Size-Dependent Temperature Variation of the Energy Gap in Lead-Salt Quantum Dots

A. Olkhovets, R.-C. Hsu, A. Lipovskii,* and F. W. Wise
Department of Applied Physics, Cornell University, Ithaca, New York 14853

(Received 27 April 1998)

We observe that the temperature coefficients of electron-hole pair energies (dE/dT) in PbS and PbSe quantum dots depend strongly on the size of the quantum dot. With decreasing size the temperature coefficient of the lowest electron-hole pair energy dE_g/dT decreases by more than an order of magnitude from the bulk value. The weak temperature dependence found in the strong-confinement limit is expected for atomiclike levels, but has not been observed previously in a semiconductor. [S0031-9007(98)07402-X]

PACS numbers: 78.66.–w, 71.35.Cc, 85.30.Vw

The effects of quantum confinement on the electronic states of semiconductors have been studied extensively in the past 20 years. Excellent introductions and overviews of the physics of confinement in 2-, 1-, and 0-dimensional systems can be found in [1]. Recently, much attention has turned to the properties of semiconductor quantum dots (QD's). The electronic and optical properties of QD's were derived from basic theoretical considerations and contrasted with those of 1- and 2-dimensional systems by Schmitt-Rink *et al.* [2]. The dominant features of the electronic structure are reasonably well established: The continuum states of the bulk semiconductor transform to the discrete states of the QD, and the shift of the interband transitions with QD size is thoroughly studied.

Given the importance of the energy gap of a semiconductor, it is perhaps surprising that the variation of electronic energies with temperature is not well established for QD's. [As is typical, we define the energy gap E_g as the energy of the lowest electron-hole pair (EHP) transition.] Studies generally report that the gap depends on temperature similarly to the energy gap of the bulk material [3]. The variation may be slightly stronger [4] or slightly weaker [5] in QD's of varying size, but the coefficient dE_g/dT is within ~30% of the bulk value.

Here we report a study of the size and temperature dependence of the EHP transition energies in PbS and PbSe QD's. The temperature coefficient of the lowest excited state dE_g/dT exhibits a dramatic size dependence: in the smallest QD's the value of dE_g/dT is reduced by an order of magnitude from the bulk value, and even changes sign. Atomiclike energy levels are expected to be independent of temperature, but this is the first observation of this property in a semiconductor. For a given transition (including higher excited states) dE/dT is determined primarily by the energy of the transition. The size dependence and energy dependence of dE/dT can be understood as consequences of quantum confinement.

IV-VI semiconductors such as PbS and PbSe provide unique access to the limit of strong quantum confinement and are excellent for investigation of the properties of a size-quantized system. In contrast to II-VI and III-V materials, both the electron and hole are individually strongly confined in lead-salt QD's. The exciton Bohr radius $a_B = 46$ nm in PbSe, 8 times larger than in CdSe. The electronic [6] and vibrational [7] spectra of lead-salt QD's are simple and sparse. The coupling of the EHP to polar phonons goes nearly to zero at small sizes [8], as expected theoretically for an ideal QD [2] but not observed in II-VI or III-V QD's owing to weak confinement of the hole and the complicated wave functions that result from valence-band mixing.

We studied high-quality PbS QD's with diameter $2R$ between 3 and 15.5 nm in oxide glass [9], phosphate glass [10], and polymer [7] hosts. $a_B = 20$ nm in PbS, so the samples span the range from nearly bulk material to the strong-confinement limit. The EHP energies are determined from peaks in the optical absorption spectra measured at temperatures from 12 to 300 K. Typical experimental data are shown in Fig. 1. Three to five distinct peaks are observed in the spectrum from each sample. For the temperature coefficient of each transition energy we take the slope of a linear fit over the range 70–300 K, where the variation of $E(T)$ is linear.

The measured values of dE_g/dT are plotted versus QD size in Fig. 2. dE_g/dT approaches the bulk value (~500 μeV/K) in the largest QD's. In 4.5-nm QD's the magnitude of dE_g/dT is a factor of 10 smaller than the bulk value, and dE_g/dT becomes slightly negative for smaller QD's. This is the first observation that the temperature coefficient of the energy gap of a semiconductor depends strongly on size. The fact that results from different samples follow the same trend indicates that it is not peculiar to a specific host or synthesis. The lines are the results of calculations to be discussed below.

The values of dE/dT for all transitions observed in the PbS samples are shown in Fig. 3. dE/dT decreases roughly linearly with energy to ~1 eV, and then flattens out at slightly negative values for higher energies. This trend is largely irrespective of size.

A theoretical treatment of the size and temperature dependence of the spectrum of a QD has not been reported, and a rigorous approach to the problem will be difficult.

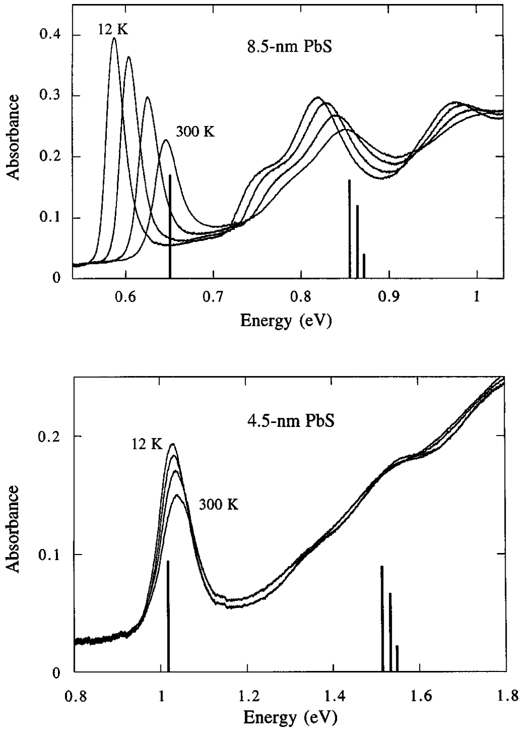

FIG. 1. Absorption spectra of 8.5 and 4.5-nm PbS QD's in oxide glass recorded at 12, 100, 200, and 300 K. Bars indicate the 300-K positions of the two lowest parity-allowed dipole transitions in each sample. Spectral features between the bars are parity-forbidden transitions [6].

The temperature dependence of the energy gap of bulk semiconductors was the subject of substantial theoretical effort [11]. For bulk materials the quantity dE_g/dT has contributions from lattice thermal expansion and electron-phonon interactions. Allen and Heine analyzed the case of a very narrow energy band, and showed that in that limit the self-energy and Debye-Waller terms cancel to give an energy level independent of temperature, as expected for an isolated atom [12]. Additional contributions from mechanical strain and thermal expansion of the wave-function envelope are expected in the QD, and it is difficult to isolate the distinct contributions experimentally. The envelope-function calculation of QD eigenstates [6] is based on bulk material parameters and would predict the same temperature dependence as bulk material. However, there is no logical basis for inserting the temperature dependence of the bulk parameters into a calculation of the temperature dependence of QD properties. Here we will estimate the magnitude of each contribution to dE_g/dT, focusing particularly on the size dependence and making simplified arguments wherever possible.

We write the temperature dependence of the energy levels of the QD in terms of contributions from distinct effects,

$$\left(\frac{dE}{dT}\right) = \left(\frac{\partial E}{\partial T}\right)_{\text{lattice}} + \left(\frac{\partial E}{\partial T}\right)_{\text{envelope}} + \left(\frac{\partial E}{\partial T}\right)_{\text{strain}} + \left(\frac{\partial E}{\partial T}\right)_{\text{el-ph coupling}} . \quad (1)$$

Thermal expansion of the QD contributes to dE_g/dT through both the lattice and the wave-function envelope, and additional contributions come from mechanical strain and electron-phonon coupling.

(i) *Thermal expansion of the lattice.*—We obtained the thermal-expansion coefficient of PbS QD's as small as 7 nm from x-ray diffraction traces and found it to be equal to the bulk value. Any size dependence of $[\partial E_g/\partial T]_{\text{lattice}} = [\partial E_g/\partial a][\partial a/\partial T]$ therefore originates in the dependence of energy on lattice constant a. In bulk PbS, lattice dilation contributes ~340 μeV/K to dE_g/dT [13]. Size-quantized energies depend weakly on lattice constant; the confining potential determines a wave vector, and the corresponding energy from the $E(\mathbf{k})$ relation.

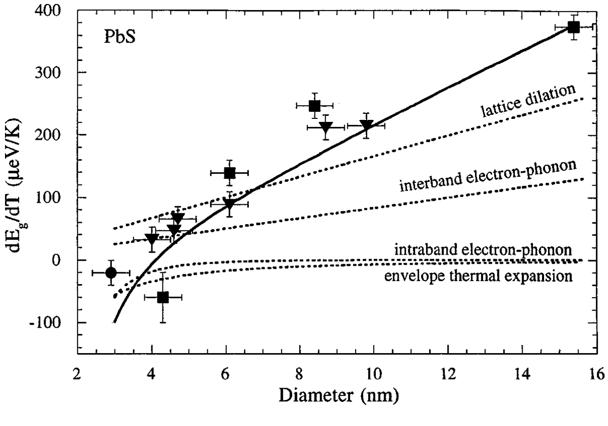

FIG. 2. dE_g/dT for PbS QD's. Symbols are experimental values. Squares: phosphate glass host; triangles: oxide glass host; circle: polymer host. Calculated contributions to dE_g/dT are shown as dotted lines, and the solid line is the sum of all contributions.

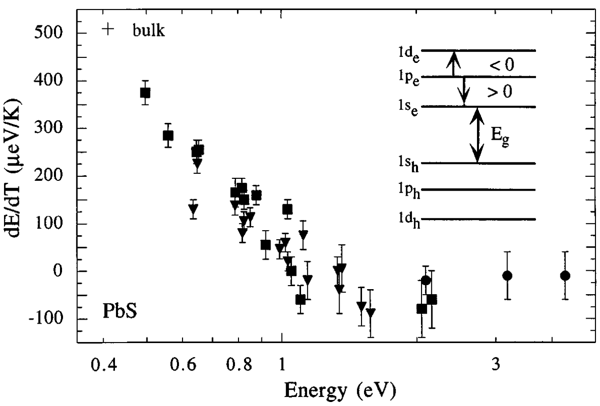

FIG. 3. dE/dT plotted versus transition energy for PbS QD's. Symbols have the same meanings as in Fig. 2. Inset: Schematic of energy levels in lead-salt QD's, with intraband couplings to the $1p_e$ state indicated.

Nomura and Kobayashi estimate $[\partial E_g/\partial T]_{\mathrm{lattice}} < 1\ \mu\mathrm{eV/K}$ in $\mathrm{CdS}_x\mathrm{Se}_{1-x}$ QD's [5]. Thus, $[\partial E_g/\partial T]_{\mathrm{lattice}}$ is known in the bulk and small-radius limits. As a first approximation we interpolate linearly between these values, and assume that the bulk value is reached when $2R = a_B$. This should be reasonable because the effects of confinement begin to appear when the diameter approaches a_B.

(ii) *Thermal expansion of the wave-function envelope.*—When a QD undergoes thermal expansion, the quantum-confined energy levels shift, with

$$\frac{dE}{dT} = \frac{\partial E}{\partial R}\frac{\partial R}{\partial T} = \frac{\partial E}{\partial R}\alpha R \propto -\frac{\alpha}{m_r}\frac{1}{R^2}, \qquad (2)$$

where α is the thermal expansion coefficient of the QD material and m_r is the reduced mass of the EHP. The last form is obtained assuming a simple parabolic-band model. Taking dE/dR from experiment yields $dE_g/dT \approx -40\ \mu\mathrm{eV/K}$ in 3-nm QD's, which accounts for $\sim 10\%$ of the observed variation.

(iii) *Mechanical strain.*—QD's in rigid hosts experience stress owing to mismatch between the thermal expansion coefficients of the dot and host, as well as pressure arising from surface tension [14]. The resulting strain produces energy shifts that we estimate directly from the pressure coefficient of energy $\partial E/\partial P$, assuming that the QD's are spherical and under uniform pressure. Since $\partial E/\partial P$ depends on the volume of the unit cell [11], it should be reasonable to use the bulk value of $\partial E/\partial P$ for the QD. For PbS QD's in glass the difference in thermal-expansion coefficients produces $[\partial E_g/\partial T]_{\mathrm{strain}} \approx -70\ \mu\mathrm{eV/K}$, varying little with size. We estimate the contribution from surface tension following Scamarcio *et al.* [14] and obtain $[\partial E_g/\partial T]_{\mathrm{surface}} \approx 10\ \mu\mathrm{eV/K}$.

(iv) *Electron-phonon coupling.*—The self-energy ΔE due to electron-phonon coupling was calculated for a bulk semiconductor using second-order perturbation theory by Fan [15], and several refinements of this calculation followed [11,16]. The change in the self-energy due to the promotion of an electron from occupied to unoccupied levels in a QD is a sum of terms of the form

$$\Delta E = \sum_{\ell_p} \frac{|\langle n'(\ell' - \ell_p); \ell_p | H_{\mathrm{el\text{-}phon}} | n\ell; 0\rangle|^2}{E_{n\ell} - E_{n'(\ell'-\ell_p)} - \hbar\omega_p},$$

where ℓ is the angular momentum of the electron, n represents all other quantum numbers for the electron, and ℓ_p and ω_p are the angular momentum and frequency of the phonon. Intraband (coupling to like-carrier states) terms are always negative, while interband (coupling to opposite-carrier states) terms are always positive for the lowest-energy transition. Interband terms in the self-energy are responsible for $dE_g/dT \approx 150\ \mu\mathrm{eV/K}$ in bulk PbS [13]. With decreasing size (increasing energy denominators), these interband contributions will decrease. The energy gap increases as $\sim 1/R^{1.3}$ for $R \geq 2.5$ nm [6]. Therefore, we approximate the interband terms as decreasing linearly from the bulk value for diameters below a_B. In QD's the intraband self-energy can be approximately related to the electron-phonon coupling strength S (the interaction energy in units of the phonon energy) and the Bose factor n:

$$\Delta E/\Delta T = -S(R)\,(\hbar\omega_p)\,\frac{d}{dT}\,n(T) \overset{T\to\infty}{\longrightarrow} -S(R)k_B\,.$$

Polar coupling to optical phonons must be considered along with deformation-potential coupling to acoustic phonons. In the strong-confinement limit the deformation-potential coupling to acoustic modes S_{ac} should dominate over the coupling to optical modes [2] and this is confirmed experimentally in 3-nm PbS QD's [8]. Deformation-potential coupling to acoustic phonons produces a temperature-linear contribution to the self-energy with $\Delta E \sim -1/R^2$ [17]. In 3-nm PbS QD's with $S_{\mathrm{ac}} \approx 0.1$ [8], we find $dE_g/dT \approx -20\ \mu\mathrm{eV/K}$.

The individual contributions to dE_g/dT are indicated in Fig. 2 as dotted lines (the contribution from mechanical strain is omitted for clarity). The sum of these terms is shown as the solid line, and agrees reasonably well with experiment. The quantitative agreement should not be taken seriously, but we can safely conclude that the size-dependence of dE_g/dT is dominated by the lattice-dilation and interband electron-phonon terms. The effect of lattice thermal expansion is weaker than in the bulk material because the QD energy levels are determined by size quantization rather than the lattice constant, and the electron-phonon self-energy term decreases because the spacing between these quantum-confined energy levels increases. (The increased spacing is evident in the spectra of Fig. 1 and systematic data are compared to theory in [6].) The overall behavior can thus be understood in terms of elementary arguments of quantum mechanics and perturbation theory.

Analogous reasoning accounts qualitatively for the variation of dE/dT with transition energy. Higher-energy states arise from the confining potential and so depend increasingly less on lattice constant. Equation (2) shows that envelope thermal expansion contributes $dE/dT \propto -E$; for $E = 2$ eV, $dE/dT \approx -50\ \mu\mathrm{eV/K}$. The effect of strain evaluated above applies to excited states, and should be approximately independent of energy for fixed size. Nothing is known experimentally about the coupling of higher excited states to phonons, but given the similarity of electron and hole wave functions connected by dipole transitions [6], we expect that the electron-phonon coupling will not vary rapidly with energy. As discussed above, interband electron-phonon terms will be negligible at high energies. For higher excited states the intraband terms can be positive (coupling to a lower-energy state) or negative (coupling to a higher-energy state), as indicated in the inset of Fig. 3. For a given QD size, the intraband energy differences are approximately constant: e.g., in the 8.5-nm dots the lowest splittings are 100 and 75 meV,

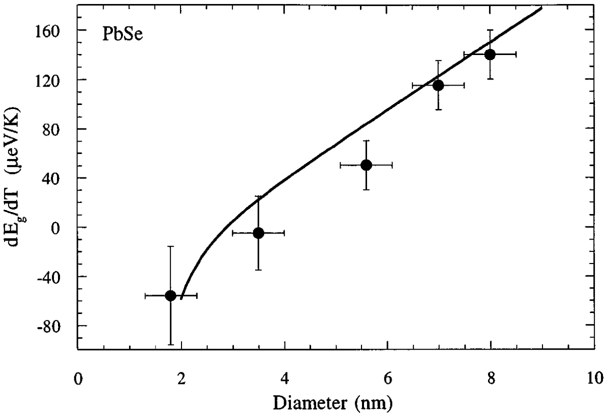

FIG. 4. Experimental and calculated values for dE_g/dT for PbSe QD's.

and in 3-nm dots 500 and 600 meV. Assuming constant electron-phonon coupling, the resulting near-cancellation of terms will produce a small negative intraband sum for higher excited states. This adds to the contributions from strain and envelope expansion to produce the values of dE/dT observed at high energies.

Similar results are obtained with PbSe QD's. Values of dE_g/dT obtained for a series of PbSe QD's with diameters 2–8 nm [18] are displayed in Fig. 4. In PbSe the Bohr radius $a_B = 46$ nm, so the confinement is extreme in these QD's. The solid line is the result of arguments similar to those made for PbS.

In II-VI materials such as CdS and CdSe, the intraband energy differences do not approach the bulk energy gap. As a result, the intraband electron-phonon terms are much larger than the interband terms, so $dE_g/dT < 0$ and is similar to the bulk value. The most detailed and systematic measurements of $E_g(R,T)$ of II-VI QD's that we have found were performed on a set of CdS QD's with diameters from 1.3 to 4 nm [4]. dE_g/dT varies approximately as $-1/R^2$ as expected for intraband terms and coupling to acoustic phonons, and the magnitude of the variation is consistent with $S_{\mathrm{ac}} \approx 1$.

In conclusion, we report strong size and energy dependence of the temperature coefficients of QD electron-hole pair energies. For the highest EHP energies dE/dT is nearly independent of temperature, as expected for atomiclike states. The approximate analysis presented here shows that the observed behavior is expected in a strongly size-quantized system, but we hope that the experimental results will motivate a rigorous theoretical treatment.

This work was supported by the National Science Foundation under Grant No. DMR-9321259. The authors thank T. Krauss and I. Kang for numerous discussions, N. Borrelli for providing samples, and S. Kycia for help with x-ray measurements.

---

*Permanent address: St. Petersburg State Technical University, Polytechnicheskaja 29, St. Petersburg, 195251 Russia.

[1] C. Weisbuch and B. Vinter, *Quantum Semiconductor Structures* (Academic Press, San Diego, 1991); C. Flytzanis and J. Hutter, *Nonlinear Optics in Quantum Confined Structures*, in Contemporary Nonlinear Optics, edited by G. P. Agrawal and R. W. Boyd (Academic Press, San Diego, 1992).

[2] S. Schmitt-Rink, D. A. B. Miller, and D. S. Chemla, Phys. Rev. B **35**, 8113 (1987).

[3] J. P. Zheng and H. S. Kwok, J. Opt. Soc. Am. B **9**, 2047 (1992).

[4] T. Vossmeyer *et al.*, J. Phys. Chem. **98**, 7665 (1994).

[5] S. Nomura and T. Kobayashi, Phys. Rev. B **45**, 1305 (1992).

[6] I. Kang and F. W. Wise, J. Opt. Soc. Am. B **14**, 1632 (1997); I. Kang, Ph.D. thesis, Cornell University, Ithaca, NY, 1998.

[7] T. D. Krauss, F. W. Wise, and D. B. Tanner, Phys. Rev. Lett. **76**, 1376 (1996).

[8] T. D. Krauss and F. W. Wise, Phys. Rev. Lett. **79**, 5102 (1997).

[9] N. F. Borrelli and D. W. Smith, J. Non-Cryst. Solids **180**, 25 (1994).

[10] A. Lipovskii *et al.*, Electron. Lett. (to be published).

[11] This work is summarized in P. B. Allen and M. Cardona, Phys. Rev. B **27**, 4760 (1983).

[12] P. Allen and V. Heine, J. Phys. C **9**, 2305 (1976).

[13] J. O. Dimmock, in *The Physics of Semimetals and Narrow-Gap Semiconductors*, edited by D. L. Carter and R. T. Bates (Pergamon, Oxford, 1971).

[14] G. Scamarcio, M. Lugara, and D. Manno, Phys. Rev. B **45**, 13 792 (1992).

[15] H. Y. Fan, Phys. Rev. **82**, 900 (1951).

[16] C. Keffer, T. Hayes, and A. Bienenstock, Phys. Rev. B **2**, 1966 (1970).

[17] T. Takagahara, Phys. Rev. Lett. **71**, 3577 (1993).

[18] A. Lipovskii *et al.*, Appl. Phys. Lett. **71**, 3406 (1997).