

Revealing the Exciton Fine Structure in PbSe Nanocrystal Quantum Dots

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We measure the photoluminescence (PL) lifetime, τ , of excitons in colloidal PbSe nanocrystals (NCs) at low temperatures to 270 mK and in high magnetic fields to 15 T. For all NCs (1.3-2.3 nm radii), τ increases sharply below 10 K but saturates by 500 mK. In contrast to the usual picture of well-separated “bright” and “dark” exciton states (found, e.g., in CdSe NCs), these dynamics fit remarkably well to a system having two exciton states with comparable - but small - oscillator strengths that are separated by only 300-900 μeV . Importantly, magnetic fields reduce τ below 10 K, consistent with field-induced mixing between the two states. Magnetic circular dichroism studies reveal exciton g -factors from 2-5, and magneto-PL shows >10% circularly polarized emission.

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Lead-salt semiconductor nanocrystals (NCs) based on PbS, PbSe, and PbTe are actively studied due to their potential impact on important technologies including telecommunication-wavelength optoelectronics (they exhibit size-tunable emission spanning the near- to mid-infrared [1–3]) and enhanced solar energy conversion (multiple excitons can be formed upon absorption of single photons [4, 5]). Other distinguishing characteristics include high photoluminescence (PL) quantum yields [6], very long exciton radiative lifetimes (τ) [6–9] and the ability to form core-shell heterostructures [10]. However, in contrast to their counterparts that emit at visible wavelengths (e.g., CdSe or CdS NCs), the fundamental electronic structure of lead-salt NCs remains an open question, despite more than a decade of experiments and often-conflicting theoretical consideration [11–14].

Electron-hole exchange interactions, crystal structure, band symmetry, spin-orbit coupling, and shape anisotropy all influence the underlying level ordering and oscillator strengths of band-edge excitons in colloidal NCs [15–18]. Understanding this “exciton fine structure” is especially important in NCs because it governs both absorptive and emissive optical properties. For example, in the common case of CdSe NCs these properties combine to split the $1S$ band-edge exciton into the now well-established fine structure of five distinct levels, wherein the lowest energy state is an optically-forbidden “dark” exciton that lies as much as $\Delta=2\text{--}15$ meV below the nearest optically-allowed “bright” exciton. Crucially, proof of dark excitons in CdSe NCs relied on measurements of PL and PL decays at low temperatures ($T < 2\text{K}$, so that $k_B T < \Delta$) and in high magnetic fields ($B > 10$ T, so that the magnetic energy $g_{ex}\mu_B B \simeq \Delta$) [15, 19, 20]. These studies revealed surprisingly long PL lifetimes at low temperature ($\sim 1 \mu\text{s}$) that shortened with applied field, consistent with optically-dark excitons that gain oscillator strength due to field-induced mixing with bright states.

In contrast with wide-gap semiconductors like CdSe (which have wurtzite/zincblende structure and direct bandgaps at the Brillouin-zone center Γ -point), lead-salt semiconductors such as PbSe are narrow-gap materials

having rock-salt crystal structure and direct gaps at the four-fold degenerate L -point at the Brillouin zone edge. In further distinction, electrons and holes in PbSe exhibit very similar masses and giant g -factors ($|g| \sim 30$) due to strong spin-orbit coupling [21]. As such, exciton fine structure in lead-salt NCs is expected to be rather different, and several theoretical studies have been reported for PbSe NCs: Four-band envelope wavefunction methods first suggested 1-5 meV exchange energies and predicted an optically-allowed exciton ground state [11], whereas tight-binding calculations anticipated that the nominally degenerate L -points are split in NCs by tens of meV by intervalley coupling [12]. More recently, empirical pseudopotential approaches [14] suggested that PbSe NCs possess a single optically-forbidden exciton ground state that lies $\Delta=2\text{--}17$ meV below a 3-fold degenerate manifold of optically-allowed exciton levels.

Experimentally, the PL decay time (τ) from PbSe NCs was first reported to be hundreds of nanoseconds at room temperature [6, 7], which is long compared to CdSe ($\tau=20$ ns). As a possible explanation, dark exciton ground states and large bright-dark splittings ($\Delta > 25$ meV) were considered, as were enhanced dielectric screening effects [6]. Subsequent studies revealed that τ increased to 1-5 μs upon cooling from 200 \rightarrow 50 K, prompting suggestions that Δ lies in this energy range ($\sim k_B \cdot 100$ K) [8]. Moreover, τ was found to increase yet *again* down to reported base temperatures of 1.4 K [8, 9], which was attributed to freezing-out of quantized acoustic phonon modes in the NC (which were thought to assist the recombination of presumed dark excitons). However, 1.4 K was not sufficiently low to saturate τ , complicating accurate fitting of the relevant energy scale. Further, no studies of τ in magnetic field, which were essential for confirming bright and dark exciton states in CdSe NCs, have been reported to date.

Here we measure PL and PL decay times τ in infrared-emitting rocksalt PbSe NCs at temperatures over five times lower than previously reported (to 270 mK), and also in high magnetic fields to 15 T. We find that τ increases sharply below 10 K, but saturates below

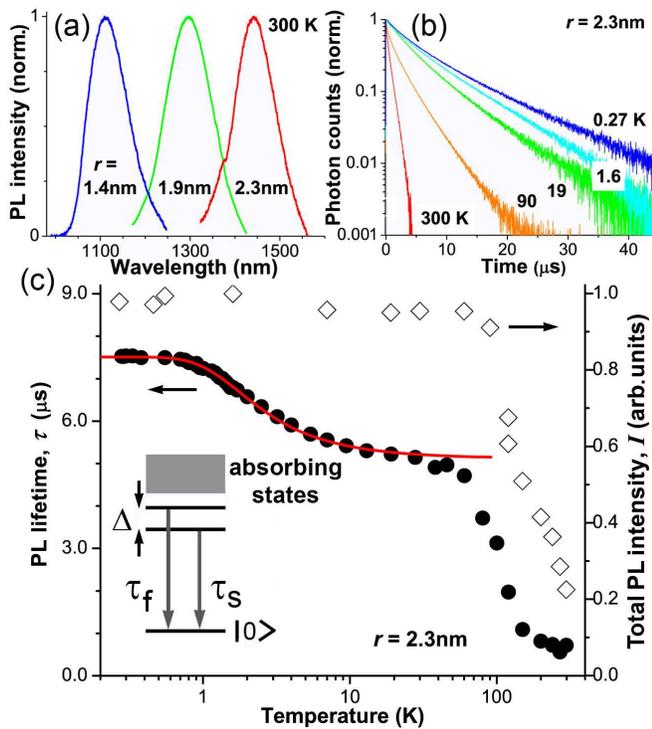


FIG. 1: (a) PL spectra from PbSe NC ensembles of different size. (b) PL decays. The lifetime τ increases as temperature T decreases. (c) Left axis: τ versus T from 270 mK to 300 K. Line is a fit of the low- T data to a two-level model (see inset). Right axis: The integrated PL emission, I . Note *both* τ and I increase \sim fivefold upon cooling to 50 K in these NCs, indicating freeze-out of competing non-radiative recombination channels. I remains unchanged below 50 K.

500 mK. In marked contrast to the ‘conventional’ exciton fine structure found in CdSe and other wide-gap NCs (i.e., clear dark and bright exciton levels with orders-of-magnitude different oscillator strengths, well-separated in energy by 2-15 meV), the dynamics in PbSe NCs fit remarkably well to a new exciton structure containing two *weakly*-emitting states with *comparable* oscillator strength, that are split by a surprisingly small energy of only 290-870 μ eV ($r=2.3$ -1.3 nm). This energy scale is much smaller than recently predicted for PbSe NCs [14], and is also much less than any quantized phonon energy in the NC. Importantly, magnetic fields reduce τ only below 10 K, consistent with field-induced mixing between these two states. Further, magnetic circular dichroism studies establish the magnetic Zeeman energy of the $1S$ absorbing exciton states in PbSe NCs for the first time ($|g_{ex}|$ ranges from 2-5), and magneto-PL from the emitting excitons reveals $>10\%$ circular polarization, also implicating contributions from Zeeman-split excitons.

Oleic-acid capped PbSe NCs having high quantum yield ($>20\%$ at 300K) were synthesized following Refs. [2, 3] and were dissolved in liquid n-octadecane to form dilute solid-solution films devoid of inter-NC energy transfer. Fig. 1(a) shows PL spectra from typical films.

NC radii r are derived from the measured bandgap [22]. PL decays were measured in the ^3He insert of a 15 T magnet. The samples were weakly excited by a 635 nm diode laser delivering 70 ps pulses at 20 kHz (1.5 μ W average power). Reducing the laser power tenfold at 270 mK did not affect τ , indicating negligible heating. A 550 μ m diameter optical fiber delivered the excitation and collected the PL, which was dispersed in a 0.3 m spectrometer and detected with an InGaAs array or an InGaAsP photomultiplier tube and photon counting electronics. PL decays were always recorded at the PL band maximum (which shifts with temperature [8, 23]).

Figure 1(b) shows that PL decays from $r=2.3$ nm PbSe NCs are predominantly single-exponential and become longer with decreasing temperature. Decay times τ were extracted from single exponential fits and are shown over three orders of magnitude in temperature in Fig. 1(c). The initial 2 μ s of data are disregarded for $T < 100$ K, to avoid artifacts from exciton cooling or residual interdot energy transfer [20]. Also shown (right axis) is the corresponding *total* (time- and spectrally-integrated) PL intensity, I . In qualitative agreement with prior work [8], $\tau=0.7$ μ s at 300 K, but increases to 5 μ s upon cooling to 50 K. Critically, however, we find that I increases by a similar factor (of about five for this film) over the same temperature range, below which it remains constant. A similar correspondence – namely, that I increases by approximately the same factor as τ – is observed for *all* NC films upon cooling to 50 K. This result strongly suggests that non-radiative recombination channels (as opposed to, e.g., an interplay between dark and bright exciton states) dominates the PL dynamics above 50 K: As competing non-radiative decay channels freeze out, both τ and I should increase correspondingly. Thus, room temperature PL decay times of order 1 μ s, measured here and in prior works, are likely *not* representative of the actual radiative exciton lifetime in PbSe NCs. Rather, these data suggest that τ measured in the 10-50 K range provides a more realistic measure.

The most striking aspect of Fig. 1(c) is that τ remains relatively constant from 50 to 10 K, but increases markedly yet again at lower temperatures. No corresponding change of I is observed, indicating an intrinsic effect consistent with a redistribution of excitons having near-unity PL quantum yield. Ultra-low temperatures <500 mK are necessary to saturate τ (at 7.5 μ s in this sample). A key feature of this data is its remarkable agreement with a simple model of two thermally-populated emitting exciton levels: a lowest-energy state with slower decay time τ_s and a higher-lying state with somewhat faster lifetime τ_f , separated in energy by Δ (see inset). In this case, the temperature-dependent lifetime is readily given by $\tau^{-1}(T) = (\tau_s^{-1} + \tau_f^{-1} e^{-\Delta/k_B T}) / (1 + e^{-\Delta/k_B T})$. Importantly, the clear saturation of τ below 500 mK effectively fixes τ_s , permitting Δ to be fit with high accuracy. In these 2.3 nm radius NCs, we find that Δ is surprisingly small – only 290 ± 6 μ eV. Although previous studies to 1.4 K ascribed the low-

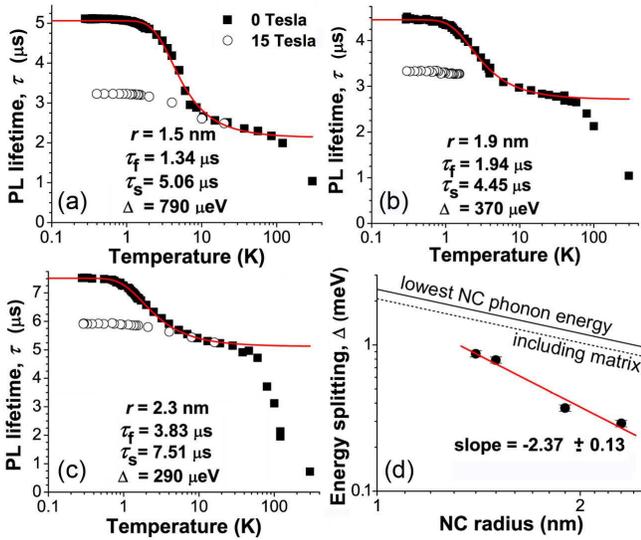


FIG. 2: (a-c) τ vs. T for three PbSe NC sizes at $B=0$ T (black points). Lines are fits to a two-level model (see text). Open symbols show $\tau(T)$ at $B=15$ T. High fields reduce τ to its value at ~ 10 K. (d) The energy splitting Δ between these two lowest exciton levels versus NC radius.

T upturn of τ with freezeout of quantized $l=2$ acoustic phonons, we note that $290 \mu\text{eV}$ is over three times less than the smallest acoustic phonon energy in PbSe NCs of this size, computed numerically [24] or using Lamb theory. Thus, this energy scale Δ likely reflects an intrinsic splitting of the lowest two states in the exciton fine structure of PbSe NCs. Moreover, τ_s and τ_f are similar (7.5 and $3.8 \mu\text{s}$), in strong contrast to the well-defined dark and bright excitons in CdSe NCs whose lifetimes typically differ by two orders of magnitude.

Figs. 2(a,b) show $\tau(T)$ data for $r=1.5$ and 1.9 nm NCs, along with similarly excellent fits of the low- T data to the model. The extracted splitting Δ decreases with NC size approximately as $1/r^2$ [Fig. 2(d)], suggesting a quantum confinement origin. For all NCs, Δ is much less than the smallest phonon energy (which falls as $1/r$), even when including realistic acoustic coupling to the surrounding organic matrix. Both τ_s and τ_f tend to increase with NC size, although the correlation is not strong.

We use high magnetic fields B to further clarify this new exciton fine structure. Figs. 2(a-c) also show $\tau(T)$ measured at 15 T. For all NCs, the low-temperature lifetime is reduced to nearly its 10-50 K value, while for $T > 10$ K, τ is unchanged by field. The total PL intensity is unaffected by field. These data suggest that the lowest-energy exciton gains some oscillator strength due to field-induced mixing with the slightly higher-lying state. That B reduces τ to its 10-50 K value, rather than its much smaller 300 K value, further confirms that τ at ~ 50 K reflects an intrinsic radiative recombination time in PbSe NCs.

An understanding of magnetic field effects requires some knowledge of the (heretofore-unknown) magnetic

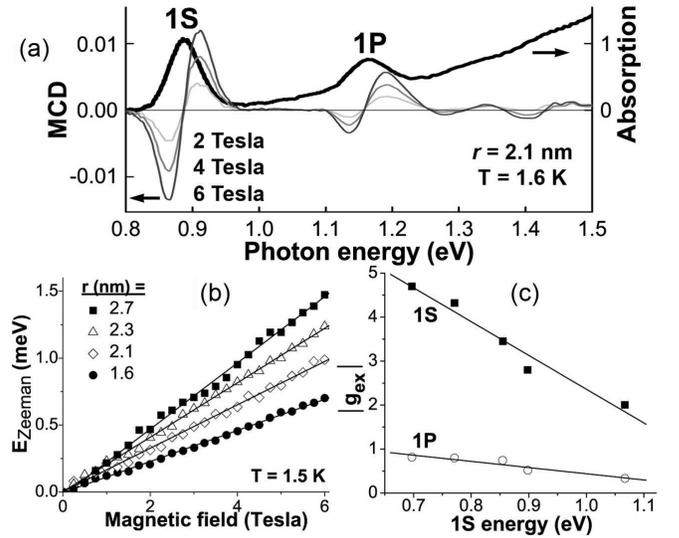


FIG. 3: (a) Optical absorption (right axis) and corresponding magnetic circular dichroism (MCD; left axis) from $r=2.1$ nm PbSe NCs. (b) Zeeman splitting of the $1S$ absorption feature, for different NCs. (c) The effective exciton g -factor $|g_{ex}|$ versus $1S$ band-gap energy.

energies of excitons in PbSe NCs. To this end, magnetic-circular dichroism (MCD) studies were performed (following Ref. [25]) in a 7 T split-coil magnet using films of NCs diluted in poly(methyl methacrylate) to minimize optical scatter. MCD, being a polarization-resolved absorption measurement, measures primarily those excitons within the fine structure that have large oscillator strength and which are responsible for absorption (these excitons are typically higher in energy than the emitting excitons from which PL originates, leading to the Stokes' shift observed in PbSe and other NCs). We measure the Zeeman splitting $E_Z = g_{ex} \mu_B B$ between right- and left-circularly polarized optically-active excitons that are split by a magnetic field. Fig. 3(a) shows the clear $1S$ absorption of $r=2.1$ nm NCs, and the derivative-lineshape MCD spectra, establishing that the $1S$ absorption is dominated by an exciton having Zeeman-type splitting. Fig. 3(b) shows $E_Z(B)$ for different NC sizes, from which the g -factors of these absorbing excitons $|g_{ex}|$ are determined. $|g_{ex}|$ increases from 2 to 5 from smallest to largest NCs, which likely results from increased spin-orbit coupling with decreasing band gap [26]. Although MCD does not explicitly reveal the Zeeman energy of the low-energy emitting states in the fine structure, these studies do provide a clear indication of the relevant magnetic energy scales in PbSe NCs.

The detailed dependence of τ on B may now be considered. Fig. 4 shows $\tau(B)$ at 1.5 K for both large and small PbSe NCs. In an applied field, τ at low temperatures is reduced by an amount that depends on the degree of mixing between the lower- and higher-energy exciton levels, which scales with the ratio of the characteristic magnetic energy E_Z to the level splitting Δ . For large PbSe NCs

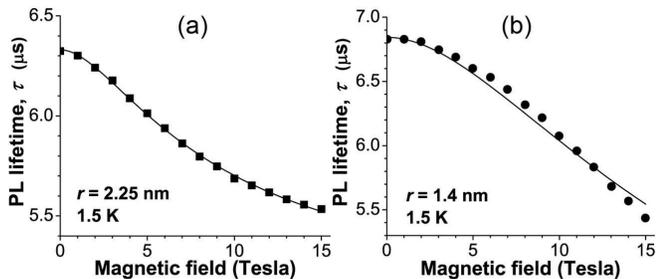


FIG. 4: Magnetic fields reduce τ at low T (1.5 K), for both (a) large and (b) small PbSe NCs. In large NCs, where Zeeman energies are large but Δ is small (see text), τ begins to saturate above 10 T. Lines show fits to the model of [27].

where MCD reveals large exciton magnetic energies and where Δ is smallest, τ clearly begins to saturate at high fields when $E_Z > \Delta$. The converse holds for small NCs: E_Z is small and Δ is big, and $\tau(B)$ does not show saturation even by 15 T. These data can be roughly modeled by adapting the theory in Ref. [27], which described B -dependent mixing between bright and dark excitons in CdSe NCs and its influence on τ .

Finally, magneto-PL studies show $>10\%$ circularly-polarized infrared emission at 2.5 K and 7 T [Fig. 5(a)], clearly implicating the role of emitting excitons in the fine structure that are Zeeman-split by magnetic fields and which couple selectively to right- or left-circularly polarized (σ^\pm) light. As shown in Figs. 5(b,c), the polarization $P=(I^+ - I^-)/(I^+ + I^-)$ increases with field (to 7 T) and decreases with temperature (to 40 K), in qualitative agreement with a thermal population of excitons occupying or mixing with Zeeman-split levels. However, since the precise symmetry, degeneracy and mixing character of the emitting excitons are not established, P cannot be used to quantify the relevant g -factors of these emitting states at this time.

In summary, studies of PL and PL decay to 270 mK and 15 T provide compelling experimental evidence for a new type of exciton fine structure in rocksalt PbSe NCs that is qualitatively different from that found in traditional wide-bandgap NCs such as CdSe. The data indi-

cate two weakly-emitting exciton levels with similar oscillator strengths that are nearly degenerate in energy ($\Delta < 1$ meV), and which mix in magnetic field. We also find that τ at 300 K is likely dominated by non-radiative channels, such that the actual radiative lifetime of excitons is much longer than previously thought, of order 5 μ s. MCD studies establish the magnetic (Zeeman) energy scale of absorbing states in the exciton fine structure, and circularly polarized infrared magneto-PL is observed for the first time. We anticipate that single-NC or resonant (line-narrowing) studies will further quantify the precise ordering, symmetry, and mixing of levels within the exciton fine structure of PbSe and other lead-salt NCs.

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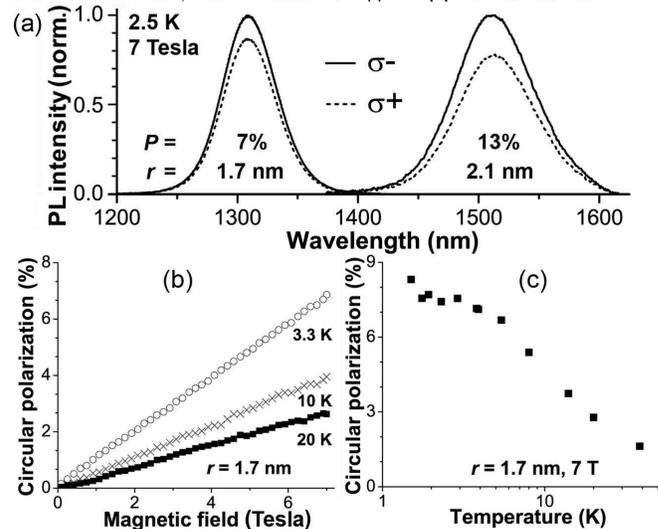


FIG. 5: (a) Circularly-polarized infrared PL emission from PbSe NCs at $B=7$ T and $T=2.5$ K. (b) PL polarization versus B . (c) PL polarization vs. T at $B=7$ T.

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