

## Bound States in Optical Absorption of Semiconductor Quantum Wells Containing a Two-Dimensional Electron Gas

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The dependence of the optical absorption spectrum of a semiconductor quantum well on two-dimensional electron concentration  $n_e$  is studied using CdTe samples. The trion peak ( $X^-$ ) seen at low  $n_e$  evolves smoothly into the Fermi edge singularity at high  $n_e$ . The exciton peak ( $X$ ) moves off to high energy, weakens, and disappears. The  $X, X^-$  splitting is linear in  $n_e$  and closely equal to the Fermi energy plus the trion binding energy. For  $\text{Cd}_{0.998}\text{Mn}_{0.002}\text{Te}$  quantum wells in a magnetic field, the  $X, X^-$  splitting reflects unequal Fermi energies for  $M = \pm 1/2$  electrons. The data are explained by Hawrylak's theory of the many-body optical response including spin effects.

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Absorption of light in a semiconductor quantum well (QW) lifts electrons from the valence band to the conduction band. In an empty QW, the lowest energy optical excitation is the exciton, an electron and a hole bound together by Coulomb interaction. The exciton is analogous to a hydrogen atom but its binding energy is greatly reduced (larger dielectric constant and smaller effective masses of the electron and hole). As shown in Fig. 1(a), the discrete optical transition that creates the exciton gives a sharp peak ( $X$ ) in the absorption spectrum below the continuum absorption (not shown) that creates unbound electron-hole pairs.

For QWs containing low concentrations of free electrons ( $n_e \approx 10^{10} \text{ cm}^{-2}$ ), a second sharp absorption peak appears, shifted down in energy from exciton peak  $X$  [Fig. 1(b)]. This additional peak corresponds to the creation of a negatively charged exciton or "trion"  $X^-$ , i.e., an exciton that has bound one of the excess electrons from the conduction band [1–4]. The trion is analogous to the negatively charged hydrogen ion. Within this framework, the trion's binding energy is constant; it would be very small in a bulk semiconductor but is considerably increased in a two-dimensional environment [1].

The absorption spectrum is very different for QWs that contain a higher density two-dimensional electron gas (2DEG). The sharp excitonic peaks  $X$  and  $X^-$  are replaced by a broad, asymmetric peak called the "Fermi edge singularity" (FES) [Fig. 1(f)]. This rises relatively quickly on the low energy side but on the high energy side its intensity falls off slowly, to merge into the continuum absorption. The FES results from multiple scattering processes involving electrons near the Fermi level. Indeed such a situation was identified in metals earlier than in semiconductors, as a singularity in the x-ray absorption spectra [5].

The QWs studied until now did not provide a precise answer to the following question: How does the spectrum of two discrete absorption peaks  $X$  and  $X^-$  transform into the FES as the electron concentration  $n_e$  increases from small to high values? Our paper replies to this question. Studying CdTe QWs with  $n_e$  ranging up to several  $10^{11} \text{ cm}^{-2}$  we find the following:

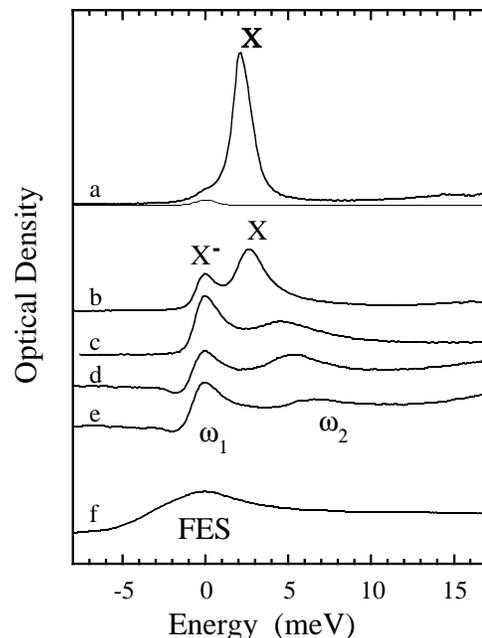


FIG. 1. Optical absorption spectra for 100 Å CdTe quantum wells at  $T = 2$  K. Electron concentrations  $n_e$  are (b) 0.2, (c) 1.0, (d) 1.3, (e) 1.8, and (f)  $3.0 \times 10^{11} \text{ cm}^{-2}$ . Sample (a) is nominally undoped. The zero of energy ( $\approx 1.61$  eV) is taken at the lowest absorption peak,  $X^-$  or  $\omega_1$ , in each case. We normalized the integrated optical density [ $= \log(1/\text{transmission})$ ] since the structures have different numbers of wells.

(a) The separation between absorption peaks  $X^-$  at energy  $\hbar\omega_1$  and  $X$  at energy  $\hbar\omega_2$  increases progressively with  $n_e$  [curves (b)–(e) in Fig. 1]. This is surprising because the  $X$ ,  $X^-$  splitting has previously been equated to the trion's binding energy  $E_{b1}$  (the energy for removing one of its two electrons), a parameter that should not increase with  $n_e$ . The separation between the two peaks turns out to be accurately linear in  $n_e$  and obeys

$$\hbar\omega_2 - \hbar\omega_1 = E_{b1} + aE_F \quad \text{with } a \approx 1, \quad (1)$$

where  $E_F$  is the Fermi energy (the energy of electrons at the Fermi level  $\mu$  relative to the bottom of the conduction band  $E_c$  that is their kinetic energy  $\hbar^2 k_F^2 / 2m_e^*$ ).

(b) As peak  $X$  ( $\omega_2$ ) moves away from peak  $X^-$  ( $\omega_1$ ) to progressively higher energy with increasing  $n_e$  it loses amplitude, until it can no longer be distinguished from the continuum absorption. It is the trion absorption peak  $X^-$  that ultimately becomes the FES seen at high  $n_e$  [Fig. 1(f)].

(c) For a CdTe (0.2% Mn) QW in a small magnetic field ( $B < 1$  T), the separation of the absorption peaks  $X^-$  and  $X$  increases with  $B$  if measured in  $\sigma^-$  polarized light, and decreases with  $B$  in  $\sigma^+$ . This fits with Eq. (1) above, where the Fermi energies ( $\mu - E_{cd}, \mu - E_{cu}$ ) are now *unequal* for the up and down spin states  $u$  and  $d$ , because the 2DEG is spin polarized via the exchange interaction with Mn atoms.

The early theories of the optical response of a QW [6] predict only one absorption peak: the exciton  $X$  at low  $n_e$  becoming the FES at high  $n_e$ . This appeared to agree with experimental spectra available at that time [7]. The present, better resolved spectra showing *two* absorption peaks do not fit with the above theories. But our results agree very well with a more recent theory by Hawrylak *et al.* [8–10]. This theory adapts the original theory [5] of the FES in 3D metals and semiconductors to the 2D case. Including essential effects of electron spin, it predicts *two* absorption thresholds. We adopt Hawrylak's labels  $\omega_1$  and  $\omega_2$  for our two absorption peaks because their evolution with  $n_e$  corresponds to the theory's predictions.

The samples studied were CdTe or Cd<sub>0.998</sub>Mn<sub>0.002</sub>Te single or multiple QWs between alloy barriers of composition Cd<sub>1-x</sub>Zn<sub>x</sub>Te ( $x \approx 0.15$ ) or Cd<sub>1-x</sub>Zn<sub>x</sub>Mg<sub>y</sub>Te ( $x \approx 0.1, y \approx 0.15$ ). The nominal well thickness was 100 Å. The structures were grown by molecular beam epitaxy (MBE) on Cd<sub>0.88</sub>Zn<sub>0.12</sub>Te substrates. Strain induced in the CdTe well by lattice mismatch with these substrates shifts light hole excitations 40 meV above heavy hole excitations and only the latter need be considered here. With 12% Zn, the substrate is transparent at the energy of heavy hole excitons in the CdTe QWs ( $\approx 1.61$  eV), so optical absorption measurements can be done easily, with a tungsten lamp source.

The barriers are doped with indium or aluminum [11] donors at a spacer distance 200 Å or greater from the edge

of the well. Donor electrons transfer into the wells creating a 2DEG. For Al doping, the transfer can be reduced by  $\approx 3$  at 2 K by blue light. From  $n_e > 10^{11}$  cm<sup>-2</sup>, the precise value of  $n_e$  could be deduced optically from the jumps in the field dependence of the absorption spectra at integer values of the Landau level filling factor. Values of  $n_e$  below  $10^{11}$  cm<sup>-2</sup> were taken to be the MBE design values.

The very weak, low energy shoulder on peak  $X$  in Fig. 1(a) is, in fact, a trion peak due to some free electrons in the undoped sample. We fit it by a Gaussian in Fig. 1(a). Then, Fig. 1 shows clearly how this  $X^-$  peak gains intensity relative to the  $X$  peak and transforms progressively to the asymmetric FES form at high  $n_e$ .

We have taken the position  $\hbar\omega_1$  of the lower peak as the zero of photon energy in Fig. 1. Its absolute energy fluctuates due to somewhat different well widths and barrier heights of the samples, and shifts progressively to slightly higher energy, by  $\approx 3$  meV at our maximum  $n_e$ ,  $3 \times 10^{11}$  cm<sup>-2</sup>. In the theory [10], this small blueshift is due to finite hole mass  $m_h$  ( $\approx 0.5m_e$ ). The upper peak at  $\hbar\omega_2$  (identified with  $X$  at low  $n_e$ ) moves off much faster as  $n_e$  increases, loses amplitude, and finally becomes undetectable.

Figure 2 gives the splitting  $\hbar\omega_2 - \hbar\omega_1$  as a function of the Fermi energy  $E_F = \hbar^2 \pi n_e / m_e^*$  (we use a cyclotron mass  $m_e^* = 0.105m_0$  for CdTe QWs [12]). We plot the splitting for the undoped sample at  $n_e \approx 0$ . A least squares fit yields Eq. (1) above, with a binding energy  $E_{b1} = 2.1$  meV and a slope  $a = 1.07 \approx 1$ .

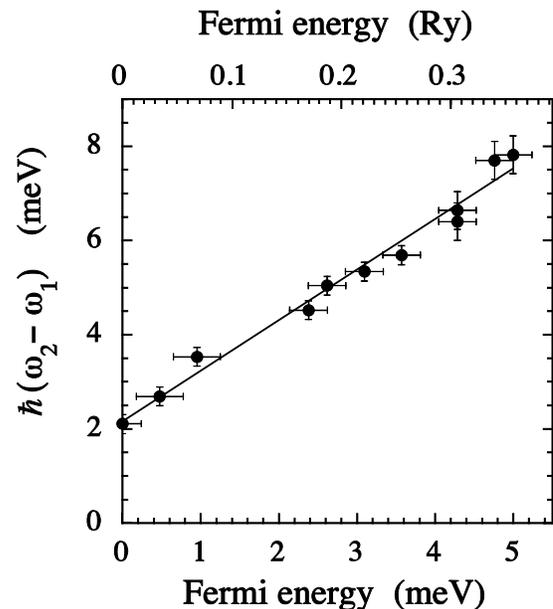


FIG. 2. Separation between upper and lower absorption peaks  $\omega_1$  and  $\omega_2$  seen for 100 Å CdTe quantum wells as a function of Fermi energy. The top scale is in Rydberg units (= 14 meV, the 3D donor binding energy). The uncertainty bars for the splitting and the Fermi energy measurements are indicated. The linear fit is Eq. (1) with  $E_{b1} = 2.1$  meV and  $a = 1.07$ .

To explain Eq. (1), we appeal to Hawrylak's theory [8–10] which provides a clear path from the  $X$  and  $X^-$  concepts to the proper many-body description of the excited states at high  $n_e$ . This theory insists that the injection of a hole into a 2DEG always creates a bound electronic state below the conduction band edge, no matter how high  $n_e$  is. In the “ground” configuration of the many electron one hole system, created by an optical transition with threshold  $\hbar\omega_1$ , the bound state is occupied by two electrons with antiparallel spins. This doubly occupied state evolves smoothly from the trion  $X^-$  of the low  $n_e$  spectrum. In the “ionized” configuration, which evolves from the exciton  $X$  and is created above a second threshold  $\hbar\omega_2$ , the bound level is singly occupied only.

In this view, the exciton is just an ionized trion, and  $\hbar\omega_2 - \hbar\omega_1$  defines the minimum energy for removing one electron from the trion. At infinitesimal  $n_e$ , this is just the trion binding energy  $E_{b1}$ , the energy for promoting one of the two electrons up to the conduction band edge  $E_c$  from the state where it is bound by the hole. At finite  $n_e$ , in the 2DEG, the  $\omega_2$  (or  $X$ ) excitation is obtained from the  $\omega_1$  (or  $X^-$ ) excitation by removal of one bound electron *up to the Fermi level*  $\mu$ , all lower conduction band levels being occupied (at 0 K). This is why the Fermi energy  $E_F = \mu - E_c$  has to be added to  $E_{b1}$  in Eq. (1) above [13].

As a corollary, the present work shows that one must go to very low  $n_e$  to see the bare trion binding energy. The straight line of Fig. 2 extrapolates to  $E_{b1}(n_e \rightarrow 0) = 2.1$  meV, which is also the value gotten by fitting the very weak trion shoulder in Fig. 1(a). This parameter was given previously as 2.6 meV for 100 Å CdTe QWs [14] from the exciton-trion splitting at  $n_e \approx 2 \times 10^{10}$  cm $^{-2}$  ( $E_F \approx 0.5$  meV). Note that  $E_{b1} = 2.1$  meV is much smaller than the neutral exciton's binding energy  $E_{b2}(n_e \rightarrow 0)$ , the energy for removing the remaining electron to  $E_c$  (about 18 meV in 100 Å CdTe QWs), since  $E_{b1} = E_{b2} - U$ , where  $U$  is the electron-electron repulsion energy. Hartree calculations [9] show  $U$  tending to zero, that is  $E_{b2} \rightarrow E_{b1}$ , at high  $n_e$ .

As a second corollary, the splitting between the two peaks  $X$  and  $X^-$ , explained in the framework of a many-body theory based on electron-electron interaction, appears to be density dependent even at low  $n_e$ . But, for these densities, one might expect to observe strong localization of the electrons and *a fortiori* of the heavier trions, [2–4,15] given the strong disorder present (as deduced from the much lower 2DEG mobility than all reported cases of GaAs QWs; only  $10^4$  cm $^2$ V $^{-1}$ s $^{-1}$  at 2 K for  $n_e \approx 10^{11}$  cm $^{-2}$ ).

Much of the evidence for this view comes from luminescence spectra, where thermalization of the emitting states may give predominance to localized states situated at low energy. In fact, our own emission spectra, for the range of  $n_e$  where  $\omega_2$  is visible, could be interpreted in this way. However, absorption spectra surely give a more faithful

picture of the true density of states. Note that the strongest evidence for localization effects comes from spectra of highly depleted GaAs Schottky diodes, where the electrostatic disorder is strong enough to induce a metal to insulator transition with perhaps only one electron per potential fluctuation [16]. We suggest that for our *ungated* CdTe QWs, regardless of the nature of the carriers (free or localized), the electron-electron interaction remains, a viewpoint already reported in very dilute 2DEG in high quality GaAs QWs [17].

The  $\omega_1$  singularity would exist even if there were no binding. The  $\omega_2$  peak exists because there is a bound state to be ionized, and one might expect to see it more easily in CdTe than in GaAs, because binding energies are twice as large in the II-VI compound. While an  $X$  peak split from  $X^-$  by  $E_{b1} \approx 1.2$  meV can be seen in GaAs QWs with a strongly depleted 2DEG [3,4,16], Brown *et al.* [9] searched for but found no clear signature of an  $\omega_2$  transition in a careful absorption study of undepleted GaAs QWs with  $n_e \approx 10^{11}$  cm $^{-2}$ . Our observations, where  $\omega_2$  is lost at  $E_F \approx 0.5$  Ry (Fig. 1), fit with this and with Hartree calculations showing the  $\omega_2$  peak strongly damped at high  $n_e$  [9].

That the binding in the lowest excited state does indeed involve two antiparallel electron spins can be demonstrated by creating a situation where spin-up and spin-down electrons have unequal populations. Application of a small magnetic field  $B$  to a QW of the very dilute magnetic semiconductor Cd $_{0.998}$ Mn $_{0.002}$ Te polarizes the  $S = 5/2$  Mn spins, and their exchange interaction with conduction electrons makes  $g_e$  (the effective  $g$  factor for the electron spins) very large. As  $B$  increases, there are progressively more spin-down than spin-up electrons in the conduction band, until the Mn magnetization saturates around 1.5 T (for 2 K).

All the optical transition energies for CdTe (0.2% Mn) wells depend strongly on  $B$ . Here we are interested in the *relative* energies of the  $\omega_2$  and  $\omega_1$  peaks, graphed in Fig. 3 as a function of  $B$ . The separation  $\omega_2 - \omega_1$  increases in  $\sigma^-$  polarization and decreases in  $\sigma^+$  as field is applied.

We explain this using Fig. 4, where distinct bound levels for spin-up and spin-down electrons are drawn at distance  $E_{b1}$  below their appropriate conduction band edge. Consider  $\sigma^-$  polarization. Absorption of a  $\sigma^-$  photon lifts an electron to the spin-up ( $m = +1/2$ ) conduction band, leaving a ( $m_z = -3/2$ ) hole in the valence band. The hole potential can bind a spin-up *and* a spin-down electron giving the  $\omega_1$  excitation. In the theory, the difference between the  $\omega_2$  and  $\omega_1$  excitations involves taking the background spin-down electron from the bound level up to the Fermi level. As shown at the right in Fig. 4, this costs the binding energy  $E_{b1}$ , plus  $E_{Fd} = \mu - E_{cd}$ , the kinetic energy at the Fermi level for *spin-down* electrons. So, as  $B$  is increased from zero, increasing the population of spin-down electrons, the  $\omega_2, \omega_1$  splitting seen in  $\sigma^-$  should increase, following Eq. (1). The *opposite* effect should be seen in

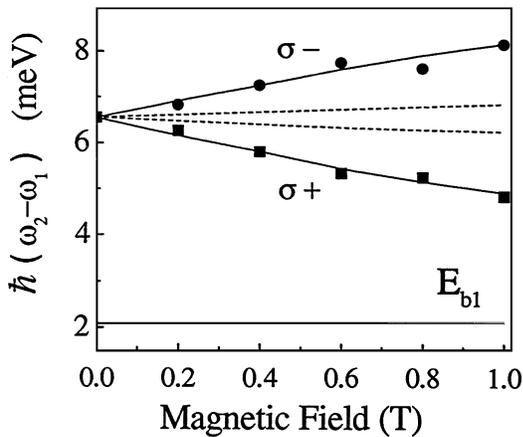


FIG. 3. Field dependence of the separation between  $\omega_2$  and  $\omega_1$  peaks in  $\sigma+$  and  $\sigma-$  polarizations at 2 K for a 100 Å CdTe (0.2% Mn) quantum well with  $n_e \approx 1.8 \times 10^{11} \text{ cm}^{-2}$ . The curves represent Eq. (1) with  $a = 1$ ,  $E_{b1} = 2.1 \text{ meV}$ ,  $E_F(B = 0) = 4.35 \text{ meV}$ , and, for  $B > 0$ , unequal Fermi energies for spin-up ( $u$ ) and spin-down ( $d$ ) electrons. The dotted curves correspond to  $E_{Fu}^d = E_F(B = 0) \pm g_c \mu_B B/2$ . The continuous curves add an exchange splitting  $E_{\text{exchange}}(n_{ed} - n_{eu})/n_e$ , where  $E_{\text{exchange}}$  is adjusted to 3.5 meV to fit the data points.

$\sigma+$  polarization. In fact, we need to add an amplification of the electron spin polarization, coming from the ferromagnetic electron-electron exchange interaction [18]. We get a good fit in Fig. 3 by modeling the equilibrium spin splitting of the conduction band with the simple form given in the legend. Thus, this paramagnetic sample illustrates the description of the  $\omega_2$  threshold as involving removal of an electron, having *opposite spin* to that of the photoelectron, from a bound state to the Fermi level.

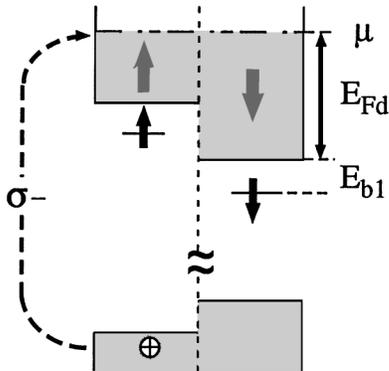


FIG. 4. For a spin polarized 2DEG, we represent the excited state created by the  $\omega_1$  transition. The light has  $\sigma-$  polarization, which adds a spin-up electron to the conduction band at the left. The hole potential binds two electrons. The  $\omega_2$  transition differs from  $\omega_1$  by removal of the spin-down electron from the bound level at the right to the Fermi level  $\mu$ .

In conclusion, a clear link between experiment and theory has been achieved, providing a better understanding of the effect of a 2DEG on the optical absorption of a QW in zero or small magnetic field. In particular, we demonstrate the density dependence of the splitting between  $X$  and  $X^-$  peaks (up to now, the negative trion was likened to a negative hydrogen ion, thus this splitting was assumed to be density independent). It is now a challenge to understand the associated emission spectra in the framework of a theory [8,10] where the lowest energy excited state is always bound. In this case the disorder, *via* the localization effects, must be taken into account.

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