PARAMETRIC EXCITATION OF EXCITONS IN SILICON

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Submitted December 15, 1970; resubmitted April 28, 1971

Zh. Eksp. Teor. Fiz. 61, 1065–1072 (September, 1971)

A theoretical analysis was made of the possibility of parametric excitation of excitons in a semiconductor subjected to intense monochromatic radiation corresponding to the Stokes region of the exciton-phonon absorption spectrum. An experimental investigation was made of the dependence of the exciton-phonon absorption coefficient of Si crystals on the radiation power density at temperatures T = 170, 134, 90, and 1.6°K. It was found that when the radiation power density was of the order of 10^7 W/cm^2 and the wavelength of the radiation corresponded to optical transitions in the Stokes region of the spectrum, the distribution of the excitons departed strongly from equilibrium. The exciton dissociation time and the relaxation time of excitons along the energy axis were estimated. An analysis was made of the role played by the absorption of light by free excitons and of the two-photon absorption processes in the observed dependences. The photon-absorption cross section of free nonequilibrium excitons was determined.

ONE of the current problems in solid-state physics, associated with the application of nonlinear optics, is the development of sources of coherent quasiparticles with large wave vectors that exceed considerably the wave vector of light. We are speaking here of the experimental realization of nonequilibrium distributions in an energy band, characterized by the concentration of the occupation numbers n(**k**) in a fairly small part of the phase space. One of the possible methods for establishing such distributions is the parametric excitation of quasiparticles by laser pumping. The general conditions for such excitation have been considered theoretically in[1]. The optical analog of such excitation is the stimulated Raman scattering of light in the Stokes region. The parametric generation of quasiparticles has been realized experimentally in the excitation of magnons by means of magnetic pumping in the microwave range.[2,3] The present paper describes an experimental investigation of the possibility of the optical excitation and the subsequent establishment of a nonequilibrium distribution of excitons in silicon single crystals.

1. Let us consider briefly the conditions for the optical excitation of excitons in the Stokes region of the exciton-phonon spectrum where the transitions obey a law of conservation of the type

$$\hbar\omega = E_g^i - G + \mathscr{E}(\mathbf{k}-\mathbf{k}_0) + \hbar\Omega(\mathbf{k}_0-\mathbf{k}), \qquad (1)$$

where E_g^i is the indirect energy gap; G is the binding energy of an exciton; $\mathscr{E}(\mathbf{k}-\mathbf{k}_0) = \hbar^2(\mathbf{k}-\mathbf{k}_0)^2/2m$; **k** and m are, respectively, the wave vector and the mass of an exciton; $\mathbf{k}_0$ is the wave vector of an energy band extremum; $\hbar\Omega$ is the energy of a phonon. We shall be interested in the dependence of the absorption coefficient on the radiation power density. This dependence is associated with the changes in the numbers of excitons n(**k**) and phonons $\nu(\mathbf{k})$ caused by the incident radiation flux and by relaxation processes. Such changes can be written in the form[4]

$$\dot{n}(\mathbf{k}) = I[n(\mathbf{k})] + w(\mathbf{k},\omega)P[n(\mathbf{k}) + \nu(-\mathbf{k}) + 1] - \gamma_{ex}(\mathbf{k})n(\mathbf{k}). \qquad (2)$$

We shall ignore the change in the number of phonons participating in indirect transitions because $\gamma_{ph} \gg \omega P$. The quantity I[n(**k**)] in Eq. (2) is the collision integral which represents collisions of excitons with acoustical phonons; $\gamma_{ex}(\mathbf{k})$ is the reciprocal of the lifetime in the exciton band (recombination time); w(**k**, ω) is a function which represents the probability of an optical transition. This probability function is related to the absorption coefficient α in the following way:

$$\alpha_1 = \hbar\omega \sum_{\mathbf{k}} w(\mathbf{k},\omega)[n(\mathbf{k}) + \nu(-\mathbf{k}) + 1] \text{ (Stokes region)} \qquad (3)$$

$$\alpha_2 = \hbar\omega \sum_{\mathbf{k}} w(\mathbf{k},\omega)[\nu(-\mathbf{k}) - n(\mathbf{k})] \text{ (anti-Stokes region).} \qquad (3')$$

In the case of a spherically symmetrical band, we can easily obtain the following relationship between the function w(**k**, ω) and the absorption coefficient $\alpha_0(\omega)$ in a weak field (this formula applies to the Stokes region of the exciton-phonon spectrum):

$$w(\mathbf{k},\omega) = \frac{2\pi}{\sqrt{2}} \frac{\hbar\alpha_0}{m^{3/2}\sqrt{\mathscr{E}}\,\omega(\nu+1)} \times \frac{\sigma}{[(E_g^i - G + \mathscr{E}(\mathbf{k}-\mathbf{k}_0))/\hbar - \Omega - \omega]^2 + \sigma^2}, \qquad (4)$$

where $\sigma = \gamma_{ex} + \gamma_{ph}$.

We shall now consider a transient situation which corresponds to the experimental conditions which will be discussed later and in which we can ignore the reciprocal of the recombination time in Eq. (2), i.e., we can assume that the laser pulse is considerably shorter than the lifetime of an exciton in the band. Under these conditions, the intraband relaxation does not alter the total number of excitons and therefore this number can increase under the action of the incident radiation. Moreover, the rise in the number of excitons in weak fields does not alter the quasiequilibrium distribution of these quasiparticles. A departure from the equilibrium distribution of the excitons, accompanied by their preferential accumulation in an energy interval of the order of $\hbar\sigma$, occurs when the following condition is satisfied:

$$wP \gtrsim 1/\tau(\mathscr{E}), \qquad (5)$$

where $\tau(\mathscr{E})$ is the average energy relaxation time.

Thus, it is evident from our discussion that the absorption coefficient in the Stokes region should increase with increasing radiation power density. If this density is sufficiently high, the excitons depart from their equilibrium distribution.

2. Our experimental investigations were carried out on silicon single crystals whose exciton spectrum was quite well known. We used high-quality n- and p-type crystals (their resistivities were 4.5×10^3 and $2.5 \times 10^4\ \Omega^{-1}\text{cm}^{-1}$, respectively; the room-temperature carrier lifetime was of the order of 1 msec).

The block diagram of the apparatus used in the nonlinear absorption measurements is shown in Fig. 1.

The second component of the stimulated Raman scattering in liquid nitrogen,[5] excited by a Q-switched ruby laser LA_1, was used as the source of radiation in the Stokes region of the exciton-phonon absorption spectrum of Si. The third component of the stimulated Raman scattering ($\lambda = 1.34\ \mu$) was used as the probing radiation. The optical paths of the main and the probing beams were identical. The powers of the main and the probing radiation reaching a crystal were measured with photodetectors Φ_1 and Φ_2 and a high-speed oscillograph O_1. The powers of the same two radiations emerging from the crystal were determined by means of photodetectors Φ_3 and Φ_4 and an oscillograph O_2. The signals from the detectors Φ_2 and Φ_4 were fed to oscillographs via suitable delay lines, denoted by DL in Fig. 1. The two oscillographs were synchronized with each other by means of a signal from the laser LA_1. The time constant of the whole recording system was ~10 nsec.

A light pulse of the main radiation was attenuated by a system of calibrating filters F_0. The power radiation density could be varied in the range 10^2–$2 \times 10^7\ \text{W/cm}^2$ by placing the filters F_0 behind the crystal ($F_0 \rightarrow F_0'$), which did not alter the total attenuation of light in the system.

A Q-switched neodymium laser with stabilized frequency ($\Delta\nu \leq 0.1\ \text{cm}^{-1}$) was used as the source of radiation in the anti-Stokes and in the overlapping Stokes and anti-Stokes regions of the exciton-phonon spectrum.

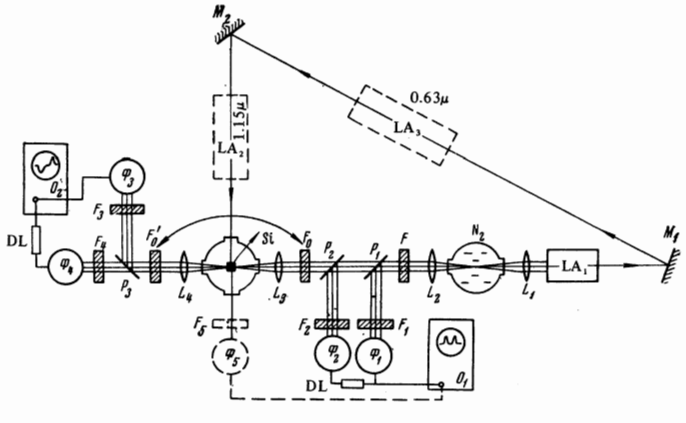

FIG. 1. Block diagram of the apparatus.

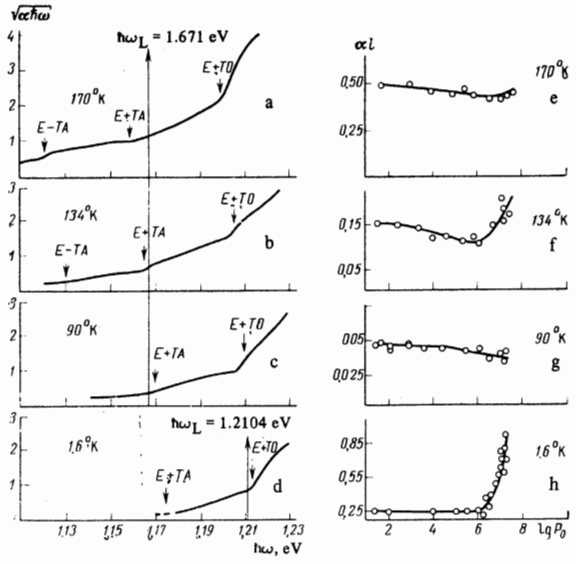

FIG. 2. a)–d) General nature of the absorption spectra representing transitions assisted by TA and TO phonons, recorded at various temperatures; e)–h) dependences of the exciton-phonon absorption coefficient on the radiation power density (at the same temperatures).

The laser frequency was stabilized by means of special selective elements placed within the resonator, as suggested in[6]. The frequency stability was checked by means of a diffraction-grating spectrograph with an image converter at its output. The experimental layout also made it possible to determine the absorption of the probing radiation of wavelength $\lambda = 1.15\ \mu$ generated by a neon-helium laser LA_2 (Fig. 1). The probing radiation reached a photodetector Φ_5 and the changes in the transmission of the Si at the moment of arrival of an excitation pulse from LA_1 were recorded with a wide-band amplifier and the oscillograph O_1. The whole system was aligned by means of a neon-helium laser LA_3 ($\lambda = 0.63\ \mu$).

3. The dependences of the exciton-phonon absorption coefficient on the power density of the monochromatic radiation are given in Figs. 2e–2h, which represent the results obtained at temperatures of 170, 134, 90, and 1.6°K. Figures 2a–2d show the general nature of the absorption spectra formed with the participation of TA and TO phonons (the arrows indicate the limits of the Stokes and anti-Stokes region),[1)] as well as the region affected by the laser radiation (the spectra were obtained at four different temperatures). The laser pumping affected the following regions of the exciton-phonon absorption in which TA phonons participated: 1) the additively overlapping Stokes and anti-Stokes regions (Figs. 2e and 2f); 2) the pure anti-Stokes region (Fig. 2g); 3) the pure Stokes region (Fig. 2h). The experimental results indicated that, in the case of optical excitation in the overlapping Stokes and anti-Stokes regions (Figs. 2e and 2f), the exciton-phonon absorption coefficient was a nonmonotonic function of the radiation power density, which exhibited some saturation at lower

[1)]The absorption spectra at temperatures T = 170 and 90°K were taken from the paper of Macfarlane et al. [7]

power densities followed by a rise at higher densities. Only a weak saturation of the absorption coefficient was observed in the anti-Stokes region (Fig. 2g). In the Stokes region of the exciton-phonon spectrum (Fig. 2h, T = 1.6°K), the dependence of the absorption coefficient on the laser pumping level was of the threshold type with a strong rise at power densities of the order of 10^6 W/cm^2: the coefficient increased by a factor of about 4.5 in a relatively narrow range of 3×10^6–2×10^7 W/cm^2.

The experimental results demonstrate clearly that the effect of laser pumping is a considerable accumulation of excitons in a band. We can easily show that the energy distribution of these excitons departs strongly from equilibrium. We shall consider first the high-temperature spectra (170 and 134°K, Figs. 2e and 2f). According to Eqs. (3) and (3′), the total absorption coefficient in that part of the spectrum where the Stokes and anti-Stokes regions overlap can be represented in the form

$$\alpha = \alpha_1 + \alpha_2 = \alpha_1^0 \frac{n_1 + \nu + 1}{\nu + 1}$$

$$+ \alpha_2^0 \frac{\nu - n_2}{\nu} = \alpha_1^0 + \alpha_2^0 + \left[\frac{\alpha_1^0 n_1}{\nu + 1} - \frac{\alpha_2^0 n_2}{\nu}\right].$$

where n_1 and n_2 are, respectively, the numbers of excitons excited in the Stokes and anti-Stokes regions and differing in energy by $2\hbar\Omega$. In the equilibrium state, the ratio of these excitons is determined by the Boltzmann factor $\exp(2\hbar\Omega/kT)$ and is independent of the incident power. The nonmonotonic nature of the dependences shown in Figs. 2e and 2f demonstrates that an increase in the power density causes the ratio n_1/n_2 to deviate from its equilibrium value because of the preferential rise of n_1.

At low temperatures (T = 1.6°K),[2)] the spectrum associated with the absorption of phonons is completely frozen out. In this case, the assumption of an equilibrium distribution is not in agreement with statistical mechanics. In fact, an equilibrium distribution of the excitons would be described by the formula

$$n = \left\{\exp\left[\frac{\mathscr{E} + |\mu|}{kT}\right] - 1\right\}^{-1},$$

which shows that

$$|\mu| / kT = \ln(1/n + 1) - \mathscr{E} / kt. \qquad (6)$$

It follows from the experimental dependence (Fig. 2d) that $n \sim 3$ and $\mathscr{E}/kT \sim 10^2$. These values are not in agreement with Eq. (6).

We shall now estimate the possibility of establishing a nonequilibrium distribution of the excitons. We shall consider separately the high- and the low-temperature regions.

At high temperatures (Figs. 2e and 2f), the excitons generated in the Stokes part of the exciton-phonon spectrum have an energy of motion $\mathscr{E}(|\mathbf{k}|)$ which is lower than the binding energy G. Such "cold" excitons cannot dissociate directly into electron-hole pairs.[8] This means that $\tilde{\tau}(\mathscr{E})$ in Eq. (5) is the average relaxation time along the energy axis associated with the intraband scattering by acoustical phonons. Using experimental parameters (for $\sigma \approx \gamma_{ph}$) and Eqs. (4) and (5), we find that

$$\gamma_{ph} / \tilde{\tau}(\mathscr{E}) \sim 10^{19} P,$$

where P is the power density in MW/cm^2. For $P = 2 \times 10^7$ W/cm^2, we obtain

$$\gamma_{ph} / \tilde{\tau}(\mathscr{E}) \sim 2 \cdot 10^{20}.$$

On the other hand, at low temperatures (T = 1.6°K, Fig. 2h), the incident radiation excites "hot" excitons whose energy is $\mathscr{E}$ = 0.0379 eV, which is greater than the binding energy. These excitons may undergo intraband scattering as well as dissociation. A theoretical estimate shows that under these conditions the dissociation time may be less than the average relaxation time along the energy axis, which is associated with the intraband scattering. This means that $\tilde{\tau}(\mathscr{E})$ in Eq. (5) is the average dissociation time.[9] It follows from Eqs. (4) and (5) that when $P \sim 2 \times 10^7$ W/cm^2, we obtain

$$\gamma_{ph} / \tilde{\tau}(\mathscr{E}) \sim 10^{21}.$$

It should be mentioned that at low temperatures the excitation of excitons occurs simultaneously with the direct excitation of electron-hole pairs as a result of the indirect electron-phonon transitions that are accompanied by the emission of TA phonons. However, we can easily show that, according to the Pauli forbiddenness rules, this process cannot result in an increase in the absorption coefficient with increasing radiation power density. Therefore, the experimentally observed increase in the absorption coefficient cannot be attributed to this process.

In fact, the electron-phonon absorption coefficient in this region is

$$\alpha = \sum_{\mathbf{k}_1, \mathbf{k}_2} w(\mathbf{k}_1, \mathbf{k}_2, \omega) \{[1 - n_c(\mathbf{k}_1)] n_v(\mathbf{k}_2) [\nu(\mathbf{k}_1 - \mathbf{k}_2) + 1] - n_c(\mathbf{k}_1) [1 - n_v(\mathbf{k}_2)] \nu(\mathbf{k}_1 - \mathbf{k}_2)\},$$

where $w(\mathbf{k}_1, \mathbf{k}_2, \omega)$ is a function representing the probabilities of electron-phonon transitions: $w(\mathbf{k}_1, \mathbf{k}_2, \omega) \propto A(\mathbf{k}_1, \mathbf{k}_2, \omega)\delta[\mathscr{E}_c(\mathbf{k}_1) - \mathscr{E}_v(\mathbf{k}_2) + \hbar\Omega_{\mathbf{k}_1 - \mathbf{k}_2} - \hbar\omega]$; $n_v(\mathbf{k}_2)$, $n_c(\mathbf{k}_1)$ are, respectively, the occupation numbers of the valence-band electrons and of the conduction-band electrons. In a weak radiation field, when $n_c = 0$ and $n_v = 1$, this absorption coefficient is

$$\alpha_0 = \sum_{\mathbf{k}_1, \mathbf{k}_2} w(\mathbf{k}_1, \mathbf{k}_2, \omega) (\nu + 1).$$

In a strong radiation field, when $n_c \neq 0$ and $n_v \neq 1$, we can easily show that $\alpha \leq \alpha_0$ because $n_c, n_v \leq 1$.

Let us consider separately the contribution of the free-exciton absorption to the observed rise of the absorption coefficient with increasing power of the incident radiation. To determine this absorption, we carried out experiments involving the optical probing of silicon crystals. In particular, the following experiment was carried out at T = 1.6°K (see block diagram in Fig. 1). We measured not only the dependence of the absorption coefficient in the Stokes region of the exciton-phonon spectrum at the wavelength of the second component of

[2)] An estimate of the possible heating of a crystal associated with the relaxation of the energy of the excitons and of the TA phonons generated by the incident radiation, gives ~8 deg for $P \approx 2 \times 10^7$ W/cm^2.

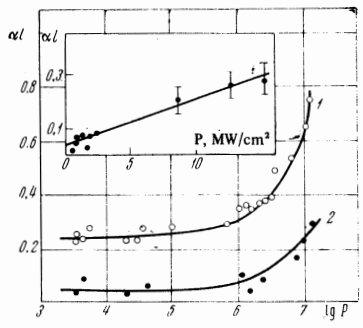

FIG. 3. Dependences of the exciton-phonon absorption coefficient on the radiation power density: 1) at the frequency of the main beam ($\hbar\omega$ = 1.2104 eV); 2) the frequency of the probing beam ($\hbar\omega$ = 0.923 eV).

the stimulated Raman scattering of ruby-laser radiation in liquid nitrogen, but also the absorption coefficient at $\lambda = 1.34\ \mu$ corresponding to the third component of the stimulated Raman scattering. The dependences obtained in this way are shown in Fig. 3. Curve 1 represents the dependence of the absorption coefficient on the radiation power at the frequency of the main beam ($\hbar\omega$ = 1.2104 eV) and curve 2 the corresponding dependence at the frequency of the probing radiation ($\hbar\omega$ = 0.923 eV). Curve 2 is replotted in the insert of Fig. 3 against a linear scale of the power of the main beam reaching the crystal. A comparison of the dependences shown in Fig. 3 demonstrates that the absorption coefficient at the frequency of the probing radiation increases linearly, as would be expected for the absorption by free excitons (or carriers). However, the absolute change in this coefficient is smaller than the corresponding change in the absorption at the frequency representing the exciton-phonon transitions. An estimate of the photon-absorption cross section of the optically generated excitons gives $\sigma \approx 2 \times 10^{-18}$ cm^2 at a wavelength $\lambda = 1.34\ \mu$. Thus, the rise in the exciton-phonon absorption coefficient with increasing power density cannot be explained solely by the absorption of the photons by free excitons, i.e., it cannot be explained by the more trivial mechanism.

We carried out additional experiments for the purpose of determining the role of the two-photon absorption in the observed rise of the absorption coefficient. A neodymium-glass laser, which emitted radiation corresponding to the transparency region of the Si crystals cooled to T = 1.6°K, was used to determine the two-photon absorption coefficient. It was found that this coefficient was $\alpha \leq 0.3$ cm^{-1} for $P \sim 2 \times 10^7$ W/cm^2, which was considerably smaller than the observed rise of the exciton-phonon absorption coefficient throughout the range of radiation powers employed.

Thus, illumination with an intense (laser) beam whose wavelength corresponds to the Stokes region of the exciton-phonon spectrum resulted in a considerable accumulation of excitons in a narrow energy interval. The observed features of the dependence of the absorption coefficient on the incident power density demonstrated that in our experiments the radiation fields were close to the threshold of the parametric generation of excitons. In other words, we observed experimentally the induced emission of excitons, i.e., the rise in the number of excitons per unit time $\dot{n}(\mathbf{k})$, which was proportional to the number of these excitons [see Eq. (2)].

The authors are grateful to V. L. Broude, V. F. Gantmakher, and I. B. Levinson for a very valuable discussion of the present paper.

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Translated by A. Tybulewicz
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