Infrared transitions between shallow acceptor states in GaAs-$Ga_{1-x}Al_xAs$ quantum wells

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We calculate energies and oscillator strengths of infrared transitions between ground and excited shallow acceptor states in quantum wells (QW's) for varying well width. The impurity states are calculated within a four-band effective-mass theory, which accounts for the valence-band mixing as well as for the mismatch of the band parameters and the dielectric constants between well and barrier materials. The envelope function is expanded into a basis set consisting of products of two-dimensional hydrogeniclike functions and impurity-free QW eigenfunctions at $\mathbf{k}_{\|} = \mathbf{0}$. The present method is suited for s-type ground states as well as for p-type excited states. We obtain the absorption spectra for well widths ranging from 50 to 200 Å. We find an overall increase of the transition energies for decreasing well widths. For polarization in the layer planes, the oscillator strengths of the lines corresponding to the bulk G and D lines maintain their oscillator strengths for decreasing well widths, whereas the lines corresponding to the bulk C line are very weak for small well widths. On the other hand, in the case of polarization along the QW axis, the oscillator strengths of the main lines decrease considerably as the well width decreases. We compare our results with absorption spectra of a recent experiment, and find a fairly good agreement.

I. INTRODUCTION

In the last decade growing interest has been devoted to the study of shallow impurities in GaAs-$Ga_{1-x}Al_xAs$ quantum wells (QW's). A good understanding of the effects due to this kind of impurity is important not only from a fundamental point of view but also because of technological applications. Shallow impurities can be present either because of intentional doping or because of uncontrolled growth conditions. In fact, a background concentration of impurities can be found in nominally undoped samples. Therefore a precise characterization of the impurities is necessary not only in order to fully exploit their properties but also to identify their presence. Owing to continuous improvements in the growth techniques as well as to a successful transfer of experimental techniques from the study of bulk materials to the study of heterostructures, it has been possible to gain detailed information on the properties of shallow impurities in QW's. Extensive studies with a large variety of techniques such as photoluminescence,[1-4] magnetospectroscopy,[5] far-infrared absorption,[6,7] resonant Raman scattering,[8,9,3,4] and two-hole transitions,[3,4] have been performed. These measurements have provided accurate determinations of transition energies between ground and excited states as a function of the well width. Furthermore selective doping has allowed one to study these properties for various impurity positions in the QW. Experiments have been performed on shallow donor states as well as on shallow acceptor states.

Some previous calculations of impurity states in QW's were based on one-band effective-mass models.[10-12] In these models, hydrogenic Hamiltonians, which have been applied successfully in bulk calculations, have been extended to the case of QW's by including a square-well potential. These models are particularly suited for donor states, which are associated with the nondegenerate conduction band. After the pioneering work by Bastard,[10] who considered infinite barriers, these models have been implemented taking successively into account the mismatch of the band parameters and the dielectric constants between well and barrier materials.[11,13]

The problem of calculating energy levels and wave functions of a shallow acceptor in a quantum well is much more complicated than the similar problem for a donor. This point has been nicely discussed by Greene and Bajaj.[14] In bulk GaAs the uppermost valence band, to which the acceptor states are associated, is fourfold degenerate at the center of the Brillouin zone. Moreover, in the acceptor problem, band warping must be accounted for. The QW potential lifts in part the degeneracy of the band producing a splitting between heavy and light holes, but the acceptor binding energy is so large that an accurate calculation has to include the full QW dispersion. Moreover, because of the more localized wave functions of the acceptor ground states the effect of

central-cell corrections has to be considered.

An attempt to address the acceptor problem including the complicated valence-band structure was made by Masselink, Chang, and Morkoç[15] who used a four-band effective-mass Hamiltonian.[16] These authors were able to calculate binding energies of the two s-type ground states, using a symmetry-adapted basis set in $\mathbf{r}$ space. Subsequently, Pasquarello, Andreani, and Buczko[17] used a similar effective-mass model, but within a $\mathbf{k}$-space approach, in order to calculate excited acceptor states. However, the formalism turned out to be unsatisfactory for the strongly bound ground states, because the wave functions had been expanded on a basis which included only the discrete subband spectrum. Very recently we have been able to include the effect due to the subband continuum yielding results for the s-type ground and excited states.[18] The comparison of calculated $1s$-$2s$ transition energies with Raman scattering and two-hole transitions measurements[3,4] showed very good agreement. Our results also agree with recent calculations by Einevoll and Chang, who obtained binding energies of s-type acceptor states using an effective tight-binding method.[19]

In this work we are interested in infrared transitions between ground and excited acceptor states in GaAs-$Ga_{1-x}Al_xAs$ QW's. Infrared transitions between impurity states in QW's are more difficult to observe with respect to the bulk case[20] because the absorption spectra present broader peaks on a stronger background. The main reasons for this difference are the following ones. In the QW the transition energy varies as a function of the position of the impurity center. Therefore the doped regions have to be small and as a consequence higher doping concentrations than in the bulk are needed in order to observe the absorption lines. The relative smaller distance between the impurity centers produces line broadening because of the increased interaction between the impurities. Broadening also occurs because of the finite spatial width of the doped layers and because of the interface roughness or other defects of the sample. Infrared transitions between QW donor states have been studied extensively from an experimental[6] as well as from a theoretical[12,13] point of view and a satisfactory agreement has been reached. On the other hand, much less work has been done on infrared transitions between acceptor states in QW's: to our knowledge only one experimental paper has been published on this subject until now.[7] From a theoretical point of view, the calculation of oscillator strengths of transitions between s-type ground and excited acceptor states and p-type excited acceptor states requires accurate wave functions and even in the bulk case calculations have not been performed until very recently.[21,22] In the QW case, until now, there has been no theory which gives wave functions of both ground and excited acceptor states with a reasonable degree of accuracy. In this work we use the theory which we have previously developed for the calculation of the binding energies of s-type states[18] and show that it is suited for acceptor states of any symmetry. We are thus able to calculate oscillator strengths of infrared transitions between ground and excited acceptor states.

In Sec. II we expose the theory which gives the energies and wave functions of acceptor states in QW's. The results are presented for well widths ranging from 50 to 200 Å. The symmetry properties of the acceptor states are briefly discussed. Section III is devoted to the calculation of the oscillator strengths of the acceptor transitions, for each of the two nonequivalent polarizations. The results are compared with experimental far-infrared absorption spectra by Reeder *et al.*[7] Concluding remarks can be found in Sec. IV.

II. SHALLOW ACCEPTOR STATES

A. Theory

In this subsection we expose a comprehensive theory for the calculation of energy levels and wave functions of acceptors in GaAs-$Ga_{1-x}Al_xAs$ QW's. A major virtue of the present theory is that, in contrast with other theories,[15,17,19] it gives accurate results for ground and excited acceptor states as well as excited acceptor states of any symmetry. We consider a quantum well grown in the [001] direction (z axis) with a single on-center (at $z = 0$) acceptor impurity. We solve the acceptor problem within a four-band effective mass theory.

The acceptor Hamiltonian is a 4×4 matrix operator

$$H = H^{\text{kin}} + H^{\text{QW}} + H^{C} + H^{s}, \tag{1}$$

where H^{kin} represents the kinetic energy of the holes, H^{QW} the confinement potential due to the valence-band discontinuity, H^{C} the potential of the impurity and of the image-charges due to the dielectric mismatch, and H^{s} the self-energy term, also due to the dielectric mismatch. In Hamiltonian (1) the kinetic energy of the hole is chosen to be positive.

The kinetic energy term H^{kin} describes the dispersion of the bulk Γ_8 valence band. H^{kin} is quadratic in $\mathbf{k} = -i\nabla$ and is given by the Luttinger-Kohn Hamiltonian.[16] Inside the quantum well ($|z| < L/2$) the Luttinger parameters[23] correspond to those of the well material, in the barrier to those of the barrier material. We use the Luttinger-Kohn Hamiltonian in the axial approximation, which has been shown to be accurate in the bulk case within 0.5 meV.[17] The confinement potential H^{QW} is a square-well potential of barrier height V and well width L. The Coulomb potential of a point charge in a system of three dielectrics separated by two infinite planes is contained in H^{C}. In order to satisfy the Maxwell boundary conditions H^{C} must contain an infinite series of image charges.[17,13] In our method of solution we will take this complete series explicitly into account. The self-energy term H^{s} represents the interaction between the hole and the polarization charge induced at the interfaces of the QW by the hole itself, because of the dielectric mismatch between well and barrier materials.[24] We have neglected this interaction because it shifts the energy levels of the hole in both the acceptor and the subband states, and therefore an effective cancellation of this effect occurs in the Coulomb binding energies. We have checked this point in first-order perturbation theory, finding negligible contributions (less than 0.1 meV) for wells ranging

from 50 to 200 Å.

We discuss now corrections which are not accounted for by Hamiltonian (1), namely the effects due to the split-off band, to the spatially-dependent screening, and to the particular chemical properties of the considered impurity.[25] All these corrections are effective very near to the acceptor site. They affect mainly the ground state because its wave function is more localized, with the highest density on the acceptor site. Acceptor states of p-type symmetry, which have a vanishing wave function on the impurity site, are barely affected. The inclusion of these corrections produces a twofold effect on the spectra calculated here. First, the transition energies are all shifted by an amount corresponding to the shift of the ground state. For the case of Be acceptors, as discussed in Ref. 18, the different corrective effects almost cancel and the ground-state shift can be neglected to a first approximation in the well width range considered here. Second, the modification of the ground-state wave function affects directly the oscillator strengths. However, a study of these corrective effects in the bulk has shown that although the absolute values of the oscillator strengths are considerably modified, their relative values remain almost unchanged.[21,25] We expect that the same conclusions hold for the QW.

The effective-mass Hamiltonian we have used is invariant for rotations around the z axis and for inversion with respect to the center of the QW. The acceptor eigenstates can be classified by two quantum numbers: the z component of the total angular momentum m and the parity ($\pm$) with respect to inversion. The acceptor levels are twofold degenerate because of time-reversal symmetry. The two states of the Kramers doublet have opposite m but the same parity, and the doublet can therefore unambiguously be labeled by $(|m|,\pm)$. In order to distinguish between the two states of a doublet, it is useful to consider the operator σ, which represents the reflection in the $z=0$ plane.[26] The two states of a doublet can be chosen to have opposite parity with respect to σ.[17] The relation between the symmetry group D_{2d}, which accounts for the zinc-blende structure, and the symmetry group $D_{\infty h}$ of the effective mass Hamiltonian (1) is given in Ref. 17.

The Hamiltonian (1) acts on a four-component envelope function F. Each component F^s is labeled by the spin index s running from $\frac{3}{2}$ to $-\frac{3}{2}$. The s component of an acceptor envelope function of definite angular momentum m reads

$$F^{m,s}(\rho,\theta,z)=e^{i(m-s)\theta}f^{m,s}(\rho,z). \tag{2}$$

Because of the angular momentum of the Bloch functions a phase factor $e^{i(m-s)\theta}$ appears in the envelope function and therefore its spin components have different transformation properties under rotations around the z axis.[27] We expand the functions $f^{m,s}$ into a basis set of functions which are separable in the coordinates ρ and z:

$$f^{m,s}(\rho,z)=\sum_n R_n^{m,s}(\rho)g_n^s(z). \tag{3}$$

The function g_n^s is chosen to be the s component of the four-component envelope function g_n, which describes a QW subband state at $\mathbf{k}_\parallel=\mathbf{0}$. The envelope function g_n is a solution of the Hamiltonian $H^{\rm kin}+H^{\rm QW}$ which describes the impurity-free QW system. The basis set of functions g_n is complete if discrete as well as continuum states of the impurity-free QW are included. The latter states are accounted for by discretizing the continuum introducing sufficiently distant infinite barriers. It is necessary to include continuum states in order to achieve numerical convergence for the binding energies of the acceptor ground states.[18] The g_n satisfy current conserving boundary conditions at the interfaces.[28]

The radial functions $R_n^{m,s}(\rho)$ in Eq. (3) are developed in an expansion of functions with the correct asymptotic behavior for large and small ρ:

$$R_n^{m,s}(\rho)=\rho^{|m-s|}\sum_l A_{nl}^{m,s}e^{-\alpha_l\rho}, \tag{4}$$

where the exponents α_l are chosen in a geometrical series and cover the relevant physical region, and where the coefficients $A_{nl}^{m,s}$ are taken as variational parameters.[18] The eigenvalue problem can be turned into a linear problem for the parameters $A_{nl}^{m,s}$. We note that, for a given symmetry, the lowest state as well as the excited ones are calculated at the same time.

A great virtue of the present basis set is that most of the integrals which appear in the matrix elements of Hamiltonian (1) can be carried out analytically. In the calculation of the matrix elements of the Coulomb potential an auxiliary integral which decouples ρ and z coordinates is introduced, using the well-known transformation

$$\frac{1}{(\rho^2+z^2)^{1/2}}=\int_0^\infty dq\, e^{-|z|q}\,J_0(\rho q), \tag{5}$$

where J_0 is the Bessel function of order zero. With this transformation all the integrals over the space coordinates are calculated analytically: only the remaining integral over the auxiliary variable q is calculated numerically. In this way we are able to include as many as 40 g_n functions and up to 9 exponentials in Eq. (4). This large number of basis functions turns out to be necessary for the calculation of the ground states, which are strongly bound. The number of basis functions can be reduced in the calculations of states of different symmetry. The use of a set of basis functions which are separable in the z and in-plane (ρ,θ) coordinates was originally suggested by the quasi-two-dimensional character of the QW system with narrow well width. However, this approach turned out to be very effective also in the case of very large well widths.[13] By a comparison with the results for the bulk case,[17] we are able to estimate that the convergence of our calculations for the binding energies of the acceptor states is within 0.2 meV.[18] As we will see in the next section, a further advantage of our basis set is that also the transition matrix elements, which are needed for the calculation of the oscillator strengths, can be carried out analytically.

B. Results

In this subsection we present numerical results for the binding energies of on-center acceptors in QW's. We have

taken the Luttinger parameters $\gamma_1 = 6.85$, $\gamma_2 = 2.1$, $\gamma_3 = 2.9$ and the dielectric constant $\epsilon = 12.53$ for GaAs, and $\gamma_1 = 3.45$, $\gamma_2 = 0.68$, $\gamma_3 = 1.29$, $\epsilon = 9.8$ for AlAs.[29] The parameters for $Ga_{1-x}Al_xAs$ are obtained by linear interpolation. The band discontinuity is taken to be $\Delta E_v = 0.35 \times 1247 \times x$ meV,[30] where an offset ratio between conduction and valence band of 65 to 35 has been assumed.

In Figs. 1 and 2 we present the energy levels for on-center acceptors in GaAs-$Ga_{0.7}Al_{0.3}As$ QW's for well widths ranging from 50 to 200 Å. The acceptor energies are given with respect to the bottom of the first heavy hole subband, which is the lowest hole level in an impurity-free QW. In Fig. 1 we plot the binding energies of the ground states as well as of the lowest-lying excited states of even symmetry with respect to inversion. Solid, dashed, and dotted-dashed curves are used for states of $(\frac{3}{2},+)$, $(\frac{1}{2},+)$, and $(\frac{5}{2},+)$ symmetry, respectively. Because of the reduced symmetry of the QW, the fourfold degenerate bulk ground state $1S_{3/2}(\Gamma_8)$ is split into two twofold degenerate states: the more strongly bound heavy-hole ground state of $(\frac{3}{2},+)$ symmetry and the light-hole ground state of $(\frac{1}{2},+)$ symmetry. The binding energies of the ground and first excited states of $(\frac{3}{2},+)$ and $(\frac{1}{2},+)$ symmetry have been reported and discussed previously in Ref. 18. These results are in good agreement with experimental data[3,4] as well as with other recent theoretical calculations.[19] In Fig. 1 we present also the binding energies of the second excited states of $(\frac{3}{2},+)$ and $(\frac{1}{2},+)$ symmetry as well as the binding energy of the lowest $(\frac{5}{2},+)$ state.

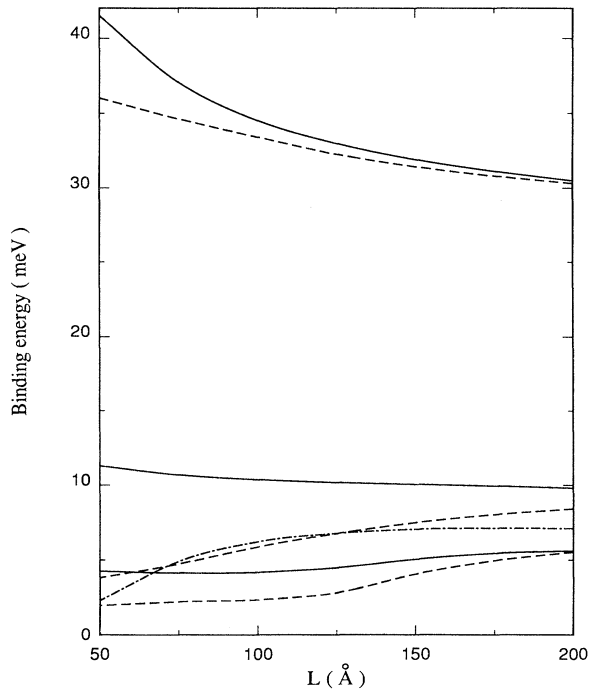

FIG. 1. Binding energy of acceptor states of even parity for an on-center impurity in GaAs-$Ga_{0.7}Al_{0.3}As$ quantum wells as a function of the well width. Solid, dashed, and dotted-dashed curves are used for states of $(\frac{3}{2},+)$, $(\frac{1}{2},+)$, and $(\frac{5}{2},+)$ symmetry, respectively. The binding energies are given with respect to the bottom of the first heavy-hole subband.

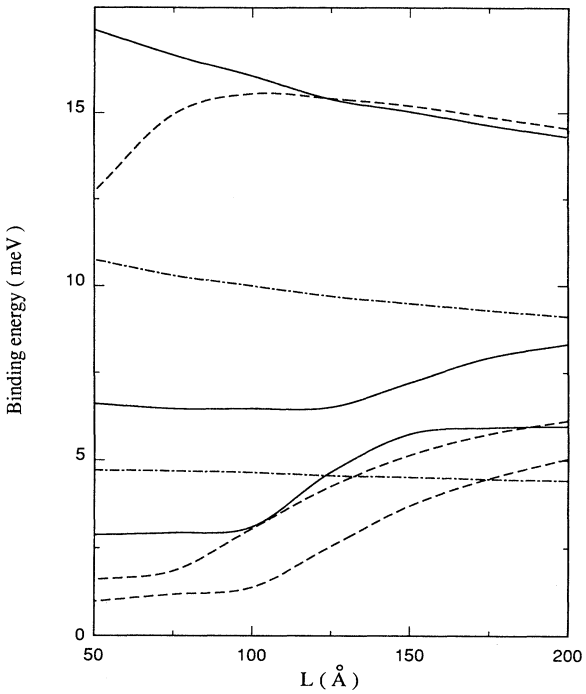

FIG. 2. Binding energy of acceptor states of odd parity for an on-center impurity in GaAs-$Ga_{0.7}Al_{0.3}As$ quantum wells as a function of the well width. Solid, dashed, and dotted-dashed curves are used for states of $(\frac{1}{2},-)$, $(\frac{3}{2},-)$, and $(\frac{5}{2},-)$ symmetry, respectively. The binding energies are given with respect to the bottom of the first heavy-hole subband.

In Fig. 2 we plot the binding energies of the lowest lying excited acceptor states of odd symmetry. The bulk excited states $2P_{3/2}(\Gamma_8)$ and $2P_{5/2}(\Gamma_8)$ are split into two doublets in the QW. The bulk $2P_{5/2}(\Gamma_7)$ state is twofold degenerate and does not split in the QW. Solid, dashed, and dotted-dashed curves are used for states of $(\frac{1}{2},-)$, $(\frac{3}{2},-)$, and $(\frac{5}{2},-)$ symmetry, respectively. The binding energies of these states had been obtained previously with an alternative procedure which consisted in an expansion of the acceptor envelope function in the $\mathbf{k}_{||}$-dependent QW subband eigenfunctions.[17] From Fig. 2 we see that the present variational method is able to reproduce these results and even to improve slightly upon them.

III. INFRARED ABSORPTION

In this section we calculate the oscillator strengths of transitions from ground and excited acceptor states to excited acceptor states in QW's in order to interpret the infrared absorption spectra of these systems.

A. Theory

The absorption cross section, defined as the absorbed energy per unit time divided by the electromagnetic flux, is given by[21]

$$\sigma(\omega,\epsilon)=\frac{2\pi^2\hbar^2\gamma_1}{nm_0}\left(\frac{e^2}{\hbar c}\right)\sum_i f_{i0}(\epsilon)\,\delta(E_i-E_0-\hbar\omega), \tag{6}$$

where n is the refractive index. The sum is over all the doublets of Kramers degenerate excited acceptor states and the label 0 indicates the ground-state doublet of the acceptor. In Eq. (6) f_{i0} is the oscillator strength of transitions from the ground doublet to the excited doublet labeled by i,

$$f_{i0}(\epsilon)=\frac{2m_0(E_i-E_0)}{g_0\hbar^2\gamma_1}\sum_{k,k'}\sum_s|\langle F^s_{ik'}|\epsilon\cdot\mathbf{r}|F^s_{0k}\rangle|^2, \tag{7}$$

where E_0, F^s_{0k} and E_i, $F^s_{ik'}$ are the energies and envelope functions of ground and excited states, respectively, $g_0=2$ is the degeneracy of the ground state, and ϵ is the polarization vector of the electromagnetic radiation. The sum indices k, k' indicate the two components of the ground and excited doublet, respectively.

We now give the selection rules for the electromagnetic transitions.[17] Only transitions between acceptor states of opposite parity with respect to inversion are allowed. Therefore only odd states can be reached starting from the even ground states. For x polarization, transitions are allowed only between acceptor states with $\Delta m=\pm1$ and of the same parity with respect to the σ reflection. On the other hand, z-polarized radiation induces only transitions between states with $\Delta m=0$ and of opposite parity with respect to σ. It should be noted that the selection rules for a D_{2d} symmetry group allow additional transitions. However, these transitions are expected to have smaller oscillator strengths.

In the bulk, for any given polarization ϵ, the oscillator strengths as defined in Eq. (7) satisfy a sum rule.[31] In the QW, because of the nonequivalence of the in-plane and z directions such a sum rule does not hold. It is however possible to derive the following sum rule (see the Appendix), which relates oscillator strengths for different polarizations to each other:

$$\sum_i[\tfrac{2}{3}f_{i0}(\hat{\mathbf{x}})+\tfrac{1}{3}f_{i0}(\hat{\mathbf{z}})]=1. \tag{8}$$

This sum rule can be used to check the precision of our calculation. In fact, we cannot perform the sum over all the exact eigenstates which appears in Eq. (8) as we diagonalize the Hamiltonian on a *finite* basis. In a variational calculation only the solutions of lowest energy accurately represent the true eigenstates. Variational solutions of higher energy have in general no specific meaning. However, it is interesting to observe that if we take the sum in (8) over the whole set of variational solutions, we find that the sum rule is verified within 4% in all cases.

B. Results

In order to interpret the absorption spectrum it is useful to start from the bulk limit.[20–22] In the bulk, the absorption spectrum is characterized by a strong doublet, whose components have been called D and C. At lower energies another line is found which is called G and is considerably weaker. The transition energies[32] and the intensities[21,22] of these lines have been explained. In this work we study QW's with well widths ranging from 50 to 200 Å. In the bulk the wave function of the acceptor ground state decreases at large distances as e^{-r/r_0} with $r_0\approx25$ Å.[32] Therefore, we expect that the acceptor spectrum at 200 Å can be interpreted starting from the bulk limit. As we have seen in the previous section, the bulk states split in the QW because of the lower symmetry. As a consequence, the G, D, and C lines split into different components in the QW.

In Fig. 3 we plot the energies of the allowed transitions in the case of x polarization in GaAs-$Ga_{1-x}Al_xAs$ QW's as a function of the well width. Analogously, the energies of the allowed transitions in the case of z polarization are plotted in Fig. 4. The QW lines have been labeled with G, D, or C according to the bulk line to which they correspond. We note that the transition energies generally increase for decreasing well widths. This

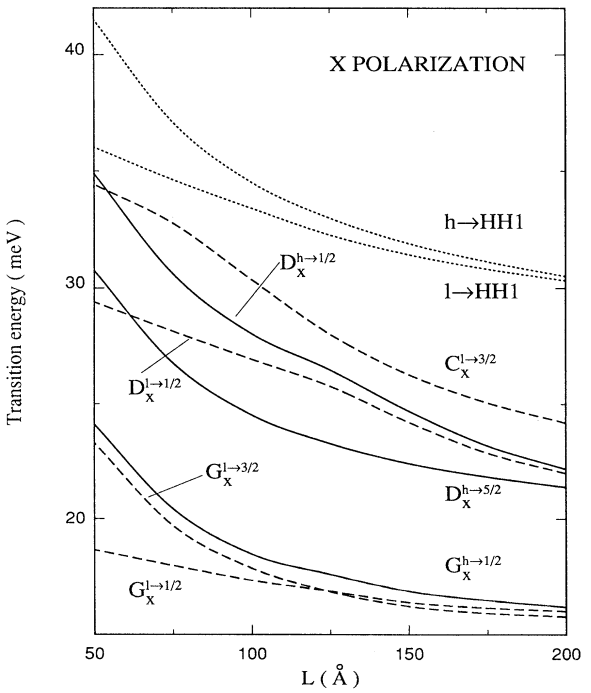

FIG. 3. Transition energies of the allowed transitions in x polarization between ground and excited acceptor states for an on-center impurity in GaAs-$Ga_{0.7}Al_{0.3}As$ quantum wells, as a function of the well width. Solid and dashed curves represent transitions from the $(\frac{3}{2},+)$ (heavy-hole) and $(\frac{1}{2},+)$ (light-hole) ground state, respectively. Dotted curves represent the onset of the transitions between the ground states and the continuum of the first heavy-hole subband.

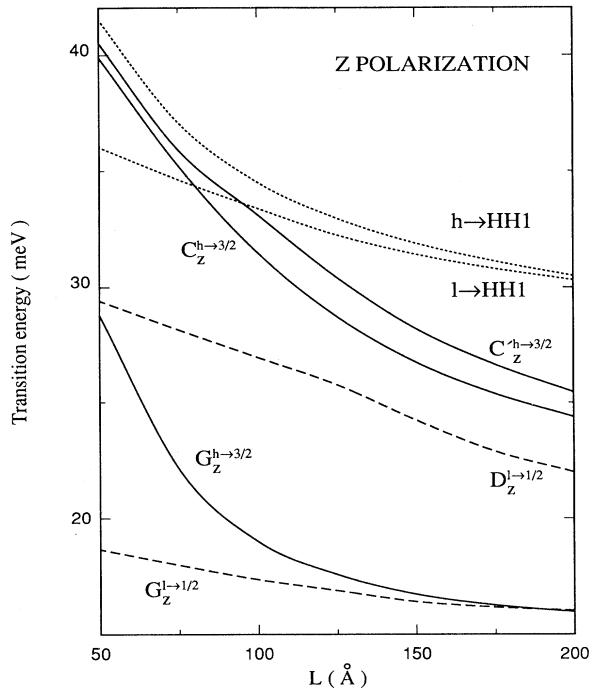

FIG. 4. Transition energies of the allowed transitions in z polarization between ground and excited acceptor states for an on-center impurity in GaAs-$Ga_{0.7}Al_{0.3}As$ quantum wells, as a function of the well width. Solid and dashed curves represent transitions from the $(\frac{3}{2},+)$ (heavy-hole) and $(\frac{1}{2},+)$ (light-hole) ground state, respectively. Dotted curves represent the onset of the transitions between the ground states and the continuum of the first heavy-hole subband.

is mainly due to the increase of the binding energies of the ground states (see Fig. 1), which is more significant than the variation of the binding energies of the excited states (see Fig. 2). The relative positions of the lines change significantly as a function of the well width. We note that in x polarization QW lines which correspond to the bulk C line cannot be excited starting from the heavy-hole ground state but only can from the light-hole ground state. In z polarization the increase of the transition energies from the heavy-hole ground state is considerably larger than in the case of x polarization. In particular for small well widths the lines which correspond to the bulk C line occur at energies very near to the onset of the transitions from the heavy-hole ground state to the continuum of the first heavy-hole subband. This can be understood as follows. The lines which correspond to the C line originate from transitions from the ground state to excited states of $(\frac{3}{2},-)$ symmetry. These states are mainly associated with the light-hole subband which is pushed towards higher energies when the well width decreases. Hence the corresponding transition energies increase. Moreover, the contribution of the light-hole subband to the lower $(\frac{3}{2},-)$ acceptor states decreases and these states are mainly associated with the heavy-hole subband.

We present in Figs. 5, 6, and 7 results for the oscillator strengths of the lines which correspond to the G, D, and C lines of the bulk spectrum, respectively. Solid and dashed lines are used for transitions from the heavy- and light-hole ground state, respectively. In Fig. 5 we plot as a function of the well width the oscillator strengths of all the lines corresponding to the bulk G line. The oscillator strengths of the five lines are rather small and of the same order of magnitude as in the bulk. The line $G_z^{l\to 1/2}$ has a negligible oscillator strength in the scale of Fig. 5 and has not been reported. In Fig. 6 we plot the oscillator strengths of the lines corresponding to the bulk D line. These lines are the strongest of the QW absorption spectrum. The oscillator strengths of transitions which are allowed in x polarization are almost independent of the well width. Only the line $D_z^{l\to 1/2}$ which is allowed in z polarization loses its oscillator strength for decreasing well widths. In Fig. 7 we give the oscillator strengths of the lines which correspond to the bulk C line. The line labeled with $C'^{h\to 3/2}_z$ represents the transition to the third level of $(\frac{3}{2},-)$ symmetry, corresponding to the bulk $3P_{3/2}[\Gamma_8]$ state. In the bulk this transition occurs at almost the same energy as the transition to the $2P_{5/2}[\Gamma_7]$ state and contributes to the intensity of the C line. In this figure the oscillator strengths of the main lines decrease for decreasing well width. This is understood as the acceptor states of $(\frac{3}{2},-)$ symmetry corresponding to the bulk C line are mainly associated with the first light hole subband. For narrow well widths, as these states are pulled towards the continuum of the first heavy-hole subband, their oscillator strengths are transferred to higher states because of mixing effects.

When the binding energies of the ground and excited acceptor states and the first-excited acceptor states are referred to the edge of the bulk valence band, it is found that at 200 Å they are close to the bulk limit.[33] The comparison between QW oscillator strengths and their bulk values is not as straightforward. The oscillator strengths of all QW transitions which correspond to the same bulk transition must be considered together.[34] We find that

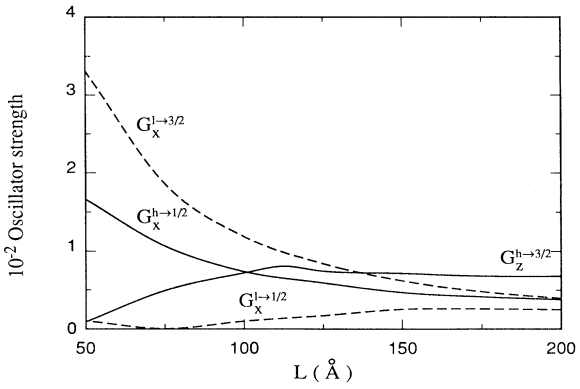

FIG. 5. Oscillator strengths of the acceptor transitions corresponding to the bulk G line in GaAs-$Ga_{0.7}Al_{0.3}As$ quantum wells as a function of the well width.

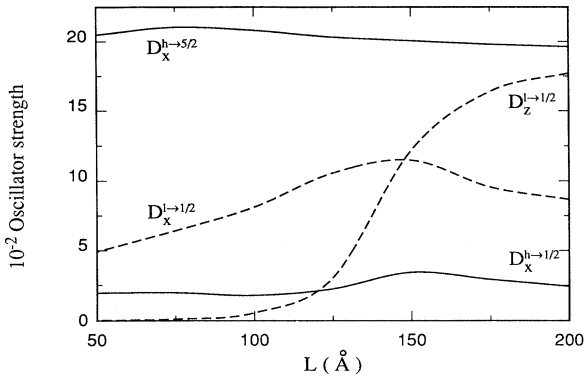

FIG. 6. Oscillator strengths of the acceptor transitions corresponding to the bulk D line in GaAs-$Ga_{0.7}Al_{0.3}As$ quantum wells as a function of the well width.

at 200 Å the correspondence is not as close as for the binding energies. In order to check the reliability of our calculations in the limit of large well widths, we have performed a calculation in the spherical approximation[32] ($\gamma_1 = 6.85$, $\mu = 0.7$) for which bulk oscillator strengths are provided in literature.[21] We have considered a QW with a well width of 265 Å. For the G line, we obtain oscillator strengths of 9.6×10^{-3} for x polarization and 8.0×10^{-3} for z polarization which have to be compared with the bulk value[21] of 8.25×10^{-3}. We are not able to determine to what extent the residual discrepancy is due to the anisotropy of the QW system or to the finite variational basis set of our calculations. We conclude that the oscillator strengths for well widths ranging from 50 to 200 Å, presented here, are reliable at least within this accuracy.

In order to reproduce the absorption spectrum in the case of x polarization we show the oscillator strengths as a function of the transition energy in Fig. 8, for various well widths. The same has been done for z polarization in Fig. 9. Solid and dashed lines indicate the oscillator strengths of transitions from the heavy- and light-hole ground state, respectively. In the figures the onset of the transitions between the ground states and the continuum of the first heavy-hole subband is indicated by thin vertical lines. The main difference between the two polariza-

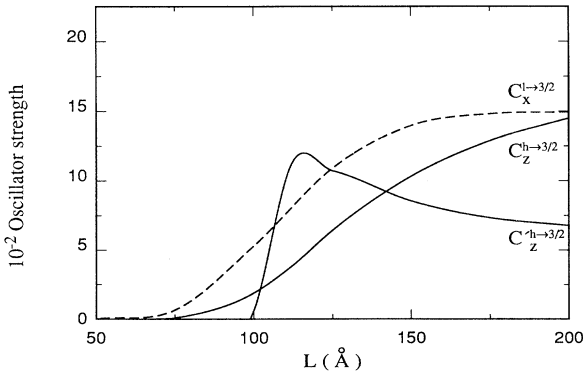

FIG. 7. Oscillator strengths of the acceptor transitions corresponding to the bulk C line in GaAs-$Ga_{0.7}Al_{0.3}As$ quantum wells as a function of the well width.

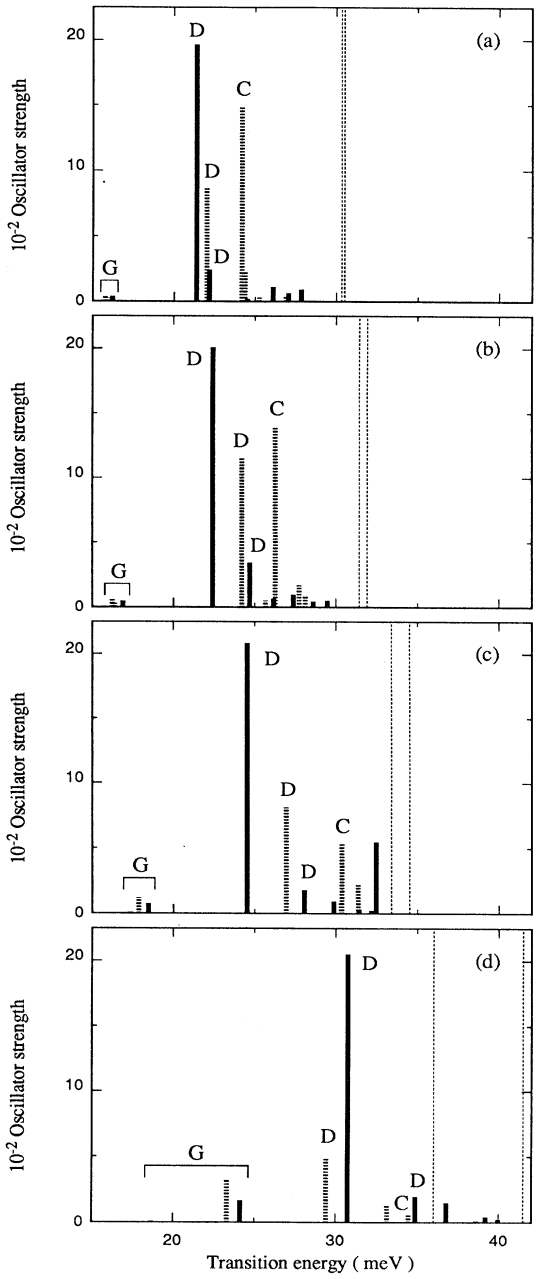

FIG. 8. Oscillator strengths of the lowest lines in the acceptor spectrum for x polarization as a function of the transition energy in GaAs-$Ga_{0.7}Al_{0.3}As$ quantum wells. Solid and dashed lines indicate the oscillator strengths of transitions from the $(\frac{3}{2},+)$ and $(\frac{1}{2},+)$ ground state, respectively. Thin dashed lines indicate the onset of the transitions between the ground states and the continuum of the first heavy-hole subband. The well width is (a) 200 Å, (b) 150 Å, (c) 100 Å, and (d) 50 Å.

tions is that the spectrum in x polarization is in general maintained for decreasing well widths whereas in the case of z polarization the intensity of the lines is suppressed for small well widths. We remark that this observation refers to the oscillator strengths of the lowest transitions, which are accurately given by our variational method and are presented in the figures. In the case of x polarization (Fig. 8), the $D_x^{h\to 5/2}$ is always the strongest line of the spectrum. As mentioned above, the line which corresponds to the bulk C line can only be reached starting from the light-hole ground state. Moreover, the oscillator strength of this line decreases for decreasing well widths. In the case of z polarization we expect that transitions from the heavy-hole ground state give rise to a strong doublet as long as the well is not too narrow. In the bulk limit these two peaks correspond to the C line. The case of 50-Å well width has not been reported in Fig. 9 because in this case all the transitions have a negligible oscillator strength on the scale of the figure.

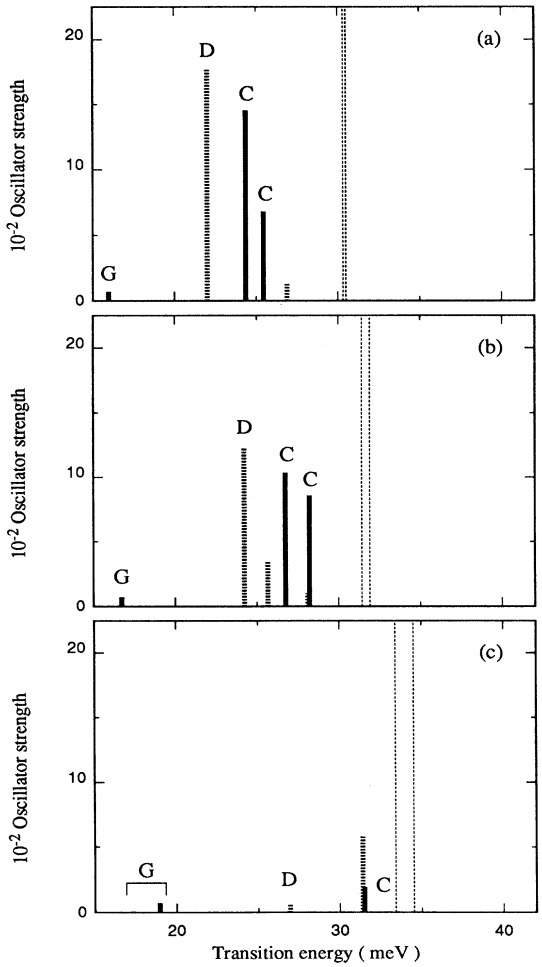

FIG. 9. Oscillator strengths of the lowest lines in the acceptor spectrum for z polarization as a function of the transition energy in GaAs-$Ga_{0.7}Al_{0.3}As$ quantum wells. Solid and dashed lines indicate the oscillator strengths of transitions from the $(\frac{3}{2},+)$ and $(\frac{1}{2},+)$ ground state, respectively. Thin dashed lines indicate the onset of the transitions between the ground states and the continuum of the first heavy-hole subband. The well width is (a) 200 Å, (b) 150 Å, and (c) 100 Å.

In order to compare our results with experimental spectra we have to consider the relative occupation of the heavy- and light-hole ground states. In fact the relative intensity of the transitions from the two ground states depends not only on their oscillator strengths but also on the relative population of the ground states, which is determined by the Boltzmann factor. The energy separation between the ground states as a function of the well width, can be obtained from the curves plotted in Fig. 1.

The only far-infrared absorption experiment on QW's has been performed by Reeder *et al.*.[7] In this experiment absorption spectra of x-polarized radiation have been obtained at a temperature $T = 4.2$ K in Be-doped QW's with well widths of 100, 150, and 200 Å. It is rather difficult to interpret the experimental results because the background is strong and quite different for each sample. We limit ourselves to the spectra of the 150- and 200-Å samples which show more evident peaks, and compare them with Figs. 8(a) and 8(b), respectively. As we have already mentioned in the previous section, we expect that, for Be impurities in this well width range, corrections not included in our pure Coulombian calculation do not modify the energies of the transitions and leave their relative intensities unchanged. Therefore we compare theoretical and experimental results without considering a global shift of the computed transition energies. The spectra at 200 and 150 Å present a major feature at ≈ 22 and ≈ 24 meV, respectively, which is considerably broadened on the low-energy side (particularly in the second spectrum). We identify this feature with the D line, which from Fig. 8 is expected to have the highest oscillator strength. Because of the lower QW symmetry, the bulk D line splits in three components. At 200 Å they are close together. We find the strongest component at 21.4 meV and the other two at 22.0 and 22.2 meV. At 150 Å the three components of the D line are more separated, the strongest being at 22.5 meV and the others at 24.2 and 24.7 meV. At higher energies than the D line a smaller feature is recognizable in both the 200- and 150-Å spectra, at ≈ 24 and ≈ 26 meV, respectively. We identify this line with the C line, which we predict at 24.2 and 26.3 meV, respectively. In the spectrum of the 200-Å sample, at lower energies than the D line, a small feature at ≈ 17 meV can be identified as the G line, which we predict at about 16 meV (there are three components rather close to each other). In the other sample, because of the noise of the background, we are not able to recognize an analogous feature in the same energy region.

In conclusion, the comparison with the experiment by Reeder *et al.*[7] is encouraging. However, because of its limited resolution it does not constitute a definitive test of the present theory and other experiments are called for. An analysis of the intensity of the observed lines versus temperature as well as of the separation of the lines in a magnetic field may be useful for identifying the peaks in the spectrum.

IV. CONCLUSIONS

We have calculated energies and oscillator strengths of transitions between ground and excited acceptor states and excited shallow acceptor states in GaAs-$Ga_{1-x}Al_xAs$ quantum wells. The acceptor states have been calculated variationally within a four-band effective mass theory which accounts for the mixing in the valence band and for the mismatch of the material parameters at the interfaces of the QW.[18] This theory is able to yield accurate wave functions for ground and excited acceptor states as well as excited acceptor states, which is an essential requisite for the calculation of oscillator strengths.

We have obtained oscillator strengths for x as well as for z polarization. The acceptor spectra for the two polarizations are identical in the bulk by symmetry. In the quantum well, the two polarizations are no longer equivalent and a considerable polarization dependence is found in the spectra. For both polarizations a general shift towards higher energies of all the transitions is found for decreasing well widths. This shift can mainly be attributed to the increase of the binding energies of the two ground states.

In the case of x polarization, the absorption spectrum is essentially similar to the bulk case. For narrow well widths some lines corresponding to transitions to excited states associated with the light-hole subbands decrease strongly. Another difference with respect to the bulk case is that the transitions from the light-hole ground state can only be observed if this state is sufficiently populated. The splitting between the two ground states can be used in order to estimate their relative population at a given temperature. For example, the intensity of the QW line which corresponds to the bulk C line is strongly reduced at low temperature.

The situation is different in the case of z polarization. In this case the intensities of the lines decrease for decreasing well widths. At 50 Å the lines are expected to be too weak to be observable. On the other hand, in the limit of large well widths (150–200 Å), there are two strong QW lines which correspond to the bulk C line. This doublet originates from transitions from the heavy-hole ground state and is therefore expected to be easily observable.

At present, only one experiment on infrared absorption in acceptor-doped quantum wells has been performed.[7] The absorption spectra have been obtained only in the case of x polarization. Comparison between theory and this experiment is encouraging but not completely satisfactory because of the low experimental resolution. As the present theory is able to reproduce with great accuracy the measured transition energies between $1s$ and $2s$ acceptor states,[3,4] we believe more experimental data are required in order to test our predictions also for transitions between ground and excited acceptor states and p-type excited acceptor states in quantum wells.

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APPENDIX: SUM RULE

For bulk systems described by Hamiltonians whose kinetic part is the Luttinger-Kohn Hamiltonian, a sum rule for the oscillator strengths holds.[31] The purpose of this appendix is to generalize this sum rule in order to cope with QW systems.

Using the double commutator of a spatial coordinate x^j with the Hamiltonian as in the derivation of the usual Thomas-Reiche-Kuhn sum rule, we derive

$$\frac{1}{3}\sum_j\sum_n \frac{2m_0(E_n-E_0)}{\hbar^2\gamma_1}\sum_{k'}\sum_s |\langle F^s_{nk'}|x^j|F^s_{0k}\rangle|^2 = 1, \tag{A1}$$

where the sum over k' is over the degenerate states of a same multiplet. The identity (A1) holds for the bulk system as well as for the QW.

A more useful sum rule may be obtained applying the following result of group theory which can easily be worked out:

$$\frac{1}{g_c}\sum_{i,l} |\langle \Gamma^i_a|\Gamma^j_b|\Gamma^l_c\rangle|^2 = \frac{1}{g_b}\sum_{i,j} |\langle \Gamma^i_a|\Gamma^j_b|\Gamma^l_c\rangle|^2, \tag{A2}$$

where, for example, Γ^i_a indicates that the envelope function (or the operator in the case of Γ_b) transforms as the ith row of the irreducible representation Γ_a of the symmetry group of the Hamiltonian, and g_a is the degeneracy of Γ_a. In the bulk, the symmetry group of the Hamiltonian is O_h and application of (A2) gives

$$\sum_n \frac{2m_0(E_n-E_0)}{\hbar^2\gamma_1}\frac{1}{g_0}\sum_{k,k'}\sum_s |\langle F^s_{nk'}|x^j|F^s_{0k}\rangle|^2 = 1, \tag{A3}$$

where $g_0 = 4$ is the degeneracy of the ground state. In the QW, because of the lower symmetry, the z direction is no longer equivalent to the in-plane directions x and y. Application of Eq. (A2) leads to the result stated in the text in Eq. (8).

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[34]In fact they have to be summed and divided by two. The factor $\frac{1}{2}$ accounts for the average of the oscillator strengths of transitions from heavy- and light-hole ground states.