Impurity photoconductivity of weakly compensated silicon under conditions of delocalization of D^- (A^+) states

L. A. Vorozhtsova, E. M. Gershenzon, Yu. A. Gurvich, F. M. Ismagilova,
L. B. Litvak-Gorskaya, and A. P. Mel'nikov

V. I. Lenin State Pedagogical Institute, Moscow

(Submitted 19 February 1987)
Zh. Eksp. Teor. Fiz. **93**, 1419–1430 (October 1987)

An investigation was made of the impurity photoconductivity of Si characterized by $N^{1/3}a_0 > 6\times 10^{-2}$ and $K = 10^{-5}$–10^{-3}, where N is the concentration of the main impurity, a_0 is the Bohr radius of this impurity, and K is the degree of compensation. The observed D^--band photoconductivity could under certain conditions be tens of times higher than the free-band conductivity. The lifetimes of free carriers (τ_c) and of carriers in the D^- band (τ_D) as functions of T, N, N^+, and W_{ph} were determined ($N^+ = KN$ is the concentration of attractive centers and NW_{ph} is the intensity of the impurity photoexcitation). The experimental results indicated that the recombination of free carriers at attractive centers was dominated by a new indirect channel involving the D^- band.

I. INTRODUCTION

The problem of band-type (impurity) photoconductivity (ε_2 conductivity) has been attracting attention of investigators for over 30 years.[1-3] Usually the ε_2 conductivity is observed in galvanomagnetic measurements under equilibrium conditions when the impurity concentration is $N \sim (0.1$–$1)N_M$, where N_M is the concentration corresponding to the Mott transition.[2,3] At present the generally accepted explanation of the ε_2 conductivity is provided by a model of a conducting D^- band, which is an analog of the upper Hubbard band[4] in a disordered system. Observation of the D^- (A^+) states[5-7] and a study of their evolution as a result of increase in N from isolated to strongly overlapping (see Refs. 8 and 9 and the bibliography given there), carried out mainly by spectral methods under nonequilibrium conditions, has made it possible to show that the ε_2 band is formed by overlapping D^- (A^+) states and to determine the influence of the concentrations of neutral and charged centers on the energy position of the lower "mobility edge" of the D^- band.[9]

The published investigations have been mainly carried out at impurity concentrations close to the delocalization threshold $N \lesssim 10^{-2} N_M$. In samples of this kind the values of ε_2 are close to $\varepsilon_0 - \varepsilon_i$ and the equilibrium conductivity is determined entirely by the conduction band; here, ε_0 and ε_i are the binding energies of an electron at a neutral donor and at a D^- center (we shall consider specifically an n-type material and mention p-type conduction only in discussing the figures). The D^- states were filled in our experiments at low temperatures via the conduction band under excitation with impurity-absorbed light. We investigated optical transitions of carriers from delocalized and localized states to the conduction band. (The localized states were complexes of the D^-–D^+ type and their energy was within the Mott–Hubbard gap.[9]) We determined the energy positions of these and other states, and the change in the degree of localization as a function of N, T, and fluctuation scatter of the levels Δ_{ij} caused by the presence of charged centers. It was found that in the range $N^{1/3}a_0 > 7\times 10^{-2}$ ($N \gtrsim 3\times 10^{16}$ cm^{-3} in Si:B for $K \lesssim 10^{-3}$) there were localized and delocalized states; the ratio of their populations n_d/n_l varied in a definite manner with N, T, and the level of illumination W_{ph}.

At low temperatures carriers are frozen out to localized states ($n_d/n_l < 1$). Relatively strong additional illumination ($W_{ph} = 10$–250 sec^{-1}), necessary in spectral measurements to reduce the resistance of a sample and the noise in it, and also to create sufficiently large numbers of excess localized and delocalized carriers, results in a situation when the scatter Δ_{ij}, which prevents delocalization from spreading to deeper states, is governed not by charged centers but by D^-–D^+ complexes.[9]

Complexes with intercenter distances R such that the energy of the ion term of the impurity molecule ($\varepsilon = \varepsilon_i + e^2/\varkappa R$) is not too close to the energy E_n of homopolar terms, which are excited impurity states, are "long-lived." An increase in temperature transfers carriers from the complexes to the D^- band where they can approach another attractive center near which there is a neutral center at a characteristic distance R_x such that

$$\varepsilon_i + e^2/\varkappa R \approx E_n,$$

and rapid recombination is then possible. Therefore, as temperature is increased, the number of D^-–D^+ complexes decreases, the fluctuation scatter Δ_{ij} becomes smaller, and the energy position of a mobility edge shifts downward; at values of T exceeding a certain critical temperature T_{cr} we find that delocalized carriers predominate ($n_d/n_l > 1$).

Observations of delocalization of carriers in the submillimeter photoconductivity spectra in the photon energy range $\hbar\omega < \varepsilon_0$ at temperatures $T > T_c$ accompanied by a simultaneous fall of the magnetoresistance $\Delta\rho/\rho$ in the range $T > T_c$ suggest that D^--band photoconductivity σ_D may be present (Ref. 9). We are then faced with the task of observing and investigating this photoconductivity.

In the present paper, a continuation and extension of an earlier study,[10] we report for the first time (to the best of our knowledge) a detailed investigation of the photoconductivity under conditions of delocalization of the D^- states. We investigated weakly compensated n- and p-type Si samples

TABLE I. Properties of samples.

Sample No.	1	2	3	4	5	6	7	8	9	10	11
Impurity	B	B	B	B	B	B	B	B	Ga	P	As
N_A, 10^{16} cm^{-3}	2.4	2.8	3.0	4.2	5.9	5.2	7.8	12	8	9	12
N_D, 10^{11} cm^{-3}	3	7	12	21	22	600	260	24	16	9	72
K, 10^{-5}	1.25	2,5	4	5	3.7	110	33	2	2	1	6

with $N^{1/3}a_0 = 6.2\times10^{-2}$–$1.1\times10^{-1}$, where delocalization was already significant[9] and the energy ε_0 had not yet decreased ($\varepsilon_0 = 45$ meV = const). The relative contribution of the D$^-$-band photoconductivity σ_D was enhanced by selecting samples with unprecedentedly low compensation in the range $10^{-5} < K < 10^{-4}$. Circuits with a leakage resistance $R_{\text{leak}} > 10^{12}$ Ω were designed which made it possible to carry out investigations at much lower (by a factor of 10^3–10^5 compared with Ref. 9) additional illumination $W_{\text{ph}} \approx 10^{-4}$–$1$ sec^{-1}. Under these conditions the number of D$^-$–D$^+$ complexes was small and estimates indicated that one could ignore the direct capture of free carriers by these complexes and by attractive centers. Therefore, we could assume that all the carriers excited from neutral centers reached the D$^-$ band and thus completed the recombination process before being captured by attractive centers.

The hypothesis of the existence of two types of the band photoconductivity, σ_c in the conduction band and σ_D, made it desirable to use a method which would make it possible to determine separately how σ_D and σ_c depend on N, $N^+ = KN$, T, and W_{ph}. The simplest and most satisfactory method was determination of the Hall emf under impurity photoexcitation conditions (photo-Hall effect) and subsequent analysis of the results using a two-band model.

An investigation of nonequilibrium processes under delocalization conditions is on the one hand important for the study of the properties of the D$^-$ band, such as the density of states $\rho_D(\varepsilon)$, where ε is the electron energy, the mobility μ_D, and the lifetime τ_D, about which very little is known at present. On the other hand, an investigation of the recombination mechanism under these conditions can give direct information on ways of achieving the maximum photosensitivity of a material.

The paper is organized as follows: Sec. II describes the experimental methods, the results of measurements, and their analysis; Sec. III discusses the electron transition scheme and gives an analysis of the results; Sec. IV presents the main conclusions.

II. EXPERIMENTAL RESULTS AND THEIR ANALYSIS ON THE BASIS OF A TWO-BAND MODEL

An investigation was made of the temperature (T) dependence of the electrical conductivity σ and of the Hall coefficient R_H in the case of impurity photoexcitation of Si:B, Si:Ga, Si:As, and Si:P, characterized by $N^{1/3}a_0 = 6.2\times10^{-2}$–$1.1\times10^{-1}$ and $K < 10^{-2}$. The parameters of the samples were determined from the $R_H(T)$ dependence under equilibrium conditions. They are listed in Table I. The photo-Hall determination of $R_H(T)$ and $\sigma(T)$ was carried out in the temperature range $T = 2$–20 K, using electric and magnetic fields $E = 2$–70 V/cm and $H = 3$–25 kOe. Carriers were photoexcited by background radiation of wavelengths in the range $\lambda = 8$–$12\,\mu$m. In some experiments we also used additional illumination from a CO$_2$ laser ($\lambda \approx 10.6\,\mu$m) and an InAs light-emitting diode ($\lambda \approx 3\,\mu$m). The results reported below were obtained mainly at low photoexcitation intensities $W_{\text{ph}}N \approx (10^{-2}$–$1)/N$. The additional illumination was calibrated on the basis of the photoconductivity of a standard Si:B sample characterized by $N = 4\times10^{13}$ cm^{-3} and $K = 0.15$.

Figure 1 shows $\sigma(T)$ and

$$\mu^*(T) = R_H(T)\sigma(T)$$

for Si:Ga, Si:P, Si:As, and Si:B samples at low values of W_{ph}. (In the case of Si:B the photoexcitation intensity was $W_{\text{ph}} \approx 0.25$ sec^{-1}; for the other materials the values of W_{ph} produced by the same background radiation in the range $\lambda \approx 8$–$12\,\mu$m differed somewhat because of the different frequency

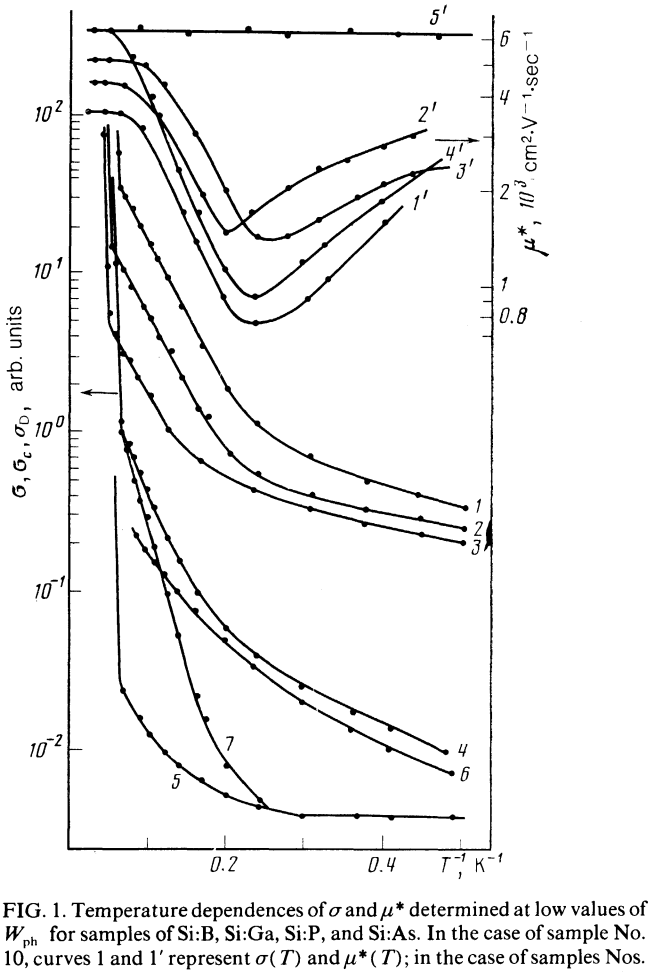

FIG. 1. Temperature dependences of σ and μ^* determined at low values of W_{ph} for samples of Si:B, Si:Ga, Si:P, and Si:As. In the case of sample No. 10, curves 1 and 1' represent $\sigma(T)$ and $\mu^*(T)$; in the case of samples Nos. 11, 9, 5, and 6, the corresponding pairs of curves are 2 and 2', 3 and 3', 4 and 4', and 5 and 5'. Curves 6 and 7 represent, respectively, the calculated values of σ_D and σ_c of sample No. 5. The values of σ are normalized to unity at $T = 15$ K and are shifted vertically by a factor of $\sqrt{10}$ for different materials.

dependence of the photoionization cross sections.) The samples were selected so that the values of K and $N^{1/3}a_0$ were as far as possible identical. At high temperatures the dependences $\sigma(T)$ were nearly exponential and the activation energy was on the order of the binding energy of the D^- (A^+) centers, amounting to $\varepsilon_i \approx 2$ meV (Ref. 8). Cooling weakened the dependences $\sigma(T)$. It was found that the dependence

$$\mu^*(T) = R_H(T)\sigma(T)$$

was nomonotonic: at high temperatures the value of μ^* was constant and corresponded to the mobility of free carriers μ_c in the case of scattering by neutral centers. Cooling caused μ^* to pass through a minimum; the depth of this minimum increased on reduction in K and W_{ph} (see below).

Figure 1 shows, for the sake of comparison, $\sigma(T)$ and $\mu^*(T)$ obtained for a sample of Si:B with the same value of N but with a higher value of K ($K \approx 10^{-3}$)—see curves 5 and 5'. Clearly,

$$\mu^*(T) = \mu_c = \mathrm{const},$$

and the dependence $\sigma(T)$ obeyed a power law $\sigma(T) \propto T^n$, where $n \approx 2$ (Ref. 10).

Note that for all the samples with $N^{1/3}a_0 \gtrsim 7 \times 10^{-2}$ and $K \approx 10^{-4}$–10^{-5} the D^- states were delocalized, as indicated by the spectral measurements[9] and by the estimates made in accordance with Ref. 11. This circumstance and the presence of a minimum of $\mu^*(T)$ allowed us to assume that, in addition to the conductivity in the conduction band, there was also conductivity in the impurity band, i.e., some mobility μ_D smaller than μ_c could be ascribed to the carriers in the impurity band whose concentration was n_D. In general, a change in the relationship between σ_c and σ_D could vary μ^* between μ_c and μ_D.

In calculating σ_c and σ_D we use, as already mentioned, the relationships which follow from a two-band model (Ref. 12). These relationships contain the following quantities: σ_c, μ_c, σ_D, and μ_D. The experimental results indicated that at low values of W_{ph} the mobility μ^* is less than μ_c by at least a factor of ten, and estimates indicated that under these conditions we can still have $\sigma_c \sim \sigma_D$ and, consequently, we assume that $b \equiv \mu_D/\mu_c < 2 \times 10^{-1}$–$10^{-3}$. Other estimates (see below) give $b \approx 3 \times 10^{-4}$. Therefore, in the range of fields H used in our study and corresponding to $\mu_D^2 H^2/c^2 \ll 1$ and for not too large values of the ratio σ_D/σ_c ($\sigma_D/\sigma_c < b^{-1}$), when the contribution of the D^--band carriers to the Hall field can be ignored, the relationships in our two-band model become

$$\mu_c(T) = \mathrm{const}(T)/N, \tag{1}$$

$$\sigma = \sigma_c + \sigma_D, \tag{2}$$

$$R_H = \frac{\sigma_c \mu_c}{(\sigma_c + \sigma_D)^2 + \sigma_D^2 \mu_c^2 H^2/c^2}. \tag{3}$$

We shall now confine our attention to the results obtained for Si:B. In addition to the experimental values of μ^* and σ, we shall give also the values of σ_c and σ_D calculated from Eqs. (2) and (3). Curves 6 and 7 in Fig. 1 represent the results of calculations for Si:B.

Figure 2 shows $\sigma_c(T)/W_{ph}$, $\sigma_D(T)/W_{ph}$, and $\mu^*(T)$ for different values of W_{ph} in the case of sample No. 3. The dependence $\sigma_c(T)/W_{ph}$ obeys the law $\sigma_c \propto \exp(\varepsilon_x/kT)$ at temperatures $T > T_{cr}$ ($T \gtrsim 4.2$–5 K), whereas in the range $T < 3.5$ K σ_c was practically independent of T. There is a

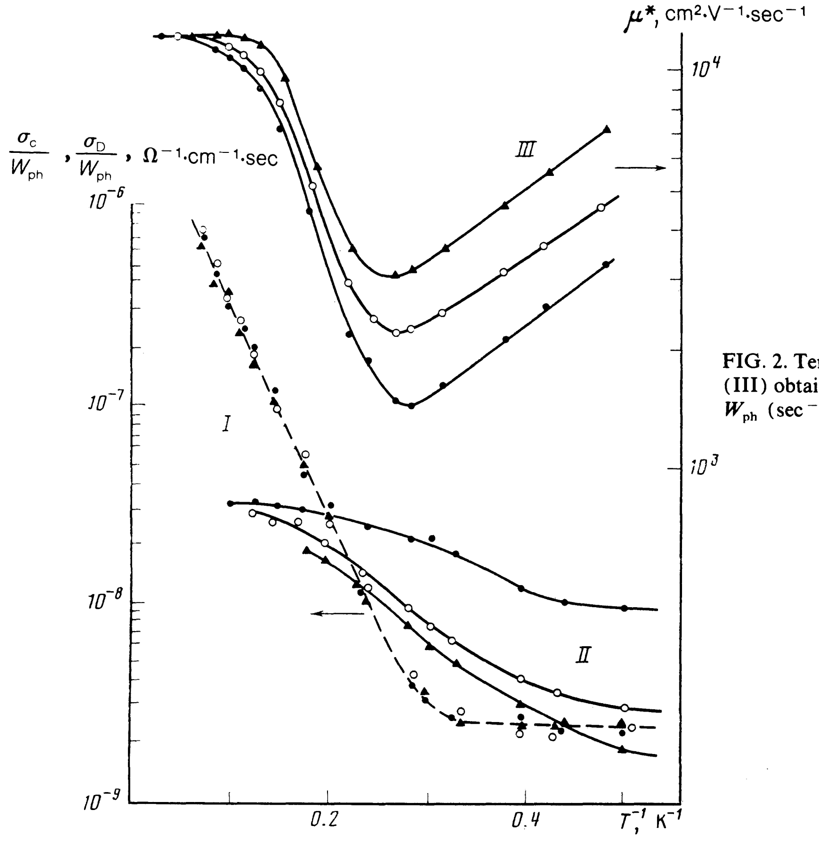

FIG. 2. Temperature dependences of σ_c/W_{ph} (I), σ_D/W_{ph} (II), and μ^* (III) obtained for sample No. 3 at different additional illumination rates W_{ph} (sec⁻¹): ●) 3×10^{-2}; ○) 0.25; ▲) 1.

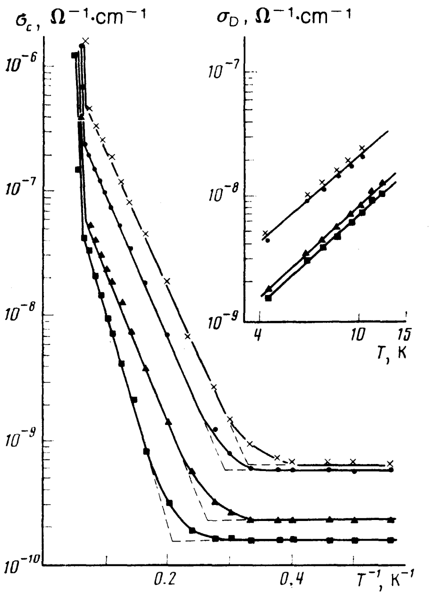

FIG. 3. Temperature dependences $\sigma_D(T)$ and $\sigma_c(T)$ for samples Nos. 2 (×), 3 (●), 4 (▲), and 5 (■) at $W_{ph} = 0.25\ \text{sec}^{-1}$ and $E = 50$ V/cm.

range of temperatures where σ_D exceeds σ_c and the ratio σ_D/σ_c increases with decreasing W_{ph}, as indicated by the increase in the depth of the minimum of $\mu^*(T)$; in this case we have $\sigma_D/W_{ph} \approx$ const throughout the investigated range of temperatures T, and σ_D/W_{ph} increases on increase in W_{ph} in the range $T < 7$ K, whereas at temperatures $T > 7$ K the ratio σ_D/W_{ph} is again constant.

Figure 3 shows the dependences $\sigma_c(T)$ and $\sigma_D(T)$ for samples Nos. 2–5 obtained for $W_{ph} = 0.25\ \text{sec}^{-1}$ and $E = 50$ V/cm. Note that the exponential dependence $\sigma_c(T)$ (observed in the range $T > T_{cr}$) has an activation energy ε_x which increases with N; at temperatures $T < T_{cr}$, we find

$$\sigma_c(T) = \text{const}.$$

The temperature T_{cr} corresponds to the transition of the dependence $\sigma_c(T)$ from $\sigma_c \propto \exp(-\varepsilon_x/kT)$ to $\sigma_c \approx$ const; this temperature increases with N. The dependence $\sigma_D(T)$ obey a power law:

$$\sigma_D \propto T^n,$$

where $n \approx 2$.

Figure 4 shows the dependences $\tau_c(N)$ calculated from

$$\tau_c = \sigma_c / e\mu_c W_{ph} N$$

and $\sigma_D(N)$ for $W_{ph} = 0.25\ \text{sec}^{-1}$, $E = 30$ V/cm, and various temperatures. Note that τ_c falls strongly as a function of N at $T = 10$ K; at $T = 1.5$ K for high values of N, we find that $\tau_c \propto 1/N$ (dashed curve). It is clear from this figure that τ_c can be less than the energy relaxation time $\tau_\varepsilon(\varepsilon)$ corresponding to $\varepsilon \approx kT$.

Figure 5 shows the dependences $\sigma(W_{ph})$ obtained for samples Nos. 1 and 5 at $T = 1.5$ K in a field $E = 30$ V/cm. It includes the values of σ_D and σ_c corresponding to several values of W_{ph} calculated using the two-band model. Clearly, $\sigma_c \propto W_{ph}$ and the ratio σ_D/σ_c increases as W_{ph} is reduced right up to $\sigma_D/\sigma_c \approx 20$–30 for sample No. 5.

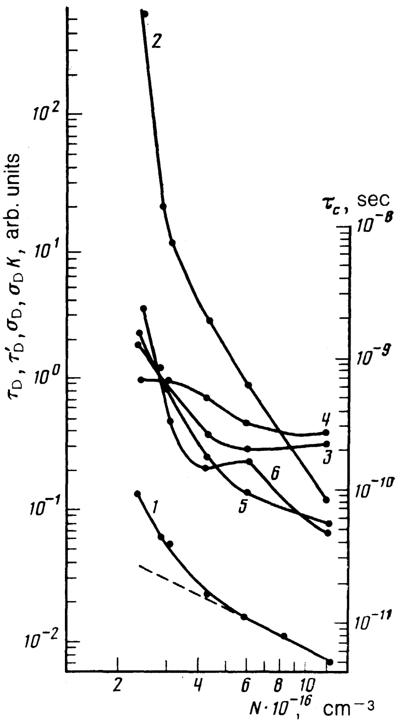

FIG. 4. Dependence $\tau_c(N)$ obtained for $W_{ph} \approx 0.25\ \text{sec}^{-1}$ in a field $E = 50$ V/cm at $T = 1.5$ K (curve 1) and $T = 10$ K (curve 2); the dashed line represents $\tau_c \propto 1/N$. Curves 3 and 4 represent the dependences $\sigma_D(N)$ and $\sigma_D K(N)$, respectively; curves and 6 give the dependences $\tau_D(N)$ and $\sigma_D'(N)$ at $T = 4.2$ K.

III. RECOMBINATION MODEL AND DISCUSSION OF EXPERIMENTAL RESULTS

Usually the lifetime τ of electrons excited from neutral centers is determined by cascade capture at attractive centers[13]

$$\tau = \tau^+ = (\alpha^+ N^+)^{-1},$$

where α^+ and N^+ are the capture coefficient and the concentration of the attractive centers; α^+ and N^+ are independent of the concentration N^0 of the neutral centers. In our case τ^+/τ reaches the values of ≈ 40 at $T = 10$ K and $\sim 10^4$ in the range $T \lesssim 4.2$ K; this can not be explained by an increase in N^+ compared with KN (Ref. 10).

In the case of the doped materials a free electron may be captured by a D^-–D^+ complex of size

$$R \approx R_c = (3\pi N/4)^{1/3}.$$

The rate of capture by the complex α^{cp} is less than α^+ (Ref. 13):

$$\alpha^+/\alpha^{cp} \approx e^2/\varkappa R_c kT > 1.$$

For example in the case of a sample with $N = 3 \times 10^{16}\ \text{cm}^{-3}$ at $T = 4.2$ K, we have $\alpha^+/\alpha^{cp} \approx 17$. The value of τ for the capture by complexes agrees with the experimental value of $\tau_c \approx 10^{-10}$ sec at $T = 4.2$ K if the concentration of the complexes N_{cp} is $10^{15}\ \text{cm}^{-3}$. We shall estimate the maximum possible value of N_{cp} on the assumption that complexes are destroyed only by thermal reemission of electrons back to the conduction band, i.e., we shall ignore the more likely release to the D^- band.[9] At $T = 4.2$ K for $W_{ph} \approx 0.25\ \text{sec}^{-1}$ in the case of sample No. 3 with $N = 3 \times 10^{16}\ \text{cm}^{-3}$ the concentration of the complexes $N_{cp} \approx 10^{12}\ \text{cm}^{-3}$ is three orders

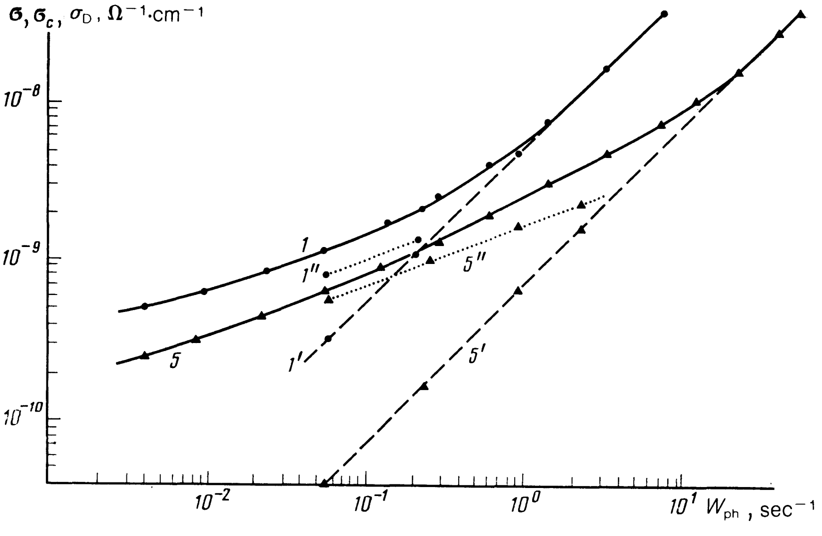

FIG. 5. Dependence of σ, σ_c, σ_D on W_{ph} at $T = 1.5$ K for $E = 10$ V/cm: 1), 1'), 1'') sample No. 1; 5), 5'), 5'') sample No. 5.

of magnitude less than that required. The value of N_{cp} becomes even less at larger values of T. If $T < 4.2$ K, then complexes cannot govern the capture if only because as these values of T we have $\tau_c < \tau_\varepsilon$. According to Ref. 13, this inequality does not apply to capture by dipoles.

Thus we obtained the following experimental results for our samples: the samples contain delocalized D^- states; $\mu^*(T)$ has a minimum; the dependence $\sigma_c(T)$ at $T > 4.2$ K is exponential; the ratio τ^+/τ reaches high values (up to 10^4 at $T = 1.5$ K); τ_c is governed mainly by the value of N. As pointed out above, the minimum of $\mu^*(T)$ indicates two photoconductivity mechanisms. The exponential nature of the dependence $\sigma_c(T)$ suggests that at temperatures $T > 4.2$ K the carriers in the conduction band are in equilibrium with those in the D^- band. A strong dependence $\sigma_c(N)$ and a weak dependence $\sigma_c(N^+)$ are evidence that recombination of free electrons at the attractive centers occurrs via the D^- band.

The experimental results and estimates provide the basis for suggesting the following transition scheme (Fig. 6). Infrared radiation ($\hbar\omega > \varepsilon_0$) of intensity $W_{ph}N$ creates positively charged donors (N^+) and electrons in the conduction band with energies $\varepsilon^* = \hbar\omega - \varepsilon_0$ (transition 1). Free electrons cool down to an energy $kT \lesssim \varepsilon_m < \varepsilon^*$ in the energy relaxation time $\tau_\varepsilon(\varepsilon_m)$ (transition 2). Then, electrons are captured by the neutral centers [capture rate $\alpha^0(\varepsilon_m)$, transition 3]. Captured electrons can be transferred thermally to the conduction band (transition 4) and then can be recaptured by the D^- band (transition 5) or they may drop down on the energy scale (cool) in the D^- band reaching states deep enough to prevent thermal release in a time τ'_D (transition 6). Cooling carriers can drift in an external electrical field and give rise to D^--band conductivity until they are captured by the attractive centers (transition 7).

Some comments should be made about these transitions. The inequality $\tau_c < \tau_\varepsilon(kT)$ (satisfied by all the samples at sufficiently low temperatures) is an indication of the dominant role of the capture of carriers by the neutral centers.[14,15] An analysis carried out in accordance with the theory of Ref. 16 demonstrates that if N is high enough ($N > 3 \times 10^{16}$ cm^{-3}) then we have $\varepsilon_m \gg kT$ and the distribution function has a maximum at $\varepsilon \gtrsim \varepsilon_m$, so that we can speak of electrons with $\varepsilon \gtrsim \varepsilon_m$. We denote the density of these electrons by n_1.

The dependence

$$\sigma_c \propto \exp(-\varepsilon_x/kT)$$

obeyed at temperatures $T \gtrsim 4.2$ K suggest the existence of an energy gap ε_x. It is due to the exponential dependence of the probability of thermal release (transition 4)

$$W_T \propto \alpha^0(kT) N_c(kT) \exp(-\varepsilon_x/kT),$$

where $\alpha^0(kT)$ is the coefficient representing the capture by the neutral centers (transition 5). The density of electrons created by thermal release ($\varepsilon \sim kT$) is n_2. Therefore, the density of free electrons n_c is equal to the sum of the densities of electrons with energies $\varepsilon \gtrsim \varepsilon_m$ (n_1) and $\varepsilon \gtrsim kT(n_2)$:$n_c = n_1 + n_2$. Since the lifetime in the conduction band is governed by the neutral centers, it follows that the transition 5 is not the only channel for depopulation of the D^- states. There should be also a flux of electrons into the interior of the D^- band from where electrons cannot escape by thermal motion. Therefore, we introduced a transition 6 character-

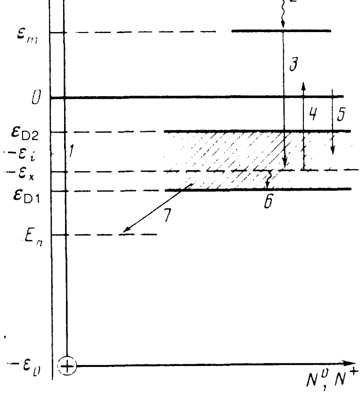

FIG 6. Electron transition scheme.

ized by a time $\tau'_{\rm D}$. The meaning of $\tau'_{\rm D}$ is that it is the time in which an electron in the $\rm D^-$ band drops down by an energy $\sim kT$ from a level of energy $-\varepsilon_x$.

On the basis of the above discussion, we can now write down the following system of equations for the recombination–generation fluxes:

$$W_{\rm ph} N^0 = n_1 \alpha^0(\varepsilon_m) N^0, \tag{4}$$

$$N^- W_t = n_2 \alpha^0(kT) N^0, \tag{5}$$

$$n_1 \alpha^0(\varepsilon_m) N^0 = N^- (\tau'_{\rm D})^{-1}, \tag{6}$$

where N^- is the concentration of the $\rm D^-$ centers in an energyband $\sim kT$ near $\varepsilon = \varepsilon_x$ and $N^0 = N - N^+ \approx N$. It follows from Eqs. (4)–(6) that

$$\sigma_{\rm c} = e n_{\rm c} \mu_{\rm c} = e \mu_{\rm c} W_{\rm ph} (1/\alpha^0(\varepsilon_m) + W_t \tau'_{\rm D}/\alpha^0(kT)). \tag{7}$$

Using the above model, we shall now consider the experimental results.

A. It follows from Eq. (7) that $\sigma_{\rm c} \propto W_{\rm ph}$. This agrees with the experimental results in the selected range of $W_{\rm ph}$ and it is true both at low (Fig. 4) and high (Fig. 2) temperatures. At high temperatures we have

$$W_t > \alpha^0(kT)/\alpha^0(\varepsilon_m)\tau'_{\rm D}$$

and it then follows from Eq. (7) that

$$\sigma_{\rm c} = e\mu_{\rm c} W_{\rm ph} N_{\rm c} \tau'_{\rm D} \exp(-\varepsilon_x/kT) \propto \exp(-\varepsilon_x/kT), \tag{8}$$

in agreement with the experimental results obtained at $T \gtrsim 4.2$ K (Figs. 1–3).

We find from Eq. (8) that

$$\tau_{\rm c} = N_{\rm c} \exp(-\varepsilon_x/kT)\tau'_{\rm D}/N. \tag{9}$$

At $T = 10$ K, it is clear from Fig. 4 that $\tau_{\rm c}(N)$ falls more rapidly than $1/N$. This can be explained by an increase in ε_x as N increases (Fig. 3) and also by a reduction in $\tau'_{\rm D}$ on increase in N. The values of ε_x and $\tau'_{\rm D}$ will be discussed in subsection C below.

At low temperatures, when

$$W_t < \alpha^0(kT)/\alpha^0(\varepsilon_m)\tau'_{\rm D}$$

(when the trapped carriers do not return to the conduction band), we have

$$\sigma_{\rm c} = e\mu_{\rm c} W_{\rm ph}/\alpha^0(\varepsilon_m), \tag{10}$$

$$\tau_{\rm c} = 1/\alpha^0(\varepsilon_m)N. \tag{11}$$

Hence, it follows that in the range of low temperatures T both $\sigma_{\rm c}$ and $\tau_{\rm c}$ are independent of T and of N^+, as confirmed by measurements carried out in the range $T < T_{\rm cr}$ (Figs. 1 and 2), but they depend only on N and $\alpha^0(\varepsilon_m)$ (curve 1 in Fig. 4). The value of ε_m increases with N (Ref. 16), whereas $\alpha^0(\varepsilon_m)$ first increases and then ceases to depend on ε_m (Ref. 15). In the latter case ($N \gtrsim 3 \times 10^{16}$ cm^{-3}), we have $\tau_{\rm c} \propto N^{-1}$ (Fig. 4). It should be stressed that the dependence $\tau_{\rm c} \propto N^{-1}$ applies not only to samples with $K \approx 10^{-4}$–10^{-5}, but also to samples with higher values of $K (K < 10^{-2})$, as shown in Fig. 1.

B. In accordance with this model, all the electrons reach the $\rm D^-$ band before being captured by the attractive centers and they can contribute to the photoconductivity when in this band. The expression for $\sigma_{\rm D}$ is

$$\sigma_{\rm D} = e\mu_{\rm D} W_{\rm ph} N \tau_{\rm D}, \tag{12}$$

where $\tau_{\rm D}$ is the lifetime in the $\rm D^-$ band. If we introduce a rate coefficient $\alpha_{\rm D}^+$ for the capture of carriers from the $\rm D^-$ band by the attractive centers ($\tau_{\rm D} = 1/\alpha_{\rm D}^+ N^+$), then

$$\sigma_{\rm D} = e W_{\rm ph} \frac{\mu_{\rm D}}{\alpha_{\rm D}^+} \frac{N}{N^+} = e W_{\rm ph} \frac{\mu_{\rm D}}{\alpha_{\rm D}^+} \frac{1}{K}. \tag{13}$$

We can expect the product $\sigma_{\rm D} K$ to depend less strongly on N than does $\sigma_{\rm D}$. Figure 4 shows $\sigma_{\rm D}$ and $\sigma_{\rm D} K$ as functions of N; we can see that $\sigma_{\rm D} K$ does indeed depend much less strongly on N than does $\sigma_{\rm D}$. The dependence $\sigma_{\rm D}(T)$, close to a power-law ($\sigma_{\rm D} \propto T^n$, where $n \approx 2$), exhibits some similarity with the temperature (T) dependence of the rate of the capture of free electrons by the attractive centers. Note that in our samples we can expect also hopping of vacancies between the ground states of the impurity. Consequently, as T and $W_{\rm ph}$ are lowered, the attractive centers are frozen out to form $\rm D^+$ $-\rm A^-$ dipoles. In our opinion, this is the reason why $\tau_{\rm D}$ ($\sim \sigma_{\rm D}/W_{\rm ph}$) increases as $W_{\rm ph}$ drops in the range of low values of T (Fig. 5), whereas at $T \gtrsim 7$ K, we have $\sigma_{\rm D} \propto W_{\rm ph}$.

We can thus see that all the main experimental results can be explained in a natural way within the framework of the present model. Our experimental method does not allow us to determine separately $\tau_{\rm D}$ and $\mu_{\rm D}$. We need independent measurements of $\tau_{\rm D}$ (for example, we could do this by investigating the relaxation time of the photoconductivity in the range $\sigma_{\rm D} > \sigma_{\rm c}$) or $\mu_{\rm D}$ (e.g., in the case of direct excitation of carriers to the $\rm D^-$ band when $\hbar\omega < \varepsilon_0$).

C. We shall now consider some additional details relating to the properties of the $\rm D^-$ band.

1. The expression for $\tau_{\rm c}$ given by Eq. (9) includes the quantities ε_x and $\tau_{\rm D}$. The energy $-\varepsilon_x$ represents the upper-limit of the distribution

$$n_{\rm D}(\varepsilon) = \rho_{\rm D}(\varepsilon) F_{\rm D}(\varepsilon)$$

of the energies of electrons in the $\rm D^-$ band [$\rho_{\rm D}(\varepsilon)$ is the density of states in the $\rm D^-$ band and $F_{\rm D}(\varepsilon)$ is the distribution function; the energy is measured from the bottom of the conduction band]. The quantity $\tau'_{\rm D}$ is the time for an electron in the $\rm D^-$ band to drop by an amount $\approx kT$ on the energy scale from a level $\varepsilon \approx -\varepsilon_x$ to states from which thermal escape is unlikely.

It is interesting to compare $\tau'_{\rm D}$ with $\tau_{\rm D}$, where $\tau_{\rm D}$ is the lifetime of an electron in the $\rm D^-$ band in the conducting state. The quantities $\tau_{\rm D}$ and $\tau'_{\rm D}$ are not identical but there should be some correlation between them because they are both related to the process of energy relaxation in the $\rm D^-$ band.

We estimated the values of $\tau_{\rm D}$ for different samples at $T = T_{\rm cr}$ by equating the two terms in Eq. (7). The results are presented in Fig. 4. It is quite clear from this figure that there is indeed a correlation between $\tau_{\rm D}(N)$ and $\tau'_{\rm D}(N)$. We shall also assume that $\tau'_{\rm D} = \tau_{\rm D}$ and calculate the values of $n_{\rm D}$, $\mu_{\rm D}$, and $\alpha_{\rm D}^+$ at $T = T_{\rm cr}$. For example, in the case of sample No. 3 ($N^+ = 1.2 \times 10^{12}$ cm^{-3}) when $W_{\rm ph} = 0.25$ sec^{-1}, we have $\tau'_{\rm D} = \tau_{\rm D} = 1.5 \times 10^{-6}$ sec, so that $\alpha_{\rm D}^+ \approx 5.8 \times 10^{-7}$ cm^3/sec and

$$\mu_{\rm D} = \sigma_{\rm D}/eW_{\rm ph} N \tau_{\rm D} = 3 \ {\rm cm^2 \cdot V^{-1} \cdot sec^{-1}},$$

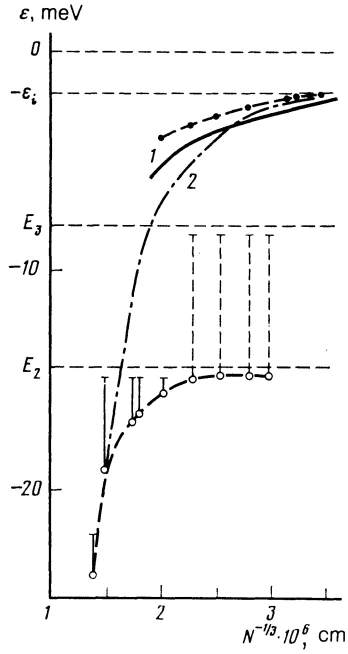

FIG. 7. Position of the bottom of the D^- band versus the reduced impurity concentration plotted in accordance with Ref. 17 (curve 1), compared with the calculated dependence of the mobility edge[9] (curve 2), with the experimental values of Σ_x (●) and with the energy position of the maximum of delocalized carriers in accordance with Ref. 9 (○).

i.e., $b = \mu_D/\mu_c = 2.5\times 10^{-4}$ and $\alpha^+/\alpha_D^+ \approx 30$. These values of μ_D and α_D^+ seem reasonable.

2. We shall denote the positions of the lower and upper mobility edges of the D^- band by ε_{D1} and ε_{D2}. Clearly, we have $\varepsilon_{D1} \lesssim \varepsilon_x < \varepsilon_{D2}$. The exact position of the level $-\varepsilon_x$ depends on the nature of $F_D(\varepsilon)$, which is not known. If the band is narrow, then all these energies are close to the level of an isolated D^- center ($-\varepsilon_i$). Consequently, at low values of N, we can assume that $\varepsilon_x \approx \varepsilon_i = 2$ meV (Fig. 7). An increase in N increases ε_x. This means that the level ε_{D1} drops.

The experimental values in Fig. 7 are compared with the dependence of the position of the bottom of the D^- band calculated by Nishimura[17] (curve 1) and with the position of the lower mobility edge of the D^- band (curve 2) taken from Ref. 9. The calculated curves 1 and 2 and the experimental dependences $\varepsilon_x(N^{-1/3})$ are qualitatively similar. The mobility edge calculations were made using the relation $\varepsilon_{D1} = -(\varepsilon_i + I)$, where $I = A\exp(-\beta N^{1/3}/a_i)$, $\beta \simeq 1.73$, $a_i = 100$ Å. The results were linked to the experimental data for a sample of Si:B with $N \approx 3\times 10^{17}$ cm^{-3}, for which the value of ε_2 was deduced from galvanomagnetic measurements under equilibrium conditions: $\varepsilon_2 = 22$ meV, i.e., $\varepsilon_{D1} = \varepsilon_0 - \varepsilon_2 - \varepsilon_1 = 21$ meV. This estimate of ε_{D1} ($N^{-1/3}$) was used successfully in Ref. 9 to determine the gap between the localized and delocalized D^- states.

It should be pointed out that the spectral measurements show that the band of delocalized states extends much deeper than the mobility edge. For example, in the case of Si:B samples with $N \approx (3\text{–}8)\times 10^{16}$ cm^{-3} it is found that the delocalized carriers have energies mainly below the first excited state of an impurity center ($E_2 \approx -14.5$ meV). The density of electrons in these states is estimated in Ref. 9 to be $n_D \approx 10^{13}$ cm^{-3}. It is difficult to see how the mobility $\mu_D(\varepsilon)$ could be high for such "deep" carriers. Clearly, the spectra provide evidence of carriers delocalized in clusters of finite dimensions. The very fact that such samples contain delocalized states with a fairly high density for ε below E_2 is in conflict with the concept of the D^- band put forward in Ref. 17.

3. A comparison of the results of measurements of the photo-Hall effect with the spectral data shows that the density of states $\rho_D(\varepsilon)$ in the D^- band falls relatively slowly as ε decreases. The distribution function $F_D(\varepsilon)$ is affected not only by the cooling process, the rate of which $[\tau_D'(\varepsilon)]^{-1}$ clearly falls as $\rho_D(\varepsilon)$ is reduced, but is also influenced significantly by the recombination of electrons from the D^- band via excited states of the impurities; the probability of this process $\tau_D'(\varepsilon)$ varies nonmonotonically with energy and falls steeply when ε becomes less than E_2 (Ref. 9). Consequently, the dependence $n_D(\varepsilon)$ is also nonmonotonic. In the range $\varepsilon_x > |E_2|$ there is one maximum of the function $n_D(\varepsilon)$, whereas in the range $\varepsilon_x < |E_2|$ there may be two maxima.

IV. CONCLUSIONS

This investigation shows that the D^--band conductivity of weakly compensated semiconductors ($K \approx 10^{-5}$–10^{-4}) appears in the impurity concentration range $N \lesssim 10^{-2} N_M$. Even close to the delocalization threshold the D^--band photoconductivity may be tens of times higher than the free-band (conduction-band) photoconductivity. The appearance of a conducting band of delocalized states alters basically the usual scheme and the laws governing photocarrier recombination: the carriers captured by the neutral centers can now cool in the D^- band, which ensures the photoconductivity in the D^- band, and, finally, they can be captured by the attractive centers thus completing the recombination process. The lifetime in the conduction band τ_c under delocalization conditions is governed mainly by the concentration of the neutral centers and by the ratio of the rate of cooling in the D^- band to the probability of thermal release from this band. The lifetime of carriers in the D^- band τ_D is governed by the concentration of the attractive centers N^+. A sharp drop in the photoconductivity when N increases in the range $N^{1/3}a_0 > 5\cdot 10^{-10}$ should be allowed for when Si is used in high-sensitive photodetector devices.

We feel that our investigation, carried out under nonequilibrium conditions, provided important information on the properties of the D^- band. Nevertheless, studies of the problem of the D^- band and of the ε_2 conductivity are far from complete at the present time and further comprehensive investigations are required.

[1] H. Fritzsche J. Phys. Chem. Solids **6**, 69 (1958).
[2] E. A. Davis and W. D. Compton, Phys. Rev. **140**, A2183 (1965).
[3] N. F. Mott and W. D. Twose, Adv. Phys. **10**, 107 (1961).
[4] J. Hubbard, Proc. R. Soc. London Ser. A **277**, 237 (1964).
[5] E. M. Gershenzon, G. N. Gol'tsman, and A. P. Mel'nikov, Pis'ma Zh. Eksp. Teor. Fiz. **14**, 281 (1971) [JETP Lett. **14**, 185 (1971)].
[6] É.É. Godik, Yu.A. Kuritsyn, and V.P. Sinis, Pis'ma Zh. Eksp. Teor. Fiz. **14**, 377 (1971) [JETP Lett. **14**, 254 (1971)].
[7] E. M. Gershenzon, Yu. P. Ladyzhinskiĭ, and A. P. Mel'nikov, Pis'ma

Zh. Eksp. Teor. Fiz. **14**, 380 (1971) [JETP Lett. **14**, 256 (1971)].

[8] E. M. Gershenzon, A. P. Mel'nikov, R. I. Rabinovich, and N. A. Serebryakova, Usp. Fiz. Nauk **132**, 353 (1980) [Sov. Phys. Usp. **23**, 684 (1980)].

[9] V. F. Bannaya, E. M. Gershenzon, A. P. Mel'nikov, R. I. Rabinovich, and I. E. Trofimov, Zh. Eksp. Teor. Fiz. **85**, 746 (1983) [Sov. Phys. JETP **58**, 434 (1983)].

[10] L. A. Vorozhtsova, E. M. Gershenzon, Yu. A. Gurvich, F. M. Ismagilova, A. P. Mel'nikov, and R. I. Rabinovich, Pis'ma Zh. Eksp. Teor. Fiz. **43**3, 480 (1986) [JETP Lett. **43**, 618 (1986)].

[11] P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

[12] R. A. Smith, *Semiconductors*, Cambridge University Press (1959) Chap. 5, § 2.

[13] V. N. Abakumov V. I. Perel' and I. N. Yassievich, Fiz. Tekh. Poluprovodn. **12**, 3 (1978) [Sov. Phys. Semicond. **12**, 1 (1978)].

[14] E. M. Gershenzon, A. P. Mel'nikov, R. I. Rabinovich, and V. B. Smirnova, Fiz. Tekh. Poluprovodn. **17**, 499 (1983) [Sov. Phys. Semicond. **17**, 311 (1983)].

[15] E. B. Gol'dgur and R. I. Rabinovich, Zh. Eksp. Teor. Fiz. **84**, 1109 (1983) [Sov. Phys. JETP **57**, 643 (1983)]; Fiz. Tverd. Tela (Leningrad) **26**, 1705 (1984) [Sov. Phys. Solid State **26**, 1034 (1984)].

[16] Yu. P. Ladyzhinskiĭ, Fiz. Tverd. Tela (Leningrad) **11**, 2282 (1969) [Sov. Phys. Solid State **11**, 1842 (1970)].

[17] H. Nishimura, Phys. Rev. A **138**, A815 (1965).

Translated by A. Tybulewicz