

Definitive Identification of D^- Centers in GaAs Quantum Wells by Tilt-Induced Line Splitting in a Magnetic Field

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D^- centers have been unambiguously identified in GaAs/(Ga,Al)As quantum wells by analysis of the dependence of the observed photoconductivity spectrum on the applied magnetic field and sample orientation. Theoretical investigations show that in magnetic fields of interest the D^- transitions do not involve photoionization of the centers as has been previously supposed but proceed from the ground state to discrete p_{-1} - or p_{+1} -like D^- levels, which lie above the $N=0$ and $N=1$ Landau-level energies, respectively. Tilting the sample leads to a predicted anticrossing of discrete p_0 - and p_{+1} -like D^- levels. Excellent agreement with experiment is obtained without any adjustable parameters.

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D^- centers, two-electron ions formed by attaching a second electron to a shallow hydrogenic donor (D^0), have proven more difficult to detect than the shallow donor centers themselves. Isolated D^- centers were found in bulk GaAs only in those rare n -type epitaxial samples which were simultaneously of high purity and very low compensation [1]. Identification of this center in GaAs was first achieved by comparing theoretical predictions of its photoionization energy [2] with measured values as a function of magnetic field.

Although shallow donors have been clearly identified in center-doped GaAs/(Ga,Al)As quantum wells by far-infrared (FIR) magnetospectroscopy [3], the D^- center has proven more elusive. It is to be expected that donor-doped GaAs quantum wells enclosed by n -type GaAlAs barriers should be rich in electrons—a condition favoring D^- formation. So far, however, no definitive evidence for such centers has been adduced. This, it appears, is due partly to a fundamentally incorrect understanding of the nature of the final states reached in D^- optical transitions, partly to a lack of relevant theoretical calculations, and partly to the fact that the D^- transition energies in a limited range of magnetic field can coincide, more or less, with those of donors located at a selected position in the well between the center and the barrier edge. It is necessary to rule out the possibility that an observed line belongs to a donor before it can be assigned with certainty to the D^- center.

There are certain important similarities between D^0 and D^- centers in quantum wells. If, for example, a magnetic field is applied along the z direction, which is defined as the direction perpendicular to the semiconductor planes, then M , the component of orbital angular momentum along z (in units of \hbar), is a good quantum number for both types of center. The free-electron levels in a quantum well in that case are discrete but have infinite degeneracy (states with the same Landau and subband quantum numbers but with different M values

are degenerate). The Coulomb potential of the donor ion breaks this degeneracy leading, in the case of infinitely high barriers, to a nondegenerate set of completely discrete quantized donor levels [4]. A similar effect occurs for the D^- center; the Coulomb potential of its D^0 core acts to break the free-electron degeneracy in M leading to a set of discrete nondegenerate quantized D^- levels. This can be most convincingly shown in the case of the two-dimensional D^- center in the limit of infinite perpendicular magnetic field, where exact solutions for all of the states can be found [5]. In that case only two possible final states can be reached from the singlet ground state in dipole transitions induced by light propagating along the field. Those are the lowest-lying singlet $M = -1$ and $+1$ levels. (Interestingly, when Zeeman spin energy is neglected, it turns out that the transition energy from the ground state to the lowest $M = -1$ state is considerably *higher* than the ionization energy of the center.)

Various workers have searched for D^- centers by doping both the barriers and quantum wells with shallow donors. Glaser *et al.* [6] and Mercy *et al.* [7] found that adding donors to the GaAlAs barriers introduced two additional lines into the magneto-optical spectrum of GaAs quantum wells of ~ 200 Å width. They concluded that neither of these lines originated from D^- transitions. More recently a similar experiment on 100-Å GaAs wells was reported by Huant, Najda, and Etienne [8] who, however, attributed two of their additional lines to D^- ions. Although those latter authors did not support this identification with calculations, they did point out that the new lines appeared in pairs separated by the GaAs conduction-band cyclotron energy $\hbar\omega_c$. Such pairs are indeed expected for D^- centers. Unfortunately they are, with one exception [9], also expected for *any electronic dipole* transition that starts from an $M=0$ level and is induced by light propagating along the magnetic field, provided that the band is parabolic and that there is cylindri-

cal symmetry about the direction of the magnetic field.

A theoretical paper by Pang and Louie [10] investigating the dependence of the D^- transition energy on magnetic field in a GaAs well 100 Å in width, and based on the assumption that the final state is a Landau level, gave energies which were systematically and significantly below the measured values. In the opinion of the present authors the theoretical results obtained do not give convincing confirmation of the presence of D^- centers in the samples examined in Ref. [8].

In the present work the relative positions of *three* D^- levels are identified in the FIR spectrum of 510-Å GaAs quantum wells. First, the separation of the ground-state level and the lowest excited $M = +1$ level is studied, as in previous work, at $\theta = 0^\circ$, where θ is the angle between the magnetic field and the z direction. In this configuration, agreement between the calculated and observed transition energies is found to be within 1 cm^{-1} . Second, an anticrossing is induced between the lowest excited $M = +1$ level and the lowest level of odd z parity by tilting the sample. (Wave functions which are odd functions of z are defined to have odd z parity.) In the present study data were taken at $\theta = 16^\circ$ and 31° . Good agreement is found between these data and the theory for D^- levels. (The agreement is obtained, moreover, without the use of any adjustable parameters.) On the other hand, attempts to fit the $\theta = 0^\circ$ and $\theta > 0^\circ$ data simultaneously with a neutral donor by postulating a spike in the concentration of donors at some position in the quantum well proved fruitless.

The experimental setup and sample employed in the present work are described in detail in Ref. [11]. Briefly, the spectral data are obtained by monitoring, as a function of swept magnetic field, the in-plane photoconductivity of a center-doped GaAs/(Ga,Al)As quantum-well sample (with no intentional barrier doping) illuminated by FIR laser radiation. Data with a high signal-to-noise ratio are obtained. A drawback to this technique is that it is difficult to observe transitions which tune slowly with magnetic field unless the energy width of the transition line is sufficiently narrow.

Line *B* of Ref. [11], a prominent feature which was described but not identified there, is here attributed to D^- centers. Another D^- line, below line *B* in energy by $\hbar\omega_c$, although expected to be present, is not observed, presumably because of its predicted slow tuning rate with magnetic field.

The strength of line *B* relative to the donor $1s \rightarrow 2p_{+1}$ transition was found to increase with increasing bias. The data shown in Fig. 1 here and in Fig. 3 of Ref. [11] were taken under "low" bias conditions. At "high" bias, line *B* appeared even stronger than the $1s \rightarrow 2p_{+1}$ donor transition in the photoconductivity spectrum. This bias dependence is qualitatively similar to the reported behavior of D^- lines in bulk GaAs [1].

At some magnetic fields line *B* appeared as a shoulder. Curve fitting was then employed to locate the magnetic

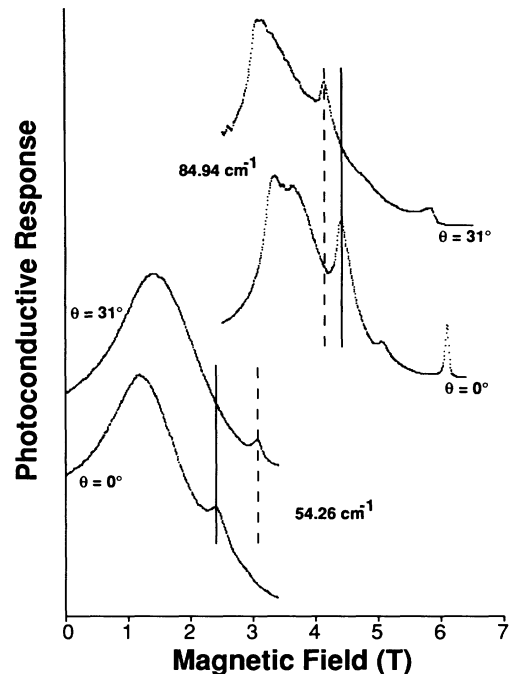


FIG. 1. Photoconductivity data above (84.94 cm^{-1}) and below (54.26 cm^{-1}) the D^- level crossing for $\theta = 0^\circ$ and 31° . Vertical lines locate the D^- peaks: the dashed lines for $\theta = 31^\circ$, the solid lines for $\theta = 0^\circ$. The strong lower-field peaks are from the donor $1s \rightarrow 2p_{+1}$ transition.

field position of the peak. Nevertheless the estimated uncertainty in the resonant field was less than 0.02 T for all data points, except for the point at 0.85 T in Fig. 2(a), which has an uncertainty of $\pm 0.05 \text{ T}$.

It is well known that the ground state of the D^- center in bulk is a spin singlet state (the space wave function is even under interchange of the coordinates of the two electrons) with $M=0$ and even z parity. The same is almost certainly true for a D^- center in the middle of a symmetrical quantum well. The selection rule $\Delta M = \pm 1$ applies for light propagating along the magnetic field; the final state must then be a singlet state of even z parity with $M = \pm 1$. Neglecting spin energy, variational calculations presented below indicate that the lowest-lying state of this type (i.e., the lowest-lying singlet $M = -1$ level) is localized and discrete but lies slightly *above* the energy of a donor in the magnetic field, E_{D^0} , plus the energy E_f of an unperturbed free electron in the lowest subband and lowest Landau level. The binding energy of a D^- state is usually defined as $E_{D^0} + E_f - E_{D^-}$. All singlet $M = -1$ levels are predicted here to be unbound (have negative binding energy). In quantum wells they are nevertheless discrete and localized in the presence of a magnetic field [12]. Binding energies of $M=0$, odd- z -parity levels, which will be referred to later, are calculated relative to the donor ground state plus the energy of a free electron in the *first excited subband* and lowest Landau level.

Variational calculations were carried out on the Hamiltonian H for an isolated D^- center. In donor atomic units (energies in units of the bulk donor Rydberg R , and lengths in units of the bulk donor Bohr radius a), H is defined by

$$H = H_0 + H_1'(1) + H_1'(2) + H_2'(1) + H_2'(2), \quad (1)$$

$$H_0 = H_D(1) + H_D(2) + 2/|\mathbf{r}_1 - \mathbf{r}_2|, \quad (2)$$

where $H_D(j)$ is the donor Hamiltonian for electron j ($j=1$ or 2) given by

$$H_D(j) = -\nabla_j^2 + \frac{\gamma_z}{i} \frac{\partial}{\partial \phi_j} + \frac{1}{4} \gamma_z^2 \rho_j^2 - \frac{2}{r_j} + V(z_j), \quad (3)$$

and H_1' and H_2' arise when the sample is tilted and are given by [11]

$$H_1'(j) = \frac{\gamma_x}{i} \left[y_j \frac{\partial}{\partial z_j} - z_j \frac{\partial}{\partial y_j} \right] - \frac{1}{2} \gamma_x \gamma_z x_j z_j, \quad (4)$$

$$H_2'(j) = \frac{1}{4} \gamma_x^2 [y^2 + z^2]. \quad (5)$$

The quantum-well potential is modeled by

$$V(z) = \begin{cases} V_0 & \text{for } |z| < L/2, \\ 0 & \text{for } |z| > L/2. \end{cases} \quad (6)$$

In the above equations L is the well width, $\gamma_z = \gamma \cos \theta$, $\gamma_x = \gamma \sin \theta$, γ is the dimensionless magnetic-field strength defined by $\gamma = \hbar \omega_c / 2R$, where $\omega_c = eB/m^*c$, B is the strength of the applied magnetic field, and m^* is the GaAs conduction-band mass. The effective mass in the barriers is taken equal to m^* .

Trial wave functions are of the Chandrasekar type with a donor-ground-state-like inner orbital $\Phi_I(\mathbf{r})$, and an outer orbital $\Phi_O(\mathbf{r})$ having the requisite symmetry. Wave functions have the general structure

$$\Psi(\mathbf{r}) = [\Phi_I(\mathbf{r}_1)\Phi_O(\mathbf{r}_2) + \Phi_I(\mathbf{r}_2)\Phi_O(\mathbf{r}_1)][1 + C|\mathbf{r}_1 - \mathbf{r}_2|]; \quad (7)$$

the inner orbital always has the form

$$\Phi_I(\mathbf{r}) = F_0(\mathbf{r})g_1(z), \quad (8)$$

whereas the outer orbitals vary depending on the state, being given by

$$\Phi_O(\mathbf{r}) = G_0(\mathbf{r})g_1(z) \quad (9a)$$

(ground state),

$$\Phi_O(\mathbf{r}) = \exp(+iM\phi)G_1(\mathbf{r})g_1(z) \quad (9b)$$

($M = +1$, even z parity),

$$\Phi_O(\mathbf{r}) = G_0(\mathbf{r})g_2(z) \quad (9c)$$

($M = 0$, odd z parity), where

$$G_{|M|}(\mathbf{r}) \text{ or } F_{|M|}(\mathbf{r}) = \rho^{|M|} \exp[-\eta\rho^2 - K(\rho^2 + az^2)^{1/2}], \quad (10)$$

and η , K , α , and C are parameters which are optimized for each state calculated. In this scheme each D^- state energy is minimized with respect to seven variational parameters. The wave functions $g(z)$ are solutions to the subband equation

$$\left[-\frac{\partial^2}{\partial z^2} + V(z) \right] g_n(z) = E_n g_n(z), \quad (11)$$

where E_1 and E_2 are the ground and first excited subband energies, respectively.

Results for $\theta = 0^\circ$ are compared to experiment in Fig. 2(a). The solid line is a spline through theoretical points representing the difference between the $M = +1$ and ground states of the D^- center; the dots are experimental data. The calculated D^- ground-state binding energies were not very sensitive to the value of V_0 assumed. (V_0 and all other sample parameters employed are the same as in Ref. [11].) The binding energy of the $M = +1$ state of the D^- center measured relative to the $N = 1$ Landau level increases in magnitude with magnetic field but is always negative (and of order -1 cm^{-1} for the range of γ of interest here when calculated with $V_0 = \infty$) [13]. (It was not considered essential to use the more realistic but more time-consuming value $V_0 = 25$ for either the $M = +1$ binding energy calculations or the $M = 0$, odd- z -parity binding energy calculations.)

Small deviations of theory from experiment evident in Fig. 2(a) are likely due to inaccuracies inherent in the tri-

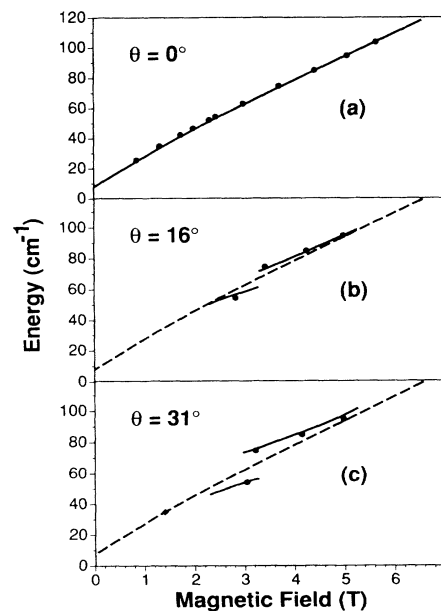


FIG. 2. Transition energy vs magnetic field for line B of Ref. [11]. The magnetic field in (a)–(c) makes an angle θ of 0° , 16° , and 31° , respectively, relative to the normal to the well planes. Dots represent data and the solid lines, theory. The diamond is a data point for $\theta = 26^\circ$. The dashed lines in (b) and (c) display the theoretical results for $\theta = 0^\circ$.

al functions of Eq. (7). The ground-state trial function of Eqs. (7), (8), and (9a) gives a D^- binding energy of 0.747 for $L=1.00$ with $V_0=35$, as compared to the binding of 0.77 ± 0.02 from Ref. [10]. [All D^- binding energies are calculated using donor wave functions of the form given by Eq. (8) to determine the corresponding donor energies.] No previous calculations of the D^- singlet p_{+1} -like levels are known to the authors.

Splitting of the D^- transition due to tilting the sample relative to the field was calculated as described below. Energies of the $M=+1$, even- z -parity (p_{+1} -like state) and the $M=0$, odd- z -parity (p_0 -like state) D^- wave functions defined earlier were separately minimized in the unperturbed Hamiltonian H_0 . This provided optimized wave functions and binding energies. From the binding energies obtained and calculations of the appropriate perturbing matrix elements the full Hamiltonian H was diagonalized in these two optimized basis functions. Deviations of the tilted energies from the $\theta=0^\circ$ energies were calculated at each field of interest and added to the experimental $\theta=0^\circ$ energy at that field. Each branch of theoretical points was splined and plotted against the experimental points (solid circles) for $\theta=16^\circ$ and $\theta=31^\circ$ in Figs. 2(b) and 2(c). The agreement appears satisfactory in view of the uncertainty in the accuracy of the calculated matrix elements.

Attempts were made to see if a location in the well could be found where a neutral donor would have a " $1s \rightarrow 2p_{+1}$ " transition energy versus magnetic field which replicates the data shown in Fig. 2(a) and which displays anticrossings comparable to those in Figs. 2(b) and 2(c). The infinite barrier model ($V_0=\infty$) was employed with the donor-excited-state calculation of Ref. [4] modified to be applicable to donors away from the well center; this gives a best fit to the data of Fig. 2(a) for a hypothetical spike in the concentration of donors located ~ 190 Å from the center of the well. The "best" $1s \rightarrow 2p_{+1}$ transition curve found deviates from the data by as much as ± 4 cm $^{-1}$ and is concave upward rather than concave downward like the data. At $\theta=0$ the nearest level to which the " $2p_{+1}$ " donor level could couple by tilting the sample is more than 4 cm $^{-1}$ away from the $2p_{+1}$ level at fields near the observed level crossing fields. Thus no behavior resembling Figs. 2(b) and 2(c) could be obtained from the donor model.

It is concluded that spectral line B of Ref. [11] has been definitively identified as the ground-state to $M=1$ singlet-level transition of a D^- center. Additional calculations suggest, moreover, that line 2 in the spectrum of Ref. [7] has the same origin as line B .

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 - [12] The barriers considered here have infinite width. As a result low-energy electrons cannot escape from the well by tunneling, and there exist localized unbound p -like states, which are strict eigenstates of H_0 . In general, localized unbound states are made possible by the complete confinement of electrons produced by the combination of the magnetic field (providing confinement in the x - y plane) and the quantum well barriers (which confine the electrons in the z direction).
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