



# Growth and decay of persistent spectral holes in CuBr semiconductor quantum dots

J. Valenta<sup>a,\*</sup>, J. Dian<sup>a</sup>, P. Gilliot<sup>b</sup>, R. Lévy<sup>b</sup>

<sup>a</sup>*Faculty of Mathematics and Physics, Department of Chemical Physics and Optics, Charles University, Ke Karlovu 3, CZ-121 16 Prague 2, Czech Republic*

<sup>b</sup>*Institut de physique et chimie des matériaux de Strasbourg, Groupe d'optique nonlinéaire et d'optoélectronique, UMR 7504 CNRS - ULP 23 rue du Loess, F-670 37 Strasbourg Cedex, France*

## Abstract

Persistent changes of absorption and photoluminescence (PL) induced by laser excitation of CuBr nanocrystals in a glass matrix are studied. Sharp resonant holes in the absorption spectrum are produced by selective excitation within the  $Z_{1,2}$  absorption band but not by the excitation above this band. Wide wavy changes of absorption are induced by both resonant and non-resonant excitation. Observed PL changes are broad and quite independent of the wavelength of the exciting laser. Trapped excitons and biexcitons seem to play a key role in the photoinduced reaction. The photoproduct is a single- or multiple-charged nanocrystal, in which the local electric field affects the electronic energy levels through the DC Stark effect. The evolution of the hole depth during burning and its relaxation after burning are described as first-order dispersive reactions, which proceed through the phonon-assisted tunneling between different excited states (forward reaction) and ground states (backward reaction) of the NC/matrix system. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 71.35.-y; 73.20.Dx; 78.55.Hx; 78.66.Jg

Keywords: Nanocrystals; Excitons; Spectral hole burning; Hole filling; Photoionization

## 1. Introduction

Semiconductor nanocrystals (NCs) imbedded in glasses or crystalline matrices exhibit a number of photo-induced modifications when exposed to strong laser excitation (see Ref. [1] for recent review). Beside the photodarkening, laser annealing or photochemical reactions the persistent spectral hole-burning (p-SHB) phenomenon has attracted

much attention in the last five years. Masumoto with co-workers observed p-SHB in CdSe,  $CdS_xSe_{1-x}$ , CuCl, CuBr and CuI nanocrystals and concluded that the selective photo-ionization of resonantly excited nanocrystals is a possible mechanism of p-SHB [2]. However, a detailed plausible explanation of how the photoinduced reaction proceeds has not yet been published.

We present here a study of p-SHB phenomenon in CuBr NCs in a glass matrix. Both resonant and non-resonant laser excitations were applied to observe induced persistent changes in absorption as well as in emission spectra. The kinetics of growth

\* Corresponding author: Fax: +420-2-21-91-12-49.  
E-mail address: valenta@karlov.mff.cuni.cz (J. Valenta)

and decay (hole filling) of spectral holes are described in detail. Our results point to the key role of trapped excitons and biexcitons in the mechanism responsible for persistent spectral changes.

## 2. Samples preparation and experimental set-ups

CuBr NCs have been grown in a borosilicate glass matrix using a diffusion controlled process. 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. For details about samples and their linear optical properties see our previous papers [3,4].

The experimental set-up is based on a pulsed nanosecond XeCl-excimer laser (308 nm, pulse duration of 30 ns and typical repetition rate of about 10 Hz). A small part of the XeCl laser output is used to excite photoluminescence (PL) and the major part pumps a dye-laser. The spectral width of the dye-laser emission is less than 0.12 meV (FWHM). Absorption changes induced by a dye-laser are tested with a spectrally broad super-radiance 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 such that they are coincident in space and time (this allows to perform simultaneously persistent and transient SHB experiments, see Refs. [3,4] for details). The probe pulses are dispersed in a single grating  $\frac{3}{4}$  m monochromator and detected by an optical multichannel analyzer. All 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.

## 3. Experimental results

### 3.1. Persistent absorption changes

The low-energy edge of the absorption spectrum of CuBr is dominated by the  $Z_{1,2}$  and  $Z_3$  excitonic absorption bands (the two excitons arise from the spin orbit splitting of the valence band [5]).

Excitonic bands are strongly blue-shifted (and broadened) with respect to the bulk CuBr due to the quantum confinement effect (Bohr radius of bulk  $Z_{1,2}$  exciton is 1.25 nm, therefore a weak or intermediate regime of quantum confinement takes place in studied NCs [6]) (see Fig. 1A).

The resonant dye-laser excitation of NCs through the lowest absorption band ( $Z_{1,2}$ ) induces two types of persistent changes in absorption spectrum (Fig. 1B and C). The most flagrant feature is the narrow spectral hole at the wavelength of pumping laser accompanied by several side holes. Such narrow holes are also observed in transient hole-burning spectra [7]. The shape of narrow resonant holes reflects the homogeneous absorption spectrum of single-sized CuBr NCs and can be used

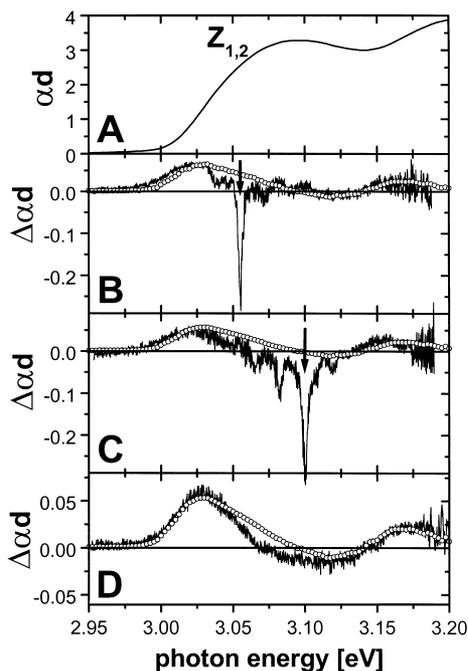


Fig. 1. Persistent changes of absorption spectrum (sample containing CuBr NCs of mean size 2.8 nm,  $T = 2$ –5 K): (A) The low-energy edge of linear absorption spectrum showing the  $Z_{1,2}$  excitonic band. (B) and (C) Absorption changes induced by the resonant excitation (indicated by arrows) at 3.055 and 3.100 eV, respectively (energy fluence was about 800 mJ/cm<sup>2</sup>). (D) Persistent absorption changes produced by the excitation of the upper part of the  $Z_3$  band, at 3.274 eV. The open circles in (B)–(D) represent simulated absorption changes produced by the red-shift of the linear absorption spectrum of 1.12, 1.00 and 0.94 meV, respectively.

to study the size dependence of energetic states of NCs, dynamics of excitons, exciton–phonon interaction in NCs, etc. [3,8].

The second feature in the persistent differential absorption spectra is a broad wavy structure which is independent of the exact wavelength of pumping laser and is even produced by the excitation of higher excitonic states ( $Z_3$ , see Fig. 1D) or band-to-band excitation (by the XeCl laser). Such absorption changes may be simulated by a simple red-shift of the linear absorption spectrum. The open dotted circles in Fig. 1B–D were calculated from the absorption spectrum (Fig. 1A) applying a red-shift of 1.12, 1.0, 0.94 meV, respectively. The simulation curves reproduce our experimental results quite well.

### 3.2. Persistent emission changes

Quasi-steady-state photoluminescence (PL) spectra of CuBr NCs excited by the XeCl laser (pulse duration 30 ps, excitation density of the order of tens of  $\text{kW}/\text{cm}^2$ ) contain two well separated peaks – labeled X and M in the present work (Fig. 2A). Both peaks are broad and their Stokes shift from the center of excitonic absorption is very large. The M peak shows a superlinear growth with increasing intensity (see inset in Fig. 2A) – even optical gain at the M peak may be induced by a strong laser pumping. These observations agree well with PL measurements and interpretation of the two PL bands published by Woggon et al. [9]. The most probable origin of the X and M bands is the radiative recombination of trapped excitons and biexcitons, respectively. (More data on PL of CuBr NCs will be published separately.) We note that the localization and trapping of biexcitons was recently observed in CuCl nanocrystals [10] and in narrow quantum wells and semiconductor alloys (see for example Ref. [11]).

PL spectra excited selectively through the  $Z_{1,2}$  absorption band (site-selective PL, see Fig. 2B) are dominated by the biexcitonic M band, whose intensity grows as the photon energy of excitation decreases. (The PL excitation spectrum of the M band has a shape similar to the wavelength dependence of a resonant hole depth [4].) The width of the M band is almost as large as that for

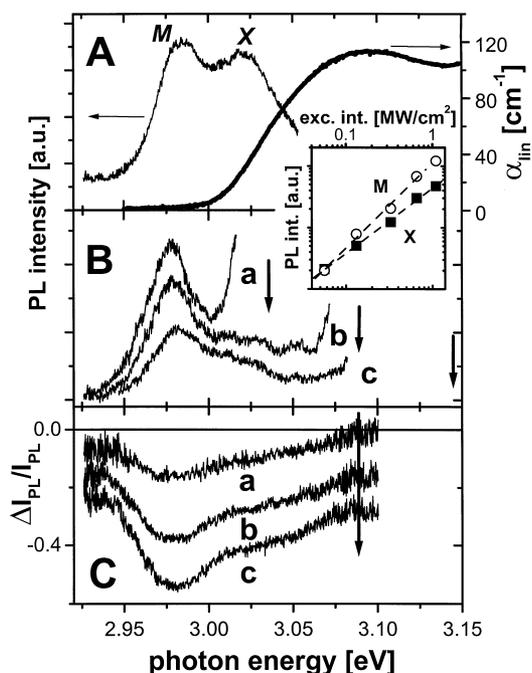


Fig. 2. Photoluminescence persistent changes (sample CuBr NCs 2.8 nm at  $T = 8$  K): (A) The linear absorption spectrum (bold line) and PL spectrum (left curve) excited by the XeCl laser (308 nm). The inset shows excitation intensity dependence of the M and X emission bands (white circles and black squares, respectively), the lines are fits of experimental points indicating slopes 1.4 and 1, respectively. (B) Selectively excited PL spectra. The position of laser excitation (indicated by arrows) was (a) 3.036, (b) 3.090, and (c) 3.146 eV. (C) Relative changes of PL induced by the excitation at 3.090 eV with fluences (a) 1, (b) 20, and (c) 130  $\text{mJ}/\text{cm}^2$ .

non-resonant excitation. No PL structures of narrow shape similar to resonant absorption holes are observed.

Prolonged resonant as well as non-resonant excitation causes a decrease of PL intensity, the M band being affected more strongly than the X band (Fig. 2C). The decrease of PL can reach up to 60% of the original intensity. As for site-selective spectra, narrow holes do not appear in differential PL spectra.

### 3.3. Kinetics of growth and decay of spectral holes

After this presentation of different photoinduced persistent spectral modifications we will describe their growth and relaxation. In Fig. 3 we compare

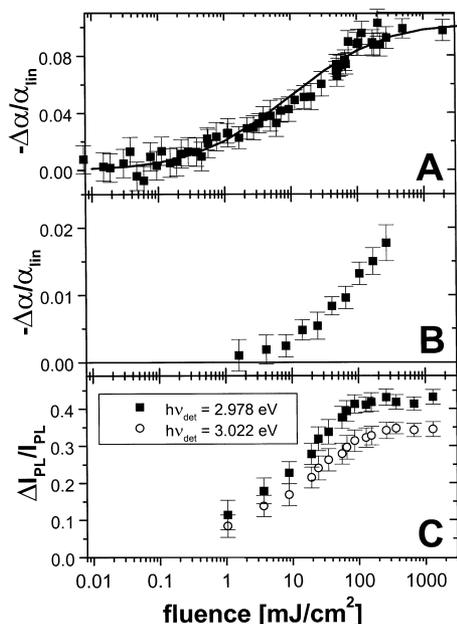


Fig. 3. (A) Growth of relative hole depth (at the centre of resonant hole) in 2.8 nm CuBr NCs ( $T = 2$  K,  $h\nu_{\text{exc}} = 3.1065$  eV). Experimental points are represented by black squares. The solid line is a fit calculated using a model of the first-order dispersive reaction (see Section 3.3). (B) Growth of the background absorption changes amplitude monitored at 3.15 eV during excitation at 3.095 eV. (C) Relative decrease of the PL intensity of the LM band (2.978 eV, black squares) and the LX band (3.022 eV, white circles) induced by excitation at 3.090 eV (at the centre of the  $Z_{1,2}$  excitonic absorption band).

the growth of the resonant hole depth (Fig. 3A) with the growth of background absorption changes (Fig. 3B) and with the decrease of the PL intensity (Fig. 3C) as a function of the excitation energy fluence.

All curves in Fig. 3 are quite similar and show nearly logarithmic dependencies of the amplitudes of changes on the energy fluence followed by saturation. The observed kinetics of the p-SHB growth cannot be, however, described by a single rate constant. Therefore, we used a model of the first order dispersive (photochemical) reaction (reaction with a significant distribution of reaction rates) in analogy with a p-SHB in glasses doped with organic molecules (for review see Ref. [12]). The model is based on the two-level system (TLS) scheme [13]: The absorption of a photon creates one free exciton

in an 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 tunnelling.

Details about the model and calculation were described in our previous paper [4]. We adopted a normal (Gaussian) distribution of the tunnelling parameter  $\lambda$ . The best fit (solid line in Fig. 3A) gives us the average value of the rate constant  $\langle R \rangle = 4.2 \times 10^7 \text{ s}^{-1}$  and the corresponding quantum efficiency  $\Phi = \langle R \rangle / k = 4.2 \times 10^{-3}$ , when we take for the absorption cross section  $\sigma \cong 10^{-13} \text{ cm}^2$  (see appendix in Ref. [4]), the excitonic decay rate  $k \cong 10^{10} \text{ s}^{-1}$ , and the LO-phonon frequency  $\omega_0 \cong 3.06 \times 10^{13} \text{ s}^{-1}$  [3].

The spontaneous changes of persistent spectral holes after the end of burning are shown in Fig. 4. While the resonant holes exhibit monotonous decrease of depth and slow broadening, the absorption background changes first slightly increase (especially at lower temperatures  $T < 50$  K) and then decay similarly as resonant holes. It seems that a resonant hole converts to a broad absorption background before it is filled out. The decrease of the resonant hole depth with time is plotted in Fig. 4C for four different temperatures.

The spontaneous hole-filling (SHF) can be understood as a backward reaction (relaxation) which transforms a photo-product of the burning reaction back to the initial educt state. SHF proceeds through the tunnelling between different ground states of the system (and not through the excited states involved in the burning reaction). The same procedure as for the hole-growth may be used to fit the SHF (the distribution of the tunnelling parameter  $\lambda$  being different). Results of the fitting procedure are shown in Fig. 4C by solid and dashed lines. We found the mean rate constant of SHF to be  $\langle R \rangle = 0.5 \text{ s}^{-1}$ , i.e., eight orders of magnitude lower than for burning [4].

The effect of heating on the backward reaction (thermally induced HF) was studied by applying

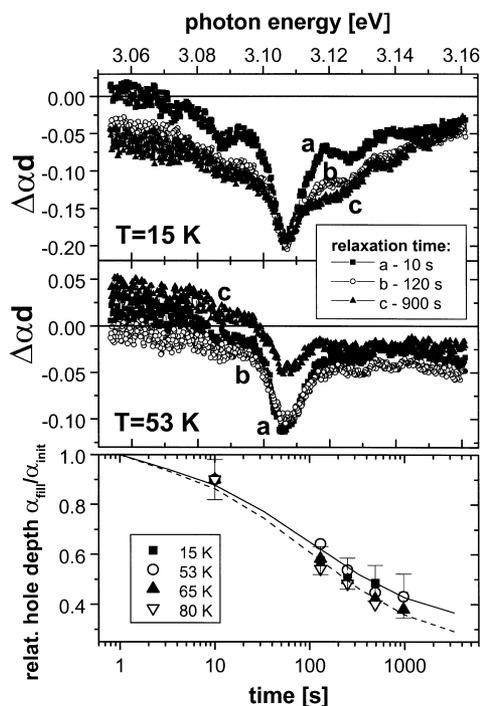


Fig. 4. Spontaneous filling of p-SHs in 2.8 nm CuBr NCs. Two upper viewgraphs show the changes of a spectral hole shape monitored with delay (a) 10, (b) 120, and (c) 900 s after the end of burning at temperatures 15 and 53 K. The lower graph represents the decay of resonant hole-depth (plotted in units of original hole depth) after 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 a model of the first-order dispersive reaction (Section 3.3).

the so-called thermal cycling procedure. Experiments are summarized in Ref. [14]. The integrated area of the ZPL hole fits well with the model derived by Köhler and co-workers [15] for molecular systems in glasses. The maximum barrier height between the product and educt state in thermally-stimulated backward reaction was found to be around  $V_{0\max} = 600$  meV.

Persistent spectral holes in our samples may be efficiently erased also by light (laser) stimulation of the backward reaction. In light-induced HF experiments we observed simultaneously a filling of a p-SH and a burning of a second spectral hole [14].

## 4. Discussion

### 4.1. Comprehensive model of persistent photo-induced changes in CuBr NCs

From the experimental facts presented above we want to point out two new findings:

- (i) The persistent modifications induced by the non-resonant and resonant excitation are very similar except the resonant absorption holes observed only with strong resonant excitation of the  $Z_{1,2}$  absorption band.
- (ii) PL spectra reveal that biexcitons are created efficiently by the resonant excitation and both excitons and biexcitons are usually trapped before they recombine.

These and previously published [2,4] experimental observations allow us to write down a detailed scenario of photoinduced persistent changes in CuBr NCs.

The sketch of our model is shown in Fig. 5. Two different paths of reaction are possible. Path A applies for absorption of photon through any state of an NC, while path B can take place only in NC where  $Z_{1,2}$  excitonic state is in resonance with laser excitation. The resonant excitation of the  $Z_{1,2}$  excitonic state has high oscillator strength, so a creation of second exciton before recombination of

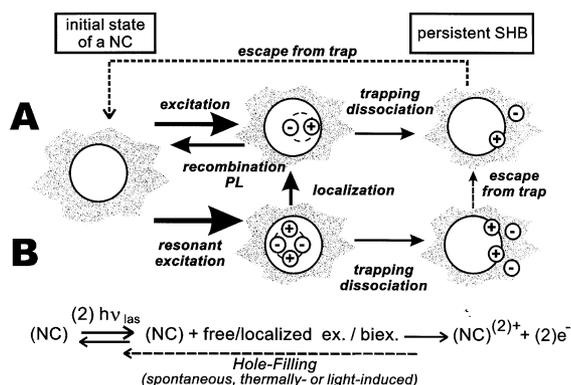


Fig. 5. Schematic representation of the sequence of processes involved in the SHB, HF, and PL processes (for details see section Discussion). Path A takes place for any excitation creating excitons in NCs. The path B can be followed only by an NC in which  $Z_{1,2}$  absorption is resonant with excitation.

the first (trapped) exciton is possible. Two excitons subsequently form a biexciton. Majority of generated excitons and biexcitons becomes localized at the surface of an NC (the surface polarization effect should be considered [16]) and then recombine back or dissociates. Electrons and holes from dissociated excitons/biexcitons can be trapped separately at the NC/glass interface or nearby (probably by the tunnelling through a potential barrier on the NC/glass interface). Finally, the NC is found back in the initial state or becomes charged (ionized). Trapped electrons and holes induce relatively strong local electric field, which causes a red-shift of excitonic absorption energies of NCs by the Stark effect (the oscillator strength of the transitions is also modified by an electric field). For resonantly excited NCs multiple ionization of an NC by dissociation of localized biexciton can happen. In such a case the Stark shift and weakening of absorption oscillator strength is much bigger. In consequence, the contribution of such NCs to the overall absorption is almost removed and a resonant spectral hole appears. A local electric field induces strong decrease of the PL intensity because it reduces the electron and hole wavefunctions overlap. This effect is stronger for biexcitons, so PL intensity of M peak decreases more than the X band intensity.

A stable photo-product (ionized NC) is formed efficiently (quantum efficiency  $4 \times 10^{-3}$  for resonant holes). 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  $0.5 \text{ s}^{-1}$  – eight orders of magnitude lower than the burning reaction). A part of the initial p-SH stays unfilled even after a long time (for temperatures  $T < 80 \text{ K}$ , see Fig. 4C). 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.

In summary, we have studied persistent photoinduced changes of absorption and emission spectra of CuBr NCs. Different structures in p-SHB spectra are caused by single or multiple charging of nanocrystals via trapping of excitons and biexcitons.

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) [17–20]. The photoionization can affect the results of spectroscopic measurements (e.g. exciton dynamics, single NC spectroscopy) or it can have influence on the performance of devices based on semiconductor quantum dots. A better understanding of the phenomenon in different nanocrystalline materials is therefore highly desirable.

## Acknowledgements

We would like to thank Prof. A.I. Ekimov (Ioffe Physical Technical Institute, St. Petersburg) for high-quality samples. We appreciate valuable and stimulating discussions with Profs. Hönerlage, Pelant and Hála. This work was supported in part by the grants No. 202/98/0669 from GACR and No. B1112901 from GA AV CR. J.V. has received the financial support from the French Government (MENRT – “réseau de formation – recherche, Europe centrale et orientale”) which is gratefully acknowledged.

## References

- [1] S.V. Gaponenko, Optical Properties of Semiconductor Nanocrystals, Cambridge Univ. Press, 1998 (Chapter VII).
- [2] Y. Masumoto, J. Lumin. 70 (1996) 386.
- [3] J. Valenta, J. Moniatte, P. Gilliot, B. Hönerlage, J.B. Grun, R. Levy, A.I. Ekimov, Phys. Rev. B 57 (1998) 1774.
- [4] J. Valenta, J. Dian, J. Hála, P. Gilliot, R. Lévy, J. Chem. Phys. 111 (1999) 9398.
- [5] M. Ueta et al., Excitonic Processes in Solids, Springer, Berlin, 1984 (Chapter 3).
- [6] L. Banyai, S.W. Koch, Semiconductor Quantum Dots, World Scientific, Singapore, 1993.
- [7] J. Moniatte, P. Gilliot, J. Valenta, A.I. Ekimov, Opt. Mater. 9 (1998) 516.
- [8] Y. Masumoto, T. Kawazoe, N. Matsuura, J. Lumin. 76–77 (1998) 189.
- [9] U. Woggon, O. Wind, W. Langbein, D. Gogolin, C. Klingshirn, J. Lumin. 59 (1994) 135.
- [10] S. Yano, T. Goto, T. Itoh, A. Kasuya, Phys. Rev. B 55 (1997) 1667.
- [11] W. Langbein, J.M. Hvam, Phys. Stat. Sol. B 206 (1998) 111.
- [12] R. Jankowiak, J.M. Hayes, G.J. Small, Chem. Rev. 93 (1993) 1471.
- [13] L. Chu, G.J. Small, J. Opt. Soc. Am. B 9 (1992) 724.

- [14] J. Valenta, J. Moniatte, P. Gilliot, R. Lévy, B. Hönerlage, A.I. Ekimov, *Appl. Phys. Lett.* 70 (1997) 680.
- [15] J. Köhler, J. Zollfrank, J. Friedrich, *Phys. Rev. B* 39 (1989) 5414.
- [16] L. Banyai, P. Gilliot, Y.Z. Hu, S.W. Koch, *Phys. Rev. B* 24 (1992) 14136.
- [17] V.J. Grabovskis, J.J. Dzenis, A.I. Ekimov, I.A. Kubrjav, M.H. Tolstoj, U.T. Rogulis, *Sov. Phys. Solid State* 31 (1989) 149.
- [18] K. Kang, A.D. Kepner, Y.Z. Hu, S.W. Koch, N. Peyghambarian, C.Y. Li, T. Takada, Y. Kao, J.D. Mackenzie, *Appl. Phys. Lett.* 64 (1994) 1487.
- [19] S.A. Emedocles, M.G. Bawendi, *Science* 278 (1997) 2114.
- [20] M. Nirmal, B.O. Dabbousi, M.G. Bawendi, J.J. Macklin, J.K. Trautman, T.D. Harris, L.E. Brus, *Nature* 383 (1996) 802.