Correlated Signals of Free Induction Decay in CdSe–CdS Nanostructures Under Two- and Three-Photon Excitation by Crossed Femtosecond Laser Beams

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Abstract. The possibility and conditions of a generation of the correlated free induction decay signals in CdSe–CdS nanostructures under two- and three-photon excitation by crossed femtosecond beams of the Ti:sapphire laser radiation are considered. It is shown that these correlated signals will be emitted in two opposite directions. The information contained in the temporal shapes and wavefronts of these signals will be correlated.

1. Introduction
Quantum dots are used widely when creating the new lasers, single photon sources and devices for optical quantum computing [1]. Among them an essential role belongs to the colloidal CdSe – CdS quantum dots [2, 3]. In our investigations of various media, including nanostructured samples, we use the various techniques of the coherent optical spectroscopy based on such phenomena as a free induction decay (FID), a photon echo (PE), a four-wave mixing (FWM), etc.

In paper [4] we predicted a possibility to observe the correlated free induction decay (CFID) signals under two-photon excitation of a CdS semiconductor crystal by the femtosecond 800-nm radiation of Ti:sapphire laser in the directions of wave vectors \( \mathbf{k}_1 \) and \( \mathbf{k}_2 \) oriented at an angle of 60° to each other. It is known [5] that these signals are formed in the superposition states [6]. Superposition means that there is no possibility to say which of the possibilities, forming the superposition, takes place in reality. Then if the system includes two particles (for example, two electrons), they may be either independent or coupled. Since we consider the coupled particles it should be noted that the predominating mechanism connecting electrons into pairs in our case is the Coulomb interaction. The two-photon femtosecond excitation of coupled electrons in the superposition state leads to the appearance of the nonequilibrium electrical polarization and to the FID generation. But the presence of the nonequilibrium electrical polarization “gratings” \( \mathbf{k}_1 - \mathbf{k}_2 \) and \( \mathbf{k}_2 - \mathbf{k}_1 \) causes the simultaneous scattering of two correlated signals CFID1 and CFID2 at once. The phase matching conditions for these signals are

\[
\mathbf{k}_{\text{CFID}_1} = \mathbf{k}_1 - \mathbf{k}_2, \\
\mathbf{k}_{\text{CFID}_2} = \mathbf{k}_2 - \mathbf{k}_1. \tag{1}
\]
The lifetime of the nonequilibrium electrical polarization “gratings” is defined by the transverse relaxation time $T_2$ which in the case of the CdS monocrystal at room temperature is equal to 170 fs [4]. The situation is illustrated in figure 1.

![Figure 1. Generation of the correlated signals CFID1 and CFID2 in CdS monocrystal under the two-photon excitation by the 800-nm Ti:sapphire laser radiation in the directions $k_1$ and $k_2$. Here $k_{\text{CFID}_1}$ and $k_{\text{CFID}_2}$ are the wave vectors of the correlated signals CFID1 and CFID2, $D_1$ and $D_2$ are the photodetectors, CS is the coincidence scheme.](image)

The novelty of this paper consists in discussion of the possibility to observe such signals in CdSe–CdS nanostructures under the conditions of two- and three-photon excitation. The fact is that unlike a monocrystal the nanostructured samples (such as CdS nanopowder or CdSe–CdS quantum dots) require the three-photon mode for resonant excitation. For the first time the three-photon excitation of nanostructured CdS sample was described by J. Chon and M. Gu in [7] which was then followed by our paper [2]. Here we would like to examine the phase matching conditions for CFID signals under three-photon excitation of CdSe–CdS nanostructures. Besides, the possibility of recording of the correlated transient holograms in such samples will be discussed.

2. Peculiarities of nanostructured CdSe–CdS samples. Formation of transient “gratings” under two- and three-photon excitation.
As it was noted above, we propose to use the nanostructured CdSe–CdS sample in our experiments. These samples are composites consisting of the CdSe–CdS nanoparticles of “core–shell” type dispersed into a PMMA matrix [3]. The process of construction of such nanoparticles was described in details in [3].

CdSe quantum dots are grown using the colloidal synthesis technique. They are then covered with the CdS shell. The average size of the constructed nanoparticles is equal to 3·10⁻⁷ cm. They have either spherical or ellipsoidal shape. The Ti:sapphire laser radiation has the wavelength of 8·10⁻⁵ cm with pulse duration of 40 fs. The area of laser excitation according to [3] is about 3·10⁻³ cm. In this case the number of working particles is estimated as 3·10⁴. The coherence length $c\tau_0$ (where $c$ is the light velocity and $\tau_0$ is the coherence time which is supposed to be equal to $T_2 = 170$ fs) is equal to 0.5 cm. The size of the sample is limited by this value which can be increased up to 1 cm.
It should be noted that the luminescence spectrum of the CdSe semiconductor having the forbidden zone in the IR range lies in the visible diapason (for the nanoparticles of size \( \leq 3 \) nm). The quantum emission is high enough since electrons and holes are localized in nanometer volume inside the quantum dot \([8]\). In our case of excitation by short femtosecond pulses the connected excitons can play the role of qubit.

Depending on the nanostructure size the bandgap width varies and the quantum size effect takes place which reveals in changing of the luminescence wavelength \([2]\). The CdSe–CdS nanoparticles of 2, 3, 6.5 and 7 nm size have a maximum of the emission line at 525, 540, 590 and 600 nm, respectively. It was established \([2]\) that covering the CdSe core with the CdS shell allows an eight-fold increase in luminescence. The fact is that such heterostructures have the special configuration of the energy zones. A smaller number of internal elementary excitations decays nonradiatively \([2]\). That is why the excitation becomes more effective. Under the excitation by the Ti:sapphire laser radiation CdSe–CdS nanoparticles demonstrate the nonlinear properties such as multi-photon absorption and luminescence at the above mentioned wavelengths. The CdSe–CdS band structure is shown in figure 2.

Let us now discuss the three-photon mode of excitation of the nanostructured CdSe–CdS sample. After excitation by three femtosecond pulses of the same wavelength (800 nm) the electrons of the sample are transferred to the upper conductive band CB2 corresponding to the wavelength of 267 nm (i.e. \( \lambda_{\text{exc}} = \lambda / 3 \)). Then according to the experimental results of paper \([9]\), the electrons decay via nonradiative transition to the conductive band CB1 corresponding to the wavelength of 534 nm (i.e. \( 267 \text{nm} \times 2 \)) and then decay radiatively. Notice that at the same time an independent two-photon transition takes place between the valence VB and conductive CB1 bands and the nonequilibrium electrical polarization “gratings” described above are formed and then scatter the CFID1 and CFID2 signals.

We would like to write the phase matching conditions for these signals under three-photon mode of excitation. If there are two exciting femtosecond beams then the third exciting pulse can act only in the directions of wave vectors \( \mathbf{k}_1 \) or \( \mathbf{k}_2 \). Suppose that the nonradiative transition is absent. In this case, the phase matching conditions could be written as:

\[
\mathbf{k}_{\text{CFID1}} = 2\mathbf{k}_1 - \mathbf{k}_2, \\
\mathbf{k}_{\text{CFID2}} = 2\mathbf{k}_2 - \mathbf{k}_1.
\]
But in the case of CdSe–CdS due to the nonradiative transition CB2→CB1 the information about the phase of the third exciting pulse and about the population of levels belonging to the conductive band CB2 is totally lost. The situation seems to be hopeless but there is the independent energy transition VZ→CB1 and thanks to this the transient gratings \( \mathbf{k}_1 - \mathbf{k}_2 \) and \( \mathbf{k}_2 - \mathbf{k}_1 \) are induced and the correlated responses CFID1 and CFID2 will be emitted.

In conclusion, let us say some words about the possibility of the femtosecond holograms recording under a multi-photon regime of absorption of laser radiation. For the first time, such possibility have been shown experimentally by A.K. Rebane with colleagues [10]. Then, in our paper [11], the formation of the correlated transient holograms (CTH) in the CdS crystal was considered for the case of the two-photon mode of an excitation. We suggested recording of the holograms into the wave fronts of signals CFID1 and CFID2 in the experimental scheme presented in figure 1. It was found that these holograms are reversed and for the spherical wave fronts the following expressions were obtained:

\[
\frac{1}{R_{\text{CTH}}} = \frac{1}{R_1} - \frac{1}{R_2},
\]

\[
\frac{1}{R_{\text{CTH2}}} = \frac{1}{R_2} - \frac{1}{R_3},
\]

where \( R_1 \) and \( R_2 \) are the radius of curvature of the corresponding exciting waves. Since CFID signals can be also observed under three-photon mode of CdSe–CdS excitation they can be used for the recording of the correlated transient holograms in such nanostructures.

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