PHYSICAL REVIEW B VOLUME 15, NUMBER 2 15 JANUARY 1977

$\vec{k}\cdot\vec{p}$ perturbation theory in III-V compounds and alloys: a reexamination

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(Received 31 August 1976)

From the recent optical conduction-electron spin-resonance (CESR) measurements of the g factors g^* in III-V compounds and the known effective masses m^*, in the framework of the $\vec{k}\cdot\vec{p}$ perturbation theory, we determine an experimental value of the interband matrix element $P^2 = (2/m_0)|\langle S|p_x|X\rangle|^2$ coupling the conduction band and the upper valence bands. P^2 ranges from 21 ± 1.5 eV in InP to 29 ± 1 eV in GaAs. This unexpected strong variation can be justified by a crude tight-binding calculation, evidencing the combined influence of ionicity and cell dimension. We show that g^* can be calculated with a precision of 10% in a three-band calculation, whereas a multiband approximation is required for m^*. The good agreement between our CESR measurements of the g factors in $Ga_{1-x}In_xAs$ and $Ga_{1-x}Al_xAs$ and the calculated values by $\vec{k}\cdot\vec{p}$ theory shows the correctness of this theory in alloys. Moreover, it is possible to obtain a satisfactory fit of the effective-mass data previously unexplained within simple $\vec{k}\cdot\vec{p}$ theory by using a multiband model and correct values of P^2. The modifications to $\vec{k}\cdot\vec{p}$ theory involving random potentials and strains are then not necessary at the precision of the experimental data available up to now.

I. INTRODUCTION

The detailed calculation of the band structure in semiconductors from first principles requires a very large computing effort. However, it appeared very early that most of their practical properties do not need the detailed knowledge of energy levels and wave functions throughout the Brillouin zone, but depend only on some quantities such as effective masses, g factors, ... defined at extremum points of energy bands.[1] Thus, a semiempirical theory, namely the $\vec{k}\cdot\vec{p}$ perturbation theory,[1,2] has been developed: It permits to calculate the shape of the energy bands in the vicinity of such special points, from the only data of experimental energy gaps and matrix elements at these points.

This paper compares the effective masses m^* and g factors g^* of conduction electrons at Γ_6^c with the predictions of $\vec{k}\cdot\vec{p}$ theory in the most common III–V compounds and alloys. The pure-compound effective masses were measured in the late fifties and had then been fitted easily, assuming a three-band interaction, i.e., a coupling only between the states of the lowest conduction band and the upper valence bands.[3] A constant coupling matrix element P^2 of 23 eV between these bands was deduced,[4] independent of the semiconductor. The comparison of the g factors calculated in this same approximation with the experimental measurements should have shown that this constancy was fortuitous. Unfortunately, at that time, the only precisely known g factors, measured by standard conduction-electron spin resonance (CESR), were those of small-band-gap semiconductors (InSb,[5] and[6] InAs) for which the three-band approximation for both m^* and g^* is sufficiently accurate and P^2 is indeed of the order of 23 eV. In GaAs, where P^2 is significantly larger, the g factor had been attributed the wrong sign,[7] so that P^2 could not be calculated properly. The other g factors were sometimes determined by nonresonant methods, with a generally rather poor precision. It is but recently that optical pumping techniques have permitted the optical detection of CESR in some more compounds (GaSb,[8] GaAs,[9] and [10]InP). This has led us in Sec. II to a reexamination of the approximations of $\vec{k}\cdot\vec{p}$ theory with the following conclusions: whereas the three-band approximation is sufficient to calculate g^* with a precision of a few percent, the calculation of m^* requires at least five bands. Moreover, the values of g^*'s calculated up to now[11,12] do not fit correctly the experimental results because they rely on wrong interband coupling parameters. We have taken the converse approach: instead of predicting the values of P^2, we determine them experimentally from the measured m^*'s and g^*'s. We show that, in opposition to the usual belief, they present a rather strong variation from one compound to another. This variation can be understood by an approximate calculation of P^2 using tight-binding wave functions. The same considerations also apply to II–VI compounds, for which sufficient experimental data exist now.

Semiconducting III–V alloys have already been extensively studied within the framework of $\vec{k}\cdot\vec{p}$ theory. They provide a situation which permits to calculate the continuous variations of effective masses and g factors with composition, in contrast with the discrete values of the pure compounds. It was observed that the three-band approximation could not fit the observed variation of the effective mass with alloy composition. The effect of band mixing due to alloy disorder was invoked to explain the breakdown of the virtual-crystal approximation.[13] A more rigorous theoretical treatment of the random potentials and strains has been made by Siggia,[14] in the coherent-potential-approximation model. It leads to modifications of $\vec{k}\cdot\vec{p}$ theory in alloys. We rather show in Sec. III that the effective-mass data can be fitted when one uses for pure compounds the values of P^2 determined in Sec. II, and assume a linear variation of P^2 with composition, in a multiband approximation of $\vec{k}\cdot\vec{p}$ theory. We use the same assumptions to explain the g factors that we measured in $Ga_{1-x}In_xAs$ and $Ga_{1-x}Al_xAs$ alloys by optical detection of CESR.[9]

II. $\vec{k}\cdot\vec{p}$ THEORY AND ITS APPLICATION TO PURE COMPOUNDS

A. $\vec{k}\cdot\vec{p}$ theory

The $\vec{k}\cdot\vec{p}$ perturbation theory gives the expressions of energies and wave functions in the vicinity of a semiconductor band extremum. In particular the effective mass is related to the k^2 term of the energy development. For a conduction electron at $k=0$ in a cubic semiconductor, the effective mass m_x^* is given by[15]

$$\frac{m_0}{m_x^*}-1=\sum_u \frac{|\langle S|p_x|u\rangle|^2}{E_c-E_u}\,, \tag{1}$$

where m_0 is the free-electron mass, S the conduction-band wave function; the wave function u corresponds to a state at energy E_u; p_x is the x component of the momentum operator. The k-dependent spin-orbit term has been neglected. As the effective mass is isotropic, we have in this case

$$m_x^*=m_y^*=m_z^*=m^*\,.$$

In the same conditions, the Landé factor g^* of the conduction electrons is expressed by[3]

$$\frac{g^*}{g_0}-1=\frac{1}{im_0}\sum_u \frac{\langle S|p_x|u\rangle\langle u|p_y|S\rangle-\langle S|p_y|u\rangle\langle u|p_x|S\rangle}{E_c-E_u}\,. \tag{2}$$

$g_0=2$ is the free-electron Landé factor. This expression strictly holds for a magnetic field parallel to z. However, in a cubic semiconductor the conduction band g^* is isotropic. The value of g^* is different from g_0 only in presence of spin-orbit interaction. From (1) and (2), it appears that the same energy gaps and matrix elements enter the developments of m^* and g^*. When simple group wave functions are considered, the matrix element $\langle S|p_x|u\rangle$ is different from zero only if u belongs to a Γ_5 representation (Koster's notations[16] are used). As spin-orbit splittings are smaller than $\Gamma_5-\Gamma_5$ band-gap energies, the spin-orbit interaction behaves as a perturbation: the double-group states of Γ_7 and Γ_8 symmetries which contribute to (5) and (6) are then issued from Γ_5 levels of the simple group.

The dominant terms come from the interaction of the Γ_1^c conduction band with the nearest bands of Γ_5 symmetry, i.e., the Γ_5^v valence bands and the Γ_5^c conduction bands, and are evidenced in Eqs. (3) and (4):

$$\frac{m_0}{m^*}-1=\frac{P^2}{3}\left(\frac{2}{E_0}+\frac{1}{E_0+\Delta_0}\right)-\frac{P'^2}{3}\left(\frac{2}{E(\Gamma_8^c)-E_0}+\frac{1}{E(\Gamma_7^c)-E_0}\right)+C\,, \tag{3}$$

$$\frac{g^*}{g_0}-1=\frac{P^2}{3}\left(\frac{1}{E_0}-\frac{1}{E_0+\Delta_0}\right)-\frac{P'^2}{3}\left(\frac{-1}{E(\Gamma_8^c)-E_0}+\frac{1}{E(\Gamma_7^c)-E_0}\right)+C'\,, \tag{4}$$

where

$$P^2=(2/m_0)\,|\langle S|p_x|X(\Gamma_5^v)\rangle|^2\,,$$

$$P'^2=(2/m_0)\,|\langle S|p_x|X(\Gamma_5^c)\rangle|^2\,,$$

$$C=\sum_{u'}\frac{P_{u'}^2}{E_c-E_{u'}}\,,$$

$$C'=\sum_{u'}\frac{P_{u'}^2}{E_c-E_{u'}}\,\frac{\Delta_{u'}}{E_c-E_{u'}}\,,$$

$$P_{u'}^2=(2/m_0)\,|\langle S|p_x|X_{u'}\rangle|^2\,.$$

u' labels all concerned bands of the double group that are neither issued from Γ_5^v nor Γ_5^c. E_0 is the $\Gamma_8^v-\Gamma_6^c$ gap, Δ_0 the valence-band spin-orbit splitting, $\Delta_{u'}$ the spin-orbit splitting related to the u' band; the energies origin is taken at Γ_8^v. The various energy levels are shown in Fig. 1. The energies $P^2, P'^2, P_{u'}^2$, describe the coupling between the conduction band and the other interacting bands.

Let us study the relative importance of the various terms of Eqs. (3) and (4):

(i) The first term of $m^*\approx P^2/E_0$ varies from 15 to 70 depending on the compound; its second term $\approx P'^2/[E(\Gamma_5^c)-E_0]$ ranges from 0 to 3. Their ratio is $(P'^2/P^2)E_0/[E(\Gamma_5^c)-E_0]$.

(ii) In the expression of g^* the first and second terms are approximately $\frac{1}{3}P^2(\Delta_0/E_0^2)$ and

$$\tfrac{1}{3}P'^2[E(\Gamma_8^c)-E(\Gamma_7^c)]/[E(\Gamma_5^c)-E_0]^2\,.$$

Their ratio is

$$(P'^2/P^2)\{E_0/[E(\Gamma_5^c)-E_0]\}^2\{[E(\Gamma_8^c)-E(\Gamma_7^c)]/\Delta_0\}\,.$$

(iii) The *relative* importance of the second term is thus reduced in g^* with respect to m^* by the factor

$$\{E_0/[E(\Gamma_5^c)-E_0]\}\{[E(\Gamma_8^c)-E(\Gamma_7^c)]/\Delta_0\}\approx\tfrac{1}{3}\times\tfrac{1}{2}=\tfrac{1}{6}\,.$$

Consequently, the term due to Γ_5^c is still an appreciable correction to m^*, but it does not influence so much the development of g^*, which converges then more rapidly than that of m^*.

The same argument can be pursued for remote bands. The residual term C should be of the same order of magnitude as in germanium,[17] where the contribution of remote bands to m_0/m^* is -2,2: the negative sign implies that the next important band is a conduction level. The relative contribution of C to m_0/m^* is then a few percent. C' should be of the order of $C(\Delta_{u'}/E_{u'})$. The spin-orbit splitting $\Delta_{u'}$ decreases for higher-lying bands[18] and is thus a fraction of eV, whereas $E_{u'} \geqslant 10$ eV. From now on, we shall take $C \approx -2, C' \approx -2\times 10^{-2}$ in all compounds.

Our purpose is to obtain P^2 and P'^2 in different III–V semiconductors from the experimental determinations of m^* and the resonance values of g^*: from (3) and (4)

$$P^2 = A\left(1 + C' - \frac{g^*}{g_0}\right)\left(\frac{2}{E(\Gamma_8^c) - E_0} + \frac{1}{E(\Gamma_7^c) - E_0}\right) - \left(1 + C - \frac{m_0}{m^*}\right)\left(\frac{1}{E(\Gamma_7^c) - E_0} - \frac{1}{E(\Gamma_8^c) - E_0}\right), \quad (5)$$

$$P'^2 = A\left(1 + C' - \frac{g^*}{g_0}\right)\left(\frac{2}{E_0} + \frac{1}{E_0 + \Delta_0}\right) + \left(1 + C - \frac{m_0}{m^*}\right)\left(\frac{1}{E_0} - \frac{1}{E_0 + \Delta_0}\right), \quad (6)$$

where

$$A = \left(\frac{1}{E_0[E(\Gamma_7^c) - E_0]} - \frac{1}{(E_0 + \Delta_0)[E(\Gamma_8^c) - E_0]}\right)^{-1}.$$

As $[1 + C' - (g^*/g_0)]$ is positive and $[1 + C - (m_0/m^*)]$ negative in all materials, P^2 is the sum of two contributions, one due to the Landé factor and the other corresponding to the effective mass. The contribution of m^* to P^2 vanishes when the spin-orbit splitting of Γ_5^c tends to zero. As this splitting is generally much smaller than the $\Gamma_1^c - \Gamma_5^c$ gap we expect the contribution of m^* to be only a correction, the value of P^2 being mainly determined by g^*. This expresses in other words the fact already mentioned that in Eqs. (3) and (4), *g^* is determined almost only by the P^2 term, whereas m^* is related to P^2 and P'^2*. The three-band approximation of $\vec{k}\cdot\vec{p}$ theory is thus almost correct for g^*, but insufficient for m^*.

Table I reports the values of P^2 and P'^2 calculated in the III–V semiconductors where values of g^* have been measured by spin resonance techniques. In all materials we took $C \approx -2$, $C' \approx -2\times 10^{-2}$. In fact the numerical value of P^2 is rather insensitive to the contribution of the higher-lying bands, its precision being mainly determined by the precision on g^* and the principal gaps, and on m^* to a smaller extent. The uncertainty on P^2 is calculated in different compounds, assuming

$$\delta m^*/m^* \leqslant 10^{-2}, \quad \delta(g^* - g_0)/(g^* - g_0) \leqslant 10^{-2},$$

$$\delta\Delta_0 \leqslant 3 \text{ meV},$$

$$\delta\left(\frac{E(\Gamma_8^c) - E(\Gamma_7^c)}{E(\Gamma_8^c) - E_0}\right) \leqslant 3\times 10^{-2}\,\frac{E(\Gamma_8^c) - E(\Gamma_7^c)}{E(\Gamma_8^c) - E_0}.$$

P^2 is determined with a precision of a few percent.[19] This is true, even in GaAs where g^* is small, because P^2 is a function of $g^* - 2$, which is known within 1%, though the precision on g^* is only 5%.[9] An important variation of P^2 from one compound to the other is evidenced.

We also indicate there the relative contribution of the g^* term to P^2: according to the compound it amounts from 80 to 90%. This shows that the Landé factor almost entirely determines P^2 and is thus the relevant quantity to be measured in order to obtain the coupling between the conduction band and the upper valence bands. This is in opposition with the previous analyses which related P^2 to

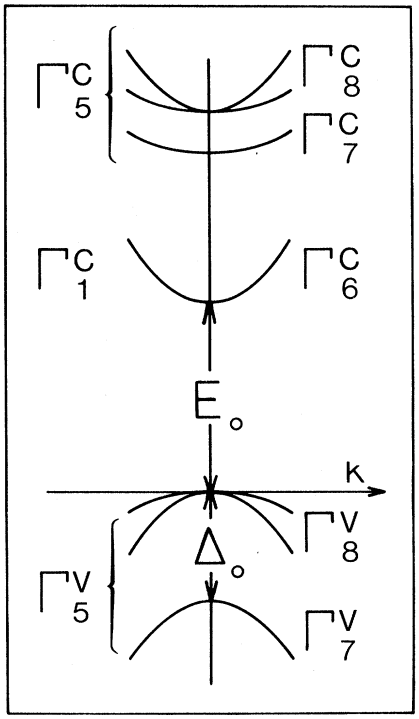

FIG. 1. Schematics of the band structure near $\vec{k} = \vec{0}$ in a cubic direct-gap semiconductor.

effective masses only and found an almost constant value in different materials.[4]

Only a range of values of P'^2 can be estimated in each compound: $[(m_0/m^*) - 1 - C]$ and $[(g^*/g_0) - 1 - C']$ being of opposite signs, P'^2 is the difference between two terms and crucially depends on the values of m^* and g^* and also on the remote bands contribution. The first line of values of P'^2 in Table I is obtained for $C = -2$, whereas the values in brackets, quite larger, correspond to $C = -1$. Anyway in most materials P'^2 is a notable fraction of P^2. Consequently a five-band approximation, taking into account the interaction of Γ_1^c with Γ_5^v and Γ_5^c, is necessary to calculate the effective mass, which strongly depends on P'^2. This remark will be used in our discussion on alloys in Sec. III.

To summarize, we have shown that experimental data of m^* and g^* yield a good experimental determination of P^2. We relate P^2 essentially to g^*, whereas m^* also depends on higher-lying bands: These approximations are similar to the low-field limit of Pidgeon and Brown's theory,[20] which is used in the interpretation of magneto-optical experiments.

B. Comparison with previous determinations of P^2

Our precise experimental determination of P^2 is made possible by the recent optical pumping measurements of g factors in GaSb,[8] GaAs,[9] InP.[10] Before that, the Landé factors were known pre-

TABLE I. Band parameters of III–V compounds and calculated interband matrix elements. The last line gives the relative importance of the first term in (5).

	InSb	InAs	InP	GaSb	GaAs
E_0	0.237 [a]	0.42 [f]	1.423 [j]	0.8137 [m]	1.519 [q]
Δ_0	0.81 [b]	0.38 [b]	0.11 [c] 0.102 [j]	0.752 [n]	0.341 [r]
$E(\Gamma_8^c)-E(\Gamma_8^v)$	3.49 [c]	4.60 [g]	4.79 [c]	3.56 [c]	4.659 [r]
$E(\Gamma_7^c)-E(\Gamma_8^v)$	3.16 [c]	4.44 [c]	4.72 [c]	3.27 [c]	4.488 [r]
$(m^*/m_0)_{\mathrm{exp}}$	0.0139 [d]	0.0230 [h]	0.0803 [k]	0.041 [o]	0.0667 [s]
g^*_{exp}	−51.3 [e]	−14.8 [i]	1.26 [l]	−9.25 [p]	−0.44 [t]
P^2 (eV)	24.4 ± 0.6	22.2 ± 0.5	20.7 ± 1.5	27.9 ± 1	28.9 ± 0.9
P'^2 (eV)	10.5 (13)	0.2 (4)	2.1 (6)	9 (11)	6 (9)
Relative contribution of g^* to P^2	.90%	.90%	.80%	.80%	.80%

[a] E. D. Johnson, Phys. Rev. Lett. 19, 352 (1967).

[b] C. R. Pidgeon, S. H. Groves, and J. Feinleib, Solid State Commun. 5, 677 (1967).

[c] M. Cardona, K. L. Shaklee, and F. H. Pollack, Phys. Rev. 154, 696 (1967). The energy gaps are measured at room temperature.

[d] E. J. Johnson and D. H. Dickey, Phys. Rev. B 1, 2676 (1970).

[e] See Ref. 5.

[f] C. R. Pidgeon, D. L. Mitchell, and R. N. Brown, Phys. Rev. 154, 737 (1967).

[g] Estimated from the values of Δ_0 and $E(\Gamma_7^c)-E(\Gamma_8^v)$ of Ref. c.

[h] C. W. Litton, R. B. Denis, and S. D. Smith, J. Phys. C 2, 2146 (1969).

[i] See Ref. 6.

[j] P. Rochon and E. Fortin, Phys. Rev. B 12, 5803 (1975).

[k] See Ref. 24.

[l] See Ref. 10.

[m] A. Filion and F. Fortin, Phys. Rev. B 8, 3852 (1973).

[n] G. Benz and R. Conradt, in *Proceedings of the Twelth International Conference on the Physics of Semiconductors, Stuttgart, 1974*, edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974), p. 1262.

[o] D. A. Hill and C. F. Schwerdtfeger, J. Phys. Chem. Solids 35, 1533 (1974).

[p] See Ref. 8; C. Hermann (unpublished).

[q] D. D. Sell, S. E. Stokowski, R. Dingle, and J. V. Di Lorenzo, Phys. Rev. B 7, 4568 (1973).

[r] D. E. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. B 12, 2527 (1975).

[s] See Ref. 24.

[t] See Ref. 9.

cisely only in InSb,[5] and InAs.[6] However, as the effective masses were determined in most materials, the authors tempted to relate band parameters to them, and to predict the values of P^2 from semiempirical theories.

1. *Three-band model*

The first approximation consisted in the restriction of the developments of m^* and g^* to Γ_5^v bands. From the measurements of m^* in different materials, it appeared that in this approximation P^2, as deduced from (3), remained almost constant in III–V semiconductors,[21] its value being approximately 23 eV.[4] Let us point out that this constancy is fortuitous: In the small-gap materials InSb and InAs, the three-band approximation is correct because of the relative values of the gaps and P^2 is indeed of the order of 23 eV. These materials do not test properly theories, which should be probed on GaAs, GaSb, and InP. In GaAs,[22] and GaSb, where g factors were measured recently by optical CESR, the experimental determinations of P^2 are larger than this value; neglecting the contribution of higher bands to m^* leads to an underestimate of P^2, which makes the value of 23 eV plausible. The measurement of the effective mass in InP was also in agreement with this value[23]; however the recent accurate measurement of[24] m^* is 10% higher, which should lead to a P^2 smaller than 23 eV.

2. *Five-band approximation*

A five-band calculation of m^* and g^* was performed by Cardona.[11] His aim is to predict the values of m^* and g^* in III–V compounds by perturbation from the properties of a symmetrical material. P^2 and P'^2 are also calculated.

In this theory P'^2, which is zero in a symmetrical material, is related to the strength of the antisymmetrical crystalline potential of the III–V compound. This potential also displaces Γ_5 and Γ_1 levels with respect to a symmetrical IV–IV material. Cardona only considers the effect of the antisymmetrical perturbation on the Γ_5 levels. He predicts correct values for m^* except in GaSb but wrong values of g^* in GaAs and GaSb, which can best test the approximations of $\vec{k}\cdot\vec{p}$ theory.

Chadi *et al.*[25] also use a five-band calculation, taking GaAs as a reference semiconductor. From the experimental determinations of m^* and g^* in GaAs they deduce $P'^2/P^2 = 0.4$, assume the same ratio in all III–V compounds, and predict g^*. Their prediction is correct, except in GaSb. Even though our determination of P'^2 is inaccurate, P'^2/P^2 does not seem to remain constant in all III–V compounds.

A first problem of these calculations is that it is difficult to relate a skew compound such as InAs or GaSb to a symmetrical material. Moreover these estimations, which are mainly based on the relative values of the $\Gamma_5^v - \Gamma_5^c$ gaps, do not take into account ionicity: Cardona predicts almost the same P^2 for InAs and GaSb, when we determine experimentally $P^2(\mathrm{InAs}) \approx 22$ eV, $P^2(\mathrm{GaSb}) \approx 28$ eV.

C. Estimation of P^2 in III-V compounds

Lawaetz's approach[12] is somewhat different as in his theory the value of P^2 in a semiconductor is related to lattice constant and ionicity, and not to the experimental $\Gamma_5^v - \Gamma_5^c$ gaps. The P^2's he predicts present the correct sense of variation, but his values vary on a smaller scale than the experimental results, because he attenuates the effect of ionicity in skew or isoelectronic compounds containing d electrons. He calculates g^* values for GaAs and GaSb which still do not fit the experiments.

We present here a crude estimation of P^2 based on simplified linear combination of atomic orbitals wave functions,[26,27] which will clearly evidence the combined influences of polarity and dimension. This tight-binding description provides a less incorrect wave function $\phi_v(\vec{k})$ for the fundamental bonding state, i.e., the valence band, than for the conduction-band state, described by $\phi_c(\vec{k})$.[26] For $\vec{k} = \vec{0}$,

$$\phi_c(\vec{0}) = a \sum_j s^+(\vec{r} - \vec{R}_j^+) - b \sum_j s^-(\vec{r} - \vec{R}_j^-)\,, \qquad (7)$$

$$\phi_v(\vec{0}) = b \sum_j p^+(\vec{r} - \vec{R}_j^+) - a \sum_j p^-(\vec{r} - \vec{R}_j^-)\,, \qquad (8)$$

where

$$a = \frac{1}{(2N)^{1/2}} \left(\frac{1 - S(1-\alpha_p^2)^{1/2}}{1 - S^2} + \frac{\alpha_p}{(1-S^2)^{1/2}} \right)^{1/2}$$

$$b = \frac{1}{(2N)^{1/2}} \left(\frac{1 - S(1-\alpha_p^2)^{1/2}}{1 - S^2} - \frac{\alpha_p}{(1-S^2)^{1/2}} \right)^{1/2}.$$

Only first neighbors are considered. N is the number of primitive cells. The jth cation (respectively, anion) is located at R_j^+ (respectively, R_j^-) from the origin; s^+ and p^+ (respectively, s^- and p^-) are the atomic s^- and p-type wave functions centered on the cation (respectively, anion) site; α_p and S are the polarity and overlap term as defined by Harrison and Ciraci.[27] The effect of d electrons is only accounted for in α_p.

Then, neglecting the overlap of wave functions and derivatives centered on different sites,

TABLE II. Polarities and lattice parameters of III–V and II–VI compounds.

	InSb	InAs	InP	GaSb	GaAs	CdS	CdSe	CdTe	ZnSe	ZnTe
α_p [a]	0.51	0.53	0.58	0.44	0.50	0.77	0.77	0.76	0.72	0.72
a [b] (a.u.)	12.242	11.406	11.090	11.561	10.684	11.047	11.489	12.246	10.710	11.510

[a] See Ref. 27.

[b] Listed in J. A. Van Vechten, Phys. Rev. 182, 891 (1969).

$$\langle \phi_c(\vec{0}) \,|\, p_x \,|\, \phi_v(\vec{0}) \rangle \approx \frac{(1-\alpha_p^2)^{1/2} - S}{2(1-S^2)} \frac{1}{N} \sum_j \left(\left\langle s^+ \middle| \frac{\delta p^+}{\delta(x-x_j^+)} \right\rangle + \left\langle s^- \middle| \frac{\delta p^-}{\delta(x-x_j^-)} \right\rangle \right) . \tag{9}$$

The p_x matrix element is the product of a decreasing function of the polarity α_p, and of atomic matrix elements. Table II gives Harrison's values of α_p in III–V compounds; InP is the most ionic, GaSb the most covalent of the considered materials. S is taken constant: $S = 0.5$. To express the variation of the atomic matrix elements from one compound to the other, from dimensional considerations we very crudely replace their sum by $\lambda\hbar/a$, where a is the lattice constant and λ a constant.

On Fig. 2 we have plotted the estimated P^2:

$$P^2_{\text{est}} = (2/m_0)\, |\langle \phi_c(\vec{0}) \,|\, p_x \,|\, \phi_v(\vec{0}) \rangle|^2 = \frac{2\hbar^2}{m_0} \left(\frac{(1-\alpha_p^2)^{1/2} - S}{2(1-S^2)} \right)^2 \frac{\lambda^2}{a^2} \tag{10}$$

for the best-fit value $\lambda^2 = (1.04 \pm 0.07) \times 10^3$ as a function of our experimental determination P^2_{exp}. The linear variation between P^2_{est} and P^2_{exp} shows that our crude model explains correctly the decrease of P^2 with ionicity and lattice constant.

The above analysis applies without change to the zinc-blende-type II–VI compounds. In wurzite-type semiconductors, the effective masses and Landé factors are anisotropic (see Appendix). However, it is still possible to deduce P^2 from the experimental data of g^*, measured either by standard EPR[28,29] or by spin-flip Raman techniques.[30-33] A value of P^2 can then be determined in these materials: the values for CdS, CdSe, CdTe, ZnSe are listed in Table III.

The above estimation of P^2 from linear-combination of atomic orbitals wave functions is still possible. The fit with the same Eq. (10) requires an overlap integral S equal to 0.25: the increase in ionicity between III–V and II–VI compounds can justify this decrease of overlap of wave functions centered on neighboring sites.

From Fig. 3 and Eq. (10), we extrapolate in ZnTe a P^2 ranging from 22 to 27 eV. This corresponds to a g^* between −0.1 and +0.3. It seems then that the Raman spin-flip line observed[33] at $g^* = 1.74$ cannot be due to conduction electrons. Though the fit is better in III–V compounds, the same elementary considerations account for the variations of P^2 with ionicity and cell dimension in III–V and II–VI semiconductors.

The only rigorous justification of the experimental values of P^2 would consist in determining P^2 from the exact wavefunctions of the different semiconductors. Bowers and Mahan,[34] in an empirical pseudopotential treatment, calculated the energy gaps and matrix elements in zinc-blende semiconductors. From their values of m^* determined in a three-band model we deduce the P^2 they obtained from the pseudowave functions (see Table IV). Apart from InSb the sense of variation of these pseudopotential P^2 is the same as what we determine, but the predicted values are all underestimated. We note that the calculated band gaps are also only approximate. A possible explanation of these discrepancies is that core effects were neglected in the calculation.

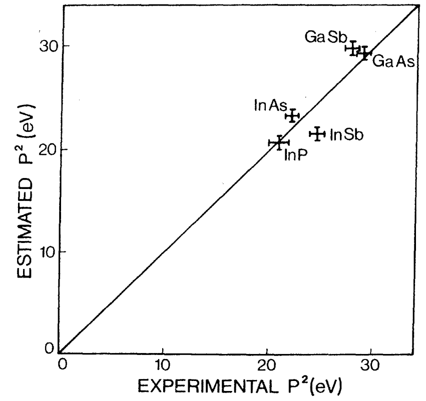

FIG. 2. Comparison of the P^2 calculated from Eq. (10) with its experimental determination in III–V compounds. The overlap term S is equal to 0.5.

TABLE III. Band parameters and calculated interband matrix elements for II-VI compounds.

	CdTe	ZnSe	ZnTe	CdS	CdSe
E_0 (eV)	1.606 [a]	2.79 [g]	2.39 [j]		
Δ_0 (eV)	0.927 [b]	0.45 [g]	0.93 [g]	For datas	
$E(\Gamma_8^c)-E(\Gamma_8^v)$ (eV)	5.70 [c]	8.62 [c]	5.85 [c]		
$E(\Gamma_7^c)-E(\Gamma_8^v)$ (eV)	5.30 [d]	8.4 [d]	5.40 [d]	See Appendix Table V	
m^*/m_0	0.090 [e]	0.17 [h]			
g^*	−0.74 [f]	1.18 [i]	1.74? [i]		
P^2 (eV)	18.5 ± 1	23 ± 1		21 ± 1	20 ± 1

[a] B. Segall and D. Marple, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967), p. 317.

[b] J. Camassel, D. Auvergne, and H. Mathieu, J. Phys. (Paris) 35, C 3-67 (1974).

[c] The spin-orbit splitting of the Γ_5^c bands is taken as half of that of Γ_5^v bands.

[d] F. Pollak, *Proceedings of the 1967 International Conference on II-VI Compounds, Providence*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 552.

[e] C. W. Litton, K. J. Button, J. Waldman, D. R. Cohn, and B. Lax, Phys. Rev. B 13, 5392 (1976).

[f] See Ref. 31.

[g] J. P. Walter, M. L. Cohen, Y. Petroff, and M. Balkanski, Phys. Rev. B 1, 2661 (1970).

[h] D. T. Marple, J. Appl. Phys. 35, 1879 (1964).

[i] See Ref. 33, and text.

III. APPLICATION TO III-V ALLOYS

A. Calculation of m^* and g^* in alloys

The expressions (1) and (2) of m^* and g^* can be used to predict m^* and g^* in alloys under appropriate assumptions, hereafter discussed, on the variations of P^2 and the band gaps with composition x.

In the virtual-crystal approximation a linear variation of certain parameters is assumed. The lattice constant a has been measured to vary linearly with x. It has been shown[35] that a linear variation of the ionic and homopolar gaps, approximately corresponding to a linear variation of ionicity[36] and of[37] α_p, could fit the band gap variation. Thus, in expression (10) of P^2, a and α_p are taken to be linear functions of x. The relative spread of their values in different III–V compounds being in general less than 10%, we shall assume a linear variation of P^2 with x, the values for $x = 0$ or $x = 1$ being taken from Table I. P'^2 is also supposed to vary linearly with x. C and C' are assumed to be constant in all materials: $C = -2, C' = -2 \times 10^{-2}$. The experimental values of the energy gaps as a function of x are used in formulas (3) and (4). The energy gaps are well fitted by a parabolic law[38]

$$E_0(x) = a + bx + cx^2\ ,$$

where c is the bowing parameter. Unfortunately, the choice of the bowing parameter is critical, as small variations of c can seriously alter the results. So, whenever possible, we use the electroreflectance measurement of c, which seems the most reliable: although this technique is usually performed at room temperature, it has been shown[39] that the bowing parameter remains the same at 300 and 80 K, and is thus temperature independent. In Figs. 4–6, which present the theoretical fit of the experimental measurements, we have indicated the uncertainty on the theoretical curve due to the scatter of c values given in the literature. The spin-orbit splitting Δ_0 has also a

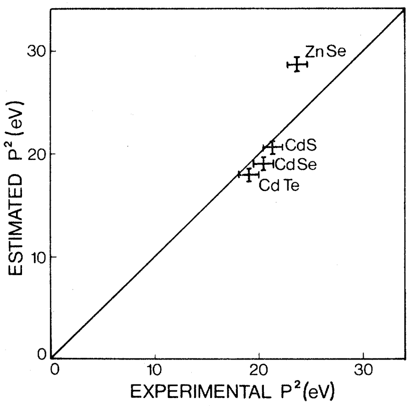

FIG. 3. Comparison of the P^2 calculated from Eq. (10) with its experimental determination in II–VI compounds. The slope is the same as on Fig. 2, the overlap term S being equal to 0.25.

TABLE IV. Interband matrix elements and band gaps from Bowers and Mahan.[34]

	InSb	InAs	InP	GaSb	GaAs	ZnSe	ZnTe	CdTe
P^2 (eV)	9.1	14.7	10.3	15.3	18.2	7.8	11.9	9.5
E_0 (eV)	0.16	0.24	1.1	0.26	0.97	2.6	2.0	1.6

quadratic dependence with composition. The bowing parameters are taken from the experiments of Berolo and Woolley.[40] Finally, we assume a linear variation of higher-lying band gaps as they are not always precisely known and anyway display small bowing parameters in the few cases which were measured.

B. Comparison with experiments

We shall first focus our attention on g factors for which precise low-temperature measurements are available.[9] Our g^* data have been fitted with $\vec{k}\cdot\vec{p}$ theory on Figs. 4 and 5. The bowing parameters of E_0 and Δ_0 for $Ga_{1-x}Al_xAs$ are 0.26[41] and 0.071,[40] respectively. The error due to the uncertainty on the bowing parameter of E_0 is indicated on the figure and is quite small, as the bowing itself is small in $Ga_{1-x}Al_xAs$. For $Ga_{1-x}In_xAs$, we take as bowing parameters 0.32[38] and 0.144.[40] The uncertainty on the theoretical curve of Fig. 5 is large due to the very different parameters given in the literature[38,42] and the sensitivity of g^* to the exact value of the bandgaps. The agreement can anyway be regarded as very satisfactory for these CESR measurements and justifies the applicability of unmodified $\vec{k}\cdot\vec{p}$ theory to alloys. The only other measurements of g factors in alloys are those of $CdS_{1-x}Se_x$,[28] and $GaIn_{1-x}Sb$.[43] In $CdS_{1-x}Se_x$, Piper fitted g^* using a five-band approximation. The systematical misfit observed, an over-all displacement of the theoretical curve, is due to a wrong choice of P^2 in the pure compounds CdS and CdSe. The g^* data on $Ga_xIn_{1-x}Sb$ present some discrepancy with our calculation, which is not really significant: the uncertainty on composition is 2% and the g^* were not corrected for electron concentration. This last correction should improve the fit with the experimental results.

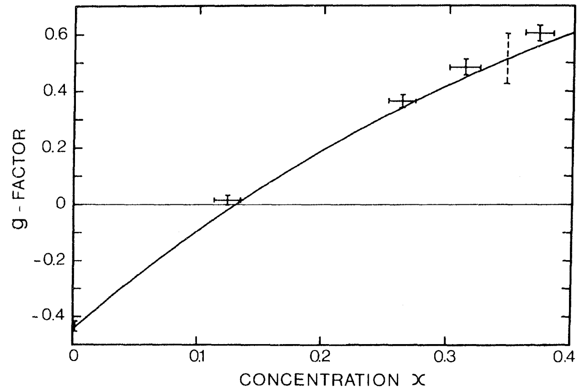

FIG. 4. CESR measurement of the g factor in $Ga_{1-x}Al_xAs$. The curve is the prediction deduced from Eq. (2), when a linear variation of P^2 is assumed. The error flag on the theoretical curve comes from the scatter on the values of the bowing parameter.

The only effective masses measured at low temperature are those of $Ga_{1-x}In_xAs$ through cyclotron resonance in high field.[44] The results are shown in Fig. 6 together with our calculation. Again, the uncertainty on the calculated curve is very large, but the measured points fall within the error flag. Let us remark that this data is not as significant as the g^* data for a test of the theory, as we are restrained to very small variations of the effective mass.

Effective masses were also determined at room temperature in $Ga_{1-x}In_xAs$,[45] $Ga_{1-x}In_xSb$,[46] and $InAs_xSb_{1-x}$[47] by different methods: Faraday rotation, magneto-thermoelectric power, and plasma reflectance. Some values were obtained by magnetoreflectance but seem less reliable. Several points complicate the analysis of these datas:
(i) the results do not yield unambiguously the mass at the bottom of the conduction band; (ii) their interpretation requires the room-temperature effective-mass band gap, which is not even known

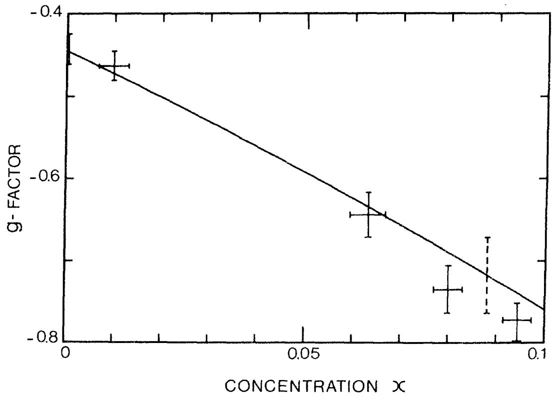

FIG. 5. CESR measurement of the g factor in $Ga_{1-x}In_xAs$.

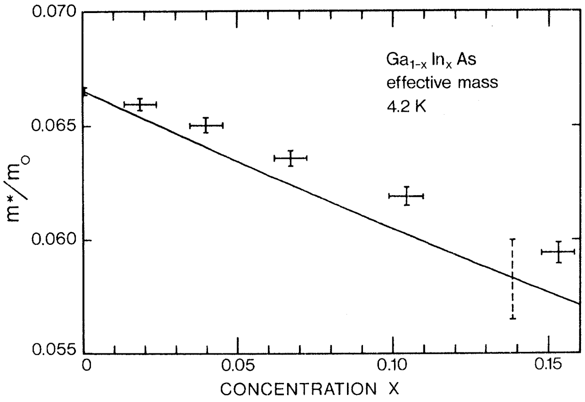

FIG. 6. Low-temperature effective mass in $Ga_{1-x}In_xAs$ measured by cyclotron resonance (Ref. 44). The curve is calculated from Eq. (1), assuming a linear variation of P^2.

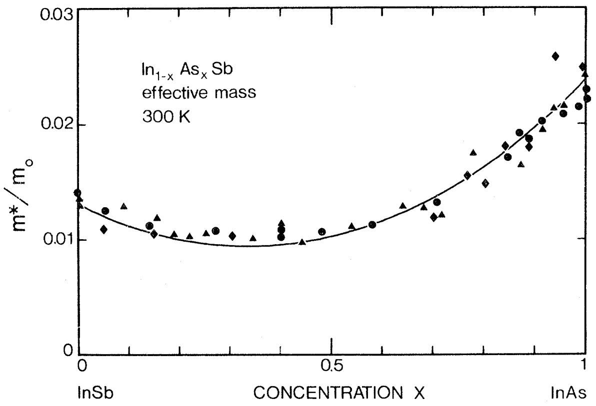

FIG. 7. Room-temperature effective mass in $In_{1-x}As_xSb$ (Ref. 47). The theoretical curve from Eq. (1) was fitted for the pure-compounds effective masses.

certainly in pure compounds. However, as these data are at the basis of the previous modifications proposed to $\vec{k}\cdot\vec{p}$ theory, we discuss them here.

The m^* data were analyzed in a three-band $\vec{k}\cdot\vec{p}$ calculation and significant discrepancies were observed. This is not surprising as we have shown in pure compounds that a three-band calculation can account approximately for g^*, but that m^* is strongly influenced by Γ_5^c bands. The three-band determination of m^* overestimates the interaction of Γ_1^c with Γ_5^v, leading to a *systematically too strong variation with composition.* Our multiband calculation gives correct relative variations of m^*. To get an overall fit with these questionable data[48] we adjust the effective-mass band gap for the pure-compounds room-temperature effective masses. Taking for P^2, P'^2, and the spin-orbit splitting the low-temperature values we get a good agreement, as is shown in Fig. 7 for $InAs_xSb_{1-x}$.

Some modifications to the $\vec{k}\cdot\vec{p}$ theory arising from the random potentials and strains existing in alloys were proposed[14] to fit these room-temperature effective masses, unexplained in a three-band approximation. They decrease P^2 of about 20% for $x=0.5$, which would increase g^* in the same proportion. These modifications would lead to discrepancies with the experimental values of g^*. On the contrary our correct predictions show that simple calculations of m^* and g^* are valid in alloys. In other words, it means that the variations of m^* and g^* with composition are contained in Eqs. (1) and (2) if we use there the measured values of band gaps and spin-orbit splittings. The influence of alloy disorder seems to be completely taken into account through its influence on the band gaps and spin-orbit splittings.

Any further study of the applicability of simple $\vec{k}\cdot\vec{p}$ theory needs cleaner datas in alloys at low temperature. In particular, it requires the simultaneous measurement of the different band gaps and effective mass or g factor in a given sample. As remarked by Siggia, $InAs_{1-x}Sb_x$ should be a good candidate, as the large difference in the lattice parameters of the pure compounds should lead to a maximum effect of the random potentials and strains. CESR should be possible there.

IV. CONCLUSION

From the recent measurements of m^* and g^* in III–V and II–VI semiconductors we have been able to determine experimental values for the interband matrix element P^2 with a precision of a few percent. The strong variation of P^2 between different materials is qualitatively explained by a simplified model which expresses the influences of ionicity and cell dimension. We predict the value of g^* in ZnTe. An important computing effort is required to calculate precisely P^2 in every semiconductor from its wave functions.

The precise g^* data at low temperature in $Ga_{1-x}In_xAs$ and $Ga_{1-x}Al_xAs$ are well interpreted in the framework of simple $\vec{k}\cdot\vec{p}$ theory, using the correct values of P^2. The modifications of $\vec{k}\cdot\vec{p}$ theory proposed to account for alloy disorder would lead to discrepancies. Thus the effect of alloying on m^* and g^* appears to be described by taking the experimental values of band gaps and spin-orbit splittings relative to the composition x. A better accuracy on m^* and g^* and band parameters is required to improve the test of $\vec{k}\cdot\vec{p}$ theory applied to alloys.

ACKNOWLEDGMENTS

We wish to thank Dr. G. Lampel for his constant interest and many helpful discussions throughout the present work.

TABLE V. Band parameters of CdS and CdSe.

	E_A (eV)	E_B (eV)	E_C (eV)	$E(\Gamma_5^c)$ (eV)	$\Delta(\Gamma_5^c)$	m^*/m_0	g^*	P^2 (eV)
CdS	2.582 [a]	2.598 [a]	2.671 [a]	6.3 ∥ [c] 6.2 ⊥ [c]	0.035 [d]	0.18 [c]	1.79 ∥ [g] 1.77 ⊥ [h]	21 ± 1
CdSe	1.87 [b]	1.895 [b]	2.342 [b]	6 ∥ [c] 5.45 ⊥ [c]	0.21 [d]	0.120 ∥ [f] 0.115 ⊥ [f]	0.68 [i]	20 ± 1

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[c] See Ref. d of Table III. The origin of energies is the upper valence band.

[d] See Ref. c of Table III.

[e] See Ref. i of Table III.

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[g] See Ref. 29.

[h] See Ref. 30.

[i] See Ref. 28.

APPENDIX: EFFECTIVE MASSES AND LANDÉ FACTORS IN WURZITE-TYPE SEMICONDUCTORS

In a noncubic material, the effective mass and Landé factor are second-rank tensors, which can be calculated by $\vec{k}\cdot\vec{p}$ perturbation theory.[49] In wurzite-type materials, two principal masses and g factors can be defined, as

$$m_x^* = m_y^* = m_\perp^*, \quad m_z^* = m_\parallel^* ,$$

$$g_x^* = g_y^* = g_\perp^*, \quad g_z^* = g_\parallel^* ,$$

The directions x, y, z being the crystal axes. The anisotropies of m^* and g^* mainly come from the interaction of the conduction band with the upper valence bands, the wave functions of which, at $k = 0$, are given by[50]

$$A(\Gamma_9)\begin{cases}(1/\sqrt{2})(X+iY)\uparrow & (m_J = \frac{3}{2}) ,\\ (1/\sqrt{2})(X-iY)\downarrow & (m_J = -\frac{3}{2}) ,\end{cases}$$

$$B(\Gamma_7)\begin{cases}(1-q_7^2)^{1/2}[(X+iY)/\sqrt{2}]\downarrow - q_7 Z\uparrow & (m_J = \frac{1}{2}) ,\\ (1-q_7^2)^{1/2}[(X-iY)/\sqrt{2}]\uparrow + q_7 Z\downarrow & (m_J = -\frac{1}{2}) ,\end{cases}$$

$$C(\Gamma_7)\begin{cases}-q_7[(X+iY)/\sqrt{2}]\downarrow - (1-q_7^2)^{1/2} Z\uparrow & (m_J = \frac{1}{2}) ,\\ -q_7[(X-iY)/\sqrt{2}]\uparrow + (1-q_7^2)^{1/2} Z\downarrow & (m_J = -\frac{1}{2}) .\end{cases}$$

The spins are quantized along z. The wave functions of a zinc-blende semiconductor are obtained for $q_7^2 = \frac{2}{3}$.

If we neglect the anisotropies due to the upper conduction bands, we get

$$\frac{m_0}{m_\parallel^*} - 1 = P^2\left(\frac{q_7^2}{E_B} + \frac{1-q_7^2}{E_C}\right) - \frac{P'^2}{E(\Gamma_5^c) - E_A} + C ,$$

$$\frac{m_0}{m_\perp^*} - 1 = P^2\left(\frac{1}{2E_A} + \frac{1-q_7^2}{2E_B} + \frac{q_7^7}{2E_C}\right) - \frac{P'^2}{E(\Gamma_5^c) - E_A} + C ,$$

$$\frac{g_\parallel^*}{g_0} - 1 = -\frac{P^2}{2}\left(\frac{q_7^2}{E_C} + \frac{1-q_7^2}{E_B} - \frac{1}{E_A}\right) - \frac{P'^2}{3}\,\frac{\Delta(\Gamma_5^c)}{E(\Gamma_5^c) - E_A} + C' ,$$

and

$$\frac{g_\perp^*}{g_0} - 1 = -\frac{P^2}{2}\left(\frac{1}{E_C} - \frac{1}{E_B}\right)[2q_7^2(1-q_7^2)]^{1/2} - \frac{P'^2}{3}\,\frac{\Delta(\Gamma_5^c)}{E(\Gamma_5^c) - E_A} + C' .$$

The origin of energies is taken at the Γ_7 conduction band; A, B label the valence bands, C the spin-orbit split-off valence band. Γ_5^c is the upper conduction band, the spin-orbit splitting of which is $\Delta(\Gamma_5^c)$.

We now compare these expressions with the experimental datas in CdS and CdSe, presented in Table V. In CdS, Gutsche and Jahne calculated $q_7^2 \lesssim 0.43$.[50] This value cannot explain the experimental anisotropy of the g factor: $g_\perp^* = 1.77$, $g_\parallel^* = 1.79$. On the contrary, we start from these measurements and assume that, as in III–V compounds, a good approximation is to consider that the g factors are only determined by the P^2 term. We deduce $q_7^2 \approx 0.31$, and $P^2 = 21.2$ eV. In CdSe, the two values $g_\parallel$ and $g_\perp$ are not known accurately enough. From $g^* = 0.68$, and[50] $q_7^2 = 0.6$, we deduce $P^2 = 20.3$ eV.

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