Observation of Negatively Charged Excitons X^- in Semiconductor Quantum Wells

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The negatively charged exciton X^- is identified by its circular polarization properties in 1.7 K magnetoabsorption spectra of CdTe-$Cd_{1-x}Zn_xTe$ multiple quantum wells modulation doped with electron concentrations $N_s \approx 2\times10^{10}$ to 1.5×10^{11} cm^{-2}. The binding energy of the second electron of X^- is 0.20 3D rydbergs at 100 Å well width. The species X^- and the neutral exciton X exist in zero field for low N_s. At $N_s = 1.45\times10^{11}$ cm^{-2} a Fermi edge singularity is seen at $B=0$ but X^- appears with field, at filling factor $\nu=2$, while X appears at $\nu=1$.

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The exciton (X), an electron and a hole bound together by their Coulomb interaction, is the analog in a semiconductor of the hydrogen atom in vacuum. The electron-hole binding energy is typically 1–50 meV. Lampert [1] hypothesized in 1958 the existence of a related species, the negatively charged exciton (X^-), that is two electrons bound to one hole, analogous to H^-. The energy of binding of the second electron in X^-, E_{b2}, was expected to be $\approx 0.055R$, by analogy with the energy of dissociation of H^- into H^0 and a free electron (here R is the effective Rydberg, $R_\infty m_e^*\varepsilon_0^2/m_0\varepsilon^2$). More precisely, calculations for bulk semiconductors taking account of the finite ratio of electron and hole masses predict somewhat lower values, e.g., $E_{b2}=0.030R$ for $m_e^*/m_h^*=0.5$ [2].

This means binding energies E_{b2} in the meV range or smaller, so X^- has been a very elusive species. It may contribute to the line shape of the luminescence from electron-hole plasmas of bulk semiconductors [3] but no clear, resolved spectra of X^- seem to have been obtained.

Stébé and Ainane [4] have pointed out that E_{b2} should increase dramatically, making the species X^- much easier to find, in a quantum well heterostructure consisting of a thin well layer sandwiched between confining barrier layers. For example, for $m_e^*/m_h^*=0.5$ they calculated a factor of 10 increase, to $E_{b2}=0.30$ 3D rydbergs in the ultimate 2D limit.

In this Letter, we propose an identification of the species X^- by its creation and annihilation transition in optical spectra of CdTe quantum wells. The relatively large value of the Rydberg in the II-VI compound CdTe ($R=13.5$ meV) helps stabilize X^-. Also the fairly large electron g factor for CdTe, $g_e=-1.6$, increases circular polarization effects that identify X^-. But our results suggest that X^- ought also to be found in other quantum well systems.

The samples [5] discussed here are CdTe quantum wells (QWs) between $Cd_{1-x}Zn_xTe$ barriers ($x\approx0.16$). Crucial for obtaining X^- is the presence of excess electrons in the CdTe wells. These can be introduced by two methods. First, it was found recently [6] that $\approx10^{10}$ cm^{-2} photoelectrons can accumulate in the wells during optical spectroscopy of nominally pure CdTe-$Cd_{1-x}Zn_xTe$ samples. This has led us to reattribute the "Y line" [7], often seen in emission spectra of such samples, to X^-. This will be presented elsewhere [8]. In the present paper, we emphasize results obtained with a second, more precise method of creating excess electrons: This is "modulation doping" during sample growth.

We grew multiple quantum well (MQW) samples in a Riber molecular beam epitaxy unit, on $Cd_{0.88}Zn_{0.12}Te$ substrates that are transparent at the QW optical gap. The samples were planar doped with indium donors, during growth interruptions under excess Cd at 220 °C as in Ref. [9]. Secondary ion mass spectrometry profiling with 30 Å resolution showed no detectable broadening of the dopant planes.

All the MQWs consist of 10 CdTe wells of thickness $L_w=100$ Å, separated by 450 or 900 Å thick barriers of $Cd_{1-x}Zn_xTe$ ($x\approx0.16$). Indium planes of nominal concentration $N_{In}=2\times10^{10}$ to 1×10^{11} cm^{-2} were placed at the barrier centers, that is at a spacing distance $d=225$ or 450 Å from the well edges. Some or all of the electrons (depending on N_{In} and d) transfer to the wells from the donor levels high in the barriers. Values quoted below for N_s, the electron concentration per unit area in the wells, are nominal [10]. We also grew an undoped reference sample (S0) and a sample doped with 10^{11} indium cm^{-2} at the centers of the wells (sample S4).

Figure 1 shows (a) emission and (b) absolute absorption spectra at 1.7 K for the most lightly doped sample, S1, with nominally $N_s=2\times10^{10}$ electrons cm^{-2} in the ten wells. The line labeled X in Fig. 1 corresponds to the free exciton in the CdTe well (E_1HH_1 exciton; a 30 meV strain splitting of the CdTe valence band means QW exciton states discussed here are made from almost pure heavy-hole states $M=\pm\frac{3}{2}$). Our main interest is the line labeled Y, at 2.65 meV below X in zero field. This is only just visible in absorption for undoped sample S0 (not

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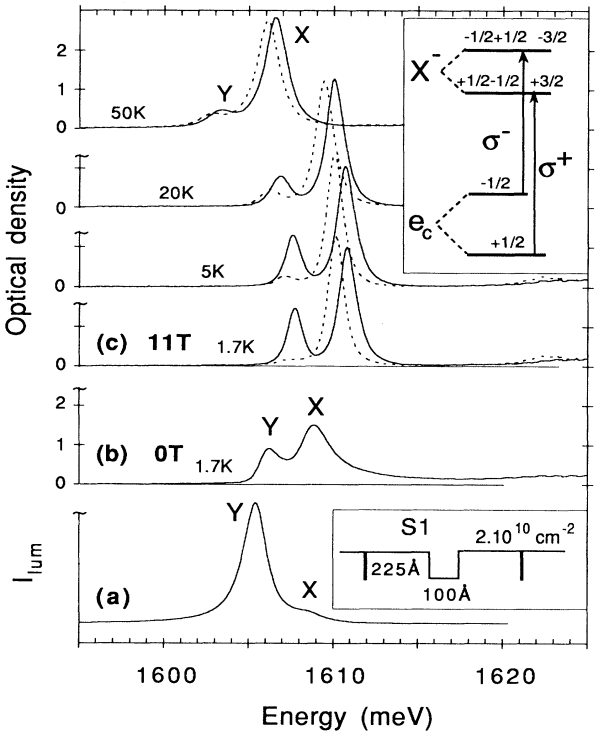

FIG. 1. Optical spectra for sample S1: a 100 Å CdTe-450 Å $Cd_{0.84}Zn_{0.16}Te$ MQW (ten periods) doped with nominally 2×10^{10} indium cm^{-2} at the barrier centers. (a) Luminescence and (b) absorption at 0 T, 1.7 K. (c) Absorption in a field $B=11$ T applied perpendicular to the QW planes for various temperatures. Full lines are σ^+ polarization; dotted lines are σ^-. The optical density scale units at left are ln(1/transmission). The inset shows the allowed ($\Delta M=\pm1$) transitions $e+h\nu\rightarrow X^-$.

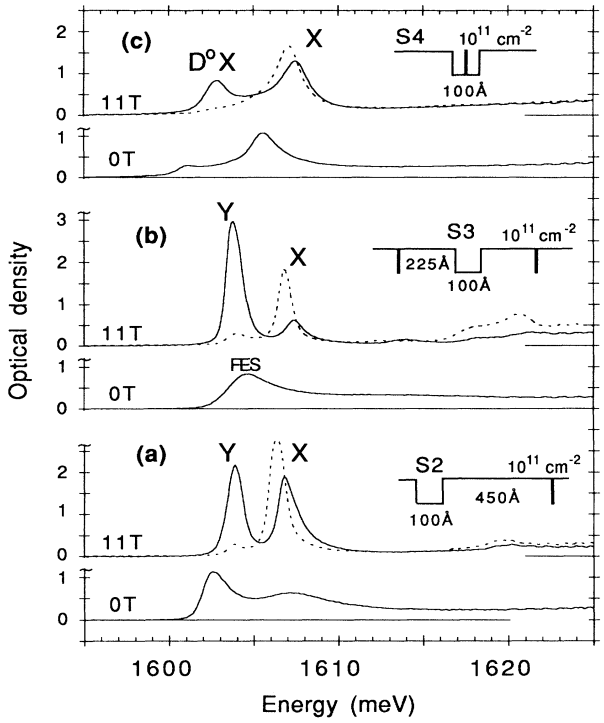

FIG. 2. Optical density, i.e., ln(1/transmission), in polarizations σ^+ (full lines) and σ^- (dotted lines) at 1.7 K for three CdTe-$Cd_{0.84}Zn_{0.16}Te$ (ten periods) MQW samples doped with nominally 10^{11} indium cm^{-2} at the barrier centers (S2,S3) or the well centers (S4).

shown), so it is doping induced.

Figure 1(c) shows spectra with an 11 T magnetic field B applied perpendicular to the plane of the QW. Lines X and Y have narrowed and shifted slightly and the splitting is now 3.1 meV. The very significant features are as follows: (i) At 1.7 K, absorption line Y is very much stronger in σ^+ polarization (solid line) than in σ^- (dotted line). (ii) Line X is only slightly polarized. (iii) The circular polarization of Y disappears with temperature. All this demonstrates that the initial state of absorption transition Y is *spin degenerate*. The ratio of its integrated σ^- and σ^+ intensities varies approximately as $\exp(-g\mu_B B/kT)$. Fits give $|g|=1.8$ to 2.0, consistent with $|g_e|=1.6$.

Hence our interpretation of the spectrum. We propose that absorption of a photon, with and without involvement of an electron present in the well, creates an X^- and a neutral X, respectively. That is, line Y is $e+h\nu_1\rightarrow X^-$ and line X is $0+h\nu_2\rightarrow X$. The energy difference $h\nu_2-h\nu_1$ gives E_{b2}, the binding energy of the second electron in X^-.

Figure 1 also shows selection rules for the Y line. The final state is X^-, which has antiparallel electron spins [2,4] so the spin state is that of the hole $M=\pm\frac{3}{2}$. The ground state is an electron spin doublet, $M=\pm\frac{1}{2}$, and absorption transitions $\Delta M=\pm1$ are allowed in σ^+ and σ^- polarizations, respectively. The electron spin splitting (if not "exchange enhanced" [11]) is $g_e\mu_B B=0.093$ meV/T and at 11 T, 1.7 K, nearly all the electrons are in the $M=+\frac{1}{2}$ state, which is why line Y is polarized σ^+.

The Zeeman splitting between the two components σ^+,σ^- of line Y is $(g_e-g_h)\mu_B B$ (see Fig. 1), where g_h is an effective g factor for the hole. This formula, which also gives the Zeeman splitting of exciton line X, is accidentally very small ($g_h\sim g_e$ at this L_w).

The magnetic properties of X^- resemble those of a better known two electron species: the exciton bound to a neutral donor (D^0X). Anticipating Fig. 2(c), concerning sample S4 with 10^{11} cm^{-2} donors placed at the well centers, we see that spin polarizations of D^0 circularly polarizes the transition $D^0+h\nu\rightarrow D^0X$. The X-D^0X separation, 4.4 meV in zero field, measures the exciton-donor binding. This binding is considerably larger than the X-Y separation, $E_{b2}(X^-)=2.65$ meV, because the positively charged donor core at the well center provides a strong localizing potential that is absent for X^-.

The value $E_{b2}=2.65$ meV is 0.20 CdTe rydbergs. This is 66% of the calculated 2D value [4] for the CdTe in-plane mass ratio $m_e^*/m_h^* \approx 0.5$ and 42% of the value for $m_h^*=\infty$. Data for line Y detected in emission spectra of undoped single QWs show E_{b2} saturating at ≈ 3 meV at small L_w for $x \approx 0.16$ barriers (whereas X-D^0X splittings reach ≈ 6 meV [12]).

Note that line Y for sample S1 (Fig. 1) has, for about one-fifth the number of electrons, about the same integrated optical density as the D^0X peak for sample S4. D^0X itself has high oscillator strength [9], so X^- has very high oscillator strength indeed. From the theory of bound-exciton oscillator strengths [13], this suggests that the X^- wave function is very diffuse, occupying many unit cells of the lattice, in contrast to D^0X where the donor potential localizes the exciton fairly strongly.

Observation of X^- in the presence of electrons is actually a paradox. In theory, with electrons filling conduction band states up to a Fermi level, exciton binding energies are drastically reduced because of screening and because occupied electron states are excluded from the exciton wave function [14]. So the existence of X^- (and of X) in sample S1 probably means the electrons are localized below a mobility edge, which would remove screening. This is not unexpected at 2×10^{10} cm^{-2} density where, with m_e^*(CdTe) $=0.09m_0$, the Fermi energy E_F is only 0.5 meV, comparable to the potential fluctuations [15] associated with the randomly distributed, distant donor cores.

Screening and exclusion effects of a 2D electron gas are observed very clearly at higher electron concentration. Figure 2 shows absolute absorption spectra for MQWs doped with nominally 10^{11} indium cm^{-2} at spacer distances $d=225$ Å (sample S3) and $d=450$ Å (sample S2).

For sample S3, where we expect complete transfer of the electrons into the well, the sharp lines X and Y no longer exist in zero magnetic field. We see instead a single broad absorption "bump" (1.605 eV) [Fig. 3(b)]. This is a "Fermi edge singularity" (FES) or "Mahan exciton," a characteristic electron gas property. It results from many-body correlations left after screening and exclusion have destroyed the conventional exciton [14].

This is classic. But Fig. 2(b) also shows, and we believe this is new, that the FES bump converts into two sharp peaks at high field. Their spacing (3.6 meV at 11 T) is close to that of the two peaks seen at low N_s, and we again use labels X and Y. Now, however, line Y is extremely strong in σ^+ polarization. An apparent corollary is that line X has become very weak in σ^+ (it is as if Y has "stolen σ^+ oscillator strength" from X).

As concerns sample S2 ($d=450$ Å), from Poisson's equation only $N_s \approx 6\times10^{10}$ cm^{-2} electrons should transfer to the well, and the zero-field spectrum is more complicated with two broad lines [Fig. 2(a)]. These evolve more quickly with magnetic field into the narrow peaks X and Y. For comparison [Fig. 2(c)], sample S4 doped in the well centers shows no electron gas effects: Line X and the less strong D^0X line are seen at all fields.

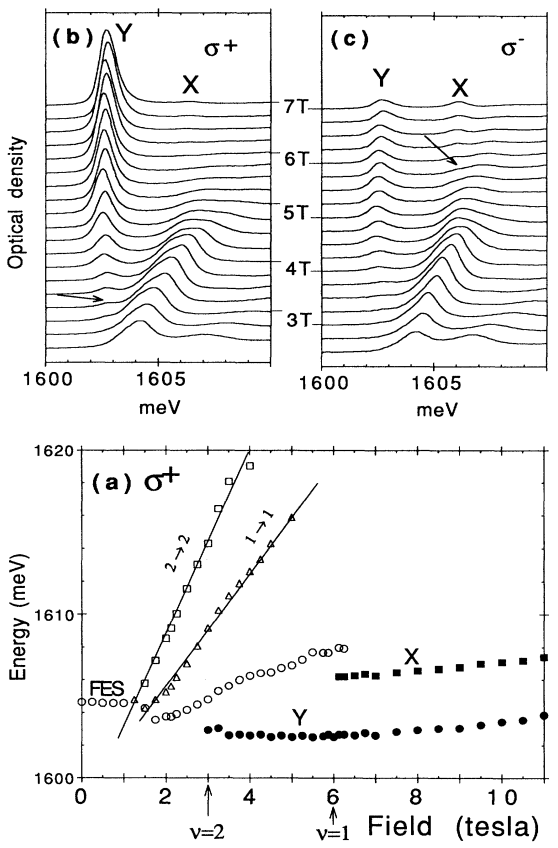

FIG. 3. (a) Positions of absorption peaks observed at 1.7 K in σ^+ polarization for modulation-doped sample S3: lines Y and X appear at 3 and 6 T, respectively. (b),(c) Optical density spectra from 2.5 to 7 T in steps of 0.25 T, with arrows marking the first appearances of Y in σ^+ and X in σ^-. Filling factor assignments $\nu=2$ and $\nu=1$ give $N_s=1.45\times10^{11}$ cm^{-2}.

As at lower N_s, we attribute lines X and Y to neutral excitons X and to X^-, respectively. Indeed, at 11 T, the spectra of the three modulation-doped samples (and of undoped sample S0 with Y just visible [8]) are very similar, the X-Y separations being 2.7, 3.1, 2.95, and 3.6 meV for S0, S1, S2, and S3, respectively. The essential difference is the large increase in the X^- intensity with increasing N_s.

Figure 3 shows how the Fermi edge singularity at 1605 meV evolves with field into Y and X lines for sample S3. At low field, transitions from valence band Landau levels λ_v to conduction band levels λ_c (peaks $2_v \rightarrow 2_c$ and $1_v \rightarrow 1_c$) resolve out from the main absorption-edge peak, moving linearly with B. Their slopes fit accurately the CdTe values of $m_e^*=0.09$ and of in-plane $m_h^*=0.19$.

At $B=3.0$ T, the narrow line Y appears below the main absorption-edge peak [see Figs. 3(a) and 3(b)] and gains intensity rapidly with increasing B. At almost ex-

actly twice the above field, $B=6.0$ T, line X appears, weakly in σ^+ polarization [Figs. 3(a) and 3(b)], and more strongly in σ^- [Fig. 3(c)]. It too gains intensity with B especially in σ^- [see at 11 T in Fig. 2(b)].

We deduce from their quite precise 1:2 ratio that the singular fields 3.0 and 6.0 T correspond, respectively, to *integer filling factors* $\nu=2$ and $\nu=1$ (where ν is the number of filled Landau levels of degeneracy eB/h). Then the exact electron concentration of sample S2 is $N_s=1.45\times10^{11}$ cm^{-2} per well and our interpretation of the Y and X branches in Fig. 3(a) is as follows.

Between $\nu=2$ and $\nu=1$, the 0_c^- Landau levels ($\lambda_c=0, M_e=-\frac{1}{2}$) are emptying progressively, but the 0_c^+ levels are still full. In this range, $0_v\rightarrow 0_c$ absorption transitions become possible but create only 0_c^- electrons. It seems that, if the electron and valence hole bind to form an excitonic state in this range, the 0_c^- electron also has to spin pair with a 0_c^+ electron, so only X^- can exist [branch Y in Fig. 3(a)].

It is only when 0_c^+ levels start to empty ($\nu<1$, 6 T in Fig. 3) that 0_c^- levels unpaired with an occupied 0_c^+ level exist. Absorption transitions to these levels or to an empty 0_c^+ level (all 0_c^- levels being empty at $\nu<1$) can then form a neutral exciton X [branch X in Fig. 3(a)]. These spectra are quite different from published absorption spectra for GaAs-$Ga_{1-x}Al_xAs$ MQWs at low ν (albeit at higher N_s) [11,16]. There, new peaks appear at $\nu=2$ and $\nu=1$ but move linearly with field and are interpreted as $0_v^-\rightarrow 0_c^-$ and $0_v^+\rightarrow 0_c^+$ inter-Landau-level transitions, not excitons. Instead of two transitions, we have four transitions, namely, Y and X in σ^+ and σ^-, and they shift quadratically with B, which is the signature of an excitonic state.

How can these exciton states X and Y be sustained in what should be a high screening environment? One explanation could be a magnetic-field-induced freeze-out of the electron gas into the potential fluctuations related to distant dopant planes [17]. But our spacing distances d are very large (450 Å for samples S2$\gg$3D donor Bohr radius 60 Å), so theoretical approaches [18] that show a magnetic field restoring excitonic binding (at low-to-medium N_s) even in the absence of disorder could also hold the answer.

Thus, our II-VI materials system is showing a variety of interesting new excitonic effects. Exclusion and screening effects disappear when the lowest two Landau levels unfill; discrete exciton states X^- and X then come into existence. For very low N_s, both states exist already at zero field. This almost certainly represents disorder-induced freeze-out, but it is less clear why magnetic field stabilizes X^- and X at higher N_s and, we suggest, this poses an interesting problem to theory.

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