Light absorption by nonequilibrium, two-photon-generated, free and localized carriers in ZnTe single crystals

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Nonlinear absorption of light in semiconducting crystals of ZnTe is studied under conditions of bulk two-photon excitation by laser radiation having $\hbar\omega_L > E_g/2$. It is shown that under these conditions there is a competition between two-photon absorption processes: two-step impurity absorption and the absorption of light by nonequilibrium free carriers, where the latter process is dominant with increasing intensity of the modulating laser radiation. It is shown theoretically and experimentally that spectroscopic investigations of this sort are a source of specific information on the band structure, the localized states, and the generation-recombination and optical properties of the free carriers in semiconductors. For specific conditions of two-photon spectroscopy practical formulas are obtained, on the basis of which a number of parameters of the free carriers and deep localized centers in different samples of ZnTe are calculated. Induced effects of selective interband absorption of light by nonequilibrium free carriers are observed simultaneously for electrons and holes in ZnTe.

1. INTRODUCTION

Under conditions of intense two-photon bulk excitation of semiconductors by pulsed laser radiation with a photon energy greater than half the band gap, i.e., $2\hbar\omega_L > E_g > \hbar\omega_L$, there occurs over the entire illuminated volume of the crystal a strong photogeneration of free charge carriers that control the processes of photoconductivity[1–3] and photoluminescence.[3–5] The effect of these excess carriers as manifested in their absorption of light has been studied to a lesser extent. The absorption of light by nonequilibrium free carriers (ANFC), excited by two-photon absorption (TPA) of laser radiation as well as by two-step absorption (TSA) via deep localized states,[6,7] frequently hamper investigations of two-photon absorption by competing with it and limit, depending on the band gaps E_g, the set of semiconducting compounds that can be studied by two-photon spectroscopy methods.

In this investigation we use two-beam methods to study the nonlinear absorption (NA) of light in ZnTe semiconductors under conditions of strong bulk two-photon excitation of the samples by laser radiation. We show that under these conditions competition between two-photon absorption, two-step absorption, and absorption by nonequilibrium free carriers takes place, and the last of these becomes dominant as the intensity of the modulating laser radiation increases. It is shown experimentally and theoretically that investigations of this sort are a source of specific information on the band structure, on localized states, and on the generation-recombination and optical properties of the free carriers in semiconductors. We note that the investigation of free carriers by classical means[8] requires special modifications of the properties of the material (doping, production of junctions, etc.). The distinctive feature of the method of two-photon-induced light absorption by nonequilibrium free carriers is the introduction of excess charge carriers of both signs by bulk optical injection through the mechanism of two-photon generation.

Impurity spectroscopy by saturation of two-step absorption, the principles of which are presented below, is distinguished by the possibility of determining directly the cross sections for the capture of photons by centers and the spectra of these cross sections, as well as the possibility of separating the contributions to the nonlinear absorption from the different deep centers even when they have overlapping absorption thresholds.[6] Investigations of absorption by nonequilibrium free carriers and of two-step absorption are important also insofar as they have a substantial effect on the operation of devices and elements in nonlinear optics.[9–12]

The spectral manifestations of absorption by nonequilibrium free carriers have, up until the present time, been studied by the two-beam method only in Ref. 13, for Ge crystals, and in Ref. 6, for GaSe. The behavior and features of two-step absorption via deep localized states in two-photon spectroscopy of semiconductors and the competition of these processes with intrinsic two-photon absorption have been studied to various degrees in a number of investigations.[6,7,14–17] In this work similar investigations are carried out for the first time for the purpose of determining specific parameters of the deep centers[18] that participate in two-step absorption.

In the second section we present a phenomenological description of the effects of two-photon-induced absorption by nonequilibrium free carriers and of two-step absorption via deep localized states, this description being specific to the experimental situation of this investigation. These theoretical results are used for the description and interpretation of the experimental data presented in section 3.

2. THEORY

Two-photon-induced absorption by nonequilibrium free carriers. Charge carriers which are generated in the bulk of a crystal by the two-photon mechanism can, in turn, absorb the laser radiation that generates them,[6,19] or can absorb the radiation of a supplementary probing light source.[6,13] Thus,

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the two-photon-induced absorption by nonequilibrium free carriers is a nonlinear, third-order effect which is, however, of an incoherent, stepwise character, the first step being two-photon absorption and the second step single photon absorption from the excited state. The two stages of the absorption by nonequilibrium free carriers are separated by relaxation processes in the intermediate state, and as a result the process depends on the population of that state, similarly to the case of two-step absorption via impurities.

Let us consider the attenuation of the intensity $I(\omega)$ of the probe light in a crystal excited by two-photon absorption of laser radiation $I_L(\omega_L, t)$. Neglecting spatial variation $I_L(z)$ of the intensity of the laser radiation in the crystal, neglecting charge carrier diffusion, and assuming that $I \ll I_L$, we can write the balance equations in the form

$$-\frac{1}{I}\frac{dI}{dz} = \alpha_\omega + \beta_{\omega+\omega_L} I_L(t) + (\sigma_e(\omega) n_e(t) + \sigma_h(\omega) n_h(t)), \quad (1)$$

$$\frac{dn_{e,h}}{dt} = \frac{\beta_{2\omega_L} I_L^2(t)}{2\hbar\omega_L} - \frac{n_{e,h}(t)}{\tau^*_{e,h}(t)}, \quad (2)$$

where α_ω is the linear loss coefficient, $\beta_{2\omega_L}$ and $\beta_{\omega+\omega_L}$ are the two-photon absorption constants for absorption of type $\omega_L + \omega_L$ and $\omega + \omega_L$, respectively, $\sigma_e(\omega)$ and $\sigma_h(\omega)$ are, respectively, the cross sections for the absorption of photons $\hbar\omega$ by free electrons and holes having, respectively, concentrations n_e and n_h and instantaneous lifetimes τ_e^* and τ_h^*. Disregarding recombination, since when pulsed laser is used, the relation $\Delta t_L \ll \tau^*$ frequently holds, we obtain from (1) and (2) an expression for the coefficient of induced absorption

$$\Delta\alpha_\omega(t) = \frac{1}{l}\ln\left(\frac{T_\omega(0)}{T_\omega(I_L, t)}\right)$$

$$= \beta_{\omega+\omega_L} I_L(t) + \frac{\sigma_\omega \beta_{2\omega_L}}{2\hbar\omega_L}\int_0^t I_L^2(t')\,dt', \quad (3)$$

where $T_\omega(0)$ is the initial transmission of the crystal, $T_\omega(I_L, t)$ is the transmission during and after the laser pulse, and l is the thickness of the crystal. The first term in (3) determines the contribution of the coherent two-photon absorption process to the induced absorption, and it can be seen that the time dependence of this contribution duplicates the shape of the modulating laser pulse. The second term determines the contribution from the incoherent process of absorption by nonequilibrium free carriers, where this process is protracted in time and reaches a maximum only at the termination of the laser pulse because of the build-up of the nonequilibrium carriers. If account were taken of relaxation processes for which $\tau^* > \Delta t_L$, then $\Delta\alpha_\omega(t)$ would be a decreasing function of t, with a characteristic time τ^*. The spectral behavior of the absorption by nonequilibrium free carriers is governed by the spectrum of the cross section, $\sigma(\omega)$ for the capture of photons by carriers.[8]

The value of $\Delta\alpha_\omega$ at the instant of time coinciding with the peak of a Gaussian-shaped laser pulse $I_L(t)$ is obtained by integrating (3) over the Gaussian shape

$$\Delta\alpha_\omega = \beta_{\omega+\omega_L} I_{L_a} + {}^1/_2 \gamma_\omega I_{L_a}^2, \quad (4)$$

where the coefficient of absorption by nonequilibrium free carriers has the form

$$\gamma_\omega \approx 2{,}35 \cdot 10^{15} \Delta t_L (\hbar\omega_L)^{-1} \beta_{2\omega_L} \sigma_\omega. \quad (5)$$

Here I_{L_a} is the maximum amplitude of the integrated laser radiation power density measured in MW/cm^2, Δt_L is in nsec, $\beta_{2\omega_L}$ is in cm/MW, σ_ω is in cm^2, $\hbar\omega_L$ is in eV, and γ_ω is in cm^3/MW. In this way, by neglecting variations in the amplitude and shape of the laser pulse as it passes through the medium that it is exciting, we find that the contribution to nonlinear absorption from absorption by nonequilibrium free carriers increases quadratically with I_L, faster than the contribution from two-photon absorption, which increases linearly with the intensity.

In a correct numerical solution of the equations that describe the absorption by nonequilibrium free carriers, without a lot of simplifying assumptions (see, e.g., the calculations in Ref. 19 for the single-beam method), "self-action" effects of the laser pulse should appear because of its absorption by free carriers produced by the laser pulse itself. A feature of this case is an asymmetrical distortion of the shape of the laser pulse, as the latter is transmitted through a medium having a band gap E_g such that $\hbar\omega_L < E_g < 2\hbar\omega_L$. This distortion is a result of the buildup of charge carriers and the consequent increased absorption by them as the laser pulse evolves in time.[6,19] As the intensity increases, the latter process leads to a decrease in the efficiency of free carrier generation, to a deviation from a quadratic intensity dependence of $\Delta\alpha = f(I_L)$, and to its linearization.[1] Therefore a criterion for the applicability of (4) is the quadratic form of the experimentally determined dependence of the nonequilibrium free carrier component of induced absorption on the intensity of the modulating laser light.

Two-step absorption via impurities. In the two-step absorption of light, a sequential excitation of electrons from the valence band into the conduction band occurs via deep impurities or defect levels in the semiconductor band gap. In contrast to two-photon absorption proper, each step of the two-step absorption involves "real" single photon transitions which change the population of the intermediate localized states, and there is a dependence of the two-step absorption on the population of these states. Because of the comparatively long lifetimes of the localized carriers, $\tau = 10^{-8}$ to 10^{-3} sec, each step of the two-step absorption can proceed separately in time (a disjunction of the order τ is possible) and space, i.e., on different localized centers. Thus, the individual two-step absorption events are completely separated by relaxation processes. In this sense both two-step absorption and absorption by nonequilibrium free carriers, in contrast to two-photon absorption, are incoherent processes, in which, so to speak, the second photon has no memory of the first. Although the concentration of localized carriers is usually small, their rather long lifetimes determine the ability of the two-step absorption processes to compete with the intrinsic two-photon absorption.

We shall consider optical transitions of the type "lamp photon—laser photon," where these transitions take place via deep donor states of energy E_M, concentration M, and

electron occupation number m. The change induced by the modulating pulsed laser radiation $I_L(\omega_L, t)$ in the impurity absorption $\Delta\alpha_\omega$ of the probing light $I(\omega)$ from the time $t = 0$, at which the laser light is turned on $[m(t=0) = m_0]$ can be expressed in the following form

$$\Delta\alpha(\omega, t) \equiv \alpha(\omega, t) - \alpha(\omega, 0) = \sigma_{vD}(\omega)\,[m_0 - m(t)]. \quad (6)$$

Here $\sigma_{vD}(\omega)$ is the cross section for the capture of a probing photon $\hbar\omega$ by a center consisting of a localized valence electron on a donor (the photoneutralization cross section). The kinetic equation for the occupation of the centers by two-step absorption is

$$\frac{dm(t)}{dt} = (M - m(t))\,(\sigma_{vD}(\omega) I(\omega) + \tau_\Sigma^{-1}) - m(t)\,\sigma_{cD}(\omega_L) I_L(\omega_L, t). \quad (7)$$

Here we introduce the lifetime τ_Σ of the carriers localized at centers in terms of the capture of free charge carriers by the centers:

$$\tau_\Sigma = \left[\gamma_{cD} n - \frac{m}{M-m}\gamma_{vD} p\right]^{-1}, \quad (8)$$

which is determined by the coefficients γ_{cD} and γ_{vD} for the capture of electrons and holes, respectively, by a center, and the concentration n of electrons and p of holes.

In the general case it is necessary to write down the corresponding equations and the conditions of neutrality for the concentrations n and p of free carriers and solve the resulting system of equations by numerical methods. In this general case it is necessary to bring in parameters relating to the recombination, capture, etc. of free carriers, and these processes are governed by a whole set of centers that we do not know about and which may or may not be involved in two-step absorption. Therefore in what follows we shall assume that $\tau_\Sigma = \text{const}$. This condition is easy to verify experimentally from the kinetics of the two-step absorption signals.

The time development of the induced absorption of the probing light as it is modulated by intense laser illumination [$\sigma_L I_L$ is the most effective of all the processes in (7)] is determined by (6) and the solution of (7)[1]:

$$\Delta\alpha(\omega; t, I_L) = m_0\sigma_{vD}(\omega)[1 - \exp(-\sigma_{cD}(\omega_L))] \times \int_0^t I_L(t')dt. \quad (9)$$

This expression describes the main features of the two-step absorption process that appear in the two-photon spectroscopy method.

a) The two-step absorption spectrum is determined by the spectral dependence of the photoneutralization cross section of a center, $\Delta\alpha(\omega) \sim \sigma_{vD}(\omega)$, which has for deep centers the form of a wide threshold band[20,21] for which the long wavelength edge is determined by $E_g - E_M$.

b) The dependence of $\Delta\alpha(I_L)$ on the light intensity has a saturating character [the limiting value of $\Delta\alpha$ is $\Delta\alpha(\infty) = m_0\sigma v_{vD}(\omega)$] which is due to the complete depopulation (or occupation) of the centers as I_L increases. It is a characteristic feature of the approximation that we are using that the saturation of the two-step absorption signal that occurs as the modulation intensity is increased is determined only by the cross section $\sigma_{cD}(\omega_L)$ for the capture of laser photons by a center. This circumstance makes it possible to make a direct experimental determination of this cross section.

c) The time variation of the signal $\Delta\alpha(t)$ at the time of the laser pulse depends on the integral over the shape of the laser pulse. This relationship stems from the time-dependent buildup of charge carriers. In the saturation region the centers are depopulated already at the initial stages of the laser pulse, and the leading edge of $\Delta\alpha(t)$ is shifted towards earlier time.

d) The relaxation of nonlinear absorption upon the termination of the modulating pulse, for low intensities of the probing light is, according to (7), determined by the lifetimes of carriers at centers (8) and provides a method of determining τ_Σ experimentally. Therefore the above assumption that $\tau_\Sigma = \text{const}$ is tested experimentally by the condition that the relaxation time of the nonlinear absorption is independent of the intensity of the illumination.

Let us write expression (9) for the nonlinear absorption coefficient in a form that is normalized to the intensity of the laser radiation ($\beta \equiv \Delta\alpha / I_L$) and is generalized to several channels of two-step absorption and which is more suitable for practical application:

$$\beta^{(\mathrm{TSA})}(\omega, I_L) = I_{L_a}^{-1} \sum_i \beta_i(\omega, 0) I_{k_i}[1 - \exp(-I_{L_a} I_{k_i}^{-1})]. \quad (10)$$

Here we have introduced the critical laser radiation intensity I_{c_i}, which characterizes the saturation of the two-step absorption via centers of type i, where these critical intensities are determined by $\sigma_{cD}(\omega_L)$ according to the relation

$$I_k = 1.6 \cdot 10^{-16} \hbar\omega_L (\Delta t_L \sigma_{cD}(\omega_L))^{-1}. \quad (11)$$

We have, in addition, introduced the quantity $\beta_i(0)$, which is obtained from the extrapolation of $\beta(\omega, I_L)$ to $I_L \to 0$, and which is determined by the parameters of the centers by the relation

$$\beta(\omega, 0) = m_0\sigma_{vD}(\omega) I_k^{-1}. \quad (12)$$

The dimensions of the quantities in (10)–(12) are as follows: β: cm/MW, I_L and I_c: MW/cm^2, σ: cm^2, m_0: cm^{-3}, t_L: nsec, and $\hbar\omega_L$: eV.

Thus, in finding the best agreement between the experimental, $\beta^\Sigma(I_L)$, and theoretical, Eq. (10), dependences, it is possible in nonlinear absorption to segregate the contributions to two-photon absorption and two-step absorption from various centers for a given $\hbar\omega$ and to determine the absolute values of $\sigma_{cD}(\omega_L)$ and $m_0\sigma_{vD}(\omega)$. By carrying out light intensity measurements on the nonlinear absorption spectra, we obtain the spectral distributions of the cross sections $\sigma_i(\omega)$ and the intensity dynamics of the effects of various centers in two-step absorption.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The experiments were carried out with the use of an automatic two-photon spectrometer[22] which records the spectral distribution of the induced absorption, the amplitude of the probe source, and the variations in the intensity of the laser radiation during the measurements. Averaging and

the preliminary mathematical processing of the signals were carried out in the automatic mode and the results were fed to a digital printer. The intensity of the laser radiation was recorded in the form

$$I_L \underset{a}{=} (\Delta t_L)^{-1} \int I_L(t)\, dt$$

by an FK-2 photocell operating in the integrating mode. The measurements were carried out at 300 K using a pulsed ($\Delta t_L = 30$ nsec) ruby laser ($\hbar\omega = 1.78$ eV) as the source of modulating light.

Three independently produced samples were investigated; these were specially undoped single crystals of ZnTe (T_d symmetry and dimensions $2\times3\times5$ mm) grown from the melt. The induced absorption spectra of these samples are shown in Fig. 1. In the spectral investigations of two-photon-induced absorption by nonequilibrium free carriers ($2\hbar\omega_L > E_g$) the laser radiation lies in the spectral range of the measurements of the laser-induced absorption. Because of the effects due to the scattering of the laser light, measurements in the range $\hbar\omega_L \pm 0.1$ eV were difficult. This circumstance dictated the choice of a ruby laser for use with ZnTe, since the radiation occurs in a spectral range where no singularities are observed in the nonlinear absorption. The spectra of Fig. 1 are bounded on the short-wavelength side by a sharp fall-off in the transmission of the probing light through the samples caused by the fundamental single-photon absorption, while on the long-wavelength end the spectra are bounded by the sensitivity threshold of the FEU-83 photomultiplier.

Figure 2 shows oscillograms of nonlinear absorption signals of $\Delta\alpha(t)$ measured in different regions of the spectrum. As can be seen, the shape of the signals corresponds to that described above for incoherent stepwise processes: the leading edge is delayed relative to the exciting pulse (due to the buildup of free and localized carriers), the peak coincides with the termination of the laser pulse, and thereafter the

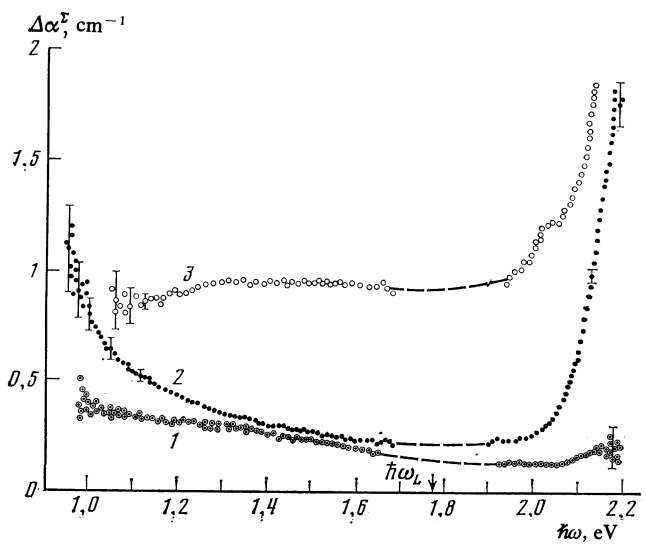

FIG. 1. Spectral dependences of induced absorption of light in ZnTe [E_g(300 K) = 2.28 eV]. Modulation by ruby laser radiation at $\hbar\omega_L = 1.78$ eV and $I_L \approx 5$ MW/cm^2. The spectra correspond to the different ZnTe samples: 1) Si; 2) YaI; 3) LI.

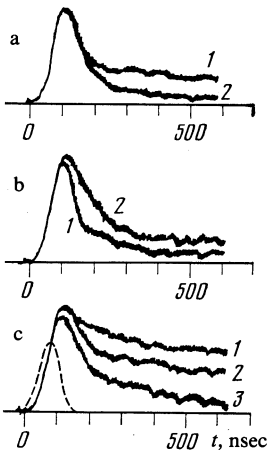

FIG. 2. Oscillograms of the signals from the induced absorption in the different ZnTe samples: a) SI; b) YaI; and c) LI. The photon energy of the probing light is: 1) 1.33 eV; 2) 2.06 eV; 3) 2.1 eV. The dashed curve indicates the pulse of modulating laser radiation.

excitation relaxes. For all the crystals the signal contains both fast (~ 100 nsec) and slow ($\sim 1\,\mu$sec) relaxation components. As the intensity of the laser radiation increases, the ratio of these two components shifts in favor of the fast component, but no substantial changes in the characteristic relaxation times are observed. This circumstance allows us to use the calculations presented above for the analysis of the processes.

The data of Fig. 3 show how the nonlinear absorption, $\beta^{\Sigma}(I_L)$, measured for various $\hbar\omega$ for the three samples, varies as a function of the intensity of the modulating laser radiation intensity. It follows from the results presented here that among the different ZnTe samples there are substantial differences in the shape of the spectra, in the absolute values

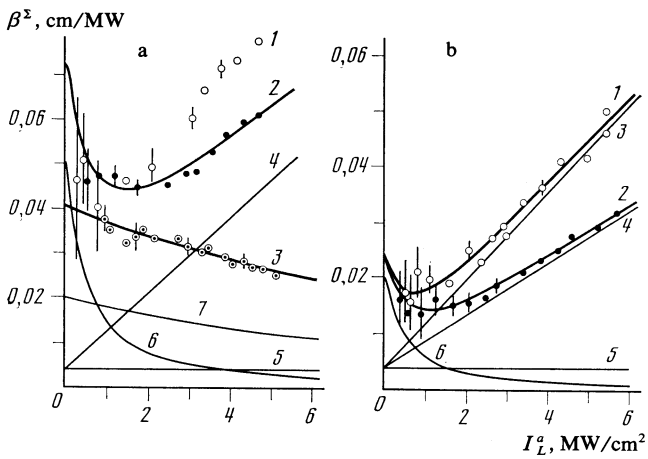

FIG. 3. Induced absorption as a function of the intensity of the modulating laser radiation, measured in the ZnTe crystals (points) and the corresponding theoretical dependences calculated according to (13) (solid heavy lines) using the parameters in Table I. In Fig. a) the curves represent: 1) ZnTe (LI) at $\hbar\omega = 2.1$ eV; 2) ZnTe (LI) at $\hbar\omega = 1.36$ eV; 3) ZnTe (SI) at $\hbar\omega = 1.36$ eV. Fig. b) shows the results for ZnTe (YaI) measured at $\hbar\omega = 2.06$ eV (1); and 1.33 eV (2). The light solid lines indicate the components of the theoretical dependences (13) due to the different nonlinear absorption processes: 4) absorption by nonequilibrium free carriers; 5) two-photon absorption; 6) and 7) two-step absorption via localized centers having different photoionization cross sections.

of $\Delta\alpha^{\Sigma}$, in the kinetics of the induced absorption signals, and in the dependences on the light intensity. This already indicates that under these experimental conditions, incoherent processes such as absorption by nonequilibrium free carriers and two-step absorption are dominant over intrinsic two-photon interband absorption.

Let us examine in detail the absorption vs light intensity curves, shown in Fig. 3, the analysis of which allows us to determine the relative degree to which the different processes participate in the nonlinear absorption and to determine the variation of these processes with increasing I_L. The solid heavy lines in Fig. 3 show the theoretical dependences of the form

$$\beta^{\Sigma}=\beta+\frac{1}{2}\gamma I_L+I_L^{-1}\sum_{i=1,2}\beta_i(0)I_{k_i}[1-\exp(-I_L I_{k_i}^{-1})], \qquad (13)$$

which, on the basis of (4) and (10), are formed from the parameters β (two-photon absorption), γ (absorption by nonequilibrium free carriers), and $\beta_i(0)$ and I_{c_i} (two-step absorption), these parameters being chosen so as to produce the best fit with the experimental points. These parameters are given in Table I, which also lists the values obtained on the basis of these parameters from (5), (11), and (12), for the cross section for the capture of photons by free carriers, $\sigma(\omega)$, and by localized charge carriers, $\sigma_{cD}(\omega_L)$. This Table also gives the values of $m_0\sigma_{vD}(\omega)$ of the intitial coefficient for the absorption of the probing light by centers (as $I_L\to 0$). In Fig. 3 the light solid lines show as a function of the light intensity the components of the absorption (13) due to the respective processes taking part in the nonlinear absorption: 1) two-step absorption (curve 5) which is characterized by $\beta=$ const, 2) absorption by nonequilibrium free carriers (curves 4 in Fig. 3a and 3 and 4 in Fig. 3b); these have the dependence $\beta\sim I_L$, that is, a linear increase with I_L, and 3) two-step absorption by centers of two types—those that saturate quickly (curve 6), and those that saturate later (curve 7) with increasing I_L (i.e., the cross section $\sigma_{cD}(\omega)$ of the former is greater than that of the latter).

As follows from Fig. 3 and Table I, as the laser intensity increases absorption by nonequilibrium free carriers dominates in the samples LI and YaI of the ZnTe crystals. On the other hand, in the Si ZnTe samples two-step absorption via centers having small cross section $\sigma_{cD}(\omega_L)$ is dominant for any I_L and it was not even possible to detect the component due to absorption by nonequilibrium free carriers. It is characteristic that in all three ZnTe samples the two-step absorption process is governed by two types of centers, where the parameters of the centers, $\sigma_{cD}(\omega_L)=2.4\cdot10^{-17}$ cm^2 and $\sigma_{cD}(\omega_L)=1.4\cdot10^{-18}$ cm^2, respectively, are the same from sample to sample, but the two types of centers occur in different combinations. Thus, the ZnTe samples (YaI) (Fig. 3b) are characterized by the fact that only the fast-saturating centers, with a large cross section $\sigma_{cD}(\omega_L)$, take part in the two-step absorption. In the CI samples of ZnTe (Fig. 3a, curve 3) only the centers with the small cross section $\sigma_{cD}(\omega_L)$ take part in the two-step absorption, whereas the LI ZnTe samples (Fig. 3a, curves 1 and 2) are distinguished by contributions to the two-step absorption from both of these centers (components 6 and 7 in Fig. 3a). Let us recall that the value of $\beta(0)$ for any component of the two-step absorption process for low intensities I_L (i.e., before the onset of saturation) is proportional to the concentration of the corresponding centers. It is difficult to draw conclusions regarding the nature of these deep centers based on measurements at a limited number of points of the nonlinear absorption spectrum. To do so one must separate out the components over the entire spectrum and determine the spectral dependences of these components which result from the different competing processes and of the centers involved in the two-step absorption. However, the fact that in three ZnTe samples, prepared by independent techniques, the same deep centers are involved in the nonlinear absorption, indicates that these centers are associated with intrinsic defects in the ZnTe.

An analysis of the change in the kinetics of the signals (Fig. 2) over the spectrum and a comparison of the kinetics with the dependences on light intensity shown in Fig. 3 indicate that the slow relaxation component is involved in the two-step absorption process (~ 1 μsec, the lifetime of the localized carriers) and the fast component is involved in the absorption by nonequilibrium free carriers (~ 0.1 μsec, the lifetime of the nonequilibrium free carriers).

Let us consider in more detail the absorption by nonequilibrium free carriers in the ZnTe sample designated YaI, in which the effect of impurity two-step absorption is the least and is quickly saturated as I_L increases (see Fig. 3b). The cross sections for the capture of photons by free carriers (Table I) at $\hbar\omega=1.33$ eV and 2.06 eV were obtained by the method described above. The value of the two-photon absorption constant for absorption of the type $\omega_L+\omega_L$ at the frequency of the ruby laser $\beta_{2\omega_L}(1.78\text{ eV})=0.010$ cm/MW, measured for ZnTe by the single-beam method,[23] was used in this determination. The nonlinear absorption spectrum of this crystal (Fig. 1, curve 2) is determined mainly (about

TABLE I.

	TPA	ANFC		TSA			
	β, 10^{-3} cm/MW	γ_ω, 10^{-3} cm^3/MW	σ_ω, 10^{-17} cm^2	$\beta_i(0)$, 10^{-2} cm/MW	$m_0\sigma_{vD}(\omega)$, cm^{-1}	I_{c_i}, MW/cm^2	$\sigma_{cD}(\omega_L)$, 10^{-18} cm^2
ZnTe (SI)	4	–	–	3.6	0.183	5	1.4
ZnTe (YaI)	4	4.7	1.4	2	0.006	0.3	24
		8 *	2.4 *				
ZnTe (LI)	4	8.5	2.5	5	0.011	0.3	24
				2	0.10	5	1.4

Note: The measurements were made at $\hbar\omega=1.36$ eV for the ZnTe samples (SI) and (LI), and at $\hbar\omega=1.33$ eV and 2.06 eV (indicated by the asterisks) for the ZnTe sample (YaI).

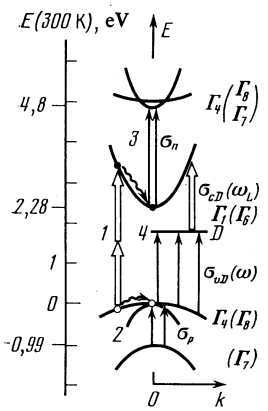

FIG. 4. Diagram of the optical processes, according to the band structure of Ref. 8, that take part in the nonlinear absorption of light: 1) two-photon absorption; 2) and 3) absorption by nonequilibrium free carriers, holes and electrons, respectively; and 4) impurity two-step absorption. The wide arrows show the absorption of laser photons $\hbar\omega_L$; the thin arrows show the laser-induced absorption of the probing light.

80%) by absorption by nonequilibrium free carriers.

The long wavelength fall-off and the short wavelength increase in the nonlinear absorption are evidently due to selective absorption by nonequilibrium free carriers involving transitions of carriers between subbands. The shape of the long wavelength part of the spectrum for $\hbar\omega < 1.4$ eV and the value $\sigma_p(1.33\text{ eV}) = 1.4\cdot10^{-17}$ cm^2 which we obtained are in agreement with the results of classical investigations of the absorption by equilibrium free carriers in p-type ZnTe,[8] in which the absorption by equilibrium free carriers was interpreted in terms of a selective absorption involving transitions of holes between the ground state Γ_8^v valence band and the Γ_7^v valence band split off by the spin-orbit interaction (see Fig. 4) and in which the value $\sigma_p(1.33\text{ eV}) = 10^{-17}$ cm^2 was obtained.

We know of no data for the selective absorption by equilibrium free carriers in ZnTe in the range $\hbar\omega > 2$ eV. The observed increase in the nonlinear absorption in ZnTe (samples YaI and LI) in the short wavelength region $\hbar\omega > 2$ eV (see Fig. 1) we believe to be due to the selective absorption by nonequilibrium free electrons involving transitions between the lowest conduction band Γ_6^c and the higher-lying band $\Gamma_{7,8}^c$ (see Fig. 4). This conclusion is favored by the following arguments: i) the kinetics of the absorption by nonequilibrium free carriers (Fig. 2b) are different in the regions $\hbar\omega < 1.4$ eV and $\hbar\omega > 2$ eV—the lifetimes of the free electrons and holes are different; ii) the ratio of the magnitudes of nonlinear absorption in these two regions are different for different ZnTe samples. It is not possible to explain this result on the basis of the absorption by free carriers of only one type, for instance, holes, with transitions from different valence subbands. Moreover, in ZnTe no valence bands were observed at this distance ($\sim$2–2.2 eV) from the upper valence band.[8] However, the position of the $\Gamma_{7,8}^c$ conduction band relative to Γ_6^c is in accord with our hypothesis ($\sim$2.5 eV, according to Ref. 8). Furthermore, the sharp increase in the nonlinear absorption for $\hbar\omega > 2$ eV is typical of the selective character of the absorption by nonequilibrium free carriers. The processes described above are depicted schematically in Fig. 4 by optical transitions in the band diagram of ZnTe.

Thus, the nonequilibrium effects of absorption by nonequilibrium free carriers in ZnTe are explained by the simultaneous occurrence of selective light absorption by both electrons and holes, which is practically impossible for steady-state absorption by equilibrium free carriers when the carriers are introduced by doping the crystal, as in e.g., Ref. 8.

In conclusion we note that the study of the nonlinear processes of absorption by nonequilibrium free carriers and two-step absorption can provide a method of measuring a number of important parameters of free carriers and deep centers in semiconductors, as we have shown using ZnTe as an example.

[1)]It is assumed that $E_M < \hbar\omega_L < E_g - E_M$, i.e., $\sigma_{vD}(\omega_L) = 0$ and $\sigma_{vD}(\omega) \gg \sigma_{cD}(\omega)$. If the last condition is not satisfied, then the processes are complicated by the appearance of induced impurity transparency along with the absorption under consideration. These effects of increased transparency have been observed often in semiconductors and they are due to the effects of the laser modulation on the steady-state two-step absorption of the "lamp photon–lamp photon" type.[18] In the present experiments these effects were not observed; therefore we shall proceed on the basis of the simplifications discussed here.

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