Effective masses of electrons and heavy holes in InAs, InSb, GaSb, GaAs and some of their ternary compounds

N. Bouarissa [*], H. Aourag [1]

Physics Department, University of M'Sila, M'Sila 28000, Algeria

Abstract

A survey is carried out for both electron and heavy-hole effective masses in InAs, InSb, GaAs, GaSb and some of their ternary compounds. Our computations are based on the pseudopotential method. To make allowance for the chemical disorder, the virtual crystal approximation is used, including a correction to the alloy potential. The agreement between our theoretical results and the experiment is very satisfying. A non-linearity dependence of the electron effective mass on the molar fraction has been shown for the ternary alloys under consideration, which indicates the alloying effect. This non-linearity disappears in the case of the heavy-hole effective mass for GaInSb. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Electrons; Heavy holes; Ternary compounds

1. Introduction

The compounds InAs, GaSb, InSb and GaAs with a total of eight valence electrons encompass some of the most technologically important materials, the tetrahedrally bonded compound semiconductors. These materials are mainly used as infrared detectors and emitters.

In recent years, efforts have been made to provide a deeper understanding of electronic properties of semiconductor devices. These efforts have revealed that in a number of cases, the simple interpolation procedures which have been relied on for more than two decades break down. In bulk semiconductor alloy materials such as, for example, InAsSb and GaInAs, the effects of long-range and local ordering, and selective localisation, respectively, have been clearly demonstrated. Such properties are strongly linked to bowing of the band structure states, and to the changes in the density of states and optical and transport parameters of alloys [1].

Effective masses of electrons and holes are important material parameters describing most carrier transport properties [2–4], exciton effects and electron-hole liquids in semiconductors [5–8], to name a few. Its importance became recently even greater as the technology of optoelectronic devices matures and its precise knowledge is becoming critical. Values of effective masses can often be determined by, for instance, cyclotron resonances [9–12] or transport measurements [3,13,14]. On the theoretical side, concepts based on the total energy and coherent poten-

---
[*] Corresponding author. Fax: +213-5-550404
[1] Permanent address: Physics Department, University of Sidi-Bel-Abbes 22000, Algeria.

tial theory have been introduced to explain these observations. However, a quantitative appreciation of the alloy electronic properties has not been accomplished. This is partly because of the failure of a priori band structure calculations on elemental and binary compounds, as well as the alloy materials, to present the excitation processes in these systems, and partly because of the practical difficulties in isolating alloy-related effects from other perturbations.

The virtual crystal approximation (VCA) treats an alloy as a perfectly periodic crystal with an average potential at each sublattice site and does not include in lowest order the effect of a periodic fluctuation [15]. This theoretical consideration gives often a linear dependence of the band gap as a function of stoichiometric coefficient. However, the measured fundamental band gap vs. x shows a bowing away from the linear interpolation of band gap of parent compounds [16]. A possible treatment of the bowing would have been to introduce into the theory a non-periodic potential with an adjustable parameter, in order to make calculations more consistent with experimental observations [17].

The present study was motivated by the need to ascertain the efficacy of the pseudopotential method combined, for ternary alloys, with the VCA, which enables to substitute the true one-electron crystal potential of the alloy by the linear part, where we add a non-periodic potential due to the compositional disorder, in describing the effective masses of electrons and heavy holes of representative semiconductors and some of their ternary compounds. We, however, focus on the effective masses as a function of the stoichiometric coefficient. We have analyzed our results in order to show the effect of the electronic bowing on the electron and heavy-hole effective masses.

2. Calculations

Simply stated, we write the pseudopotential Hamiltonian for an electron in the cubic semiconductors of zincblende type as:

$$H = (-\hbar^2 / 2m)\nabla^2 + V(r) \qquad (1)$$

The potential $V(r)$ can be expanded in reciprocal lattice vectors G and can be expressed as the product of a structure factor $S(G)$ times a pseudopotential form factor $V(G)$. It is convenient then to rewrite this in terms of a symmetric and antisymmetric potential, giving:

$$V(r) = \sum_G \left[V^{\mathrm{s}}(G)\cos(G\tau) + iV^{\mathrm{A}}(G)\sin(G\tau) \right]$$
$$\times \exp(-iG \cdot r) \qquad (2)$$

$\tau = (a/8)(1,1,1)$, where a is the length of the unit cube, V^{s} and V^{A} are the symmetric and antisymmetric form factors.

In terms of atomic potentials:

$$V^{\mathrm{s}}(G) = \tfrac{1}{2}(V_1(G) + V_2(G)) \qquad (3)$$

$$V^{\mathrm{A}}(G) = \tfrac{1}{2}(V_1(G) - V_2(G)) \qquad (4)$$

$$V_1(G) = (2/\Omega)\int V_1(r)\exp(-iG \cdot r)\mathrm{d}^3r \qquad (5)$$

and similarly for $V_2(r)$, where $V_1(r)$ and $V_2(r)$ are the pseudopotentials due to single atoms in the lattice and Ω is the volume of the unit cell.

The basis states used to form the Hamiltonian matrix consist of plane waves with wave vector $G + k$, where G is a reciprocal lattice vector and k is a wave vector lying within the first Brillouin zone.

$$\Psi_{nk}(r) = (1/\Omega)^{0.5}\Sigma C_{nk}(G)\exp(i(k + G) \cdot r) \qquad (6)$$

The coefficients $C_{nk}(G)$ are found by solving the secular equation:

$$\left((|k + G|^2 - E_{nk})\delta_{G,G'} + V(|G - G'|) \right)C_{nk}(G') = 0 \qquad (7)$$

The zincblende matrix is complex since the matrix elements of the antisymmetric potential are imaginary. The eigenvalues of this matrix are found by diagonalizing a matrix twice as large as the original complex one.

The lattice constant of the alloy $A_x B_{1-x}C$ is determined by using Vegard's rule as:

$$a(x) = xa_{\mathrm{AC}} + (1 - x)a_{\mathrm{BC}} \qquad (8)$$

where a_{AC} and a_{BC} are the lattice constants of the pure semiconductors AC and BC, respectively.

The alloy potential is calculated within the virtual crystal approach (VCA) as:

$$V_{\mathrm{VCA}} = xV_{\mathrm{AC}} + (1 - x)V_{\mathrm{BC}} \qquad (9)$$

To make allowance for the chemical disorder, we add the compositional disorder as an effective periodic potential [17]:

$$V_{\text{alloy}} = V_{\text{VCA}} + V_{\text{dis}} \tag{10}$$

where:

$$V_{\text{dis}} = -p\big[\, x(1-x)\,\big]^{0.5} \sum_{j} \Delta(r - R_j) \tag{11}$$

j indicates the summation on the AC and BC molecular sites.

$$\Delta(r) = V_{\text{AC}}(r) - V_{\text{BC}}(r) \tag{12}$$

The potential $\Delta(r)$ decreases more rapidly owing to screening, thus ensuring the rapid convergence of p.

By adding this effective disorder potential to the virtual crystal potential, we have the final expression for the pseudopotential form factors:

$$V_{\text{alloy}}(r) = x V_{\text{AC}}(r) + (1-x) V_{\text{BC}}(r)$$
$$- p\big[\, x(1-x)\,\big]^{0.5}\big(V_{\text{AC}}(r) - V_{\text{BC}}(r)\big) \tag{13}$$

p is then treated as an adjustable parameter.

We used this potential over different compositions by varying p until agreement with experiments was achieved.

In our calculations, we have used five pairs of states k_i and k_j: $(\Gamma\text{–}\Gamma)$, $(\Gamma\text{–}X)$, $(\Gamma\text{–}L)$, $(X\text{–}X)$ and $(L\text{–}L)$.

The dimension of our eigenvalue problem is a (136×136) matrix. However, 59 plane waves give a good convergence.

A theoretical effective mass in general turns out to be a tensor with nine components m^*_{ij} defined as [18]:

$$\frac{1}{m^*_{ij}} = \frac{4\pi^2}{h^2}\frac{\partial^2 E(k)}{\partial k_i \partial k_j} \tag{14}$$

where E is the carrier energy and k_i are the components of the wave vector k in a periodic potential field of a semiconductor. Thus, the effective mass is a direction dependent quantity.

For a very idealized simple case, i.e., for the band extremum occurring precisely at $k = 0$ and the parabolic $E(k)$ relationship (as in the case of the $A^{\text{III}}B^{\text{V}}$ compounds), the effective mass becomes a scalar and is a value independent of direction. Therefore, we may use one scalar effective mass defined as:

$$\frac{1}{m^*} = \frac{4\pi^2}{h^2}\frac{\partial^2 E(k)}{\partial k^2} \tag{15}$$

In our case, it is particularly easy to evaluate the band energies at a sequence of points around $k = 0$ and evaluate m^* from Eq. (15) directly.

3. Results

The adjusted local pseudopotential form factors for gallium antimonide (GaSb), indium antimonide (InSb), indium arsenide (InAs) and gallium arsenide (GaAs) are summarized in Table 1. The electronic band structures of all mentioned above binary semiconductors have been calculated using the empirical pseudopotential method (EPM). Our results for the principal energy gap are given in Table 2. The agreement with experiment is generally very good. In the case of the ternary compounds $\text{InAs}_x\text{Sb}_{1-x}$ and $\text{Ga}_x\text{In}_{1-x}\text{Sb}$, the EPM has been combined with the VCA with and without including the disorder effect and used for the band gap energy calculations. We found that the agreement with experiment is reached only when the disorder effect is taken into account.

In this section, we concentrate on the results of our calculations of hole and electron effective masses at the valence-band maxima and the conduction-band minima of the studied semiconductors. Table 3 lists our theoretical results along with the available experimental values, for convenience some theoretical results of other methods are also listed. As can be

Table 1
The adjusted local pseudopotential form factors in Ry for GaSb, InSb, InAs and GaAs

Compound	$V^s(3)$	$V^s(8)$	$V^s(11)$	$V^A(3)$	$V^A(4)$	$V^A(11)$
GaSb	−0.1910	0.005	0.0434	0.0454	0.0300	0.000
InSb	−0.2032	0.010	0.0294	0.0601	0.0300	0.015
InAs	−0.2116	0.000	0.0457	0.0492	0.0450	0.010
GaAs	−0.2662	0.014	0.0643	0.0146	0.0380	0.001

Table 2
The calculated energy levels spacing in eV compared with experiment [19]

Band-gap energy (eV)	GaSb		InSb		InAs		GaAs	
	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp
$\Gamma^c - \Gamma^v$	0.72	0.72	0.17	0.18	0.36	0.36	1.42	1.42
$X^c - \Gamma^v$	1.01	1.05	1.63	1.63	1.37	1.37	1.95	1.91
$L^c - \Gamma^v$	0.77	0.76	0.93	0.93	1.07	1.07	1.73	1.73

seen, for InAs, Nakwaski [18] has recommended for the electron effective mass a value of 0.023 m_o, where m_o stands for the electron mass in free space. Our calculated value is bigger than this one, but is in a good agreement with those measured by Ukhanov and Mal'tsev [21] and Kazakova et al. [22]. For InSb, our calculated value is much higher than that of Ref. [3]. Unfortunately, we have no other experimental data which are available for comparison. Similarly, as for InSb, we have only one available experimental value of the electron effective mass taken from Ref. [3], which is in a reasonable agreement with our calculated value. However, in the case of GaAs, many theoretical and experimental values of effective masses are available from the scientific literature. A nearly general agreement between many researchers using different theoretical approaches or experimental techniques shows that the value $m_e^* = 0.067\, m_o$ of the band-edge electron effective mass in GaAs seems to be determined very correctly [18], which is in a very good agreement with our calculated one. We may then conclude that our calculated electron effective masses and experiment compare favorably, although the agreement is not quite as good as for GaAs and GaSb. This can be explained by the fact that the energy band gap of both materials InAs (0.36 eV) and InSb (0.17 eV) is less than those of GaSb (0.72 eV) and GaAs (1.42 eV), since the narrow gap between the conduction and valence bands in InAs and InSb leads to a strong interaction between them which makes the energy dispersion relation $E(k)$ vary non-parabolically with k (E not proportional to k^2). The conduction band non-parabolicity is a result of mixing between states in different bands, especially conduction and valence bands. Due to the non-parabolic nature of the energy band, the polar interactions of the electrons with the longitudinal phonons through the electric field of

polarization wave play an important role at room temperature for these materials, where in this interaction, the phonon energy is comparable to the electron energy. Another complication which is due also to the narrowness of the band gap implies a non-negligible number of thermally excited electrons, so screening has to be taken into consideration. The inclusion of screening and the subband wave-function effects decreases, however, the mass correction appreciably [27–29]. This may improve our calculated electron effective masses of InAs and InSb.

The calculated heavy-hole effective masses for our studied materials are tabulated and compared with other theoretical estimates and available experimental data in Table 4. We notice that the agreement between our theoretical results and the experiment is generally very good.

Since we have neglected spin–orbit coupling in our work, we cannot say anything about the so-called split-off mass band resulting from the spin–orbit coupling.

Let us now try to find relations for the band-edge density of states electron and heavy-hole effective masses in the ternary compounds $InAs_xSb_{1-x}$ and $Ga_xIn_{1-x}Sb$.

Table 3
Conduction band-edge electron effective mass (in units of free electron mass) in InAs, InSb, GaSb and GaAs determined by various experimental and theoretical methods

Material	m_e^*	Method
InAs	0.018 [20][b]	Self-consistent ab-initio calculations
	0.029 [21][c]	Faraday rotation
	0.030 [22][c]	Reflection
	0.04 [23][b]	Thermoelectric power
	0.026 [3]	
	0.023 [18]	Recommended value
	0.034[a,b]	Pseudo-potential method
InSb	0.015 [3]	
	0.03[a,b]	Pseudo-potential method
GaSb	0.047 [3]	
	0.05[a,b]	Pseudo-potential method
GaAs	0.0636 [24][c]	Photoluminescence
	0.069 [25][c]	Faraday rotation
	0.07 [26][b,c]	Thermoelectric power
	0.07 [3]	
	0.067 [18]	Recommended value
	0.07[a,b]	Pseudo-potential method

[a] Present work. [b] At room temperature. [c] At 300 K.

Table 4
Valence band-edge heavy-hole effective masses (in units of free electron mass) in InAs, InSb, GaSb and GaAs determined by various experimental and theoretical methods

Material	m_{hh}^*	Method
InAs	0.90 [4][b]	LCAO method
	0.41 [3]	
	0.57 [18]	Recommended value
	0.40[a,b]	Pseudo-potential method
InSb	0.39 [3]	
	0.41[a,b]	Pseudo-potential method
GaSb	0.3 [3]	
	0.31[a,b]	Pseudo-potential method
GaAs	0.5 [18][b]	Thermoelectric power
	0.85 [4][b]	LCAO method
	0.68 [3]	
	0.57 [18]	Recommended value
	0.42[a,b]	Pseudo-potential method

[a] Present work. [b] At room temperature.

Figs. 1 and 2 give the variation of the electron effective mass as a function of the stoichiometric coefficient x for $InAs_xSb_{1-x}$ and $Ga_xIn_{1-x}Sb$, respectively. The results show clearly a linear dependence of the electron effective mass on the alloy composition, when the disorder potential is not taken
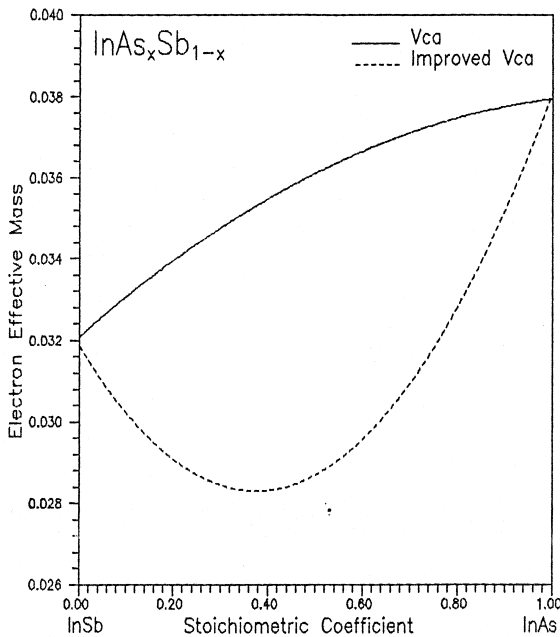
Fig. 1. Conduction band-edge electron effective mass (in units of free electron mass) vs. alloy composition in $InAs_xSb_{1-x}$.

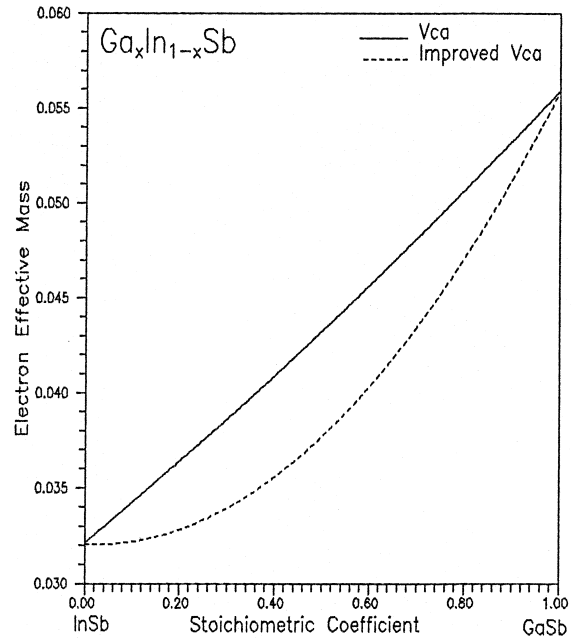Fig. 2. Conduction band-edge electron effective mass (in units of free electron mass) vs. alloy composition in $Ga_xIn_{1-x}Sb$.

into account (VCA alone). However, by taking this effect into consideration (improved VCA), a non-linearity dependence on the alloy composition is observed (bowing effect). This means that the disorder effect on the electron effective mass is important. Therefore, we can conclude that in any attempt to calculate the electron effective mass in ternary semiconductor alloys, we should take into account the disorder potential.

A least square fit of these two curves exhibits a sublinearity, yielding for the linear and quadratic electron effective mass coefficients (in units of free electron mass):

$m_e^* = 0.03 + 0.01 x - 0.004 x^2$
(VCA; $InAs_xSb_{1-x}$)
$m_e^* = 0.03 + 0.02 x + 0.003 x^2$
(VCA; $Ga_xIn_{1-x}Sb$)
$m_e^* = 0.03 - 0.01 x + 0.025 x^2$
(improved VCA; $InAs_xSb_{1-x}$)
$m_e^* = 0.03 - 0.001 x + 0.025 x^2$
(improved VCA; $Ga_xIn_{1-x}Sb$).

The quadratic term stands for the bowing parameter. This behaviour is not similar to the linear dependence of the electron effective mass on the alloy
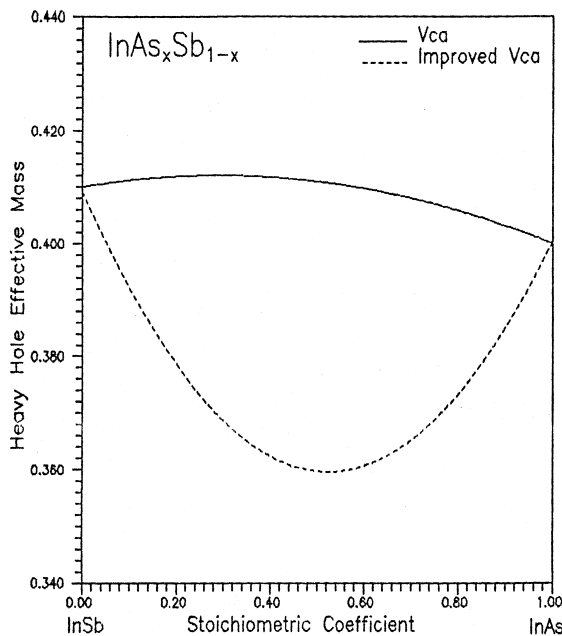
Fig. 3. Valence band-edge heavy-hole effective mass (in units of free electron mass) vs. alloy composition in $InAs_xSb_{1-x}$.

that for $Ga_xIn_{1-x}Sb$ (0.41 eV). As previously with the electron effective mass, a least square fit of these two curves yields for the linear and quadratic heavy-hole effective mass coefficients (in units of free electron mass):

$m_{hh}^* = 0.40 + 0.01x - 0.023x^2$
(VCA; $InAs_xSb_{1-x}$)
$m_{hh}^* = 0.40 - 0.10x + 0.005x^2$
(VCA; $Ga_xIn_{1-x}Sb$)
$m_{hh}^* = 0.40 - 0.18x + 0.180x^2$
(improved VCA; $InAs_xSb_{1-x}$)
$m_{hh}^* = 0.40 - 0.10x - 0.004x^2$
(improved VCA; $Ga_xIn_{1-x}Sb$).

Once again this result for $InAs_xSb_{1-x}$ does not agree with the recommended formulae describing band-edge heavy-hole effective mass in the $A^{III}B^V$ ternary compounds proposed by Nakwaski [18]. This difference is due to the fact that in Ref. [18], the author has just assumed a linear dependence of the effective mass on the alloy composition, by taking into consideration the recommended values listed in Tables 3 and 4 without doing any calculations. However, in o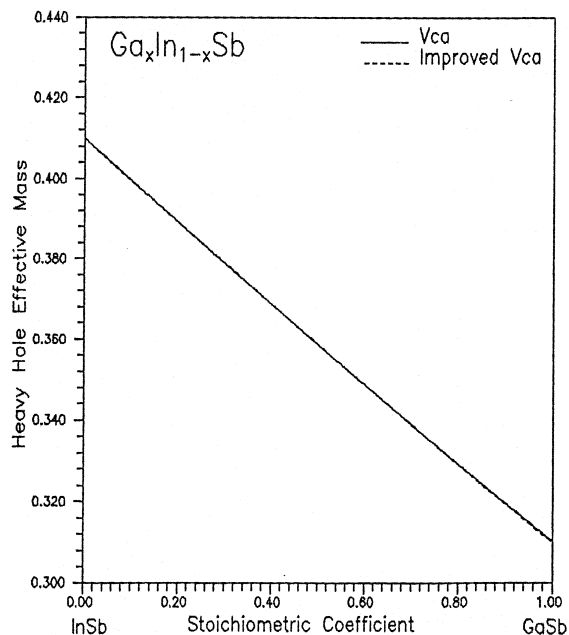ur case, we have calculated the effective composition recommended by Nakwaski [18] for some $A^{III}B^V$ ternary compounds.

The variation of the heavy-hole effective mass vs. alloy composition is plotted in Figs. 3 and 4 for $InAs_xSb_{1-x}$ and $Ga_xIn_{1-x}Sb$, respectively. Through Fig. 3, we notice similarly as for the electron effective mass, that the disorder effect on the heavy-hole effective mass is also important, since as one can see, the inclusion of the compositional disorder (improved VCA) leads to a non-linearity dependence on the alloy molar fraction. However, we note through Fig. 4 that the mentioned curves calculated separately with the VCA alone and with the inclusion of the disorder potential (improved VCA) for the alloy $Ga_xIn_{1-x}Sb$ are insensitive to the method used. The fact that the disorder effect on the heavy-hole effective mass has no effect in $Ga_xIn_{1-x}Sb$ could be ascribed to the similarity of the fourth valence bands of its parents in the vicinity of the Γ-point [30]. The fact that the disorder effect on the heavy-hole effective mass is important in $InAs_xSb_{1-x}$ and has no effect in $Ga_xIn_{1-x}Sb$, could be ascribed to the difference in their band gap bowing, since the bowing parameter for $InAs_xSb_{1-x}$ (0.58 eV) is higher than

Fig. 4. Valence band-edge heavy-hole effective mass (in units of free electron mass) vs. alloy composition in $Ga_xIn_{1-x}Sb$.

masses for each value of x and then we have done the best fit.

We have tentatively proposed a relation expressing the energy gap dependence of the electron effective mass for the binary semiconductors under consideration, in the following form:

$$\frac{m_e^*}{m_o} = 0.0310 - 0.0218Eg + 0.1000Eg^2$$
$$- 0.0460Eg^3.$$

where Eg (in eV) stands for the energy gap. This form is very similar to that proposed by Kolbas [18]. All the above facts leads us to believe that the disorder effect is essential not only for the band gaps and other physical properties of semiconductor alloys [31] but also for the electron and heavy-hole effective masses in these materials. Additional experimental measurements for systems of varying degrees of covalency, ionicity, and metallicity could be useful for determining ways of improving the theory.

4. Conclusion

In conclusion, a pseudo-potential calculation of the electron and heavy-hole effective masses in InAs, InSb, GaSb and GaAs has been carried out. Our theoretical results are in reasonable agreement with the available experimental ones. Generally, the theoretical–experimental differences are due to the narrowness of the band gap which leads to non-parabolicity of the energy dispersion relation.

An illustrative result of the electron effective mass calculations for both studied alloys $InAs_xSb_{1-x}$ and $Ga_xIn_{1-x}Sb$, shows a deviation from linearity which is due to the bowing effect. However, this non-linearity for the heavy-hole effective mass is still present only for the ternary alloy $InAs_xSb_{1-x}$. This may be due to the difference in the band gap bowing of the ternary compounds under consideration.

The relation expressing the variation of the electron effective mass as a function of the energy gap of the above studied materials was in turn proposed, and its form is in good agreement with that proposed by Kolbas.

References

[1] M. Jaros, Rep. Prog. Phys. 48 (1985) 1091.
[2] D.L. Rode, Semiconductors and semimetals, in: R.K. Willardson, A.C. Beer (Eds.), Vol. 10, Transport Phenomena, Academic Press, New York, 1975, p. 1.
[3] C. Kittel, Introduction to Solid State Physics, 5th edn., Wiley, New York, 1976.
[4] W.A. Harrison, Electronic Structure and the Properties of Solids, Freeman, San Francisco, 1980.
[5] T.M. Rice, Solid State Phys. 32 (1978) 1.
[6] J.C. Hensel, T.G. Phillips, G.A. Thomas, Solid State Phys. 32 (1978) 88.
[7] G. Beni, T.M. Rice, Solid State Commun. 23 (1977) 871.
[8] G. Beni, T.M. Rice, Phys. Rev. B 2 (1978) 768.
[9] G. Dresselhaus, A.F. Kipp, C. Kittel, Phys. Rev. 98 (1955) 368.
[10] J.M. Luttinger, Phys. Rev. 102 (1956) 1030.
[11] B. Lax, J.G. Mavroides, Phys. Rev. 100 (1955) 1650.
[12] C. Kittel, Quantum Theory of Solids, Wiley, New York, 1963.
[13] P.I. Baranskii, A.E. Belyaev, O.P. Gorodnichii, Sov. Phys. Semicond. 10 (1976) 110.
[14] P.I. Baranskii, O.P. Gorodnichii, A.U. Savchuk, Sov. Phys. Semicond. 10 (1976) 931.
[15] R.H. Parmenter, Phys. Rev. 97 (1955) 587.
[16] A.B. Chen, A. Sher, Phys. Rev. B 10 (1981) 5360.
[17] S.J. Lee, T.S. Kwon, K. Nahm, C.K. Kim, J. Phys. Condens. Matter 2 (1990) 3253.
[18] W. Nakwaski, Physica B 210 (1995) 1, and references therein.
[19] S. Adachi, J. Appl. Phys. 61 (1987) 4869.
[20] P. Boguslawski, A. Baldereshi, Solid State Commun. 70 (1989) 1085.
[21] Y.I. Ukhanov, Y.V. Mal'tsev, Sov. Phys. Solid State 5 (1963) 1124.
[22] L.A. Kazakova, V.V. Kostsova, R.K. Karymshakov, Y.I. Ukhanov, V.P. Yagup'ev, Sov. Phys. Semicond. 5 (1972) 1495.
[23] R.P. Chasmar, R. Stratton, Phys. Rev. 102 (1956) 1686.
[24] D.M. Szmyd, P. Porro, A. Majerfeld, S. Lagomarsino, J. Appl. Phys. 68 (1990) 2367.
[25] C. Constantinescu, S. Nan, Phys. Status Solidi A 18 (1973) 277.
[26] O.V. Emelyanenko, D.N. Nasledov, V.I. Sidorov, V.A. Skirpin, G.N. Talalakin, Phys. Status Solidi 12 (1965) K93.
[27] H. Sigg, P. Wyder, J.A.A.J. Perenboom, Phys. Rev. B 31 (1985) 5253.
[28] F.M. Peeters, X. Wu, J.T. Devreese, Solid State Commun. 65 (1988) 1505.
[29] S. Das Sarma, Phys. Rev. B 27 (1983) 2590.
[30] N. Bouarissa, unpublished data.
[31] N. Bouarissa, H. Aourag, Solid State Commun. 101 (1997) 205.