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Photoluminescence spectroscopy of PbSe nanocrystals

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The low-energy electronic states of PbSe quantum dots are investigated using photoluminescence spectroscopies. Size-selective photoluminescence measurements produce unexpectedly broad (~50 meV) emission lines. In addition, significant anti-Stokes luminescence is observed. Finally, we observe a size-dependent splitting of the lowest emission feature. Possible origins of the broad emission lines observed despite size-selective excitation and the splitting of the emission spectrum will be discussed.

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INTRODUCTION

Studies of lead-salt (PbS, PbSe, PbTe) nanocrystals or quantum dots (QDs) were originally motivated by the possibility of achieving strong confinement of both charge carriers, along with size-quantized optical transitions in the infrared spectral region between 1 and 3 μm.[1] Interest in lead-salt QDs has increased significantly since the development of a reliable and flexible colloidal synthesis in 2001.[2] The IV-VI lead-salt semiconductors, with their simple band structures differ substantially from their II-VI and III-V counterparts. The electronic structure and consequent electronic and optical properties, of lead-salt QDs are not completely understood. Calculations of the electronic states within the framework of effective-mass theory,[3–5] tight-binding approaches,[6] and atomistic pseudopotential techniques[7] have been reported. None of these consistently explains all experimentally observed features of lead-salt nanocrystals. The questions that are still subject to debate include, for example:

(i) What is the nature of the "band-edge" states, which are most relevant to radiative relaxation?

(ii) What is the role of intervalley coupling versus other effects that could break degeneracies, such as electron-hole exchange interaction?

(iii) What circumvents the expected phonon bottleneck to intraband carrier relaxation?

(iv) Why is the luminescence lifetime in the microsecond range, rather than tens or hundreds of nanoseconds?

Systematic experimental measurements of the properties of lead-salt QDs will be needed to develop a thorough understanding of these structures. The aim of the work presented here is to provide some spectroscopic data that will begin to close this gap. These data will have to be reconciled with theoretical treatments of the electronic structure.

The first systematic treatment of the electronic states of lead-salt nanocrystals was the work of Kang and Wise based on the effective mass approximation. This produced sparse electron and hole levels, in contrast to the states of most II-VI and III-V semiconductors. In Kang's theory, single-particle states are eight-fold degenerate (with spin) owing to the equivalent L valleys at which the band extrema occur.[3] Allan and Delerue reported a tight-binding calculation of PbSe QDs, which shows that the degeneracies are broken.[6] Groups of eight s orbitals and 24 p orbitals are found for electrons, spread over tens of millielectron volts for typical particle sizes. Furthermore, the mirror symmetry of electron and hole begins to break: the hole p-levels split into two groups. An *et al.* recently reported calculations that emphasize the coupling of the (anisotropic) equivalent valleys along with the finite potential barrier surrounding the dot.[7] These calculations produce spectra with dense hole states, qualitatively similar to the hole spectra of II-VI QDs. One would expect the more detailed and realistic atomistic calculations[6,7] to be superior to analytic calculations performed within the effective-mass and envelope-function theories. However, the effective-mass models quite accurately describe recent experimental results on multiple-exciton generation in PbSe QDs.[8,9]

Fine structure in the energy spectra of QDs has been a subject of much interest and has been invoked to explain both the shift between absorption and emission peaks as well as the observation of long radiative lifetimes in CdSe.[10,11] The envelope function calculations of the electronic structure of the IV-VI QDs by Kang *et al.* included many-body perturbations. It was found that the Coulomb interaction does not split the lowest transition and that the electron-hole exchange interaction is small (10 meV in comparison to the ~1 eV transition energies).[3] Very recent atomistic calculations predict that the lowest-energy excitonic manifold of PbSe QDs is split by electron-hole Coulomb and exchange interactions, in addition to the intervalley and interband couplings mentioned above.[12]

We are motivated specifically by recent studies of the relaxation of photoexcited electrons and holes in PbSe quantum dots. These investigations found that the "intraband" relaxation occurs on the picosecond time scale,[13,14] and the inferred energy-loss rate is comparable to that in the corresponding bulk crystal. The picosecond relaxation exhibited by PbSe QDs could be facilitated by the presence of additional states that would "bridge" the energy-level separation predicted by the effective-mass model. The dense hole states predicted by An *et al.* could enable the Auger-like process put forth to explain rapid intraband relaxation in CdSe QDs to be an effective energy-loss mechanism in the lead-salt QDs.[15] Guyot-Sionnest *et al.* suggest that the surface ligands may play a major role in the intraband relaxation.[16] The ground-state recovery of photoexcited PbSe and PbS QDs occurs on the microsecond time scale at room temperature,[13,17,18] a strong contrast to the ~10 ns room-temperature lifetime of CdSe nanocrystals. Dielectric screening has been suggested as the underlying cause of the long lifetime.[13] Exchange splitting could produce a dark lowest exciton, which would also contribute to the long lifetime.[19] A recent experimental study of PbS QDs in glass suggests the existence of such a dark exciton.[20]

These issues point out the clear need for more-detailed experimental knowledge of the electronic states of lead-salt nanocrystals. Here we report measurements of the photoluminescence (PL) spectra of PbSe QDs.[21] Measurements at low temperature reveal spectroscopic features that have not been reported previously. With high-photon-energy excitation, the lowest-energy emission feature splits, with larger splitting in smaller QDs. Size-selective excitation is expected to produce fluorescence line narrowing, but the fluorescence spectrum only narrows by a factor of 2–3, which implies a very broad (25–50 meV) single-particle linewidth. Significant anti-Stokes luminescence is observed in the same experiments. These observations will be discussed in light of current theoretical models of the electronic states of the QDs.

EXPERIMENT

High-quality colloidal PbSe and PbS NCs were synthesized as reported previously in the literature.[2,17] The size of the QDs varied by $-/+5\%$ of the nominal size in each sample. To perform temperature-dependent PL measurements, an optically transparent low-temperature host is required. Several suitable low-temperature glass formers were investigated; however, all of these compounds have significant absorptions in the infrared. For example, 2,2,4,4,6,6,8-heptamethylnonane (HMN), typically used in the visible region of the electromagnetic spectrum, absorbs wavelengths longer than 1500 nm, and thus precludes optical measurements of all but the smallest PbSe QDs in this host. To circumvent this problem with low-temperature hosts, we fabricated solid-state films by drop casting the QDs from hexane onto a glass coverslip. All data presented in this paper are from these drop-cast, solid-state QD films.

The samples were loaded into a helium vapor cryostat and cooled to temperatures as low as 15 K. The PL was excited with a tungsten-halogen lamp spectrally filtered by a monochromator, or one of several narrow-band laser sources: a tunable continuous-wave Ti:sapphire laser (775–930 nm), a commercial grating-tuned diode laser (1520–1570 nm), and a fixed wavelength diode laser (980 nm). The excitation conditions resulted in less than one photoexcited electron-hole pair per QD on average. The emitted light from the QD sample was collected perpendicular to the excitation, spectrally resolved by a 0.2-m monochromator, and detected with a cooled, extended InGaAs photodiode. The excitation source was modulated with a chopper and the in-phase component of the detected signal was collected and digitized by a lock-in amplifier. The spectral resolution of the system was typically less than 5 meV.

The difficulty of arranging for an adequate light source, sensitive detector, and transparent host for a specific nanocrystal sample is a serious challenge to spectroscopy in the infrared, especially by comparison to working at visible wavelengths up to ∼800 nm. These technical difficulties impede systematic spectroscopic studies of infrared nanocrystal materials. However, useful information can still be obtained from relatively isolated combinations of nanocrystal size and specific hosts.

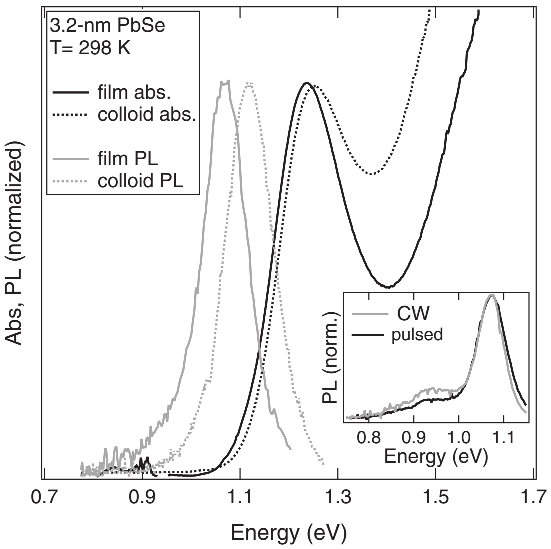

FIG. 1. Comparison of the absorption and globally excited PL spectra (excitation photon energy=1.7 eV) of 3.2-nm diameter PbSe QDs in solid state film and colloidal samples. The absorption of the film has been corrected for scatter by subtracting a $1/\lambda^4$ background. The small peak in absorption of the film at ∼0.9 eV is from oleic acid. The inset shows PL spectra excited at 1.55 eV with CW (average intensity=0.8 $\mathrm{W/cm^2}$) and high peak-intensity pulsed (pulse energy ∼1 mJ, pulse duration=70 fs, peak intensity =50 $\mathrm{GW/cm^2}$) Ti:sapphire lasers.

Overall features

Room-temperature optical transmission measurements of the films reveal excitonic absorption features superimposed with scatter. A simple $1/\lambda^4$ background subtraction corrected for the contribution of scatter to the film's attenuation. Although this analysis is not rigorous and some details of the corrected spectra depended on the specifics of the subtraction, we verified that the energies of the excitonic peaks were essentially unchanged (Fig. 1). The excitation photon energy is well above the energy of the lowest transition. In this case, all of the QDs in the size distribution are excited and contribute to the ensemble emission spectrum. This is referred to as global excitation. The PL from the films is still dominated by band-edge emission although we consistently find that the emission spectra are redshifted with respect to emission from the colloids. Transmission electron micrographs of the films of PbSe QDs show nearly close-packed QD ordering within a given domain, likely separated by the oleic acid on the surface (∼2–3 nm, head-to-tail).[17] A redshifted absorption spectra could be due to scatter, as shown by Dollefeld *et al.*[22] However, systematic measurements of fluorescence quenching and lifetimes show the redshifted emission spectra we observe is due to electronic energy transfer from smaller to larger QDs in the ensemble.[18] Because we observe the emission from the larger QDs in the ensemble, we might expect

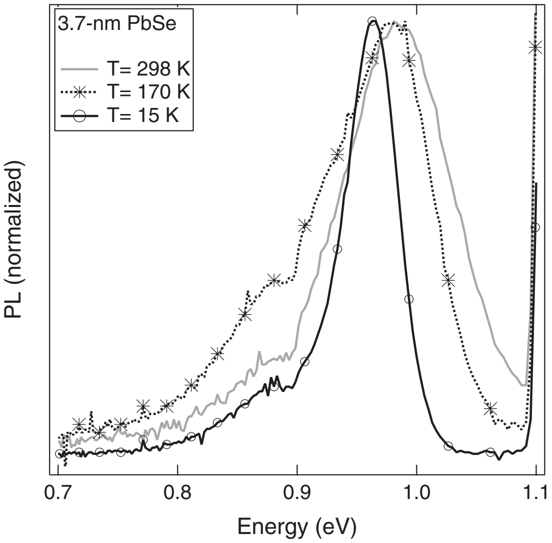

FIG. 2. The peak of the PL spectrum shifts to lower energy [peak energy position: 0.984 eV (298 K), 0.981 eV (170 K), 0.963 eV (15 K)] and narrows [full width at half maximum: 112 meV (298 K), 111 meV (170 K), 51 meV (15 K)] with decreasing temperature. The excitation energy is 1.1 eV. The feature observed in all of the traces at 0.9 eV is an artifact of the monochromator grating.

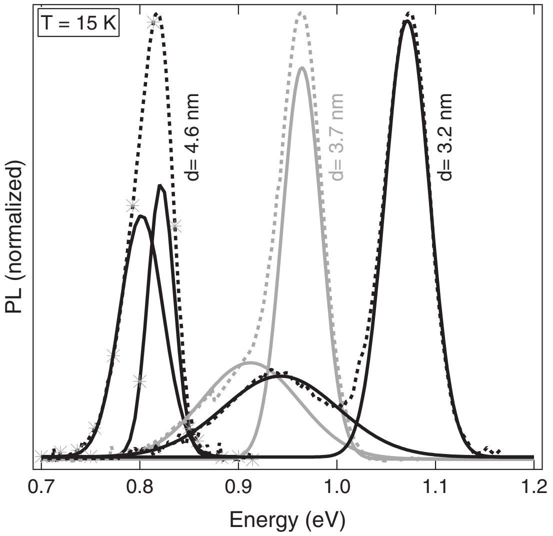

FIG. 3. PL spectra from PbSe QD solid state films at $T=15$ K. The dashed curves are the measured PL spectra for the indicated QD sizes. The solid curves are the best-fit two-Gaussian decomposition of the measured spectra.

to observe some line-narrowing owing to the effective size-selective excitation. However, this effect is apparently small, as the luminescence linewidths from the colloid and film samples are almost equal (Fig. 1). The spectra recorded from the drop-cast films and from QDs in HMN exhibit features at identical energies, but there are quantitative differences in the magnitudes of the luminescence peaks.

An asymmetric low-energy tail to the emission spectrum is consistently observed in our experiments despite differences in QD synthesis and film fabrication. As a simple test of the possibility that the emission arises from traps or defects associated with the surface of the QDs, we looked for an intensity dependence to the emission spectrum. Previously, it has been shown that traps or defect states may be saturated by increasing the intensity of the excitation source.[23] We find that the PL spectrum maintains its shape (Fig. 1, inset) as the peak excitation intensity is varied over 10 orders of magnitude by using 1.55-eV CW (0.8 $\mathrm{W/cm^2}$) and pulsed laser (50 $\mathrm{GW/cm^2}$) sources. We take these observations as experimental evidence that structure in the PL spectrum is not derived from defect states. This is consistent with the fluorescence quantum yield of at least 10% at room temperature estimated for these QDs previously. The asymmetric low-energy tail of the spectrum will be discussed further below.

Temperature-dependent luminescence spectra

Figure 2 shows the change in the global PL spectrum with temperature for a solid state film of 3.7-nm PbSe NCs. The room-temperature PL spectrum is broad and comparable to the width of the absorption peaks (see, for example, Fig. 1), which suggests that the bandwidth is a consequence of the particle-size distribution. The peak of the emission spectrum generally shifts slightly to lower energy as the sample temperature is reduced. However, in films of smaller QDs, the peak barely shifts at all. These observations are consistent with the size-dependent temperature variation of the lowest transition of PbSe QDs reported by Olkovets *et al.*[24] The luminescence peak narrows by a factor of ~2.5 between 300 and 15 K. This indicates that a significant portion of the observed linewidth is a consequence of homogeneous broadening; i.e., the homogeneous linewidth is relatively large. The asymmetric tail to lower energies is maintained, and even seems to be accentuated owing to the reduction of the full-width at half-maximum linewidth.

The globally excited PL spectra measured at 15 K for three different sizes of PbSe QDs (Fig. 3) shed some light on the asymmetric spectral shape. Larger PbSe QDs exhibit the asymmetric PL spectra. The asymmetry increases in smaller QDs, and in 3.2-nm dots a clear second emission peak splits off from the main peak. The observed splitting suggests the empirical decomposition of the PL spectra into a sum of two features. For convenience we fit the spectra to a sum of two Gaussian emission lines, and the fits are also shown in Fig. 3. We find that the widths and the separation of the component emission peaks increase with decreasing QD size. For fixed QD size, the splitting increases with decreasing temperature. The widths of the components are in the range 50–100 meV. At 15 K, the separation between the peaks varies from approximately 20 to 130 meV as the PbSe QD size decreases from 4.6 to 3.2 nm. The temperature dependence is remarkably strong for the smallest nanocrystal. A 2-nm diameter PbS QD was also measured and exhibited a peak separation of 310 meV. Perhaps surprising is the fact that the higher-energy of the two emission peaks is always the more intense one. The magnitude of the lower-energy peak approaches the higher-energy peak in larger QDs. The two peaks have

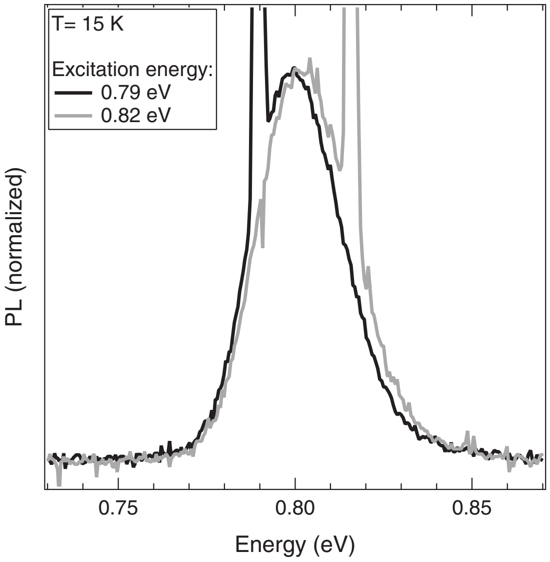

FIG. 4. PL from 4.6-nm PbSe QDs at $T=15$ K. The first absorption peak (not shown) is at 0.95 eV. The size-selective excitation was tunable between 0.82 and 0.79 eV. The two curves peaked near 0.80 eV are emission spectra for the indicated excitation energies.

nearly-equal integrated emission intensity for all three sizes of QD.

Size-selective excitation of PL spectra

One way to circumvent the inhomogeneous broadening of optical spectra that arises from the particle-size distribution is to use size-selective excitation. In contrast to the global excitation experiments discussed above, a narrow-band excitation source with a photon energy tuned within the low-energy tail of the QD absorption spectrum is used to photoexcite only the largest QDs within the sample. Subsequently, only this subset of the largest QDs contributes to the emission spectrum. We note that in this case, energy transfer from smaller to larger QDs will not play a role; the largest particles in the ensemble will be excited directly. Based on the availability of suitable laser sources in our laboratory, we could only access the line-narrowing spectral regime for one size of nanocrystal. The results are shown in Fig. 4 for 4.6-nm PbSe QDs.

The intent of size-selective excitation is to produce a narrower emission line (nominally approaching the single-particle or homogeneous spectrum), and some line narrowing is observed. As the excitation photon energy decreases from 0.95 down to 0.79 eV, the linewidth initially decreases quickly, but then seems to reach a limiting width of ~30 meV. This is significantly broader than that observed for CdSe QDs in either size-selective PL (1–10 meV) (Ref. 25) or single-dot PL (<1 meV) experiments.[26]

Another interesting feature is the appearance of some anti-Stokes luminescence in the spectra. With excitation at 0.82 eV, there appears to be some luminescence that can be distinguished from the residual excitation light, up to energies of ~0.85 eV. With excitation at 0.79 eV, the anti-Stokes emission is pronounced. The peak of the emission clearly occurs at higher energy than the excitation, and more than half of the integrated emission is at energies above the excitation energy. The emission spectrum largely coincides with the position of the lower-energy component in the decomposition of the asymmetric profile (refer to Fig. 3). Within the enumerated experimental constraints the pronounced anti-Stokes PL was reproducible; different film samples prepared from the same QD stock yielded the same results.

DISCUSSION

If we assume that the narrowest observed linewidth is the homogeneous linewidth, it would imply an exciton dephasing time <~50 fs for an isolated line. The luminescence spectra of single 3-nm PbS QDs are ~3 times narrower than the ensemble emission spectrum,[27] which is similar to the narrowing we observe in size-selective excitation of PbSe QDs reported here. The single-particle spectrum of 3-nm PbS QDs is extremely broad: the 100-meV width recorded at room temperature corresponds to a dipole dephasing time of ~20 fs.[27] Initial photon-echo experiments in our laboratory yield transients that cannot be resolved with the ~100-fs resolution of the apparatus,[28] which also imply rapid dephasing. In addition, attempts to observe spectral hole burning in small PbS QDs produce only a weak and broad bleach of the lowest transition, which again seems to imply ultrafast dephasing.[29] Considering the similarities in the electronic structures of PbSe and PbS QDs, it is not surprising that distinct experiments produce fairly similar results for the two materials. However, such rapid dephasing is difficult to reconcile with what is known about electron-phonon coupling in lead-salt QDs.

Another possible explanation for the apparently large homogeneous linewidth is that highly degenerate low-energy states are split into groups of states that span the corresponding energy ranges. The 64-fold degenerate lowest transition is shifted and split by several effects: Coulomb and exchange interactions, intervalley couplings, and possibly shape asymmetry.[6,7,12]

According to Allan and Delerue,[6] intervalley coupling begins to produce appreciable (and possibly observable) splitting of the lowest energy levels when the QD diameter is ~5 nm. With decreasing size, the splitting of electron states increases up to ~80 meV, and the splitting of hole states increases up to ~40 meV. Thus, observed splitting in the optical spectra will be on the order of ~100 meV. The energy range for each group of states increases with decreasing size, up to ~50 meV in 2-nm crystals, so the widths are comparable to the splitting, and the split groups may be barely resolved. Within the overall trend of increasing splitting with decreasing size, the evolution is not always monotonic, and the remaining twofold or fourfold degeneracies can also vary in energy position.[6] Considering these "oscillations" in the behavior, we do not have enough experimental data to sensibly compare to these details of the calculation. However, this seems to be the only theoretical prediction that agrees even roughly quantitatively with the measured splitting of the luminescence spectra as well as the broad widths

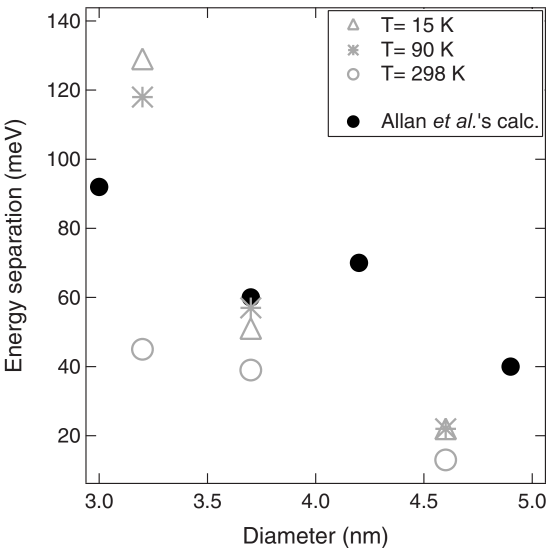

FIG. 5. The experimentally measured PL splitting for three different PbSe QD sizes. The splitting is found to increase with both decreasing temperature and size. Solid circles: maximum splitting predicted in calculations by Allan *et al.* (Ref. 6).

of the two emission components. In Fig. 5, the maximum energy splitting from this calculation is compared to the measured energy separation of the two PL features obtained from the Gaussian decomposition of the global PL spectra over a range of temperatures.

A decaying anti-Stokes tail in PL has been observed in the emission from InP QDs at room temperature.[30] This spectral feature was explained reasonably well by a model involving surface states, and the energy up-conversion occurred by phonon absorption. A general feature of II-VI and III-V semiconductor QDs is that surface ligands and surface reconstruction can have a major influence on the band-edge electronic states and optical properties.[31,32]

The combination of energies that are below the exciton energies (corresponding to the peaks of the absorption spectrum) and the observation of anti-Stokes luminescence suggest consideration of the role of surface states in the emission, as invoked by Poles *et al.*[30] A calculation of the electronic states of PbSe QDs with imperfect surface passivation, along the lines of Ref. 28, e.g., would be interesting in this regard, but such a calculation has not been reported. Atomistic calculations have found that PbSe, because of its large ionicity, does not require special care to saturate dangling bonds and remove surface states from the energy gap.[33] Even if the origin of the states were postulated, we can only conjecture as to the mechanism that underlies the anti-Stokes shift. Photon absorption to a low-energy state (0.79 eV for the 4.6-nm dots of Fig. 5, e.g.) clearly occurs. From that state, phonon absorption to an emitting state at 0.8 eV can be ruled out at 15 K. Photon absorption to a higher excited state could occur, but would presumably require that the absorbing state have a much longer lifetime than the emitting state. We have measured the luminescence lifetimes of PbSe and PbS QDs at energies across the full-width at half-maximum of the global emission spectrum at room temperature, and we find negligible variation of the lifetime. Future work will include similar measurements at low temperatures.

CONCLUSIONS

In conclusion, we have investigated the band-edge electronic structure of PbSe QDs using PL spectroscopies. We observe splitting of the emission spectrum. The magnitude of this splitting (reaching up to ~100 meV in the smallest nanocrystals) and its variation with QD size is roughly consistent with a tight-binding calculation of the splitting of the lowest transition due to the coupling of equivalent *L* valleys. Attempts to access the homogeneous line shape by size-selective excitation produce linewidths of ~50 meV, narrowed somewhat compared to the global photoluminescence but much broader than the corresponding spectra in other QDs. Anti-Stokes photoluminescence is observed at low temperature with the lowest-energy excitation, and the origin of this luminescence is currently not understood. We hope that these results stimulate further theoretical and experimental work on lead-salt nanocrystals.

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