Effect of hydrostatic pressure on GaAs-$Ga_{1-x}Al_xAs$ microstructures

P. Lefebvre, B. Gil, and H. Mathieu

Groupe d'Etude des Semiconducteurs, Université des Sciences et Techniques du Languedoc, place Eugene Bataillon, 34060 Montpellier Cédex, France

(Received 10 November 1986)

Some detailed experimental studies of the effect of hydrostatic pressure on the energy levels of GaAs-$Ga_{1-x}Al_xAs$ quantum-well heterostructures have been recently published. The heterostructures used are grown by molecular-beam epitaxy and consist of several single GaAs wells with different widths separated by wide $Ga_{1-x}Al_xAs$ barriers. Photoluminescence measurements at low temperature and up to 70 kbar show that all the peaks move to higher energy as the pressure is applied. The pressure coefficients of the heavy- and light-hole excitonic transitions appear to be different. On the other hand these coefficients decrease with decreasing well widths. In this paper we present a theoretical calculation of these pressure coefficients and of their well-width and barrier-height dependence, which quantitatively fits the experimental results.

I. INTRODUCTION

Hydrostatic pressure has been proved to be a valuable tool for studying the influence of the band-structure parameters on the electronic properties of semiconductors, bulk crystals, or two-dimensional (2D) systems.[1] It was not the purpose of the present paper to review exhaustively the large quantity of experimental works along these lines; however, some behaviors very characteristic of impurities have been noticed for a long time in the case of 3D crystals: Although hydrogenlike centers tend to follow the band structure, isoelectronic traps *do not*.[2–4] Experimental investigations of the behavior of 2D systems under hydrostatic pressure have actually been made in a wide series of quantum wells[5–7] and superlattices,[8–11] like GaAs-$Ga_{1-x}Al_xAs$,[4–10] GaSb-AlSb,[7] or $In_yGa_{1-y}As$-GaAs,[11] etc.

In type-I quantum wells, strongly allowed excitonic transitions occur between the quantized levels in the conduction band and the light- (l) and heavy- (h) hole subbands of the same quantum number n. The energies of such transitions are higher than the band gap of the material constituting the quantum well (QW), because of the size quantization which induces a raise of the conduction- and valence-band extrema.

The problem of band offset in GaAs-$Ga_{1-x}Al_xAs$ QW has recently found an experimental solution, namely use pressure-induced crossover between the Γ minimum in GaAs and the X one in $Ga_{1-x}Al_xAs$.[4–6] The result allows one to assume a valence- band offset of about 30% of the band-gap discontinuity.

Another interesting experimental result in this case is the weak—but remarkable—decrease of the pressure coefficients of the transition energies with decreasing well widths.[4–7] In fact, the case of the GaAs-$Ga_{1-x}Al_xAs$ QW, as shown in Ref. 6, there seems to be a relation between the pressure coefficients (α) and the well width. This behavior is a typical result of quantum-size effects that appear as well for microstructures with well heights smaller than a few hundred meV [the case of the GaAs-$Ga_{1-x}Al_xAs$ QW and superlattices (SL)] as for strained QW with well heights ranging up to 1.5 eV [the case of GaSb-AlSb (Ref. 7)].

In the present paper we propose a model calculation for the excitonic recombinations and their pressure coefficients in type-I quantum wells, such as the GaAs-$Ga_{1-x}Al_xAs$ ones. This model, which has successfully been used for a GaSb-AlSb strained quantum well between 0 and 7 kbar,[7] is extended to the case of GaAs-$Ga_{1-x}Al_xAs$ quantum wells of different widths under pressures up to 30 kbar.

The paper is organized as follows. In the next section we present our model calculation, which takes into account the pressure-induced modifications of the microstructures: well width, barrier height, dielectric constant, carrier effective masses, and the excitonic rydberg. Then a quantitative comparison between our findings and the experimental results recently given in the literature is made in Sec. III. All contributions are analyzed in detail.

II. THEORETICAL MODELIZATION

A. Basic equations

Our calculation is based on the envelope-function approximation of Bastard.[12] We resolve the effective-mass equation, giving the ground quantized level in the conduction- (valence-) band potential well of the confining layer. This equation reads

$$[-\hbar^2\nabla^2/2m^*(z)-E+V(z)]F(z)=0 , \qquad (1)$$

where $F(z)$ is the envelope function along the z axis of the structure modulating the free-electron (-hole) part of the wave function. $V(z)$ is the potential perturbation due to the gap mismatch between the two materials and $m^*(z)$ is the mass of the particle under consideration. The boundary conditions are standard and given by the continuity of both $F(z)$ and $1/m^*(z)(\partial F/\partial z)$.[13]

In this paper we concentrate on the GaAs-$Ga_{1-x}Al_xAs$ system; as a consequence, in the framework of the formalism, the transition energy corresponding to a QW is obtained by adding the electron and hole confinement energies and by subtracting the effective rydberg to the energy of the GaAs fundamental energy gap:

$$E(\mathrm{QW})=E_g(\mathrm{GaAs})+E_e+E_{\mathrm{hole}}-E_{\mathrm{rydberg}} . \tag{2}$$

We have to consider the dimensional properties of the excitons in the QW's. It is well known[14–17] that the binding energy of the free exciton in a type-I QW increases towards 4 times its three-dimensional value while the well width decreases (this is exact in the case of an infinite potential well; we will assume it to be true for our finite ones[18]). The variation of the 2D rydberg in units of the 3D rydberg versus well width in units of the 3D Bohr radius is shown in Fig. 2 of Ref. 15. In fact, since both heavy and light holes are quantized, we will have to consider heavy and light excitons (see, for instance, Fig. 3 of Ref. 18). The behavior of the QW under hydrostatic pressure is rather complicated since several effects have to be considered.

(i) The well width diminishes with the pressure; this results in a rise in energy for the conduction- (valence-) band levels and then in the transition energy between the ground states. The pressure dependence of the well width L_z with the pressure is taken from the elasticity theory:

$$L_z(P)=L_z(0)[1-(S_{11}+2S_{12})P] , \tag{3}$$

where P is the magnitude of the external pressure, which is positive for a compression; S_{11} and S_{12} are the elastic constants of GaAs.

(ii) Both GaAs and $Ga_{1-x}Al_xAs$ exhibit different pressure coefficients. In the case of the aluminum concentration of the samples investigated here, the barrier height decreases versus pressure and as a consequence the pressure reduces the confinement of the carriers in the sandwiched GaAs layer.

(iii) The size quantization and the change of the gaps with the pressure lead to an increase of the effective masses in the well and in the barriers. This change contributes negatively to the pressure coefficient of the transition energy.[7]

We have taken Kane's three bands model[19] in order to express the change of the effective mass under pressure:

In the barriers,

$$\frac{m_e^b(P)}{m_e^b(0)}=\frac{E_g^b+C^bP}{E_g^b}\,\frac{E_g^b+C^bP+\Delta}{E_g^b+\Delta}\,\frac{2\Delta+3E_g^b}{2\Delta+3(E_g^b+C^bP)} , \tag{4}$$

$$\frac{m_{\mathrm{lh}}^b(P)}{m_{\mathrm{lh}}^b(0)}=\frac{E_g^b+C^bP}{E_g^b} , \tag{5}$$

$$\frac{m_{\mathrm{hh}}^b(P)}{m_{\mathrm{hh}}^b(P)}=1 . \tag{6}$$

In the quantum wells,

$$\frac{m_e^w(P,E_e,E_{\mathrm{lh}})}{m_e^w(0,0,0)}=\frac{E_g^w+C^wP+E_e+E_{\mathrm{lh}}}{E_g^w}\,\frac{E_g^w+C^wP+E_e+E_{\mathrm{lh}}+\Delta}{E_g^w+\Delta}\,\frac{2\Delta+3E^w}{2\Delta+3(E_g^w+C^wP+E_e+E_{\mathrm{lh}})} , \tag{7}$$

$$\frac{m_{\mathrm{lh}}^w(P,E_e,E_{\mathrm{lh}})}{m_{\mathrm{lh}}^w(0,0,0)}=\frac{E_g^w+C^wP+E_e+E_{\mathrm{lh}}}{E_g^w} , \tag{8}$$

$$\frac{m_{\mathrm{hh}}^w(P,E_e,E_{\mathrm{hh}})}{m_{\mathrm{hh}}^w(0,0,0)}=1 , \tag{9}$$

where C^b and C^w are the band-gap pressure coefficients in the barriers and wells, respectively. E_g^b and E_g^w are the band gaps and E_e and E_{lh} the confinement energies of the electrons and light holes which are concerned by the $\mathbf{k}\cdot\mathbf{p}$ coupling. The expressions for the QW show that a self-consistent calculation is necessary to know the values of the energy levels and masses. Equations (4)—(9) show that the effective masses increase while increasing pressure both in the well and in the barriers. This is a point which is interesting to discuss because this is a very important contribution to the change of the pressure coefficient of the optical transitions.

In the well, this increase leads to a "collapse" of the levels toward the bottom of the potential wells. *Outside the well*, this increase induces a reduction of the real-space extension of the wave function. For instance, if the well center is at $z=0$ we can write, for $|z|>L_z/2$ (L_z being the well width), $F_{(z)}=K\exp(-\rho|z|)$, where K is a normalization constant and

$$\rho=[2m^b(E)(V-E)/\hbar^2]^{1/2}$$

E being the confinement energy of the particle in the well and $m^b(E)$ the varying effective mass of this particle in the barrier. We can say that the change with pressure of the effective masses in the barrier makes the energy levels in the well collapse only if these masses increase *more rapidly* than the masses in the well. On the contrary, if the masses increase more rapidly in the well, the levels tend to rise.

Now let us consider the pressure dependence of the rydberg. It is not easy to calculate because its variations are function of the change of the well width, effective masses, and dielectric constant. The change of the dielectric constant has been measured by Samara;[20] he found $\kappa=(1/\epsilon)(d\epsilon/dP)\sim-0.14\%$ kbar^{-1}. As a consequence, the 3D rydberg experiences a variation which reads

$$R_{3\mathrm{D}}^*(P)=R_{3\mathrm{D}}^*(0)\exp(2\kappa P)\mu(P)/\mu(0) ,$$

$\mu(0)$ and $\mu(P)$ being the proper effectives masses for the excitons at atmospheric pressure and for a pressure P.

This change of the effective free rydberg has not been measured for GaAs, but it was measured by reflectivity at liquid-helium temperature for its companion indium phosphide by Chen *et al.*;[21] they found a change of the effective rydberg of 3%/kbar while the prediction of the effective-mass theory was the third. Some expressions of the effective mass for heavy and light excitons can be found in Ref. 22 and will not be repeated here.

The change of the Bohr radius of the 3D exciton under pressure reads

$$a_{B\,3D}^{*}(P)=a_{B\,3D}^{*}(0)\exp(-\kappa P)\mu(0)/\mu(P)\ .$$

Taking into account all these variations, we are able to calculate the values of both heavy and light excitons for each pressure.

B. Numerical calculation

We have performed a series of numerical calculations in the case of the GaAs-$Ga_{1-x}AlAs$ QW in order to explain the experimental findings collected at 80 K by Venkateswaran *et al.*[6] and at 8 K by Wolford *et al.*[4,23] The numerical values of the hole effective masses have been expressed as a function of the Luttinger parameters given by Lawaetz;[24] a linear interpolation has been made between GaAs and AlAs in order to obtain the values corresponding to the alloy composition of the barriers in the samples.

Concerning the electron effective mass, we have taken the empirical formula of El Jani:[25]

$$m_e^*(Ga_{1-x}Al_xAs)=0.0657+0.0174x+0.145x^2 \quad \text{for } x<0.35\ .$$

The 80 K and atmospheric-pressure values of the $Ga_{1-x}Al_xAs$ band gap are 1502, 1857, and 1893 meV when $x=0$, 0.3, and 0.33, respectively, according to Refs. 6 and 26. The spin-orbit splitting has been taken to be equal to 340 meV for GaAs and 330 meV for the alloy. The band-gap structure at 8 K is given accurately in Ref. 23. Now we need the pressure coefficients of the band gap. AlAs exhibits a smaller pressure coefficient than GaAs.[27] The optical measurements of the GaAs band-gap pressure coefficient tend to converge toward a value of 10.7 meV $kbar^{-1}$.[4,6,28] On the other hand, the pressure coefficient of $Ga_{1-x}Al_xAs$ band gap has been measured decreasing with x.[27] For $x=0.30$ the value of 9.8 ± 0.1 meV/kbar has been measured;[26] this enables us to estimate a value of 9.9 for $Al_{0.28}Ga_{0.72}As$. Finally, we take a standard value of 4.6 meV for the three-dimensional exciton rydberg in GaAs and a relative change of the dielectric constant of 14×10^{-4} $kbar^{-1}$.[20] The elastic compliance constants of GaAs are[29]

$$S_{11}=1.16\times10^{-6}\ \text{bars}^{-1}\ ,$$

$$S_{12}=-0.370\times10^{-6}\ \text{bars}^{-1}\ ,$$

$$S_{44}=1.670\times10^{-6}\ \text{bars}^{-1}\ .$$

III. RESULTS AND DISCUSSION

Figure 1 displays the pressure coefficient of the free-exciton transition energies measured in GaAs-$Ga_{0.7}Al_{0.3}As$ QW's (open and solid circles) and the results of our calculation preformed for both heavy holes (dashed-dotted line) and light holes (solid line). Two

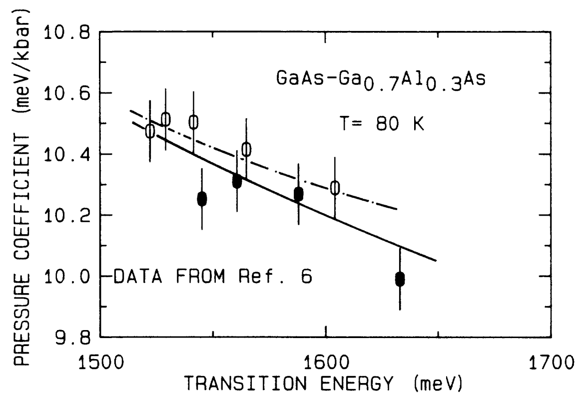

FIG. 1. Comparison between the pressure dependence of the $Ga_{0.7}Al_{0.3}As$ quantum well measured at 80 K (open circles for the heavy holes and solid ones for the light holes) and the results of that calculation (dash-dotted line for the heavy holes and solid line for the light hole). The experimental uncertainty has been represented by a vertical line, which corresponds to the measurements of the experimental pressure coefficients of GaAs (Ref. 28) and $Ga_{0.7}Al_{0.3}As$ (Ref. 6), 10.7 ± 0.1 and 9.8 ± 0.1 meV/kbar. The calculation has been performed with the average values of these pressure coefficients.

asymptotic behaviors should be noticed. In the large-width limit, the 2D character of the microstructures vanishes, the quantum-size effects disappear as soon as the well width exceeds the de Broglie wavelength of the carriers, and we tend toward the pressure coefficient of GaAs. On the other hand, our calculation gives an asymptotic behavior which reaches the pressure coefficient of the barrier in the case of the small-width sample. In that case, as it has been displayed in Fig. 2, the envelope functions of electrons and holes are mainly localized in the barriers. The probability to find the electron (light hole) in the barriers are 79%, 9.4%, and 2.6% (82.6%, 14.8%, and 5.1%) for well widths of 10, 60, and 110 Å, respectively. Figure 3 shows the pressure dependence of the quantized light exciton as a function of the probability of finding the electron in the GaAs layer ($\int |F_e^w|^2 dz$). Obviously, we rediscover the asymptotic behaviors of two limit cases: (i) the pressure coefficient of the barrier in the limit of narrow well, and (ii) the pressure dependence of bulk GaAs when the 2D character of the microstructures vanishes in the case of wide wells. In a previous paper[4] it was pointed out that the lower-pressure coefficient in the case of narrow wells arose from hybridization between Γ- and X-like Bloch states. Such a hybridization should be a second-order effect; the first-order effects are (i) the increase of the effective mass of the carriers with the transition energy, (ii) the change of the barrier heights with the pressure, since both the binary and ternary phases have different pressure coefficients, (iii) the change of the well width, and (iv) the change of the rydberg. In the case of a 50-Å-wide QW (sample 2-E of Ref. 6), the change of the rydberg versus pressure makes the pressure coefficient of the exciton decrease by 0.082 meV $kbar^{-1}$, while it has been measured as ~ -0.7

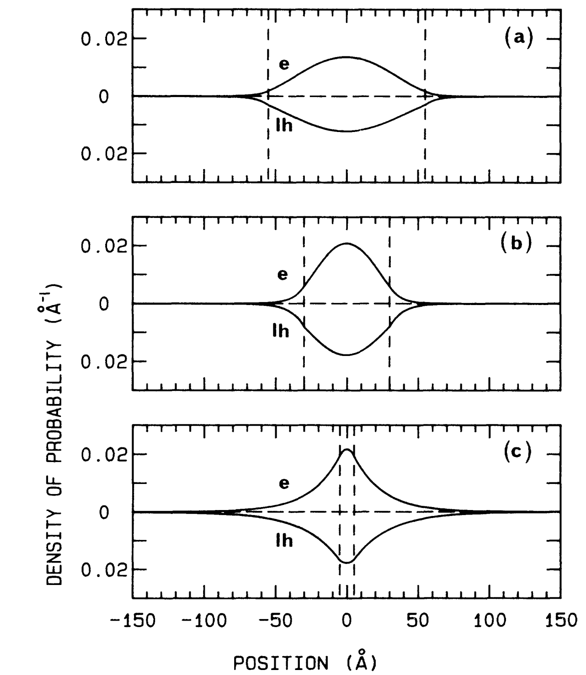

FIG. 2. Schematic representation of the real-space density of probability obtained for the electron (e) and the light hole (lh) in the case of three widths of the GaAs-$Ga_{0.7}Al_{0.3}As$ QW. The corresponding widths are (a) 10 Å, (b) 60 Å, and (c) 110 Å. The wave functions are more delocalized in the real space in the case of narrow wells than in the case of wide wells. The probabilities inside the well, $\int |F_e^w|^2 dz$, are, respectively, (a) 20.99%, (b) 90.63%, and (c) 97.39%, for the electron. In the case of the light hole, $\int |F_h^w|^2 dz$ are (a) 17.34%, (b) 85.20%, and (c) 94.93%.

meV/kbar between bulk GaAs and 2-E excitons. This change of the exciton is 1 order of magnitude smaller than the experimental finding; this change is the same for these QW as for the GaSb-AlSb strained QW.[7]

Finally, we have calculated the pressure coefficients of excitons quantized in GaAs-$Ga_{0.72}Al_{0.28}As$ microstructures, and we find results in reasonable agreement with the works summarized in Ref. 4, as has been displayed in Fig. 4.

We have obtained satisfactory agreement between the calculation and the experimental data obtained at 80 K (Ref. 6) and 8 K. This agreement is in the limit of experimental uncertainty. From this work and our previous one,[7] we can say that a general trend of optical transitions in QW is to exhibit a smaller pressure coefficient than that of the 3D sandwiched material. The effective mass of the carriers increases with the pressure and, simultaneously, their confinement. This is the case of the GaSb-AlSb type-I strained QW's, where the potential wells (espcially for the electron) are deep. In the case of GaAs-$Ga_{1-x}Al_xAs$ QW's, the depth of the potential wells does not exceed a few hundred meV (the gap mismatch is of the order of 350 meV in the range of aluminum concentrations investigated here); as a consequence, the carriers are less localized than in the previous system and they can tunnel into the barriers. The effective mass of the carriers increases faster in the barriers than in the well; this results in a decrease of the transmission rate inside the barriers when the sample is pressed; the carriers are confined more strongly and the value of the pressure coefficient is intermediate between GaAs and $Ga_{1-x}Al_xAs$. The narrower the well, the heavier the effective mass of the carriers, and the smaller the pressure coefficient. Concerning the narrowing of the wells under pressure, they are found to give a contribution compensated for by the increase of the effective rydberg.

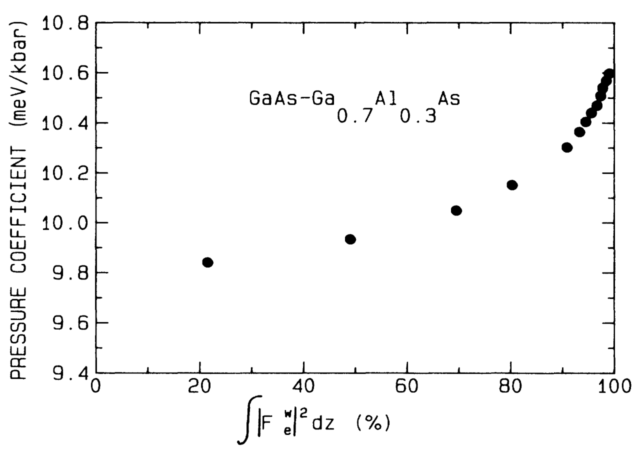

FIG. 3. Calculation of the pressure coefficient of the quantum well as a function of the probability $\int |F_e^w|^2 dz$ of finding the electron in the GaAs-$Ga_{0.7}Al_{0.3}As$ microstructures. The asymptotic values of 10.7 and 9.8 meV/kbar correspond to bulk GaAs (Ref. 4) and $Ga_{0.7}Al_{0.3}As$ (Ref. 6).

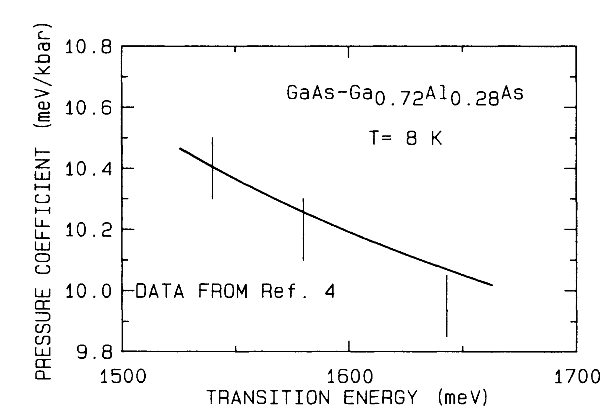

FIG. 4. The same as Fig. 1, but for GaAs-$Ga_{0.72}Al_{0.28}As$ QW's, and at 8 K; thus the experimental data from Ref. 4 only concern the transitions involving the heavy holes. The reasonable experimental uncertainty is represented by a vertical line, which takes the same origin as that discussed for Fig. 1.

IV. CONCLUSIONS

In summary, we have shown that the pressure dependence of GaAs-$Ga_{1-x}Al_xAs$ QW's decreases with the well width for essentially the following reasons.

(i) In the case of narrow wells, the quantized level tends to follow the pressure dependence of the barrier edge because of the delocalization of the carriers into the barrier.

(ii) The increase of the carrier effective mass in the well and in the barriers under pressure reduces the transmission rate into the barriers but increases the confinement of the carriers. This second effect plays an important role in the case of wide wells, when most of the wave function of both the electron and hole are located inside the well, while the first effect is predominant in the case of narrow wells.

[1]For a review, see, for instance, G. A. Samara, Physica **139&140B**, 3 (1986).

[2]B. Gil, M. Baj, J. Camassel, H. Mathieu, C. Benoit á la Guillaume, N. Nestres, and J. Pascual, Phys. Rev. B **29**, 3398 (1984).

[3]M. Leroux, G. Neu, and C. Verie, Solid State Commun. **58**, 289 (1986).

[4]D. J. Wolford (invited speaker), in Proceedings of the XVIIIth International Conference on the Physics of Semiconductors, Stockholm (1986) (unpublished), and references therein.

[5]B. A. Weinstein, S. K. Hark, and R. D. Burnham, J. Appl. Phys. **58**, 4662 (1985).

[6]U. Venkateswaran, M. Chandrasekhar, H. R. Chandrasekhar, B. A. Vojak, F. A. Chambers, and J. M. Meese, Phys. Rev. B **33**, 8416 (1986).

[7]P. Lefebvre, B. Gil, J. Allegre, H. Mathieu, Y. Chen, and C. Raisin, Phys. Rev. B **35**, 1230 (1987).

[8]V. Venkateswaran, M. Chandrasekhar, H. R. Chandrasekhar, T. Wolfram, R. Fisher, W. T. Masselink, and H. Morkoc, Phys. Rev. B **31**, 4106 (1985).

[9]S. W. Kirchoefer, N. Holonyak, Jr. K. Hess, K. Meehan, D. A. Gulino, H. G. Drickamer, J. J. Coleman, and P. D. Dapkus, J. Appl. Phys. **53**, 6037 (1982).

[10]J. E. Epler, R. W. Kaliski N. Holonyak, Jr., M. J. Peanasky, G. A. Hermannsfeldt, H. G. Drickamer, R. D. Burnham, and R. L. Thornton, J. Appl. Phys, **57**, 1495 (1985).

[11]E. D. Jones, H. Ackermann, J. E. Schirber, T. J. Drummond, L. R. Dawson, and I. J. Fritz, Appl. Phys. Lett. **47**, 492 (1985).

[12]G. Bastard, Phys. Rev. B **24**, 5693 (1981).

[13]J. P. Leburton and K. Kahen, Superlattices and Microstruct. **1**, 49 (1985).

[14]R. C. Miller, D. A. Kleinman, W. T. Tsang, and A. C. Gossard, Phys. Rev. B **24**, 1134 (1984).

[15]G. Bastard, E. E. Mendez, L. L. Chang, and L. Esaki, Phys. Ref. B **26**, 1974 (1982).

[16]Y. Shinozuka and M. Matsuura, Phys. Rev. B **28**, 4878 (1983); **29**, 3217 (1984).

[17]R. L. Greene, K. K. Bajaj, and D. E. Phelps, Phys. Rev. B **29**, 1807 (1984).

[18]J. C. Maan, G. Belle, A. Fasolino, M. Altarelli, and K. Ploog, Phys. Rev. B **30**, 2253 (1984).

[19]E. O. Kane, *Semiconductors and Semimetals,* edited by R. K. Willardson (Academic, New York, 1966), Vol. 1.

[20]G. A. Samara, Phys. Rev. B **27**, 3494 (1983).

[21]Y. Chen, B. Gil, A. Kadri, J. Camassel, J. Allegre, and H. Mathieu, Physica **139&140B**, 491 (1986).

[22]C. Priester, G. Allan, and M. Lannoo, Phys. Ref. B **30**, 7302 (1984).

[23]D. J. Wolford, T. F. Kuech, J. A. Bradley, A. A. Gell, D. Ninno, and M. Jaros, J. Vac. Sci. Technol. B **4**, 1043 (1986).

[24]P. Lawaetz, Phys. Rev. B **4**, 3460 (1971).

[25]B. El Jani, P. Gibart, J. C. Portal, and R. L. Aulombard, J. Appl. Phys. **58**, 3481 (1985).

[26]M. Chandrasekhar, U. Venkateswaran, H. R. Chandrasekhar, B. A. Vojak, F. A. Chambers, and J. M. Meese, in Proceedings of the XVIIIth International Conference on the Physics of Semiconductors, Stockholm (1986), Ref. 4.

[27]N. Lifshitz, A. Jayaraman, R. A. Logan, and R. G. Maines, Phys. Rev. B **20**, 2398 (1979).

[28]D. J. Wolford and J. A. Bradley, Solid State Commun. **53**, 1069 (1985).

[29]A. Gavini and M. Cardona, Phys. Rev. B **1**, 672 (1969).