Band-Edge Exciton Fine Structure of Single CdSe/ZnS Nanocrystals in External Magnetic Fields

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We report a spectroscopic study of the two lowest-energy exciton levels of individual CdSe/ZnS nanocrystals under applied magnetic fields. Field-induced coupling between the bright and the dark excitonic states is directly observed in the low-temperature photoluminescence spectrum and decay and allows the determination of the angle between the nanocrystal c axis and the field. Orientation-dependent Zeeman splittings of the dark and bright exciton sublevels are measured and provide the corresponding exciton Landé factors, as well as spin-flip relaxation rates between Zeeman sublevels.

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Over the past decade, significant efforts have been spent on magneto-optical properties of semiconductor quantum dots, motivated by the need to understand the fundamental spin structure of the quantum dot electronic states and by potential applications in solid-state spintronics [1] and quantum information processing [2]. Among quantum dots, chemically synthesized CdSe nanocrystals (NCs) have already shown suitable properties for nanoscale electronics [3–5], laser technology [6], and biological fluorescent labeling [7,8]. They are particularly attractive due to their bright luminescence, which is size tunable across the visible spectrum.

It is well established that the photoluminescence (PL) of spherical or nearly spherical NCs at low temperature arises from the two lowest levels of the band-edge exciton fine structure, namely, the long-lived ground excitonic state $|F\rangle$ (also called the ''dark'' state, with a total spin projection $J = \pm 2$ on the crystal c axis) and the lowest-energy optically active state $|A\rangle$ ($J = \pm 1^L$), which lies a few meV above the ground state [9–11]. Indeed, recent studies based on temperature dependence of PL spectra [12,13] and PL decay [12], as well as polarization-resolved spectroscopy [14], showed that luminescence of individual CdSe NCs with cylindrical symmetry display two sharp zero-phonon lines (ZPLs), which are attributed to purely radiative recombination from the two lowest (bright and dark) exciton states. Yet, the origin of the $|F\rangle$ ZPL remains an open question.

Magneto-optical methods largely contributed to the understanding of the NCs band-edge exciton fine structure. Most of the magneto-optical studies have been applied to ensembles of NCs [9,15–18], where averaging over orientations and size distributions reduces the amount of available quantitative information. As a consequence, Zeeman splittings of fine structure exciton levels are not resolved, and the corresponding Landé g factors are not well known. A recent low-temperature study of single NCs under magnetic fields allowed measurements of Zeeman shifts within an exciton state doublet attributed to a distortion-induced splitting of the bright state [19].

In this Letter, we report a cw and time-resolved spectroscopic study of individual CdSe NCs in an external magnetic field (up to 7 T). Besides the direct observation of the field mixing between the two lowest fine structure states, we measure the Zeeman energy splitting of the dark and bright exciton states, extract their g factors, and determine the spin relaxation rates between dark exciton Zeeman sublevels. Furthermore, we observe an unexpected lifetime lengthening of the dark excitonic state with increasing fields, which suggests that the dark exciton ZPL takes its origin in an intrinsic magnetic coupling of bright and dark exciton states.

Samples of CdSe/ZnS core-shell NCs (Qdot655 from Quantum Dot Corporation, peak emission at 655 nm at room temperature) are prepared by spin coating clean glass coverslips with a nanomolar solution of NCs in polyvinyl alcohol. A home-built scanning confocal microscope is used to image single NCs excited with the 532 nm line of a cw frequency doubled Nd:YAG laser. It is based on a 0.95 numerical aperture objective which is inserted in a magnetic cryostat together with the sample and a piezoscanner. The objective axis is perpendicular to the magnetic field, allowing magneto-optical studies in the Voigt configuration. The emitted photons are filtered from the scattered excitation light by a bandpass filter (60 nm FWHM) and sent to a single-photon-counting avalanche photodiode and a spectrometer. The PL decay measurements are performed with a conventional time correlated single-photon-counting setup, using a pulsed laser source (optical parametric oscillator at 570 nm, 6 ps pulse width, 76 MHz repetition rate) and a pulse picker which reduces the repetition rate.

At 2 K, the luminescence intensity of most of the single NCs is remarkably stable and did not show any blinking. This high photostability allows the acquisition of resolution-limited PL spectra of single NCs. The NCs

that we studied display two ZPLs in their zero-field emission spectrum [12–14] as shown in the lowest spectrum of Fig. 1(a). These ZPLs, named F and A, have been attributed to the radiative recombination from the two lowest levels of the band-edge exciton fine structure. Tens of single NCs were studied as a function of the external magnetic field. We observed various spectroscopic behaviors which result from different relative orientations between the NC c axis and the magnetic field.

Figure 1(a) shows the evolution of a single NC PL spectrum as a function of the external magnetic field. This NC does not display a resolved Zeeman splitting of the ZPLs but only a broadening of the F ZPL at large magnetic fields. Moreover, the weight of this ZPL dramatically increases upon raising the field from zero to 7 T [Fig. 1(c)]. These observations suggest that the magnetic field is nearly perpendicular to the NC c axis and induces a mixing of the bright and dark exciton states, enhancing the oscillator strength of the latter. In order to determine the relative angle θ between the field and crystal axis, we recorded the field-dependent PL decay of this NC at 2 K. The decay is biexponential with a fast decay occurring in the nanosecond range and a much slower one with a lifetime of hundreds of nanoseconds at zero field [12,20,21]. The long decay time, which is assigned to the dark exciton radiative recombination, drastically shortens with increasing fields [from ~200 ns at 0 T to ~40 ns at 7 T, in Fig. 1(b)]. Indeed, the magnetic coupling opens an additional channel for ground exciton recombination via admixture in the $|F\rangle$ state of the $|A\rangle$ state. The decay rate of the dark exciton in a magnetic field B is given by [10]

$$\tau_F^{-1} = \frac{\sqrt{1+\zeta^2+2\zeta\cos\theta}-1-\zeta\cos\theta}{\sqrt{1+\zeta^2+2\zeta\cos\theta}}\frac{3}{4}\tau_0^{-1} + \tau_F^{-1}(0), \quad \text{with } \zeta = \mu_B g_e B/3\eta, \tag{1}$$

η being the exchange interaction energy ($\eta \sim 0.28$ meV for 4 nm-radius NCs [10]), μ_B the Bohr magneton, and $g_e \sim 0.9$ the electron g factor [22–24]. $\tau_F^{-1}(0) = 5.3 \times 10^{-3}$ ns^{-1} is the zero-field radiative decay rate of the dark exciton and τ_0^{-1} the decay rate of the $J = 0$ fine structure state of the band-edge exciton. By taking $\tau_0 = 2$ ns [10,25], and using θ as a fitting parameter, the field dependence of the long component decay rate is reproduced by the expression (1), for $\theta = (75 \pm 5)°$ [see Fig. 1(c)].

A markedly different spectroscopic behavior is obtained for small angles between the magnetic field and the NC c axis. As displayed in Fig. 2(a), a well resolved Zeeman splitting of the dark exciton sublevels $J = \pm 2$ is indeed observed in the emission spectra of single NCs, leading to 2 ZPLs named F_+ and F_-. The energy splitting is linear with the field [Fig. 2(b)], and its slope $\mu_B g_F \cos\theta$ is proportional to the dark state g factor g_F. Moreover, the evolution of the PL decay in a magnetic field shows a striking lengthening of the long time component with raising fields in the range 0–1 T [see Fig. 2(c)] which is

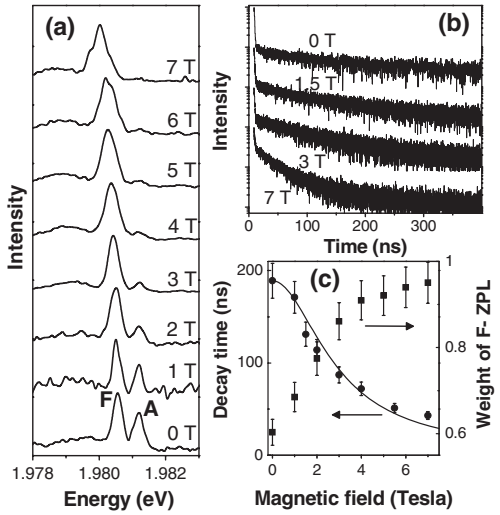

FIG. 1. (a) PL spectra of a single NC in a magnetic field nearly perpendicular to the c axis. The lines labeled A and F are the recombination ZPLs of the bright and the dark excitons, respectively. (b) PL decay of this NC for various intensities of the magnetic field. (c) Circles: Field-induced shortening of the PL long decay time. The solid curve is a fit which leads to the relative angle $\theta = (75 \pm 5)°$ between the NC c axis and the field, taking $\tau_0 = 2$ ns and $\tau_F(0) = 190$ ns in expression (1). Squares: Relative weight of the F line in the ZPL structure, as a function of the magnetic field.

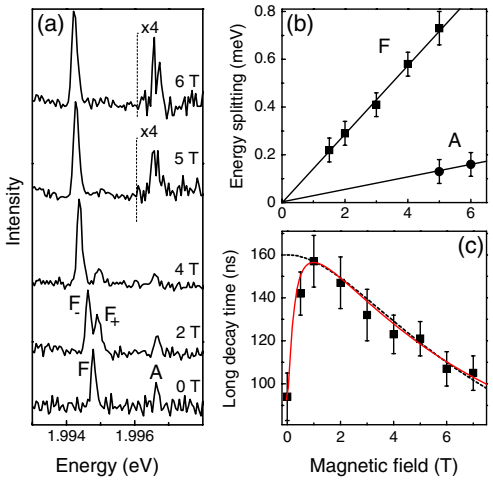

FIG. 2 (color online). (a) PL spectra of a single NC at 2 K, for various intensities of the magnetic field which is almost parallel to the c axis. (b) Zeeman energy splittings of the dark (F) and bright (A) exciton sublevels. Linear fits of Zeeman splittings yield $g_F \cos\theta = 2.5$ and $g_A \cos\theta = 0.45$. (c) Evolution of the long decay time with the magnetic field. The dashed curve is a fit with expression (1) for fields larger than 1 T, which yields $\theta = (25 \pm 5)°$, taking $\tau_0 = 2$ ns and $\tau_F(0) = 160$ ns. The solid curve is a modelization which takes into account the contribution of an intrinsic magnetic field to the mixing of bright and dark exciton states (see text).

discussed at the end of this Letter. At larger fields, the mixing between bright and dark states induced by the magnetic component normal to the c axis explains the shortening of the dark state lifetime and allows the determination of the NC orientation $\theta = (25 \pm 5)°$ using expression (1) [see dashed curve in Fig. 2(c)]. From the linear Zeeman splitting we further deduce the dark exciton g factor $g_F \sim 2.7$ for this NC. This value is in agreement with the theoretical estimation of $g_F = g_e - 3g_h \sim 3$ (g_h being the hole g factor) and consistent with the value $\sim$1.7 deduced from PL polarization measurements and averaged on ensembles of 4 nm-radius NCs [22]. At high magnetic fields ($B \geq 5$ T) a weak Zeeman splitting of the bright exciton sublevels shows up in the PL spectra. The bright exciton g factor g_A is then estimated to $g_A \sim 0.5$ for this NC. This value is smaller than $g_A \sim 1$ deduced from time-resolved Faraday rotation studies performed on NC ensembles [22]. Theoretical calculations led to disparate g factors which depend on the NC shape and size, as well as surface boundary conditions [22–24]. The g factors are also expected to display anisotropy [23,26]. This could explain the large difference between the g_A of our NCs with cylindrical symmetry and that obtained on nonsymmetric NCs [19].

An interesting feature of the emission spectra of Fig. 2(a) is the field-dependent intensity of the dark exciton Zeeman components. The weight of the higher energy ZPL (F_+) clearly drops with increasing fields. This is a signature of a spin-flip relaxation between dark exciton Zeeman sublevels which occurs with absorption and emission of acoustic phonons. Indeed, the existence of such spin-flip relaxations has previously been demonstrated from polarization-resolved magnetophotoluminescence studies of the dark exciton ground state on NC ensembles [11,17]. The spin-flip rates can be determined with a simple thermal mixing model [12,13] of $|F_-\rangle$ and $|F_+\rangle$ with rates $\gamma_1(N_B + 1)$ for $|F_+\rangle \rightarrow |F_-\rangle$ and $\gamma_1 N_B$ for $|F_-\rangle \rightarrow |F_+\rangle$, where $N_B = 1/[\exp(\Delta E_F/k_B T) - 1]$ is the Bose-Einstein number of phonons whose energy matches the Zeeman splitting ΔE_F and γ_1 the zero-temperature relaxation rate of the transition $|F_+\rangle \rightarrow |F_-\rangle$. Assuming identical pumping rates to the states $|F_+\rangle$ and $|F_-\rangle$, and identical radiative recombination rates $\Gamma_F(B)$ of these sublevels at a magnetic field B, we use rate equations to derive the populations of the states $|F_+\rangle$ and $|F_-\rangle$ in the stationary regime and at low saturation. The relative intensity of the luminescence arising from $|F_+\rangle$ in the dark exciton emission is given by $[\gamma_1 N_B + \Gamma_F(B)/2]/[\gamma_1(2N_B + 1) + \Gamma_F(B)]$. We can estimate the spin-flip rate at different energy splittings: $\gamma_1 \sim 4 \times 10^{-3}$, 8×10^{-3}, and 2×10^{-2} ns^{-1} for $B = 2$, 3, and 4 T, respectively. The decrease of γ_1 for reduced energy splittings ΔE_F is likely due to the decrease of the phonon density of states [27]. Indeed, a field-induced coupling between $J = +2$ and $J = -2$ states is unlikely for these NCs with the c axis nearly parallel to $\vec{B}$, although a high order effect cannot be completely ruled out. It is interesting to compare values of γ_1 to the zero-temperature spin-flip rate γ_0 between bright and dark exciton states in zero field. Typical values of the order of $\gamma_0 \sim 1$ ns^{-1} have been measured on those NCs [12], where the energy splitting between bright and dark states lies in the meV range. Such a large difference ($\sim$ 2 orders of magnitude) between γ_1 and γ_0 is related to the fact that high order phonon processes might be involved in $J = +2 \rightarrow J = -2$ spin-flip mechanisms.

In Fig. 3, we present the magnetic field dependence of the dark exciton energy splitting and decay rate of several NCs having different orientations. For comparison, decay rates are normalized to their zero-field values. The orientation θ of each NC is obtained from the fit of the decay rate evolution with the magnetic field for $B \geq 1$ T, taking $\tau_0 = 2$ ns in expression (1) [see Fig. 3(a)]. For all the NCs, the Zeeman splitting [see Fig. 3(b)] can be well reproduced by using the same value of $g_F = 2.7$. Note that varying the value of τ_0 in the range 1–4 ns also gives acceptable fits of the decay rates and leads to a confidence interval of 2.2–2.9 for g_F values.

Interestingly, we observe that NCs with small orientation angles θ display a lengthening of the dark exciton lifetime with increasing fields for $B \leq 1$ T. This

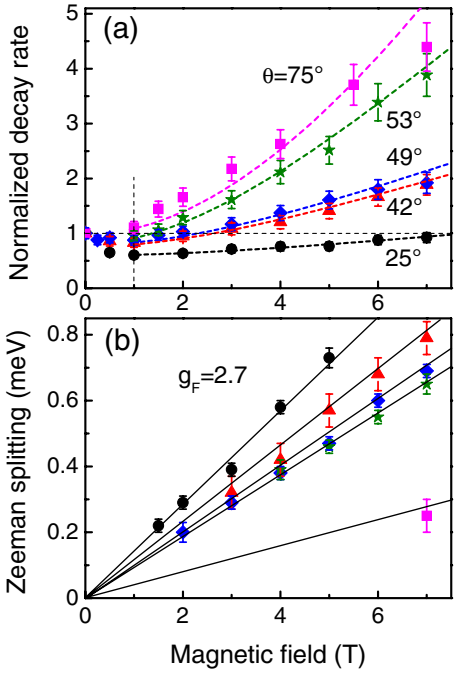

FIG. 3 (color online). (a) Evolution of the long decay rate as a function of the magnetic field, for five NCs. The decay rates are normalized to the zero-field decay rate. The data relative to the NC presented in Fig. 1 (squares), and that presented in Fig. 2 (circles), are included. The angle θ between the magnetic field and the NC c axis is derived for each NC from fits of the decay rates with expression (1) at fields larger than 1 T, taking $\tau_0 = 2$ ns. (b) Zeeman splitting of the dark exciton sublevels, for the same NCs. The solid lines are the calculated Zeeman splittings, taking the angles θ from (a), and $g_F = 2.7$ for all NCs.

observation indicates that the longitudinal component of the magnetic field decreases the $|F\rangle$ exciton oscillator strength by reducing an intrinsic contamination of the dark state by the optically active state. It also suggests that this intrinsic admixture takes its origin from an interaction with magnetic defects in the NC which can generate strong internal magnetic fields, enabling zero-phonon recombination to occur [10]. The external field tends to orient the intrinsic magnetic moment of these defects along its direction. If this direction is close to the c axis, the effect of a moderate external field is therefore a reduction of the contamination of $|F\rangle$ by $|A\rangle$. At large fields and for $\theta \neq 0$, the normal component of the external field will then strengthen the mixing between $|A\rangle$ and $|F\rangle$ states. This behavior can be qualitatively reproduced with a simple orientation model of an intrinsic magnetic moment in a field which is the superposition of the external field $\vec{B}_{\text{ext}}$ and a weak field $\vec{B}_0$ responsible for the alignment of the defect magnetic moments. In the NC, the field $\vec{B}_i$ created by these magnetic moments adds to the external field, resulting in an effective field which is written

$$\vec{B} = \vec{B}_{\text{ext}} + B_i \frac{\vec{B}_{\text{ext}} + \vec{B}_0}{\|\vec{B}_{\text{ext}} + \vec{B}_0\|}. \quad (2)$$

By using this expression for B in Eq. (1), the field evolution of the dark exciton lifetime is reproduced with $B_0 = 0.15$ T oriented perpendicularly to the c axis, $B_i = 3$ T, and $\tau_F^{-1}(0) = 4.4 \times 10^{-3}$ ns^{-1} [see the solid curve in Fig. 2(c)].

In the same vein, a longitudinal spin relaxation time lengthening with the magnetic field followed by shortening has been reported by Gupta *et al.* in a time-resolved Faraday rotation experiment performed on NC ensembles [22]. This observation was tentatively explained with a mechanism involving the hyperfine interaction with unpolarized nuclear spins. However, the hyperfine field contribution is most likely negligible in CdSe [28] since only a small fraction of ions (25% of Cd ions) have nuclear spins (and these spins are only 1/2). Instead, magnetic defects which potentially generate strong effective internal magnetic fields might be involved [10]. Magnetic properties have indeed been reported for CdSe NCs and attributed to a variety of sources, including dangling bonds [29], surface ligands [30,31], and defects in the nanocrystals [32]. Further magneto-optical investigations and theoretical models are needed to elucidate the physical origin of the alignment field $\vec{B}_0$ and the large internal fields $\vec{B}_i$.

In summary, various spectroscopic behaviors were found when applying an external magnetic field to single CdSe NCs, depending on the relative orientation of the NC c axis in the field. For the first time, coupling between the two lowest-energy excitonic levels, as well as Zeeman splittings of these levels, were clearly identified on single NCs and allow estimations for the bright and the dark exciton g factors. In further investigations, Zeeman splittings of exciton sublevels will be precious tools to probe the density of states of acoustic phonons as a function of energy, without the need to change the NC size. The ability to tune energy levels and spin relaxation rates within the band-edge exciton fine structure of single NCs also has potential applications in quantum information processes.

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