ISSN 1063-7834, Physics of the Solid State, 2010, Vol. 52, No. 9, pp. 1941–1946. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © V.S. Dneprovskiĭ, E.A. Zhukov, M.V. Kozlova, T.Wumaier, Dau Sy Hieu, M.V. Artem'ev, 2010, published in Fizika Tverdogo Tela, 2010, Vol. 52, No. 9, pp. 1809–1814.

LOW-DIMENSIONAL SYSTEMS AND SURFACE PHYSICS

Absorption Saturation and Self-Action Processes under Resonant Excitation of the Basic Exciton Transition in CdSe/ZnS Colloidal Quantum Dots

V. S. Dneprovskiĭ[a], E. A. Zhukov[a], M. V. Kozlova[a], T. Wumaier[b], Dau Sy Hieu[c], and M. V. Artem'ev[d]

[a] *Moscow State University, Moscow, 119991 Russia*

e-mail: scon281@phys.msu.ru

[b] *Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 40-1 Beijing Road, Urumqi, Xinjiang, 830011 China*

[c] *Saigon Institute of Technology, Quang Trung Tower, Lot 14, Road 5, Quang Trung Software City District 12, Ho Chi Minh City, Vietnam*

[d] *Research Institute of Physical-Chemical Problems, Belarussian State University, ul. Leningradskaya 14, Minsk, 220030 Belarus*

Received November 3, 2009

Abstract—The revealed absorption saturation and Fresnel diffraction of ultrashort laser pulses under resonant excitation of the basic exciton transition in CdSe/ZnS quantum dots (a strongly absorbing colloidal solution) have been explained by the processes of filling of states of a two-level system with the excited-state lifetime dependent on the light intensity and self-diffraction of the laser beam due to the formation of the transparency channel and the induced diaphragm.

DOI: 10.1134/S106378341009026X

1. INTRODUCTION

In recent years, growing interest has been expressed by researchers in the study of nonlinear optical phenomena in semiconductor nanostructures (quantum wells, multiple quantum wells, superlattices, quantum wires, and quantum dots) and in their use for the design of new optoelectronic devices. Two types of nonlinear optical processes can manifest themselves in semiconductor nanostructures.

(1) Nonlinear optical phenomena that are associated with the inertialess (classical) nonlinearities and appear as a result of the interaction of high-intensity optical fields with bound electrons. These are optical harmonic generation, multiphoton absorption, focusing and defocusing of laser radiation, etc.

(2) Nonlinear optical phenomena determined by the dynamic (inertial) nonlinearities in absorbing media under excitation of free carriers by intense light. The magnitudes of dynamic nonlinearities can sharply increase (they are called giant) under resonant excitation of nanostructures. The giant nonlinearities can be used for designing optical switches, saturable absorbers for laser mode locking, nonlinear light filters over a wide spectral range, etc.

The present work is devoted to the study of nonlinear optical processes in semiconductor quantum dots under resonant excitation of the basic discrete optical electron–hole (exciton) transition by ultrashort laser pulses, i.e., to nonlinear optical phenomena of the second type. It is well known [1] that the dominant nonlinear optical process in semiconductor quantum dots under excitation of one and more electron–hole pairs in the individual quantum dot is the filling of states, which is accompanied by a decrease (saturation) in the absorption. It should be noted that the development of nonlinear optics began in 1926 when Wawilov with colleagues [2] started to study the nonlinear absorption under resonant excitation of the discrete optical transition in an uranium glass by a high-power light spark. The deviation from the linear Bouguer law (a decrease in the absorption with an increase in exciting radiation) was explained in [2, 3] by the finite lifetime of a molecule in the excited state: "... the higher the luminosity, the more pronounced the decrease in the fraction of the absorbed energy, because the excited molecules cease to absorb light in a previous manner until they return to the normal state" [3].

In order to analyze the nonlinear absorption under resonant excitation of a medium (including quantum dots) by a high-power light flux, it is convenient to use the model of saturation of absorption in a two-level system with a specified excited-state lifetime, which allows one to determine a change in the population with time due to the stimulated and spontaneous transitions [4]. In [1, 5, 6], the experimental data on the measured dependence of the nonlinear absorption in quantum dots on the intensity of exciting laser light

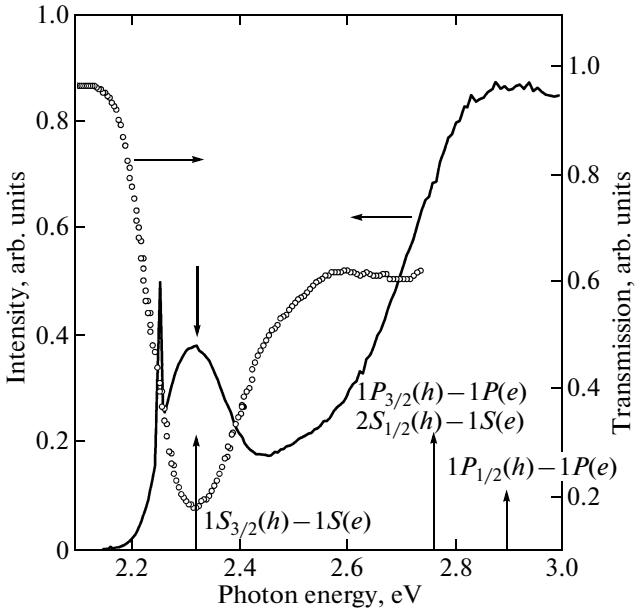

Fig. 1. Transmission and photoluminescence excitation spectra of CdSe/ZnS quantum dots. The thick arrow denotes the energy of the second harmonic radiation of the Nd : YAG laser, which excites excitons in quantum dots.

were compared with the results of the calculations under the assumption that the excited-state lifetime is constant (does not depend on the excitation level), which seems to be valid only for moderate excitation intensities.

In [7–9], it was shown that, in the case of excitation of more than one electron–hole pair in the quantum dot, the excited-state lifetime decreases sharply due to the Auger recombination. We can assume that the Auger recombination should lead to a decrease in the rate of absorption saturation with an increase in exciting radiation intensity. In the first part of our work, we investigated how the lifetime of the excited state of the quantum dot, which varies with an increase in the exciting radiation intensity, affects the saturation of absorption in the quantum dot.

The objective of the second part of this work was to study the specific features of propagation of the laser beam (self-action effects) that results in the saturation of absorption (bleaching) of the colloidal solution of CdSe/ZnSe quantum dots.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The experiments on the nonlinear absorption and self-action of ultrashort light pulses under resonant excitation of the basic optical exciton transition were performed using spherical quantum dots CdSe with a ZnS shell and hydrophobic trioctylphosphine layer at the outer surface in order to prevent their coalescence. The quantum dots were prepared through the metalorganic synthesis (NFM LTD, Belarus). The resonant excitation of the $1S_{3/2}(h)$–$1S(e)$ basic exciton transition in the CdSe/ZnS quantum dots was provided by the high-power (separated from a pulse train and amplified) single short (30 ps) pulses of a Nd : YAG laser operating in the mode-locked mode; in this case, the pulses were converted into second harmonic radiation (2.33 eV). The resonant excitation was performed by choosing the quantum dots with an appropriate size (radius). The energy of the basic exciton transition in the CdSe/ZnS quantum dots was determined from the transmission and photoluminescence excitation spectra. A variation in the concentration of quantum dots in a colloidal solution (in hexane) made it possible to choose the sample with a required linear absorption at the resonant wavelength.

It should be noted that the photoluminescence excitation spectra were measured by the modified method described in [10]. In the conventional method, the narrow band is separated from the inhomogeneously broadened (due to the size dispersion of quantum dots) luminescence spectrum and the dependence of the luminescence intensity on the wavelength of exciting light is measured in this spectral range. The capabilities of a Pixis 256 CD camera allow one to measure a large number of photoluminescence spectra for a short time, so that, in each case, the light beam with a new wavelength with the step $\Delta\lambda \approx 1$ nm is used for the excitation. Therefore, the photoluminescence excitation spectra with different wavelengths of the measurement (for quantum dots with different sizes) can be obtained from the ensemble of photoluminescence spectra.

Figure 1 shows the transmission spectrum of the colloidal solution of quantum dots and the photoluminescence excitation spectrum at a wavelength of 552 nm. This luminescence wavelength corresponds to the quantum dots in their ensemble characterized by the size dispersion that have a maximum absorption at the wavelength of the basic exciton transition. The spike at a wavelength of 552 nm is a trace of the exciting light beam at the wavelength corresponding to the maximum of the luminescence spectra. In the CdSe quantum dots, the frequencies of the optical transitions associated with the absorption and luminescence do not coincide with each other. The Stokes shift (the revealed long-wavelength shift in the maximum of the luminescence spectrum by 80 meV with respect to the maximum of the absorption spectrum) arises as a result of the internal crystal field in the hexagonal lattice, the deviation of the quantum dot from a spherical shape, and the electron–hole exchange interaction [11–13]. The exchange interaction depends on the quantum dot radius ($\approx R^{-3}$) and significantly increases in quantum dots of small radii. The exchange interaction is responsible for the splitting of the exciton transition into the optically active absorbing state and the optically passive radiative state. The optically passive exciton (dark exciton) is responsible for the lumines-

cence of CdSe quantum dots, which is accompanied by the interaction with LO phonons.

The quantum dot radius (2.5 ± 0.4 nm) and the size dispersion were determined by comparing the energies of the maximum of the photoluminescence excitation spectrum and half-width of the transmission spectrum (Fig. 1) with the results of the theoretical calculations [14] of the dependence of the energy of the quantum transitions in the CdSe quantum dots on their radii.

In order to determine the dependence of the transmission of the cell with the colloidal solution of CdSe/ZnS quantum dots on the excitation intensity, we measured the energy of laser pulses at its input and at its output. Furthermore, the use of the photodetector with a special CCD array allowed us to measure the profile of the intensity of the laser beam at the output of the cell. The concentration of quantum dots in the colloidal solution was about 10^{17} cm^{-3}, and the measured linear transmission of the cell with the colloidal quantum dots was equal to 0.02.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The dependence of the ratio between the energy of the pulse transmitted through the cell with the colloidal solution of quantum dots and the energy of the pulse at the input of the cell on the exciting radiation intensity is plotted in Fig. 2. It should be noted that the rate of increase in the transmission decreases and even the transmission itself decreases (!) at high excitation levels. We attribute this circumstance to the change (decrease) in the lifetime of excitons in quantum dots due to the Auger recombination that is dominant at high excitation levels.

In order to analyze the nonlinear absorption of ultrashort high-power laser pulses under resonant excitation of the basic optical exciton transition $1S_{3/2}(h)$–$1S(e)$ in the CdSe/ZnS quantum dots, we used the two-level model for the filling of states (absorption saturation). For the two-level system (the colloidal solution of quantum dots in our case), one can obtain the following equations for the determination of the change in the population of n electrons in the excited state with time and the change in the light absorption [15]:

$$\frac{\partial n}{\partial t} = I(x, t)(N - 2n)\sigma - \frac{n}{\tau_{ex}}, \quad (1)$$

$$\frac{\partial I}{\partial x} = -I(x, t)(N - 2n)\sigma. \quad (2)$$

In Eqs. (1) and (2), $I(x, t)$ is the photon flux at the depth x and the instant of time t, σ is the absorption cross section for one quantum dot, τ_{ex} is the excited-state lifetime, and N is the total number of quantum dots per unit volume.

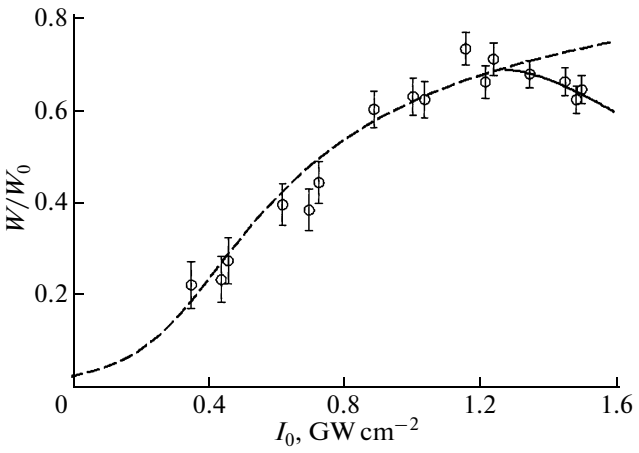

Fig. 2. Dependence of the ratio between the energies of the pulse passed through the cell with the colloidal solution of CdSe/ZnS quantum dots and the pulse at the input of the cell on the input pulse intensity. The dashed line indicates the results of the calculations for the constant lifetime of the excited exciton (moderate excitation intensities, less than one electron–hole pair in the single quantum dot). The solid line represents the results of the calculations for the decreasing excited-state lifetime (more than one electron–hole pair in the single quantum dot).

Following [15] and taking into account Eqs. (1) and (2), we can derive the equation for the determination (in the dimensionless form) the change in the transmission $T(\chi_1, \tau)$ of the colloidal solution of quantum dots with a fixed width x_1 with time (where $\chi_1 = N\sigma x_1 = -\ln T_0$):

$$\frac{d}{d\tau}(\ln T) + \ln T = 2\beta f(\tau)(1 - T) + \ln T_0. \quad (3)$$

In Eq. (3), $\tau \equiv t/\tau_{ex}$ is the dimensionless time, $\beta \equiv \sigma I_0 \tau_{ex}$, I_0 is the flux of photons of the laser at the input of the cell with the colloidal solution, T_0 is the transmission of the colloidal solution with the width x_1 for the low-power excitation (in the absence of the nonlinear absorption), and the function $f(\tau)$ approximates the shape of the laser pulse. It is convenient to represent the shape of the pulse in the form $f(\tau) = \frac{1}{2}(1 - \cos C\tau)$ for the change in the dimensionless time $0 \le \tau \le \frac{2\pi}{C}$. As a result, we have

$$f(\tau) = \frac{1}{2}\left(1 - \cos\pi\frac{\tau}{\Delta\tau}\right) = \frac{1}{2}\left(1 - \cos\pi\frac{t}{\Delta t}\right),$$

where $\Delta t = (\Delta\tau)\tau_{ex}$ is the laser pulse duration.

A comparison of the measured dependence of the transmission on the exciting radiation intensity I_0 and the results of the numerical solution to Eq. (3) demonstrates that it is necessary to take into account the decrease in the relaxation time τ_{ex} with a increase in I_0

(Fig. 2). The relaxation time is constant for moderate intensities, whereas, for high intensities (under excitation of more than one electron–hole pair in the individual quantum dot), we have $\tau_{ex} \approx I_0^{-2}$ due to dominant Auger recombination process [7–9]. For high excitation levels, Eq. (3) can be transformed as follows:

$$\frac{d}{d\tau}(\ln T) + \ln T = 2\sigma\gamma I_0^{-1} f(\tau)(1 - T) + \ln T_0. \quad (4)$$

One can see from Fig. 2 that the results of the numerical calculations using Eq. (4) agree with the experimental data for high intensities of the laser pulses exciting the quantum dots.

It should be noted that, for the two-level system and moderate intensities of the exciting pulses, the effect of filling of the states leads to a change in the shape [15] of the pulse transmitted through the sample, namely, to its contraction and asymmetry due to the significant absorption of its leading edge. Therefore, for comparison of the experimental results and the results of calculations using Eqs. (3) and (4), we determined the intensities of the transmitted pulses $I_{tr} = f(\tau)T(\tau)$, as well as their energies after the integration with respect to the time.

Apart from the effect of filling of the states, a number of processes can cause the change in the absorption at the frequency of the basic exciton transition in the quantum dots under excitation by high-power laser radiation: the Stark shift of the exciton transition, heating of the sample due to the light absorption, and degradation (increase in the absorption) for significant irradiation doses of the samples.

At high intensities of exciting radiation, either an electron or a hole after overcoming of the corresponding barriers can be trapped at the surface due to Auger process [16]. The Stark effect caused by the local electric field is responsible for the ionization of the quantum dots and for the low-frequency shift of the exciton transition. It can be seen from Fig. 1 that the Stark shift of the absorption spectra to the range of shorter wavelengths under the high-power excitations can lead to a decrease in the absorption. However, for high excitation levels, we revealed the increase in the absorption (Fig. 2).

The heating of the colloidal solution of CdSe/ZnS quantum dots (we estimated that the increase in the temperature upon absorption of the ultrashort laser pulses did not exceed 10 K) and the corresponding low-frequency shift of the basic exciton transition can lead only to an additional decrease rather than to an increase in the absorption.

Above a specific threshold of the intensity of exciting laser pulses and at a high irradiation dose (a large number of exciting pulses), the absorption in the quantum dots increases [17, 18]. The results presented in Fig. 2 were obtained for intensities of exciting radiation that did not exceed the threshold of this effect. The last circumstance was confirmed by identical dependences of the transmission of the quantum dots with both an increase and a decrease in the intensity of exciting laser pulses. Therefore, the saturation effect can be considered the dominant process that causes the bleaching of the colloidal solution of CdSe/ZnS quantum dots.

In order to study the specific features of laser beam propagation in the regime of absorption saturation of the $1S_{3/2}(h)$–$1S(e)$ basic exciton transition in the colloidal CdSe/ZnS quantum dots, we measured the profiles of the laser beam intensity at the input and output of the cell. Figures 3a and 3b show the measured profiles of the laser beam intensity at the output of the cell with the strongly absorbing ($\alpha \cong 40$ cm^{-1}) colloidal solution of quantum dots under resonant excitation of the basic exciton transition. The annular intensity distribution with a maximum or minimum value of the intensity at the center was found at the output of the cell only in the case of high intensities of exciting laser pulses at the input. For the exciting laser beam, the measured intensity distribution in the cross section has a Gaussian shape, i.e., the radiation intensity decreases gradually from the center to the periphery.

The revealed radiation intensity distribution at the output of the cell with the colloidal solution of quantum dots can be explained by the propagation of the high-power laser beam with a confined cross section in the nonlinear medium with local parameters dependent on the light intensity. Most likely, we can separate several coexisting processes.

(1) The process of filling of the states (the absorption saturation phenomenon) results in the bleaching of the colloidal solution of quantum dots, which is nearly opaque for a low intensity of light. As was shown above, even with a decrease in the exciton lifetime at high excitation levels, the transmission remains significant due to the nonradiative Auger relaxation (Fig. 2). Therefore, the high-power beam at the doubled laser frequency corresponding to the resonant excitation of the $1S_{3/2}(h)$–$1S(e)$ electron–hole transition in the CdSe/ZnS quantum dot produces the transparency channel, inside which the absorption is small owing to the strong saturation. The intense light can penetrate into the colloidal solution through considerably larger distances as compared to nonsaturating low-power light in the linear regime.

(2) With penetration into the colloidal solution of quantum dots, the light beam, which has a normal distribution in the cross section, loses its low-intensity layers due to the considerably stronger absorption than at the center on its axis. There occurs a beam "stripping" [19, 20], i.e., the strip effect that results in a change in the profile of the beam, whose edges transform from smooth into sharp ones. There arises an induced "rigid" diaphragm.

(3) The formation of rings with a maximum or a minimum of the intensity at the center (Figs. 3a, 3b)

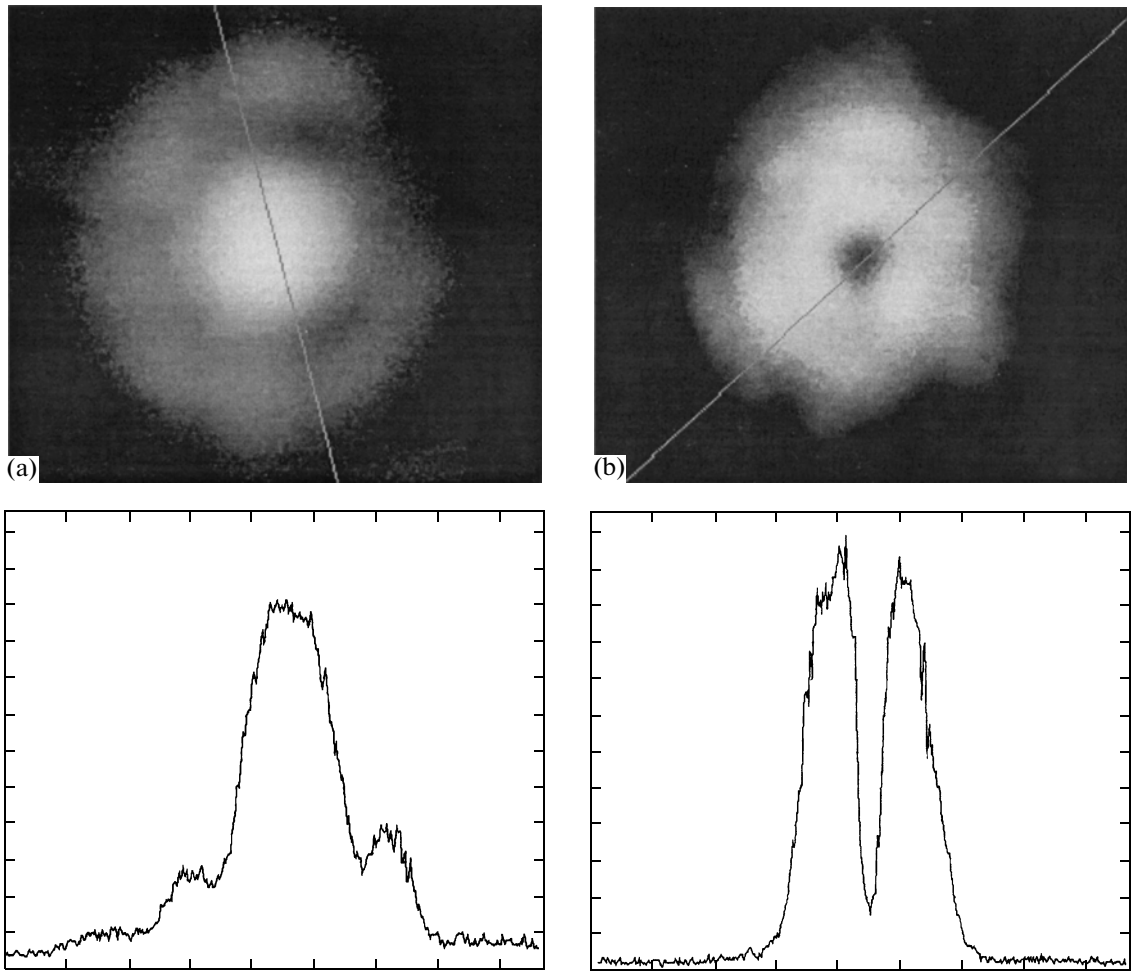

Fig. 3. Profiles and laser beam intensity distributions along the specified direction at the output of the cell with the colloidal solution of CdSe/ZnS quantum dots for laser pulse intensities of (a) 1.0 and (b) 1.2 GW/cm^2 at the input of the sample.

can be explained by the Fresnel diffraction from a circular aperture, because the diameter of the induced diaphragm depends on the light intensity.

4. CONCLUSIONS

In semiconductor quantum dots absorbing light, the main nonlinear optical effect, namely, the absorption saturation (bleaching) associated with the filling of the states, can be explained using the simple model of saturation of the two-level medium. The results of the present work suggest that, in this case, it is necessary to take into account the dependence of the excited-state lifetime on the light intensity for high light intensities. It is this inclusion of the decrease in the exciton lifetime in the quantum dot due to the Auger recombination that has allowed us to explain the decrease in the rate of increase in the transmission and even the decrease in the transmission with an increase in the intensity of exciting radiation in the colloidal solution of CdSe/ZnS quantum dots under resonant excitation of the $1S_{3/2}(h)$–$1S(e)$ exciton transition by high-power ultrashort pulses of the second harmonic of the Nd : YAG laser.

The revealed Fresnel diffraction under resonant excitation of excitons in the colloidal quantum dots is most likely associated with the dominant process of self-diffraction, i.e., the self-action phenomenon when the light affects the parameters of the medium and the modified medium influences the propagation of light. The absorption saturation leads to a change in the refractive index, namely, to its increase or decrease depending on the deviation of the frequency of exciting radiation from the resonance frequency. With an increase in the light intensity, the refractive index decreases at frequencies below the resonance and increases at the frequencies above the resonance. The corresponding dependence of the refractive index on the light intensity can result in the development of the self-defocusing or self-focusing process [1]. In the present work, the experiments have been performed at the exact resonance for the majority of quantum dots having a size dispersion, which allows us to explain the results obtained by the dominant nonlinear change in

the absorption coefficient (bleaching of the colloidal solution of quantum dots), the formation of the transparency channel, the confinement of the beam cross section due to strip effect, the appearance of the induced "rigid" diaphragm, and the self-diffraction of the beam of the second harmonic of neodymium laser.

The revealed phenomena should be taken into account when developing optoelectronic devices (nonlinear saturable filters, optical switches, lasers, etc.), which contain quantum dots at high concentrations (e.g., colloidal solutions, crystals with a regular arrangement of quantum dots, and glasses with semiconductor nanocrystals).

ACKNOWLEDGMENTS

This study was supported in part by the Russian Foundation for Basic Research (project nos. 08-02-00205 and 08-02-90102).

REFERENCES

1. H. M. Gibbs, G. Khitrova, and N. Peyghambarian, *Nonlinear Photonics* (Springer, Berlin, 1990).
2. S. I. Wawilov and W. L. Lewschin, Z. Phys. **35**, 932 (1926).
3. S. I. Vavilov, *Microstructure of Light* (Academy of Sciences of the USSR, Moscow, 1950), p. 70 [in Russian].
4. D. N. Klyshko, *Physical Bases of Quantum Electronics* (Nauka, Moscow, 1986) [in Russian].
5. S. H. Park, M. P. Casey, and J. Falk, J. Appl. Phys. **73**, 8041 (1993).
6. S. H. Park, R. Morgan, M. Lindberg, S. W. Koch, and N. Peyghambarian, J. Opt. Soc. Am. B **7**, 2097 (1990).
7. D. Chepic, A. L. Efros, A. Ekimov, M. Ivanov, V. A. Kharchenko, and I. Kudriavtsev, J. Lumin. **47**, 113 (1990).
8. V. A. Kharchenko and M. Rosen, J. Lumin. **70**, 158 (1996).
9. V. Dneprovskii, A. Efros, A. Ekimov, V. Klimov, I. Kudriavtsev, and M. Novikov, Solid State Commun. **74**, 555 (1990).
10. V. Dneprovskii, D. Kabanin, V. Lyascovskii, A. Santalov, T. Wumaier, T. G. Dang, and E. Zhukov, Phys. Status Solidi C **5**, 2507 (2008).
11. A. L. Efros, Phys. Rev. B: Condens. Matter **46**, 7448 (1992).
12. A. L. Efros and A. Rodina, Phys. Rev. B: Condens. Matter **47**, 10005 (1993).
13. M. Nirmal, D. Norris, M. Kuno, M. Bawendy, A. L. Efros, and M. Rosen, Phys. Rev. Lett. **75**, 3728 (1995).
14. A. I. Ekimov, F. Hashe, M. C. Schanne-Klein, D. Ricard, C. Flytzanis, I. A. Kudryavtsev, T. V. Yaseva, A. V. Rodina, and A. L. Efros, J. Opt. Soc. Am. B **10**, 100 (1993).
15. A. C. Selden, Br. J. Appl. Phys. **18**, 743 (1967).
16. D. Norris, A. Sacra, C. Murray, and M. Bavendi, Phys. Rev. Lett. **72**, 2612 (1994).
17. P. Roussignol, D. Ricard, J. Lucasik, and C. Flytzanis, J. Opt. Soc. Am. B **4**, 5 (1987).
18. M. Mitsunaga, H. Shinojima, and K. Kubodera, J. Opt. Soc. Am. B **5**, 1448 (1988).
19. K. Tai, H. V. Gibbs, M. Rushford, N. Peyghambarian, J. S. Satchell, M. G. Boshier, R. J. Ballagh, W. J. Sandle, M. LeBerre, E. Ressayre, A. Tallet, J. Teichmann, Y. Claude, E. P. Mattar, and P. D. Drummond, Opt. Lett. **9**, 243 (1984).
20. V. L. Debrov, L. A. Melnikov, A. D. Novikov, and S. K. Potapov, J. Opt. Soc. Am. B **7**, 1079 (1990).

Translated by A. Kapustin