Excitonic Coupling in GaAs/GaAlAs Quantum Wells in an Electric Field

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We have observed coupling between excited and ground states of excitons in GaAs quantum wells under an electric field. Low-temperature photoluminescence excitation spectra show peaks corresponding to excited states of the heavy-hole exciton and to the ground state of the light-hole exciton. With increasing field, the peaks converge and then they show anticrossing and share their oscillator strengths. As a result of this interaction, fine structure attributed to the $2p$ state of the heavy-hole exciton is resolved.

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The optical spectra of GaAs/Ga$_{1-x}$Al$_x$As quantum wells are dominated by sharp excitonic structure.[1,2] Improvement in the quality of the samples allows routine observation of excitonic transitions between the different subbands in the conduction and valence bands of the GaAs wells. Parity-allowed as well as parity-forbidden excitonic transitions are easily observed in absorption[3] and absorption-related measurements,[4] but the excited states of excitons are much more elusive. Their presence in optical spectra of GaAs/Ga$_{1-x}$Al$_x$As quantum wells was first reported by Miller *et al.*,[2] yielding a measurement of the heavy- and light-hole excitonic term value $B_{1s}-B_{2s}$ [$B_{1s(2s)}$ represents the two-dimensional exciton $1s$-ground-state ($2s$-excited-state) binding energy]. More recently, Dawson *et al.*[5] have observed well-resolved excited-state peaks in photoluminescence excitation (PLE) spectra, as well as structure on the high-energy side of the heavy-hole line in photoluminescence (PL) spectra.[6] Polarization measurements and comparison with PLE spectra led them to assign this new structure to the $2s$ excited state of the heavy-hole exciton, whose binding energy was in reasonable agreement with variational calculations.[2,5,7-10]

In this Letter we report the observation of coupling between excited states of the heavy-hole (h_1) and the ground state of the light-hole (l_1) excitons in the PLE spectra of GaAs/Ga$_{1-x}$Al$_x$As quantum wells. As a result of the coupling, the hydrogenic $2s$ and $2p$ states of h_1 are resolved for the first time. The energy separation between the excited states of h_1 (hereafter called $h_1^{(2x)}$, where x stands for both the s and p state) and l_1 was tuned by application of an external electric field perpendicular to the layers. Because of the larger heavy-hole effective mass, the heavy-hole excitons are predicted to show a stronger Stark shift than the light-hole excitons,[11,12] as has been confirmed experimentally.[4,13] When the thickness of the quantum wells is such that $h_1^{(2x)}$ lies at a slightly higher energy than l_1, the peaks converge with increasing electric field, and eventually, when they become sufficiently close, repel each other, leading to an anticrossing. Coupling between ground and excited excitonic states in bulk GaAs was reported before,[14] achieved by application of an external uniaxial stress. In contrast, we realized the interaction in a quantum well by a moderate electric field without significantly altering the bond structure. Until now, this field effect had been limited to atomic physics, where Stark maps of Rydberg atoms show strong repulsions between closely lying levels.[15] Our observation of separate $2s$ and $2p$ states, similar to the fine structure of the hydrogen atom, should stimulate theoretical effort for a better understanding of the excitonic spectra in solid-state systems.

The sample used in our experiments was a p-i-n heterostructure grown by molecular beam epitaxy. A n^+-GaAs buffer layer, followed by 800-Å Ga$_{0.65}$Al$_{0.35}$As, was deposited on a Si-doped GaAs (100) substrate. A series of five GaAs quantum wells (160 Å), with 250-Å-thick Ga$_{0.65}$Al$_{0.35}$As barriers, were capped by 800-Å Ga$_{0.65}$Al$_{0.35}$As and 1.5-μm p^+-GaAs. The region between the n^+- and p^+-GaAs was nominally undoped, except the first 400 Å of the Ga$_{0.65}$Al$_{0.35}$As adjacent to the buffer layer, which were slightly Si doped. The electric field, perpendicular to the layers, was applied by biasing of the structure between the p^+- and n^+-GaAs regions. The magnitude of the electric field, estimated from growth parameters and from the bias corresponding to flat-band condition ($\sim$1.7–1.75 V), is believed to be accurate to about 10%. Excitation spectra were recorded at 4.8 K with a resolution of 0.2 meV. An LD700 dye, pumped by a Kr$^+$-ion laser, was used to excite the sample with power densities below 0.5 W/cm^2.

Figure 1 shows a low-field PLE spectrum covering the spectral region from the ground to the excited states of the light-hole exciton. Also depicted is the heavy-hole PL, which shows a rising background from the p^+-GaAs PL on its low-energy side, and does not have any observable Stokes shift relative to the PLE. The low electric field has already shifted all the structures by $\sim$0.1 meV with respect to the flat-band condition. The peak labeled h_{12a} is associated with the $n=2$ heavy-hole and $N=1$ conduction subbands.[16] We assign the shaded structures to the excited states of the heavy-hole and light-hole ex-

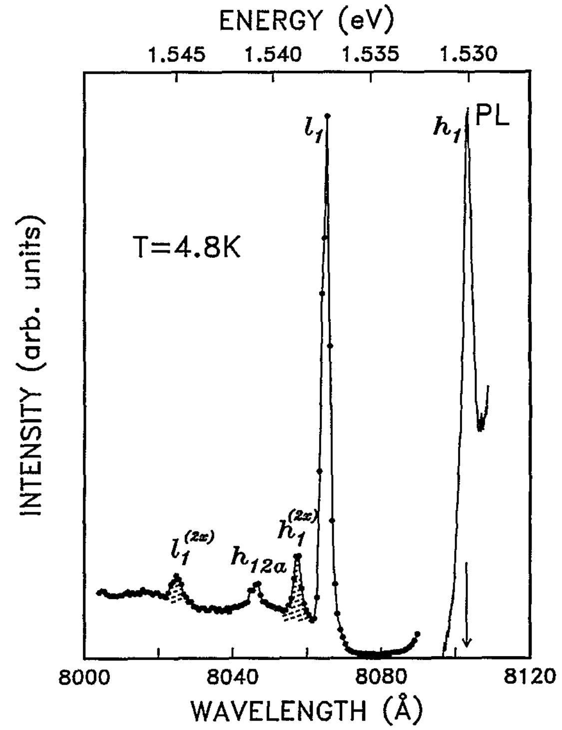

FIG. 1. Low-temperature excitation spectrum of a 160-Å quantum well at 7.1 kV/cm. h_1 and l_1 denote the ground states of the heavy and light excitons, respectively. The shaded structures, $h_1^{(2x)}$, and $l_1^{(2x)}$, correspond to excited states of the heavy- and light-hole excitons, respectively. h_{12a} is an exciton related to the $n=1$ conduction and $n=2$ heavy-hole valence band. Also shown is the photoluminescence (PL) spectrum of the heavy-hole exciton. The arrow indicates the setting of the spectrometer for the excitation spectrum.

citons, $h_1^{(2x)}$ and $l_1^{(2x)}$, respectively. The assignment is based on a comparison with previous data,[2,5] and on the agreement between the excitonic term values $B_{1s}^{[h(l)]} - B_{2s}^{[h(l)]}$ with calculated ones.[2,5,7,9] (For the thickness of our sample, the theories also predict a small splitting, 0.4 meV, between the 2s and the 2p states.[7,9]) Experimentally we obtain term values of 8.2 ± 0.2 meV and 8.0 ± 0.2 meV for the heavy- and light-hole excitons, respectively. Extrapolation of the data from Ref. 6 to 160 Å yields a value for the heavy-hole exciton between 7 and 8 meV, while theoretical calculations obtain lower limits of ~6.5 and ~7.5 meV for the heavy- and light-hole excitons,[2,9] respectively. The ratios of the oscillator strengths of the excited to the ground states of the heavy- and light-hole excitons have an experimental value of 0.07, in reasonable agreement with the theoretical value of 0.11.[7,10]

The peaks in the spectrum of Fig. 1 are extremely sharp, with a full width at half maximum (FWHM) of 0.5 meV, which is comparable to the 0.4-meV thermal broadening. This indicates the exceptional quality of the sample, which enabled us to resolve all the structures in the spectrum as clearly defined peaks. In other samples, with well thicknesses ranging from 100 to 250 Å, which also showed relatively sharp h_1 and l_1 peaks (FWHM =1.2 meV), the excited states of heavy and light excitons could only be seen as shoulders similar to those reported previously.[2]

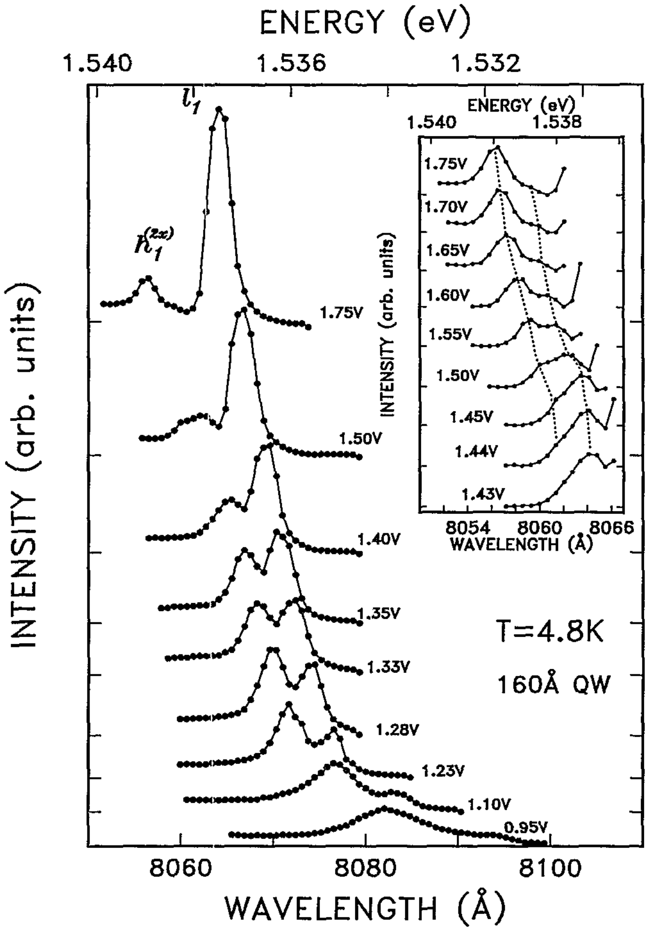

FIG. 2. Excitation spectra for several biases, ranging from flat band (1.75 V) to 22.8 kV/cm (0.95 V), in the spectral range of the ground light-hole exciton (l_1) and the excited states of the heavy-hole exciton ($h_1^{(2x)}$). Inset: Spectra corresponding to the excited states for different voltages where fine structure is resolved. The dashed lines are a visual aid to help in following the structures.

In the following we will focus on the spectral range covering the l_1 and $h_1^{(2x)}$ excitons. PLE spectra for different bias are shown in Fig. 2. At flat band (1.75 V) $h_1^{(2x)}$ lies 1.5 meV higher than l_1, and the ratio of their oscillator strengths is ~0.25. As the electric field is increased, i.e., the voltage decreased, $h_1^{(2x)}$ moves closer to l_1 and the intensities of the two structures become comparable (see, for example, the spectrum at 1.33 V, which corresponds to ~12 kV/cm). This fact demonstrates the coupling between the two excitons, as they increasingly share their oscillator strengths when they become energetically closer. For even higher electric fields the excitons separate; $h_1^{(2x)}$ moves to the low-energy side of l_1

(reversing the original order) and its strength decreases steadily. Eventually, the structure becomes a shoulder, partially because of electric-field–induced broadening.

In the intermediate-field range a repulsion between $h_1^{(2x)}$ and l_1 becomes noticeable, as seen more clearly in Fig. 3, where their energies are plotted as a function of the electric field. The dashed and dotted lines depict calculations, described elsewhere,[17] of the Stark shifts of uncoupled heavy- and light-hole excitons, respectively. A 60%-40% distribution was chosen for the conduction–valence-band discontinuity and standard effective-mass values were used.[17] The theoretical results for the ground state of the heavy-hole exciton have been shifted to higher energies by the excitonic term value, $B_{1s}^h - B_{2s}^h$, to match the experimental value of $h_1^{(2x)}$ at flat band. In doing this, small changes of the binding energies of the excitons with increasing electric field[12] have been neglected. As seen in Fig. 3, the agreement between theory and experiment is very good, except in the region around 15 kV/cm, where the coupling, which is not included in the theory, occurs.

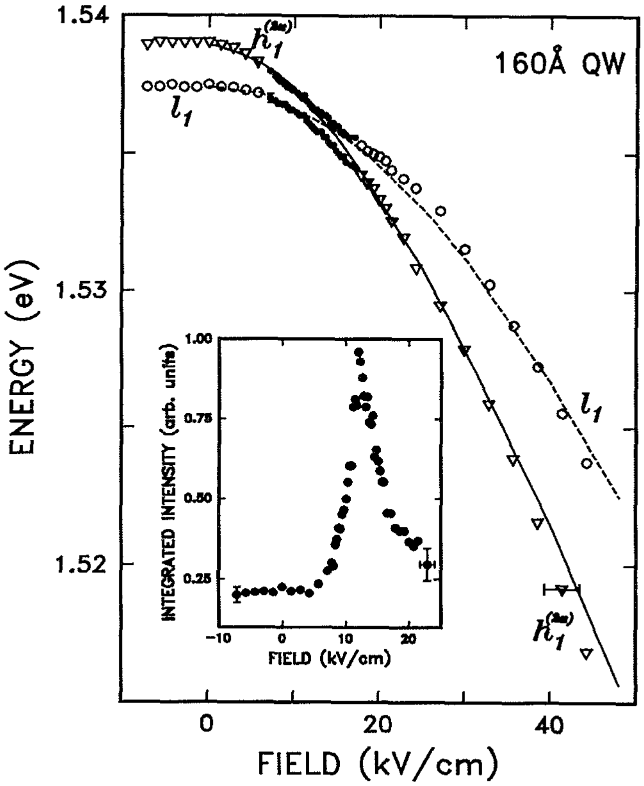

FIG. 3. Energy thresholds of the ground state of the light-hole exciton (l_1, open circles) and excited states of the heavy-hole exciton ($h_1^{(2x)}$, triangles) as functions of electric field strength. The data are shown as solid circles in the region of strong coupling. The lines correspond to calculations of Stark shifts with use of the effective-mass approximation and neglect of changes in binding energies and coupling among excitons. Inset: The integrated intensity of the $h_1^{(2x)}$ structure normalized to that of l_1 as a function of electric field. Error bars show the uncertainties in field and intensities.

For fields larger than ~20 kV/cm the two peaks diverge, an inversion in their energetic position has taken place, and they again follow the theoretical results. The inset in Fig. 3 shows the integrated intensity of $h_1^{(2x)}$ normalized to that of l_1 as a function of the electric field. A clear increase is observed up to ~12 kV/cm as a result of the interaction with the light-hole exciton. At this field, which is close to the predicted crossing under neglect of interaction between the excitons, the coupling reaches its maximum. The subsequent decrease in the normalized intensity shows a strong correlation with the increasing energy separation between the excitonic structures. The minimum separation between l_1 and $h_1^{(2x)}$ amounts to 0.7 ± 0.2 meV. This value is larger than 0.3 meV, which was found in uniaxial stress experiments in bulk GaAs and attributed to exchange interaction between the ground state of the light-hole and excited states of the heavy-hole excitons.[14] If the effect of the external electric field can be viewed mainly as a change of the subband energies, which is not unreasonable considering the small effect of the field on exciton binding energies,[12] our data indicate an enhancement of the interaction, by a factor of 2, in quantum wells relative to the bulk.

In the discussion given above we have labeled the excited states of the heavy-hole exciton as $h_1^{(2x)}$. Actually, a closer examination of this peak reveals additional fine structure. The inset in Fig. 2 shows spectra of $h_1^{(2x)}$ from flat band up to ~9.1 kV/cm (1.43 V). With increasing field a shoulder appears on the low-energy side of the structure. This shoulder becomes comparable in amplitude to the original peak at 1.55 V and is the dominant feature at higher fields. The energy separation between these two structures amounts to ~0.45 meV, and it is field independent. Because of the close agreement of this value with the predicted difference (0.4 meV) between the 2s and 2p states of excitons in a 160-Å quantum well,[7,9] we tentatively assign the high- (low-) energy counterpart of the doublet to the 2s (2p) excited state of the h_1 exciton [$h_1^{(2s)}$ ($h_1^{(2p)}$)].

In a quantum well, the confinement reduces the symmetry of the GaAs layers from the T_d to the D_{2d} group, lifting the degeneracy of the $h_1^{(2s)}$ and $h_1^{(2p)}$ excitons. Their relative oscillator strengths cannot be predicted from symmetry arguments, and calculations of the strengths are not available. On the basis of our assignment, the data at flat band indicate that the strength of $h_1^{(2p)}$ is ~0.25 of that of the 2s exciton. Group-theory considerations show that both excited states, $h_1^{(2s)}$ and $h_1^{(2p)}$, can couple with the ground state of the l_1 exciton. The data indicate that, as a result of the increasing electric field and the increasing coupling with l_1, $h_1^{(2p)}$ grows in strength and finally overwhelms $h_1^{(2s)}$. This enhancement may be due to a smaller $h_1^{(2p)}$-l_1 separation relative to $h_1^{(2s)}$-l_1, but a difference in the strengths of the couplings cannot be ruled out. Observations of forbidden transitions (e.g., h_{12}) in the presence of an electric field have been reported in the literature,[4,18] and the effects of band mixing on the optical properties of quantum wells have been studied theoretically.[19] The present situation is different from that of h_{12}, since the enhancement of $h_1^{(2x)}$ is due to excitonic coupling instead of breaking of the inversion symmetry in the well. The theoretical treatment is also more complicated in our case, because it involves the whole excitonic problem including excited states and coupling among them, as well as with the ground state of a different exciton (l_1). A comparison of our data with calculations that include coupling should help to clarify the mechanism and the strength of the interaction.

In conclusion, we have observed coupling between excited states of the heavy-hole and the ground state of the light-hole excitons in GaAs/$\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ quantum wells in the presence of an external electric field. An anticrossing behavior as well as a sharing of oscillator strength for fields of the order of 10 kV/cm has been shown. Fine structure in the excited states of the heavy-hole exciton has been resolved, and the two components of the structure are assigned to the 2*s* and 2*p* states of the h_1 exciton. The results reported here demonstrate that optical spectroscopy in solid-state quantum systems can approach systems can approach the level of resolution found in atomic physics.

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[1] R. Dingle, in *Festkörperprobleme,* edited by H. J. Queisser, Advances in Solid State Physics Vol. 15 (Pergamon/Vieweg, Braunschweig, 1975), p. 21.

[2] R. C. Miller, D. A. Kleinman, W. T. Tsang, and A. C. Gossard, Phys. Rev. B **24**, 1134 (1981).

[3] See, for example, R. C. Miller and D. A. Kleinman, J. Lumin. **30**, 520 (1985), and references therein.

[4] R. T. Collins, K. von Klitzing, and K. Ploog, Phys. Rev. B **33**, 4378 (1986).

[5] P. Dawson, K. J. Moore, G. Duggan, H. I. Ralph, and C. T. B. Foxon, Phys. Rev. B **34**, 6007 (1986).

[6] K. J. Moore, P. Dawson, and C. T. Foxon, Phys. Rev. B **34**, 6022 (1986).

[7] Y. Shinozuka and M. Matsuura, Phys. Rev. B **28**, 4878 (1983).

[8] M. Matsuura and Y. Shinozuka, J. Phys. Soc. Jpn. **53**, 3138 (1984).

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

[10] K. S. Chan, J. Phys. C **19**, L125 (1986).

[11] G. Bastard, E. E. Mendez, L. L. Chang, and L. Esaki, Phys. Rev. B **28**, 3241 (1983).

[12] D. A. B. Miller, D. S. Chemla, T. C. Damen, A. C. Gossard, W. Wiegmann, T. H. Wood, and C. A. Burrus, Phys. Rev. B **32**, 1043 (1985).

[13] L. Viña, R. T. Collins, E. E. Mendez, and W. I. Wang, Phys. Rev. B **33**, 5939 (1986).

[14] C. Jagannath and E. S. Koteles, Solid State Commun. **58**, 417 (1986).

[15] See, for example, D. Kleppner, M. G. Littman, and M. L. Zimmerman, in *Rydberg States of Atoms and Molecules,* edited by R. F. Stebbings and F. B. Dunning (Cambridge Univ. Press, Cambridge, England, 1983), Chap. 3.

[16] R. T. Collins, L. Viña, W. I. Wang, L. L. Chang, L. Esaki, K. v. Klitzing, and K. Ploog, in Proceedings of the Eighteenth International Conference on the Physics of Semiconductors, Stockholm, Sweden, 1986 (to be published).

[17] L. Viña, E. E. Mendez, W. I. Wang, L. L. Chang, and L. Esaki, J. Phys. C (to be published).

[18] D. A. B. Miller, J. S. Weiner, and D. S. Chemla, IEEE J. Quantum Electron **22**, 1816 (1986).

[19] See, for example, Y. C. Chang, and J. N. Schulman, Phys. Rev. B **31**, 2069 (1985).