Kinetics of electron and hole binding into excitons in germanium

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The kinetics of binding of free carriers into excitons under stationary and nonstationary conditions is studied by investigating the submillimeter photoconductivity of Ge in a wide range of temperatures and of excitation levels. It is shown that the absolute values and the temperature dependence of the binding cross section ($\sigma \sim T^{-2.5}$) can be satisfactorily described by the cascade recombination theory. The value of σ and its temperature dependence differ significantly from the cross sections, measured in the same manner, for capture by attracting small impurities. Under nonstationary conditions, just as in the case of recombination with shallow impurities, a significant role is played by the sticking of the carriers in highly excited states.

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1. INTRODUCTION

The study of kinetic phenomena made a major contribution to our present knowledge of the properties of a system consisting of free carriers, an exciton gas, and an electron-hole liquid in a semiconductor. The kinetic equations that describe the behavior of the system with time contain different parameters that characterize the processes of binding of the free carriers into excitons, the dissociations of the excitons, the capture of free carriers and of excitons into electron-hole drops, the decay of the drops, etc. Some of these parameters, such as the lifetimes of the free excitons and of the particles in a drop, were reliably measured both in Ge and in Si. At the same time, the experimental data on the binding of free carriers into excitons are skimpy. We know of only one paper devoted to this question in the case of Si.[1] The apparent reason is that the traditional methods of studying excitons in the optical band are not suitable for the investigation of the binding process, owing to the influence of competing mechanisms of interband recombination via deep impurity centers, dissociation of the excitons at high temperatures, and their condensation at low temperatures. For Ge, great advantages in the study of the carrier binding into excitons are offered by measurements in the submillimeter band, which is characterized by emission-photon energies comparable with the exciton binding energy. The submillimeter photoconductivity arising in the case of photoionization and photothermal ionization of the excitons (excitonic photoconductivity) is not masked by other effects.[2] Particularly promising are investigations of submillimeter photoconductivity with the aid of monochromatic tunable generators in this wavelength band, namely backward wave tubes (BWT). They make it possible not only to carry out spectral investigations, but, owing to the possibility of high-frequency modulation of the BWT radiation at any point of the spectrum, to measure the absolute values of the characteristic times of the nonstationary submillimeter photoconductivity, down to 10^{-8} sec.[3] In conjunction with measurements of the lifetimes of the optically excited carriers, this makes it possible to study the binding of the free carriers into excitons in a wide temperature range even when the excitons undergo intensive thermal dissociation or are condensed, and to obtain the absolute values of the binding parameters.

Experimental investigations of the binding of carriers into excitons are stimulated by the success of the theory. In Ref. 4, a reliable calculation was made, for the first time ever, of the absolute values and of the temperature dependence of the cross section for binding of free carriers into excitons in semiconductors. It was shown that the binding of the carriers into excitons has much in common with trapping of carriers by a shallow attracting impurity center, and can be regarded as diffusion of an electron-hole pair in total-energy space at positive and negative energy values. However, the appearance of an additional energy scattering channel when the exciton moves as a unit, and exchange of energies between the interval and translational motions of the electron + hole pair, lead to a different temperature dependence of the binding cross section than in the case of capture of a hole by an impurity.

In this paper we present the results of an investigation of the kinetics of submillimeter excitonic photoconductivity of germanium. We obtain the values of the characteristic times of stationary and nonstationary submillimeter excitonic photoconductivity, the cross sections for binding the free carriers into excitons, and the probabilities of thermal dissociation of the excitons in a wide temperature range and a wide range of excitation levels. The values and the temperature dependence of the binding cross section are compared with the values and temperature dependences, obtained by the same methods, of the cross sections for carrier capture by charged donors and acceptors in germanium[3] and are compared with the theory.[4] Preliminary results of the measurements were published in Ref. 5.

2. DETERMINATION OF THE PARAMETERS OF THE BINDING OF FREE CARRIERS INTO EXCITONS

Free excitons in semiconductors (Ge and Si) are usually investigated with interband illumination of the sample, which excites free electrons and holes. In order for them to recombine predominantly via binding into excitons, it is necessary to choose for the investigation samples with sufficiently low density of shallow and deep inpurities, and also

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limit the temperature interval of the measurements and the range of the excitation levels. Indeed, one of the competing mechanisms of band-to-band recombination (for Ge at $T \lesssim 2$ K) can be trapping of the free carriers by neutral shallow impurities with formation of D^- or A^+ centers, followed by trapping of the carriers of opposite sign.[6] Since the coefficient of carrier trapping by a neutral center is $\sim 3\times 10^{-7}$ $cm^3 \cdot sec^{-1}$ (Ref. 6), and the expected values of the coefficient of binding into excitons at $T \lesssim 2$ K are $\sim 10^{-4}$ cm^3/sec (Ref. 4), recombination via $D^-(A^+)$ centers can be neglected at $N_n < 3\times 10^2 n$(N_n is the total density f the shallow impurities in the material, which are completely neutralized under conditions interband light, and n is the density of the free carriers). Investigations of the binding of carriers into excitons are of interest in a wide temperature range in the absence of condensation, therefore, the excitation level must be kept as low as possible. In this case the minimum excitation level is determined by the sensitivity of the measurement method, and amounts in our experiments to $\sim 10^{16}$ cm^{-3}/sec. This limits the permissible density of the shallow impurities in the investigated samples to $\sim 3\times 10^{-12}$ cm^{-3}. Thus, band-to-band recombination via $D^-(A^+)$ centers becomes significant only at sufficiently high densities of the shallow impurities.

Another recombination method that competes with the excitonic method is capture of free carriers by deep impurity centers. This recombination channel cannot be completely excluded from consideration, inasmuch as at high temperatures the exciton dissociation leads to a sharp growth of the density of the free carriers and to an increase of the rate of recombination via deep centers.

The scheme of significant generation and recombination fluxes in the absence of exciton condensation is shown in Fig. 1. It corresponds to the following equations of the kinetics of the system under stationary conditions (assuming $n \approx p$):

$$G - n^2\gamma_b + N_e\alpha_0 - n/\tau_{imp} = 0, \quad n^2\gamma_b - N_e/\tau_e - N_e\alpha_0 = 0. \qquad (1)$$

Here G is the interband generation flux, γ_b and α_0 are the coefficient of binding of free carriers into excitons and the probability of thermal dissociation of the excitons, τ_e and τ_{imp} are the lifetimes of the excitons and of the free carriers in recombination via impurity canters. From the solution of the system (1) it follows that the free-carrier lifetime

$$\tau_1^{-1} = G/n = n\gamma_b - N_e\alpha_0/n + 1/\tau_{imp} \qquad (2)$$

depends on several unknown parameters—γ_b, α_0, and τ_{imp}. It is possible therefore to determine the value of the binding coefficient in the investigation of band-to-band recombination only if the following two conditions are satisfied: a) $n\gamma_b \gg 1/\tau_{imp}$, and b) $n\gamma_b \gg N_e\alpha_0/n$, i.e., in the absence of thermal dissociation of the excitons and of recombination via impurity states. The condition a) is attainable when the level of excitation is increased and a sufficiently pure material with large value of τ_{imp} is chosen. The condition b) is satisfied only in a limited temperature interval ($T < 3K$ for germanium). At low temperatures and high excitation levels, however, the recombination process becomes complicated because of the presence of a condensed phase. Therefore the determination of γ_b from measurements of τ_1 is possible only in a very narrow interval of temperatures and of excitation levels.

The influence of thermal dissociation of excitons on the recombination times of the photocarriers produced via additional excitation of a semiconductor in the region of the exciton binding energy is much weaker. Indeed, from Eqs. (1), with allowance for the additional generation flux from the exciton levels g, we obtain for the characteristic time τ_2

$$\tau_2^{-1} = g/\Delta n = 2n\gamma_b + \tau_e\alpha_0/\tau_{imp} + 1/\tau_{imp}, \qquad (3)$$

where Δn is the density of the free carriers produced as a result of photoionization of the excitons [expression (3) was obtained under the assumption $n \gg \Delta n$]. Under conditions when $N_e/n \gg \tau_e/\tau_{imp}$, the second term in the right-hand side of (3), which determines the contribution of the thermal dissociation of the excitons to τ_2^{-1}, can be neglected in a larger temperature region than in expresson (2). In addition, the simultaneous solution of Eqs. (1) and (3) yields γ_b and α_0 in the entire range of T:

$$\gamma_b = \left[2n\tau_2\left(1 + \frac{\tau_e n}{2\tau_{imp}N_e}\right)\right]^{-1}, \quad \alpha_0 = \frac{n^2\gamma_b - N_e/\tau_e}{N_e}. \qquad (4)$$

It can be seen from (4) that the experimental determination of γ_b and α_0 in a large temperature interval is possible, but calls for measurements of a large number of parameters, namely n, τ_{imp}, τ_2, N_e, and τ_e.

The main difficulty, in our opinion, is the determination of the characteristic time τ_2 of the excitonic photoconductivity, since measurement by stationary methods usually does not yield the absolute value with sufficient accuracy, while measurement by nonstationary methods, e.g., of the relaxation time of the excitonic photoconductivity τ_{r2}, while sufficiently accurate, can yield values of τ_{r2} that differ substantially from τ_2 because of the sticking of the carriers in high-excited states of the recombination centers.[3] Therefore only the determination of the values of τ_{r2} and τ_2 and their dependences on the temperature and on the excitation level, jointly with measurements of n, τ_{imp}, N_e, and τ_e make it possible to obtain the values of γ_b and α_0 in a wide temperature interval. Comparison of the cross sections for binding free carriers into excitons and for trapping by shallow im-

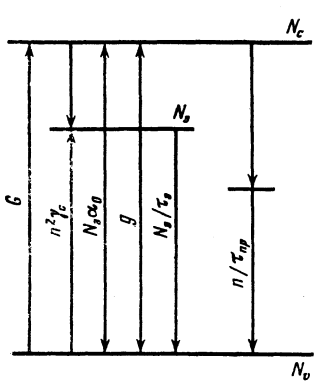

FIG. 1. Kinetics of recombination of free carriers in the case of interband excitation.

purities[3] can bring to light the features of the binding into excitons.

3. PROCEDURE AND EXPERIMENTAL TECHNIQUE

To measure the parameters listed above we used various experimental methods that determined the distinguishing features of the experimental setup.

First, to solve the problem posed it is necessary to have extremely pure semiconducting specimens, in which the exciton lifetime is long and the influence of recombination on impurities can be neglected in a sufficiently large temperature interval. When working with such a material, however, difficulties are raised by contact and surface phenomena that complicate greatly the interpretation of the photoconductivity-measurement results. This makes it necessary to forgo *dc* investigations of the photoconductivity and use contactless methods of measuring the free-carrier density and the photoconductivity by determining the absorption of microwave power under conditions of cyclotron resonance of the free carriers.

The investigations were carried out in a wide temperature range (1.6–12 K), the free carriers were excited with light from the intrinsic absorption region ($n \approx p$). The values of τ_e, N_e, n, Δn, τ_{r2}, and τ_2 were determined from the following measurements.

The exciton density N_e was calculated from the measured values of the absorption coefficient of submillimeter radiation for the quantum energy corresponding to photoionization of the exciton, $\alpha = 7.5 \times 10^{-14} N_e$ (Ref. 2), and their lifetime was determined from measurements of the dependence of α on the frequency of the amplitude modulation of the intnesity of the interband light. The values of N_e and τ_e obtained in this manner under conditions when the condensation of the excitons and the rcombination of the carriers by impurities can be neglected ($T = 4.2$ K) have made it possible to calculate the intensity of the generation flux $G = N_e/\tau_e$. The densities of the free carriers n (p) and of the carriers excited in photoionization of the excitons Δn (Δp) were determined from the area under the cyclotron resonance (CR) line. To increase the sensitivity in the measurement of n, the microwave-power absorption signal under CR conditions was recorded with the intensity of the interband light modulated, and when Δn was measured it was recorded with modulation of the power of the submillimeter radiation that caused the photoionization of the excitons. The area under the CR absorption line is uniquely connected with the density of the free carriers that take part in the resonance:

$$n = \eta \varkappa'' \Delta H / 4\pi dek,$$

where η is the microwave-radiation absorption coefficient at the maximum of the CR line, ΔH is the line width, k is the fraction of the electrons for which the given magnetic field is resonant, and d is the thickness of the sample. To monitor the absolute values obtained in this manner an additional comparison was made of the values obtained for the area under the CR line for unipolar conductivity (in the absence of interband light) and from measurements of the Hall constant under the same conditions. We note that the two methods yield results that differ by not more than 10%.

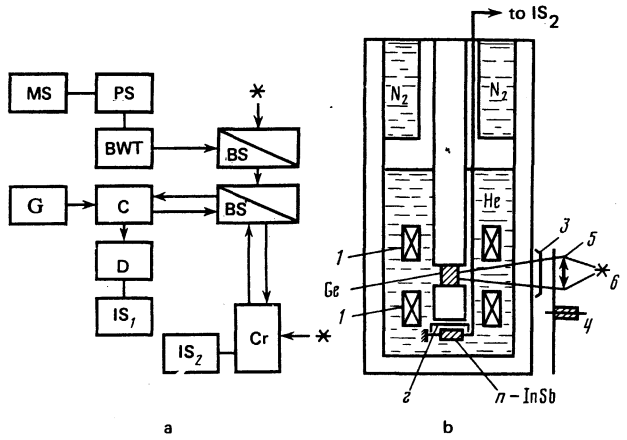

FIG. 2. Block diagram of experimental setup (a) and diagram of the cryostat (b) for the study of the kinetics of exciton photoconductivity of Ge: PS—power supply of BWT; BS—beam splitter, MS—modulation system, G—microwave generator, C—circulator, $IS_{1,2}$—indication system, D—crystal detector, Cr—cryostat, 1—superconducting Helmholtz coils, 2—filter for interband illumination of n-InSb detector; 3—IR filter, 4—modulator, 5—optical system, 6—illuminator.

The relaxation time τ_{r2} of the submillimeter photoconductivity was determined from the dependence of the photoconductivity signal on the amplitude-modulation frequency of the submillimeter radiation.

A block diagram of the setup is shown in Fig. 2. The submillimeter spectrometer, used previously to observe the absorption spectra *dn* the photoconductivity spectra of free excitons in Ge (Ref. 2), as well as the kinetics of the submillimeter photoconductivity of Ge with shallow impurities,[3] was coupled with an 8-mm-band microwave spectrometer with the aid of a reticular beam splitter used "in transmission" for submillimeter radiaiton and "in reflection" for 8 mm. The submillimeter and millimeter radiation is transmitted through a quasi-optical channel and exciting a Ge sample in a liquid-helium cryostat in the cavity of a superconducting magnet constructed in the form of Helmholtz coils to permit optical excitation of the sample through the side window of the cryostat. To measure the absorption coefficient of the submillimeter and millimeter radiation an n-InSb detector, covered with a filter to block the interband light, was placed behind the Ge sample outside the cavity of the superconducting magnet. Volume excitation of the sample by the interband light from an incandescent lamp was achieved by placing IR filters ahead of the optical window of the cryostat. In the measurement of N_e, τ_e, and n the light intensity was modulated with a mechanical chopper at a frequency varied in the range 0–35 kHz by changing the supply voltage of the chopper motor. The photoconductivity of the sample was determined by measuring, under CR conditions, the change of the level of the microwave radiation power reflected from the sample and passing through the sample. In this case, for aboslute measurements of n and Δn the microwave spectrometer must be used "in transmission," meaning that the absorption signal is recorded by the n-InSb detector. Since it is more convenient to operate the microwave spectrometer "in reflection." All the relative measure-

ments of n and Δn in the temperature and excitation-level range were carried out by means of a signal from a crystal detector connected in the mcirowave spectrometer channel through a circulator. The quantity recorded was then the change of the microwave-radiation power reflected from the Ge sample. The same microwave-spectrometer regime was used also for the measurements of τ_{r2}, for which a low-inertia indication circuit is necessry (the time constant of the n-InSb receiver is too large and amounts to $\sim 10^{-6}$ sec).

The submillimeter radiation at a frquency up to $\sim 10^8$ Hz was modulated by varying the anode voltage of the BWT in accordance with the scheme described in Ref. 3. The temperature of the Ge sample was set in the 4.2–1.4 K range by pumping off liquid-helium vapor. To raise the temperature (above 4.2 K), the quasi-optical channel with the sample were placed in an evacuated jacket. In this case the measurements were performed at relatively low levels of optical excitation ($G \lesssim 3\times 10^{17}$ cm^{-3}/sec). To prevent overheating, the sample was secured with vacuum grease to a quartz plate clamped to a copper radiator. The temperature was measured with a carbon thermometer located in the immediate vicinity of the sample. The illumination of the sample with interband light in this range of temperatures was effected through the upper warm window of the cryostat. In this case an additional beam splitter was included in the quasi-optical channel.

Investigations of the exciton photoconductivity was carried out on several samples of sufficiently pure Ge ($N_d + N_a \lesssim 10^{12}$ cm^{-3}). The obtained values of γ_b and α_0 were independent of the parameters of the invstigated samples.

4. RESULTS OF EXPERIMENT

All the experimental results presented below pertain to an ultrapure Ge sample with $N_d + N_a \approx 10^{10}$ cm^{-3}, in which the exciton lifetime τ_e amounts to 4×10^{-6} sec. It does not depend on the temperature of the sample in the range 1.4–12 K and on the level of the optical excitation at $G = 10^{16}$–10^{19} cm^{-3}/sec. The latter is confirmed also by

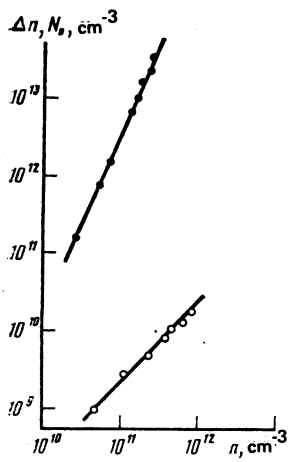

FIG. 3. Dependence of the exciton density N_e(●) and of the photocarrier density Δn(○), excited by submillimeter radiation, on the free-carrier density n, at $T = 4.2$K.

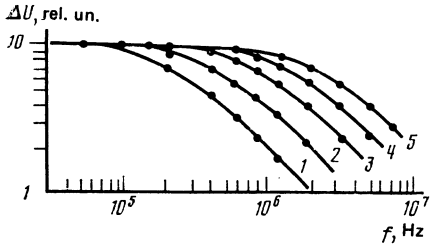

FIG. 4. Dependence of Δn on the submillimeter-radiation modulation frequency ($T = 4.2$K) at different excitation levels corresponding to the following values of n: 1–10^{10} cm^{-3}; 2–2.3×10^{10} cm^{-3}; 3–6.3×10^{10} cm^{-3}; 4–1.5×10^{11} cm^{-3}; 5–2.7×10^{11} cm^{-3}.

measurements of $N_e(n)$ (Fig. 3): $N_e \sim n^2$ in a wide range of variation of G (this follows from the second equation of the system (1) if the excitons do not condense into electron-hole drops). The same figure shows the $\Delta n(n)$ dependence. We note that $\Delta n \sim$ n.

The investigations of γ_b and α_0 were divided into two groups: the study of the binding mechanism at constant temperature under stationary and nonstationary conditions, and the study of the temperature dependences of γ_b and α_0.

Figure 4 shows plots of Δn against the modulation frequence f of the submillimeter radiation for different excitation levels. The measurements have shown that in photo- and photothermal ionization of the excitons the form of $\Delta n(f)$ does not change when the submillimeter radiation wavelength is changed. For clarity, the curves for $\Delta n(f)$ are shown in relative units and the plots of $\Delta n(f)$ have the same ordinate at small f. All the plots are well described by the expression

$$\Delta n = \Delta n(0)\,[1+(2\pi f\tau_{p2})^2]^{-1/2}$$

(the solid curves of Fig. 4). The corresponding values of τ_{r2} are plotted in Fig. 5 as functions of the free-carrier density. The figure shows also a plot of $\tau_2 = \Delta n/g$ obtained from the data of Fig. 3 with allowance for the fact that $g \sim N_e$ (the method of calculating the absolute values of τ_2 is described below). It can be seen from Fig. 5 that $\tau_2 \propto n^{-1}$, and that τ_{r2} exceeds τ_2 considerably at large n and has a much weaker dependence on n. With decreasing n, the $\tau_{r2}(n)$ dependence approaches $\tau_2(n)$ asymptotically.

Figure 6 shows plots of $N_e(T)$, $n(T)$, and $\Delta n(T)$ measured at a constant excitation level $G_1 = 3\times 10^{17}$ cm^{-3}/sec; for

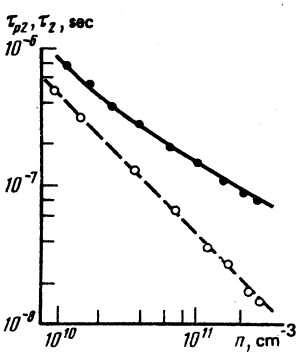

FIG. 5. Plots of τ_{r2}(●) and τ_2 (○) vs the free-carrier density n, $T = 4.2$ K.

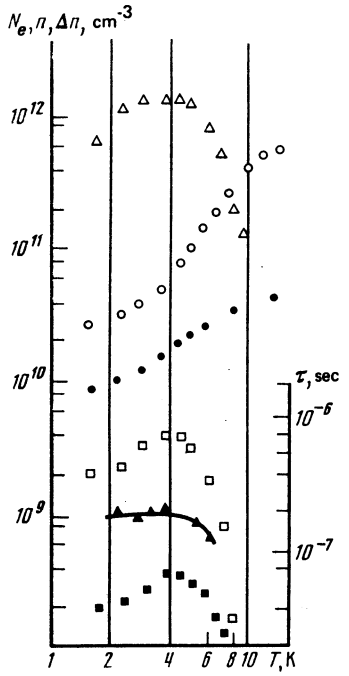

FIG. 6. Temperature dependences of $N_e(\Delta)$, n(○), Δn(□), τ_{r2}(▲), τ_2(■) at $G = 3\times10^{17}$ cm^{-3}/sec and of n(●) at $G = 3\times10^{16}$ cm^{-3}/sec.

comparison, the plot of $n(T)$ is given also for a smaller value of G ($G_2 = 3\times10^{16}$ cm^{-3}/sec). The values of $\tau_2(T)$ obtained from the measurements of Δn(T), $N_e(T)$, and $\tau_{r2}(T)$ for $G = G_1$ are shown in the same figure.

It can be seen that the functions $n(T)$ and $\Delta n(T)$ differ substantially: the $\Delta n(T)$ curve passes at $T\approx4$ K through a maximum, and n increases with increasing T, but at $T>8$–10 K the growth slows down rapidly; at large G the change of n in the same interval of T is greater. The plot of $N_e(T)$ is similar to that of $\Delta n(T)$.

The plots of $\tau_{r2}(T)$ and $\tau_2(T)$ differ greatly and the difference between the values of τ_{r2} and τ_2 increases with decreasing T. We note in conclusion that the character of the $n(T)$ and $\tau(T)$ dependences practically coincide at $T\lesssim4$ K.

5. DISCUSSION OF EXPERIMENTAL RESULTS

1. We consider first the data obtained by stationary methods. With change of temperature, a change takes place in the contributions of the different processes that determine the equilibrium in the excitons + free carriers + condensate system. At the employed excitation levels, the condensed phase is observed only at the very lowest temperatures. Thus, at an excitation level 3×10^{17} cm^{-3}/sec (see Fig. 6) the excition condensation determines the decrease of their density at $T<2.5$ K. However, the density of the free carriers does not depend on the presence of electron-hole drops (EHD) in the sample. Indeed, at such low temepratures it is possible to neglect the evaporation of the free carriers from the EHD. In addition, the contribution of the recombination of the free carriers on the impurities and the dissociation of the excitons are negligible already at $T\approx4.2$ K: from the $\tau_2 \propto 1/n$ dependence observed at 4.2 K it follows that $2n\gamma_b \gg \tau_e\alpha_0/\tau_{imp}$ and $2n\gamma_b \gg 1/\tau_{imp}$ [see (3)]. It appears that also the Auger flux of the free carriers from the drops, which is substantial at higher excitation levels, is small under these conditions compared with G. Therefore the appearance of drops in the sample changes the density of the excitons, and n turns out to be determined only by the probability of the process of binding into excitons at the given excitation level. The same is valid also for Δn, as is confirmed by a calculation of the kinetic equations under these conditions. The foregoing explains the similarity between the temperature dependences of τ_2, Δn, and n at $T = 1.5$–4 K and at the different excitation levels, and makes it possible to determine the values of τ_2 and the binding coefficient γ_b. From the numerical data of Fig. 6, with account taken of the value $\tau_e = 4\times10^{-6}$ sec, one calculates $G = N_e/\tau_e = 3\times10^{17}$ cm^{-3}/sec (in the calculation, N_e is taken from Fig. 6 at $T = 4.2$ K, where N_e does not depend on T). Next we obtain at $T = 2$ K the value $\gamma_b = G/n^2 = 3.6\times10^{-4}$ cm^3/sec and $\tau_2 = 1/2n\gamma_b = 4.7\times10^{-8}$ sec ($n = 2.9\times10^{10}$ cm^{-3}). The value of τ_2 calculated in this manner is used in fact to construct the plots of $\tau_2(n)$ and $\tau_2(T)$ in absolute units in Figs. 4 and 6. The value of γ_b at $T = 2$ K was obtained in the same manner also from the experimental data corresponding to the lower excitation level $G = 3\times10^{16}$ cm^{-3}/sec, at which the condensation of the excitons into EHD is observed only at $T<2$ K. The values of γ_b turned out to be independent of G within the limits of experimental accuracy; this is evidence of the small contribution of the Auger flux of the free carriers from the drops at $T<2.5$ K to the kinetics of the free carriers + excitons- + condensate system.

The sharp decrease of N_e and the increase of n at $T>4$ K (Fig. 6) show that in these conditions the contribution of the dissociation of the free exciton to the kinetics becomes substantial. This leads not only to an increse in the density of the free carriers, but also to a change in the recombination mechanism: at $T>10$ K, practically the entire recombination flux proceeds via deep impurity centers, and the n(T) plot flattens out. Indeed in the absence of condensation we have $G = N_e/\tau_e + n/\tau_{imp} \approx n/\tau_{imp}$ (if $n/\tau_{imp} \gg N_e/\tau_e$). At $T = 12$ K we have $N_e \ll 10^{11}$ cm^{-3}, $N_e/\tau_e \ll 3\times10^{17}$ cm^{-3}/sec, $n = 4\times10^{11}$ cm^{-3}, and $\tau_{imp} = 1.30\times10^{-6}$ sec. Since $\tau_e \approx \tau_{imp}$, recombination on impurities is substantial in the region where $n \gtrsim N_e$. At the employed excitation level this corresponds to the temperature region $T\geqslant8$ K. Calculation of τ_{imp} from the data of Fig. 6 shows that $\tau_{imp} \sim T^{1/2}$, in good agreement with the calculations by Lax.[7] From the results obtained for $G = 3\times10^{17}$ cm^{-3}/sec, using expression (4), we can calculate now the values of γ_b and α_0 in a wide range of temperatures (Figs. 7 and 8). In the region $T>2K$ (Fig. 7) we have $\gamma_b(T)\sim T^{-2}$. The values and the temperature dependence of γ_b are in good agreement with the calculaton[4] (solid line in Fig. 7) for the region of intermediate temperatures, satisfying the condition

$$\frac{M^2}{m_p^*}s^2 < kT < \left(\frac{M^2}{m_p^*}s^2E_B\right)^{1/2},$$

where M is the summary effective mass of the pair, M_p^* is the effective mass of the hole, s is the speed of sound in the crystal, E_B is the exciton binding energy. For Ge this condition corresponds to the temperature interval $1<T<7$ K, in

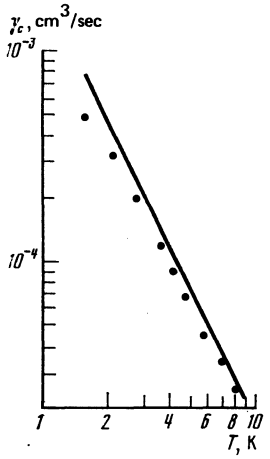

FIG. 7. Temperature dependence of the binding coefficient γ_b.

which γ_b is described by the expression

$$\gamma_b=\frac{1}{\sigma_c v},\quad \sigma_b=\frac{4\pi}{3l_0}\left(\frac{e^2}{\varkappa kT}\right)^3\left(\frac{kT}{Ms^2}\right)^{1/2}\left(\frac{8}{3\pi}\right)^{1/2}\frac{m_p^*}{M},$$

where $\varkappa$ is the dielectric constant of the crystal, v is the mean squared velocity, $l_0=v\tau_\varepsilon$, and τ_ε is the relaxation time of the energy of the free carriers. At $T<2$ K one observes a small weakening of the energy dependence of γ_b, apparently due to the inelasticity of the interaction between the carriers and the acoustic phonons.[4]

The $\alpha_0(T)$ dependence is shown in Fig. 8. The ratio of the exciton dissociation coefficient to the coefficient of the binding of the free carriers can be calculated for the case of thermodynamic equilibrium of exciton levels with allowed ands,[8] with account taken of the degeneracy multiplicity of the lower exciton level, for the translational mass of the exciton ($M_t=0.335\,m_0$, Ref. 9), and for the nonparabolicity of the exciton band[10]:

$$\frac{\alpha_0}{\gamma_b}=2C(T)\left(\frac{2\pi m_n^* m_p^* kT}{h^2 M}\right)^{3/2}\exp\left(-\frac{\Delta E_B}{kT}\right). \qquad (5)$$

Here m_n^* and m_p^* are the masses of the density of states of the

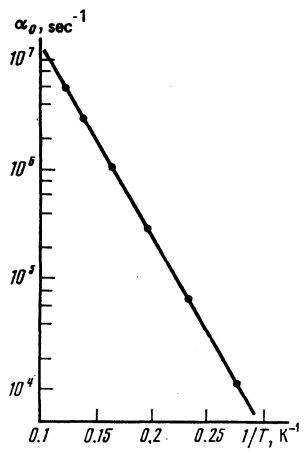

FIG. 8. Temperature dependence of the thermal-dissociation probability α_0.

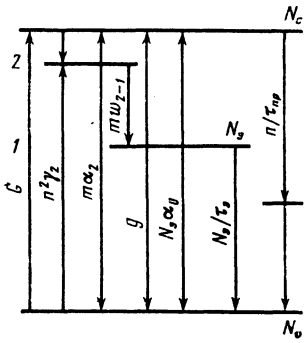

FIG. 9. Recombination kinetics in interband excitation with account taken of the sticking levels.

electrons and holes, and $C(T)$ takes into a ccount the nonparabolicity of the exciton band.

A comparison of the data on Fig. 8 with calculation in accordance with (5) (the values of γ_b are taken in this case from Fig. 7) shows that the temperature dependences practically coincide at $E_B=4.1$ meV, while the absolute values differ by more than one order of magnitude, with the experimental values of α_0 turning out to be less than the theoretical ones. The causes of this discrepancy are not clear to us.

2. We turn now to the results on the kinetics of nonstationary submillimeter photoconductivity. According to the cascade-recombination therory,[4] the process of binding of free carriers into excitons can be regarded as diffusion of an electron-hole pair in the total-energy space. The pair can be regarded as bound if its total energy is negative and larger in absolute magnitude than kT. Initially the carriers are bound in states with total energy $|E|<kT$, whose thermal-dissociation probability is large compared with the probability of descent of the pair into the region of large negative values of the total energy. Thus, these states can play the role of sticking levels in the process of nonstationary exciton photoconductivity. Figure 9 shows a simplified two-level scheme of the binding of free carriers into excitons. Here 1 is the ground state of the thermalized exciton, 2 replaces all the states with total energy $|E|<kT$, γ_2 is the coefficient of binding of an electron and hole into state 2, α_2 is the probability of thermal dissociation of these states, m is the density of the carriers bound into states 2, and w_{21} is the probability of the transition of the exciton from the state 2 into the state 1, i.e., $mw_{21}=n^2\gamma_b$.

At $T\approx 2.5$–6 K, i.e., under conditions when the dissociation of the excitons in the ground state, the recombination via impurity centers, and condensation can be neglected, the kinetics of the binding is described by the following system of equations:

$$\begin{aligned} d\Delta n/dt&=-2n\Delta n\gamma_2+\Delta m\alpha_2+g,\\ d\Delta m/dt&=2n\Delta n\gamma_2-\Delta m\alpha_2-\Delta m w_{21}. \end{aligned} \qquad (6)$$

Since $2n\gamma 2,\alpha_2\gg\omega_{21}$, we have in the stationary case ($dn/dt=0$, $dm/dt=0$)

$$2n\Delta n\gamma_2=\Delta m\alpha_2,\quad \Delta m/\Delta n=2n\gamma_2/\alpha_2,\quad \Delta m w_{21}=2n\Delta n\gamma_c. \qquad (7)$$

Simultaneous solution of Eqs. (6) yields the relaxation time of the submillimeter exciton photoconductivity

$$\tau_{p_2}=\frac{1}{2n\gamma_b}\left(1+\frac{\Delta m}{\Delta n}\right)=\tau_2\left(1+\frac{2n\gamma_2}{\alpha_2}\right). \quad (8)$$

To calculate the ratio γ_2/α_2 we used the expression[1)] (5). Since the important states here are those with $|E|<kT$, the exponential in (5) is close to unity and

$$\frac{\Delta m}{\Delta n}=2n\sum_i\frac{\gamma_i}{\alpha_i}=2Mn\left(\frac{2\pi m_r kT}{h^2}\right)^{-3/2}. \quad (9)$$

The summation is carried out over all the states with energy E in the interval $e^2/\varkappa r_n<|E|<kT$, where $r_n=n^{-1/3}$ is the average distance between the free carriers and M is the number of such states. Equation (9) is similar to the ratio obtained in Ref. 3 of the number of bound and free states in the presence of Coulomb impurity centers in the semiconductor, with the only natural difference that the role of recombination centers is assumed by double the density of the free carriers, and the carrier mass is replaced by the reduced exciton mass. Therefore, without repeating here the calculation of the number of levels of the Coulomb centers in the semiconductor, we use the ratio obtained in Ref. 3

$$\Delta m/\Delta n=\tfrac{5}{6}(2n)^{1/2}(\pi e^2/A\varkappa kT)^{3/2}. \quad (10)$$

We obtain the parameter A from a comparison of τ_{r2} and τ_2 (Fig. 6) at a free-carrier density $n=2\times10^{11}$ cm^{-3}. The value $A=0.26$ obtained in this manner is practically the same as given in Ref. 3 ($A=0.22$) for the ratio of the number of bound and free states in germanium with shallow impurities. The solid lines in Figs. 5 and 6 are the values of τ_{r2} calculated from τ_2 with the aid of (10). The agreement between calculation and experiment indicates that the model of carrier sticking in high excited states of the excitons is correct and that the absolute values of τ_2 were correctly determined.

3. The investigations of the kinetics of the stationary and nonstationary submillimeter exciton photoconductivity yielded in the values and the temperature dependences of the parameters for the binding of free electrons and holes into excitons in germanium. It should be noted that the investigated temperature interval 1.6–8 K is of greatest interest from the viewpoint of comparison of the experimental results with the theory. According to Ref. 4, for germanium in this temperature range the principal role in the binding is played by the distances between the electron and the hole at which the relaxation rate of the total energy becomes comparable with the rate of energy exchange between the interval and translational motion of the exciton. In this case, the energy scattering in the motion of the exciton as a unit becomes significant; this leads, within the framework of the theory,[4] to a large binding cross section and to a somewhat different dependence of the cross section on the temperature compared with trapping by an immobile charged impurity center. Calculation of the binding cross section in this temperature interval is most complicated (diffusion of a pair in a two-dimensional space). At lower temperatures ($T<1$ K) the binding process does not differ in any way from trapping by an impurity, and at $T>8$ K the relaxation of the energy is determined by the cooling of the hot excitons in the ground state. In Fig. 10, the data obtained on the cross section for binding of free carriers into excitons are compared with the

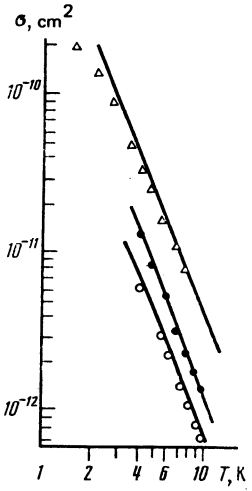

FIG. 10. Temperature dependences of the cross sections for capture of carriers by shallow donors σ_d (●) and acceptors σ_a (○) and of the cross section for binding of free carriers into excitons σ_b (Δ) in Ge.

corresponding results for trapping by shallow donors and acceptors in germanium.[3] The figure shows also the theoretical plots (solid lines) for excitons in accordance with Ref. 4 and for impurities in accordance with Ref. 11. It can be seen that the cross section for binding into excitons agrees with the theory and exceeds the cross section for trapping by both donors and acceptors. For example, at $T=4.2$ K the binding cross section amounts to $\sigma_b=3.2\times10^{11}$ cm^2, while the cross section for capture by donors and acceptors are respectively $\sigma_d=1.4\times10^{-11}$ cm^2 and $\sigma_a=6\times10^{-12}$ cm^2. In addition, σ_b has a weaker temperature dependence. All this indicates that the binding of carriers into excitons differs from their trapping by impurity centers in this temperature interval; it is due to the random motion of the exciton as a whole.

Notice should be taken also of another important, in our opinion, result: we have shown that the model of carrier sticking in high-excited states of attracting centers[3] is applicable to the process of binding of free carriers into excitons. This indicates that the model of sticking in high excited states of attracting centers is universal in the case of the cascade recombination mechanism.

[1)]For high excited states, the nonparabolicity of the exciting band can apparently be neglected. In addition, in the calculation that follows we introduce an adjustment parameter A which automatically takes into account also the effective density of states.

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