557 (1967); **57** 1329 (1969) [Sov. Phys. JETP **25**, 365 (1967); **30**, 721 (1970)].

[33] E. G. Brovman and Yu. Kagan, Usp. Fiz. Nauk **112**, 369 (1974) [Sov. Phys. Usp. **17**, 125 (1974)].

[34] E. A. Kaner and L. V. Chebotarev, Zh. Eksp. Teor. Fiz. **73** 1813 (1977) [Sov. Phys. JETP **46**, 953 (1977)].

[35] A. P. Zhernov and Yu. M. Kagan, Fiz. Tverd. Tela (Leningrad) **20**, 3306 (1978) [Sov. Phys. Solid State **20**, 1906 (1978)].

[36] E. G. Maksimov, Zh. Eksp. Teor. Fiz. **69**, 2236 (1978) [Sov. Phys. JETP **42**, 1138 (1978)].

[37] É. A. Kaner and L. V. Chebotarev, Preprint ITF-78-70R, Kiev.

[38] D. Pines, Elementary Excitations in Solids, Benjamin, 1963.

[39] L. D. Landau, Zh. Eksp. Teor. Fiz. **30**, 1058 (1956); **32**, 59 (1957) [Sov. Phys. JETP **3**, 920 (1956); **5**, 101 (1957)].

[40] Yu. Kagan and A. P. Zhernov, Zh. Eksp. Teor. Fiz. **50**, 1107 (1966) [Sov. Phys. JETP **23**, 737 (1966)].

[41] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[42] A. M. Kosevich, Osnovy mekhaniki kristallicheskoĭ reshetki (Fundamentals of Crystal Lattice Mechanics), Nauka, 1972.

[43] I. G. Lang and S. T. Pavlov, Fiz. Tverd. Tela (Leningrad) **12**, 1068 (1970); **12**, 2412 (1970) [Sov. Phys. Solid State **12**, (1970); **12**, (1970)].

Capture of photoexcited carriers by shallow impurity centers in germanium

E. M. Gershenzon, G. N. Gol'tsman, V. V. Multanovskiĭ, and N. G. Ptitsyna

Moscow State Pedagogical Institute
(Submitted 2 March 1979)
Zh. Eksp. Teor. Fiz. **77**, 1450–1462 (October 1979)

Measurements were made of the lifetimes τ_f of free carriers and the relaxation time τ_r of the submillimeter impurity photoconductivity when carriers are captured by attracting shallow donors and acceptors in Ge. It is noted that in samples with capture-center concentration $N_{rec} \gtrsim 10^{11} \text{cm}^{-3}$ the relaxation time τ_r greatly exceeds τ_f in the temperature range 4.2–12 K. The measured values of τ_f are compared with the calculation of cascade recombination by the classical model. To evaluate the data on τ_r, the distinguishing features of this model are considered for the nonstationary case. The substantial difference between the values of τ_f and τ_r is attributed to re-emission of the carriers from the excited states of the shallow impurities.

PACS numbers: 72.20.Jv, 72.40. + w, 71.55.Dp

1. INTRODUCTION

One of the important mechanisms of recombination of free carriers by attracting Coulomb centers in semiconductors is cascade capture with participation of the excited impurity states; the theory of this mechanism was developed by a number of workers.[1-4] The calculations were made only for the stationary case, and the possible differences between the characteristic times in stationary and nonstationary conditions were not discussed. Generally speaking, however, such differences can exist. In fact, according to Abakumov et al.[4] the recombination of the carriers proceeds via their diffusion in energy space over highly excited states of the impurity centers in the region of negative energies up to a binding level with energy $|\varepsilon| \approx kT$, and the probability of the thermal ejection from highly excited states $|\varepsilon| < kT$ into the free band is large compared with the probability that the carriers will drop down via cascade of excited states to the ground state. Thus, high excited states of the impurities exchange carriers in practice only with the free band, and consequently, can play the role of sticking levels. The number of such states under definite conditions can be quite large.

Usually the sticking centers and recombination centers are separated in space, and direct exchange of carriers between them does not take place. In the case of cascade recombination on shallow impurity centers

this is not so, so that the sticking levels discussed by us belong to the recombination centers themselves. The presence of sticking levels should manifest itself primarily in the values of the characteristic times measured by stationary and nonstationary methods. In an experimental verification of the calculations performed in Refs. 1–4, the lifetimes were determined by different methods. The published experimental data on carrier recombination on impurity centers in semiconductors are on the whole in agreement with the calculations of Abakumov et al.[4] Attention is called, however, to the large scatter of the data obtained by different authors.[5-8] The measured lifetimes differ both in the values and in the temperature dependence.

On the one hand this is partially due to the inadequacy of the procedures in a number of cases when the relaxation time τ_r of the excess carrier density is identified with the stationary lifetime of the carriers without valid grounds, or when the measured τ_r is in fact determined not from the carrier recombination but, for example, from the dielectric relaxation of the space charge in the semiconductor. On the other hand, the mechanism of cascade recombination is not always decisive in the capture, even in the case of Coulomb attracting centers. For deep impurities, a large role can be played by recombination with participation of optical phonons.[9] At high concentrations of the centers, this mechanism can be substantial also for shallow impuri-

0038-5646/79/100728-07$02.40

ties.[10] Nevertheless, it is precisely for shallow impurities that the model of cascade recombination is applicable, apparently, in the widest possible range, and in the study of carrier capture by shallow impurities it is possible to obtain a detailed comparison of theory and experiment.

This comparison must be made primarily for the simplest case of low concentration of the recombination centers and relatively high temperatures, when the centers can be regarded as isolated, and the interaction of the carriers with the acoustic phonons can be regarded as quasielastic. It is also possible here to neglect the overlap of the neighboring centers that are important for the capture, the freezing-out of the Coulomb centers into dipoles, and other complicating factors.

Our purpose was to study the capture of free carriers by shallow impurities in Ge at low concentration of the recombination center and at relatively high temperatures by stationary and nonstationary methods. To this end we measure the lifetimes of the free carriers and the relaxation time of the impurity photoconductivity. These data are compared with one another and with the theory.

It turned out that the relaxation time τ_r at helium temperatures greatly exceeds the lifetime τ_f of the free carriers even in very pure samples with recombination-center concentration $N_{rec} \sim 10^{11}$ cm^{-3}. An analysis of the experimental data and of the calculations has shown that this difference is due to re-emission of the carriers from highly excited states of the same shallow impurities, which are recombination centers. A comparison of the times measured by stationary and nonstationary methods makes it possible to study these states and their role in the capture of free carriers. Since the singularities of the nonstationary case have not yet been considered in the theory of cascade recombination, it became necessary, for a comparison with the theory, to carry out the corresponding calculations. Here we confine ourselves to a simplified model of an impurity center, and also to the case of low concentration of the recombination centers.

The choice of Ge as the material for the study of the capture of the carriers by shallow impurities was dictated by several factors. First, this is the purest semiconductor in which it is easy to attain conditions such that the shallow recombination centers can be regarded within a wide range of the concentrations as interacting sufficiently weakly. Second, the experimental data on carrier capture by shallow impurities in Ge are less plentiful than, for example, for Si. In particular, the kinetics of the impurity photoconductivity of Ge with shallow impurities has hardly been investigated. The carrier capture process was investigated so far mainly by other methods: the relaxation of the conductivity after application of an electric-field pulse,[6] from the value of the stationary photoconductivity,[6] or from the generation-recombination noise.[7] This situation is apparently due to the experimental difficulties, since the characteristic frequencies of the photoconductivity for Ge with shallow impurities correspond to the submillimeter band, which became technically accessible only

relatively recently. Third, the investigation of the kinetics of submillimeter photoconductivity is important also from the practical point of view, since Ge is one of the most promising materials for the preparation of submillimeter and long-wave infrared impurity photoresistors, in which the time delay of the response is determined directly from these measurements.

It should also be noted that the photoconductivity relaxation times τ_r which had to be measured turned out to be quite short (~30 nsec). Such measurements in the submillimeter band are not a trivial task. We registered for this purpose the photoconductivity in transitions of bound carriers between excited states of donors and acceptors using a submillimeter spectrometer[11] with backward-wave tubes (BWT). The amplitude of the radiation in the spectrometer was modulated at a frequency up to 20 MHz. An important feature of the experiment is the use of photothermal ionization of the impurity, which makes it possible to obtain an excess concentration of thermalized carriers, for in this case the photoexcited carriers turned out to be free only after interacting with the equilibrium phonons.

2. EXPERIMENTAL PROCEDURE

The kinetics of impurity photoconductivity of n- and p-Ge were investigated by us in the wavelength band $\lambda = 0.3-1.5$ mm at temperatures $T = 4.2-12$ K. The measurements were made with a submillimeter spectrometer with BWT previously used to observe the lines of the transitions between the excited states of donors and acceptors in Ge and for a detailed study of their energy spectrum.[11] In the present study we registered the dependence of the intensity of these photoconductivity lines on the modulation frequency of the submillimeter radiation. For lack of sufficiently rapid modulators for the submillimeter band, amplitude modulation with frequency up to 20 MHz was produced by varying the anode voltage of the BWT. The measurement procedure is illustrated by Fig. 1. In the upper part of the figure is shown by way of example, a section of the photoconductivity spectrum of a Ge sample; this section contains only one line at 318 GHz. To record this spectrum with scanning of the radiation frequency, the BWT was ad-
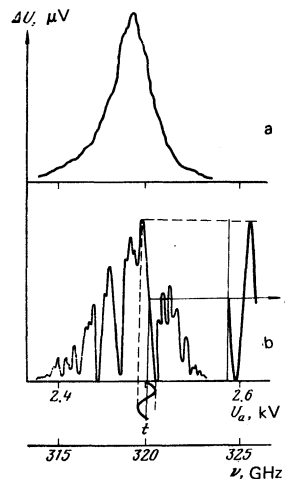

FIG. 1. Section of the photoconductivity spectrum of a p-Ge sample (see the table, sample 15), recorded with (a) and without (b) stabilization of the radiation power level.

TABLE I.

justed in the magnetic field in such a way that the dependence of the radiation power P on the anode voltage U_a, and consequently on the frequency, was as smooth as possible. The spectrum was scanned by varying U_a and maintaining the radiation power P constant with the aid of electromechanical feedback based on a signal from an n-InSb detector. For high-frequency modulation of the radiation we needed another adjustment of the BWT in the magnetic field, wherein the $P(U_a)$ curve was strongly cut up and had individual sections in which no generation was produced. In this case the power is not stabilized and the same section of the spectrum takes the form shown in Fig. 1(b). It is seen that for amplitude modulation of the BWT radiation it suffices to superimpose on the anode voltage an alternating component (5–10 V) at the modulation frequency Ω. The resultant frequency modulation is insignificant, since it is small compared with the line widths of the observed impurity transitions.

The photoconductivity signal of the investigated sample was registered at the frequency Ω by a narrow-band voltmeter (V6-2 or V6-1). To eliminate the influence of the capacitance C of the conducting leads, the sample was shunted with a resistor R_{sh} ($R_{sh} \ll 1/\Omega C$).

The samples were in the form of dumbbells, so that they could be used directly to measure the concentrations N_D and N_A of the donor and acceptor impurities by using the Hall effect.

In the study of recombination by nonstationary methods it is necessary to pay careful attention to prevent the relaxation of the space charge from distorting the measurement results. Shunting the sample in an external measuring circuit does not always exclude the influence of the dielectric relaxation, so that at low temperatures it is difficult to obtain in pure Ge samples ohmic contacts and a homogeneous illumination with the submillimeter radiation. We used therefore in the experiments samples with impurity compensation $K \lesssim 0.5$; illumination by the background radiation at room temperature decreased their resistivity ρ to $\lesssim 10^4 \Omega$-cm. The samples with the largest number of recombination centers ($N_{rec} \sim 3$–$5 \cdot 10^{13}$ cm^{-3}) were chosen more carefully (with $K \lesssim 0.1$) and had $\rho \lesssim 10^3 \Omega$-cm. This made it possible to get rid of the influence of the dielectric relaxation on the kinetics results, since its characteristic time $\tau_d = \rho\varkappa$ ($\varkappa$ is the dielectric constant of the crystal) was always much shorter than the measured τ_r.

To determine the stationary lifetime τ_f we measured the photoresponse voltage ΔU at sufficiently low modulation frequency (150 Hz) of the background radiation and the concentration n of the free carriers. At low temperatures, at $n \ll N_D - N_A, N_A, N_D$, we have

$$\Delta U = U \frac{\Delta n}{n} = U \frac{\Delta G \tau_f}{n}, \tag{1}$$

where U is the bias voltage on the sample; Δn and ΔG are the alternating parts of the free-carrier concentration and of the generation flux. Since the employed samples had $\Delta G \sim N_D - N_A$ at the given background radiation power, it follows that $\tau_f \sim \Delta U n / U(N_D - N_A)$. To

Sample No.	Type	N_D	N_A	Sample No.	Type	N_D	N_A
1	p	$8 \cdot 10^{10}$	$6.4 \cdot 10^{11}$	9	p	$1.4 \cdot 10^{13}$	$2.9 \cdot 10^{13}$
2	p	$2 \cdot 10^{11}$	$6 \cdot 10^{11}$	10	p	$1.7 \cdot 10^{13}$	$3.8 \cdot 10^{13}$
3	p	$3 \cdot 10^{11}$	$8 \cdot 10^{11}$	11	p	$3.2 \cdot 10^{13}$	$3.1 \cdot 10^{14}$
4	p	$6.3 \cdot 10^{11}$	$3.1 \cdot 10^{12}$	12	p	$4 \cdot 10^{13}$	$1.7 \cdot 10^{14}$
5	p	$7.2 \cdot 10^{11}$	$1.7 \cdot 10^{12}$	13	p	$5.1 \cdot 10^{13}$	$5.3 \cdot 10^{14}$
6	p	$8.7 \cdot 10^{11}$	$2.2 \cdot 10^{12}$	14	n	$1.6 \cdot 10^{13}$	$2.6 \cdot 10^{12}$
7	p	$4.4 \cdot 10^{12}$	$8 \cdot 10^{12}$	15	n	$1.1 \cdot 10^{13}$	$1.6 \cdot 10^{12}$
8	p	$1.1 \cdot 10^{13}$	$2.3 \cdot 10^{13}$				

modulate the additional background illumination, a rotating disk with holes was placed in front of the entrance window of the cryostat; the intensity of the thermal radiation of its metallic blades was less than that passing through the openings (modulation depth ~1%). This method makes it possible to determine τ_f in relative units up to $T \lesssim 12$ °K.

3. EXPERIMENTAL RESULTS

For all the n- and p-Ge samples (see the table) the impurity photoconductivity relaxation times were measured at several submillimeter frequencies corresponding to transitions between different excited states of the donors and acceptors. We chose for the measurements transitions whose initial and final states differed substantially in energy.

Figure 2 shows by way of example the amplitude-frequency dependence of the photoconductivity signal $\Delta U(\Omega)$ of a p-Ge sample for a line with energy 1 MeV at $T = 9$ °K. The points here are the experimental results and the solid line is calculated from the formula[12]

$$\Delta U(\Omega) = \Delta U_{\Omega \to 0} / (1 + \Omega^2 \tau_r^2)^{1/2}. \tag{2}$$

The agreement between the calculation and experimental data indicates that the photoconductivity kinetics is described by a single relaxation time τ_r ($\tau_r = 10^6$ sec for Fig. 2). For each sample, the values of τ_r obtained from measurements at different frequencies of the submillimeter radiation turned out to be the same. This indicates that the function $\Delta U(\Omega)$ is not sensitive in our case to the details of the ionization of the excited states by the impurity atoms, and is determined only by the capture of the free carriers. The latter is not surprising, since the ionization times of the excited states of the impurity atoms are as a rule much less than the lifetimes of the free carriers. In fact, the times of the phonon transition between the excited levels of the shallow impurities in Ge are small (10^{-9}–10^{-11} sec),[13] and the probability of ionization of the final states for transitions between the excited states does not differ strongly from unity in the temperature range 4–12 °K.[14]
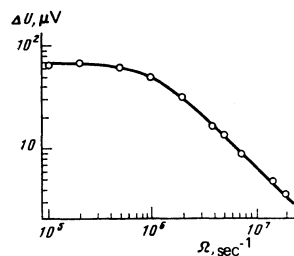

FIG. 2. Amplitude-frequency dependence of the photoresponse voltage of p-Ge sample No. 5.
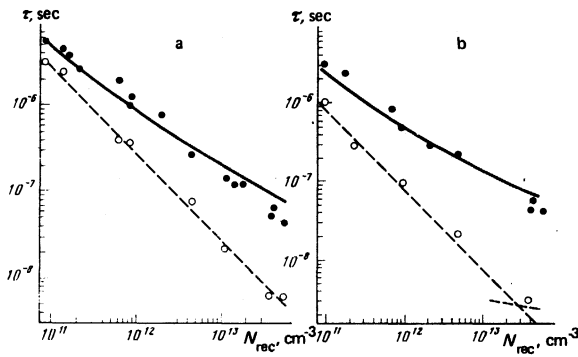
FIG. 3. Plots of the photoconductivity relaxation time τ_r (●) and of the free-carrier lifetime τ_f (○) against the concentration of the attracting centers in p-Ge samples at $T = 8$ K (a) and 4.2 K (b). Dashed curves—calculated from Ref. 4, solid—calculated from Eq. (6) with Eq. (9) taken into account.

Figure 3 shows the dependences of the relaxation time τ_r of the submillimeter photoconductivity and the lifetime τ_f of the free carriers on the concentration N_{rec} of the attracting centers for Ge with shallow acceptors at $T = 8$ K (a) and 4.2 K (b). The absolute values of τ_f for all the measured samples were obtained by reconciling the experimental value of the stationary lifetime for the sample with $N_D = 8 \cdot 10$ cm^{-3} (sample No. 1 in the table) at $T = 8$ K with the theoretical value calculated from the formula

$$\tau_f^{-1} = N_{rec} v \sigma, \qquad (3)$$

where v is the mean squared thermal velocity of the carrier, and σ is the cross section for capture of the carrier by an isolated Coulomb attracting center. In accordance with Ref. 4,

$$\sigma = \frac{4\pi}{3 l_0} \frac{e^2 Z}{\varkappa kT} \left[\frac{e^2 Z}{\varkappa (kT + 2,74 m_d s^2)} \right]^2 ; \qquad (4)$$

here eZ is the charge of the impurity ion, m_d is the state-density mass, s is the speed of sound in the crystal, $l_0 = v \tau_\varepsilon$, and τ_ε is the carrier-energy relaxation time.
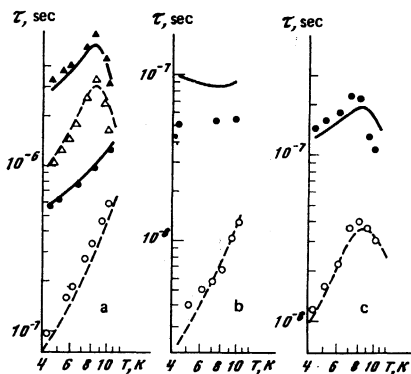
For both temperatures and all samples, including the

FIG. 4. Temperature dependence of τ_f (light symbols) and τ_r (dark symbols) for p-Ge and n-Ge samples: a) △, ▲— sample No. 1, ○, ●—sample No. 5; b) sample No. 13; c) sample No. 14 (see the Table). Dashed curves—calculated from Ref. 4, solid line—calculated from Eq. (6) with account taken of Eq. (9).

purest ones, the condition $p \ll N_D$ is satisfied (where p is the concentration of the free holes), therefore the concentration of the recombination centers N_{rec} is equal to N_D. It is seen from Fig. 3 that τ_f is practically proportional to N_{rec}^{-1}. The $\tau_r (N_{rec})$ is much weaker: at relatively high temperature and small values of N_{rec} it approaches asymptotically the $\tau_f (N_{rec})$ dependence, that even at $N_{rec} = 4 \cdot 10^{13}$ cm^{-3} and $T = 4.2$ K the value of τ_r exceeds τ_f by more than an order of magnitude.

Figure 4 shows the temperature dependence of τ_r and τ_f for three p-Ge samples and one n-Ge sample. The $\tau_r(T)$ dependence is much weaker than $\tau_f(T)$. Thus, for pure n- and p-Ge samples (Figs. 4a and 4c) with recombination-center concentration $N_{rec} \lesssim 5 \cdot 10$ cm^{-3} we have $\tau_f(T) \propto T^\alpha$, where α ranges from 2.5 to 2 when the temperature is decreased; under the same conditions the $\tau_r(T)$ dependence is close to linear. In dirtier samples with $N_{rec} = (1 - 4 \cdot 10$ cm^{-3} at $T < 7$ K, a gradual weakening of the $\tau_f(T)$ dependence is observed, and τ_r is independent of T within the limits of the experimental accuracy. For all the samples, the functions $\tau_f(T)$ and $\tau_r(T)$ go through a maximum at high temperatures; the position of the maximum varies with the densities of the main and compensating impurities.

4. DISCUSSION OF RESULTS

We discuss first the experimental data on the lifetime τ_f of the free carriers. The dashed curves in Figs. 3 and 4 show the calculations of the functions $\tau_f(N_{rec})$ and $\tau_f(T)$ in accordance with formulas (3) and (4). Inasmuch as at relatively high temperatures the concentration $p(n)$ of the free carriers becomes comparable with the concentration of the compensating impurity N_D (N_A), and then also with the differential concentration $N_A - N_D$ ($N_D - N_A$), we calculate, for example, τ_f of holes we use the expression[15]

$$\tau_f = [\sigma v (N_d + 2 p_0 + p_i)]^{-1}, \qquad (5)$$

where

$$p_i = \frac{N_f}{\beta} \exp\left(-\frac{\varepsilon_{gr}}{kT}\right)$$

ε_{gr} is the energy of the ground state, β is the multiplicity of its degeneracy, and N_f is the density of the free states.

The experimental plots of $\tau_f(N_{rec})$ and $\tau_f(T)$ practically coincide with the theoretical ones. We note that for shallow impurities in Ge the dependence $\tau_f(T) \propto T^{2.5}$ expected[4] from the cascade model of capture for isolated Coulomb centers in quasielastic interaction with phonons is observed only in a very narrow temperature region and for pure samples (with $N_{rec} \lesssim 5 \cdot 10$ cm^{-3}, Figs. 4a and 4c). The upper bound on the temperature is due to the increase in the number of recombination centers with increasing concentration of the free carriers [see (5)]. This explains the decrease of τ_f and τ_r at high temperatures. For low temperatures, the weakening of the temperature dependence is due to the inelastic interaction of the carriers with the acoustic phonons. It becomes noticeable in Ge already at $T \lesssim 6$ K.

In dirtier samples and higher temperatures, the carriers may not manage to become thermalized prior to capture; in addition, an essential role is assumed by the overlap of the neighboring-center levels, which are important for the capture. For these reasons the section with $\tau_f \propto T^{2.5}$ is not observed at all at $N_{rec} \gtrsim 10^{13}$ cm^{-3} (Fig. 4b).

We turn now to the results on τ_r. In the purest samples at high temperatures, the values of τ_r approach the theoretical values τ_f. This makes it possible to assume, with sufficient grounds, that the theory of cascade capture[4] well describes not only the functions $\tau_f(N_{rec})$ and $\tau_f(T)$, but yields also sufficiently accurate absolute values of the lifetimes and cross sections for capture of the free carriers by shallow impurities in germanium.

At the same time, as already noted, at high impurity concentrations and low temperatures, τ_r exceeds τ_f substantially. Usually an excess of τ_r and τ_f is evidence of the presence in the sample of sticking levels of type α or β in Ryvkin's terminology.[12] When the sample contains sticking levels of one type with concentration M and ionization energy ε_M, and the equilibrium between the sticking levels and the free-state band is established within a time τ_θ much shorter than the lifetime of the free carriers τ_f (α sticking), the photoconductivity relaxation time is defined as[12]

$$\tau_r = \tau_f(1 + M/N_{cM}),\tag{6}$$

where N_{cM} is the effective free-state density referred to the sticking-center level, $N_{cM} = N_f \exp(-\varepsilon_M/kT)$.

If $\tau_\theta \gg \tau_f$ (β sticking), then the frequency dependence of the photoresponse is described by two times: τ_θ and τ_f. Obviously the form of frequency dependence in this case is connected with the value of the ratio M/N_{cM}.

In semiconductors with shallow impurities, the sticking centers can be neutral impurity atoms capable of becoming attached to an excess electron or hole (D^- or A^+ centers). Since the binding energy of a D^- (A^+) state in Ge is $\lesssim 1$ MeV,[16] in the temperature interval 4.1–12 K the probability of disintegration of such states is quite high. Depending on the concentration N_{rec}, they can appear as α- or β-sticking levels. However, the number of these states, which is determined by the concentration of the neutral impurity atoms, was much less in the samples investigated by us than N_{cM}. Therefore the D^- (A^+) centers cannot influence noticeably the relaxation of the photoconductivity under these conditions.

As already noted above, the sticking of the carriers in semiconductors can occur also on high excited states of the same shallow impurities that determine the recombination of the free carriers. To avoid confusion, we must define more precisely the meaning of the term "sticking." Lax introduced a quantity called by him the sticking probability of a carrier in a given state. It characterizes the probability of a process wherein the carrier captured from a band into a given state reaches subsequently the ground state and will not be ejected again into the free band. We use the term "sticking" in the opposite meaning, just as, for example, in Ref. 12,

where sticking centers are defined as traps for which the probability of the inverse thermal ejection (reemission) is very high. In this sense, since τ_θ for high excited states is very small (10^{-9}–10^{-11} sec,[13]) and the probability of ionization of these states is of the order of unity,[14] they act as α-type sticking levels.

Expression (6) for τ_r was obtained in Ref. 12 for a model in which the capture and sticking centers are spatially separated. In our case, as already noted, this is not so. According to the cascade model,[4] carrier capture is regarded as their direct descent to all the cited states of the impurity center from the region of positive energies into the region of negative energies. The carrier remains captured when it drops below the level with energy $\sim kT$. Thus, all the excited states having an energy $|\varepsilon| \lesssim kT$ participate in the capture and at the same time, by virtue of the sufficiently large ionization probability, are sticking levels.

We calculate now the relaxation time of the photoconductivity for a simplified two-model of such an impurity recombination center—see Fig. 5. The arrows in the figure indicate the optical and phonon transitions. Level 2 is practically in thermal equilibrium with the band and replaces all the higher excited states with energy $|\varepsilon| \lesssim kT$. The carrier recombines when it goes from level 2 to level 1. The probability w of this transition, in contrast to the usual case of spatially separated recombination and sticking centers, is in this case not equal to zero, although it is small compared with the ionization probability of level 2. The nonequilibrium free carriers are produced by the impurity light, and the corresponding generation flux is directed from level 1 into the free band. The kinetic equations for this model are of the form

$$dn/dt = m\gamma_M N_f \exp(-\varepsilon_M/kT) - n\gamma_M M + G,$$
$$dm/dt = n\gamma_M M - m\gamma_M N_f \exp(-\varepsilon_M/kT) - mw,\tag{7}$$

where n is the concentration of the free carriers, M is the total number of bound states with energy $|\varepsilon| \lesssim kT$ for N_{rec} attracting centers, m is the number of electrons in these states, and γ_M is the coefficient of carrier capture by level 2. Since $\varepsilon_M \lesssim kT$, the exponential in (7) is close to unity.

For the stationary case, in the approximation in which w is small compared with $\gamma_M N_f$ at low temperatures, when $m \ll N_{rec}$, we obtain $m/n = M_{N_f}$ and $\tau_f = N_f/Mw$. In the nonstationary case we can seek a general solution of the system (7), since the equilibrium between level 2 and the band is established within the time $\tau_\theta \ll \tau_f$. It is easy to show that when G is changed (the additional illumination is turned on and off) the photoconductivity relaxation is described by a single
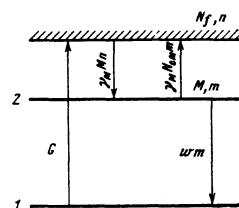

FIG. 5. Transition scheme for a two-level model of an impurity atom.

time $\tau_r = \tau_f(1 + M/N_f)$. This expression is identical with the expression obtained in Ref. 12 for the case of α sticking for spatially separated capture and sticking centers.

Thus, the problem of the influence of the highly excited states on the kinetics of the photoconductivity of an impurity semiconductor reduces to a calculation of the ratio M/N_f. Under conditions of quasi-equilibrium of the excited states and the free band (α sticking), we calculate M/N_f by using the known expression for the concentration of the electrons (holes) on the degenerate impurity level[17]:

$$\frac{M}{N_f} = \frac{m}{n} = \frac{N_{rec}}{N_c e^{F/kT}} \sum_M \beta_M \exp\left(\frac{F - \varepsilon_M}{kT}\right)$$

$$= \frac{N_{rec}}{N_f} \sum_M \beta_M \exp\left(-\frac{\varepsilon_M}{kT}\right), \tag{8}$$

where β_M is the degree of degeneracy of the Mth impurity excited state, and F is the Fermi energy reckoned from the bottom of the conduction (valence) band. It is seen that although on each center (regardless of how large the number of excited states) there can be not more than one electron, and the ratio m/n (and consequently also M/N_f) is determined by the total number of bound states with energy $|\varepsilon| \lesssim kT$ on N_{rec} attracting centers.

At relatively large distances from the attracting center, which correspond to highly excited states, the potential of the center is very close to the Coulomb potential $-e^2/\varkappa r$. Therefore at $|\varepsilon| \lesssim kT$ the energy spectrum of the bound states can be regarded as quasi-continuous and the sum in (8) can be replaced by an integral. Then the quantity $\rho_{bound}(\varepsilon)d\varepsilon$ appears in place of β_M and we use for the density of states $\rho_{bound}(\varepsilon)$ the known expression

$$\rho_{bound} = N_{rec}\left(\frac{m_d e^4}{2\hbar^2 \varkappa^2}\right)^{3/2} \varepsilon^{-5/2},$$

where the customarily employed effective mass is replaced by the density mass $m_d = 0.2m_0$ for the conduction band and $0.38m_0$ for the valence band. The state density in the free bands is calculated in the known fashion:

$$\rho_{free} = 2\frac{(2m_d)^{3/2}}{4\pi^2\hbar^3} \varepsilon^{1/2}.$$

As $\varepsilon \to 0$ the density $\rho_{bound} \to \infty$. However, near the edge of the band, the growth of the density of the bound state is limited by the fluctuations of the impurity potential, the swing of which is $\pm\varepsilon_0$ ($\varepsilon_0 = Ae^2N^{1/3}/\varkappa$).

Figure 6 shows the energy dependences of the densities ρ_{bound} and ρ_{free} of the bound and free states in the crystal. The bound-state region includes all the states lying below the percolation level ε_0. In the potential-fluctuation region, the function $\rho_{bound}(\varepsilon)$ is unknown. To calculate M/N_f we match together the densities of the free and bound states in the manner shown in Fig. 6, and integrate $\rho_{free}(\varepsilon)$ and $\rho_{bound}(\varepsilon)$ with account taken of the occupation of the free and bound states. For fewer samples ($N_{rec} < 4 \times 10^{13}$ cm^{-3}) and relatively high temperatures ($T > 4$ K) used in the experiment we have $\varepsilon_0 < kT$.

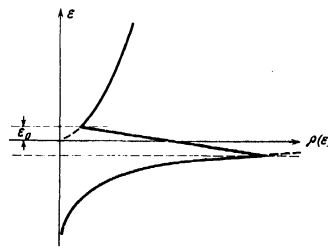

FIG. 6. Dependence of the density of the bound and free states in a crystal on the carrier energy.

Then

$$\int_{\varepsilon_0}^{\infty} \rho_{free}(\varepsilon)f(\varepsilon)d\varepsilon \approx 2\left(\frac{2\pi m_d kT}{h^2}\right)^{3/2} = N_f.$$

The calculation of M can be greatly simplified by taking into account the fact that the energy of the excited states of interest to us is $|\varepsilon| \lesssim kT$ and the value of the exponential in (8) is close to unity, while the maximum of the density of the bound states lies in the region $|\varepsilon| \lesssim kT$ (Fig. 6), and finally, the density of the bound states $\rho_{bound}(\varepsilon)$ decreases sharply with increasing $|\varepsilon|$. Then the units of integration in (8) can be chosen to be ε_0 and $-\infty$. As a result we obtain for M/N_f

$$\frac{M}{N_f} = \frac{5}{6}N_{rec}^{1/2}\left(\frac{\pi e^2}{A\varkappa kT}\right)^{3/2}. \tag{9}$$

We compare now our results with experiment. We calculate the value of the constant A from the measurements of τ_r and τ_f for one of the samples at a certain temperature (for sample No. 5 at $T = 8$ K we have $A = 0.22$) and plot the calculated functions $\tau_r(N_{rec})$ and $\tau_r(T)$ for all the samples, using this value of A. The corresponding calculated plots are shown in Figs. 3 and 4 by solid lines. They agree with the experimental ones for most measured samples. The only exception is the group of samples with $N_{rec} \approx 2-4 \cdot 10^{13}$ cm^{-3} (for example, Fig. 4b), for which the theoretical and experimental temperature dependences differ somewhat. This is not surprising, inasmuch as $\varepsilon_0 \sim kT$ for these samples and the assumptions made in the calculation of M/N_f are not fully valid in this case.

We note that the experimental value $A = 0.22$ differs somewhat from the theoretical one for weakly compensated samples ($A = 0.3$, Ref. 18), a fact that can be fully attributed to the simplifications made in the calculation.

Thus, the relaxation of the impurity photoconductivity of Ge with shallow-impurity concentration $10^{11} - 10^{14}$ cm^{-3} in the range $T = 4-12$ K is determined by the re-emission of the carriers from the high excited states, which act as sticking levels. The difference between the relaxation time and the stationary lifetime increases with increasing concentration of the captured centers and with decreasing temperature. The temperature dependence is obvious: the number of bound states that act as sticking levels does not depend on T (at least so long as $\varepsilon_0 < kT$), while the effective number of free states increases in proportion to $T^{3/2}$. The dependence on N_{rec} can be qualitatively explained in the following manner. With increasing number of recombination centers, ε_0 increases, the number of bound states per center decreases like $N_{rec}^{-1/2}$ (the maximum of the density of

the bound states in Fig. 6 drops into the region of larger negative energies), but the number of centers increases. Therefore N turns out to be an increasing function of N_{rec} and is proportional to $N_{rec}^{1/2}$.

In samples with a large number of recombination centers, when $\varepsilon_0 > kT$, the ratio M/N_f should apparently decrease with increasing N_{rec}. This is determined by the fact that the bound states that can act as sticking levels in this case only in the region of the impurity potential fluctuations in the energy interval $\varepsilon_0 - (\varepsilon_0 - kT)$. The large number of deeper levels with $|\varepsilon| > kT$ can be disregarded, since the probability of ionization of the carriers in these states is low. The number of free states at $\varepsilon_0 > kT$ also turns out to depend on N_{rec}. Estimates show that in the limiting case $\varepsilon_0/kT > 1$ the values of M and N_f increase in proportion to $N_{rec}^{1/6}$, and the ratio M/N_f is close to unity and does not depend on either N_{rec} or T. As a result, at $\varepsilon_0 \gtrsim kT$ the difference between τ_r and τ_f should decrease.

CONCLUSION

The influence of highly excited states of shallow impurities on the kinetics of the impurity photoconductivity should apparently be observed not only in Ge. Estimates similar to those presented above show that, for example, in silicon with shallow impurities the relaxation time of the impurity photoconductivity τ_r at low temperatures can also greatly exceed τ_f. In the other purest semiconductors, such as GaAs or InSb, the degree of extreme purification which is for the time being much worse than that of Ge or Si, the sticking effect described in this paper is apparently insignificant, inasmuch as below the impurity depletion temperature the swing of the potential fluctuations exceed kT.

A difference between the stationary and nonstationary time connected with the re-emission of the carriers in highly excited states should be observed also in the case of carrier recombination in deep Coulomb centers, if the cascade mechanism of capture is decisive in this case.

The results of this study impose definite limitations on the inertia of photoreceivers made of Ge with shallow impurities. Until now the response time of such photoresistors was identified with the stationary lifetime. Our experiments show that for the customarily employed Ge with $N_{rec} \sim 10^{13}$ cm^{-3} under standard conditions ($T \sim 4.2$ K) the inertia should be larger by at least one order of magnitude, namely $\sim 10^{-7}$ sec. To decrease the inertia it is necessary to use materials with larger concentration of attracting centers ($N_{rec} \gtrsim 10^{14}$) for which the times τ_r and τ_f come closer together. The limiting values of τ are determined by the energy relaxation time[4] and amount to $\sim 10^{-9}$ sec.

However, the sensitivity of such photoreceivers is worse than when material with smaller N_{rec} is used.

In conclusion, the authors thank Yu. A. Gurvich, V. I. Perel', M. N. Nassievich, and V. N. Abakumov for useful discussions.

[1] M. Lax, Phys. Rev. 119, 1502 (1960).
[2] G. Ascarelly and S. Rodrigues, Phys. Rev. 124, 1321 (1962); J. Phys. Chem. Solids 22, 57 (1968).
[3] F. Belesnay and G. Pataki, Phys. Status Solidi 13, 499 (1966).
[4] V. N. Abakumov and I. N. Yassievich, Zh. Eksp. Teor. Fiz. 71, 657 (1976) [Sov. Phys. JETP 44, 345 (1976)]. V. N. Abakumov, V. I. Perel', and I. N. Yassievich, Fiz. Tekh. Poluprovodn. 12, 3 (1978) [Sov. Phys. Semicond. 12, (1978)].
[5] S. H. Koenig, R. D. Brown, and W. Schillinger, Phys. Rev. 128, 1668 (1962).
[6] V. F. Bannaya, E. M. Gershenzon, Yu. A. Gurvich, Yu. P. Ladyzhenskii, and T. G. Fuks, Fiz. Tekh. Poluprovodn. 7, 1306 (1973) [Sov. Phys. Semicond. 7, 876 (1973)].
[7] S. A. Kaufman, K. M. Kulikov, and N. P. Likhtman, Fiz. Tekh. Poluprovodn. 4, 129 (1970) [Sov. Phys. Semicond. 4, 102 (1970)].
[8] R. Norton and H. Levinstein, Phys. Rev. B 6, 489 (1972).
[9] V. N. Abakumov and V. N. Sokolova, Fiz. Tekh. Poluprovodn. 12, 1625 (1978) [Sov. Phys. Semicond. 12, 962 (1978)].
[10] V. N. Bannaya, E. M. Gershenzon, and T. G. Fuks, Fiz. Tekh. Poluprovodn. 13, 264 (1979) [Sov. Phys. Semicond. 13, 153 (1979)]. V. N. Abakumov, Fiz. Tekh. Poluprovodn. 13, 59 (1979) [Sov. Phys. Semicond. 13, 34 (1979)].
[11] E. M. Gershenzon, G. N. Gol'tsman, and N. G. Ptitsina, Zh. Eksp. Teor. Fiz. 64, 587 (1973) [Sov. Phys. JETP 37, 299 (1973)]. E. M. Gershenzon, G. N. Gol'tsman, and A. I. Elant'ev, Zh. Eksp. Teor. Fiz. 72, 1062 (1977) [Sov. Phys. JETP 45, 555 (1977)]. E. M. Gershenzon, G. N. Gol'tsman, and M. L. Kagane, Zh. Eksp. Teor. Fiz. 72, 1466 (1977) [Sov. Phys. JETP 45, 769 (1977)].
[12] S. M. Ryvkin, Fotoélektricheskie yavleniya v poluprovodnikakh (Photoelectric Phenomena in Semiconductors), Fizmatgiz, Moscow, 1963.
[13] E. M. Gershenzon, G. N. Gol'tsman, and N. G. Ptitsina, Zh. Eksp. Teor. Fiz. 76, 711 (1979) [Sov. Phys. JETP 49, 355 (1979)].
[14] E. M. Gershenzon, G. N. Gol'tsman, L. A. Orlov, and N. G. Ptitsina, Proc. Thirteenth Intern. Conf. Phys. Semicond., Rome, 1976, p. 631.
[15] D. S. Blakemore, Proc. 9th Internat. Conf. on Semiconductor Physics, Nauka, 1969, p. 514.
[16] E. M. Gershenzon, G. N. Gol'tsman, and A. M. Mel'nikov, Pis'ma Zh. Eksp. Teor. Fiz. 14, 217 (1971) [JETP Lett. 14, 142 (1971)] M. Taniguchi and S. Narita, J. Phys. Soc. Jpn. 43, 1262 (1977).
[17] V. L. Bonch-Bruevich and S. G. Kalashnikov, Fizika poluprovodnikov (Physics of Semiconductors), Nauka, 1977.
[18] A. L. Efros, B. J. Shklovskij, and J. Janchev, Phys. Status Solidi 13, 5045 (1972).

Translated by J. G. Adashko

734   Sov. Phys. JETP 50(4), Oct. 1979

Gershenzon et al.   734