Persistent spectral hole-burning and hole-filling in CuBr semiconductor nanocrystals

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Persistent spectral holes (p-SHs) are induced in the $Z_{1,2}$ excitonic absorption band of CuBr nanocrystals (NCs) in glass by selective excitation with nanosecond dye-laser pulses at low temperatures. The effect can be observed only in samples containing NCs with mean radius smaller than about 5 nm. The kinetics of p-SHs growth and the long-time relaxation (spontaneous hole-filling) after burning are studied. The burning process may be described as the first order dispersive reaction, which proceeds through a phonon-assisted tunneling between different excited states of the NC/matrix system. The same model apply in the backward reaction (hole-filling) but the tunneling takes place between different ground states of the NC/matrix system and the reaction rate is much lower. The photoproduct of persistent spectral hole-burning reaction is a charged NC which energy states are modified by the Stark effect. The quantum efficiency of burning reaction is quite high 4×10^{-3} (mean rate constant is 4×10^{7} s^{-1}) while the rate of spontaneous HF reaction is very low (0.5 s^{-1}). © *1999 American Institute of Physics.* [S0021-9606(99)70144-3]

I. INTRODUCTION

The transient selective saturation of excitonic absorption under strong narrow-band excitation [transient spectral hole-burning (t-SHB)] in semiconductor nanocrystals (NCs) was observed already at the end of eighties in the beginning of laser-spectroscopic studies of NCs.[1] This phenomenon was not surprising because it is a straightforward consequence of the inhomogeneous broadening due to the NC-size distribution. On the other hand selective absorption saturation similar to t-SHB but lasting for time significantly longer than any excited state lifetime of the studied system—called persistent spectral hole-burning (p-SHB)—was an unexpected effect. A semiconductor NC is a rather big object—containing thousands of atoms—bigger and more stable than organic molecules or impurity and defect centers in which the p-SHB phenomenon was observed.[2] The first studies on p-SHB in NCs were published by Masumoto's group in 1994.[3] From the present point of view, it is probable that p-SHB is always present (to a certain extend) when studying semiconductor NCs in glass by strong selective excitation at low temperatures. However, the phenomenon was escaping an attention for several years (or it was considered to be marginal), probably because its relatively rapid saturation (exposition of about 1 J/cm^2 or less is sufficient in most cases).

Spectral hole-burning spectroscopy in semiconductor NCs has been applied to study the excited-state dynamics, to overcome the inhomogeneous broadening, and to obtain various microscopic parameters of nanocrystalline materials (as, e.g., NC size-dependence of the exciton energy, exciton–phonon interaction, etc.).[4–6] On the other hand the mechanism of p-SHB in semiconductor NCs itself is an interesting topic. The NC/matrix surface effects are most probably responsible for the p-SHB (but a detailed mechanism is not yet well understood[7]) and the investigation of the SHB phenomenon can provide information about photochemical properties of semiconductor NCs embedded in different types of matrices.

We present here a study of persistent-SHB phenomenon in CuBr NCs in a borosilicate glass matrix. The shape of spectral holes, changes of hole depth with size of NCs and especially the kinetics of growth and decay (hole-filling) of spectral holes are described in details. The aim of this work is better understanding of the mechanism responsible for persistent spectral changes in semiconductor nanocrystalline systems.

II. EXPERIMENT

A. Experimental setups

The experimental setup is based on a pulsed nanosecond XeCl-excimer laser serving as an excitation source for a dye-laser (with PBBO, Exalite 389 or DPS dye in dioxane solution as active medium). The spectral width of the laser emission is less than 0.12 meV (FWHM). Excitation intensities as high as 570 kW/cm^2 can be reached when focusing pulses of typical energy of 0.5 μJ and 5 ns duration into spots of about 150 μm diam. Absorption changes induced by a dye-laser are tested with a spectrally broad superradiance of a laser-dye solution excited by a part of the excimer laser emission. Probe and pump pulses are focused on to the sample surface

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such that they are coincident in space and time (this allows to perform simultaneously persistent and transient SHB experiments, see Ref. 8 for details). The probe pulses are dispersed in a single grating 3/4 m monochromator and are detected by an optical multichannel analyzer connected to a computer.

For the seek of comparison we use also a one-beam pump-and probe setup to measure p-SHB. In this configuration the pumping dye-laser serves also to probe induced absorption changes. The testing of sample transmission before and after burning is achieved by scanning frequency of the attenuated (about 1000 times) laser beam around the center of a spectral hole. The transmitted light is detected directly by a photomultiplier placed behind the cryostat. The advantages of the one-beam method are a higher spectral resolution (it is determined by the spectral width of dye-laser emission) and the perfect spatial coincidence of the spots of the pumping and the testing beam on the sample. On the other hand, the advantages of the two-beam method are a multichannel detection of the wide part of a transmission spectrum and the possibility to observe transient changes during burning.

The experiments are performed at low temperatures using a pumped helium-bath cryostat ($T = 2$ K) or a continuous flow cryostat which allows to adjust the temperature between 5 and 300 K.

Room temperature linear absorption is measured by a conventional two beam spectrophotometer (Hitachi UV3000).

B. Sample preparation and characterization

CuBr NCs have been grown in a borosilicate glass matrix using a diffusion controlled process.[9] The semiconductor concentration in the matrix is about 1%. We study a set of five samples made of glass containing CuBr NCs of different mean radius, 12, 9.5, 5.1, 3.9, and 2.8 nm, respectively. (Note: the Bohr radius of exciton is 1.25 nm in the bulk CuBr). The mean radius of the NCs is determined from the spectral positions of the maxima of the $Z_{1,2}$ and Z_3 excitonic absorption bands using the model of donorlike excitons.[10] Samples have a rectangular form of sheets with thickness of about 0.4 mm.

Room-temperature absorption spectra of two representative samples are shown in Fig. 1 (spectra of the whole set of samples were presented in Ref. 8, Fig. 1). The important blue-shift of $Z_{1,2}$ and Z_3 excitonic absorption bands due to the quantum confinement is clearly observed [see also Fig. 2(A) for low-temperature linear absorption spectra of three samples containing NCs of mean radius of 5.1 nm or smaller].

Two other interesting absorption bands are observed at high photon energies around 4.5 and 5.7 eV (see Fig. 1). We attribute the peak at 5.7 eV to the E_1 peak of a band-to-band transition in CuBr according to results from bulk CuBr, where this peak is placed at 5.5 eV.[11,12] The peak at 4.5 eV may correspond to the Cu^+-ion absorption (transitions $3d^{10} \rightarrow 3d^9 4s$ and $3d^{10} \rightarrow 3d^9 4p$) because it is shifted to lower energy only by about 20–300 meV compared to Cu^+-ion absorption in alkali halides.[13–15]
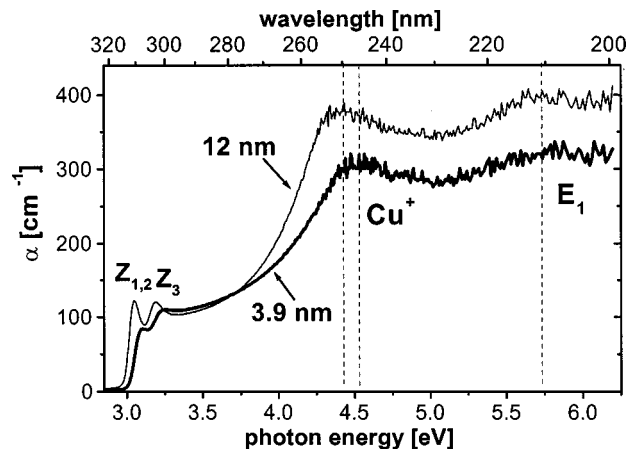

FIG. 1. Linear UV absorption spectra (taken at room temperature) for two samples 3.9 nm (bold line) and 12 nm (narrow line). Apart from the excitonic absorption bands $Z_{1,2}$ and Z_3 two another UV-bands around 4.5 and 5.75 eV are distinguished. For details, see Sec. II B.

III. EXPERIMENTAL RESULTS

Strong excitation of CuBr NCs by a pulsed nanosecond dye-laser radiation (photon energy being resonant with the $Z_{1,2}$ excitonic absorption band) produces two types of changes in absorption spectra (see Figs. 3 and 4):

(i) relatively *narrow spectral holes* resonant with the laser photon energy and

(ii) *broad overall changes* of excitonic absorption bands (absorption background changes).

One part of both types of changes lasts only during the excitation (transient changes with sub-ns decay time[8]), the second part has a very long decay time (several hours) at low temperatures (persistent changes, Figs. 3 and 4). In this paper we concentrate on the p-SHB effect. The comparison of the persistent and transient changes was presented in our previous paper.[8]

We have to note that both the t-SHB and p-SHB are observed only in three samples from our set, namely in those with mean sizes of NCs of 2.8, 3.9, and 5.1 nm. The other two samples with bigger NCs have narrower size distributions and consequently the inhomogeneous broadening of the excitonic absorption bands is smaller and the peak absorption of the $Z_{1,2}$ band is much higher. This makes the observation of t-SHB more difficult. Also the efficiency of the p-SHB mechanism seems to decrease with increasing size of NCs as illustrated in the Fig. 2. Part A of Fig. 2 shows the low-temperature (2 K) linear absorption spectra of 2.8 nm (black triangles), 3.9 nm (white triangles), and 5.1 nm (black circles) samples. Figures 2(B) and 2(C) show the size-dependence of relative hole depths (at the burning laser photon energy) for the transient and persistent SHB, respectively. For the seek of comparability the values of hole depths were taken at identical excitation intensity of 100 kW/cm^2 in the case of t-SHB and for energy fluence of 300 mJ/cm^2 in the case of p-SHB. The relative hole-depth always decreases with increasing photon energy in the $Z_{1,2}$ absorption band for any of the three samples. For samples with smaller mean size of NCs, however, the relative depth increases (if compared for any photon energy inside the $Z_{1,2}$
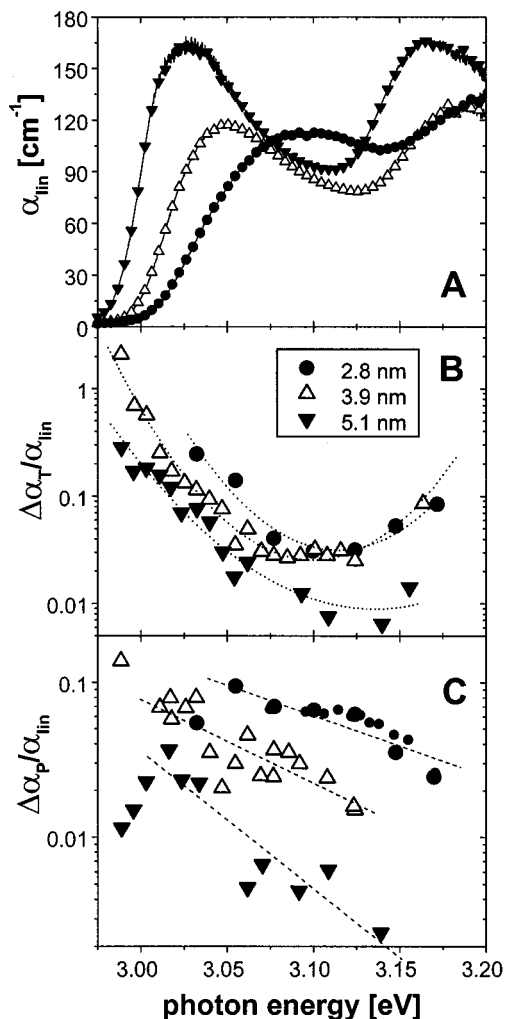
FIG. 2. Size dependence of the relative hole depths (for resonant holes). (A) Linear absorption of three samples (mean size 2.8 nm—full circles, 3.9 nm—open up-triangles, and 5.1 nm—full down-triangles) exhibiting hole burning effects. (B) Relative transient absorption changes. (C) Relative persistent absorption changes. The transient hole depths at any wavelength are monitored for an excitation density of 100 kW/cm^2, the persistent holes are monitored for an exciting laser fluence of 300 mJ/cm^2.

FIG. 3. Persistent changes (differential absorption) of the $Z_{1,2}$ excitonic absorption band under resonant excitation (CuBr NCs, $a = 2.8$ nm). (A) Persistent absorption changes ($T = 2$ K) measured in the two beam configuration for excitation at 3.054 eV and fluences of 2.0 (a), 16 (b), and 270 mJ/cm^2 (c). The deepest component of spectral holes coincide with the laser frequency (resonant holes). Dashed lines mark positions of side-holes. (B) Detail of the central part of persistent SHs ($T = 7$ K) measured in the one-beam configuration for excitation at 3.045 eV and burning fluences; 64 (a), 130 (b), 250 (c), 500 (d), and 1000 mJ/cm^2 (e). Full dots represent experimental data, while solid lines are Lorentzian fits of SHs. (C) Broadening of above plotted SHs with increasing fluence. The zero-fluence limit width (dashed line) is about 1.3 meV.

band), especially for the case of p-SHB [Fig. 2(C)]. This paradox—increasing importance of SHB in samples with small NCs but decreasing depth with decreasing size within one sample—may be understood by considering the different preparation conditions of our samples. Bigger NCs are formed by annealing at higher temperatures and for a longer time. They have better spherical shape and better quality of interfaces. If the mechanism of photochemical changes is related to surface defects and imperfections, its efficiency will be reduced in bigger (more regular) NCs.

A. Shape of resonant spectral holes

Resonant spectral holes consist of a hole centered at the excitation wavelength (central hole) and of several side-holes at both shorter and longer wavelengths [Fig. 2(A)].

Central holes have almost a perfect Lorentzian shape without any apparent structure. We suppose that they corre-
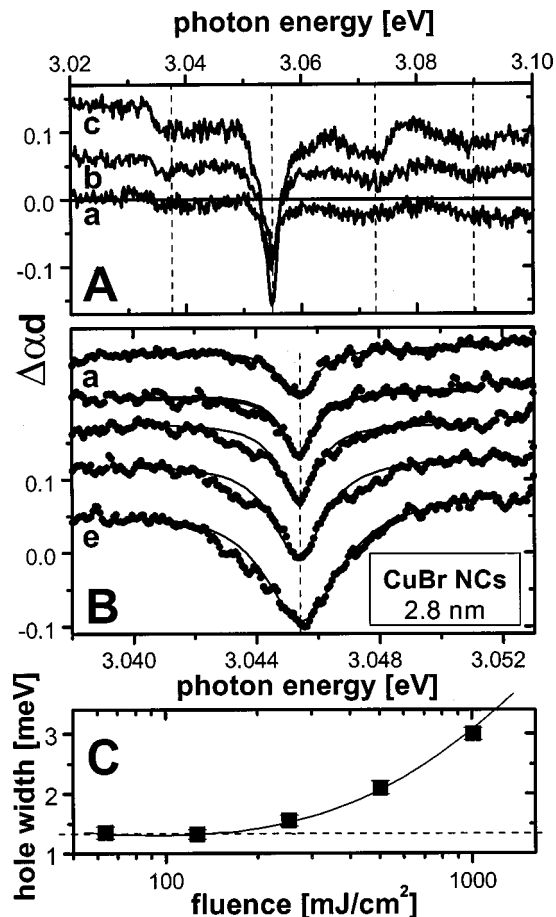
spond to zero-phonon absorption lines of almost single-sized NCs. No side-bands coming from low-frequency acoustic phonons [observed by Matsumoto group in similar experiments on CuCl (Ref. 16)] are resolved near the burning frequency. Figure 3(B) shows details of the central part of persistent SHs. These high-resolution spectra were measured in the one-beam configuration. There is no apparent difference compared to the two-beam experiments [Fig. 3(A)]. Therefore we can state that the two-beam experiments have a high enough resolution and provide us with essentially identical results as the one-beam configuration but in significantly (about 10 times) shorter detection time. Part C of Fig. 3 shows the width of the hole as a function of fluence for data from Fig. 3(B). Small broadening at low fluences becomes stronger for fluences higher than about 250 mJ/cm^2. This is the value of fluences at which the persistent-hole depth becomes almost saturated [see Sec. III C, (Fig. 5)].
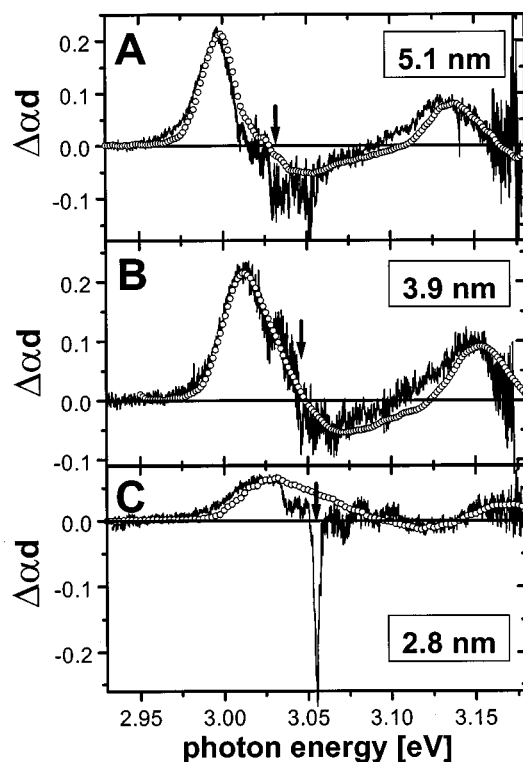
FIG. 4. Wide spectral-range persistent differential absorption spectra for the fluence of 800 mJ/cm² in samples; 5.1 nm (A), 3.9 nm (B), and 2.8 nm (C). The position of the laser is marked by arrows. For comparison we add dotted curves to each spectrum. These spectra represent calculated absorption changes corresponding to 0.21 (A), 1.9 (B), and 1.12 meV (C) red-shifts of respective linear absorption spectra.

In our previous papers[8,17] we have estimated excitonic dephasing time from the widths of central holes and compared them with direct measurements by femtosecond transient four-wave-mixing. Also a discussion of a LO-phonon origin of side holes may be found in Ref. 8.

B. Absorption background changes

In wide-range differential absorption spectra (see Fig. 4) we can observe that narrow spectral holes around the excitation wavelength are superposed with some broad wavy structures.

The shape of broad absorption changes may be reconstructed by a small red-shift (of a few meV) of the linear absorption spectrum. (We note the evident fact that the shape of differential absorption spectra obtained by such a small red-shift is identical to the shape of the first derivative of linear absorption spectra.) The dotted curves in Figs. 4(A), 4(B), 4(C) are the absorption changes calculated by linear absorption red-shifts of 0.21, 1.9, and 1.12 meV, respectively. The correspondence between measured and modeled background changes is quite good. The magnitude of the background differential absorption grows with increasing fluence in the same way as the depth of a resonant hole, i.e., approximately as the logarithm of fluence. A possible origin of the absorption background changes will be discussed in Sec. IV.
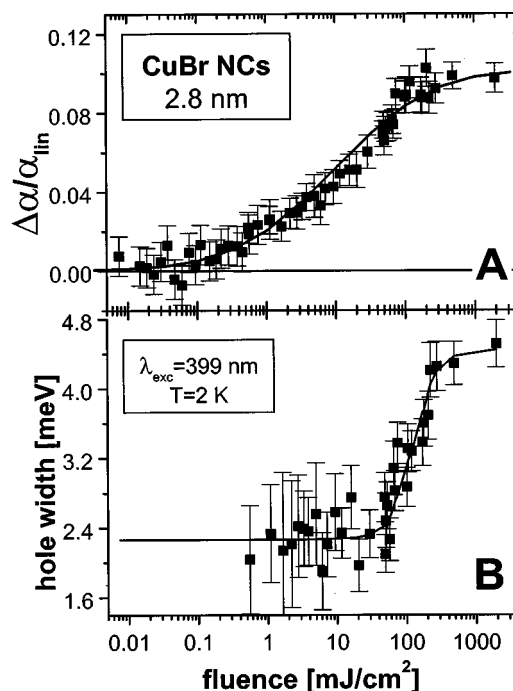

FIG. 5. Growth of relative hole depth (at the center of resonant holes) of persistent SHs in 2.8 nm NCs ($T=2$ K, $h\nu_{exc}=3.1065$ eV). Experimental points are represented by black squares. The solid line is a fit calculated using a model of the first order dispersive reaction described in text (Sec. III C 1). The best fit is obtained for parameters, $\sigma_G=1.14\pm0.54$ and $C=63\pm9$ cm²/J. (B) Broadening of persistent holes with energy fluence. The black squares are the full-widths at half-maximum of the Lorentzian fits of holes. The solid line is only the guide for eyes.

C. Kinetics of growth and decay of persistent spectral holes

The study of the kinetics of growth and decay (recovery) of p-SHs gives us an interesting insight into the mechanism of the p-SHB phenomenon. It allows us to estimate the distribution of rates of the corresponding reaction as well as its quantum efficiency.

1. Persistent spectral hole-burning kinetics

Figure 5 shows the resonant hole depth (A) and width (B) as a function of the energy fluence extending over five orders of magnitude. Our laser was tuned to the center of the $Z_{1,2}$ absorption band (3.1065 eV). For practical reasons (the duration of experiment) we increase energy of laser pulses from 1.2 nJ/pulse up to 130 nJ/pulse to achieve energy fluence extending over five orders of magnitude (the repetition rate was kept constant at about 10 Hz). The correctness of this procedure was verified by measuring the p-SH growth with different intensities of laser pulses. We observed that the kinetics of p-SHB depends only on the integral exposition of the samples and not on the intensity of exciting laser pulses (within the range of energies specified above and within our experimental accuracy). We did not find any threshold pulse energy (down to 1 nJ/pulse) below which the p-SHB is not observed.

These facts exclude the Auger-type mechanism of SHB, i.e., the creation of some stable product by exciton–exciton or exciton–electron (exciton–hole) scattering which can give
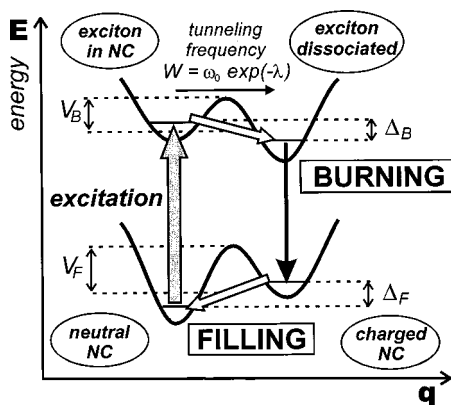
FIG. 6. Sketch of the model [based on the two-level systems (TLS) scheme] adopted to explain the kinetics of p-SH growth (see Sec. III C 1). V_B, V_F and Δ_B, Δ_F are the barrier heights and the asymmetry parameters for barriers involved in the burning and filling reaction, respectively. $W = \omega_0 \exp(-\lambda)$ is a tunneling frequency for the phonon-assisted tunneling between two different excited states of the NC/glass system (where ω_0 is a phonon frequency and λ is a tunneling parameter).

to an electron (hole) enough energy to overcome energy barrier at the NC/matrix interface. In such a case the efficiency of the reaction should depend superlinearly on the pulse intensity.

Concerning the width of the holes [Fig. 5(B)] we observe a small broadening up to energy fluences of about 0.1 J/cm^2 (around this fluence the hole-depth becomes saturated), then the hole-widths increase to approximately the double of its minimal value.

It is evident that the observed kinetics of the p-SH growth cannot be described by a single rate constant. Therefore we use a model of the *first order dispersive (photochemical) reaction* (reaction with a significant distribution of reaction rates) in analogy with a persistent-SHB in glasses doped with organic molecules (for review see Ref. 18).

In this model,[19] the rate-determining step is phonon-assisted tunneling between two different excited states of the impurity-glass matrix system. After relaxation the system is found in a different ground state configuration (with different position of absorption line) than before excitation. A persistent SH can be created at the laser burning wavelength just because the spontaneous backward-reaction has a much lower probability,

We suppose that a similar mechanism may be adopted to explain the growth of p-SHs in CuBr NCs in a glass matrix. Figure 6 gives a schematic representation of our model based on the two-level systems (TLS) scheme.[20] The absorption of a photon creates one free-exciton in a NC. It recombines back or becomes localized at the NC/matrix interface. Now, the electron–hole pair can either recombine or the electron (hole) can tunnel through a barrier to the matrix creating permanent charges—trapped quasiparticles—near the interface. So in analogy with amorphous molecular solids the NC/glass system has more than one ground state configuration and the transfer between two ground states is possible via excited state tunneling. The phonon-assisted tunneling rate is $W = \omega_0.\exp(-\lambda)$, where ω_0 is a phonon frequency and λ is a tunnelling parameter. The parameter λ depends on

several other quantities which are subject to statistical fluctuations because of the disorder on the interface NC/glass.

The value of the tunnelling rate R is highly sensitive to tunneling parameters and it can extend over several orders of magnitude. For nonphotochemical SHB involving the downward phonon-assisted tunneling in the excited electronic state of the molecule, the reaction rate takes the form $R = \Omega_0.\exp(-2\lambda)$, where $\Omega_0 \approx \omega_0$.[18] So the distribution of R values stems primarily from the distribution of λ values. Different shapes of the λ distribution have been adopted, e.g., the square distribution[21] or a normal (Gaussian) distribution.[22] In the following we use the Gaussian λ-distribution.

The expression for the relative central hole depth (i.e., normalized number of burned NCs) $D_h(t) = \Delta \alpha / \alpha_{\text{lin}}$ as a function of burning time t has the form,[18]

$$D_h(t) = 1 - \int_0^{\Omega_0} f(R).\exp(-P\sigma\Phi(R)t).dR, \qquad (1)$$

where $f(R)$ is the normalized distribution function for R, P is the photon flux, and σ the peak absorption cross section of the transition. The quantum yield for the reaction is equal to $\Phi(R) = R/(R+k)$, where k is the excited state decay rate. Usually, the relation $R \ll k$ is fulfilled and $\Phi(R) \approx R/k$.

Because the hole kinetics is measured as a function of photon flux P in our case (we use different pulse intensities), the hole depth $D_h(t)$ has to be expressed as a function of photon fluence $F = P(t).t$

$$D_h(F) = \frac{1}{\sqrt{2\pi} \cdot \sigma_G} \int_{-\infty}^{+\infty} \exp\left(-\frac{x^2}{2\sigma_G^2} - C \cdot F \cdot \exp(2x) \right).dx, \qquad (2)$$

where $x = \lambda - \lambda_0$ and $C = (\sigma/k).\Omega_0.\exp(-2\lambda_0)$. We adopt here the Gaussian distribution of λ values (λ_0 is the center and σ_G the width of the Gaussian distribution). Equation (2) has been used to fit the hole-growth kinetics [see Fig. 5(A)]. The two fitting parameters are the width of the Gaussian distribution σ_G and the constant C. The best fit has been obtained for the following values of parameters: $\sigma_G = 1.14 \pm 0.54$ and $C = 63 \pm 9$ cm^2/J. Using the values of the absorption cross section $\sigma \cong 10^{-13}$ cm^2 (see Appendix), the excitonic decay rate $k \cong 10^{10}$ s^{-1}, and the LO-phonon frequency $\omega_0. \cong 3.06 \times 10^{13}$s^{-1},[8] we find from C the mean value of the λ-distribution $\lambda_0 = 11.0$. We can also calculate the average value of the rate constant $\langle R \rangle = \Omega_0 \exp(-2\lambda_0)\exp(2\sigma_G^2) = 4.2 \times 10^7$ s^{-1} and the corresponding quantum efficiency $\Phi = \langle R \rangle / k = 4.2 \times 10^{-3}$. All the values of λ distribution parameters as well as reaction quantum efficiency are of the same order as the values found in glasses doped by organic molecules.[18]

The value of quantum efficiency $\Phi = 4.2 \times 10^{-3}$ is quite high but is only about the half of the value 9.7×10^{-3} measured by Kawazoe and Masumoto for CuBr NCs in glass (mean radius of 3.4 nm, $T = 5$ K).[23] Nevertheless, their procedure for elucidation of Φ is different from ours because only the onset of hole-growth curve is considered for calcu-
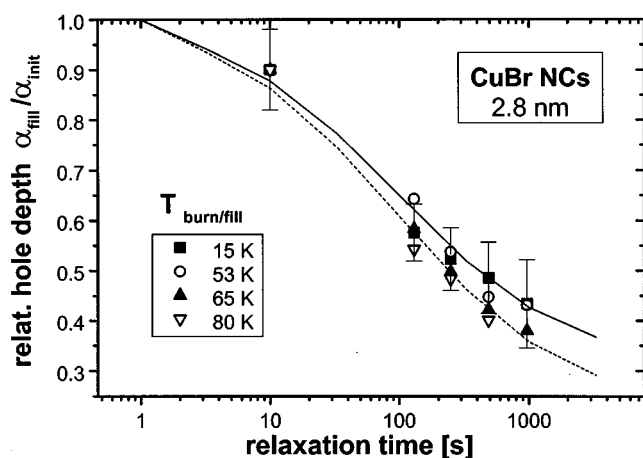
FIG. 7. *Spontaneous filling of persistent SHs for 2.8 nm CuBr NCs*. The hole-depth is plotted in units of original hole depth at the end of burning ($h\nu_{exc} = 3.1065$ eV). The temperature of the burning/filling process was 15 K (black squares), 53 K (white dots), 65 K (black triangles), and 80 K (white triangles). The solid and dotted lines are the best fits calculated using Eq. (3) (see Sec. III C 2). The fitting parameters are $\sigma_G = 1.0 \pm 0.5$ and $B = 6.8 \pm 2.1 \times 10^{-3}$ s^{-1}. The unfillable part of the original hole was taken 0.33 and 0.25, for the upper (solid) curve and the lower (dashed) curve, respectively.

FIG. 8. Schematic representation of the sequence of processes involved in the SHB and HF processes (for details see Sec. IV).

lation. Such treatment is preferential for nanocrystals with higher probability of the p-SHB photoreaction while our calculation gives the mean value of Φ.

We have to note that the relative hole-depth is saturated at about 10% of the linear absorption [Fig. 5(A)]. The reason may be, that not all NCs are able to undergo the photoinduced reaction with a stable photoproduct. Also the influence of the exciton–phonon coupling may affect the depth of hole.[24]

2. Spontaneous hole-filling

The spontaneous hole-filling (SHF) is a backward reaction (relaxation) which transforms a photoproduct of the burning reaction back to the initial educt state. SHF proceeds through the tunneling between different ground states of the system (and not through the excited states involved in the burning reaction). The equation for the hole-depth kinetics will be similar to Eq. (2) (but the distribution of the tunnelling parameter λ is not the same as that found for p-SHB),

$$D_h(t) = \frac{1}{\sqrt{2\pi} \cdot \sigma_G} \int_{-\infty}^{+\infty} \exp\left(-\frac{x^2}{2\sigma_G^2} - B \cdot t \cdot \exp(2x) \right) . dx,$$

(3)

where $B = \Omega_0 . \exp(-2\lambda_0)\exp(2\sigma_G^2)$.

In Fig. 7 the decay of saturated persistent SHs is shown for different burning/filling temperatures. The best fit is obtained for the following values of parameters: $\sigma_G = 1.0 \pm 0.5$ and $B = 6.8 \pm 2.1 \times 10^{-3}$ s^{-1}. Using the same value of the LO-phonon energy as in the previous calculation we find $\lambda_0 = 18$, and $\langle R \rangle = 0.5$ s^{-1}. The width of the λ-distribution is approximately the same as for the burning process, but the mean value λ_0 is significantly higher. The average rate constant of the filling reaction is eight orders of magnitude lower than for burning.
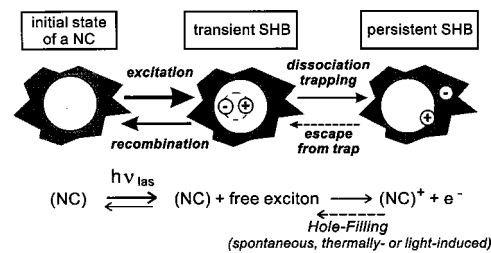
An interesting feature of the SHB process is also the fact that a part of the initial p-SH stays unfilled even after a long relaxation time. The unfillable portion of p-SH decreases from 0.33 to 0.25 with a temperature rise from 15 to 80 K.

We have to note that persistent spectral holes in our samples may be efficiently erased also by thermal or light (laser) stimulation of backward reaction. Both thermally and laser-induced hole filling phenomena were described in Ref. 25.

IV. DISCUSSION: MODEL OF PERSISTENT SPECTRAL HOLE-BURNING IN SEMICONDUCTOR QUANTUM DOTS

Generally, two main types of p-SHB mechanisms are described in literature;[18,26] *photophysical* (or nonphotochemical) and *photochemical*. The photophysical SHB occurs due to a rearrangement of the host environment around the absorber. The photoproduct absorption appears usually close to the burning wavelength (inside the inhomogeneously broadened band in this case). The photochemical mechanism labels a (reversible) reaction that is initiated in an excited state of the absorber (molecule) and its photoproducts absorb usually far from the burning wavelength. In the case of semiconductor nanocrystals, however, it is difficult to distinguish between the photochemical or photophysical mechanisms. Our p-SHB spectra (see Fig. 4) show an induced absorption on the red edge of the $Z_{1,2}$ excitonic absorption band but we cannot decide whether this is really a photoproduct absorption or simply the effect of a red-shift of the whole linear absorption spectrum due to an electric field effect.

Masumoto and co-workers proposed a straightforward model of persistent SHB in copper halide NCs; the photoionization of NCs.[27] It is worth mentioning that such a model was previously used to explain photoinduced permanent increase of absorption—the so-called photodarkening effect—in CdS$_x$Se$_{1-x}$ ($x = 0...1$) NCs in glass (color filters).[28,29] Let us now propose a similar model for the persistent SHB in CuBr NCs, which will explain our experimental observations.

A schematic picture of our model is in Fig. 8. A photon absorbed by a NC (whose exciton energy is resonant with the laser frequency) creates an exciton inside a NC. The presence of one exciton in a NC saturates its absorption at the laser wavelength but creates induced (biexcitonic) absorption at a higher energy. This causes transient spectral holes as well as changes of absorption in a wide spectral range. Then the exciton recombines (the initial state of a NC is reconstructed) or it is localized on the surface of the NC and

afterwards dissociates. An electron (or hole) escapes from the NC (probably by tunneling through the potential barrier on the NC/glass interface) and both particles are trapped separately in a glass matrix around the NC and on the surface of the NC. In such a way the NC becomes charged (ionized) and its absorption is shifted away from the initial position (or even disappears completely) and a resonant hole appears. We suppose that background absorption changes are caused by the photoproducts of laser-induced reaction. Separately localized electrons and holes cause relatively strong local electric field and consequently the excitonic absorption energies are red-shifted by the *Stark effect* (the oscillator strength of the transitions is also modified by an electric field). The Stark shift may have a broad distribution due to the variation of magnitude of a local electric field which depends on exact position of the charges. In consequence the photoproduct absorption is smoothed and has no sharp structure (similar to observed background absorption changes, Fig. 4). The eventual creation of a local electric field by charge diffusion from burned to unburned NCs through the glass matrix has a low probability at low temperatures (< 10 K).

The Stark effect in II–VI semiconductor quantum dots has been studied extensively because of their potential application as optical modulators.[30,31] Stark shift in ensembles of NCs was found to be a quadratic function of the applied field, it means that the polarizability of NC excited-state plays a key role. The recent work of Empedocles and Bawendi[32] on single CdSe NC Stark spectroscopy indicates clearly the importance of both the polar and polarizable character of the lowest excited state. The excited-state dipole moment (its average in an ensemble of NCs goes to zero due to the random orientation of dipoles) is explained by the polarization of a highly polarizable excited state in a strong, rapidly changing local field. This field has a magnitude of the order of $10^5 - 10^6$ V/cm^2 and it is caused by the localization of charge carriers on or near the NC surface (such a photoionization has been also proposed as the source of single-NC fluorescence intermittence[33]). The Stark shift due to the local electric field causes spectral diffusion which is probably the main source of the inhomogeneous broadening of NC spectral lines. We suppose that a similar mechanism is involved in the persistent spectral hole-burning in our CuBr/glass samples. (Unfortunately, there are not any data on electroabsorption of copper halides in literature as far as we know.) It seems probable, that the photoionization effect inducing strong local electric fields is a common feature in various semiconductor nanocrystalline materials (in both the strong and weak quantum confinement regimes).

Let us now return to our description of the p-SHB mechanism. A stable photoproduct (ionized NC) is formed efficiently (quantum efficiency 4×10^{-3}) but only in a small part of the total number of excited NCs. (The depth of saturated p-SHs is only about 10% or 20% in extreme cases.)

The backward reaction may proceed either spontaneously or it may be induced by a thermal or light excitation. The spontaneous backward reaction—escape and recombination of trapped quasiparticles by tunnelling—has a very low rate (about 0.5 s^{-1}, eight orders of magnitude lower than the burning reaction). A part of the initial p-SH stay unfilled

even after a long time (for temperatures $T < 80$ K, see Fig. 7). On the other hand, the filling by heating of the sample can erase the hole completely since trapped quasiparticles are released efficiently by a thermal activation.

What is the nature of photoinduced centers? Okamoto and Masumoto suggested that the Cu$^+$-ion displacement triggers p-SHB in CuCl NCs in NaCl.[34] We observe a peak assigned to the Cu$^+$-ion absorption in the linear absorption spectra of our samples. More information about the role of Cu$^+$-ions may be elucidated from the comparison of simultaneously observed photoluminescence and absorption changes. These experiments are under development.

V. CONCLUSIONS

We have performed pump-and-probe transmission experiments (using a nanosecond dye-laser) on CuBr nanocrystals (NCs) embedded in a borosilicate glass matrix. The persistent spectral hole-burning (SHB) phenomenon is observed in the low temperature excitonic absorption band of NCs with mean radius smaller than 5 nm. The evolution of spectral holes during burning and their relaxation after burning are studied. We show that both the persistent SHB and the spontaneous hole-filling (HF) may be described as the first order dispersive reactions. The SHB (HF) reaction proceeds through phonon-assisted tunneling between different excited (ground) states of the NC/matrix system. The persistent product of such reaction is a charged NC which energy states are modified by the Stark effect. The quantum efficiency of the burning reaction is quite high 4×10^{-3} (average rate constant is 4×10^7 s^{-1}) while the rate of spontaneous HF reaction is very low (0.5 s^{-1}).

APPENDIX: ABSORPTION CROSS SECTION OF A NANOCRYSTAL

Our estimation of the NC absorption cross section (ACS) σ is based on the relation between the absorption coefficient α and the ACS σ,[35]

$$\alpha = \sigma(N_1 - N_2), \tag{A1}$$

where N_1 and N_2 are the populations of the ground and the excited state, respectively. For very low photon flux, fast relaxation and low thermal population [$kT \ll (E_2 - E_1)$] we can use the approximation $N_2 = 0$, $N_1 = N_t$. Here N_t stands for the total population, i.e., the number of absorption centers, molecules or nanocrystals in our case.

The problem is now reduced to the calculation of the number of NCs participating in absorption when the laser is tuned, for example, to the center of the inhomogeneously-broadened absorption band.

We know that semiconductor material occupies about 1% of the sample volume but not the whole mass of semiconductor can be active in a selective absorption. To estimate the part of semiconductor material, which will be resonant with a selective laser excitation, we take the ratio of homogeneous/inhomogeneous linewidth. This parameter is equal to 1/100 if calculated as the ration of the zero-intensity limit value of a hole-width (1.25 meV, see Fig. 3) and the width of the inhomogeneously-broadened $Z_{1,2}$ absorption band [125 meV, see Fig. 2(A)]. The volume of a NC with radius of 2.8 nm is 9.2×10^{-20} cm^3. Consequently the volume of 1×10^{-4} cm^3 represents 1.1×10^{15} of nanocrystals ($a = 2.8$ nm) and our estimation of N_t is 1.1×10^{15} cm^{-3}. Finally, when we take the absorption coefficient at the center of the $Z_{1,2}$ band $\alpha = 110$ cm^{-1} [see Fig. 2(A)] we obtain from Eq. (6) the value of the NC cross section $\sigma = 1 \times 10^{-13}$ cm^2.

Let us compare the result of our estimation with a procedure adopted by Kawazoe and Masumoto.[23] They assume that the ACS for unite volume does not change from a bulk crystal to nanocrystals. The ACS is given as a product of the ACS for a unit volume κ and the volume V of nanocrystal in resonance with laser. For the Z_3 absorption of CuCl they found $\kappa = 3 \times 10^6$ meV/cm (but they give no explicit value for $Z_{1,2}$ in CuBr). This is exactly what we can find from bulk absorption spectrum in Ref. 11. From the same reference we estimate $\kappa = 5 \times 10^6$ meV/cm for $Z_{1,2}$ absorption of CuBr. This gives us $\sigma = 1.5 \times 10^{-13}$ cm^2 in good agreement with our estimation.

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