Phonon Broadening and Spectral Hole Burning in Very Small Semiconductor Particles

P. Roussignol, D. Ricard, and C. Flytzanis

Laboratoire d'Optique Quantique, Ecole Polytechnique, 91128, Palaiseau CEDEX, France

N. Neuroth

Central Research and Development, Schott Glaswerke, 6500 Mainz, Federal Republic of Germany

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We report on experimental evidence of the important role of phonon broadening in very small CdSSe crystallites. At low temperature, spectral hole burning is observed. These results are in agreement with the special conditions of quantum confinement and with the polar character of this semiconductor.

When photoexcited carriers in semiconductors are artificially confined into volumes whose dimensions are all below a critical length, their quantum behavior and dynamics undergo drastic changes with respect to those of the bulk. The optical properties of such systems are particularly affected by this quantum confinement effect[1,2] and at present much effort is being focused on the understanding of the physical mechanisms that shape their optical nonlinearities, mostly the optical Kerr effect. The goal is certainly the design of promising nonlinear optical materials, but these are of fundamental interest as well since they throw new light on some physical aspects which are suppressed in the infinitely large systems.

Up until now the main experimental effort in this respect has been directed in semiconductor-doped glasses containing $CdS_{1-x}Se_x$ crystallites, which are also commercially available as color filters. In their case, the diameter (≈ 7-8 nm) of the particles is not small enough to show a sizeable quantum confinement effect.[3,4] With a suitable heat treatment, however, glasses containing smaller crystallites can be prepared and the implications of quantum confinement on the linear optical properties are now well established.[5,6] Colloidal suspensions have also been studied.[7,8]

Schmitt-Rink, Miller, and Chemla[9] have studied theoretically the nonlinear properties of these very small particles, especially in the case of GaAs and InSb. In the vicinity of the lowest-energy structure, when it is prominent, each quantum dot should behave as a two-level system whose saturation is responsible for the nonlinearity. A large nonlinearity is anticipated since a large fraction of the oscillator strength is concentrated in a single structure. The spectral width of the structure therefore plays a central role. It was argued that intrinsic mechanisms such as electron-phonon coupling should play a minor role compared with the statistical nature of the growth process of the semiconductor crystallites leading to a possibly large inhomogeneous broadening. The electron-phonon coupling may vary over a wide range in different semiconductors, in particular, if their polarity does so and it is important to also have experi-

mental evidence about its impact as it drastically conditions the magnitude as well as the time scale of the nonlinear saturation and, by the same token, the optical nonlinearity.

In the present Letter, we report on experimental evidence of the important role of intrinsic phonon broadening in very small CdSSe crystallites, especially at room temperature. We will show, however, that at a lower temperature (≈ 12 K), spectral hole burning is observable. The burnt holes are observed to be broad and blue shifted relative to the excitation wavelength. These results are discussed in terms of conventional models of phonon broadening for localized electronic transitions.

Our measurements were performed on samples grown by heat treating melts prepared for the manufacture of the Schott filters RG610 and RG630. Before the heat treatment, the melts contain Cd, S, and Se ions and are transparent. They are then tempered for 72 h in a temperature ranging from 500 to 700°C over a 15-cm-long bar. Samples were then cut in different portions of the bars and subsequently polished. The size of the crystallites were determined by small-angle x-ray scattering. The spread in our particle size is $\approx 10\%$-15%. Nonlinear absorption was studied with a picosecond excite and probe technique. The primary source was a 25-psec-long pulse delivered by a mode-locked Nd-doped yttrium aluminum garnet laser at the wavelength $\lambda = 1064$ nm. Part of this pulse was frequency doubled to yield the excitation pulse at the wavelength $\lambda = 532$ nm, the rest of the laser pulse being focused in a water cell. Through self-phase modulation, a white picosecond pulse is created and serves as the probe pulse to monitor the absorption of our sample. The absorption spectrum is measured with the use of a spectrometer and an optical multichannel analyzer. The probe beam is focused at the sample to a size small compared with that of the excitation beam so that only a uniformly excited zone is probed. The time delay between the excitation and probe pulses can be varied, allowing us to study the change in the absorption spectrum due to picosecond excitation and, when so desired, its time evolution.

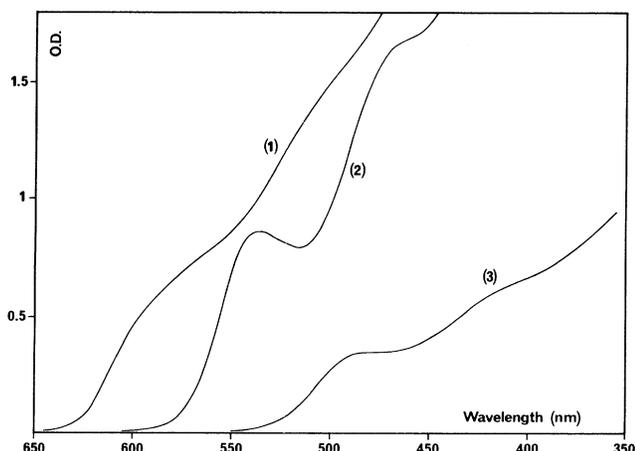The implications of the quantum size effect are al-

FIG. 1. Absorption spectra (optical density vs wavelength) at room temperature for three samples grown from an RG610 melt. Samples 1, 2, and 3 were grown at 700, 600, and 500 °C, respectively. The mean particle diameters are 12, 5, and ≈ 2.5 nm, respectively.

ready apparent when looking at the heat-treated bars whose color changes gradually from yellow (low temperature and very small particles) to red (high temperature and larger particles). Three absorption spectra taken at room temperature on samples cut in the bar grown from the RG610 melt are shown in Fig. 1. The spectrum for

sample 1 treated at ≈ 700 °C is the same as that of the commercial glass. The spectra for samples 2 and 3 treated at ≈ 600 °C and ≈ 500 °C, respectively, clearly show the blue shift and the structures due to transitions between quantized levels. However, as exemplified by the first or $1s$-$1s$ band, the structure is more clearly visible for intermediate-size particles; it broadens for smaller particles. We note that the structure is superimposed on the tail of higher-energy features.

Figure 2 shows how the absorption spectrum changes when one goes from room temperature to low temperature (≈ 12 K) for two different samples. The absorption edge shifts to the blue as the temperature is lowered as observed for the bulk semiconductor. The absorption edge also steepens and the structure becomes narrower indicating that phonon broadening significantly contributes to the width observed, at least at room temperature. The width of this $1s$-$1s$ band is reduced by about 25% when going from room temperature to low temperature.

With homogeneous broadening being important at room temperature, we anticipated that spectral hole burning would be unlikely under such conditions. We studied the change in the absorption spectrum after picosecond excitation at 532 nm on several samples cut in the bar grown from the RG630 melt, especially when the peak of the $1s$-$1s$ structure falls in the vicinity of the excitation wavelength corresponding to a particle size of ≈ 4–5 nm. A typical result is shown in Fig. 3. We do not observe any spectral hole burning although the spec-
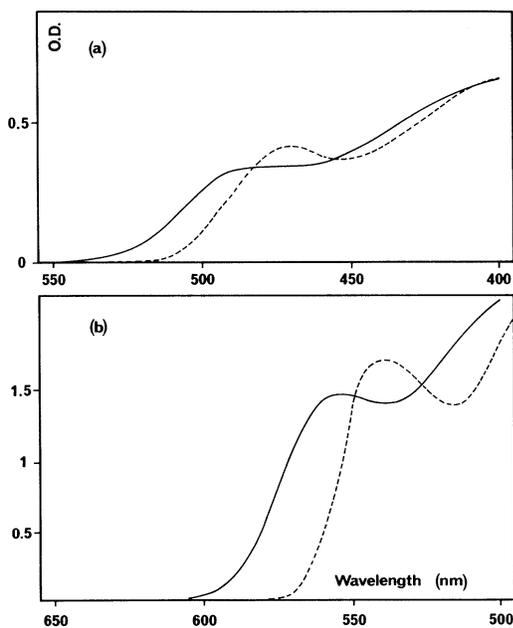

FIG. 2. Absorption spectra at room temperature (solid lines) and at low temperature (12 K, dashed lines) for two different samples. (a) Sample 3 of Fig. 1. (b) The sample was grown from an RG630 melt at ≈ 580 °C.
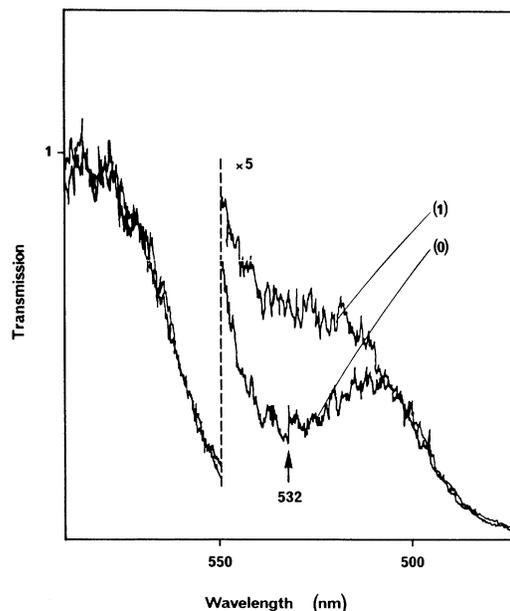

FIG. 3. Transmission vs wavelength measured at room temperature for a sample grown from an RG630 melt at ≈ 550 °C before (0) and immediately after (1) picosecond excitation at 532 nm.

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tral width of the excitation pulse is small (a fraction of a wave number). The $1s$-$1s$ structure is uniformly saturated implying that, on our 25-psec time scale, this transition behaves as a homogeneously broadened line. Different samples led to the same observation. Since the volume fraction occupied by the semiconductor particles is small ($\approx 1\%$), these particles are far enough from one another for cross relaxation to be slow and our conclusion would hold even for faster time scales.

We repeated the same measurements at low temperature (≈ 12 K). When the excitation wavelength is on the high-energy side of the structure, we do not observe hole burning. However, when the excitation wavelength corresponds to the peak of the structure, as shown in Fig. 4 or to the low-energy side, hole burning is clearly ob-

served. The burnt holes are fairly broad, indicating a still important homogeneous contribution, and they appear on the high-energy side of the excitation. Figure 4 also shows the temporal evolution of the absorption spectrum which relaxes back to the normal spectrum within ≈ 1 nsec with a slower component probably due to trapped carriers.

Broadening of transitions between localized electronic distributions by longitudinal-optical (LO) phonons or by piezophonon and deformation potential coupling has been treated theoretically.[10,11] The implications for small semiconductor particles are discussed by Schmitt-Rink, Miller, and Chemla.[9] Our taking only LO phonons of frequency ω_0 into account leads to a set of phonon sidebands in the imaginary part of the susceptibility which assumes the form

$$\text{Im}\chi = C e^{-S(2\bar{n}+1)} \sum_p \left[\frac{\bar{n}+1}{\bar{n}}\right]^{p/2} I_p\{2S[\bar{n}(\bar{n}+1)^{1/2}\}\delta(E - E_x + S\hbar\omega_0 - p\hbar\omega_0) ,$$

where

$$\bar{n} = [\exp(\hbar\omega_0/k_B T) - 1]^{-1}$$

is the phonon occupation number and

$$S = \sum_q |M_{0q}/\hbar\omega_0|^2$$

is the Huang-Rhys parameter. C is a constant; p is the number of phonons created ($p > 0$) or destroyed ($p < 0$) in the transition; I_p is the modified Bessel function; $E_x - S\hbar\omega_0$ is the energy of the zero-phonon line; and

FIG. 4. Same as Fig. 3 but at low temperature (≈ 12 K). The sample was grown from an RG630 melt at $\approx 565\,^\circ$C and the spectrum is also shown for various positive values of the probe-pulse delay.

$M_{0q} \propto \int d^3 r e^{i\mathbf{q}\cdot\mathbf{r}} |\phi(\mathbf{r})|^2$ is the electron-phonon matrix element for the phonon of quasimomentum $\hbar\mathbf{q}$. Each LO phonon sideband is then broadened via electron-acoustic phonon interaction. Although the electron may be size quantized, because of the high ionic masses, phonons are not.

We have in good approximation spherical semiconductor particles of radius a. Schmitt-Rink, Miller, and Chemla[9] consider the first case treated by Efros and Efros[1] for which $a \ll a_e, a_h$ where a_e and a_h are the Bohr radii of an electron and hole, respectively. Under such conditions, both the electron and hole are size quantized with, if we assume infinite potential barriers, identical wave functions. This leads to a vanishing local charge density $e|\phi(\mathbf{r})|^2$ and to a vanishing polar coupling to LO phonons. III-V compounds being, furthermore, weak-coupling materials, this explains the conclusion reached in Ref. 9, i.e., the prediction of a very weak phonon broadening in this case. The case of CdSSe, however, is closer to the second case considered by Efros and Efros[1] for which $a_h \ll a \ll a_e$. Under such conditions, only the electron is size quantized and the hole moves in the nearly parabolic Coulomb potential due to the electronic distribution. In such a case, the local charge density $e|\phi(\mathbf{r})|^2$ does not vanish and, CdS or CdSe being more polar than III-V's and therefore strong-coupling materials, this explains the important phonon broadening that we observe. At room temperature, phonon broadening dominates the inhomogeneous broadening due to size distribution; at low temperature, it is still non-negligible (the width of the spectral holes we burn is about 60 meV). Also, as already pointed out,[9] because of confinement, an increasing coupling to short-wavelength phonons is expected when the size is reduced. This is consistent with our observation of a broadening of the $1s$-$1s$ structure when the particle size is reduced at room
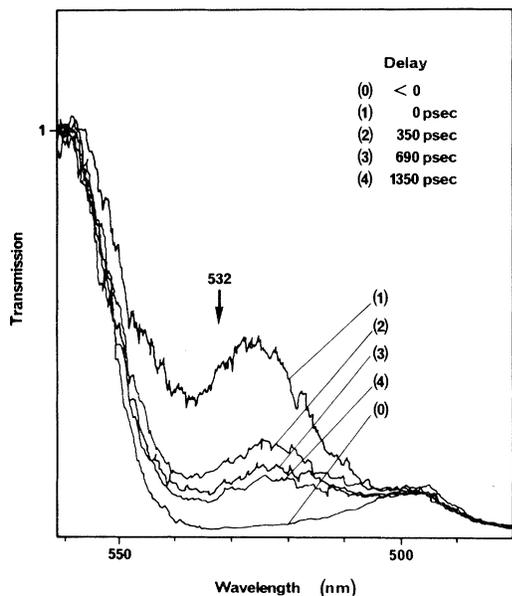
temperature.

The spectral shape of the hole burning has been discussed theoretically for a single line.[12] When features specific to the microcrystallite size distribution are properly taken into account, certain of these results pertain to our case too. Thus, because of weighting by the *asymmetric*[13] size distribution, the burnt hole may be shifted with respect to the excitation wavelength. Furthermore, as was previously pointed out, when the size is reduced the electron hole coupling and, concomitantly, the Huang-Rhys factor S are increased; this implies that the intrinsic homogeneous broadening is *larger* on the high-energy side ($a < \bar{a}$ where $\bar{a}$ is the average size radius) than on the low-energy side ($a > \bar{a}$). These two features explain the observed blue shift of the spectral hole we burn when we excite on the low-energy side and the absence of hole burning when we excite on the high-energy side of the $1s$-$1s$ band. A quantitative analysis, however, is complicated because the $1s$-$1s$ line is superimposed on the tail of higher-energy features.

An alternative explanation for the broadening of the $1s$-$1s$ band was proposed by Efros and Efros[1] and experimental evidence for this mechanism was claimed to be observed recently.[14] It corresponds to the quantization of the hole motion in the harmonic potential discussed above. We do not believe that this mechanism can explain our results. Whereas phonon broadening leads to a roughly symmetric band shape, for this second mechanism the oscillator strength steadily decreases with the harmonic-oscillator quantum number because of the oscillatory behavior of the wave function, leading to an asymmetric band. Furthermore, this mechanism cannot explain the narrowing we observe when the temperature is lowered. We do not believe either that impurities play an important role since we consider only above band-gap properties.

We finally note that our observations are in agreement with preliminary phase-conjugation measurements performed at room temperature at the fixed wavelength 532 nm. As the size of the semiconductor particles is reduced and the absorption edge is shifted to the blue, the ratio $\chi^{(3)}/\alpha$ of the Kerr susceptibility to the absorption coefficient passes through a maximum when the $1s$-$1s$ band is the most apparent, whereas it is roughly constant for commercial glasses.[4] This is consistent with a spectral confinement of the oscillator strength which is optimum for intermediate-size particles.

In summary, we have shown experimentally and explained theoretically that phonon broadening is quite important in small CdSSe particles, especially at room temperature. This is an important feature for the design of better nonlinear optical materials. However, at low temperature, spectral hole burning in the quantum structure is observed in agreement with theoretical predictions.

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