1-y}P_y$ isogap contour ($E_0 = 0.94$ eV) in the (x, y) plane (curve a). The perfect lattice matching of this alloy on a given substrate ($a(x, y) = a_0$, a_0 is the substrate lattice parameter) yields the relation $y = f(x)$ shown in curve (b) for InP and curve (c) for GaAs substrates.

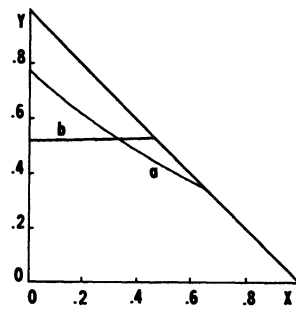


Fig. 2. — $Al_{1-x-y}Ga_xIn_yAs$ ($x + y \leq 1$) isogap contour ($E_0 = 0.94$ eV) in the (x, y) plane (curve a). The perfect lattice matching of this alloy on a given substrate ($a(x, y) = a_0$, a_0 is the substrate lattice parameter) yields the relation $y = f(x)$ shown in curve (b) for InP.

4. Discussion and conclusion.

In the present paper, we have presented a complete method for calculating the physical properties of general crystalline alloys. The main approximations have been studied : in the virtual crystal approximation an interpolation scheme for alloy internal parameters (Q) (e.g., lattice parameter) and physical properties (E), here fundamental optical gaps, between those of the pure constituents is described. This scheme allows us to determine

Table IV. — General expansion of optical gaps (E) as a function of the composition in $A_{1-x-y}B_xC_yD$. The $\alpha(1-m)$ parameter for each sublattice is obtained from (2.19) : $\gamma(B-C) = 2 \cdot \frac{\Gamma_A^{(B)} \cdot \Gamma_A^{(C)}}{B_{BC}}$; $\gamma(A-m) = \frac{|\Gamma_A^{(m)}|^2}{B_{Am}}$. The last row corresponds to the lattice parameter expansion.

E	$1-x-y$ $E(AD)$	x $E(BD)$	y $E(CD)$	$-x(1-x-y)$ $C^I(ABD)$	$-y(1-x-y)$ $C^I(ACD)$	$-xy$ $C^I(BCD) - \gamma(B-C)$	$-x(1-x)$ $\gamma(A-B)$	$-y(1-y)$ $\gamma(A-C)$
	$Al_{1-x-y}Ga_xIn_yAs$							
E_0 (eV)	2.982	1.551	0.583	0.00	0.629	-0.05	0.27	0.5 (*)
E_1 (eV)	3.610	3.112	2.510	0.00	0.277	-0.26	0.48	0.5 (*)
E_2 (eV)	4.881	5.013	4.420	0.00	0.073	-0.149	0.02	0.5 (*)
a (Å)	5.662 2	5.653 4	6.058 5	0.0	0.0	0.0	0.0	0.0

(*) Due to the lack of experimental data, the bandwidth parameters for the Al-In pair are taken as 1.0 eV.

the VCA or intrinsic bowing effects from those of the pseudobinary alloys based on the same group of pure compounds. This interpolation scheme is quite general since it does not refer to any specific band structure calculation method for the determination of the relation $E(Q)$. On the other hand a second order alloy model has been used to describe the disorder induced (extrinsic) bowing effects for the general alloys. Though this method shares its parameterized nature with the well known dielectric method (DM), it is different for the latter on two points : first, the adjustable parameters involved in our calculation are given a clear physical significance as embodying the information about the disorder state in the alloy. Secondly, in the present method, the disorder state is shown to affect differently the alloy band structure at different k points in the Brillouin zone. This effect is proved to exist even when a short range fluctuating alloy potential is assumed. This finally leads to the adoption of three bandwidth parameters (B) for the higher symmetry Γ , L , X points, instead of a single one as in classical DM. This approach has been applied to the III-V ternary (pseudo binary) alloys where the B parameter has been determined using the existing experimental data. This determination has been made such that they only depend on the substituents pair dealt with (e.g., Ga-Al ; Ga-In ; ... etc.). It must be emphasized that the accuracy of such a determination was limited by two factors : (i) the scatter in the reported experimental bowing (ii) the lack of data for some pairs to which few experimental studies have been devoted e.g., Al-In or P-Sb. The present calculations give a better description of the band structure (E_0 , E_1 , E_2) of ternary alloys than previous calculations based on the classical DM. The present theory has also been applied to the quaternary alloys. In this case, the calculations are greatly reduced since most of the needed parameters have been previously obtained in the ternary alloys. However, all these simplifications are still based on firm physical grounds including a more correct description of disorder effects with respect to previously published theories [9-11], where a purely geometrical approach has led to somewhat inconsistent assumptions.

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Appendix.

The statistical parameters $\langle \xi_k^{(i)} \cdot \xi_m^{(i)} \rangle$ are explicitly known when a given solid solution type (probability distribution law of the $C_k^{(i)}$) is assumed. For instance in an ideal solid solution the respective probabilities of occupancy of a given site on the sublattice (i) by the $A_k^{(i)}$ atomic species are $x_k^{(i)}$. This is a consequence of the assumption of statistically independent sublattices. Therefore, one can explicitly calculate the average composition at a given site for all species $A_k^{(i)}$. For instance the site concentration of any $A_k^{(i)}$ is 1 if the site is occupied by $A_k^{(i)}$ and 0 otherwise. Then, in this case,

$$\langle C_k^{(i)} \rangle = (1 - x_k^{(i)}) \cdot 0 + x_k^{(i)} \cdot 1 = x_k^{(i)}; \quad \text{for all } i \text{ and } k$$

and

$$\langle \xi_k^{(i)} \rangle = \langle C_k^{(i)} \rangle - x_k^{(i)} = 0; \quad \text{for all } k \text{ and } i.$$

In this case, one can also calculate the correlation parameter associated with the composition fluctuations $\langle \xi_k^{(i)} \cdot \xi_m^{(i)} \rangle$. We obtain

$$\begin{aligned} \langle \xi_k^{(i)} \cdot \xi_k^{(i)} \rangle &= x_k^{(i)} \cdot (1 - x_k^{(i)}); \quad \text{for } k = m \\ \langle \xi_k^{(i)} \cdot \xi_m^{(i)} \rangle &= -x_k^{(i)} \cdot x_m^{(i)}; \quad \text{for } k \neq m. \end{aligned}$$

These equations A.2 may be written in a compact form as

$$\langle \xi_m^{(j)} \cdot \xi_k^{(i)} \rangle = \langle \xi_k^{(i)} \cdot \xi_m^{(i)} \rangle = \delta_{ij} (x_k^{(i)} (1 - X_k^{(i)}) \delta_{km} + 2 \cdot x_m^{(i)} x_k^{(i)} (\delta_{km} - 1)) \quad (\text{A.3})$$

δ_{km} is the Kroenecker delta. The factor 2 on the right hand side of (A.3) arises from the fact that in (2.13) each pair (k, m) is considered once in the sum. For non ideal solid solutions, the statistical parameters are unknown and thus may be taken as disorder characteristic parameters. See section 2.3.

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