Far-infrared absorption profiles for shallow donors in GaAs-Al$_x$Ga$_{1-x}$As quantum-well structures

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Previous variational calculations of the ground and 2p-like excited states of a shallow donor in a quantum well are extended to include the effects of an applied magnetic field and arbitrary donor position. The extended wave functions are then used in a theory for the absorption profiles of shallow donor transitions in quantum wells. Absorption profiles for several donor-impurity distributions are calculated and compared with recent far-infrared absorption experiments. The comparison with experiment is somewhat ambiguous, but the theory does suggest that some experimental samples may possess thin donor-impurity layers at the interfaces between semiconductors.

I. INTRODUCTION

Current crystal epitaxial growth techniques such as molecular-beam epitaxy and metal organic chemical vapor deposition make it possible to grow systems of alternate layers of different semiconductors (usually referred to as heterostructures) or layers of a single semiconductor with different doping properties. Such systems with large-scale periodicity (typically 50–500 Å) along the growth direction are known as superlattices. Perhaps the most commonly studied heterostructure system consists of alternating layers of GaAs and Ga$_{1-x}$Al$_x$As, where the Al fraction $x \leq 0.4$. In this paper we shall confine our attention to such systems.

The band gap of Ga$_{1-x}$Al$_x$As varies with x, and is larger than that of GaAs. When it is grown in alternating layers with GaAs, discontinuities in the conduction- and valence-band edges occur at the interfaces. For sharp interfaces the potential felt by an electron moving in the conduction band is that of a one-dimensional array of square wells and barriers, with the wells formed in the GaAs and the barriers in the Ga$_{1-x}$Al$_x$As. The presence of these quantum wells causes the normal three-dimensional band structure to be split into subbands along the k_z direction. In the effective-mass approximation the subband edges correspond to the energy levels of an effective-mass electron moving in the one-dimensional potential.

Studies of shallow donor states in bulk semiconductors have yielded considerable information about the host semiconductor, so that it is not surprising that similar studies have been made of shallow donors in heterostructures. The energy levels associated with such shallow states in a GaAs-Ga$_{1-x}$Al$_x$As quantum well are found near the conduction subband edges. The Coulomb binding energy has been the focus of most of the theoretical work to date.[1-8]

Recently far-infrared absorption experiments have be-
gun to measure the shallow donor 1s-like to 2p-like transitions in GaAs-Ga$_{1-x}$Al$_x$As quantum-well structures.[9] The differences in binding energies for shallow donors located at arbitrary positions with respect to the GaAs wells result in broadened profiles for such transitions. The purpose of this paper is to present the results of theoretical calculations of the shape of these profiles. In principle, such theoretical profiles, in combination with experimental profiles, can be used to extract information concerning the distribution of donor impurities in a given sample.

Prior to this work there has been one calculation of the absorption line shape for the 1s to 2p shallow donor transition in these heterostructures.[10] There are several aspects of this calculation which make it difficult to compare its results with experiment. First, the model chosen was that of a quantum well with infinitely high barriers. This has been shown to be not a very good approximation for narrow wells ($L \leq 50$Å). Second, the line shape was calculated for zero external magnetic field. The experimental data, on the other hand, is much better for moderate-size magnetic fields. Finally, the authors arbitrarily considered only donors within the GaAs well in their calculation of the line shape. Tanaka et al.[5] have shown that the binding of electrons within the well to donors outside it can be appreciable. This, plus the fact that the density of states continues to increase for donors outside that well, means that they should not be neglected. In fact, as will be pointed out later, neglecting such impurities leads to the prediction of a spurious second peak in the absorption profile.

II. THEORY OF THE ABSORPTION PROFILE

The theory of absorption of light by atomic systems is well known, and can be found in standard texts on quantum mechanics (see, for example, Ref. 11). We only sketch it here, and indicate specifically how it can be applied to the problem of shallow donor absorption. We

first assume that our donors are sufficiently well separated that they do not interact with each other. Since the effective Bohr radius of a shallow donor in GaAs is about 100 Å, and our donors will be constricted still further by the applied magnetic field and the quantum well, this is not a very restrictive approximation for lightly doped samples ($< 10^{16}$ cm^{-3}). We also assume that the experiments will be performed at very low temperature so that all the donors are initially in their ground states. We choose our coordinate system such that the z axis is directed along the growth direction for the heterostructure, and consider the incident light polarized in the x direction with intensity I_0.

The probability per unit time for an electric dipole transition from an initial state i to a final state f is given by

$$P_{i \to f} = \frac{4\pi^2 e^2 \hbar^2}{m^2 E_{fi}^2 c} I_0 \, | \langle f | \nabla_x | i \rangle |^2 \delta(\hbar\omega - E_{fi}) , \quad (1)$$

where ω is the angular frequency of the incident light and E_{fi} is the energy difference between the final state and the initial state—$E_{fi} = E_f - E_i$. In the effective-mass approximation the mass in Eq. (1) is the effective mass of the donor electron.[12] If we multiply this expression by E_{fi} and sum over final states, we obtain the rate of energy loss from the field caused by absorption as a donor electron is excited from an initial state i to any other final state. Then if we multiply the resulting expression by ρ_i, the probability that the donor electron is initially in the state i, and sum over all initial states, we get the following expression for the power absorbed from the incident radiation:

$$P(\omega) = \frac{4\pi^2 e^2 I_0}{m^2 \omega c} \sum_{i,f} | \langle f | \nabla_x | i \rangle |^2 \rho_i \delta(\omega - E_{fi}/\hbar) . \quad (2)$$

Kohn[12] has shown that within the effective-mass approximation

$$| \langle f | \nabla_x | i \rangle |^2 = \frac{m^2 E_{fi}^2}{\hbar^4} | \langle f | x | i \rangle |^2 . \quad (3)$$

Substituting this into Eq. (2) yields the following expression for the absorbed power:

$$P(\omega) = \frac{4\pi^2 e^2 \omega I_0}{\hbar^2 c} \sum_{i,f} | \langle f | x | i \rangle |^2 \rho_i \delta(\omega - E_{fi}/\hbar) . \quad (4)$$

In the presence of an applied magnetic field, $-i\hbar\nabla$ should be replaced by $-i\hbar\nabla - (e/c)\mathbf{A}$, where $\mathbf{A}$ is the magnetic vector potential. However, the relationship in Eq. (3) is changed with the result that Eq. (4) is still valid.[13]

For a bulk semiconductor the sum over i reduces to a single term since the ground-state energies of all isolated donors are the same. However, for a quantum-well system the ground-state energy of a given donor depends on its location relative to the quantum well. The sum over i, then, is actually a sum over all the possible positions of the donor impurity.

In this work we are interested in the shape of the absorption profile, rather than its absolute expression. For this reason we define a function $I(\omega)$ as follows:

$$I(\omega) = \omega \sum_{f,i} | \langle f | x | i \rangle |^2 \rho_i \delta(\omega - E_{fi}/\hbar) . \quad (5)$$

$I(\omega)$ is usually called the absorption line shape because it contains most of the frequency dependence of the power spectrum of Eq. (4). It is closely related to the imaginary part of the complex dielectric function.[10]

The sum over donor positions in Eq. (5) is a sum over the Ga and Al sites in the GaAs-Ga$_{1-x}$Al$_x$As heterostructure for group-IV donors, or over As sites for group-VI donors. However, since the size of the donor is many times larger than the lattice spacing, the sum may be approximated by an integral with little error. The energy of a donor is dependent only upon its z coordinate (z_i), so we can replace the sum over i by an integral over z_i. The probability ρ_i in this case becomes the linear density distribution of donors, $p(z_i)$.

As we have noted, the transition energy E_{fi} is a function of the impurity position z_i. We may formally invert the relationship to obtain z_i as a function of angular frequency $\omega_{fi} = E_{fi}/\hbar$. This allows us to perform the integration to obtain

$$I(\omega) = \omega \sum_f \int_{-\infty}^{\infty} dz_i \, p(z_i) | \langle f | x | i \rangle |^2 \delta(\omega - \omega_{fi})$$

$$= 2\omega \sum_f \left| \frac{d\omega_{fi}}{dz_i} \right|_{\omega_{fi}=\omega}^{-1} | \langle f | x | i \rangle |^2 p(z_i) . \quad (6)$$

Because of the cylindrical symmetry of the problem, the initial (ground) states are states with zero angular momentum projection along the z axis (i.e., $m = 0$ states as discussed below). The matrix elements of the x operator will then vanish for all states except those for which $m = \pm 1$. At this point we assume that the frequency of the incident radiation is such that only the $2p$-like states contribute significantly to the line shape in the region of interest. This point will be discussed later. This approximation reduces the sum over final states to just two terms, the $2p_\pm$-like states, which from here on we will refer to as $2p_\pm$. We defer a description of these states until the next section. Furthermore, the application of a magnetic field will cause the $2p_+$ and $2p_-$ states to split, so that possibly only one term will be important for the line shape over a given range of frequency.

III. SHALLOW DONOR WAVE FUNCTIONS

In order to obtain a numerical absorption profile it is necessary that we have available accurate representations of the ground and $2p_\pm$ states for the shallow donor in a quantum well. This problem, with an applied magnetic field along the growth direction, has been examined by Greene and Bajaj.[8] We will sketch the analysis here; see Ref. 8 for details.

In the effective-mass approximation the Hamiltonian for the shallow donor electron may be written in the following form:

$$H = \frac{-1}{m^*} \nabla^2 - \frac{2}{r} + \gamma L_z + \tfrac{1}{4}\gamma^2 \rho^2 + V_w(z) . \quad (7)$$

This equation has been written in dimensionless form. The unit of energy is the effective Rydberg and the unit of

length is the effective Bohr radius—both determined using the parameters of bulk GaAs. (These quantities are 5.83 meV and 98.7 Å, respectively.) The quantity m^* in the above expression is the effective mass of the electron in units of the bulk GaAs effective mass. Inside the well $m^* = 1$; in the $Ga_{1-x}Al_xAs$ barrier material it is assumed to vary with x as[2]

$$m^* = 1 + 1.24x .\tag{8}$$

In Eq. (7), L_z is the z component of angular momentum (in units of $\hbar$), $\rho = (x^2 + y^2)^{1/2}$, and γ is a dimensionless measure of the magnetic field, the ratio of the lowest Landau energy of a "free" effective-mass electron to the effective Rydberg. The quantum-well potential $V_w(z)$ is assumed to be a simple square well. Neighboring wells are considered to be sufficiently far away that there is virtually no penetration of the donor-electron wave function into another well. This requires the $Ga_{1-x}Al_xAs$ barrier to be wide (> 200 Å).

The variational wave functions that we use to evaluate the line-shape function are of the same form as we used to find the binding energies of a shallow donor in a well with an applied magnetic field. Since the Hamiltonian in Eq. (7) is cylindrically symmetric, the component of angular momentum along the z axis is conserved, so that the ϕ dependence of the wave function has the form $\exp{(im\phi)}$. The "magnetic" quantum number, m, is an integer. Furthermore, since for most well widths the Coulomb contribution to the energy is considerably smaller than the contribution from the square-well potential, it is helpful to explicitly factor the solution for the ground state of the one-dimensional square-well problem out of our variational wave function. We label this square-well function $f(z)$. Its explicit form can be found in Ref. 8 or any general quantum mechanics text.[11] The form for the effective-mass envelope function that we have used is then given by

$$\Psi(\mathbf{r}) = \rho^{|m|} e^{im\phi} f(z) \sum_{j,k} A_{jk} G_{jk}(\rho, z - z_i) ,\tag{9}$$

where the basis functions $G_{jk}(\rho, z - z_i)$ are taken to be the product of Gaussian functions in ρ and $z - z_i$,

$$G_{jk}(\rho, z - z_i) = e^{-(\alpha_j + \beta)\rho^2} e^{-\alpha_k(z - z_i)^2} .\tag{10}$$

The parameters A_{jk}, α_j, and β are determined variationally. For the results presented in the next section, 13 terms were used in the expansion of Eq. (9) for both the ground and excited states.

IV. RESULTS AND DISCUSSION

As we indicated earlier, the major broadening effect for shallow donor transitions in these heterostructures is the dependence of energy on the position of the donor with respect to the well. This is clearly indicated in Fig. 1, which shows the dependence of the $1s$-$2p_-$ transition energy as a function of the position of the donor. The value of the Al concentration x in the barrier layers is taken to be 0.3 throughout this work. For these results the conduction-band discontinuity has been taken to be 85% of the total band discontinuity. Preliminary calculations
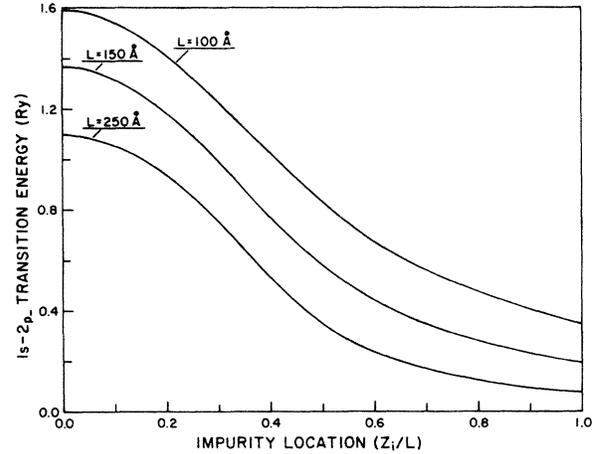
FIG. 1. Variation of the $1s$-$2p_-$ transition energy (expressed in terms of an effective Rydberg, 5.83 meV) as a function of the position of the donor ion (expressed in terms of the quantum-well width L) for three different widths. The value of the magnetic field parameter is $\gamma = 1$, and the origin of the coordinate system is chosen to be the center of the well. The value of the Al concentration x in the barrier layers is chosen to be 0.3.

using a value of 60% as suggested by more recent experimental work[14] give similar results. The magnetic field chosen for Fig. 1 corresponds to $\gamma = 1$, and the energy units are effective Rydbergs (Ry). In GaAs $\gamma = 1$ corresponds to a magnetic field of about 64 kG. (The $1s$-$2p_+$ energy can be obtained by adding 2γ to the $1s$-$2p_-$ transition energies.) The donor position z_i is given as a fraction of the well width L, with $z_i = 0$ being the center of the well. As can be seen in the figure, the $1s$-$2p_-$ energy decreases monotonically as the donor is moved from the center of the well to the edge ($z_i = L/2$) and on into the barrier material. Note the wide range (~ 1 Ry) of the transition energy for donors at different well positions.

As seen in Eq. (6), the derivative of the transition energy with respect to the donor position is an important factor in determining the absorption profile. The inverse of this derivative as a function of transition energy is shown in Fig. 2. It becomes infinite at the center of the well, causing the ideal profile to have an infinite spike at the energy corresponding to $z_i = 0$. Other broadening mechanisms neglected in Eq. (6) will remove the singularity, but there will be a peak characteristic of donors located in the center of the well.

The theoretical $1s$-$2p_+$ far-infrared absorption profiles are shown in Figs. 3 and 4. As before, the magnetic field value is $\gamma = 1$. This value results in a large Zeeman splitting between the $2p_+$ and $2p_-$ states. Consequently, we have neglected the contribution of the $2p_-$ states to the profiles in the energy range shown. The solid line of Fig. 3 shows the profile for a uniform impurity distribution versus transition energy over a range of about 1 effective Rydberg. The well width is 150 Å. The points shown on the solid curve correspond to equally spaced z_i values, each separated from the two neighboring points by 0.05L, or 7.5 Å. The edge position, $z_i = L/2$, is indicated on the figure while the center position is at the right side, at the
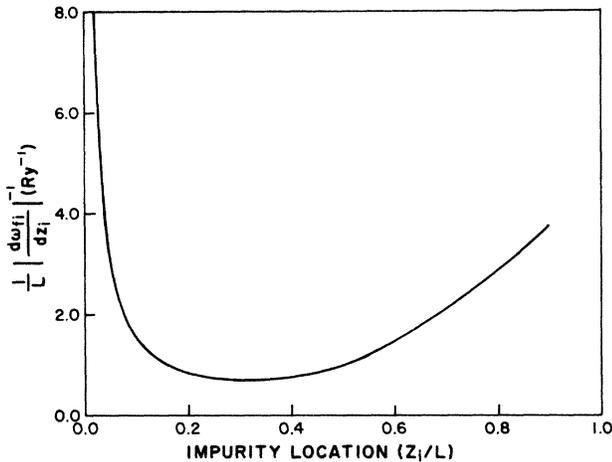
FIG. 2. Variation of the inverse of the derivative of the $1s$-$2p_+$ transition energy, $|d\omega_{fi}/dz_i|^{-1}$, as a function of the position of the donor ion, z_i. (This is proportional to the density of transition energies). The value of the magnetic field parameter is $\gamma = 1$, the Al concentration is $x = 0.3$, and the well width $L = 150$ Å.

FIG. 4. Variation of the relative absorption associated with $1s$-$2p_+$ transitions as a function of the transition energy in a quantum well of width $L = 150$ Å. The value of the magnetic field parameter is $\gamma = 1$. The solid curve represents the case where the well is spike-doped (width ~ 50 Å) at the center and the dashed curve corresponds to the case where the spike-doped peaks are located at the interfaces between the two semiconductors. The value of the Al concentration x in the barrier layers is chosen to be 0.3.

location of the absorption spike predicted in the preceding paragraph. Note that there is only the single spike in the uniform donor distribution curve. This result differs from that reported in Ref. 10. In Ref. 10 the authors obtain two peaks, one for the on-center donors, the second for the on-edge donors, assuming uniform doping only in the well region using infinite potential barriers. The reason our results differ from those of Ref. 10 is that we

FIG. 3. Variation of the relative absorption associated with $1s$-$2p_+$ transitions as a function of the transition energy in a quantum well of width $L = 150$ Å. As in Fig. 1, the magnetic field parameter is $\gamma = 1$. The solid curve corresponds to the case where the donors are distributed uniformly, and the dashed curve to the situation where a 10-Å-wide Gaussian donor impurity distribution is superimposed on a uniform background distribution. The Gaussian distribution is taken to be centered at the semiconductor interfaces and has an arbitrarily chosen peak value of 2 times that of the background. The value of the Al concentration x in the barrier layers is chosen to be 0.3.

assume uniform doping both in the well and in the barrier region. This leads to only one peak for $1s \rightarrow 2p$ or $1s \rightarrow \infty$ transition regardless of whether the potential barriers are infinitely high or not. For the case of $1s \rightarrow \infty$ transition this can be seen by examining Bastard's (Ref. 1) binding energy versus donor position plot (Fig. 3 of Ref. 1). The slope continues to decrease as the donor is moved further into the barrier. The same holds for the $1s \rightarrow 2p$ transition as shown in Fig. 2. In our case the absorption continues to increase for still smaller energy values than shown in Fig. 3. This is due to the fact that the derivative of the transition energy with respect to z_i becomes smaller with increasing z_i (see Fig. 1). This increase will not continue indefinitely in a real heterostructure with finite-width barriers because as a donor moves further into a barrier away from one quantum well, it gets closer to a neighboring well. Thus a finite-width barrier results in some maximum value for z_i, and for uniform doping, should exhibit a peak characteristic of donors at the center of each barrier.

As noted above, if the donor-impurity distribution is uniform in the well and in the barrier regions, there is only one peak associated with the $1s \rightarrow 2p_+$ transition. Another peak can be caused by a local concentration of impurities as might be found at the interfaces between the two semiconductors. The dashed curve in Fig. 3 illustrates the absorption profile with a 10-Å-wide Gaussian donor-impurity distribution superimposed on a uniform background distribution. The Gaussian distribution is centered at the interface between the GaAs and $Ga_{1-x}Al_xAs$, and has an arbitrarily chosen peak value of 2 times that of the background. The presence of a local impurity concentration at the interfaces between semiconductors is suggested by the photoluminescence spectra of Shanabrook and Comas,[15] who observed two peaks, one associated with recombination of a bound electron of an

on-center donor with a free heavy hole, and the other probably associated with recombination of a bound electron of an on-edge donor with a free heavy hole. They determined the binding energies of the on-center and the on-edge donors from their spectra and found them to be in fair agreement with those calculated by Mailhiot, et al.[2] (The theoretical prediction of Bastard[1] that there should be a second peak in the photoluminescence spectrum of a uniform donor distribution is in error. His prediction applies to heterostructures whose donor impurities are found only in the well material.)

Figure 4 shows the effect of a "spike-doped" donor distribution upon the absorption profile. Spike doping has been employed in several experimental studies of shallow donors in GaAs-Ga$_{1-x}$Al$_x$As heterostructures. The profiles in Fig. 4 are for a 150-Å-wide quantum well, with 50-Å-wide Gaussian doping spikes. Any background impurity distribution is assumed negligible. The applied magnetic field again corresponds to $\gamma = 1$. Two cases are presented in the figure. The solid line represents the case in which the peak of the spike occurs at the center of the well, while the dashed curve represents the results for doping spikes whose peaks are at the interfaces between the two semiconductors. Not surprisingly, the on-center case yields an absorption profile with a single peak whose maximum transition energy is that of a donor located at the center of the well.

The on-edge case is more complicated. There is still a spike associated with donors at the center of the well. However, its presence may be misleading. The amount of absorption seen in a real profile is proportional to the area under the curve in any given energy range. The area under the central spike is relatively much smaller in this case than it is for either the uniform distribution or the on-center spike doping. Another interesting point about the dashed curve of Fig. 4 is that the low-energy peak of the absorption does not occur at the same place as the peak of the doping spike. This is because the doping spike is very broad and is multiplied by a factor that increases with smaller energies—the inverse of the derivative of the transition energy with respect to donor position z_i. The combination causes the peak to be shifted to lower energies than would be expected for a very narrow distribution centered at the interface (as in the dashed curve of Fig. 3).

It should be pointed out that our wave functions [Eq. (9)] for the donors located away from the center have a p_z-like character only in the $f(z)$. The contribution of the p_z-like component, however, increases as the donor moves near to the edge. The variational part $G(\rho,z)$ does not have a p_z-like character. How this particular choice of

the variational wave function affects the results is not clear.

Recently Jarosik et al.[9] have obtained data from far-infrared absorption experiments on shallow donors in spike-doped GaAs-Ga$_{1-x}$Al$_x$As quantum-well structures. In one of the samples, for example, with magnetic field strengths in the range $0.5 \leq \gamma \leq 1.5$, they observe three peaks in a broad absorption feature approximately centered around the bulk GaAs $1s$-$2p_+$ transition. This particular sample is doped with a 50-Å-wide spike at the center of the well. Let us assume that, in addition to the doped spike, their heterostructures contain a narrow concentration of impurities at the interface. As mentioned earlier, this assumption is consistent with their photoluminescence data on some of the same samples. The two theoretical peaks corresponding to donors at the center and at the edges of the 150-Å- wide GaAs well fall rather close to the two higher energy peaks seen by Jarosik et al., so it is tempting to identify these experimental peaks with our theoretical ones. Although the third (low-energy) peak is at about the right energy for the peak corresponding to donors at the center of the finite barrier width layers (not shown in Figs. 1—4, which treat only the infinite barrier width case), the much lower donor concentration in the barrier makes it unlikely that such a peak would appear in the experimental profiles.

More recent absorption profiles from spike-doped GaAs-Ga$_{1-x}$Al$_x$As quantum-well structures do not show multiple peaks.[16] The position of the single observed peak is in good agreement with our calculated transition energies for donors located at the center of an isolated quantum well. However, the experimental profiles are roughly symmetric about the central peak, in contrast to the highly asymmetric peak illustrated by the solid line of Fig. 4. Further study is called for, but one possible explanation is that the high-energy portion of the experimental profile is due to transitions to $3p$-like states of donors distributed throughout the well.

V. SUMMARY

To summarize, we have developed a theory of far-infrared absorption profiles for the case of shallow donors in quantum-well structures, in the presence of an applied magnetic field. Assuming broadening dominated by the positional dependence of the donors, we have calculated theoretical absorption profiles for several distributions of donor impurities within GaAs-Ga$_{1-x}$Al$_x$As heterostructures. The theoretical calculations suggest that a lower-energy peak in some of the experimental profiles may be due to thin impurity accumulation layers at the semiconductor interfaces.

[1]G. Bastard, Phys. Rev. B 24, 4714 (1981).

[2]C. Mailhiot, Yia-Chung Chang, and T. C. McGill, Phys. Rev. B 26, 4449 (1982).

[3]Ronald L. Greene and K. K. Bajaj, Solid State Commun. 45, 825 (1983).

[4]S. Chaudhuri, Phys. Rev. B 28, 4480 (1983).

[5]Kazuyoshi Tanaka, Masataka Nagoka, and Tokio Tamabe, Phys. Rev. B 28, 7068 (1983).

[6]C. Priester, G. Bastard, G. Allan, and M. Lannoo, Phys. Rev. B 30, 6029 (1984).

[7]S. Chaudhuri and K. K. Bajaj, Solid State Commun. 52, 967 (1984).

[8]Ronald L. Greene and K. K. Bajaj, Phys. Rev. B 31, 913 (1985).

[9]N. C. Jarosik, B. D. McCombe, B. V. Shanabrook, J. Comas, and G. Wicks, in *Proceedings of the 17th International*

Conference on the Physics of Semiconductors, edited by, J. D. Chadi and W. A. Harrison (Springer-Verlag, New York, 1985), p. 507.

[10]G. Bastard, E. E. Mendez, L. L. Chang, and L. Esaki, Solid State Commun. 45, 367 (1983).

[11]Leonard I. Schiff, Quantum Mechanics, 3rd ed. (McGraw-Hill, New York, 1968).

[12]W. Kohn, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5.

[13]C. Aldrich and R. L. Greene, Phys. Status, Solidi B 93, 343 (1979).

[14]R. C. Miller, D. C. Gossard, D. A. Kleinman, and O. Munteanu, Phys. Rev. B 29, 3740 (1981).

[15]B. V. Shanabrook and J. Comas, Proceedings of the 5th International Conference on Electronic Properties of Two-Dimensional Systems, Oxford, 1983 [Surf. Sci. 142, 502 (1984)].

[16]N. C. Jarosik, B. D. McCombe, B. V. Shanabrook, J. Comas, John Ralston, and G. Wicks, Phys. Rev. Lett. 54, 1283 (1985).