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Definitive observation of the dark triplet ground state of charged excitons in high magnetic fields

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The ground state of negatively charged excitons (trions) in high magnetic fields is shown to be a dark triplet state, confirming long-standing theoretical predictions. Photoluminescence (PL), reflection, and PL excitation spectroscopy of CdTe quantum wells reveal that the dark triplet trion has lower energy than the singlet trion above 24 T. The singlet-triplet crossover is "hidden" (i.e., the spectral lines themselves do *not* cross due to different Zeeman energies), but is confirmed by temperature-dependent PL above and below 24 T. The data also show two bright triplet states.

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A central problem found in atomic, solid-state, and nuclear physics is the case of a three-particle system of fermions, bound together by long-range Coulomb interactions. In atomic physics, this situation is most simply realized by the two-electron hydrogen ion, H^-, in which the two identical electrons can exist in either a singlet or triplet state with total electron spin $S_e=0$ or 1, depending on external parameters. The semiconductor analog of the H^- ion is the negatively charged exciton (trion), consisting of two conduction electrons bound to a single valence hole. Optical signatures from trions have been observed in GaAs, CdTe, and ZnSe quantum wells (QWs) (Refs. 1–4). Unlike the H^- ion, the hole and two electrons comprising the trion have comparable masses and typically experience strong QW confinement in one dimension, making trions a genuine quantum three-particle system with Coulomb interactions for which no general analytical solutions exist.

Much attention has focused on the evolution of trion optical signatures with applied magnetic field.[5–9] In the limit of zero magnetic field, theory predicts just one bound trion state: the $S_e=0$ singlet trion (T_s) (Refs. 10,11). This is consistent with Hill's theorem,[12] which states that the H^- ion (with an infinitely massive proton) supports exactly one bound singlet state. In the opposite limit of extremely high magnetic fields, it can be rigorously shown that a $S_e=1$ triplet is the only bound trion state in a strictly two-dimensional (2D) system.[11,13] Model-independent symmetry considerations[14] demonstrate that this lowest triplet state is "dark" (T_{td}) (i.e., optically inactive), due to the exact selection rules imposed by spatial axial and translational symmetries that exist in a disorder-free QW. Thus, at finite magnetic fields one expects both singlet and triplet bound trions.[11,13] More importantly, at some critical magnetic field B_c the spin configuration of the trion ground state must cross over from the singlet to the triplet. Theoretical estimates suggest this crossover field is very large ($B_c>20$ T) and depends sensitively on the strength of the Coulomb interaction (dielectric constant) and the details of the QW confinement.[11,15–18] Numerical calculations also point to the existence of weakly bound, optically active "bright" triplet states (T_{tb}), although there is a large disparity amongst the predicted regions of stability and binding energies.[15,16] Distinction between T_{td} and T_{tb} is due to *orbital motion* and *is not related* to the spin selection rules.[14–16] Note, T_{td} and T_{tb} have identical spin configuration.

In this Communication we present conclusive evidence that the high-field ($B>B_c=24$ T) ground state of negatively charged trions in CdTe-based QWs is (1) a triplet state and (2) optically dark, i.e., it has no absorption oscillator strength. Three distinct and complementary polarization-resolved spectroscopies—photoluminescence (PL), reflection, and PL excitation (PLE) (Ref. 19)—proved to be essential for identifying and conclusively determining the spin properties of trions in magnetic fields below *and above* the singlet-triplet crossover field B_c. As such, this work represents a comprehensive picture of the evolution of the trion ground-state's spin over a complete range of magnetic fields. Two important aspects of the singlet-triplet crossover, revealed particularly in high-field PL spectra, require careful accounting of the Zeeman energies of the initial trion and the final electron states. First, the actual crossover point is shifted to much lower fields ($B_c=24$ T) than the ~70 T that is expected when Zeeman energies are disregarded. Second, and less obvious, the singlet-triplet crossing is *hidden* from direct observation, i.e., the measured T_s and T_{td} PL peaks themselves do *not* cross. This is because, following emission, the spin (and therefore energy) of the final remaining electron is different for T_s and T_{td}. Rather, the crossover is revealed by an exchange of *intensity* between the T_s and T_{td} lines in PL, and by their temperature dependence above and below B_c.

Single 120-Å CdTe/Cd$_{0.85}$Mg$_{0.15}$Te QWs were grown by molecular-beam epitaxy on (100)-oriented GaAs substrates

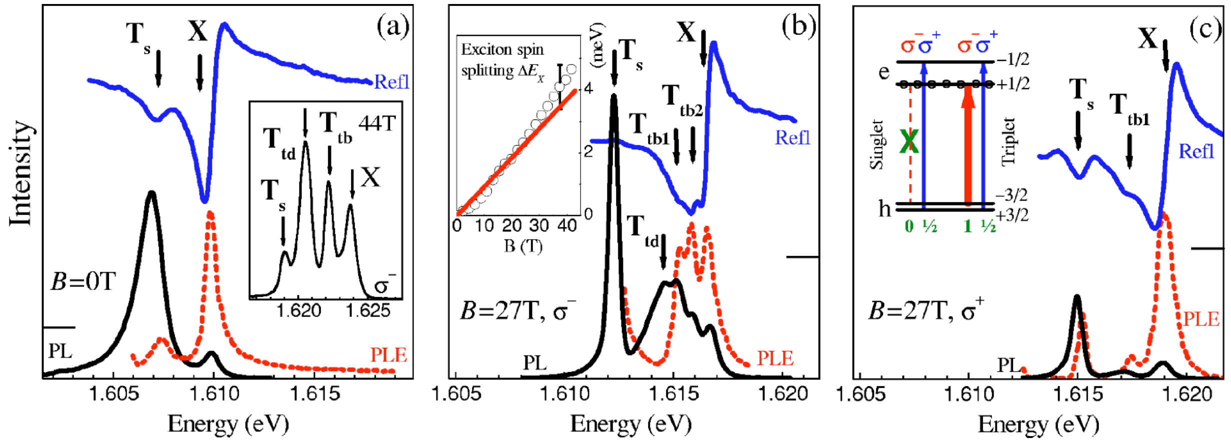

FIG. 1. (Color online) PL, PLE, and reflectivity (Refl) spectra of a 120-Å CdTe/Cd$_{0.85}$Mg$_{0.15}$Te QW with $n_e = 2\times10^{10}$ cm^{-2} at $T = 1.3$ K. The singlet (T_s), dark triplet (T_{td}), two bright triplet (T_{tb1} and T_{tb2}) trions, and the neutral exciton (X) are clearly seen. (a) Spectra at 0 T. Inset: σ^- PL at $B = 44$ T. (b,c) Spectra at 27 T in σ^- and σ^+ polarizations. Inset (b): X Zeeman splitting (circles) and electron splitting (line) for $g_e = -1.60$. Inset (c): Schematic of transitions leading to photocreation of T_s and T_{tb}. Transition probabilities are coded by the arrow thickness; the dashed line means the forbidden transition.

by wedge doping, which allows different electron densities n_e on the same wafer.[20] The data presented here were from a structure with $n_e = 2\times10^{10}$ cm^{-2}. Polarized optical spectra were measured at low temperatures (1.3–10 K) and in magnetic fields applied parallel to the growth axis (Faraday geometry). DC fields to 33 T (Nijmegen) and pulsed fields to 44 T (Los Alamos) were used. Ti:sapphire or He-Ne lasers with power density <1 W/cm^2 were used for excitation via fibers or by direct optical access. Circularly polarized light was used to resolve the exciton and trion spin orientation.

Zero-field optical spectra are shown in Fig. 1(a), where the well-known pair of resonances associated with the neutral exciton X and singlet trion T_s are clearly seen in PL, PLE, and reflectivity. Triplet states, being unbound at zero field, are not observed. Linewidths are <1.5 meV, much smaller than the 3-meV trion binding energy (taken as the energy difference between X and T_s lines). The $T_s:X$ ratio of oscillator strengths is 1:9 (from PLE and reflectivity), permitting evaluation of the two-dimensional electron gas (2DEG) density.[21] At 44 T (inset), the PL spectra develop two additional strong peaks between the X and T_s lines, which we assign to dark and bright triplets based on their polarization, energy, and evolution with magnetic fields as discussed below.

In finite magnetic fields, correct assignment of the various optical transitions to the proper exciton or trion state is essential. Figures 1(b) and 1(c) show the polarized optical spectra at 27 T. The neutral exciton X is readily identified in reflectivity, where it dominates all other resonances, exhibits equal oscillator strength in both σ^+ and σ^- polarizations, and also appears in an undoped reference sample. The features observed at the same energy in PL and PLE spectra are therefore also assigned to X. Note that while X is strong in PLE spectra, it is weak in PL due to thermalization to lower-lying trion states.

At 27 T, the X Zeeman splitting is ~2.7 meV. The field dependence of the X and electron Zeeman splittings are shown in the inset. The latter, determined by spin-flip Raman scattering,[22] indicates an electron g factor $g_e = -1.60$. The exciton spin splitting, $\Delta E_X = (g_{\mathrm{hh}} - g_e)\mu_B B$, therefore implies a small heavy-hole g factor ($|g_{\mathrm{hh}}| < 0.2$) which actually changes sign at ~18 T.

Trion formation involves a photocreated electron-hole pair and a background electron from the 2DEG. In high magnetic fields, when the 2DEG is totally spin polarized ($B > 4$ T in this sample), singlet and triplet trion states can be identified by their distinct polarizations in PLE, reflectivity, and PL spectra. The singlet trion T_s with the lowest Zeeman energy has net spin projection $S_z = S_{ez} + S_{hz} = 0 - \frac{3}{2} = -\frac{3}{2}$ (see Fig. 2). This singlet emits a σ^- photon upon recombination, leaving the remaining electron in the *upper* $\left(-\frac{1}{2}\right)$ Zeeman state. Formation of T_s, requiring a photoexcited electron with spin antiparallel to the 2DEG electrons, should therefore exhibit a strong PLE and reflectivity resonance *only* in σ^+ po-

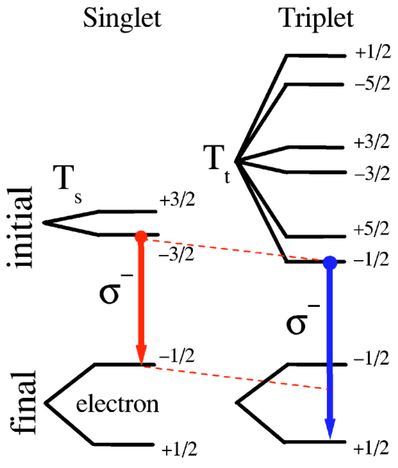

FIG. 2. (Color online) Schematic of the hidden singlet-triplet crossover of trion states in CdTe QWs. At high magnetic fields, the lowest dark triplet state has less energy than the lowest singlet. After recombination, however, the remaining electron is left in different spin states. Thus, the observed triplet PL energy remains *larger* than that of the singlet, as indicated by the lengths of the arrows.

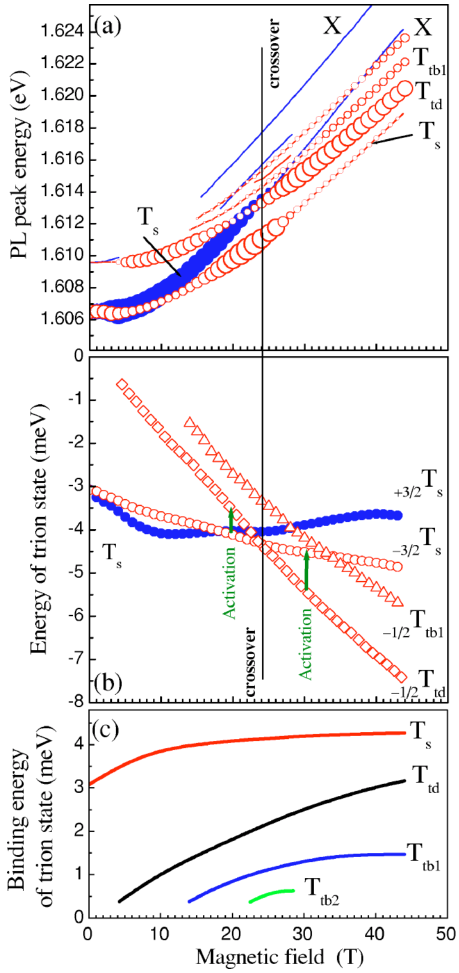

FIG. 3. (Color online) (a) Evolution of trion PL peaks in σ^- (open) and σ^+ (solid) polarizations. Symbol size indicates PL intensity. (b) Energies of the T_s (circles), $T_{\rm td}$ (diamonds), and $T_{\rm tb1}$ (triangles) trion states, measured from the neutral exciton X, showing B_c=24 T. Arrows mark the thermal activation processes measured in Fig. 4. (c) Trion binding energies from Coulomb interactions alone (no Zeeman terms).

larization, as observed. Indeed, T_s is quite strong in σ^+ PLE and reflectivity, and completely absent in the σ^- reflectivity (its absence in σ^- PLE is obscured by scattered light, where we always detect σ^- emission).

In contrast, triplet trions are predominantly polarized opposite to the singlet. The lowest-energy triplet has net spin $S_z = S_{ez} + S_{hz} = +1 - \frac{3}{2} = -\frac{1}{2}$. This triplet also emits a σ^- photon upon recombination, but unlike T_s, leaves the remaining electron in the *lower* $\left(+\frac{1}{2}\right)$ Zeeman state. This distinction will prove important shortly, when discussing the hidden singlet-triplet crossover. Formation of triplet trions, requiring predominantly spin-parallel electrons, should therefore exhibit resonances largely in the σ^- PLE and reflectivity. Indeed, two additional resonances in σ^- PLE and reflectivity are clear, and both have corresponding σ^- PL emission [Fig. 1(b)]. We therefore assign these lines to two "bright" (optically active) triplet trion states $T_{\rm tb1}$ and $T_{\rm tb2}$. Most importantly, however, an additional strong σ^- polarized PL peak is seen at energy 1.6145 eV. It has *no counterpart* in PLE or reflectivity spectra, meaning that the corresponding transition has no oscillator strength and is optically inactive. Thus, we assign this PL peak to the dark triplet $T_{\rm td}$. It has the largest binding energy among the triplet states, consistent with theoretical predictions.[11,15,16] The reason dark triplet PL appears at all is due to the small but nonzero probability of allowed radiative recombination via disorder scattering[14] or interaction with excess electrons, as demonstrated even in low-density 2DEGs ($n_e \sim 10^{10}$ cm^{-2}) (Ref. 24).

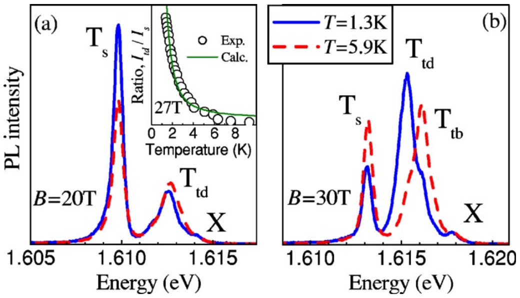

FIG. 4. (Color online) The temperature dependence of PL spectra measured in σ^- polarization at 20 T (a) and 30 T (b). Inset: the $T_{\rm td}$:T_s intensity ratio vs temperature. The line is a calculation based on a two-level model with 0.45 meV energy splitting.

Figure 3(a) shows the energy shifts of the trion PL with magnetic field, where symbol size indicates the PL intensity and weak transitions are traced by lines. We concentrate primarily on the evolution of the T_s and $T_{\rm td}$ peaks. For all accessible fields (0–44 T), the T_s PL peak occurs at the lowest measured energy. However, at about 24 T, the T_s PL intensity is significantly redistributed in favor of $T_{\rm td}$, strongly suggesting that the bound dark triplet has crossed the singlet to become the trion ground state. However, the observed PL lines themselves *do not cross*. This seeming contradiction is resolved by recalling that the electrons which remain after recombination of T_s and $T_{\rm td}$ reside in the upper $\left(-\frac{1}{2}\right)$ and lower $\left(+\frac{1}{2}\right)$ spin states, respectively, and these final states are split by the electron Zeeman energy $\Delta E_e = \mu_B |g_e| B$. As shown schematically in Fig. 2, the $T_{\rm td}$ state can have lower energy than T_s, but emission from $T_{\rm td}$ may still have the greater energy. At the crossover field B_c, when the T_s and $T_{\rm td}$ states themselves have identical energies, the energy of $T_{\rm td}$ emission still exceeds the energy of T_s emission by exactly ΔE_e. We describe the change of trion ground state as a "hidden" crossing between T_s and $T_{\rm td}$ (Ref. 23).

The hidden crossover is revealed particularly well by the temperature dependence of the trion PL peaks above and below B_c=24 T (Fig. 4). At 20 T (below B_c), increasing the temperature from 1.3 to 5.9 K depopulates the T_s state in favor of $T_{\rm td}$, implying thermal excitation of trions from a singlet ground state to a higher-energy dark triplet. In contrast, the same temperature increase at 30 T (above B_c) has the opposite effect—an increase in T_s emission and a reduction in $T_{\rm td}$ emission, implying thermal excitation from a dark triplet ground state to a higher-lying singlet state. In other words, the trion ground state has crossed over from singlet to dark triplet. A fit to the ratio of PL intensities versus temperature (the inset of Fig. 4) reveals that the radiative recombination times of the trion states satisfy $t_{\rm td} \gg t_s$ (Ref. 25), independently confirming the identification of T_{td} as a dark state.

Whereas the Zeeman splitting of the final electron states causes the "hidden" nature of the crossover, the different Zeeman splittings of the initial T_s and T_{td} states have an additional important consequence. Namely, the crossover occurs at a much lower magnetic field than it would in the absence of Zeeman effects. Figure 3(b) shows the *initial* energies of all trion states, measured with respect to the "center of gravity" of the neutral exciton Zeeman doublet, which accounts for the overall diamagnetic shift. Each trace has a contribution from the trion's Coulomb binding energy, as well as the additional Zeeman energy of the initial trion state. The striking feature of Fig. 3(b) is the evident crossover between T_{td} (with spin projection $S_z=-\frac{1}{2}$) and T_s (with $S_z=-\frac{3}{2}$) which occurs at 24 T. This value coincides very well with the field at which the PL intensity redistribution occurs. Note also that a bright triplet state T_{tb1} (with $S_z=-\frac{1}{2}$) crosses the singlet at ~34 T. For future comparison with theory, we also plot in Fig. 3(c) the trion binding energies resulting from Coulomb interactions alone (i.e., *without* Zeeman terms). It is evident that the actual crossover field is indeed reduced due to the electron Zeeman splitting ΔE_e, without which B_c would be estimated to ~70 T, in good qualitative agreement with theoretical predictions for II-VI QWs (Ref. 17).

As discussed briefly above, the data also reveal another unique feature: a second bright triplet state T_{tb2}. It is detected in PL, PLE, and reflectivity spectra between 22 and 28 T [see Figs. 1(b) and 3(c)]. While CdTe QWs are characterized by strong Coulomb interactions, this enhancement is not enough to ensure binding of additional trion states because the neutral exciton—relative to which a trion may or may not be bound—is also more tightly bound. Some additional physics is needed here. One possibility is that trion binding energies are enhanced in these QWs by "bipolaron" effects, wherein the polarization clouds of two electrons in the trion partly overlap, lowering the total energy relative to the neutral exciton X (Ref. 26).

In conclusion, combined PL, PLE, and reflectivity studies reveal the detailed energy spectrum of charged trions over a wide range of magnetic fields. These trions exemplify a canonical problem of interest in many solid-state, atomic, and nuclear physics problems: a three-particle spin system with long-range Coulomb interactions. We have confirmed a high-field crossover from the singlet to dark triplet trion state, upholding long-standing theoretical predictions. It has been shown that the Zeeman spin splitting of electrons both reduces the crossover field to experimentally accessible values $B_c=24$ T, and also causes the crossover to be "hidden" from direct observation of the emission energies themselves. We have also observed a unique feature in the spectra, an additional bound bright triplet trion state, and indicated the physics that might explain its stability.

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