RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 4 15 JULY 1993-II

Vibronic quantum beats in PbS microcrystallites

Janet L. Machol and Frank W. Wise
Department of Applied Physics, Cornell University, Ithaca, New York 14853

Ramesh C. Patel
Department of Chemistry, Clarkson University, Potsdam, New York 13676

David B. Tanner
Department of Physics, University of Florida, Gainesville, Florida 32816

(Received 1 June 1993)

We have used femtosecond optical spectroscopy to study the dynamics of excitons strongly confined in microcrystallites of the narrow-band-gap semiconductor PbS. The transient absorption of the lowest exciton level exhibits terahertz-frequency vibronic quantum beats. Far-infrared measurements show that the vibrations are confined transverse-optical phonons.

Although there has been considerable interest in the electronic and optical properties of semiconductor microcrystallites, or quantum dots, only a small portion of this work has been done on samples which strongly confine the excitons, i.e., for which the crystallite is much smaller than the bulk exciton Bohr radius.[1] Large absorptive and dispersive nonlinearities are predicted for such systems if the quantum-dot transitions are not broadened excessively.[2,3] The magnitude and origin of this line broadening are critical; any broadening counteracts the spectral concentration of oscillator strength due to quantum confinement, and thus reduces the nonlinearity. The dominant intrinsic source of line broadening is expected to be exciton-phonon coupling, and this motivates studies of the strength and time scale of carrier-phonon interactions in quantum dots.

Strong confinement is most readily achieved in narrow-band-gap semiconductors, in which the excitons have large Bohr radii.[2] We have chosen to study PbS, for which the strong-confinement regime is attained for particle diameters much less than the bulk exciton Bohr radius of 18 nm. Spherical PbS crystallites approximately 4 nm in diameter can be synthesized with a narrow size distribution.[4] These 4-nm particles satisfy the condition of strong confinement as defined by Éfros and Éfros,[1] in which the particle radius is much less than the Bohr radii of both the electron and the hole. Furthermore, the analysis of Banyai *et al.*[3] predicts that for a given particle size the nonlinearities of PbS will be 30 times as large as those of GaAs,[5] and three orders of magnitude larger than those of CdS.

Here we report on the initial relaxation of photocreated excitons in PbS microcrystallites. In particular we focus on an ultrafast oscillatory response which can be explained as quantum beats between confined vibrational states of the microcrystallite. The vibronic nature of the quantum beats and the identity of the vibrational mode associated with the beats are determined by Raman and far-infrared measurements.

PbS colloids, stabilized with poly(vinyl alcohol), were prepared in an aqueous solution.[6] An average particle diameter of 4.3 nm was measured from images taken with a scanning transmission electron microscope (STEM). Electron and x-ray diffraction experiments by other researchers have shown that the crystallites have the cubic structure of bulk PbS,[6] and thus also the bulk phonons. The colloidal solution, which had a lifetime of several days, was dried into a thin flexible film which had an indefinite lifetime. The absorption spectrum of the film was identical to that of the initial solution.

Quantum confinement in the PbS microcrystallites results in discrete energy levels and an increase in the effective band gap from the bulk value of 0.41 eV. The room-temperature absorption spectrum of a film of the crystallites (Fig. 1) exhibits a confinement energy greater than 1.5 eV and a series of distinct exciton peaks. We attribute the peaks near 600, 400, and 300 nm to the $1s_e$-$1s_h$, $1s_e$-$1p_h$, and $1p_e$-$1p_h$ transitions, respectively. These assignments are based on solutions of the single-particle Schrödinger equation assuming an infinite potential well and parabolic energy bands; the best match to the measured spectrum occurs with a particle diameter of 4.0 nm. The linewidths are consistent with the observed distribution of particle sizes. Analysis of the spectrum is simplified by the fact that in PbS the valence band is nondegenerate near the L point of the Brillouin zone, where the minimum energy gap occurs.

The dynamics of the lowest-energy excitons in PbS microcrystallites were studied at 300 K with standard time-resolved nonlinear absorption techniques. Pulses from a mode-locked dye laser were amplified at kilohertz repetition rates[7] and used to generate a white-light continuum from which excitation and probe wavelengths were selected. The pulses were 90 fs in duration and the focused excitation pulses had peak intensities of 0.5–4 GW/cm^2. PbS microcrystallites are known to exhibit permanent absorption bleaching after illumination, perhaps due to photoanodic dissolution.[4] During our experiments the absorption of the sample decreased by up to 15%, but the transient signals did not change qualitatively.

The nonlinear absorption of the crystallites was exam-

0163-1829/93/48(4)/2819(4)/$06.00

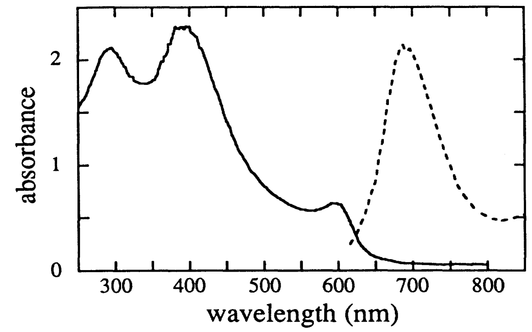

FIG. 1. Room-temperature absorption (solid line) and luminescence (dotted line) spectra of the PbS microcrystallites. Identical absorption results are obtained at 10 K. The luminescence was measured with excitation at 581 nm.

ined for several combinations of excitation and probe wavelengths relative to the $1s_e$-$1s_h$ exciton transition. When the crystallites are excited at the peak of the resonance (602 nm), we observe (1) saturation at the pump frequency and (2) induced absorption on the low-energy side of the resonance. The absorption bleaching [Fig. 2(a)] exhibits a coherent artifact near zero delay and a decay component lasting several picoseconds. In addition, there is a sinusoidal component with a frequency of 2.6 THz (corresponding to a period of 385 fs); this is evident in the Fourier transform of the data [Fig. 2(a) inset]. The induced absorption [Fig. 2(b)] appears in <200 fs and also has a decay component of several picoseconds. Any oscillations which might be present in this induced absorption are below the sensitivity of the experiment.

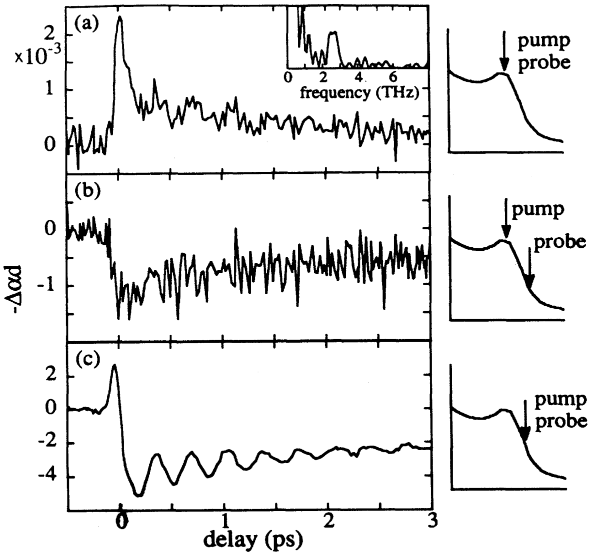

FIG. 2. Time-dependent nonlinear absorption measured at wavelengths of (a) 602 nm, (b) 602 nm (pump) and 626 nm (probe), and (c) 616 nm. The inset shows the power spectrum of the data of (a). The excitation and probe wavelengths are indicated on the $1s_e$-$1s_h$ absorption resonance.

Identical pump and probe wavelengths on the low-energy side of the $1s_e$-$1s_h$ resonance produce an oscillatory response superimposed on induced absorption. An experimental trace for excitation and probe wavelengths of 616 nm is shown in Fig. 2(c), and similar results have been recorded with wavelengths as long as 626 nm. We believe that the positive spike near zero delay is a coherent artifact since its duration is less than the temporal resolution of the experiment. The oscillations are more apparent at 616 than at 602 nm because the continuum was more stable at this wavelength.

The nonlinear absorption of a microcrystallite excited at the peak of its lowest exciton resonance has been investigated theoretically by Hu, Lindberg, and Koch[8] and the results apply to the electronic phenomena (i.e., induced or saturated absorption) which we observe. The oscillatory component, which is vibrational in origin, will be discussed below. Absorption bleaching at the peak is due to saturation of the exciton transition. Induced absorption near the resonance is due to the formation of biexcitons (two-electron-hole-pair states) via the absorption of one pump and one probe photon;[8,9] this has been observed on both the high- and low-energy sides of the exciton resonance.[9,10] The ground-state biexciton is theoretically observable as an induced absorption on the low-energy side of the exciton resonance, but only when the exciton transition is not strongly damped.[8] For a damping rate $\hbar\Gamma$ greater than the bulk exciton binding energy, the induced absorption is suppressed by the saturating one-pair resonance. For PbS this corresponds to a damping time of much less than 1 ps. The fastest relaxation process observed in the PbS quantum dots is the 1-ps damping of the oscillations. Since there is relatively little damping, we attribute the absorption induced by pumping on resonance and observed below resonance to the creation of ground-state biexcitons.

Excitation on the low-energy side of the exciton resonance of the PbS crystallites induces absorption at the excitation wavelength. We assume a transition to the biexciton ground state is also responsible for this induced absorption. This requires some homogeneous broadening, so that the low-energy tail of the exciton transition will overlap the ground-state–biexciton transition.

The frequency of the observed oscillations is essentially independent of the underlying electronic process. The best fit of the function

$$\Delta\alpha(t)=C_1\exp(-t/\tau_1)+C_2\exp(-t/\tau_2)\cos(2\pi\nu t)$$

to the data of Fig. 2(c) yields $\tau_1=5$ ps, $\tau_2=1.1$ ps, and $\nu=2.9$ THz. We attribute the modulation to quantum beats. The generation of beats in a three-level system can be understood as follows.[11] Assume that optical transitions are allowed from a ground state $|0\rangle$ to excited states $|1\rangle$ and $|2\rangle$ with associated energies E_1 and E_2. Absorption of a short light pulse, the spectrum of which spans the energies E_1 and E_2, produces an initial state which is a coherent superposition of these levels,

$$|a(t=0)\rangle=\alpha|1\rangle+\beta|2\rangle ,$$

where α and β depend on the excitation spectrum and the transition probabilities. At times longer than the pulse duration, the superposition state becomes

$$|a(t)\rangle = \alpha \exp(-iE_1 t/\hbar)|1\rangle + \beta \exp(-iE_2 t/\hbar)|2\rangle \ .$$

The relaxation of the exciton population will contain modulation terms of the form

$$\mathrm{Re}\{(\alpha\beta \exp[-i(E_1 - E_2)t/\hbar]\}$$

which evolve with a period $T = h/(E_2 - E_1)$; the absorption of a probe pulse will be modulated at the same frequency. If the energy levels E_1 and E_2 are different excitations of the same normal mode, the beat frequency will be equal to the mode frequency. Here the measured beat frequencies around 2.8 THz imply an energy-level spacing of about 11 meV or 90 cm^{-1}.

If a vibrational mode is coupled to an optical transition as a phonon sideband, it can often be observed either by Raman scattering or by infrared absorption. In bulk PbS, the zero-wave-vector optical modes are Raman inactive and infrared active.[12] In resonance-Raman measurements of the PbS crystallites at 10 K, we observe no peak in the spectrum in the vicinity of 11 meV. Fourier-transform infrared measurements, however, reveal a temperature-independent absorption which peaks at 90 cm^{-1} as shown in Fig. 3. The observation of a peak in the far-infrared (FIR) absorption at the required energy confirms that vibronic quantum beats are responsible for the observed oscillations.

The dielectric function of binary semiconductors typically has a strong resonance at the frequency of the transverse-optical (TO) phonon.[13] In bulk PbS, the energy of the zero-wave-vector (Γ-point) TO phonon is 8.1 meV.[14] In a crystallite of radius R, however, confinement of the phonons[15] results in a minimum allowed wave vector q on the order of $qR \sim \pi$; for $R = 2$ nm, $q \sim 2\times10^7$ cm^{-1}. The energy of the bulk PbS TO phonon increases with wave vector around the zone center and is near 11 meV for $q > 2\times10^7$ cm^{-1} along the [001] and [110] directions.[14] Thus we conclude that phonon confinement in the crystallites shifts the FIR absorption to this higher energy and we assign the measured infrared absorption peak to the confined TO phonons. A detailed analysis of the infrared absorption of the crystallites will be presented separately.

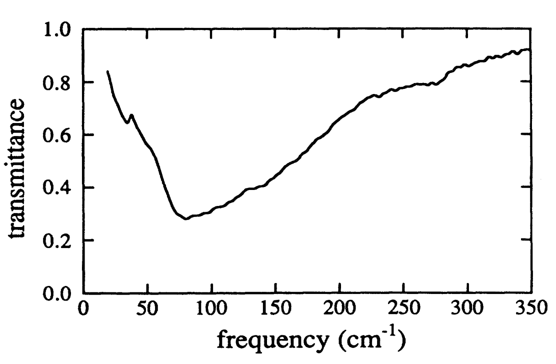

FIG. 3. Far-infrared transmittance of one sample of PbS microcrystallites at 300 K. The absorption spectra vary among samples; however, all samples exhibit a peak near 90 cm^{-1}. The spectra are essentially temperature independent over the range 20–300 K.

Other vibrational modes of PbS are unlikely to be responsible for the observed FIR absorption. The energy of the longitudinal-optical (LO) phonon is about 27 meV for $q < 4\times10^7$ cm^{-1}.[14] Due to the large difference between the static ($\varepsilon_0 = 170$) and high-frequency ($\varepsilon_\infty = 17$) dielectric constants of PbS, the calculated surface-optical (SO) modes[16] are clustered just below the LO-phonon frequency, between 23 and 24 meV. With one free charge per crystallite, the calculated SO mode frequencies[16] are 8 and 160 meV. The SO modes are expected to absorb strongly in the FIR; we are currently investigating why this mode is not apparent in the measured spectrum. Finally, the calculated lowest spheroidal-mode energy[17] is about 4 meV.

The observation of a beat frequency corresponding to a nonzero phonon wave vector raises the question of whether there is significant exciton-phonon coupling at wave vectors away from the zone center. Schmitt-Rink, Miller, and Chemla predict that the exciton-phonon coupling at large wave vectors will increase with decreasing microcrystallite size due to exciton confinement.[2] The coupling will be maximum for $qR \sim \pi$ and for $R = 2$ nm, $q \sim 2\times10^7$ cm^{-1}. Nomura and Kobayashi have performed a detailed calculation of the dependence of the exciton-phonon coupling on crystallite size and phonon wave vector.[18] For GaAs quantum dots the size of the bulk exciton, they found significant exciton-phonon coupling for wave vectors as large as 2×10^7 cm^{-1}. In the 4-nm PbS microcrystallites, where the excitons are more strongly confined, one would expect coupling to be at least as strong to phonons at such large wave vectors. The exciton is most likely coupled to the TO mode by a deformation potential interaction.[19]

Previous observations of quantum beats in bulk and quantum-well semiconductors have generally involved electronic states.[20] Quantum beats in CdSe microcrystallites observed by Schoenlein *et al.* in photon-echo experiments were attributed to LO phonons.[21] The observation of vibronic quantum beats is related to the work of Cho, Kütt, and Kurz, in which coherent phonons were generated in GaAs by the separation of photogenerated carriers in a surface-space-charge field.[22] In quantum beats the phonons are directly coupled to the optical transition while in the coherent-phonon experiments the phonons are created by impulsive charge separation. Finally, phonon-polariton beats have recently been excited and detected in bulk $\mathrm{LiTaO_3}$.[23]

In conclusion, we have used femtosecond spectroscopy to study the dynamics of excitons strongly confined in PbS quantum dots. Relatively small damping of the exciton transition allows us to observe the ground-state biexciton as well as an ultrafast sinusoidal relaxation. We attribute the oscillatory response to quantum beats involving confined TO phonons in the microcrystallites.

We thank T. Krauss and S. Lyon for assistance with Raman measurements, M. Thomas for help with the

STEM measurements, and R. Proctor for help with noise reduction in the time-resolved experiments. We acknowledge useful discussions with S. FitzGerald and A. Sievers. This work was supported by the National Science Foundation under Grants Nos. DMR-8957988 and DMR-9101676 and by the MRL Program of the National Science Foundation under Grant No. DMR-9121654.

---

[1] Al. L. Éfros and A. L. Éfros, Fiz. Tekh. Poluprovodn. **16**, 1209 (1982) [Sov. Phys. Semicond. **16**, 772 (1982)]. See also L. E. Brus, J. Chem. Phys. **79**, 5566 (1983).

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

[3] L. Banyai, Y. Z. Hu, M. Lindberg, and S. W. Koch, Phys. Rev. B **38**, 8142 (1988).

[4] S. Gallardo, M. Gutiérrez, A. Heinglein, and E. Janata, Ber. Bunsenges. Phys. Chem. **93**, 1080 (1989).

[5] M. A. Olshavsky, A. N. Goldstein, and A. P. Alivisatos, J. Am. Chem. Soc. **112**, 9438 (1990).

[6] M. T. Nenadović, M. I. Čomor, V. Vasić, and O. I. Mićić, J. Phys. Chem. **94**, 6390 (1990).

[7] D. Nickel, D. Kühlke, and D. von der Linde, Opt. Lett. **14**, 36 (1989).

[8] Y. Z. Hu, M. Lindberg, and S. W. Koch, Phys. Rev. B **42**, 1713 (1990).

[9] Y. Z. Hu, S. W. Koch, M. Lindberg, N. Peyghambarian, E. L. Pollock, and F. F. Abraham, Phys. Rev. Lett. **64**, 1805 (1990).

[10] M. G. Bawendi, W. L. Wilson, L. Rothberg, P. J. Carroll, T. M. Jedju, M. L. Steigerwald, and L. E. Brus, Phys. Rev. Lett. **65**, 1623 (1990).

[11] W. Lange and J. Mlynek, Phys. Rev. Lett. **40**, 1373 (1978); M. Mitsunaga and C. L. Tang, Phys. Rev. A **35**, 1720 (1987).

[12] W. Jantsch, *Dynamical Properties of IV-VI Compounds* (Springer-Verlag, New York, 1983).

[13] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971).

[14] M. M. Elcombe, Proc. R. Soc. London Ser. A **300**, 210 (1967).

[15] S. W. Marshall and R. M. Wilenzick, Phys. Rev. Lett. **16**, 219 (1966).

[16] R. Ruppin, in *Electromagnetic Surface Modes,* edited by A. D. Boardman (Wiley, New York, 1982).

[17] H. Lamb, Proc. Math. Soc. London **13**, 187 (1882); A. P. Alivisatos, A. L. Harris, N. J. Levinos, M. L. Steigerwald, and L. E. Brus, J. Chem. Phys. **89**, 4001 (1988).

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

[19] B. K. Ridley, *Quantum Processes in Semiconductors* (Oxford, New York, 1988).

[20] See, e.g., E. O. Göbel, K. Leo, T. C. Damen, J. Shah, S. Schmitt-Rink, W. Schäfer, J. F. Müller, and K. Köhler, Phys. Rev. Lett. **64**, 1801 (1990); K. Leo, T. C. Damen, J. Shah, E. O. Göbel, and K. Köhler, Appl. Phys. Lett. **57**, 19 (1990); H. Stolz, V. Langer, E. Schreiber, S. Permogorov, and W. von der Osten, Phys. Rev. Lett. **67**, 679 (1991); S. Schmitt-Rink *et al.*, Phys. Rev. B **46**, 10460 (1992).

[21] R. W. Schoenlein, D. M. Mittleman, J. J. Shiang, A. P. Alivisatos, and C. V. Shank, Phys. Rev. Lett. **70**, 1014 (1993).

[22] G. C. Cho, W. Kütt, and H. Kurz, Phys. Rev. Lett. **65**, 764 (1990).

[23] H. J. Bakker, S. Hunsche, and H. Kurz, Phys. Rev. Lett. **69**, 2823 (1992).