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Far-infrared study of confinement effects on acceptors in GaAs/$Al_xGa_{1-x}As$ quantum wells

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Results of a far-infrared absorption study of beryllium acceptors in GaAs/$Al_xGa_{1-x}As$ quantum wells with widths between 300 and 100 Å, as well as a bulk sample of Be-doped GaAs for comparison, clearly show the effects of confinement on the acceptor. The observed increase in transition energy is in qualitative agreement with recent calculations. The intra-acceptor transition data will provide a useful basis for comparison with calculations of higher excited p-like states.

Shallow donors in GaAs/$Al_xGa_{1-x}As$ quantum wells have been studied extensively both theoretically[1] and experimentally[2] over the past few years. The behavior of the donors is understood sufficiently well that dopant redistribution on a length scale of 15 Å can be investigated.[3] Because of its more complex nature, the electronic states of an acceptor in a GaAs/$Al_xGa_{1-x}As$ quantum well are still not fully understood. The valence band of bulk GaAs is fourfold degenerate and contains a cubic term which must be taken into account to describe the acceptor states. Initial calculations of acceptor states in a GaAs/$Al_xGa_{1-x}As$ quantum well have been made by Masselink, Chang, and Morkoc,[4] and Raman[5] studies of transitions between s-like states are in reasonable agreement with calculations. To the present date, however, there are no reported calculations of the p-like acceptor states in quantum wells. In far-infrared transmission experiments, the dominant features are due to transitions between the s-like ground states and higher p-like states.

In this paper we report the first far-infrared transmission study of the Be acceptor in GaAs/$Al_xGa_{1-x}As$ ($x=0.3$) quantum wells with widths between 300 and 100 Å. A thick Be-doped GaAs epitaxial layer was also studied as a limiting case and to provide a basis for understanding the quantum-well results.

Because of the more complicated nature of the valence band of GaAs the acceptor states are complex, and it is helpful to consider these states in the bulk prior to introducing the confining quantum-well potential. The topmost valence-band states of GaAs near the Γ point (Brillouin zone center) consist of three p-like ($l=1$) states that are triply degenerate (sixfold with spin) in the absence of spin-orbit interaction. Including spin these states may be characterized by their total angular momentum quantum number J and its projection along an axis, M_j as $J=\frac{3}{2}$ ($M_j=\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$) and $J=\frac{1}{2}$ ($M_j=\frac{1}{2}, -\frac{1}{2}$). With spin-orbit coupling included the $J=\frac{3}{2}$ and $J=\frac{1}{2}$ bands are split by $\Delta=340$ meV, with the fourfold degenerate (at $k=0$) $J=\frac{3}{2}$ bands lying highest in energy. The $J=\frac{3}{2}$ bands are split into two Kramers degenerate bands, $M_j=\pm\frac{3}{2}$ and $M_j=\pm\frac{1}{2}$, usually referred to as the "heavy-hole" and "light-hole" bands. An acceptor in bulk GaAs in lowest order can be thought of as a spin-$\frac{3}{2}$ particle in Coulomb potential, essentially a one-particle spin-$\frac{3}{2}$ atom. The total angular momentum F of the "atom" is obtained by adding the total spin of the hole ($\frac{3}{2}$) and the orbital angular momentum of the hydrogenic envelope L; thus F takes the integer-spaced values between $L+\frac{3}{2}$ and $|L-\frac{3}{2}|$. The valence band, however, has cubic symmetry which leads to splittings of the acceptor states of a spherically symmetric potential. Acceptor states must therefore be given an irreducible representation of the valence-band point group to identify them uniquely. The lowest acceptor states are identified as $1s_{3/2}\Gamma_8$, $2p_{3/2}\Gamma_8$, $2s_{3/2}\Gamma_8$, $2p_{5/2}\Gamma_8$, $2p_{5/2}\Gamma_7$, and $2p_{1/2}\Gamma_6$. Notice that the $F=\frac{5}{2}$ states are split as a result of the lower cubic symmetry of the valence band.

For the limit of large spin-orbit interaction the energy of the acceptor levels can be obtained from the following Hamiltonian which takes into account the highest ($J=\frac{3}{2}$) valence bands:[6]

$$H=\frac{1}{2m_0}(\gamma_1+\tfrac{5}{2}\gamma_2)\hat{P}^2-\frac{\gamma_2}{m_0}(\hat{P}_x^2\hat{J}_x^2+\hat{P}_y^2\hat{J}_y^2+\hat{P}_z^2\hat{J}_z^2)$$
$$-\frac{2\gamma_3}{m_0}(\{\hat{P}_x\hat{P}_y\}\{\hat{J}_x\hat{J}_y\}+\{\hat{P}_y\hat{P}_z\}\{\hat{J}_y\hat{J}_z\}$$
$$+\{\hat{P}_z\hat{P}_x\}\{\hat{J}_z\hat{J}_x\})-\frac{e^2}{\epsilon_0 r}, \quad (1)$$

where γ_1, γ_2, and γ_3 are the Luttinger parameters of the valence band $\{AB\}=(AB+BA)/2$, m_0 is the free-electron mass, $\hat{P}$ is the linear momentum operator, and $\hat{J}$ is the angular momentum operator. Solutions to the Schrödinger equation with this Hamiltonian have been obtained under different approximations.[7,8] Selection rules for optical transitions can be obtained from the "zeroth-order" wave function method of Lin-Chung and Wallis,[9] in which the acceptor envelope wave function is used to evaluate the matrix elements. Kirkman, Stradling, and Lin-Chung[10] used this method to determine the allowed optical transitions and the absorption coefficients for acceptors in GaAs. For the transitions relevant to this discussion ($1s_{3/2}\Gamma_8$ to $2p_{5/2}\Gamma_8$ and $2p_{5/2}\Gamma_7$) the strongest absorption

lines in the Faraday geometry arise from $\Delta m = \pm 1$ and weaker transitions from $\Delta m = \pm 3$. These authors also reported calculations of the g values for the ground state and the p-like excited states which agree within 20% with their far-infrared studies.

The only reported calculation of acceptor states in $GaAs/Al_xGa_{1-x}As$ quantum wells are those of Masselink *et al.*[4] These workers used the Hamiltonian of Eq. (1) with the addition of a confining potential $V(z)$,

$$V = \begin{cases} 0, & |z| < \frac{W}{2}, \\ V_0, & |z| > \frac{W}{2}, \end{cases}$$

where V_0 represents the valence-band discontinuity, and W is the well width.

The presence of the quantum-well potential reduces the symmetry of the valence band to D_{2d}. In this reduced symmetry the $J = \frac{3}{2}$-like valence-band states are split into "heavy" ($M_j = \pm \frac{3}{2}$) and "light" ($M_j = \pm \frac{1}{2}$) hole bands. Additionally, the $1s_{3/2}\Gamma_8$ acceptor ground state and the $2p_{5/2}\Gamma_8$ excited state must be split accordingly into $1s_{3/2}(\Gamma_6+\Gamma_7)$ and $2p_{5/2}(\Gamma_6+\Gamma_7)$, respectively. In Fig. 1 the expected splittings of the acceptor states for an acceptor at the center of a $GaAs/Al_xGa_{1-x}As$ quantum well are shown schematically. Masselink *et al.*[4] solves Eq. (1) variationally in the presence of the confining potential $V(z)$, with and without the Coulomb potential. When the Coulomb term is omitted, the resulting energy is the appropriate confinement subband energy. The acceptor binding energy was obtained by subtracting the subband energy from the solution of Eq. (1) with the Coulomb term included. This calculation was performed separately for the Γ_6- and Γ_7-like acceptor states. The boundary conditions were dealt with by considering the fraction of the acceptor wave function in the quantum well when Eq. (1) is solved with GaAs and then with AlGaAs valence-band parameters. A linear combination of the two energies was then taken. Only the results of the subband energies and the acceptor states $1s_{3/2}\Gamma_8$ and $2s_{3/2}\Gamma_8$ in quantum wells were reported. Their calculations show that as the quantum-well width decreases from infinity (bulk) to 100 Å the acceptor ground state splits by about 2.5 meV, and the binding energy increases by about 4 meV. As with a donor in a quantum well an increase in the binding energy of the acceptor states with decreasing well width is found. Since the acceptor ground-state wave function in the bulk is much less extended than the donor ground-state wave function, the percentage effect over this range of well width is much smaller for acceptors. Confinement effects on the excited states are much greater due to their more extended wave functions.

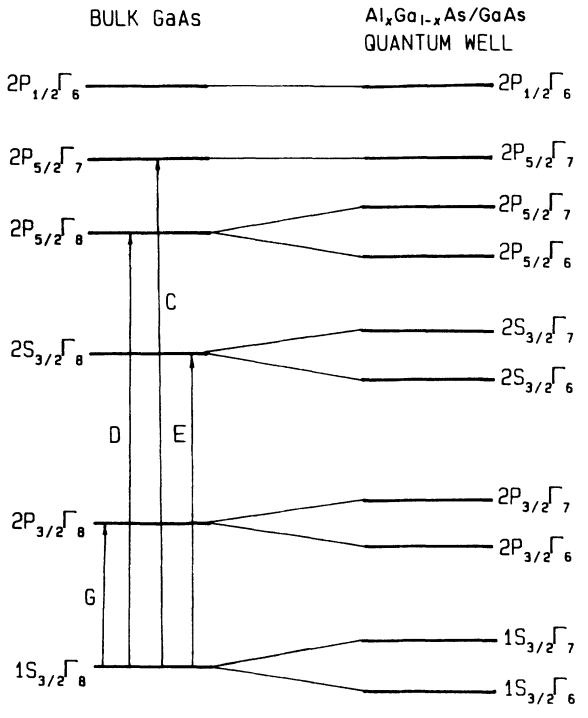

FIG. 1. Left, a schematic energy-level diagram of an acceptor in bulk GaAs, T_d. Right, the expected splittings of an acceptor under D_{2d} symmetry of a quantum well.

Far-infrared 80–250 cm^{-1} absorption measurements were made with a Specac 40.000 or Bomem DA3.02 Fourier-transform spectrometer. Conventional light-pipe optics were used to couple the interferometer to a 9.0-T superconducting magnet and Ge:Ga photoconductive detector-operated samples were mounted in He-exchange gas in the Faraday geometry in a two-position rotatable sample holder. An acceptor-doped sample and a section of semi-insulating GaAs, which was used to provide reference spectra, were mounted in this holder. Transmittance spectra were obtained by ratioing sample spectra to reference spectra taken under the same conditions during the same run. All samples were molecular-beam-epitaxy-(MBE-) grown on semi-insulating GaAs substrates. Table I shows the characteristics of the samples studied. The GaAs quantum wells were doped over the center $\frac{1}{3}$ of each well; the $Al_{0.3}Ga_{0.7}As$ barriers were 150 Å in thickness and were nominally undoped.

The transmission spectrum of 3 μm of Be-doped (3×10^{16} cm^{-3}) GaAs at zero field and 4.2 K is shown in Fig. 2(a). Several transmission minima are evident at 135, 167, 184, and 220 cm^{-1}. These features are labeled G, D, C, and A, respectively, consistent with the literature. When a magnetic field was applied, the D line moved to higher energies, and the C feature also moved up slightly

TABLE I. Characteristics of the samples studied.

Well width	Number of wells	Dopant density	Dopant position
Bulk	. . .	3×10^{16}	Uniform
300	33	3×10^{17}	Center $\frac{1}{3}$
200	50	3×10^{17}	Center $\frac{1}{3}$
150	50	3×10^{17}	Center $\frac{1}{3}$
100	100	3×10^{17}	Center $\frac{1}{3}$

in energy. Heating the sample to 20 K caused new lines to appear at frequencies below the D feature. At lower magnetic fields a similar temperature dependence was observed but with proportionally smaller splittings. In Figs. 2(a)–2(e) the zero-field transmission spectra of the bulk, 300, 200, 150, and 100 Å samples are shown. A series of absorption lines which move systematically to higher energies as the well width decreases is evident. The dominant feature displays the same magnetic field dependence as the bulk D line.

The relative separation of the features G, D, C, and A is consistent with the photoconductive peaks observed by Kirkman *et al.*[10] These lines arise from transitions between the $1s_{3/2}\Gamma_8$ ground state and $2p_{3/2}\Gamma_8$, $2p_{5/2}\Gamma_8$, $2p_{5/2}\Gamma_7$, and $2p_{3/2}\Gamma_6$ states, respectively. Since the energy of the acceptor ground state has a much larger chemical shift than the p-like states, the absolute position of these features depends on the chemical identity of the impurity while their relative separation is independent of impurity species.

The appearance of lower-energy features associated with the D line at 20 K at 9.0 T is due to splitting of the ground state $1s_{3/2}\Gamma_8$ in the magnetic field. When K_BT is comparable to the field splitting, the "higher" ground states are populated and the absorption intensity for transitions originating in these states becomes appreciable. With the g values given in Ref. 10, we cannot explain the temperature dependence of the absorption found in the present work. We therefore suggest that the calculated g values are in error, most likely for the higher p-like state. Errors in g values have been noted before[11,12] and are generally due to the sensitivity of the g value on the wave function used.

The dominant absorption feature labeled D' in Fig. 2(b) displays a magnetic field dependence, approximately 1 cm^{-1}/T, similar to the highest component of the D line of the bulk acceptor. The relatively high dopant density 3×10^{17} cm^{-3} used in the quantum wells would lead to very broad C and D features in bulk GaAs. Although the C and D features are much sharper in the quantum well than would be expected for a bulk sample with the same dopant density, they are still quite broad, and it is difficult to identify any fine structure as was the case with the present bulk sample. As the quantum well width decreases from 300 to 100 Å the C and D features move to higher energies (see Fig. 3). This is due to the quantum well "pushing" the hole closer to the negative core thereby increasing its binding energy. Thus the energy of all the states will increase at a rate that depends on the Bohr radius of the state and the orientation of the lobes of its wave function relative to the confinement axis. Clearly the transition energy will move to higher energy as the well width decreases. This behavior is similar to the donor system for which extensive calculations are in good agreement with experiment.[2] The calculations in Ref. 4 are for the s-like ground and excited states from which only the E transition can be calculated. This transition is parity forbidden for the infrared experiments. However, confinement effects are expected to be of similar magnitude for the D-like transition due to the similar Bohr radii of the $2s_{3/2}\Gamma_8$ and $2p_{5/2}\Gamma_8$ states.[7]

As the quantum well width is decreased the heavy-hole–light-hole splitting of the acceptor ground state increases, with the heavy hole having the highest energy (see Fig. 1). In a quantum well transitions from the heavy-hole states should therefore be stronger than those from light-hole states. The strongest absorption in the D manifold in bulk GaAs arises from the $M_j = \pm\frac{3}{2}$ heavy-hole-like acceptor states,[10] and the observed decrease in absorption intensity with decreasing well width is attributed to depopulation of the light-hole-like states.

The absorption spectra of Be acceptors in $GaAs/Al_xGa_{1-x}As$ quantum wells have been measured, and clear effects of the confinement have been observed in the form of an increase in the transition energy with decreasing well width. This behavior is similar to that observed for shallow donors.[1,2] The energy increase of the transition energy of the dominant absorption line (D line) is of the same magnitude as predicted for the E transition. For

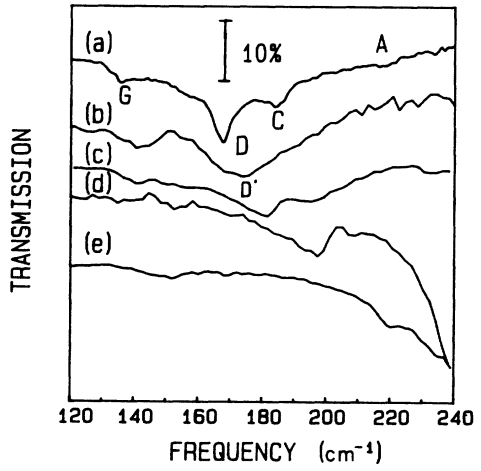

FIG. 2. Zero-field transmission spectra taken at 4.2 K of (a) Be-doped GaAs 3 μm thick and Be-doped $GaAs/Al_xGa_{1-x}As$ quantum wells are center $\frac{1}{3}$ at 3×10^{17} with widths (b) 300 Å, (c) 200 Å, (d) 150 Å and (e) 100 Å.

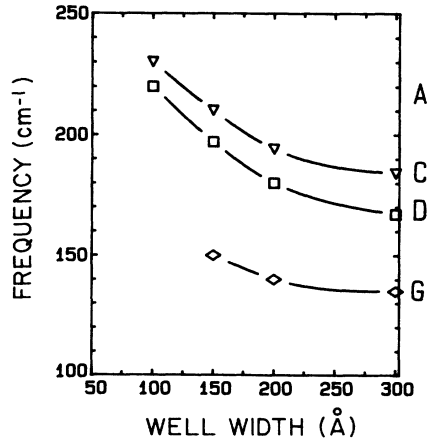

FIG. 3. Position of the zero-field C, D, G features as a function of well width.

more quantitative comparison with the present data calculations of the *p*-like excited states are required. Although the bulk acceptor *g* values previously determined appear to be of the correct order of magnitude, in a magnetic field the observed temperature dependence of the split *D* lines is inconsistent with the ordering of the levels predicted. It is suggested that this discrepancy is due to slight inaccuracies in the trial wave functions.

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