

# Carrier lifetime in excited states of shallow impurities in germanium

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The lifetimes and densities of the carriers in excited states of donors and acceptors, as functions of the temperature and of the impurity illuminator intensity, are obtained from investigations of Ge submillimeter photoconductivity spectra due to electron transitions between the excited states of shallow impurities under nonequilibrium conditions.

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Up to now attempts to investigate the populations of excited states of impurities and to determine the lifetimes of electrons in these states were unsuccessful, despite the importance of this information for various photoelectric phenomena in semiconductors. The development of a sensitive high-resolution spectrometer with backward-wave tubes for the 2-0.25 mm band,<sup>[1]</sup> where the transitions between the excited states of the impurities take place, adds greatly the experimental possibilities.

TABLE I. Binding energy  $\epsilon$  and lifetime  $\tau$  of carrier in excited states of impurity.

level	donor							acceptor
	$2p_0$	$2s$	$3p_0$	$3s$	$2p_{\pm 1}$	$4p_0$	$3d_0$	$8-01$
$\epsilon$ , MeV	4.75	3.60	2.56	2.14	1.73	1.67	1.48	4.36
$\tau \times 10^9$ , sec	3.0	1.25	0.50	0.3	2.0	0.2	0.2	300

The purpose of the present study was to determine the density  $N$  and the lifetime  $\tau$  of the electrons in the excited states of donors (Sb) and acceptors ( $B$ ) in pure Ge with  $N_g + N_a \lesssim 10^{13} \text{ cm}^{-3}$  both under equilibrium conditions at  $T = 4.2-10 \text{ K}$ , and under nonequilibrium conditions—in photoionization of the impurities by background radiation at room temperature (intensity  $I$  of the excitation was smoothly varied over several orders of magnitude). We investigated in detail the lower excited states of the donors. In the case of acceptors we investigated only the first excited state, which was of greatest interest, and for which one could expect an anomalously large  $\tau$ .<sup>[2]</sup>

Since the values of  $N$  at low  $T$  are very small, to raise the sensitivity we registered the photoconductivity spectra.<sup>[1]</sup> The intensities of the individual lines of this spectrum, while providing definite information on the population of the excited states, cannot serve directly as a means of measuring  $N$  and  $\tau$ . Indeed, even at a sufficiently low temperature and at a low excitation level,

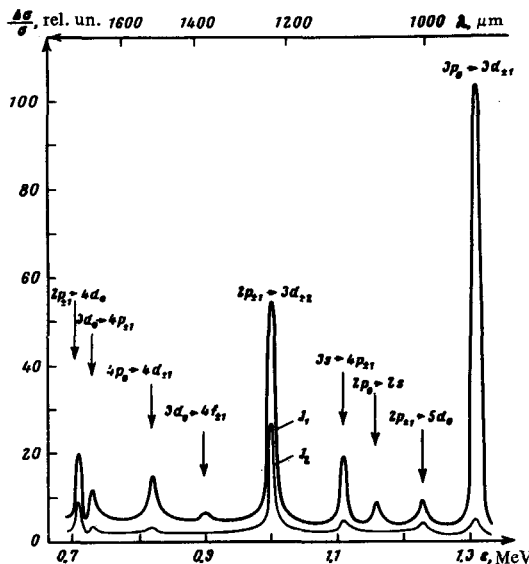


FIG. 1. Section of the spectrum of the photoconductivity of  $n\text{-Ge}$   $N_g = 10^{13} \text{ cm}^{-3}$ ,  $N_a = 2 \times 10^{12} \text{ cm}^{-3}$  at two levels of the background photoexcitation of the sample  $I_1 \ll I_2$ ,  $T = 4.2 \text{ K}$ .

the photoresponse under photothermal ionization of the excited state depends on many factors:

$$\Delta U = U \Delta n / n = U P \tau_c N W S_\lambda / h \nu n S, \quad (1)$$

where  $U$  is the constant bias,  $P$  and  $\epsilon = h\nu$  are the radiation power and its quantum energy,  $n$  and  $\tau_c$  are the concentration and the lifetime of the free carriers,  $N$  and  $W$  are the concentration at the starting state and the probability of thermal ionization of the final state,  $S_\lambda$  is the absorption cross section for the given transition,  $S$  is the area of the front surface of the sample. The  $N(I)$  dependence, however, can be easily determined from the experimental values of  $\sigma \times \Delta U(I)$ , where  $\sigma$  is the conductivity, inasmuch as in this product only  $N$  depends on  $I$  [see (1)]. At small  $I$ , the concentrations  $N$  remain at equilibrium,<sup>[3]</sup> and  $\sigma \times \Delta U$  does not depend on  $I$ . This makes it possible, at small  $I$ , to tie in the experimental values of  $\sigma \times \Delta U$  with the equilibrium values of  $N_p$ ,<sup>[7]</sup> and to obtain the numerical values of  $N$  at different  $I$ .

To determine  $\tau$  from the values of the nonequilibrium concentrations it is necessary to know the recombination fluxes through the excited state. An analysis of the calculations<sup>[4,5]</sup> with allowance for the energy positions of the starting states of the investigated transitions<sup>[6]</sup> (see Table I) shows that the probability of a transition with emission of a phonon between excited states that are closest in energy greatly exceeds the probability of other transitions and, furthermore, at  $T = 4.2$  K the capture of free carriers goes mainly to higher states. Therefore the nonequilibrium recombination flux through the investigated excited states is the same and equals  $I = n/\tau_c$ , making it possible, if  $n$  and  $\tau_c$  are known, to determine the lifetimes of the electrons in the excited states.

Figure 1 shows a section of the photoconductivity spectrum of  $n$ -Ge at low intensity  $I$  of the background photoexcitation of the sample, corresponding to equilibrium population of the starting states of the transitions, and also at  $l_2 \gg l_1$ , which corresponds to a strong disequilibrium of the population. It is seen that the relative intensity of the lines in the nonequilibrium situation differs substantially from the equilibrium situation. In the presented section of the spectrum, at  $I = I_2$ , the dominant spectral lines are those with starting state  $2p_{\pm 1}$ . Figure 2 shows plots of  $\sigma \times \Delta U$  against  $\sigma$  ( $\sigma$  at  $T = 4.2$  K,  $\sigma$  is proportional to  $I$ ) for the lines  $3p_0 \rightarrow 3d_{\pm 1}$ ,  $2p_0 \rightarrow 3d_{\pm 1}$  and  $2p_{\pm 1} \rightarrow 3d_{\pm 2}$ . The experimental values of  $\sigma \times \Delta U$  at small  $I$  are normalized to  $N_p$ . The fact that  $W$  does not depend on  $I$  was manifested in the measurements of the ratio of the intensities of lines with common starting states  $2p_0 : 2p_0 \rightarrow 3d_{\pm 1}$ ,  $2p_0 \rightarrow 4d_{\pm 1}$ ,  $2p_0 \rightarrow 5d_{\pm 1}$ ,  $2p_0 \rightarrow 5g_{\pm 1}$  and  $2p_{\pm 1} : 2p_{\pm 1} \rightarrow 4d_0$ ,  $2p_{\pm 1} \rightarrow 3d_{\pm 2}$ ,  $2p_{\pm 1} \rightarrow 5d_0$ , and also of other similar series of transitions.

Figure 3 shows the temperature dependences of the intensity ratio of the lines  $3p_0 \rightarrow 3d_{\pm 1}$  and  $2p_0 \rightarrow 3d_{\pm 1}$ , (" $\blacktriangle$ " -  $I_1$ , " $\triangle$ " -  $I_2$ ,  $I_1 < I_2$ ), and also of the lines  $2p_{\pm 1} \rightarrow 3d_{\pm 2}$  and  $2p_0 \rightarrow 5d_{\pm 1}$  (" $\bullet$ " -  $I_1$ , " $\circ$ " -  $J_2$ ). The values of  $\Delta U_1/\Delta U_2$  on Fig. 3 are proportional to the ratio of the populations of the starting states of the transitions ( $N_{3p_0}/N_{2p_0}$  and  $N_{2p_{\pm 1}}/N_{2p_0}$ ). This follows from (1), inasmuch as for the first pair of transitions the final state is common, and for the second pair the energies of the final states are low and are very close to each other, so that  $W_{3d_{\pm 2}} = W_{5d_{\pm 1}} \approx 1$ . If it is now recognized that the degeneracy multiplicity of the  $2p_{\pm 1}$  level is twice that of  $2p_0$  and  $3p_0$ , and if we normalize the plots of Fig. 3 as  $T \rightarrow \infty$  to the values 1 for  $N_{3p_0}/N_{2p_0}$  and to 2 for  $N_{2p_{\pm 1}}/N_{2p_0}$ , then we obtain the

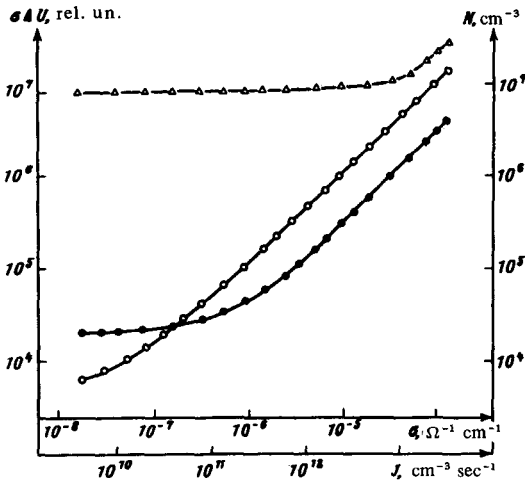


FIG. 2. Plots of  $\sigma \times \Delta U$  against  $\sigma$  at  $T = 4.2$  K for the transitions  $-2p_0 \rightarrow 3d_{\pm 1}$ , "●"  $-3p_0 \rightarrow 3d_{\pm 1}$ , "○"  $-2p_{\pm 1} \rightarrow 3d_{\pm 2}$ .

right-hand relative-concentration scale of Fig. 3. It is seen that at small  $I$  the relations are exponential; the argument of the exponential corresponds, accurate to  $\approx 5\%$ , to the difference between the energies of the starting states. This is evidence of a uniform distribution of the electrons over the excited states of the impurities at small  $I$ . At large  $I$  the plots of Fig. 3 deviate from the exponential ones below a certain value of  $T$ , when the population of the levels  $2p_{\pm 1}$  or  $3p_0$ , in contrast to  $2p_0$ , is no longer at equilibrium, and finally, they saturate at still lower values of  $T$ , since the populations of all levels are not at

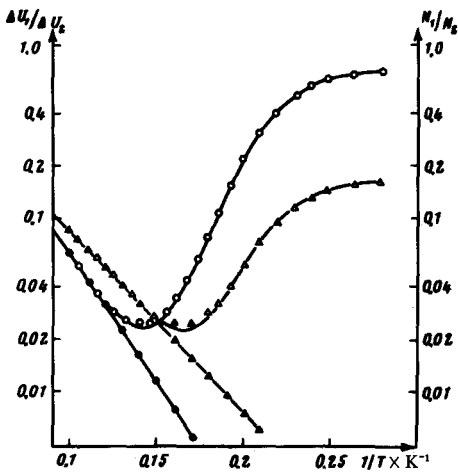


FIG. 3. Temperature dependences of the ratio of the intensities of two pairs of photoconductivity lines at two levels of the background photoexcitation of the sample "▲", "△"  $-\Delta U_{3p_0-3d_{\pm 1}} / \Delta U_{2p_0-3d_{\pm 1}}$  at  $I_1$  and  $I_2$ , respectively; "●", "○"  $-\Delta U_{2p_{\pm 1}-3d_{\pm 2}} : \Delta U_{2p_0-5d_{\pm 1}}$  at  $I_1$  and  $I_2$ , respectively.

equilibrium and do not depend on  $T$ . The solid curves of Fig. 3 were calculated by us under the assumption that does not depend on  $T$ . The agreement between the calculation and experiments indicates, in particular, that at  $T \approx 8$  K the value of  $\tau$  for all the investigated states is practically independent of  $T$ .

From the data of Figs. 2 and 3 we obtained the lifetimes of the electrons in the excited donor states  $2p_0$ ,  $3p_0$ ,  $2p_{\pm 1}$ . Similar measurements were performed also for other excited states of the donor, and for the first excited state of the acceptor (see Table I).  $\tau_c$  was determined by us from measurements of the dependence of the submillimeter radiation, on the amplitude-modulation frequency ( $\Omega$ ), while  $n$ ,  $p$ ,  $N_g$  and  $N_a$  were obtained from measurements of the Hall effect. It is seen that  $\tau$  in the state  $2p_{\pm 1}$  exceeds the lifetime not only in the high-lying states  $4p_0$  and  $3d_0$ , but also in the low-lying states  $3p_0$  and  $3S$ . The apparent reason is that the level  $2p_{\pm 1}$  is the lowest in energy among all levels with nonzero projection of the angular momentum, and a phonon transition from it to lower levels is hindered. It is also of interest that the lifetime of the carrier in the first excited state of the acceptor turns out to be lower by two orders of magnitude than that of the donor.

We note in conclusion that the attained values of  $\tau$  are the lower bounds of the true values, since a fraction of recombination flux can become closed and bypass the given excited state. For low excited states, the lifetimes  $\tau$  are much larger than the values<sup>[1]</sup> calculated from the widths of the investigated lines in pure samples ( $\approx 10^{-10}$ sec), whereas for relatively high donor levels  $4p_0$  and  $3d_0$  these values are close.

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