Spin spectroscopy of dark excitons in CdSe quantum dots to 60 T

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Polarization-resolved magnetophotoluminescence spectroscopy is used to study exciton spin states in 40–80 Å diameter chemically synthesized CdSe quantum dots (QDs) at temperatures $T=1.2-50$ K. The spin polarization is found not to saturate in magnetic fields to 60 T and time-resolved studies indicate a thermal population of exciton states. A simple model incorporating the angle-dependent Zeeman splitting and bright-dark level mixing in these randomly oriented quantum dots is constructed in quantitative agreement with the data. Fits using this model yield a dark exciton g factor of ~ 0.9 at $T=1.45$ K, which is independent of QD diameter and exhibits a surprising increase with increasing temperature.

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In light of recent interest in the exploitation of the optical and spin-dependent properties of quantum dots (QDs) for applications ranging from QD-based lasers[1] to quantum computation[2] to fluorescent tagging of biological systems,[3] it has become increasingly important to understand the nature of the fundamental optical transitions in these systems. Chemically synthesized CdSe QDs are promising for many of these applications due to their bright luminescence, which is size tunable across the visible spectrum.[4] However, the ground state of these QDs is thought to be an optically inactive, or dark, exciton.[5] It is therefore of great interest to understand the radiative pathway of this nominally forbidden optical transition.

Here we measure the polarization-resolved magnetophotoluminescence (PL) of chemically synthesized CdSe QDs in pulsed magnets up to 60 T, generating Zeeman splittings ($\Delta E_Z \sim 3.5$ meV for $g \sim 1$) that approach the electron-hole exchange energies (~ 5 meV) in these mesoscopic systems. We determine that the PL polarization from these QDs, while well fitted by a simple two-level model at fields $B < \sim 20$ T, shows a surprising lack of saturation at higher fields up to $B=60$ T. Coupled with time-resolved photoluminescence measurements, these results appear to confirm the theoretical prediction[6] that the dark exciton ground state experiences a strong, polarization-preserving, field-induced coupling to the optically active excitonic states. Further, we are able to construct a simple model based on these theoretical predictions that is in quantitative agreement with our data and which allows us to extract the g factor of the dark exciton. The values obtained disagree with both earlier theoretical predictions[6] and previous measurements of the optically active exciton states.[7,8]

Samples consist of an ensemble of randomly oriented, nearly monodisperse ($\sim 5\%$ rms distribution in diameter) CdSe QDs with diameters of 40, 57, or 80 Å, suspended in insulating polymer films.[9] PL is excited and detected using a single optical fiber coupled to the sample, which is located in a ^{4}He cryostat in the bore of either a 60 or 40 T pulsed magnet such that both excitation and collection occur parallel to the applied field. Thin-film circular polarizers between the fiber and sample permit detection of either $\sigma+$ or $\sigma-$ helicities of PL, and full optical spectra are acquired every 1.5 ms throughout the entire 2000 ms (60 T magnet) or 500 ms (40 T magnet) magnet shot.[10] The excitation, at 442 or 400 nm (2.81 or 3.10 eV), is kept in the low-power regime (~ 0.3 W/cm^2, corresponding to less than 0.1 exciton per QD) to avoid Auger and biexciton effects. Furthermore, measurements in a low-field (<4 T) optical cryostat show no pump-induced polarization of the excitonic luminescence when pumping with circularly polarized light at these energies. This is likely due to the nonresonant nature of the pump (~ 1 eV above the band gap).

Figure 1(a) shows a characteristic PL spectrum from the 57 Å diameter QDs at $T=1.45$ K in 0 and 60 T magnetic fields. The linewidth of $\Gamma \sim 60$ meV is typical of all QDs measured and arises due to the finite QD size distribution. The PL is unpolarized in zero field, and becomes circularly polarized with increasing magnetic field, with the $\sigma-$ ($\sigma+$) polarized emission gaining (losing) intensity with increasing field, as shown in Fig. 1(b).[11] Further, if we consider the PL polarization $P=(I_{\sigma-}-I_{\sigma+})/(I_{\sigma-}+I_{\sigma+})$ [Fig. 1(c)], we find that P never attains full saturation. At 1.45 K, the polarization starts to level off at $P \sim 0.60$ at low fields ($B < \sim 20$ T) and subsequently increases slowly to a value of $P \sim 0.73$ by $B=60$ T, still well below $P=1$. Figure 1(c) also shows that the polarization drops quickly with increasing temperature, reminiscent of the behavior of optically active excitons thermally populating two Zeeman-split spin levels.[12]

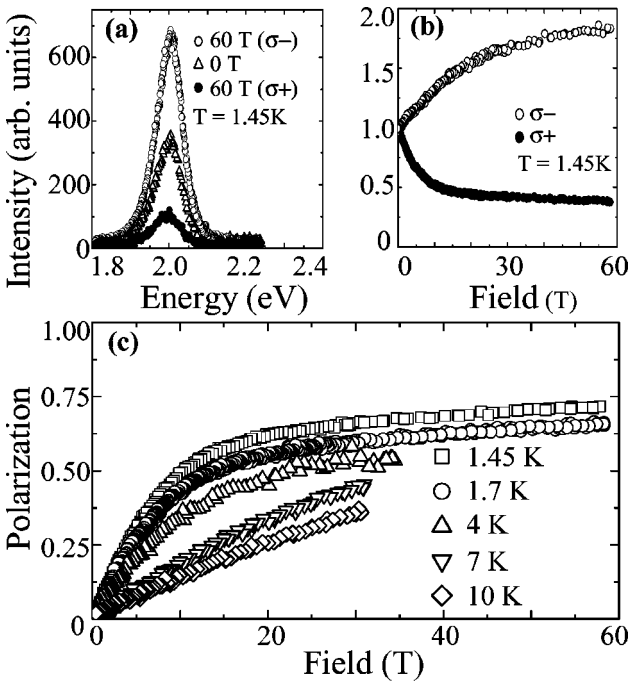

FIG. 1. (a) PL spectra from 57 Å quantum dots at $T=1.45$ K and $B=0$ and 60 T ($\sigma+$ and $\sigma-$). (b) The normalized intensity of the $\sigma+$ and $\sigma-$ PL vs field. (c) PL circular polarization at different temperatures. At $T=1.45$ K, data show an initial saturation near $0.6(B\sim 20$ T) and subsequent slow growth to $0.73(B=60$ T), still well below complete polarization ($P=1$).

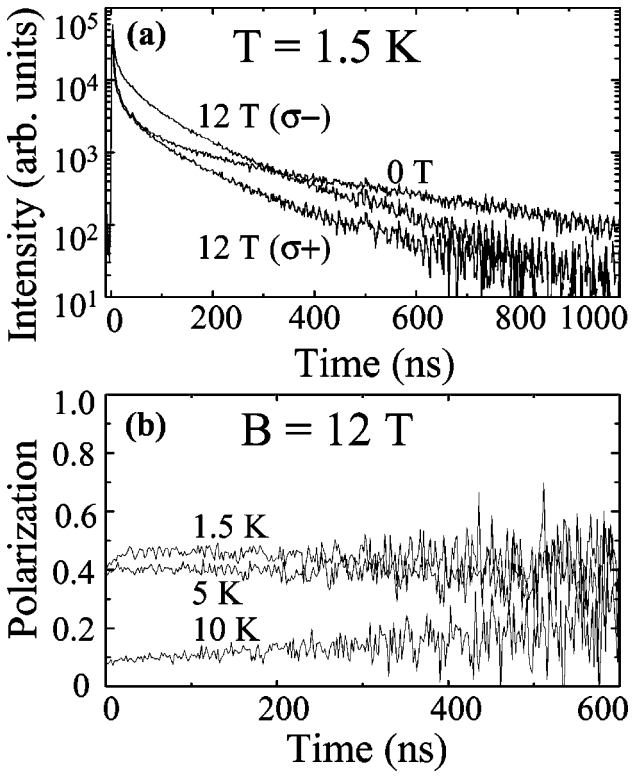

FIG. 2. (a) Time- and polarization-resolved PL (logarithmic scale) at $B=0$ T and for $\sigma+$ and $\sigma-$ at $B=12$ T for 40 Å diameter QDs. (b) Time-resolved PL polarization at different temperatures from the same sample.

Time-resolved studies of the PL decay in an 18 T superconducting magnet (Fig. 2) further support the notion of a thermal distribution of excitons. The QDs are excited at a wavelength of 400 nm by optical pulses from a frequency-doubled Ti:sapphire laser, pulse picked from $f=76$ MHz to 540 kHz due to the long (of order 100 ns) radiative lifetime of the QDs, and the PL decay is measured using time-correlated single-photon counting. Modal dispersion through the optical fiber coupling to the sample limits the temporal response to $\sim$160 ps. Characteristic decay curves at $T=1.5$ K are shown in Fig. 2(a) at $B=0$ T, and for both circular polarizations at $B=12$ T. As observed previously,[5,13] the PL decay is nonexponential and slow, becoming faster with increasing applied field. Immediately following excitation [Fig. 2(b)], the degree of circular polarization remains roughly constant throughout the decay and is approximately equal to the value obtained in the time-integrated PL (Fig. 1). The lack of any significant structure in the time-resolved PL indicates a thermal distribution of excitons within Zeeman-split spin sublevels and limits any spin-relaxation processes to time scales less than $\sim$1 ns.[5,14]

In order to understand these data we must take a more detailed look at the energy spectrum of the ground-state exciton in these QDs. Previous work[15] has established that the PL from small ($\leqslant$100 Å diameter) CdSe QDs is significantly redshifted from the absorption edge due to the effects of quantum confinement on the photoexcited carriers. This confinement also gives rise to a large electron-hole exchange energy, which lifts the degeneracy of the bulk exciton state and generates a pronounced fine structure. The energy levels are calculated[6] and shown in Fig. 3(a), where solid lines indicate optically active and dashed lines nominally forbidden transitions. The result is an excitonic energy spectrum where the eigenstates are linear superpositions of the bulk band electron and hole eigenstates. Superscripts differentiate between superposition states with the same total angular momentum but different total energy.

Within this picture the exciton ground state is located $\sim$5 meV below the lowest-energy optically active exciton state ($J=\pm 1^L$) and is dark, having total spin projection on the crystal hexagonal axis $J=\pm 2$.[5,6,15,16] While optical transitions to and from a $J=\pm 2$ state are normally forbidden within the electric dipole approximation, transitions may occur with optical phonons, or via magnetic-field-dependent mixing with optically active $J=\pm 1^L$ exciton states.[5,6] Support for this scenario comes from the observation of a decrease in both PL lifetime and LO-phonon line intensity (in fluorescence-line-narrowing studies[5]) with increasing magnetic fields up to 10 T, and also from the apparent insensitivity of the optical response to the properties of the QD surface.[15]

This field-dependent energy level mixing is geometry dependent. The crystalline and shape anisotropy of these slightly ellipsoidal (prolate) wurtzite CdSe QDs breaks the rotational symmetry of the exciton spin in zero field, constraining it to lie along the c axis of the crystal [Fig. 3(b)]. As a result, magnetic fields applied parallel to the c axis induce

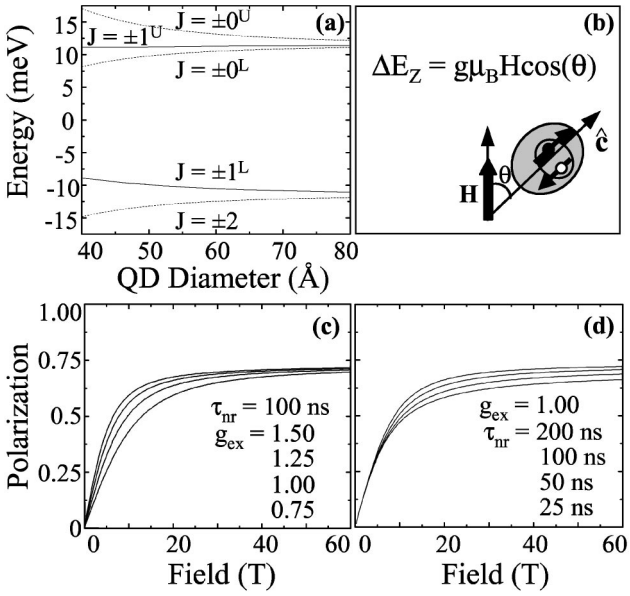

FIG. 3. (a) Calculated energies of the exciton fine structure in CdSe QDs for optically active (solid lines) and dark (dashed lines) states. The $J=\pm 2$ dark exciton ground state mixes with the lower branch ($J=\pm 1^L$) of the optically active exciton in fields applied perpendicular to the QD c axis. (b) Schematic of a CdSe QD, with intrinsic c axis oriented randomly with respect to the field and observation axis. (c), (d) The modeled polarization [Eq. (4)], for various g_{ex} and τ_{nr}.

a Zeeman splitting proportional to the exciton g factor g_{ex}. In contrast, magnetic fields orthogonal to the c axis generate no Zeeman splitting, but rather admix the $J=+2(-2)$ dark state with the optically active $J=+1^L(-1^L)$ excitons, thus inducing direct, circularly polarized optical transitions from the dark exciton and increasing the overall radiative recombination rate.

These high-field studies thus effectively measure the PL polarization from an ensemble of randomly oriented QDs with varying Zeeman splittings as well as varying admixtures of ground and excited states. Within the electric dipole approximation the relative probabilities of detecting $\sigma\pm$ light from a $J=\pm 1^L$ exciton oriented at an angle θ to the field (and observation) axis are $\chi_{J=+1}(\sigma\pm)\propto(1\pm\cos\theta)^2$ and $\chi_{J=-1}(\sigma\pm)\propto(1\mp\cos\theta)^2$. However, the population of the $J=\pm 2$ levels is the relevant thermodynamic quantity for these mixed states and given an angular-dependent Zeeman splitting we have a Boltzmann factor of the form $\Delta=g_{ex}\mu_B\mathbf{H}\cdot\mathbf{c}=g_{ex}\mu_B H\cos\theta$. Assuming a thermal distribution between these spin-split levels, the intensity of the detected PL in $\sigma+$ and $\sigma-$ polarization is therefore

$$I_{\sigma\pm}(x)=[(1\mp x)^2 e^{\Delta\beta/2}+(1\pm x)^2 e^{-\Delta\beta/2}]/[e^{\Delta\beta/2}+e^{-\Delta\beta/2}], \tag{1}$$

where $x=\cos\theta$ and $\beta=(k_BT)^{-1}$. Integrating over all orientations and computing the PL polarization yields

$$P(H,T)=\int_0^1 2x\tanh(\Delta\beta/2)dx \Big/ \int_0^1 (1+x^2)dx. \tag{2}$$

In the limiting case of low temperatures (or high fields) when $\Delta\beta\gg 1$, this polarization $P(H,T)\to 0.75$. This is the maximum possible PL polarization that can be reached in a system of randomly oriented wurtzite QDs, and it should be noted that the data in Fig. 1(c) indeed approach this limit at the lowest temperatures and highest fields.

One must also account for the influence of the perpendicular component of magnetic field, which mixes the dark and bright exciton states, thus increasing the radiative quantum efficiency $q(H,x)$ for dots oriented orthogonal to the field. In this case the relative contribution of different QDs to the PL depends on the ratio of radiative (τ_r) and nonradiative (τ_{nr}) decay times as $q(H,x)=[1+\tau_r(H,x)/\tau_{nr}]^{-1}$. We can then express the radiative lifetime[6] as

$$\frac{1}{\tau_r(x)}=\frac{3}{4\tau_0}\frac{\sqrt{1+\zeta^2+2\zeta x}-1-\zeta x}{\sqrt{1+\zeta^2+2\zeta x}}. \tag{3}$$

Here, τ_0 is the radiative decay time of the bright exciton ($=1.6$ ns) and $\zeta=g_{ex}\mu_B H/3\eta$, where η is the electron-hole exchange splitting[6] (calculated to be 2.22, 0.81, and 0.28 meV in the 40, 57, and 80 Å diameter QDs, respectively). Physically, Eq. (3) describes how the lifetime for mixing-induced recombination of dark excitons ranges from infinity (when $H\to 0$, or when $c\|\mathbf{H}$, and neglecting phonon-mediated recombination) down to a value near the $J=\pm 1^L$ exciton radiative lifetime when mixing is maximized ($c\perp\mathbf{H}$ and $H\to\infty$). Thus, the polarization becomes

$$P(H,T)=\int_0^1 2x\tanh(\Delta\beta/2)q(H,x)dx \Big/ \int_0^1 (1+x^2)\times q(H,x)dx, \tag{4}$$

which reduces to Eq. (2) in the limit $\tau_{nr}\gg\tau_r$ where nonradiative transitions are negligible.

In the opposite limit of low radiative quantum efficiency ($\tau_r\gg\tau_{nr}$), such as may be realized in low fields where mixing is small, $q(H,x)\propto(1-x^2)$ and the PL polarization $P(H,T)$ approaches a maximum value of only 0.625 at low temperatures. This is because QDs with $c\perp\mathbf{H}$ radiate more efficiently, but have zero g factor, thus lowering the overall polarization. With increasing magnetic field, however, the radiative decay time τ_r is decreased for the majority of QDs and a gradual growth of the maximum allowed polarization from 0.625 to 0.75 may be realized. Precisely such behavior is observed in Fig. 1(c), where the low-temperature polarization initially approaches saturation near $\sim$0.6 and grows slowly to $\sim$0.73 by the highest fields. Simulations of the PL polarization from the 57 Å QDs are shown in Figs. 3(c) and 3(d) for different values of g_{ex} and τ_{nr}. Finally, it should be noted that while according to this model the PL polarization does not saturate in fields up to 60 T, the occupancy of the lowest-energy spin-split level is completely saturated by $B\sim 10$ T.

This model [Eq. (4)] provides an excellent fit to the measured PL polarization, as shown in Fig. 4(a) where data from all three sizes of QD are shown at $T=1.45$ K, along with the modeled polarization for the 57 Å QDs. Interestingly, the data are all roughly equivalent—this stems from the similar and balancing role played by τ_{nr} and the exchange interac-

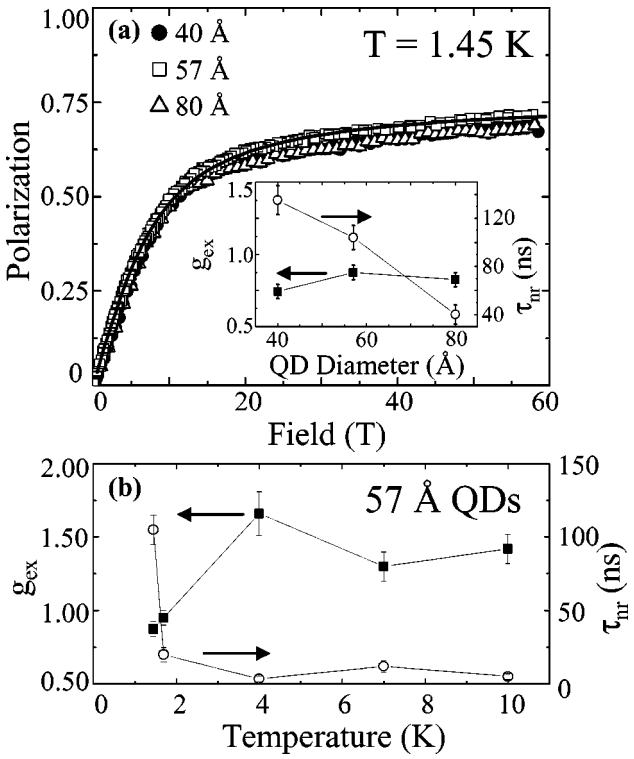

FIG. 4. (a) The nearly identical PL polarization in 40, 57, and 80 Å diameter QDs to magnetic fields of 60 T at low temperature, along with the theoretical polarization given by Eq. (4). Inset: Extracted values of g_{ex} and τ_{nr} for these QDs. (b) Extracted values of g_{ex} and τ_{nt} vs temperature, for the data in Fig. 1(c) (57 Å diameter QDs).

tion η [see Eq. (3)], both of which decrease with QD size. The best-fit values of g_{ex} and τ_{nr} are shown in the inset. While g_{ex} and τ_{nr} are rather sensitive to the input values of η, which may be calculated but are difficult to measure directly, one general trend is worthy of note: the exciton g factors at this low temperature exhibit values between 0.74 ± 0.05 and 0.87 ± 0.05, which is less than expected for either the dark or bright exciton states ($g_{ex}=1.004-1.5$ for the bright states[7,8] and $g_{ex}\sim4$ for the dark states,[6] detailed below).

Finally, we model the temperature-dependent polarization data shown in Fig. 1(c) to extract g_{ex} and τ_{nr} as a function of temperature in the 57 Å QDs. Figure 4(b) shows these best-fit parameters, and reveals a surprising growth of the measured exciton g factor with increasing temperature, from $g\sim0.9$ at the lowest temperatures to $g\sim1.4$ at $T=10$ K. The high-temperature values are consistent with previously measured values of the bright exciton states,[7,8] but are considerably smaller than $g_{ex}=g_e-3g_h\sim4$ calculated for the dark exciton state.[6] This difference may be connected with the uncertainty in our knowledge of the Luttinger γ parameters, with small variations resulting in dramatic changes in g_h, including sign reversal. Further, calculations of g_h were done using the standard boundary condition that the hole wave function is zero at the nanocrystal surface. However, a more general form of the boundary condition demands that only the current density vanish at the surface, leading to a surface contribution to the electron and hole g factors that can considerably change their values.[17] This explanation may also account for the difference in g factors measured in samples grown by different techniques,[7] and hence yielding different surface structures.

The unexpected behavior of g_{ex} with temperature has strong parallels to behavior observed in diluted magnetic semiconductors (DMS).[18] In those materials, as the temperature drops, the coupling to the magnetic dopants becomes more pronounced, and can lead to changes in the electron g factor of an order of magnitude or more. In a similar vein, the temperature dependence of g_{ex} in these CdSe QDs can be interpreted as arising from an exchange interaction. Though the sign of this temperature dependence is opposite that observed in DMS, this may be explained by a change in the sign of the exchange constant. We therefore suggest that this variation in g_{ex} may be due to an interaction with the QD surface, which likely contains uncompensated spins[19] weakly coupled to the photogenerated carriers within the QDs.

In conclusion, we have measured the polarization properties of the dark exciton ground state in chemically synthesized CdSe QDs. We find that this polarization does not saturate in fields to 60 T and time-resolved studies confirm a thermal population of the dark exciton states. Through simple but quantitative modeling we obtain good agreement with our data and are able to extract the dark exciton g factor. We find that our measured values are roughly consistent with experimental measures of the optically active excitons at temperatures above $T\sim4$ K,[7,8] but are in disagreement with theoretical predictions[6] and show a surprising decrease with decreasing temperature. An interaction of the photogenerated carriers with uncompensated spins at the QD surface is proposed as a possible explanation for this unexpected behavior.

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[19] Such spins could arise from, e.g., uncompensated bonds due to imperfect passivation at the nanocrystal surface.