Theory of Low-Temperature Impact Ionization in High-Purity Germanium

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An analysis of low-temperature electrical breakdown of semiconductors shows that the main theoretical problem is to find the distribution function $f(\epsilon, E)$ of the charge carriers, depending on the applied electric field E. In the case of high-purity n-type germanium $(N_D+N_A<4\times10^{13} \text{ cm}^{-3})$, it is shown that the only important interactions are the electron-acoustical phonon ones. The distribution function has been calculated under equivalent assumptions by Stratton. It is used here in order to find the rates of creation and recombination of the charge carriers. Direct radiative recombination is found to be negligible; and the prebreakdown characteristics are mainly governed by the decrease of the thermal recombination rate. The impact ionization rate is calculated under the simplifying assumption of a cross section independent of the energy, thus introducing the only adjustable parameter. The breakdown field dependence on both temperature and compensation of the material is obtained. The results are compared with the data of Koenig and Brown. The agreement is found to be satisfactory. Conclusions to be drawn from this agreement are discussed, together with the limitations introduced by the chosen models.

I. INTRODUCTION

OW-TEMPERATURE electrical breakdown caused by impact ionization of the neutral impurities by the free carriers is a well-known property of germanium; the breakdown field E_b is typically of the order of a few volts per centimeter. This phenomenon, discovered in 1953,¹ has been studied in a rather extensive way, on germanium doped either with hydrogenlike impurities²⁻⁵ or with deep-level impurities.^{2,5,6} For shallow impurities the results may be summarized as follows: (a) For $N_D + N_A > 10^{15} \text{ cm}^{-3}$ (where N_D and N_A are the densities of donors and acceptors, respectively), the breakdown field depends linearly on the concentration of impurities^{2,5,7}; (b) when $N_D + N_A < 4 \times 10^{13}$ cm⁻³, E_b depends on the compensation degree of the sample as shown by Koenig^{8,9}; (c) the value of E_b is sensitive to the temperature.10

The first theoretical treatment was made by Chuenkov.¹¹ He calculated the distribution function of the charge carriers by solving the kinetic equations, assuming that when the carrier energy ϵ is larger than the activation energy ϵ_i of the impurities, the distribution function $f(\epsilon, E)$ is determined mainly by the energy losses caused by impact ionization. This leads to $E_b \propto \epsilon_i^{5/4}$ when $N_D - N_A < 10^{15}$ cm⁻³ and $T < 19^{\circ}$ K, thus independent of both the temperature T and the compensation $(N_D - N_A)/N_A$, which disagrees with experiment; for larger concentrations the results are not better since theory gives $E_b \propto (N_D - N_A)^{\frac{1}{2}}$. A different approach was chosen by Yamashita,¹² who considered the problem in the viewpoint of hot-electrons theory. The distribution function was assumed to be Maxwellian, with an electronic temperature T_e . At first sight, the results seem to be fairly good, but the choice of the distribution function, as well as that of some constants, presents some arbitrariness, as will be shown later.

In a preliminary paper¹³ it has been shown how it is possible, in the case of high-purity germanium, to account approximately for the prebreakdown region $(1 \text{ V/cm} < E < E_b)$ under simple assumptions on the relative importance of the various energy losses of the electrons. In the present article these assumptions are established on better theoretical foundations, and the dependence of the breakdown field E_b is given in terms of both temperature and compensation, for high-purity $(N_D + N_A < 4 \times 10^{13} \text{ cm}^{-3})$ *n*-type germanium. The agreement between experiment and theory is found to be satisfactory. This might lead to a new method of determination of the compensation degree in high-purity samples, which is a delicate problem; however, one must be prudent since the models available until now to describe the different processes involved present some limitations. These are discussed, and conclusions are drawn from the different results.

II. GENERAL THEORETICAL EXPRESSIONS

In order to obtain a criterion for breakdown we shall follow an idea originally due to Price¹⁴ and also used by Chuenkov¹¹ and Yamashita.¹² Let us take the case of an *n*-type semiconductor. In a steady state (dn/dt=0,where n is the electron density), and at very low temperatures $(N_D - N_A, N_A \gg n)$ the balance equation for

¹N. Sclar, E. Burstein, W. J. Turner, and J. W. Davisson, Phys. Rev. 91, 215 (1953).

N. Sclar and E. Burstein, J. Phys. Chem. Solids 2, 1 (1957) ³ S. H. Koenig and G. R. Gunther-Mohr, J. Phys. Chem. Solids 2, 268 (1957).

<sup>2, 268 (1957).
&</sup>lt;sup>4</sup> G. Finke and G. Lautz, Z. Naturforsch. 12a, 223 (1957).
⁵ E. I. Abaulina-Zavaritzkaya, Zhur. Eksptl. i Teoret. Fiz. 36, 1342 (1959); [translation: Soviet Phys.—JETP 9, 953 (1959)].
⁶ A. Zylbersztejn, J. Phys. Chem. Solids, 23, 297 (1962).
⁷ A. L. McWhorter and R. H. Rediker, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague 1961), p. 134.
⁸ S. H. Koenig, J. Phys. Chem. Solids 8, 227 (1959).
⁹ S. H. Koenig, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961), discussion 2, p. 150.
¹⁰ S. H. Koenig, Phys. Rev. 110, 986, 988 (1958).
¹¹ V. A. Chuenkov, Fizika Tverdogo Tela U.S.S.R. 2, 799 (1960).

¹¹ V. A. Chuenkov, Fizika Tverdogo Tela U.S.S.R. 2, 799 (1960).

¹² J. Yamashita, J. Phys. Soc. Japan 16, 720 (1961).

 ¹³ A. Zylbersztejn, J. Electronics and Control 10, 429 (1961).
 ¹⁴ P. J. Price (unpublished). The first discussion of this idea was published by Koenig (see reference 10).

the various creation and recombination processes is given by

$$\frac{dn/dt=0=(A_{p}+A_{0}+A_{i}n)(N_{D}-N_{A})}{-(B_{p}+B_{0}+B_{i}n)N_{A}n, \quad (1)}$$

where A_p is the thermal creation rate, A_0 the photoionization rate, and A_i the impact ionization rate; B_p , B_0 , and B_i , respectively represent the corresponding recombination processes.

At the onset of breakdown the Auger recombination rate $B_i n$ is assumed to be negligible (there are few free electrons); this will be verified later. Let us write $A_p + A_0 = A_T$ and $B_p + B_0 = B_T$; hence,

$$n(T,E) = \frac{A_T(T,E)(N_D - N_A)}{B_T(T,E)N_A - A_i(E)(N_D - N_A)}.$$
 (2)

The criterion for breakdown is then

$$B_T(T, E_b) N_A = A_i(E_b) (N_D - N_A).$$
(3)

The thermal recombination must decrease with the applied electric field and the impact ionization must be enhanced. This means that $\bar{E_b}$ must decrease when $(N_D - N_A)/N_A$ is increased. This was, in fact, observed in high-purity samples.8

Now, if $f(\epsilon, E)$ is the distribution function for the electrons, any of the three coefficients A_i , B_0 , or B_p [written C(T,E) for generality] is given by

$$C(T,E) = \int_{0}^{+\infty} v\sigma_{c}(\epsilon,T) f(\epsilon,E) \epsilon^{\frac{1}{2}} d\epsilon \bigg/ \int_{0}^{+\infty} f(\epsilon,E) \epsilon^{\frac{1}{2}} d\epsilon, \quad (4)$$

where $\sigma_c(\epsilon, T)$ is the cross section for the considered process. At this step of the development, the distribution function must be explicitly known in order to predict theoretically the behavior of the semiconductor in an applied electric field. Therefore, assumptions must be made concerning the importance of the various collisions that a free electron in the conduction band can undergo.

III. SOLUTIONS IN THE CASE OF HIGH-PURITY GERMANIUM

A. Distribution Function

In a general case, the low-field mobility of the electrons may be considered as mainly limited by scattering from acoustical and optical phonons, and ionized or neutral impurities. At liquid-helium temperatures the optical modes are not to be taken into account since they are practically unexcited. Furthermore, the last two types of scattering become unimportant when $(N_D + N_A) < 4 \times 10^{13}$ cm⁻³, i.e., in high-purity germanium. This may be readily seen by using the Brooks-Herring formula¹⁵ for ionized impurities and Erginsoy's

formula¹⁶ for neutral ones, and by comparing them with the mobility limited by acoustical phonons:

$$\mu_a = 2.4 \times 10^7 T^{-\frac{3}{2}} \text{ cm}^2/\text{V-sec.}$$

This expression was verified in the range 50°-250°K,¹⁷ and we assume it to be valid at very low temperatures.¹⁸ When an electric field is applied, the distribution function $f(\epsilon, E)$ must depend on three mechanisms: electronacoustical phonon interaction, interelectronic collisions, and energy losses due to impact ionization of the neutral impurities. Fröhlich and Paranjape¹⁹ have shown that electron-electron interaction is negligible when $n \ll n_e$ $=2 \times 10^{14} (T/293) \text{ cm}^{-3}$ which at 4°K gives $n_e = 3.6 \times 10^{10}$ cm⁻³. This condition is nearly always realized $(n \sim 10^7)$ cm⁻³ in a typical case). The hot-electron approximation, i.e., a Maxwellian distribution with an electronic temperature T_e , is valid for $n \gg n_e$, and therefore is somewhat incorrect in the present case.

We show here that the impact ionization does not disturb the high-energy tail of the distribution function. In other words, the electrons with $\epsilon \ge \epsilon_i$ lose much more energy by means of phonon emission than by ionization of the neutral impurities. In a collision with an acoustical phonon the momentum is conserved and the exchanged energy is $\hbar\omega \simeq (2\epsilon m^*)^{\frac{1}{2}s}$ (s: velocity of sound). At 4°K, $\hbar\omega \gg kT$ for an electron with $\epsilon > \epsilon_i$ and the mean energy loss is $\Delta \epsilon \simeq \hbar \omega$; only emission is important. The rate of energy loss is then, if τ is the relaxation time for acoustical phonon scattering

$$\left(\frac{d\epsilon}{dt}\right)_{\rm ph} = \frac{\Delta\epsilon}{\tau} (2m^*\epsilon_i)^{\frac{s}{2}} \left(\frac{\epsilon}{\epsilon_i}\right)^{\frac{1}{2}}.$$

The optical phonon emission is to be neglected, these phonons having an energy $\hbar\omega_0 \simeq 0.037$ eV, somewhat larger than $\epsilon_i \simeq 0.01$ eV for donors in germanium, and the relaxation time for optical phonon scattering being very large in the helium range. With $\tau \simeq 2.5 \times 10^{-17} \epsilon^{-\frac{1}{2}} T^{-1}$ sec and $s=5.39\times10^5$ cm/sec, for $T=4^{\circ}$ K one finds $(d\epsilon/dt)_{\rm ph} \simeq 3 \times 10^{-5} (\epsilon/\epsilon_i)$. The rate of energy loss due to impact ionization is

$$(d\epsilon/dt)_i = (N_D - N_A)(2\epsilon/m^*)^{\frac{1}{2}}\sigma_i(\epsilon)\epsilon_i,$$

where $\sigma_i(\epsilon)$ is the cross section for impact ionization. Its maximum in terms of ϵ is probably close to the geometrical cross section σ_g of a neutral donor, as it occurs for hydrogen.²⁰ Here we shall take $\sigma_i(\epsilon) = \sigma_g \simeq 4 \times 10^{-13}$ cm^2 as an upper limit. Then, with $N_D - N_A = 4$ $\times 10^{13}$ cm⁻³, one finds $(d\epsilon/dt)_i \simeq 3 \times 10^{-6} (\epsilon/\epsilon_i)^{\frac{1}{2}}$. There-

¹⁵ H. Brooks, Advances in Electronics and Electron Physics (Academic Press Inc., New York, 1955), Vol. 7, p. 156.

 ¹⁶ C. Erginsoy, Phys. Rev. 80, 1104 (1950); 88, 893 (1952).
 ¹⁷ F. J. Morin, Phys. Rev. 93, 62 (1954).

¹⁸ The applicability of this result in the helium-temperature region may be checked by noting that it yields a mobility at 4° K of 3×10^{6} cm²/V-sec in agreement with the mobilities observed by Koenig (references 8, 10) in high-purity samples in the He range. ¹⁹ H. Fröllich and B. V. Paranjape, Proc. Phys. Soc. (London)

B69, 21, 866 (1956).
 ²⁰ N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions (Oxford University Press, New York, 1949), p. 245.

fore it is seen that

$$\left(\frac{d\epsilon}{dt}\right)_{\rm ph} \left/ \left(\frac{d\epsilon}{dt}\right)_i \simeq 10 \left(\frac{\epsilon}{\epsilon_i}\right)^{\frac{1}{2}}$$

in the worst case. As a matter of fact, a mean cross section $\sigma_i \simeq 10^{-14}$ cm² will be found, showing that the calculated ratio is certainly too small. This means that the only process of energy loss for the electrons to consider when $\epsilon \ge \epsilon_i$ is the acoustical phonon emission. For $\epsilon < \epsilon_i$, emission of acoustical phonons is preponderant if the average energy of the electrons $\bar{\epsilon} \gg (kT)^2/2m^*s^2$. By writing that the energy gained from the field is restored to the phonon system, a limit of validity for this theory is found straightforwardly:

$$E \gg (s/\mu_a \sqrt{2}) (kT/m^* s^2).$$
(5)

At 4°K the approximations are correct since the breakdown fields are of the order of a few volts per centimeter. Under these conditions the distribution function has been calculated by Stratton²¹:

$$f_0(\epsilon, E) = a \exp\left[-\left(\frac{\epsilon}{kT}\right)^{\frac{5}{2}} \frac{\sqrt{2}}{6\pi} \left(\frac{16}{5} \frac{s}{\mu_a E}\right)^2 \left(\frac{m^* s^2}{kT}\right)^{\frac{1}{2}}\right], \quad (6)$$

where a is a normalization constant. It must be pointed out that this distribution function has been already used to explain hot-carrier experiments in p-type germanium, at 31°K,²² and gave good agreement with the data. In order to obtain expressions which are easy to handle, and to have a better physical representation of the electron gas, let us introduce the parameter T_e , which has the dimensions of a temperature. The distribution function will be written as

 $f_0(\epsilon, T_e) = a \exp[-(\epsilon/kT_e)^{\frac{5}{2}}],$

where

$$T_e = \alpha E^{4/5}, \tag{8}$$

(7)

with

$$\alpha = \left[\frac{\sqrt{2}}{6\pi} \left(\frac{16s}{1.2 \times 10^8}\right)^2 \left(\frac{m^* s^2}{k}\right)^{1/2}\right]^{-2/5}.$$
 (9)

When α is calculated in cgs units, E in Eq. (8) is to be expressed in volts per centimeter. By taking s=5.39 $\times 10^5$ cm/sec and $m^*=0.12m_0$, the numerical value is $\alpha = 31.1.^{23}$ It must be pointed out that T_e may effectively be regarded as an electronic temperature, since the mean energy calculated with the aid of Eq. (7) is $\bar{\epsilon} = kT_e/k$ $\Gamma(3/5) \simeq kT_e$.

B. Direct Radiative Recombination Rate

In order to calculate the direct radiative recombination rate $B_0(T_e)$, we shall use the cross section $\sigma_0(\epsilon)$ for the hydrogen atom with the usual correction for hydrogen like centers in a semiconductor. Such a method was employed by Sclar and Burstein,²⁴ to evaluate $B_0(T)$ at zero field. One has

$$\sigma_0(\epsilon) = \frac{(n')^3}{D} \frac{2^8 \pi^2 e^2 \hbar}{3m^{*2} c^3} \frac{\epsilon_i}{\epsilon} \exp(-4) \text{ cm}^2,$$

where n' is the refractive index, D the dielectric constant, and c the speed of light. By applying Eq. (4) with $f(\epsilon, T_e)$ given by (7), one finds

$$B_{0}(T_{e}) = \frac{(n')^{3}}{D} \frac{2^{8}\pi^{2}e^{2}\hbar}{3m^{*2.5}c^{3}} \epsilon_{i} \exp(-4) \\ \times \frac{\sqrt{2}\Gamma(2/5)}{\Gamma(3/5)} (kT_{e})^{-\frac{1}{2}} \text{ cm}^{3}/\text{sec.} \quad (10)$$

This recombination rate decreases with the applied electric field and is independent of the lattice temperature, but the limit of validity depends on it. Numerically, by taking $\epsilon_i = 0.01$ eV, n' = 4, $m^* = 0.25m_0$, D = 16, one finds the value

$$B_0(T_e) = 2.4 \times 10^{-20} (kT_e)^{-\frac{1}{2}} \text{ cm}^3/\text{sec.}$$
 (11)

For an applied electric field E=3V/cm, $B_0=2.36$ $\times 10^{-13}$ cm³/sec.²⁵ This value may be compared with that found by Sclar and Burstein²⁴ in the case of a Maxwellian distribution at $T=4.2^{\circ}$ K, $B_0=1.3\times10^{-12}$ cm³/sec; the increase in "electronic temperature" in our case must be taken into account.

C. Cascade Capture Process

Enormous capture cross sections, of the order of 10^{-12} to 10⁻¹⁰ cm², were observed for donors in germanium at liquid helium temperatures.^{10,26} Whereas multiphonon transitions to the ground state yield cross sections five to ten orders of magnitude too small,27 capture into excited states of large radius followed by a cascade of one-phonon transitions leads to cross sections of the right order of magnitude as was shown by Lax.²⁸ This theory of "giant traps" will be used here in order to evaluate $B_p(T_e)$.

In the case of interactions with acoustical phonons only, Lax finds the recombination cross section in terms

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 ²¹ R. Stratton, Proc. Roy. Soc. (London) A242, 355 (1957).
 ²² R. Bray and D. M. Brown, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961), C7, p. 82.
 ²³ The conductivity effective mass was taken here, as the

distribution function is derived from transport equations. An average effective mass $m^*=0.25m_0$ will be used everywhere in the following.

²⁴ N. Sclar and E. Burstein, Phys. Rev. 98, 1757 (1955).

²⁵ N. Scar and E. Bursten, Phys. Rev. 70, 1137 (1995).
²⁵ This result is slightly different from that formerly given¹³ because of a more reasonable choice for the electron effective mass.
²⁶ G. Ascarelli and S. C. Brown, Phys. Rev. 120, 1615 (1960).
²⁷ H. Gummel and M. Lax, Ann. Phys. 2, 28 (1957).
²⁸ M. Lax, Phys. Rev. 119, 1502 (1960).

(13)

of the electron energy as

$$\sigma_{p}(x) = \frac{4^{6} \sigma_{1} F(x)}{6 \gamma^{4} x},$$
(12)

where

and

$$x=\epsilon/kT, \quad \gamma=kT/\frac{1}{2}m^*s^2,$$

$$F(x) \simeq \frac{1}{4} [x + (\delta/\gamma)]^{-1}$$

for $x \ll 1$. The quantity δ is given graphically vs γ and corresponds to the cutoff of the binding energy. The dependence of F(x) is more complicated for $x \gg 1$, but owing to the distribution function the expression (13)may be employed in the whole x range as was shown by Lax with a Maxwell-Boltzmann distribution. Here this approximation is better because of the much more rapid decrease of $f(\epsilon, T_{\epsilon})$. The quantity σ_1 , which has the dimensions of a cross section, is given by

$$\sigma_1 = (\pi/12) \left(Z e^2 / D_{\frac{1}{2}} m^* s^2 \right)^3 l_c^{-1}, \tag{14}$$

where l_c is the room-temperature mean free path associated with acoustical phonon scattering; one has $l_c \simeq 8 \times 10^{-6}$ cm. By taking D = 16 and $s = 5.39 \times 10^{5}$ cm/sec, a value $\sigma_1 = 2.13 \times 10^{-9}$ cm² is found.²⁹ The recombination rate $B_p(T_e)$ is then

$$B_{p}(T_{e}) = \frac{2^{4}\sigma_{1}s\sqrt{2}}{\Gamma(8/5)} \left(\frac{m^{*}s^{2}}{kT}\right)^{2} \left(\frac{m^{*}s^{2}}{kT_{e}}\right)^{\frac{3}{2}} \\ \times \int_{0}^{+\infty} \frac{e^{-(\epsilon/kT_{e})^{\frac{5}{2}}}d\epsilon}{\epsilon + (\delta m^{*}s^{2}/2)}.$$
(15)

By setting

$$I(\beta) = \frac{5}{2} \int_{\beta}^{+\infty} \frac{\exp\left[-(u-\beta)^{\frac{5}{2}}\right]}{u} du, \qquad (16)$$

the calculated expression for the recombination rate becomes

$$B_p(T_e) = 5 \times 10^{-6} T^{-2} E^{-1.2} I(\beta) \text{ cm}^3/\text{sec},$$
 (17)

with $\beta = \delta m^* s^2 / 2k \alpha E^{4/5}$, where E must be expressed in volts per centimeter. The integral $I(\beta)$ cannot easily be calculated in the general case; however, an approximate expression can be given for small values of β . When $\beta \ll 1$, it may be neglected in the integrand of $I(\beta)$. Therefore

$$I(\beta) \simeq \frac{5}{2} \int_{\beta}^{+\infty} \frac{\exp(-u^{\frac{5}{2}})}{u} du,$$

which may be approximated by³⁰

$$I(\beta) \simeq \left[\ln\left(1/1.78\beta^{\frac{1}{2}}\right) + \beta^{\frac{1}{2}} \right].$$
(18)

The second term may be neglected compared to the logarithm, and the approximate expression for $B_{p}(E)$ is then

$$B_{p}(E) \simeq 10^{-5} T^{-2} E^{-1.2} \left[\ln E + \frac{1}{2} \ln \frac{3.2 \times 10^{3}}{(0.24\delta)^{\frac{5}{2}}} \right].$$
(19)

This recombination rate decreases with the applied electric field and the temperature.³¹ For $T = 4.2^{\circ}$ K and an applied electric field E=3 V/cm, a value $B_p=7.83$ $\times 10^{-7}$ cm³/sec is found. Thus it is seen that the formerly calculated optical recombination rate $B_0(E)$ is totally negligible compared to $B_p(E)$.

The magnitude of B_i , the Auger recombination rate, has been directly measured⁸ for the range of lattice temperatures 4°-10°K, near breakdown; the result is $B_i \simeq 10^{-17}$ cm⁶/sec. This means that in the case under consideration, considering the electronic density, the three-body recombination may also be neglected. Therefore, the only efficient recombination process before and at the outset of breakdown is the giant-trap-type one. In the following we shall take $B_T(E) = B_p(E)$.

D. Impact Ionization Rate

In order to calculate $A_i(T_e)$, the cross section $\sigma_i(\epsilon)$ for impact ionization of an hydrogen-like center must be known. An evaluation of A_i at thermal equilibrium was made by Sclar and Burstein.24 They used the cross section of a hydrogen-like atom calculated in the Born approximation.

$$\sigma_i(\epsilon) = (0.285\pi e^4/D\epsilon_i\epsilon) \ln(4\epsilon D/0.048\epsilon_i).$$

This expression is only valid for high energy electrons $(\epsilon \gg \epsilon_i)$, and moreover it does not go to zero for $\epsilon = \epsilon_i$: the value is then $\sigma_i(\epsilon_i) = 2.78 \times 10^{-11}$ cm², which is somewhat overestimated.32

The simplest assumption is to consider the cross section σ_i as constant. Because of the very rapid decrease of the distribution function, the results should not be sensitive to this very crude approximation.³³ This was made by Yamashita,¹² and he took $\sigma_i = \pi (Da_0)^2$ =2.26×10⁻¹⁴ cm². This choice is somewhat arbitrary, since it does not correspond to any physical quantity in the semiconductor. Here it will also be taken $\sigma_i(\epsilon) = \sigma_i$ = constant, but this will be adjusted to the experiment, thus introducing the only adjustable parameter of this theory.

Now the impact ionization rate is

$$A_{i}(T_{e}) = (\sigma_{i}/\Gamma(3/5))(2kT_{e}/m^{*})^{\frac{1}{2}}\Gamma[\frac{4}{5},(\epsilon_{i}/kT_{e})^{\frac{5}{2}}], \quad (20)$$

²⁹ With slightly different values (D=12 and $s=4\times10^5$ cm/sec), Lax²⁸ finds $\sigma_1=7\times10^{-9}$ cm².

³⁰ The value of $I(\beta)$ obtained in Eq. (18) has been compared to the one calculated by a computing machine using the correct expression (16). The approximation is found to be good, better than 10% for $\beta \leq 2 \times 10^{-2}$. For example, at $T = 4^{\circ}$ K, $\beta < 2 \times 10^{-2}$ as soon as $E \geq 3$ V/cm.

³¹ It must be pointed out that in their experiments Ascarelli and Brown²⁶ found a variation of $B_p(T)$ in T^{-2} . However, it is im-probable that the electrons were somewhat "heated" and in fact the observed law would be in $T^{-3.5}$. This would seem to indicate a ³² The geometrical cross section of a hydrogen-like center is

 $[\]sigma_g = \pi (mDa_0/m^*)^2$ and in germanium $\sigma_d = 3.62 \times 10^{-13} \text{ cm}^2$. ³³ Such an attitude was already suggested by Sohm [J. C. Sohm, J. Phys. Chem. Solids **18**, 181 (1961)].



FIG. 1. The impact ionization rate vs the applied electric field.

where

$$\Gamma(a,x) \equiv \int_x^\infty t^{a-1} e^{-t} dt$$

is the incomplete Γ function.

Expression (20) cannot be easily calculated for any value of $x = (\epsilon_i / kT_e)^{\frac{5}{2}}$ and it was calculated by an analog computer. The result is shown in Fig. 1. The constant σ_i was adjusted by using the sample 45-10 (see Table I) measured by Koenig and Brown.³⁴ For this, Eq. (3) and the formerly calculated expression for $B_T(E)$ were used. This sample was chosen since its properties are known with a good accuracy; the error on the compensation degree is felt to be less than 15%.³⁴ A value $\sigma_i = 1.05$ $\times 10^{-14}$ cm² is found in this way.

The theoretical curve $A_i(E)$ shows an edge near 3 V/cm. This is quite satisfactory for it shows that breakdown will hardly be observed below this value of the applied field. This agrees with the data (see below). Furthermore, this confirms that A_i is negligible at thermal equilibrium.

IV. DISCUSSION OF RESULTS. CONCLUSIONS

There were until now few available data concerning high-purity germanium.8 Fortunately, many samples were very recently measured by Koenig and Brown.^{34,35} The details concerning these specimens are given in Table I. The measurements were performed at a temperature $T = 5^{\circ}$ K.

The data are compared to the theory in Fig. 2 (also shown is the theoretical curve obtained by Koenig). The agreement may be regarded as satisfactory, considering the scatter in the data. The estimate of the compensation degree in high-purity semiconductors is a delicate

problem, and in the present case it was calculated by determining the partial scattering due to ionized impurities. The theoretical results might lead to a new method for determining the compensation degree by measuring the breakdown field at liquid-helium temperatures. However, the accuracy would be rather poor mainly for two reasons. First, the value of the breakdown field becomes very sensitive to $(N_D - N_A)/N_A$ only for large compensation degrees. This is connected with the fact that the impact ionization rate $A_i(E)$ presents an edge near E=3 V/cm. The second reason is directly related to the method here employed to calculate $A_i(E)$. Since the constant σ_i is adjusted to an experimental value, there is an uncertainty introduced. However, it must be pointed out, considering the agreement between theory and experiment, that the effective dependence of the ionization cross section with the electron energy is certainly damped out by the use of the distribution function. The knowledge of this quantity would therefore only allow us to entirely separate the theoretical results from the experimental uncertainties. This refinement would, however, be fairly important in this point of view.

The theoretical variation of the breakdown field E_b with temperature is compared with the data for Koenig's sample n-WLB 28-6¹⁰ in Fig. 3. The agreement may be considered as satisfactory. It must be pointed out that the shift between the two curves might well be explained by a difference in the experimental and theoretical criterions for breakdown. In the first case the breakdown field is taken as the value where the J-Ecurve shows a marked change in slope, when in the second case the breakdown field is the asymptotic value [see Eq. (3)]. In the present case, the agreement is to be considered as a qualitative one.

A further limitation arises from the dependence of the results on the theory describing the recombination process. Lax²⁸ assumed that the recombination probability is independent of the binding energy of the electron to the impurity. However, it has been found experimentally26 that the nature of the special hydro-

TABLE I. Experimental results of Koenig and Brown.³⁴

Sample	Net donor concen- tration ND-NA (cm ⁻³)	Acceptor concen- tration N _A (cm ⁻³)	Compen- sation $(N_D - N_A) / N_A$	Break- down field E _b (V/cm)
$\begin{array}{c} \text{n-WLB-33-A^{ab}} \\ 46-2 \\ 31 \\ 42-1 \\ 41-15 \\ (As) \\ 44-1 \\ 28 \\ \text{n-WLB-28-6^{b}} \\ 45-10^{c} \\ 45-2 \end{array}$	$\begin{array}{c} 1.0 \times 10^{12} \\ 4.3 \times 10^{12} \\ 7 \times 10^{12} \\ 2.5 \times 10^{13} \\ 3.1 \times 10^{13} \\ 6.4 \times 10^{13} \\ 1.5 \times 10^{13} \\ 1.5 \times 10^{13} \\ 1.87 \times 10^{13} \\ 3.9 \times 10^{18} \end{array}$	$\begin{array}{c} \simeq 1.3 \times 10^{12} \\ \simeq 2.6 \times 10^{12} \\ \simeq 2 \times 10^{12} \\ \simeq 8.7 \times 10^{12} \\ \simeq 6.8 \times 10^{12} \\ \simeq 4.8 \times 10^{12} \\ \simeq 1.6 \times 10^{12} \\ \simeq 1.6 \times 10^{12} \\ \simeq 6.3 \times 10^{11} \\ \simeq 1.6 \times 10^{12} \end{array}$	$\begin{array}{c} \simeq 0.77 \\ \simeq 1.7 \\ \simeq 3.5 \\ \simeq 2.9 \\ \simeq 4.6 \\ \simeq 13 \\ \simeq 9.3 \\ \simeq 9.3 \\ \simeq 30 \\ \simeq 25 \end{array}$	$ \begin{array}{r} 14 \\ 15.1 \\ 14.9 \\ 8 \\ 7.6 \\ 5.5 \\ 4.8 \\ 4.6 \\ 4 \\ 3.6 \\ \end{array} $

^a For this sample, the breakdown field was measured at a temperature T = 4.55 °K. Its orientation was [110]. However, correcting for this would rise E_b by 15%. ^b Compensation for these samples was carefully reestimated. ^c The constant σ_i was adjusted using this sample, since it is the one for which things are best known.

³⁴ S. H. Koenig and R. D. Brown (private communication).

³⁵ A detailed account of these experiments, together with a theoretical interpretation, will be soon published [S. H. Koenig (private communication)].

gen-like impurity which is involved has an influence on the value of the recombination cross section. This shows that some progress is to be made in the theoretical treatment of the cascade capture process. Possible refinements of the theory of the low-temperature behavior of a semiconductor in high electric fields directly depend on these features.

Finally, it must be pointed out that effects arising from the anisotropy of the constant energy surfaces were neglected here. It is known experimentally¹ that the value of the breakdown field slightly depends on the orientation of the sample along the applied electric field. However, as this effect is of second order, it is felt that the use of an anisotropic distribution function would only introduce minor changes in the results. The formerly discussed limitations of the theory are felt to be much more important.

In any case, some positive results may be deduced from this theoretical study. The relative importance of the various energy losses for the electrons is clearly established. In the case of high-purity germanium containing shallow impurities only the acoustical phonon emission is to be considered. For silicon, however, the emission of an optical phonon will have some probability



FIG. 2. The breakdown field E_b vs $(N_D - N_A)/N_A$, at $T = 5^{\circ}$ K. Sample 41–15 was As-doped, and correcting for this increases the theoretical value of E_b by 25%, thus fitting fairly well the experimental value. The dashed line corresponds to Koenig's theoretical interpretation (to be published).

FIG. 3. The breakdown field E_b vs the temperature. The continuous curve corresponds to Koenig's data for sample n-WLB-28-6; the theory is represented by the dashed line.



of occurring. This was at one time advanced as the cause for nonobservation of low-temperature breakdown in silicon.³⁶ A theoretical analysis of this phenomenon would certainly give some information on this scattering process. Unfortunately there is as yet a lack of experimental results.³⁷

In high-purity germanium the breakdown process is mainly governed by the relative variations of the impact ionization rate and of the recombination rate with successive one-phonon transitions, as the applied electric field is increased. Other processes are negligible. This means that the emission of light detected when a sample breaks down^{26,38} is mainly due to photon emission at the last step of the cascade capture process, i.e., when the electron jumps from the first excited state down to the ground state. To confirm this theoretical result, a study of the emitted recombination light would be in order.

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⁸⁸ S. H. Koenig and R. D. Brown, III, Phys. Rev. Letters 4, 170 (1960).

⁸⁶ M. A. Lampert, F. Herman, and M. C. Steele, Phys. Rev. Letters 2, 394 (1959).

³⁷ Experiments on high-purity *n*-type silicon are in progress in this Laboratory.