Direct-capture threshold effects in silicon superconductivity

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(Submitted 29 March 1991)
Zh. Eksp. Teor. Fiz. **100**, 1547–1555 (November 1991)

The photoconductivity (PC) of silicon with degree of compensation $K < 10^{-3}$ and with main-impurity density N exceeding somewhat the delocalization threshold of the D^- states was experimentally investigated at helium temperatures (T) and in various electric fields (E). An abrupt PC threshold (σ_g) was observed in the D^- band for samples with $K > 10^{-4}$ at $T > T_{cr}$ (or $E > E_{cr}$). The effect on E on the free-carrier conductivity (σ_c) turned out to be stronger the higher T. The results are explained using the indirect-recombination method. It is shown that the second recombination stage, carrier capture from the D^- band by an attracting center (AC) can be represented as carrier drift toward the AC under the influence of the Coulomb field of the latter. The threshold of the onset of the conductivity σ_g is explained. Estimates of T_{cr}, of E_{cr}, and of the coefficient of carrier capture by the AC from the D^- band are explained. The values obtained on the basis of this model are close to those obtained in experiment.

1. INTRODUCTION

We have shown earlier[1,2] that the D^- states influence substantially at helium temperatures the photoconductivity (PC) in doped silicon ($N > 10^{16}$ cm^{-3}) with very small compensation ($K \leqslant 10^{-3}$). According to Refs. 1 and 2, the recombination of free electrons with attracting centers (AC) is effected at $K \leqslant 10^{-3}$ in two stages (indirect recombination): the electron is first captured by a neutral center (NC) and then goes over from the NC to the AC. For small N and "large" K($N < 2\cdot 10^{16}$ cm^{-3}, $K \geqslant 10^{-4}$) the number of NC participating in the recombination is relatively small; their distance R from the AC does not exceed a certain value $R_{\rm eff}(T)$. The second stage is in this case a hopping approach of the electron to the AC. The NC located at a distance $R > R_{\rm eff}$ from the AC take no part in the recombination and act as sticking centers. At large N and small K($N > 4\cdot 10^{16}$ cm^{-3}, $K \leqslant 10^{-4}$) the D^- states are in the main already delocalized. The second recombination state is therefore effected by electron motion over the D^- band and an appreciable fraction of the NC participate in the recombination. A distinguishing feature of such samples is the possible appearance in the D^- band of a photoconductivity (PC) σ_g that can be comparable with or even larger than the PC σ_c in the free band (c band).

The above division of samples into two groups is to a certain degree arbitrary.[2] In some intermediate samples the physical situation is different, depending on the temperature T and on the electric field E. The present paper is devoted to the properties of such samples. Principal attention is paid to the investigation of the conditions under which σ_g sets in when T, E, and K are varied, and also of the dependences of σ_g and σ_c on these quantities.

Our most important results can be formulated as follows: Samples exist in which the conductivity σ_g is zero at small T and E but increases when they increase. It has turned out that the onset of σ_g has a threshold—it appears almost jumpwise at a certain $T = T_{cr}$ or $E = E_{cr}$. The field dependences of σ_c are radically different from those in cascade capture: the effect of E on σ_c is weaker the lower T.

We were able to explain the results using an indirect-recombination model. The heretofore ignored capture of D^--band electrons by AC can be regarded as electron drift to the AC by the action of the Coulomb field of the center. The jumplike onset of σ_g and the unusual behavior of $\sigma_c(T,E)$ are explained by this model. The coefficient α_g^+ of capture of a D^--band electron by an AC and the values of T_{cr} and E_{cr} are estimated without using any adjustment parameters. The values obtained for σ_g^+, T_{cr}, and E_{cr} have turned out to be close to the measured ones.

2. EXPERIMENTAL PROCEDURE AND RESULTS

We investigated a set of Si:B samples with $n = (2$–$12)\cdot 10^{16}$ cm^{-3} and $K = 10^{-5}$–10^{-3}. The free carriers were photoexcited by background radiation at room temperature in a photon energy range $\hbar\omega = 80$–120 meV (interference filter). The excitation intensity ($W_{\rm ph}N$) was relatively low ($W_{\rm ph} \simeq 0.1$–1 s^{-1}). We measured the conductivity σ and the Hall constant R_H. At $\mu^* \equiv R_H\sigma \simeq \mu_c$, where μ_c is the free-carrier mobility, the conduction was only via the c-band (all the reasoning that follows pertains to n-type material): $\sigma = \sigma_c$. At $\mu^* < \mu_c$ a contribution is made by conduction through the D^- band: $\sigma = \sigma_c + \sigma_g$. In this case σ_c and σ_g were calculated using the two-band model (see Ref. 3 for more details). Under the experimental conditions the mobility μ_c was determined by scattering from neutral impurities: $\mu_c(E,T) = \mu_n = $ const. The shown measurement results for two most typical samples are representative of the large batch.

Figures 1 and 2 show the temperature dependences of σ_c and σ_g for samples 1($N \simeq 6\cdot 10^{16}$ cm^{-3}, $KN \approx 4\cdot 10^{13}$ cm^{-3}) and 2($N \approx 6\cdot 10^{16}$ cm^{-3}, $KN \approx 6\cdot 10^{12}$ cm^{-3}) for different E. Three sections can be distinguished on the $\sigma_c(T)$ curves; low $T(T < T_2) - \sigma_c = $ const, intermediate $(T_2 < T < T_1) - \sigma_c(T) \propto \exp(-\varepsilon_x/kT)$, and high $(T > T_1) - \sigma_c(T) \propto T^{2.5}$. As E increases the σ_c curves undergo a certain evolution: T_2 decreases and T_1 increases, i.e., the intermediate-temperature region broadens. For sample 1

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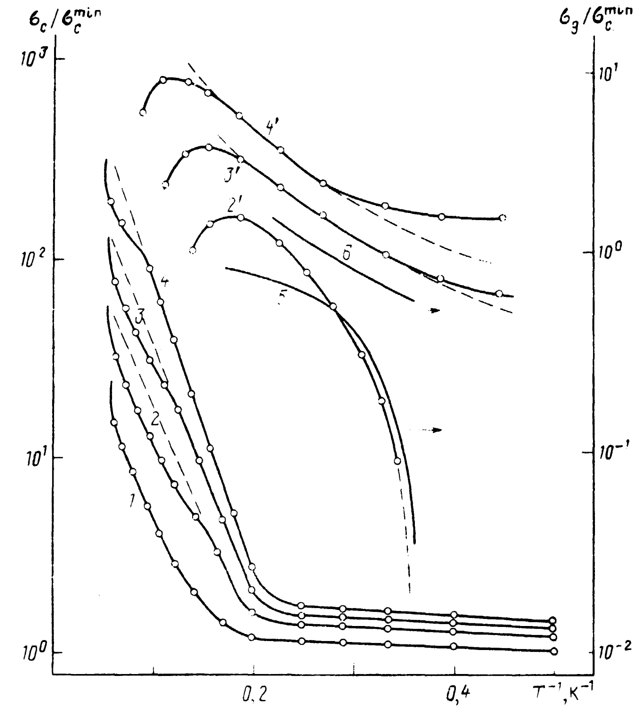

FIG. 1. Dependences of $\sigma_c(T)$ and $\sigma_g(T)$ (numbers of primed curves) for sample 1 at different values of E(V/cm): 1—5; 2,2′—40; 3,3′—60, 4,4′—80. Dashed curves—dependences of $\sigma_g(T) \propto T^2$. Curve 5—calculated dependence of $x_T(T)$; curve 6—dependence of $\sigma_g(T)/x_T(T)$ for curve 2′.

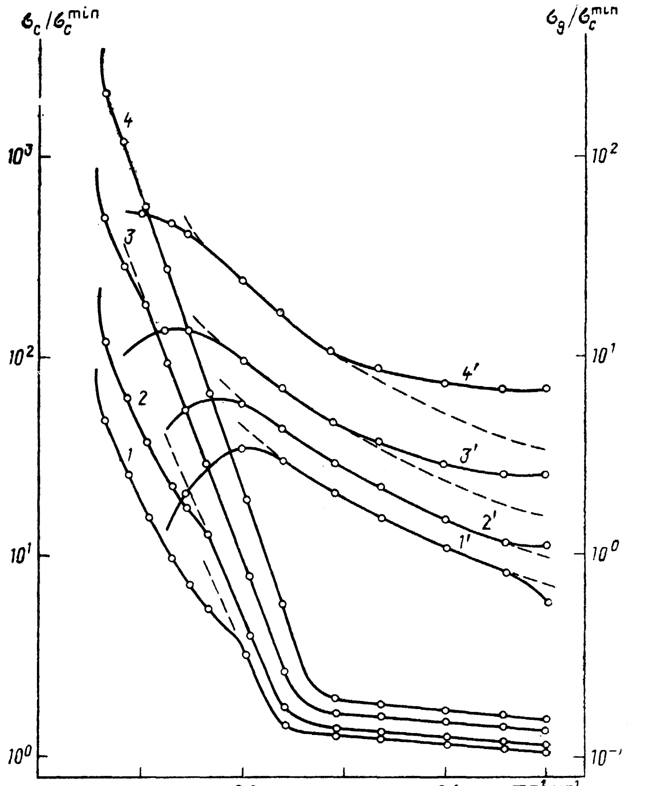

FIG. 2. Dependences of $\sigma_c(T)$ and $\sigma_g(T)$ (numbers of primed curves) for sample 2 at different values of E(V/cm): 1—10; 2—20; 3—60; 4—100. Dashed curves—dependences of $\sigma_g(T) \propto T^2$.

at $E = 5$ V/cm this region is nonexistent, $T_1 \leqslant T_2$, and no σ_g is observed. At $E = 40$ V/cm the conductivity σ_g is zero up to a certain critical temperature $T_{cr} \simeq 2.8$ K, after which $\sigma_g(T)$ is seen to grow abruptly. At $T \simeq 5$ K the value of σ_g is already comparable with σ_c and increases smoothly with further increase of T. The $\sigma_g(T)$ dependence becomes weaker when E increases at low T. At intermediate T we have $\sigma_g(T) \sim T^2$, after which σ_g has a maximum. The temperature corresponding to the maximum of $\sigma_g(T)$ is higher the larger E. In sample 2 the conductivity σ_g exists in all fields, while in a field 10 V/cm the increasing σ_g also has a threshold at $T = T_{cr} \leqslant 2$ K. Note that σ_g increases with decrease of $NK \equiv N^+$ (it follows from measurements of sample batches that $\sigma_g \sim 1/N^+$ for equal T and E).

Figure 3a shows a plot of $\sigma_c(E)$ for sample 2 at various T. Evidently, the $\sigma_c(E)$ dependence becomes stronger with increase of T. We emphasize that this fact is not at all understandable in light of the usual assumptions concerning the heating and capture of electrons. Figure 3b shows the $\sigma_g(E)$ dependence for samples 1 (curve 7) and 2 (curves 5 and 6). In sample 1, σ_g is zero up to a certain critical value $E_{cr} \simeq 30$ V/cm, where it rises above a threshold. In sample 2 σ_g increases monotonically with the field. The σ_g dependence weakens when the temperature is raised.

3. DISCUSSION OF RESULTS

Let us show that the dependences of σ_g and σ_c on T and E can be explained using the indirect recombination mech-

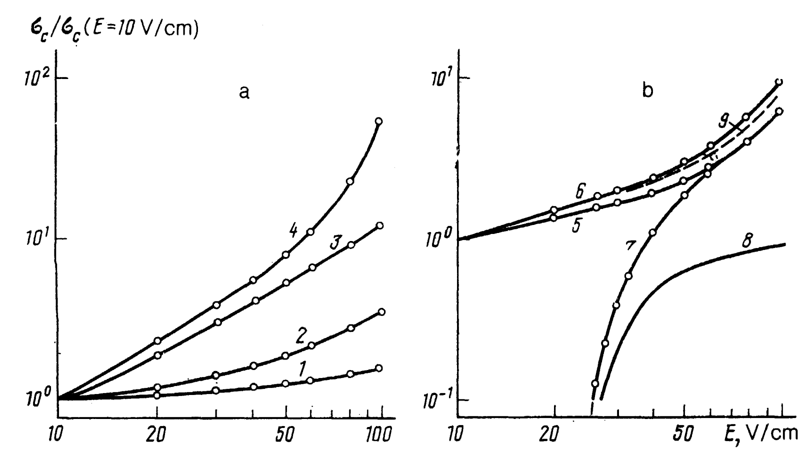

FIG. 3. a) Dependences of $\sigma_c(E)$ for sample 2 at 1—$T = 2$ K; 2—4.2 K; 3—6 K; 4—10 K. b) Dependences of $\sigma_g(E)$ for sample 1 at 5—$T = 2.5$ K; 6—4.2 K. Curve 7—dependence of $\sigma_g(E)$ for sample 1 at $T = 2.5$ K; junction with curve 5 at $E = 100$ V/cm. Curve 8—calculated dependence of $x_E(E)$. Curve 9 (dashed)—dependence of $\sigma_g(E)/x_E(E)$ for curve 7.

anism proposed by us earlier,[1,2] if it is assumed that D^--band electron recombination on an AC is the result of directed motion of these electrons to the AC in its Coulomb field.

1. Consider the dependence of σ_c on E and T. The increase of σ_c with E is due to the increased density n_c of the free electrons as the lifetime increases [$\mu_c(E) = \text{const!}$].

It was shown in Refs. 1 and 2 that under the considered conditions σ_c cannot be attributed to cascade capture by an AC. One more argument must be added to the statements there. We have already emphasized that the $\sigma_c(E)$ dependence increases with T. This dependence becomes weaker in cascade capture.

The $\sigma_c(T)$ dependences are attributed in Ref. 2 to indirect recombination for two limiting cases (see the Introduction): small N and large K ($K \geqslant 10^{-4}$), and large N and small K ($K \leqslant 10^{-4}$). The lifetime τ_{c1} of the free electrons takes in the first of these cases the form[2]

$$\tau_{c1}^{-1} = (4\pi/3)R_{\text{eff}}^3 N^+ \tau_n^{-1} \xi \propto T^{-2,5}, \tag{1}$$

where $\xi \simeq 1$, $\tau_n^{-1} = \alpha^0 N$, and α^0 is the coefficient of capture by an NC. In the second case ($K < 10^{-4}$) an appreciable fraction of the NC takes part in the recombination. An electron trapped on an NC far from an AC contributes to the conductivity through the D^- band until it is captured by an AC (capture probability $\alpha_g^+ N^+ = 1/\tau_g^+$) or is thermal ejected to the c band (ejection probability $W_T = \alpha^0 N_c \exp(-\varepsilon_x/kT)$, N_c is the c-band, ε_x is the energy gap between the c-band bottom and the maximum of the D^--band electron distribution). The corresponding lifetime τ_{c2} is

$$\tau_{c2}^{-1} = \tau_n^{-1}(1 + W_T \tau_g^+)^{-1}. \tag{2}$$

Our samples are intermediate with respect to N and K. Depending on the external conditions (T,E) the main transport of a trapped electron to an AC in the samples can be effected by either method. A somewhat simplified expression for τ_c is

$$\tau_c^{-1} = \tau_{c1}^{-1} + \tau_{c2}^{-1} = \tau_{c1}^{-1} + \tau_n^{-1}(1 + W_T \tau_g^+)^{-1}. \tag{3}$$

We shall analyze this equation assuming that $\tau_{c1} \gg \tau_n$: owing to the very small K this inequality holds for all the employed samples. W_T increases exponentially with T, the values of τ_{c1} and $\tau_g^{(+)}$ have power-law growth rates, and τ_n is independent of T. We denote the temperatures at which $W_T \tau_g^+ = 1$ and $W_T \tau_g^+ = \tau_{c1}/\tau_n$, by T_2 and T_1 respectively. Obviously, $T_2 < T_1$, since $\tau_{c1} \gg \tau_n$. If $T < T_1$ we can neglect the first term of (3). The number 1 can be neglected in the denominator of the second term if $T < T_2$, and must be retained if $T > T_2$. If, however, $T > T_1$, the second term of (3) should be omitted. The $\sigma_c(T) \propto \tau_c(T)$ dependence takes as a result the form

$$\begin{gathered} \sigma_c \propto \tau_n = \text{const}(T), \\ \sigma_c \propto \tau_n \tau_g^+ W_T \propto \exp(-\varepsilon_x/kT), \\ \sigma_c \propto \tau_{c1} \propto T^{2,5} \end{gathered} \tag{4}$$

for the three temperature regions $T < T_2$, $T_2 < T < T_1$ and $T > T_1$ respectively.

We see that the qualitative results that follow from the analysis of Eq. (3) are fully valid: all three characteristic regions are observed in experiments. This casts light on the physical meanings of the temperatures T_1 and T_2 introduced in the discussion of Figs. 1 and 2. Expressions (4) describe correctly the $\sigma_c(T)$ dependence in the entire temperature interval. The quantitative estimates of σ_c yield quite reasonable values.[2]

2. We use now the same model to analyze σ_g, supplementing it with ideas concerning capture of D^--band electrons by AC.

From the kinetic equations we obtain for the lifetime σ_g in the D^- band

$$1/\tau_g = 1/\tau_g^+ + (1 + W_T \tau_g^+)\tau_n/\tau_{c1}\tau_g^+. \tag{5}$$

We assume that the change of σ_g is due mainly to the change of the electron density n_g in the D^- band. Since $n_g \propto \tau_g$, the $\sigma_g(T)$ dependence should have two characteristic regions:

$$\begin{gathered} \sigma_g \propto \tau_g^+ \quad (T < T_1), \\ \sigma_g \propto \tau_{c1}/\tau_n W_T \quad (T > T_1). \end{gathered} \tag{6}$$

In the last case σ_g decreases with increase of T in view of the depletion of the D^- band by thermal ejection of electrons into the c band. Experiment confirms the presence of the two regions: It is seen from Figs. 1 and 2 that near $T = T_1$ the $\sigma_g(T)$ dependence changes: the increase of σ_g due to the increase of τ_g^+ with T (see below) is replaced by a decrease.

3. Let us discuss the field dependences. The electric field deforms the Coulomb potential well. Just as in cascade capture, this deformation decreases the probability of capture by AC and lengthens the times τ_g^+ and τ_{c1}. Thus, the conductivity σ_g should increase with E, as is in fact the case.

Turning to Eqs. (4), we conclude that the conductivity σ_c should not depend on E at $T < T_2$ and should increase with E at $T \geqslant T_2$. This is precisely what is observed in experiment. This explains also the enhancement of the $\sigma_c(T)$ dependence with increase of T. Thermal excitation causes the D^- band to supply electrons to the c-band. The increase of n_g with the field causes therefore n_c to increase, and more strongly the higher the temperature.

It can be seen from Figs. 1 and 2 that T_2 decreases somewhat with increase of E. This is understandable: the condition $W_T \tau_g^+ > 1$ is easier to satisfy the longer τ_g^+. The temperature T_1 determined by the condition $\tau_{c1} = \tau_n W_T \tau_g^+$, increases with E. It can apparently be concluded from this that when E increases τ_{c1} increases faster than τ_g^+.

Curve 1 of Fig. 1 has no regions of intermediate T. It can be seen that for this sample, in a field 5 V/cm, the first term of (3) becomes predominant when T is increased precisely when the inequality $W_T \tau_g^+ > 1$ begins to be satisfied.

It is thus possible to understand fully our experimental results from the standpoint of an indirect recombination mechanism if it assumes that τ_g^+ increases with increase of E. This assumption is intuitively quite reasonable. An estimate of τ_g^+ can be obtained by starting from the condition $W_T(T_2)\tau_g^+ = 1$. For curve 3 of Fig. 2 we have $\varepsilon_x \simeq 2.75$ meV and $T_2 \simeq 4$ K. Using for N_c the density of states in the valence band of silicon ($\approx 2 \cdot 10^{15}\ T^{3/2}\ \text{cm}^{-3}$) and $\alpha^0 \approx 10^{-7}\ \text{cm}^3 \cdot \text{s}^{-1}$ (Ref. 2) we obtain $1/\tau_g^+ \approx 6 \cdot 10^5\ \text{s}^{-1}$. For curve 2 of Fig. 1 ($T_2 \approx 5$ K) similar calculations yield $1/\tau_g^+ = 3 \cdot 10^6\ \text{s}^{-1}$.

4. We have not yet attempted in Refs. 1–3 and in the present paper to specify concretely the course of D^- band electron capture by AC. We try this now. The capture can be regarded as a slow (owing to the very small mobility μ_g) slippage of electrons to AC under the action of the center's Coulomb field $e/\varkappa R^2$ (named "creeping recombination" by B. I. Shklovskiĭ[1)]). The electron flux to an AC through the surface of a sphere of radius R is obviously equal to $n_g\mu_g(e/\varkappa R^2)4\pi R^2$. Dividing this expression by n_g we obtain the capture coefficient

$$\alpha_g^+=4\pi e\mu_g/\varkappa. \tag{7}$$

In the paper by Vorozhtsova *et al.*,[3] measurements at small E at $T\simeq 3$ K yielded by an independent method, for an Si:B sample with $N=3\cdot 10^{16}$ cm^{-3} and $K=4\cdot 10^{-5}$, $\mu_g=3$ cm^2/V·s and $\alpha_g^+\simeq 5.8\cdot 10^{-7}$ cm^3·s^{-1}. Substitution of this value of μ_g in (7) yields the very close value $\alpha_g^+=4.8\cdot 10^{-7}$ cm^3·s^{-1}. So good an agreement is to some degree fortuitous, since the experimental μ_g was quite approximate. On the other hand, from the values obtained above for τ_g^+ we obtain $\alpha_g^+\approx 8\cdot 10^{-8}$ cm^3·s^{-1} at $E\simeq 60$ V/cm for sample 1 and $8\cdot 10^{-7}$ cm^3·s^{-1} for sample 2 ($E=40$ V/cm). In this case, too, α_g^+ can be regarded as in full accord with the creeping recombination. (It must be recognized that the field E should decrease α_g^+ somewhat.)

5. It was assumed above that the time τ_g^+ increases, and therefore σ_g rises somewhat at $T<T_1$ with growth of T and E. For low T and small E, however, the growth of σ_g is very abrupt and attests to some qualitative change of the conducting properties of the D^- band in this sample at temperature somewhat below 3 K.

Let us set forth our understanding of the nature of the threshold of the conductivity σ_g. The electron is directed ("trickles" down) towards the nearest AC. This does not mean that the electron is necessarily captured by this center. The "trickling" process is hindered by diffusion. If the distance to the AC is not too short, and the diffusion is intense enough, the electron can go from the vicinity of the given AC to the vicinity of another, then reach the vicinity of a third, etc. In this case the electron covers in the crystal a distance $\sim(D_g\tau_g^+)^{1/2}$ much longer than the average distance $R_c^+\sim(N^+)^{-1/3}$ between the AC (D_g is the diffusion coefficient in the D^- band). Such an electron can be called "free": it contributes to the conductivity σ_g. If, however, $(D_g\tau_g^+)^{1/2}<R_c^+$, the electron should be regarded as captured and does not contribute to σ_g. An estimate of the critical temperature T_{cr} above which "free" electrons appear in the D^- band can be obtained from the relation

$$(D_g\tau_g^+)^{1/2}\approx R_c^+. \tag{8}$$

Substituting here the equations

$$(\tau_g^+)^{-1}=(4\pi e\mu_g/\varkappa)N^+,\quad \mu_g=eD_g/kT,$$

we obtain

$$e^2/\varkappa R_c^+\approx kT_{cr}. \tag{9}$$

Note that the quantity on the left is the mean fluctuation of the potential produced by the randomly disposed AC. It can be regarded as the energy distance between the mobility edge and the percolation level in the D^- band.

The experimental value of T_{cr} of sample 1 in a field 40 V/cm is $\simeq 2.8$ K (Fig. 1). From relation (9) we obtain $T_{cr}=4$ K. Recognizing that our estimate is crude, the agreement should be regarded as good. For sample 2, calculation yields $T_{cr}\simeq 2$ K. The experimental value of T_k is somewhat lower (see curve 1′ of Fig. 2).

It is customary in recombination theory to introduce a distance $R_T=e^2/\varkappa kT$ (see, e.g., Ref. 4). It can be regarded as the radius of a sphere surrounding the recombination center, in which the capture takes place. Condition (9) means that $R_T\approx R_c^+$, or

$$N^+R_T^3\approx 1. \tag{10}$$

At $R_T\geqslant R_c^+$ the capture spheres cover fully the entire crystal. Since $\sigma_g\simeq 0$ in this case, all the D^--band electrons contained in the capture sphere should be regarded as captured. Assume this to be the case also at $R_T<R_c^+$ (a free electron passing through this sphere has only a certain capture probability[4]). The crystal-volume capture in which the D^--band electrons can be regarded as free is then

$$x_T=1-N^+R_T^3. \tag{11}$$

Expressing d in terms of T we get

$$x_T=1-(T_{cr}/T)^3. \tag{12}$$

At $x_T\ll 1$ the $\sigma_g(T)$ dependence should be determined by the function $x_T(T)$: $\sigma_g(T)\propto x_T(T)$. We have used dashed lines for the plots of $x_T(T)$ in Fig. 1, in relative units, using a fit parameter $T_{cr}=2.77$ K (curve 5). In addition, the figure shows a plot of $\sigma_g(T)/x_T(T)$ in a field 40 V/cm (curve 6). We see that the function $x_T(T)$ agrees well with the form of curve 2′ near $T=T_{cr}$ and that the ratio $\sigma_g(T)/x_T(T)$ varies smoothly with temperature in a manner close to the σ_g dependence at large values of $E(\sigma_g(T)\propto T^2)$ (Ref. 3).

6. The Coulomb well becomes deformed in the presence of E. At a distance $R>R_E$, where $e^2/\varkappa R_E^2=eE$, the influence of the field is stronger than that of the AC. The effect of the field on the recombination becomes substantial at $R_E<\min(R_c^+,R_T)$. The relative number of "free" electrons in the D^- band can be expressed, by analogy with (11), as

$$x_E(E)=1-N^+R_E^3. \tag{13}$$

If $R_T>R_c^+$, a fast growth of $\sigma_g(E)$ should be expected near the critical value $E=E_{cr}$ is determined from the relation

$$N^+R_E^3(E_{cr})\approx 1. \tag{14}$$

Curve 7 of Fig. 3b ($T\approx 2.5$ K) applies to the case $R_T>R_c^+$ and corresponds to $E_{cr}\approx 26$ V/cm. An estimate using (14) yields the very close value $E_{cr}=30$ V/cm. Expressing N^+ in terms of E_{cr} we obtain from (13)

$$x_E(E)=1-(E_{cr}/E)^{3/2}. \tag{15}$$

For $x_E\ll 1$ we have $\sigma_g(E)\propto x_E(E)$. Curve 8 of Fig. 3b shows the $x_E(E)$ dependence for $E_{cr}=26$ V/cm, while curve 9 (dashed) shows the smooth part of the function $\sigma_g(E)$, [i.e., the ratio $\sigma_g(E)/x_E(E)$] for $T=2.5$ K. Everything stated above concerning the functions represented by curves 2′, 5, and 6 of Fig. 1 can obviously be restated for the field dependences represented in Fig. 3b by curves 7, 8, and 9 respectively.

7. At $T < T_1$ the conductivity $\sigma_g \sim \mu_g \tau_g^+$ does not contain μ_g and is inversely proportional to N^+. The relation $\sigma_g \propto 1/N^+$ was actually observed in our measurements. Thus, for example, according to Figs. 1 and 2, at $E = 60$ V/cm and $T = 3$ K the value of σ_g for the second sample is approximately 6 times larger than for the first. The corresponding ratio of the densities N^+ is $0.15 = (6.7)^{-1}$.

8. We conclude with a few remarks. The function $x_T(T)$ [or $x_E(E)$] is the fraction of the "free" electrons in the D^- band; τ_g^+ is the lifetime in the D^- band. The product $x_T\tau_g^+$ [or $x_E\tau_g^+$] can be regarded as the lifetime of the electrons of the D^- band in the conducting state. We note in this connection that the assumption that two lifetimes exist in the D^- band was set forth earlier in Ref. 3.

In the discussion of the form of $\sigma_g(T)$ we have implicitly assumed that the D^--band electrons are thermalized to a considerable degree. This assumption is corroborated by the strong dependence of σ_g on T for small E.

The analysis set forth is, of course, very crude and many premises call for substantial refinement. In particular, the introduction above of a T_{cr} independent of E (or E_{cr} independent of T) is apparently permissible only if $R_E \gg R_T(T_{cr})$ [or respectively $R_T \gg R_E(E_{cr})$]. In general, T_{cr} should be a function of E, just as E_{cr} a function of T. Further, in an electric field, the volume in which an electron is trapped is no longer spherical. Equation (13) should therefore read $x_E(E) = 1 - \theta(E)N^+R_E^3$, where $\theta(E)$ is a numerical factor of order unity.

The here-developed picture of D^--band electron recombination on AC permits a qualitative description of the aggregate of the experimental result and, most importantly, account for the threshold-like onset of σ_g when T and E increase. The obtained T_{cr} and E_{cr} turn out to be close enough to the experimental values.

The authors thank V. I. Perel' and B. I. Shklovskiĭ for a discussion of the mechanism of D^--band electron capture by AC and A. G. Aronov for a helpful discussion.

[1)]The terminology belongs to B. I. Shklovskiĭ.

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Translated by J. G. Adashko