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Impact ionization in n-germanium, 4–9.5 °K

W. Pickin

Escuela Nacional de Estudios Profesionales Cuautitlán, Apartado Postal No. 25, Cuautitlán Izcalli, Estado de México, México

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A new theory for describing nonequilibrium phenomena involving shallow donor states is applied to the problem of impact ionization of shallow donors in n-germanium at low temperatures; it allows the calculation of the whole electron-concentration–field characteristic $n(E)$, and not just the breakdown field E_B. The results are in good agreement with experiment, especially so for the purer samples considered. The excited states of the donors are shown to be of utmost importance both for the ionization and for the recombination. At one extreme they produce nonlinear effects which provide a strong mechanism for the S breakdown (current-controlled negative resistance) observed experimentally; Kurosawa's mechanism is shown to be correspondingly weak and to be vanishing for electric fields much above 6 V/cm. In normal (non-S) breakdown a regime is identified in which, with allowance for the effect of the excited states on ionization, some analogy can be drawn with the usual Price breakdown criterion. A new, non-Price-breakdown regime is shown to result from the effect of impact processes on transitions from the excited states. The border between the two regimes is marked by a strongly temperature-dependent sample-compensation ratio, the purer samples considered lying in the new regime at 7 °K. The distribution functions considered for electrons in the conduction band were supposed dominated by acoustic-phonon scattering; some indications were found of the presence of additional scattering mechanisms in less pure samples and at high values of n. The conduction-band anisotropy of germanium was taken into account; the donor levels were not assumed to be hydrogenic. No appeal was made to the principle of detailed balance. The results indicate that calculations of this type on nonequilibrium phenomena are now practicable, and that despite the apparent complexity of such systems their qualitative behavior can be understood in terms of a few simple concepts.

INTRODUCTION

Application to a sample of n-germanium at temperatures less than some 15 °K of an increasing electric field E is known to result in a steep increase of current density j near a "breakdown" field E_B which is typically of several V/cm; in some cases a genuine S-shaped breakdown results in which the current can later be sustained by a field $E_S < E_B$. The same phenomena occur in other semiconductors at temperatures sufficiently low that in zero field the carriers are "frozen out" into shallow traps; it has long been established that they are due to impact ionization of the traps by hot carriers, this leading to an increase of several orders of magnitude in carrier concentration n and thus in current.

Experimental curves of $n(E)$ for pure samples of n-germanium at 7 and 9.5 °K have been published by Koenig, Brown, and Schillinger[1] (KBS). Previous theoretical work[2] has attempted the calculation of breakdown fields for these samples, using a breakdown criterion due to P. J. Price.[3]

Analysis[1,4,5] has usually been based on an equation

$$\frac{dn}{dt} = (N_D - N_A - n)(A^P + nA^I) - n(N_A + n)(B^P + nB^I) . \tag{1}$$

Here N_D and N_A are the donor and acceptor concentrations and A^P, A^I, B^P, and B^I are suitably defined rate coefficients; A refers to (ionizing) transitions from donor to conduction band, B to the corresponding inverse (recombination) transitions; the superscripts P and I refer to phonon and impact processes, respectively; in the former the transition energy is provided by or lost to a phonon; in the latter a conduction electron plays the same role. $N_D - N_A - n$ is the number of filled donors, $N_A + n$ the number of empty donors.

To first order in n, (1) gives in the steady state, with neglect of a small term A^P in the denominator,

$$n \approx (N_D - N_A)A^P / [B^P N_A - (N_D - N_A)A^I] . \tag{2}$$

The Price criterion for breakdown is then the vanishing of the denominator of (2).

Pioneering work by Lax,[6] later refined,[7-11] showed that the donor excited states were important in low-temperature recombination, since electrons could "cascade" down through the ladder of states, emitting a phonon on each transition. The net recombination rate would then be proportional to $\sum_i B_i^P P_i$ (summed over all states i of the donor), P_i being the "sticking probability" that an electron in state i would indeed reach the ground state ($i = 1$); and the terms for higher states in this sum turned out to be much greater than the ground-state term B_1^P ($P_1 = 1$ by definition).

The sticking probabilities P_i were defined by a

set of equations "analogous to the Kolmogorov equation for Markov processes"[10]:

$$P_i = \sum_{j \neq i} P_{ij} P_j , \tag{3}$$

P_{ij} being the probability that an electron in state i would go to state j rather than to any other state, so that

$$P_{ij} = W^P_{ij} / \left(A^P_i + \sum_{k \neq i} W^P_{ik} \right), \tag{4}$$

where W^P_{ij} is the rate coefficient for phonon transitions from state i to state j.

The only account taken of the excited states in the impact theories of Refs. 1–5 was a replacement of B^P and B^I in (1) by the appropriate Lax formula. It will be seen that such a procedure is wholly inadequate.

The present paper (of which preliminary results[12] have already appeared) deals with low-temperature nonequilibrium phenomena involving shallow donors in germanium, and stems from the realization that the donor excited states dominate every aspect of these phenomena, not just the recombination aspects treated by Lax.[6] Instead of his formulation in terms of Markoff processes, all these phenomena are treated as solutions of the rate equations for the system of donors and conduction band; these may be written

$$\frac{dn_i}{dt} = -n_i \left(\sum_{j \neq i} W_{ij} + A_i \right) + \sum_{j \neq i} W_{ji} n_j + n(N_A + n) B_i , \qquad i = 1\text{–}N . \tag{5}$$

Here n_i is the population (per unit volume) of donor level i, and N (~6) is the number of donor levels; the donors are supposed to be capable of no more than single occupancy, so that the number of filled donors is still $N_D - N_A - n$ and the number of empty donors is still $N_A + n$. The various rate coefficients would in general contain contributions from impact (Auger), phonon, and radiative (superscript R) processes, with

$$W_{ij} = nW^I_{ij} + W^P_{ij} + W^R_{ij} ,$$

$$A_i = nA^I_i + A^P_i + A^R_i ,$$

$$B_i = nB^I_i + B^P_i + B^R_i$$

(though the latter may be neglected in the absence of photoexcitation in the experimental conditions). Together with the conservation condition

$$N_D - N_A = n + \sum_i n_i , \tag{6}$$

Eqs. (5) form a set of $N+1$ equations in the $N+1$ unknowns n_i, $i = 1\text{–}N$, and n. Given that all $N(N+1)$ rate coefficients for each process may be calculated as functions of temperature and field (which implies, of course, a knowledge of the electron distribution function) and that the above equations may be solved for the (experimentally most significant) variable n, one is then in possession of a complete description of all such nonequilibrium phenomena.

The author has described elsewhere[12-14] the solution of the (nonlinear) rate equations for both steady-state and transient conditions. It is the former solution that is of interest here. The result may be expressed as a balance between ionization and recombination of the form

$$(N_D - N_A - n) A = n(N_A + n) B , \tag{7}$$

where A is a net ionization rate coefficient given by

$$A = A_1 + \sum_{i=2}^{N} W_{1i} (1 - q_i) , \tag{8}$$

and B is a net recombination rate coefficient given by

$$B = \sum_{i=1}^{N} B_i q_i . \tag{9}$$

The q_i are modified sticking probabilities, analogous to the P_i of the former cascade theories,[6,8,10] though including terms for impact processes as well as the phonon terms; they satisfy

$$\left(\sum_{j \neq i} W_{ij} + A_i + W_{1i} \right) q_i - \sum_{\substack{j \neq i \\ j \neq 1}} (W_{ij} - W_{1j}) q_j = W_{i1} + \sum_{j \neq 1} W_{1j} + A_1 , \qquad i = 2\text{–}N , \tag{10}$$

with $q_1 = 1$. The derivation is directly from (5) and (6) without appeal to Markoff processes, but (9) is clearly analogous to Lax's result already quoted, and means that capture occurs by a cascade process. (8) clearly shows that ionization occurs by inverse cascade, $1 - q_i$ being analogous to an "escape probability"; the direct term A_1 in (8) is nearly always negligible in comparison with the indirect terms. Apart from small terms involving excitation from the ground state, (10) can be seen to be analogous to (3) and (4). It should be borne in mind that the q_i are functions of n through their dependence on the rate coefficients, and that (7) is thus highly nonlinear in n; however, all the nonlinearity is concentrated there, the q_i being solutions of the linear equations (10), and the obvious properties of the q_i as sticking probabilities will be seen below to remove any difficulty in the solution of (7). Indeed, the nonlinearity will be shown to be interesting in its own right, as leading to S breakdown.

The numerical program of the present work is

thus as follows: given a field E, all phonon and impact rate coefficients are calculated; the q_i are then obtained from (10) as functions of n; (7) is then solved, essentially by an intersection technique, as will now be described.

SOLUTION OF THE BALANCE EQUATION (7)

Define a "donor function" $D(n)=A/B$, and a "sample function" $S(n)=n(N_A+n)/(N_D-N_A-n)$, so that (7) becomes

$$D(n)=S(n) \tag{11}$$

and for given E the appropriate steady-state value of n can be found as the intersection of the curves $S(n)$ and $D(n)$.

$D(n)$ hides a formally very complicated dependence on n and E, but is, again formally, a property of a single donor.

$S(n)$, on the other hand, is independent of the type of donor (e.g., of its energy-level structure) and dependent only on the values of N_D and N_A in a particular sample. Since the behavior of $S(n)$ is trivial, interest resides mainly in the form of the curve $D(n)$, and in its variation with field; a knowledge of this for a particular type of donor enables $n(E)$ to be obtained for any sample.

By definition

$$D(n)=\frac{\left(A_1^P+\sum_j W_{1j}^P(1-q_j)\right)+n\left(A_1^I+\sum_j W_{1j}^I(1-q_j)\right)}{\left(\sum_j B_j^P q_j\right)+n\left(\sum_j B_j^I q_j\right)}, \tag{12}$$

or, following the large parentheses,

$$D(n)=\frac{A^P(\vec{q})+nA^I(\vec{q})}{B^P(\vec{q})+nB^I(\vec{q})} \tag{13}$$

in analogy with (1); but now A^P, A^I, B^P, and B^I depend on the q_i and through them on n and on both phonon and impact rate coefficients. And, as mentioned, the terms A^P and A^I in (13) do not represent the terms A^P and A^I that would appear in a $D(n)$ deduced from (1), but are usually completely dominated by the terms $\sum_j W_{1j}^P(1-q_j)$ and $\sum_j W_{1j}^I(1-q_j)$. In other words, ionization occurs by a type of inverse cascade process. Previous neglect of this has led in effect to gross underestimates of the magnitude of $D(n)$, as will be seen.

In equilibrium (i.e., in zero field) $D(n)$ is flat, since then $A^P/B^P=A^I/B^I$, each being equal to a quantity determined by purely statistical considerations. With increasing field the curve $D(n)$ is monotonically raised.

An obvious approximation $D_1(n)$ to $D(n)$ is obtained by supposing that the q_i maintain always

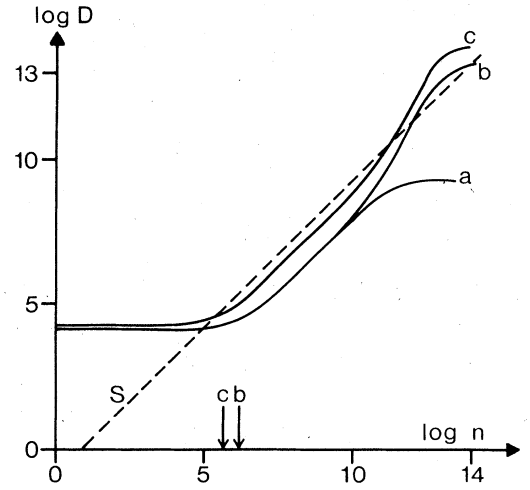

FIG. 1. General behavior of $D(n)$ and $D_1(n)$ (Maxwellian distribution, $T=4$ °K), a: $D_1(n)$, $T_e=18.0$ °K; b: $D(n)$, $T_e=18.0$ °K; c: $D(n)$, $T_e=22.6$ °K. The arrows mark the values of $\tilde{n}$ for curves b and c. The value of n_q ($\sim 10^9$ cm^{-3}) can be seen from the point at which curves a and b part company. Note that $D(n)$ is flat for $n<\tilde{n}$, is a straight line of unit slope for $\tilde{n}<n<n_q$, goes supralinear for $n>n_q$, and then flattens off for $n\sim 10^{14}$ cm^{-3}. [S denotes a typical curve for $S(n)$; for such a sample curve c corresponds to a field a little below (Price) breakdown.]

their equilibrium values q_i', i.e., that impact terms do not affect the q_i. This turns out to be true for $n<n_q$ with $n_q\sim 10^9$ cm^{-3} in reasonable breakdown fields. So for $n<n_q$

$$D(n)\approx D_1(n)=\frac{A^P(\vec{q}')+nA^I(\vec{q}')}{B^P(\vec{q}')+nB^I(\vec{q}')}. \tag{14}$$

It is also found that $nB^I(\vec{q})$ is only comparable to $B^P(\vec{q})$ for $n\gg n_q$.

On a log-log plot $D_1(n)$ is thus flat for small n, switching sharply to a straight line of unit slope at $n=\tilde{n}$ where $\tilde{n}=A^P(\vec{q}')/A^I(\vec{q}')$. It flattens off again as $nB^I(\vec{q}')$ comes into play; see curve a of Fig. 1. As the field is raised $\tilde{n}$ is reduced since $A^I(\vec{q}')$ increases and $A^P(\vec{q}')$ is independent of field. And the whole curve $D_1(n)$ is shifted upwards by a slight decrease in $B^P(\vec{q}')$, as shown by the behavior of the lower half of curve c of Fig. 1.

For $n\ll N_A$, $S(n)\approx Cn$, where $C=N_A/(N_D-N_A)$. On the log-log plot $S(n)$ is thus also a straight line of unit slope, which begins to curve upwards as n nears N_A and goes to infinity at $n=N_D-N_A$; examples can be seen in the figures. As E is increased there must eventually come a breakdown value E_B for which $S(n)$ and $D_1(n)$ become coincident in their linear parts; comparing intercepts one obtains

$$A^I(\vec{q}')=CB^P(\vec{q}'), \tag{15}$$

in obvious analogy to the Price criterion [cf. (2)], and so referred to hereafter, but with the new forms for A^I and B^P.

Curve b of Fig. 1 shows the full curve $D(n)$ corresponding to the $D_1(n)$ of curve a. For $n > n_q$ $D(n)$ increases supralinearly, as $D_1(n)$ never can [cf. (14)]; this is because once impact transitions are operative among the excited states the q_i are reduced from their equilibrium values, so that the numerator in (13) is increased and the denominator decreased [with respect to the values of (14)].

As is shown in Fig. 1 $D(n)$ can thus cut $S(n)$ a second time, which is suggestive of S breakdown, discussed below. Finally $D(n)$, too, flattens off.

NON-PRICE BREAKDOWN: A NEW REGIME

Figure 1 presupposed $\tilde{n} < n_q$. Figure 2 shows a case in which the sample is well into breakdown, but in which $\tilde{n} \gg n_q$ so that the breakdown is coming almost entirely from the change of the q_i [since $D_1(n)$ remains flat]; the breakdown is thus due in this case to the excited states. Such breakdown cannot, of course, be described by the Price criterion but needs brute numerical calculation of $n(E)$.

That n_q can be greater than $\tilde{n}$ arises because n_q is determined by impact transitions among the excited states, which are relatively little affected by changes of field (see below), whereas $\tilde{n}(=A^P/A^I)$ involves the impact transitions from the ground state, which are strongly affected. Given therefore the "usual" situation where $n_q > \tilde{n}$, a reduction of the field must eventually produce a $D(n)$ with $n_q < \tilde{n}$. If C is so small and $S(n)$ thus so far to the right that the sample is already in breakdown, then the breakdown is "non-Price."

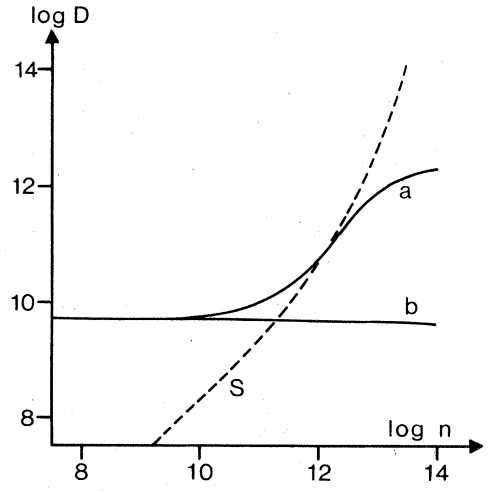

FIG. 2. $D(n)$ and $D_1(n)$ in a non-Price regime (Stratton distribution, $E = 3.0$ V/cm, $T_e = 18.1$ °K, $T = 7$ °K). a: $D(n)$; b: $D_1(n)$; S is $S(n)$ for sample 45-2 of KBS. Here $D_1(n)$ is flat, so that $\tilde{n} > 10^{14}$ cm^{-3}; on the other hand, n_q is still about 10^9 cm^{-3} so that $D(n)$ is far from flat. For this sample $S(n)$ is far enough to the right for the sample to be clearly in breakdown, and the breakdown is due entirely to the difference between $D(n)$ and $D_1(n)$, i.e., to the excited states.

For a given temperature, and as always for a given donor, the boundary between the two regimes is thus marked by a value C_0 of C, with $C_0 = A^I/B^P$ precisely for that electric field for which $\tilde{n} = n_q$. Breakdown is "Price" for $C > C_0$, "non-Price" for $C < C_0$. As C decreases below C_0 the breakdown is expected to become progressively less sharp from simple geometrical consideration, $D(n)$ being considered as pinned at a nearly constant value of n_q.

Rough calculations for the present donors show $C_0 \sim 10^{-6}$ at 4 °K, $\sim 10^{-1}$ at 7 °K, and ~ 1 at 9.5 °K. The steep rise of C_0 with temperature is again because of the different behavior of $\tilde{n}$ and n_q, the former being strongly affected by change of temperature and the latter little affected.

Thus at 4 °K the Price criterion applies for all reasonable samples. But at 7 °K samples 45-10 and 45-2 of KBS already lie in the new regime (see Table VI). Previous calculations[2] for these samples which applied the Price criterion must be regarded as largely meaningless.

SIMPLIFIED ANALYSIS

Table I confirms that the excited states are capable of producing the required increase in $D(n)$. It also emphasizes further how a complicated situation involving 84 rate coefficients (with $N = 6$ in this case) is susceptible of simple analysis using the concept of sticking probability. It is based on the idea that only $W_{12}(1 - q_2)$ makes a significant contribution to A (usually a very good assumption) and that only $B_6 q_6$ makes any contribution to B (about 50% right). Then

$$D(n) \approx \frac{W_{12}^P(1-q_2) + n\,W_{12}^I(1-q_2)}{B_6^P q_6 + n B_6^I q_6} \tag{16}$$

$$= \frac{1-q_2}{q_6}\,\frac{W_{12}^P + n\,W_{12}^I}{B_6^P + n B_6^I} \tag{17}$$

$$= \frac{1-q_2}{q_6}\,\frac{q_6'}{1-q_2'}\,D_1(n). \tag{18}$$

Table I then shows the two sides of (18) for a field at which $D_1(n)$ is nearly flat. Agreement is astonishingly close. Table II shows the same for a higher field in which $D_1(n)$ is far from flat. For both tables the temperature is 4 °K, q_2' is virtually unity, and a large contribution to the difference between D and D_1 is made by the factor $(1 - q_2)/(1 - q_2')$ in (18).

At 7 °K, on the other hand, $q_2 \sim 0.3$, so that the

TABLE I. D^{approx} defined by (18) as an excellent approximation to $D(n)$ at 4 °K (Stratton distribution, $E=2$ V/cm, $T_e=18$ °K). The flatness of $D_1(n)$ shows that any breakdown here would be due entirely to the changes in the q_i.

n	$D(n)$	D^{approx}	$D_1(n)$
10^{10}	2.954×10^{4}	2.940×10^{4}	2.117×10^{4}
10^{11}	1.417×10^{5}	1.388×10^{5}	2.817×10^{4}
10^{12}	4.620×10^{6}	4.562×10^{6}	3.919×10^{4}
10^{13}	2.214×10^{8}	2.358×10^{8}	4.217×10^{4}
10^{14}	8.373×10^{8}	9.631×10^{8}	4.252×10^{4}

factor $(1-q_2)/(1-q_2')$ can change by at most 50% with increasing n. So at 7 °K the additional liberty can be taken with (18) of putting that factor equal to unity. Table III shows the results.

TEMPERATURE DEPENDENCE OF $D(n)$

Figure 3 shows the variation of $D(n)$ with (lattice) temperature T. The most significant change as T increases is the large increase of $A^P(\vec{q}')$; this raises $D(n)$ for $n<\tilde{n}$, and moves $\tilde{n}$ to the right by the same amount. Of themselves these changes would leave the Price regime E_B unaltered.

In fact, E_B is slightly decreased, because of a slight reduction of $B^P(\vec{q}')$ (caused by reduction of the q_i') which again raises $D(n)$.

S BREAKDOWN

It is clear in all cases that $D(n)$ must cut $S(n)$ at least once, so that the existence of at least one solution to the equation $D(n)=S(n)$ is assured. The presence of a supralinear bulge in $D(n)$ implies that it can cut $S(n)$ twice more, so that three values of n may exist for which the rates of entry and departure of electrons are in balance in the conduction band. However, the middle value (point B of Fig. 4) is clearly unstable. For suppose n to be increased from there by a fluctuation; then we pass to a part of the graph where $D>S$; here $A(N_D-N_A-n)>Bn\,(N_A+n)$, so that electrons are entering the conduction band faster than they are leaving it; thus n increases further, and we run immediately up the graph to point C. Point C is stable, as D there cuts S from above.

To prove S breakdown it is necessary to show a sustaining field E_S less than E_B. Consider again the situation shown in Fig. 4. If this has arisen by the field increasing from zero it appears likely that the physical solution would be that represented by A; the solution already developed at C appears inaccessible, as it would require a huge fluctuation in the value of n for such a solution to appear in any region of the sample, and such a fluctuation would be "opposed" by the large difference between S and D, between points A and B. So the field shown is less than the breakdown field E_B. If, on the other hand, Fig. 4 shows a situation in which the field is decreasing from a value slightly beyond E_B, then it appears that the physical solution would be that represented by C; point A remains as yet inaccessible, blocked by the large difference between D and S between points

TABLE II. D^{approx} defined by (18) as an excellent approximation to $D(n)$ at 4 °K (Stratton distribution, $E=4$ V/cm, $T_e=23$ °K). $D_1(n)$ is not flat in this case.

n	$D(n)$	D^{approx}	$D_1(n)$
10^{10}	7.371×10^{7}	7.546×10^{7}	4.124×10^{7}
10^{11}	3.057×10^{9}	3.174×10^{9}	2.946×10^{8}
10^{12}	3.047×10^{11}	3.235×10^{11}	7.650×10^{8}
10^{13}	1.602×10^{13}	1.955×10^{13}	9.104×10^{8}
10^{14}	4.445×10^{13}	6.156×10^{13}	9.280×10^{8}

TABLE III. D^{approx} defined by $(q_6'/q_6)D_1(n)$ as a good approximation to $D(n)$ at 7 °K (Stratton distribution, $E=3$ V/cm, $T_e=18$ °K).

n	$D(n)$	D^{approx}	$D_1(n)$
10^{10}	5.63×10^{9}	5.42×10^{9}	5.05×10^{9}
10^{11}	9.67×10^{9}	8.05×10^{9}	4.90×10^{9}
10^{12}	5.54×10^{10}	3.89×10^{10}	4.56×10^{9}
10^{13}	7.30×10^{11}	5.40×10^{11}	4.46×10^{9}
10^{14}	1.92×10^{12}	1.57×10^{12}	4.40×10^{9}

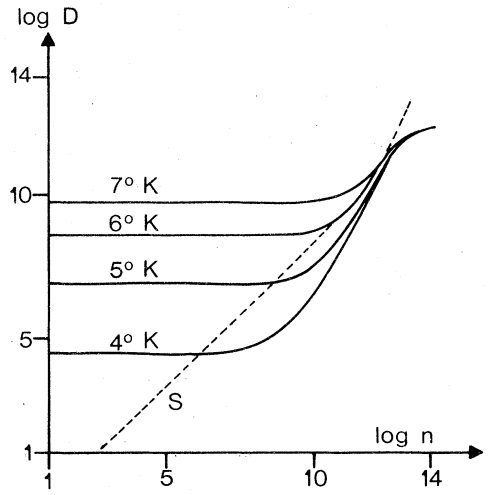

FIG. 3. Temperature dependence of $D(n)$ (Stratton distribution, $E=3.0$ V/cm, $T_e=18.1$ °K). S is $S(n)$ for sample 45-2 of KBS. This sample would be just in breakdown at 6 °K, well into breakdown at 7 °K, and far short of breakdown at 4 and 5 °K.

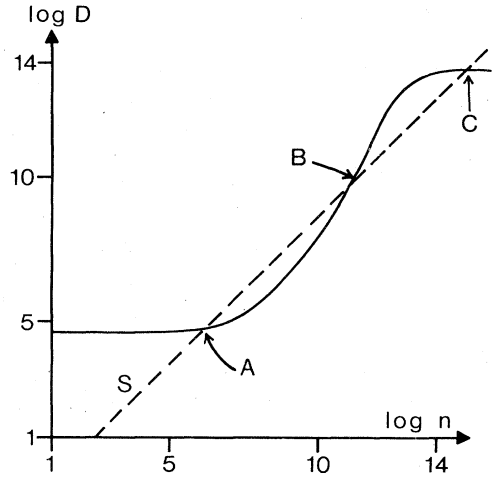

FIG. 4. Supralinearity of $D(n)$ and S breakdown (Stratton distribution, $E=4.0$ V/cm, $T_e=22.8\,^\circ$K, $T=4\,^\circ$K). S is $S(n)$ for a typical sample with fairly high N_A. Points A and C represent stable values of n; that of point A will obtain if the field shown is increasing, that of point C if it is decreasing. Point B represents an unstable solution of the equation $D(n)=S(n)$.

C and B. So the field shown is greater than E_S.

A fortiori $E_S < E_B$; the difference ΔE between E_B and E_S is clearly related to the width of the bulge in $D(n)$, and is found to be nontrivial in magnitude, typically of several V/cm.

The present calculations thus show that S breakdown can be due to excited states, and in order to explain the occurrence of S breakdown it is not now necessary to postulate some dependence of the distribution function on donor population.

Indeed, it is rather that some such dependence is necessary to explain its experimentally observed nonoccurrence in many situations, for the "excited-states" mechanism as presented above is clearly too strong to explain the experimental facts; it predicts almost universal occurrence of S breakdown in the Price regime, and possible occurrence in the new regime, as $D(n)$ can show some supralinearity even when $D_1(n)$ is nearly flat.

The dependence required is thus one which makes the distribution *harder* to heat as n is increased, as this would be capable of removing the bulge in $D(n)$ in some circumstances. The matter is discussed further below in connection with ionized-impurity scattering.

On the other hand, supralinearity of $S(n)$ does not always guarantee the occurrence of S breakdown; for pure samples (i.e., with small N_A) the upward curving of $S(n)$ near N_A can deny the extra intersections.

DISTRIBUTION FUNCTIONS

All impact rate coefficients and the B_i^P are integrals of cross sections over the spherical part $f_0(\epsilon)$ of the electron distribution in the conduction band, with due attention to the threshold energies involved. The behavior of $f_0(\epsilon)$ is critical to the results; indeed, it is the only point at which the electric field enters the theory. Only fields applied in the (100) direction were considered, to ensure equal heating of all four valleys of the conduction band, as in the experiments of KBS. Ideally Monte Carlo calculations would be used; in their absence the present calculations follow Zylbersztejn[2] in supposing that the (non-Maxwellian) distribution function is determined only by acoustic phonon scattering, but consider three resulting analytic forms of distribution function.

Preferred for $E \gtrsim 3$ V/cm (again following Zylbersztejn[2]) is the Stratton[15] distribution, based upon the zero-point approximation for the phonons. This gives a first possible distribution function

$$f_0^{(1)}(\epsilon) \propto \exp[-(\epsilon/kT_e')^{5/2}], \tag{19}$$

with an electron temperature $T_e=0.45\ T_e'$. The conduction-band anisotropy in germanium was taken into account, based on the work of Budd,[16] by the use of an $E-T_e$ relationship:

$$T_e' = 16.78E^{4/5} \quad (E \text{ in V/cm}), \tag{20}$$

in contrast to the isotropic result

$$T_e' = 31.1E^{4/5}$$

used by Zylbersztejn[2]; anisotropy makes the electrons harder to heat.

For lower fields the lattice oscillators are better treated by the equipartition approximation.[17] This gives a second choice, from Conwell,[18] again including the effects of anisotropy:

$$f_0^{(2)}(\epsilon) \propto (\epsilon/kT + S^*)^{S^*} \exp(-\epsilon/kT), \tag{21}$$

with

$$S^* = 503.1E^2/T^3 \quad (E \text{ in V/cm}), \tag{22}$$

and an $E-T_e$ relationship,

$$E = [2T_eT(T_e - T)/503.1]^{1/2}. \tag{23}$$

The usual data on germanium constants were used above in (20) and (22), apart from the values of the deformation potentials where Keyes' values[19] $\Xi_u = 18$ eV and $\Xi_d = -8$ eV were used.

(19) is the solution of a differential equation valid strictly speaking only for $\epsilon \gg \epsilon_m$, where $\epsilon_m = \gamma kT^2$ and γ is of the order of unity.[20] (21) is the solution of a differential equation valid for $\epsilon \ll \epsilon_m$. Since in impact problems one is often especially interested in a small part of the dis-

tribution, that where ϵ is greater than some threshold energy, it is useful to be able to use a Stratton form valid for that region even when the majority of the distribution would be better described as of equipartition form. Accordingly we define a "matched" distribution (unnormalized) as

$$f_0^{(3)}(\epsilon) = f_0^{(1)}(\epsilon_m) f_0^{(2)}(\epsilon), \quad \epsilon < \epsilon_m,$$
$$f_0^{(3)}(\epsilon) = f_0^{(1)}(\epsilon) f_0^{(2)}(\epsilon_m), \quad \epsilon \geq \epsilon_m, \tag{24}$$

which matches $f_0^{(1)}$ and $f_0^{(2)}$ at $\epsilon = \epsilon_m$.

(Matching of the slopes, which would make the procedure exact were ϵ_m well defined, appears to be an unwarranted refinement given the real width of the transition region around ϵ_m). $f_0^{(3)}(\epsilon)$ can then be used indiscriminately at all values of field, a substantial computational advantage, the problem being converted into one of choice of γ. This was determined by the usual idea[16] that since the acoustic phonons with which an electron of energy ϵ can interact have a maximum energy of $2(\epsilon m^* s^2)^{0.5}$, where m^* is the effective mass and s the sound velocity, zero-point conditions apply for $2(\epsilon m^* s^2)^{0.5} > kT$. The appropriate averages are given in Appendix II of Budd's paper[16] on the anisotropic case, and lead to $\epsilon > 0.83\, kT^2$, i.e., $\gamma = 0.83$. Since more complicated criteria could clearly be derived, the calculations were repeated for various values of γ. Numerical results for the $E - T_e$ relationship [which in fact is responsible for much of the variation in $D(n)$ from one value of γ to another] are given in Table IV, and certain insensitivity to the precise value of γ may be seen in some regions of temperature and field.

Finally, the usual Maxwellian distribution

$$f_0^{(4)}(\epsilon) \propto \exp(-\epsilon/kT_e) \tag{25}$$

was included in the calculations. This allowed consideration of Kurosawa's theory[21] of S breakdown, which depends on a change of the distribution during breakdown to Maxwellian form as a result of increased electron-electron scattering, as predicted by Fröhlich and Paranjape,[22] for $n > n_e$, where $n_e \sim 10^{10}$ cm^{-3} at 4 °K in germanium.

Since n has to be yet an order of magnitude greater before the electron-electron scattering enters into the total energy-balance equation,[23] the appropriate $E - T_e$ relationship for use with (25) remains substantially the same as (20) or (23) according to whether zero-point or equipartition conditions are supposed to hold. The supposed change to Maxwellian form must thus occur at constant T_e.

The neglect of other scattering mechanisms is clearly justifiable in the limit of small N_D, N_A, and n; when it begins to become unjustified is discussed below in connection with the results of the calculations.

RATE COEFFICIENTS

The calculation of the rate coefficients will now be summarized. Phonon ones were obtained from previous work,[24,25] and impact ones from results

TABLE IV. T_e as a function of E calculated for the matched distribution of (24) for various values of its defining parameter γ at (a) 4 °K and (b) 7 °K. (The value $\gamma = 0$ corresponds to a Stratton distribution, the value $\gamma = \infty$ to an equipartition distribution.) E in V/cm.

(a) 4 °K

E	$\gamma =$ 0	0.41	0.83	1.50	2.00	2.37	4.74	∞
1.6	10.94	10.92	10.92	11.48	12.24			14.90
1.8	12.02	12.01	12.00	12.46	13.18			16.41
2.0	13.08	13.07	13.06	13.43	14.10	14.73	17.66	18.00
2.5	15.63	15.63	15.61	15.86	16.39	16.97	20.79	21.89
3.0	18.09	18.08	18.07	18.24	18.66	19.16	23.47	25.87
4.0	22.77	22.77	22.76	22.85	23.12	23.47	27.91	33.78
5.0	27.22	27.22	27.21	27.27	27.45			41.70

(b) 7 °K

E	$\gamma =$ 0	0.41	0.83	1.50	2.00	2.37	∞
1.6	10.94	10.79	12.41	13.87	13.95	13.95	13.96
1.8	12.02	11.81	13.24	14.94	15.06	15.08	15.08
2.0	13.08	12.83	14.06	15.98	16.18	16.20	16.22
2.5	15.63	15.38	16.16	18.48	18.95	19.04	19.08
3.0	18.09	17.87	18.32	20.80	21.64	21.84	21.98
4.0	22.77	22.62	22.73	25.06	26.61	27.19	27.73
5.0	27.22	27.12	27.11	29.04	31.03	32.07	33.67

on impact ionization[26] and excitation[27] of the hydrogen atom. Up to five excited levels were considered. Various advances over previous work[7-11] (on photoconductivity) may be mentioned. The donor energy-level structure was not taken to be hydrogenic, as indeed it is not in n-germanium because of the mass anisotropy; it was necessary to assume a donor system with hydrogenic degeneracies and hydrogenic wave functions, but it was found possible to adjust the energy levels to agree with averages of the known energy levels[28] in germanium, which might be expected to be the most important of the three aspects; indeed, the results proved sensitive to the energy separations of the lower levels. The donor ground state was allowed to be split, and adjustments were made to matrix elements for transitions from the lower ground-state level to take account of "central-cell" corrections,[29] using the "quantum-defect method" pioneered by Bebb and Chapman[30] for photoionization of shallow donors. Multivalley degeneracy was allowed for on the assumption of negligible intervalley processes. Rate coefficients for downward transitions were calculated explicitly, without appeal to the principle of detailed balance, whose use in a strongly nonequilibrium situation would have been inappropriate.

Nonetheless, considerable uncertainties remain. It is not clear that the effective-mass approximation can be applied in calculating phonon matrix elements, as the phonon wave vectors involved are too large (there is no such problem for impact transitions). Given that it can, there is still little information available on donor wave functions associated with anisotropic conduction bands, and the treatment given above remains somewhat arbitrary.

Further difficulty was encountered in the calculation of rate coefficients for "forbidden" transitions between levels of a split ground state, and such transitions were found to be important if the splitting is large, as it is for arsenic donors (~4.0 meV).[1] The results are thus only reliable for antimony donors, where ground-state splitting has little significance (0.57 meV).[1]

CALCULATIONS

The numerical program outlined above now presents no special difficulty since $D(n)$ has been shown to be monotonic (in both n and E). In cases in which the equation $D(n)=S(n)$ had more than one solution only the lowest was obtained (corresponding, as explained, to a situation in which the electric field is increasing).

As the q_i were often very close to unity at the lower temperatures, the terms involving $\rho_i = 1 - q_i$ in $A(\tilde{q})$ were obtained directly by matrix inversion from

$$\left(\sum_{j\neq i} W_{ij} + A_i + W_{1i}\right)\rho_i - \sum_{\substack{j\neq i \\ j\neq 1}} (W_{ij} - W_{1j})\rho_j = A_i - A_1\,, \qquad i = 2-N\,, \quad (26)$$

which follows trivially from (10). This inversion and that of (10) for the q_i were checked on each performance, the product of the matrix and its inverse having to produce the unit matrix to 10^{-8}; this check succeeded in all cases in which the ground state was not split; in those cases a check that q_i should be equal to $1-\rho_i$ succeeded mostly to 10^{-5}, occasionally to only 10^{-3}. A further check was that the equilibrium value n^0 of n calculated laboriously by the above procedure should agree with the value calculated[31] in one line from statistical considerations; a similar check is possible for the value of n that one would obtain with a Maxwellian distribution function at electron temperature T_e and with all phonon rate coefficients set equal to zero. Both succeeded.

All integrals over electron energy in the conduction band were cut off at the energy of the optical phonon in germanium (0.037 eV), as the distributions would be invalid at higher energies in any case. A check was made by doubling this energy. At $T_e = 64\,^\circ$K, with a Maxwellian distribution, even the impact rate coefficients for upward transitions (which depend strongly on the tail of the distribution) were changed by at most 5%; significant changes required electron temperatures as high as 100 °K. Optical-phonon scattering can thus safely be ignored.

In general the values of the rate coefficients were calculated to within 1%, an excessive accuracy in view of the uncertainties in the theory. An exception is B_i^I, whose values for non-Maxwellian distributions depend on a double integral over a coarsely tabulated partial impact cross section[32]; the resulting errors of some 30% in B_i^I would still not be critical in view of the relatively small influence of B_i^I on the important parts of $D(n)$.

RESULTS ON $D(n)$

Figures 5 and 6 show the behavior of $D(n)$ with varying field for a Stratton distribution at 4 and 7 °K, and confirm the general analysis developed above. Examples of $S(n)$ are included for samples of KBS. Note how despite a slight supralinearity of $D(n)$ at 3.5 V/cm at 7 °K, the upward curvature of $S(n)$ prevents the development of extra solutions of $D(n)=S(n)$. Note also the monotonicity of $D(n)$ in n and E, with the exception of the curve for 1.6 V/cm at 7 °K; in this case the fall in $D(n)$ with n

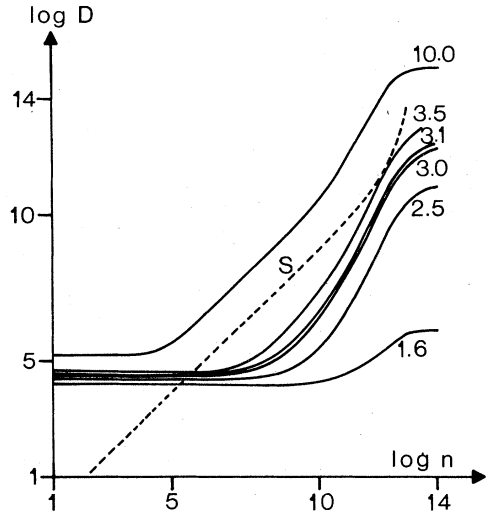

FIG. 5. $D(n)$ for different fields (shown in V/cm), at 4 °K (Stratton distribution). The corresponding electron temperatures in °K are 10.9, 15.6, 18.1, 18.4, 20.4, and 47.4. S is $S(n)$ for sample 45-10 of KBS. ($E_B \sim 5$ V/cm for this sample at 4 °K.)

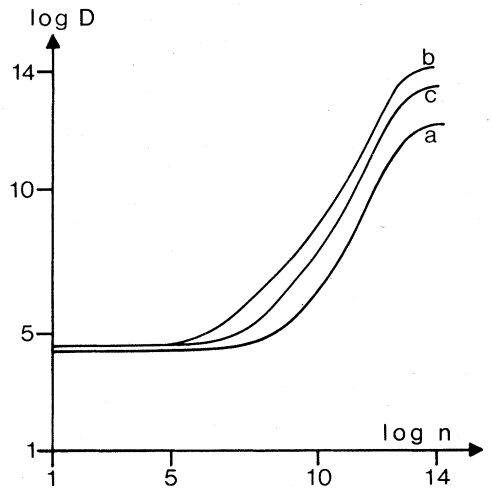

FIG. 7. $D(n)$ at 4 °K for the same field and different distribution functions ($E = 3.0$ V/cm). a: Stratton distribution, $T_e = 18.1$ °K; b: equipartition distribution, $T_e = 25.8$ °K; c: matched distribution with $\gamma = 4.7$, $T_e = 23.5$ °K. $D(n)$ for a matched distribution with $\gamma = 2.0$ gives a curve substantially identical to curve a. Note the relative strengths of the distributions.

is spurious, the field being too low for the Stratton distribution to be realistic.

Figures 7 and 8 show the variation of $D(n)$ with choice of distribution for constant field. The equipartition distribution function is seen to be "stronger" than the Stratton. This is simply because of its longer "tail"; electrons with sufficient energy to cause impact excitation out of the ground state (the first step of the inverse cascade process) need energies of at least $I_{12} = I_1 - I_2$, and such energies lie well in the tail of the distributions at the low field shown (3 V/cm), as is obvious from the corresponding values of T_e. The matched distributions (for various values of γ) lie intermediate between the Stratton and equipartition results, as expected.

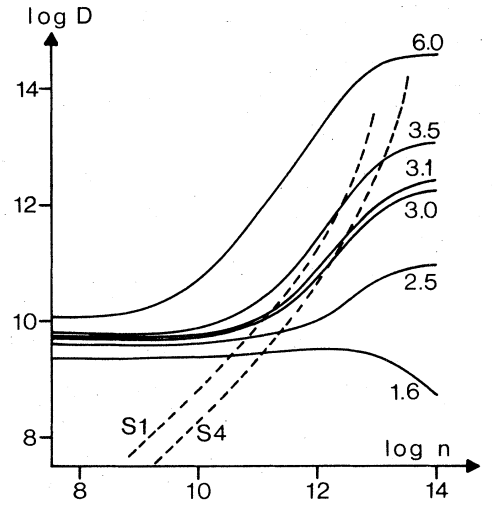

FIG. 6. $D(n)$ for different fields (shown in V/cm), at 7 °K (Stratton distribution). The corresponding electron temperatures in °K are 10.9, 15.6, 18.1, 18.4, 20.4, and 47.4. $S1$ and $S4$ are $S(n)$ for samples 45-10 and 45-2, respectively, of KBS. (For the former sample $E_B \sim 3$ V/cm at 7 °K.) The curve for 1.6 V/cm is spurious, as zero-point conditions do not apply at 7 °K for such a low field.

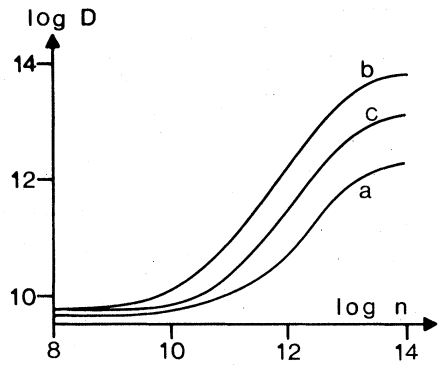

FIG. 8. $D(n)$ at 7 °K for the same field and different distribution functions ($E = 3.0$ V/cm). a: Stratton distribution, $T_e = 18.1$ °K; b: equipartition distribution, $T_e = 22.0$ °K; c: matched distribution with $\gamma = 1.5$, $T_e = 20.8$ °K. The $D(n)$ for matched distributions with $\gamma = 0.8$ and $\gamma = 2.0$ are substantially identical to curves a and b, respectively. Note the relative strengths of the distributions.

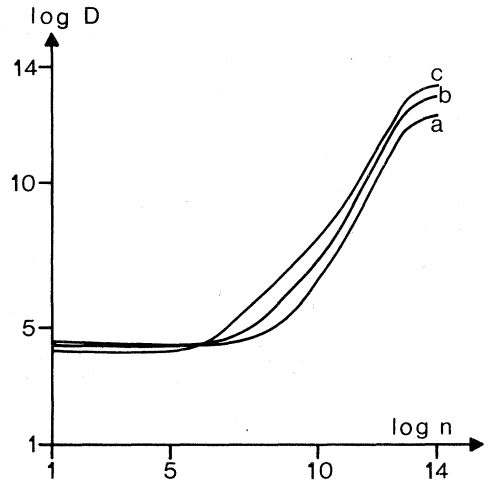

FIG. 9. $D(n)$ at 4 °K for the same electron temperature and different distributions (T_e=18 °K). *a*: Stratton distribution, E=3.0 V/cm, T_e=18.1 °K; *b*: equipartition distribution, E=2.0 V/cm, T_e=18.1 °K; *c*: Maxwellian distribution, T_e=18.0 °K. Note that the difference between curves *a* and *b* is much less than that shown in Fig. 7. Note that the Maxwellian distribution is the strongest.

Figures 9 and 10 show the variation of $D(n)$ with choice of distribution for constant electron temperature T_e; this is much less than the variation at constant field, and shows the advantages that would be gained by independent knowledge of the

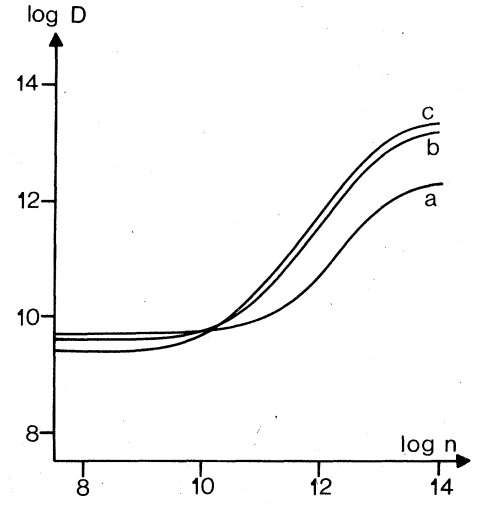

FIG. 10. $D(n)$ at 7 °K for the same electron temperature and different distribution functions (T_e=18 °K). *a*: Stratton distribution, E=3.0 V/cm, T_e=18.1 °K; *b*: equipartition distribution, E=2.4 V/cm, T_e=18.3 °K; *c*: Maxwellian distribution, T_e=18.0 °K. Note that the difference between curves *a* and *b* is much less than that shown in Fig. 8. Note that the Maxwellian distribution is the strongest.

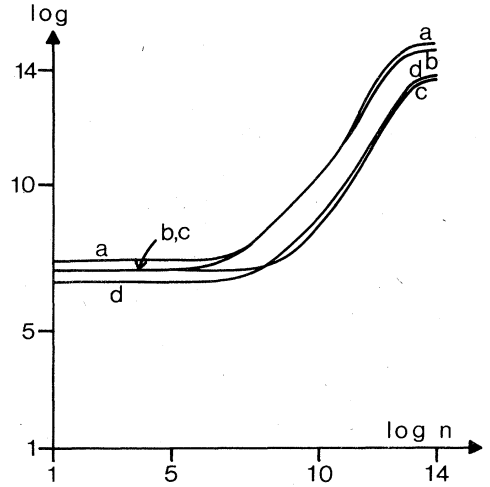

FIG. 11. $D(n)$ at 5 °K for Stratton and Maxwellian distributions: reversal of strengths in high field. *a*: Stratton distribution, E=7.5 V/cm, T_e=37.7 °K; *b*: Maxwellian distribution, T_e=38.0 °K; *c*: Stratton distribution, E=4.0 V/cm, T_e=22.8 °K; *d*: Maxwellian distribution, T_e=20.4 °K. Curves *c* and *d* show the Maxwellian distribution to be stronger than a Stratton one, even though the electron temperature of the latter is greater. Curves *a* and *b* show that this position is reversed in higher fields. (Kurosawa's mechanism for *S* breakdown is thus nonexistent for T_e>38 °K, and possibly earlier.)

$E - T_e$ relationship. Indeed, a large part of the variation with γ at constant field can be seen to be due to consequent changes in electron temperature; cf. Table IV above.

The Maxwellian distribution can be seen to be stronger than the others; again this simply reflects its longer tail.

For higher fields, on the other hand, when kT_e becomes of the order of I_{12}, the difference between the various distributions would be expected to disappear, as the main impact processes would not then be dominated by electrons in the tail of the distribution. This is confirmed by Fig. 11, which shows a slight inversion of the normal order for $T_e \sim 40$ °K, corresponding to a field of some 7.5 V/cm in the zero-point case. While some differences remain (due, for example, to differing values of B^P), the various distributions would now predict much the same breakdown fields, at least in a Price regime.

ERROR ESTIMATES

Given a state of uncertainty as to the distribution function, the expected error in terms of the electric field required to produce a given value of n can be obtained by comparing Figs. 7 and 8 with Figs. 5 and 6. Total uncertainty between the Strat-

TABLE V. Rate of change $\tilde{v}$ of log $\tilde{n}$ with field E. (Stratton distribution, $T=5$ °K.) Note that $D(n)$ thus becomes progressively less sensitive to change of field as the field increases. E in V/cm.

E	log$\tilde{n}$	$\tilde{v}$ (approximate) (cm V^{-1})
3	9.725	1.5
4	8.614	0.73
5	8.017	0.45
6	7.631	0.33
7	7.353	0.23
8	7.139	0.19
10	6.828	0.11
15	6.394	0.06

ton and equipartition functions (or, equivalently, total ignorance of γ) then implies at 3 V/cm an error of the order of 1 V/cm. Errors associated with the approximate treatment of the donor parameters (energy-level structure, etc.) can be estimated by explicit variation of those parameters; an error of some 0.5 V/cm at 3 V/cm is not an unreasonable estimate.

Further error can result from experimental uncertainty in the characterization of the sample. Values of N_A are rarely precise,[1] and a consequent error by a factor of 2 in C will produce a lateral shift in log$S(n)$ of log 2 = 0.3 and an error of about 0.4 V/cm in a field of 3 V/cm.

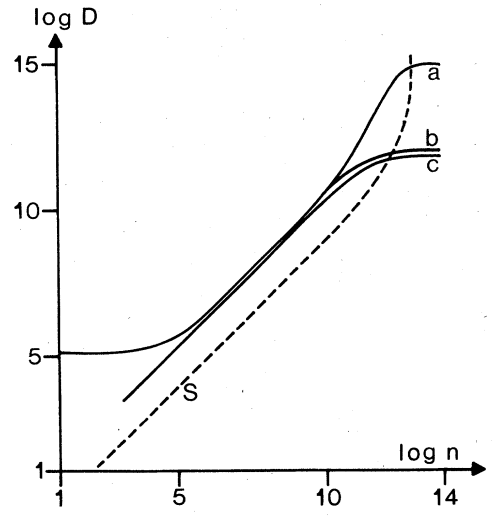

FIG. 12. Comparison of $D(n)$, $D_1(n)$, and $D_2(n)$ at high field and low temperature, showing a region in which previous theories would give reasonable results for E_B. (Equipartition distribution, $E=5.7$ V/cm, $T_e=47.0$ °K, $T=4$ °K.) a: $D(n)$; b: $D_1(n)$; c: $D_2(n)$. S is $S(n)$ for sample 45-10 of KBS. Note that $D_2(n) \approx D(n)$ for $\tilde{n} < n < n_q$, and would successfully predict E_B in a Price regime. $D_2(n)$ remains wrong outside these limits.

At higher fields the differences between the distributions become less serious, as already stated, but the characterization question is unaffected. It is then important to realize that the error in terms of field can be substantially increased, simply because $D(n)$ becomes less sensitive to changes in field; more precisely, $\tilde{n}$ does not move back uniformly along $D(n)$ for uniformly increasing field. It is helpful to define the "velocity" $\tilde{v}$ at which log $\tilde{n}$ moves by

$$\tilde{v} = -\frac{d}{dE}(\log \tilde{n}) \quad (\mathrm{cm V^{-1}}). \tag{27}$$

Table V gives rough values of $\tilde{v}$. An error of 0.5 V/cm at 3 V/cm can then correspond at 15 V/cm to an error an order of magnitude greater.

COMPARISON WITH PREVIOUS THEORIES

As explained above, previous theories[1-5] have taken account of the effect of the excited states on recombination, using the Lax model, and have ignored their effect on ionization. In the terminology of the present work, that implies an attempt to approximate $D(n)$ by a curve

$$D_2(n) = \frac{A_1^P + nA_1^I}{\sum_j B_j^P q_j' + n\sum_j B_j^I q_j'}. \tag{28}$$

Such a curve can, of course, never produce the supralinear behavior of $D(n)$, nor can it describe non-Price breakdown. It can in certain circumstances be a reasonable approximation to $D_1(n)$ in

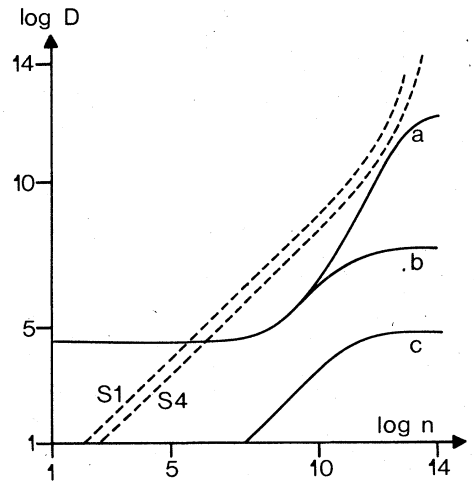

FIG. 13. Comparison of $D(n)$, $D_1(n)$, and $D_2(n)$ still at low temperature but now at lower field, showing inadequacy of previous theories (Stratton distribution, $E=3$ V/cm, $T_e=18.1$ °K). a: $D(n)$; b: $D_1(n)$; c: $D_2(n)$. $S1$ and $S4$ are $S(n)$ for samples 45-10 and 45-2, respectively, of KBS. Note that $D_2(n)$ is now grossly wrong, and would badly overestimate E_B. The situation would be even worse at higher temperature.

TABLE VI. Data for the samples of KBS (Ref. 1). Some of the values of N_A, indicated "?", are doubtful. The pairs of values of C given for the first two samples are for low-field and high-field donor concentrations, in that order.

Sample	Nominal dopant	N_D-N_A (10^{13} cm^{-3})	N_{Sb} (10^{13} cm^{-3})	N_{As} (10^{13} cm^{-3})	N_A (10^{12} cm^{-3})	C
45-10	Sb	1.84	1.02	0.86	0.64	(0.067, 0.035)
45-2	Sb	3.87	2.11	1.83	0.73	(0.036, 0.019)
28-6	Sb	1.26	~0.7	~0.7	1.4	0.111
44-1	Sb	6.41	···	···	6.8	0.106
49-1	As	15.6	···	···	16.9	0.108
41-15	Sb	3.1	···	···	6.5?	0.210
42-1	Sb	2.5	···	···	8?	0.320
46-2	P	0.43	···	~0	2.9	0.674

the linear region, as shown in Fig. 12; the requirements are a field sufficiently high for the threshold energy (I_1) involved in A_1^I to be not significantly greater in its effects than that (I_{12}) involved in W_{12}^I, and/or a temperature sufficiently low for the factor $(1-q_2')$ to weight the term $W_{12}^I(1-q_2')$ disadvantageously in comparison with A_1^I. Figure 12 thus shows that the previous theories would have some meaning for $T_e > 47$ °K and $T < 4$ °K. Figure 13 shows that they would be largely meaningless for $T_e \sim 18$ °K ($E \sim 3$ V/cm) even at 4 °K. At 7 °K, of course, $D_2(n)$ is an even worse approximation. And in all cases $D_2(n)$ is hopeless for small n, as it underestimates A^P by orders of magnitude.

RESULTS ON $n(E)$ IN A NON-PRICE REGIME: COMPARISON WITH EXPERIMENT

Table VI assembles data on the samples of KBS considered in the present work. Curves of $n(E)$ are given by KBS only for samples 45-10 and 45-2 at 7 °K and 9.5 °K; and for these there is a slight difficulty in that the donors were not all of one type, a situation not treated explicitly by the present theory. However, the ground state of the arsenic donors (~12 meV) is so much deeper than that of the antimony donors (~9 meV) that the former may be left out of account for the breakdown fields (~3 V/cm) of these samples.[1] At high fields, on the other hand, they would be indistinguishable from the antimony donors. The results for $n(E)$ are here presented as two curves, one for "low-field N_D" (antimony donors only) and one for "high-field N_D" (all donors included); the true $n(E)$ curve would pass from the first curve to the second sometime after breakdown. The matter is perhaps of little immediate importance, as the experimental results were spoiled at high field by injection from the contacts.[1]

Figure 14 represents a first comparison with the experimental results for sample 45-10, based on a Stratton distribution function and with a neglect of the ground-state splitting of the antimony donor. Good agreement is obtained for E_B.

However, Fig. 14 does not do justice to the theory; first, because the Stratton distribution, though sound in the breakdown region, cannot be expected to hold at low field (< 2 V/cm) since zero-point conditions do not then apply; and second, because the ground-state splitting of the antimony donor, though small (0.57 meV), is sufficient to

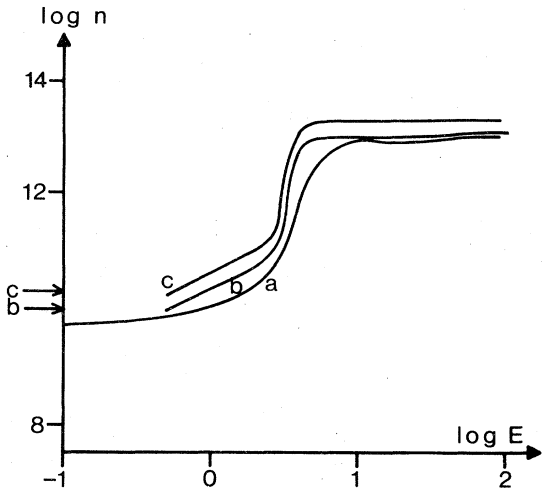

FIG. 14. $n(E)$ compared with experiment: simplified case. Sample 45-10 of KBS, $T = 7.04$ °K. *a*: experiment; *b*: theory (Stratton distribution, $T = 7.04$ °K, low-field donor concentration for antimony donors, with neglect of donor ground-state splitting; the latter makes the curve a shade too high); *c*: as *b* but with high-field donor concentration. The arrows denote the (statistically calculated) equilibrium values of n for samples represented by curves *b* and *c*, which are also too high for the same reason. The Stratton distribution is clearly inadequate at low field, as n appears to fall below the arrows, which is unphysical.

produce a noticeable lowering of n *even in equilibrium*, where n can be calculated from standard statistical results. The appearance of Fig. 14 can thus be improved by minor cosmetic adjustments which do not affect the breakdown field, but which treat the low-field region more realistically.

The first point is obvious from the tendency of the theoretical $n(E)$ of Fig. 14 to fall below the (statistically calculated) equilibrium value of n at low field; this would be clearly unphysical. The matter could be taken care of by using the equipartition distribution at low field, since, as shown in curve c of Fig. 15, this distribution has no such tendency, and then the Stratton distribution at high field, with an (uncertain) transition region between the two. However, it is computationally more convenient to use the matched distribution already defined, which is automatically "equipartition" at low field and "Stratton" at high. Figure 15 shows that with the previously calculated value of $\gamma = 0.8$ the two approaches are identical, curve b (matched distribution) passing smoothly from curve c (equipartition) to curve a (Stratton) in a narrow transition region a little before the predicted breakdown field; in this picture uncertainties in γ translate into uncertainties in the transition region. Curve d of Fig. 15, for example, shows the result with $\gamma = 1.5$, which is now intermediate between those for the zero-point and equipartition cases. In summary, the distribution function used in the final calculation is the matched distribution with $\gamma = 0.8$; in one sense γ is here an adjustable parameter that in the event needed no adjustment; in another sense one is relying on the calculation of γ as $\simeq 0.8$, and on the results of previous work[2] that zero-point conditions already apply at breakdown.

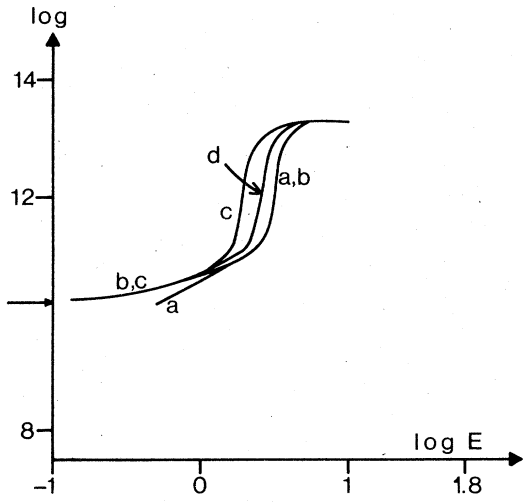

FIG. 15. $n(E)$ for different distribution functions. (Sample 45-2, low-field donor concentration, for antimony donors, with neglect of ground-state splitting, $T = 7$ °K.) a: Stratton distribution; b: matched distribution with $\gamma = 0.8$; c: equipartition distribution; d: matched distribution with $\gamma = 1.5$. The arrow denotes the (statistically calculated) equilibrium value of n. Note that the unphysical behavior of the Stratton distribution at low fields is removed by a slight admixture of equipartition behavior, and that the resulting matched distributions give identical results to those of the equipartition distribution at such fields. At higher field the matched distribution with $\gamma = 0.8$ gives results identical to those of the Stratton distribution; that with $\gamma = 1.5$ represents an intermediate case.

The second point was taken care of by including the lower level of the split ground state, so that the upper one became in effect the first excited level; Eqs. (7)–(10) remain valid, so that this is perfectly permissible. The value of n in zero field then drops, as it automatically must, to the experimental value. The only difficulty is in knowing the values of the phonon and impact rate coefficients for transitions *between* these split levels. They were thus parametrized with small values (since these transitions are to a first approximation forbidden in any case). The reduction in n (below the result of Fig. 14) then decreases smoothly from its small known value in zero field to zero at high field, as is to be expected. No adjustment was made to these parameters, as the effects would be scarcely noticeable. In the case of arsenic donors, on the other hand, where the ground-state splitting is much larger (4.0 meV), the values chosen for the parameters would become significant; for this reason results are given here only for antimony donors.

A slight but noticeable error in the $n(E)$ curve also results if one does not properly allow for the drop in the conduction-band edge caused by the donor attraction, as described by KBS; this is another example of the sensitivity of the results to the exact donor ionization energies. (In impure samples this effect can be much stronger, since the conduction band can drop by some 20% of the ionization energy, leading at 4 °K to an increase of n by a factor of order 100 in equilibrium, and to corresponding changes in the rate coefficients.)

The final result is now shown in Fig. 16. Agreement is excellent until well into breakdown. Indeed, its extent is rather surprising given the dubious nature of the analytic distribution functions used in the present work, and the difficulties involved in calculating the rate coefficients. The chief discrepancy (apart from those in the injection region referred to) appears to be that the breakdown is predicted to be too sharp; for the second time (cf. the discussion on S breakdown) there are indications that the electrons become harder to heat as n increases.

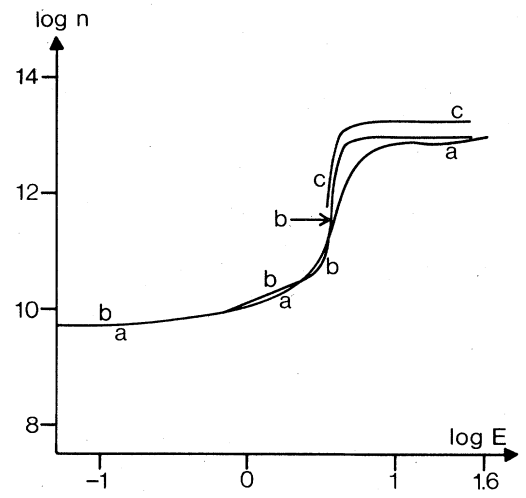

FIG. 16. $n(E)$ compared with experiment: definitive case. (Sample 45-10 of KBS, $T = 7.04\,^{\circ}\mathrm{K}$). *a*: experiment; *b*: theory (matched distribution with $y = 0.8$, low-field donor concentration, for antimony donors, with account taken of ground-state splitting); *c*: as *b* but for high-field donor concentration. The theoretical prediction is curve *b*, except in the postbreakdown region where curve *c* might be more appropriate; but the experimental result is uncertain in that region anyway (Ref. 1). The only flaw is that the breakdown is predicted to be a little too sharp. Note that the regime is non-Price.

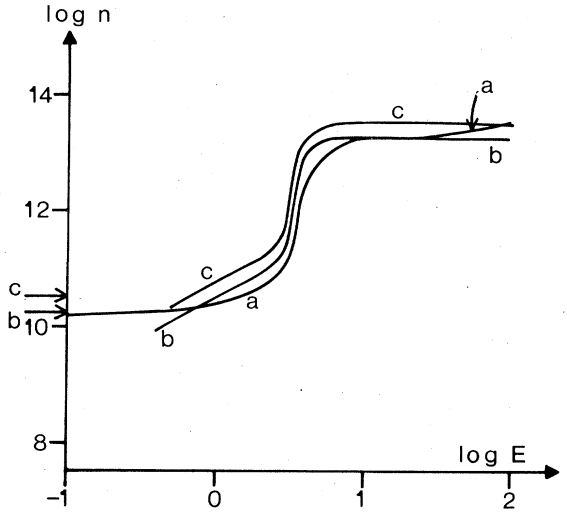

FIG. 17. $n(E)$ for sample 45-2 of KBS at $7.14\,^{\circ}\mathrm{K}$ (results for the simplified case, analogous to those of Fig. 14). *a*: experiment; *b*: theory (Stratton distribution, $T = 7.14\,^{\circ}\mathrm{K}$, low-field donor concentration, for antimony donors, with neglect of ground-state splitting); *c*: as *b* but with high-field donor concentration. The arrows denote the (statistically calculated) equilibrium values of n. (Agreement appears equally good for this sample; it would be improved in the analogous figure to Fig. 16.)

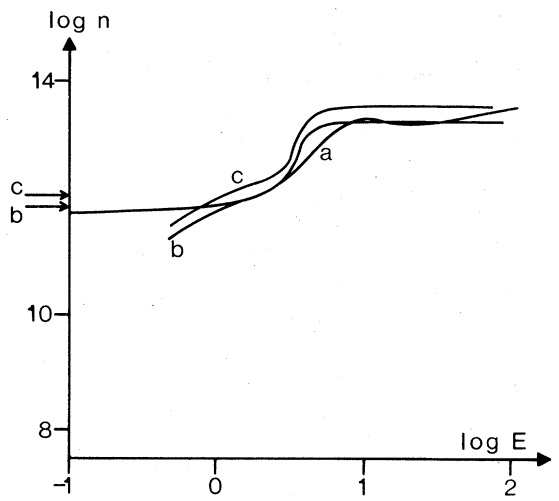

FIG. 18. $n(E)$ for sample 45-2 of KBS at $9.5\,^{\circ}\mathrm{K}$ (results for the simplified case, analogous to those of Fig. 14). *a*: experiment; *b*: theory (Stratton distribution, $T = 9.5\,^{\circ}\mathrm{K}$, low-field donor concentration, for antimony donors with neglect of ground-state splitting); *c*: as *b* but with high-field donor concentration. The arrows denote the (statistically calculated) equilibrium values of n.

Figures 17 and 18 show results for $n(E)$ for sample 45-2 of KBS at 7 and $9.5\,^{\circ}\mathrm{K}$, respectively. They omit the cosmetic modifications of the results of Fig. 16 and are based on the simple Stratton distribution. Agreement appears as good as for sample 45-10.

All these results pertain to a non-Price regime.

RESULTS ON E_B IN A PRICE REGIME: COMPARISON WITH EXPERIMENT

KBS give breakdown fields, but not $n(E)$, for various samples at $5\,^{\circ}\mathrm{K}$. This is now a Price regime, and $n(E)$ is predicted to be substantially vertical at E_B; see the calculated $n(E)$ curves of Fig. 19.

Theory and experiment are compared in Table VII, due account being taken of ground-state splitting. Some indication is given of the expected error, based on an error of 0.5 V/cm at 3 V/cm adjusted for higher fields to take account of the reduction of $\tilde{v}$. For some of the samples the values of N_A are doubtful, and only the nominal dopant is given for N_D, so that there are also uncertainties in characterization. The results are in agreement within the expected error. However, it appears possible to detect a trend in the discrepancies, E_B being underestimated for impure samples. This represents the third indication that the electrons become harder to heat when n is large.

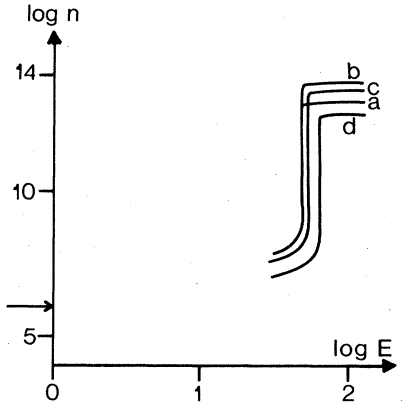

FIG. 19. $n(E)$ at 5 °K for various samples of KBS (theory). (Stratton distribution, $T=5$ °K.) a: sample 28-6; b: sample 44-1; c: sample 41-15; d: sample 46-2. The arrow shows the equilibrium value of n for sample 46-2. Note that this is a Price regime, and that the breakdown is predicted to be substantially vertical. No experimental curves for $n(E)$ are available for these samples, only values of E_B.

IONIZED-IMPURITY SCATTERING: DISCUSSION

The nonoccurrence of predicted S breakdown, the overestimate of the sharpness of breakdown for pure samples, and the underestimate of breakdown fields for less pure samples are all indications that increasing sample conductivity makes the electrons harder to heat. Possible causes are ionized-impurity scattering (the number of ionized scatterers being equal to $2N_A+n$) and/or some heating of the phonon distribution at high current densities (which would also lead to increased scattering as n increases). Some experimental evidence for the former was found by KBS in the form of a dip in the (Hall) mobility during breakdown.

There is no formal difficulty involved in incorporating into the present theory such a dependence of the distribution function on n; the function $D(n)$ could still be defined, though the rate coefficients would now have to be recalculated for every value of n if the whole curve of $D(n)$ were to be obtained (as would be necessary for a discussion of S breakdown). On the other hand, if one is interested only in the curve $n(E)$ in a situation in which S breakdown does not occur, and if one is prepared to treat ionized-impurity scattering as a perturbation that merely adjusts the $E-T_e$ relationship while having an insignificant effect on the shape of the distribution, then the only change required in, say, Fig. 16 is a rightward shift of every point of the curve to take account of the new E value for the corresponding n value. For ionized-impurity scattering there would be no significant change in the curve $n(E)$ until n reached a value greater than $2N_A$, i.e., 1.3×10^{12} cm^{-3} for sample 45-10 of Fig. 16. The rightward shift of the curve for greater values of n could then smooth out the fairly sharp corner shown in Fig. 16, much as required by the experimental results.

It should be noted that if the inelastic scattering due to the impact processes were to affect significantly the distribution function, then the present theory would entirely break down. The distribution function would become a function of the n_i, and the function $D(n)$ could not then be defined.

TABLE VII. E_B at $T=5$ °K for the samples of KBS appearing in Table VI above, in a Price regime. $E_B^{\rm exp}$ is the experimental result of KBS for each sample. The results of the present theory are $E_B^{(1)}$ and $E_B^{(2)}$, the latter taking into account ground-state splitting, the former neglecting it; upper and lower bounds are given for E_B. For the first two samples the results are based on use of the low-field donor concentrations. The error estimate quoted is based on 0.5 V/cm at $E=3$ V/cm, adjusted at higher fields to take account of the variation of $\tilde{v}$ displayed in Table V.

Sample	$E_B^{\rm exp}$ (V/cm)	$E_B^{(1)}$ (V/cm)	$E_B^{(2)}$ (V/cm)	Error (V/cm)
45-10	4.0	4.2/4.5	4.5/4.6	1.0
45-2	3.6	3.8/4.0	4.1/4.2	1.0
28-6	4.8	4.5/4.8	4.8/5.0	1.7
44-1	5.5	4.5/4.8	4.8/5.0	1.7
49-1	6.6	4.5/4.8	6.0/6.5	2.5
41-15	7.6	5.0/5.2	5.2/5.5	2.0
42-1	8.05	•••	5.5/6.0	2.3
46-2	15.1	6.0/6.5	8.0/9.0	4-5

S BREAKDOWN: DISCUSSION

This is not predicted for samples 45-2 and 45-10 at 7 or 9.5 °K, because of the sharp upward curving of $S(n)$. It is predicted at 5 °K for all samples, but was not found experimentally. Supposing that the reason for its nonoccurrence is the effect of ionized-impurity scattering, then it is possible to discuss qualitatively when S breakdown *would* be expected to occur. The best hope would appear to lie in impure samples, with large values of N_A, since in such a case there would be little *additional* ionized-impurity scattering during the breakdown process; this implies large values of C, and consequently large breakdown fields; and this again implies a relative decrease in the importance of ionized-impurity scattering, since fast electrons are scattered less than slow ones by this process. (Of course, the sample must not be so impure as to lose the excited states by impurity

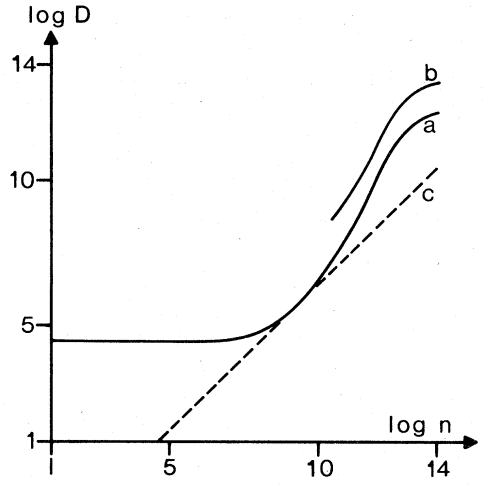

FIG. 20. $D(n)$ at 4 °K for Stratton and Maxwellian distributions, at field low enough to show Kurosawa's mechanism for S breakdown (cf. Fig. 11). a: Stratton distribution, $E=3$ V/cm, $T_e=18.1$ °K; b: Maxwellian distribution, $T_e=18.0$ °K (shown for $n>10^{10}$ cm^{-3}); c: a line of unit slope tangent to curve a (to aid in judging the size of the bulge). If we suppose a distribution function Stratton for $n<10^{10}$ cm^{-3} and Maxwellian for $n>10^{10}$ cm^{-3} its $D(n)$ would be curve a for $n<10^{10}$ cm^{-3} and curve b for $n>10^{10}$ cm^{-3}, and would indeed show an extra bulge over curve a. (On the other hand, curve a already shows a considerable bulge due solely to the excited states.)

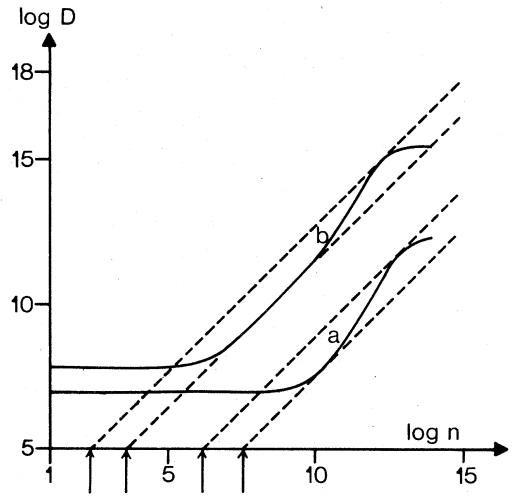

FIG. 21. $D(n)$ for Stratton distribution showing substantial bulge due to excited states at both high and low field ($T=5$ °K), and thus a strong mechanism for S breakdown at both fields. a: $E=3.0$ V/cm; b: $E=15.0$ V/cm. The broken lines are of unit slope and thus indicate the width of the bulges. This width is little reduced by increasing field, going from 1.4 for curve a (in terms of intercept on the log n axis) to 1.25 for curve b; given the associated decrease of $\bar{v}$ there is in fact a strong increase in predicted values of E_B-E_S with increasing field, in contrast to the predictions of Kurosawa's mechanism, which disappears long before one reaches a field as high as 15 V/cm.

overlap.) These qualitative requirements appear consonant with experimental results on S breakdown,[33-36] which occurs in germanium for impurity concentrations between 5×10^{14} and 2×10^{16} cm^{-3}, and disappears as C decreases.[35,36]

That excited states can be responsible for S breakdown, though a surprise to the author, has in fact been known since 1943, when Davydov[37] showed that S breakdown would occur in a gas whose molecules have two excited states. His work seems to have been forgotten in the solid-state literature already referred to. Kastalskii[36] produced a similar theory for the solid-state case in 1973, considering donors with a single excited level, and ascribed various experimentally observed features of S breakdown to changes in the position of this level. The present theory is both more quantitative and more general, since it can deal with an arbitrary number of states. And its formulation in terms of the intersection of the curves $D(n)$ and $S(n)$ avoids the necessity for solution of the transient rate equations of Kastalskii's method, whose implications as regards change of level it of course subsumes.

Some comment on Kurosawa's theory[21] of S breakdown can now be made. He supposed a transition of the distribution function to Maxwellian form during breakdown (induced by the corresponding increase in electron-electron scattering[22,23]), the longer tail of that distribution then increasing the impact ionization rate. In the language of the present work this means that $D(n)$ would be that appropriate for a Stratton distribution for small n, and that appropriate for a Maxwellian for large n. For low fields this does indeed lead to an (extra) bulge in $D(n)$, as shown in Fig. 20, and to consequent S breakdown. Figure 11 has already shown, however, that for fields higher than some 7 V/cm that bulge entirely disappears, together with Kurosawa's theory. If indeed S breakdown requires high field, then Kurosawa's theory appears untenable.

By contrast, the bulge due to the excited states remains vigorous at such fields, and predicts substantial differences between breakdown and sustaining fields, as shown in Fig. 21. But until account is taken of the effects of ionized-impurity scattering explicit calculations of E_B-E_S would appear to be premature.

SUMMARY AND CONCLUSIONS

The description of any nonequilibrium phenomenon involving shallow donors at low temperature

requires (a) knowledge of the electron distribution function, (b) calculation of the rate coefficients (many of which involve the distribution function), and (c) the solution of the rate equations. We have seen that (c) may be performed exactly, at least in the steady-state case; but (a) and (b) contain considerable uncertainties.

Nonetheless, this paper has shown that practical calculations on such phenomena are possible, and that the results are both illuminating for theory (in uncovering the important variables), and in good agreement with experiment. Indeed, the extent of this agreement in an essentially parameter-free calculation is surprising, since it has been seen that the results are quite sensitive to the form of the (uncertain) distribution function; this might be some indication that relatively simple analytic distribution functions behave reasonably well in n-germanium, provided that the material is pure and that due account is taken of the anisotropy of the conduction band. On the other hand (a) and (b) go together, and a finding that the phonon rate coefficients were dominated by multiphonon processes[38] (not considered here) would then throw doubt on these simple distribution functions.

In all events the basic conclusion of this work, that the donor excited states are critical to a description of such phenomena, appears well established, and proof against reasonable future changes of outlook on (a) and (b). The inadequacy of making minor modifications to take account of these states has been clearly shown; they must be there in the basic equations (5), and if not one will both produce nonsense and fail to pick up nonlinear behavior such as S breakdown. And it has furthermore been shown that despite the computational difficulties associated with 84 rate coefficients, 48 of which vary with field, the overall behavior of the system can be understood very simply in terms of a small number of parameters ($\tilde{n}$, n_q, $\tilde{v}$, etc.) and its consequent division into Price, non-Price, and S breakdown. Finally it has been shown that the effect relied upon by Kurosawa to explain S breakdown is vanishingly weak in the conditions in which such breakdown is usually found, and that the strong mechanism proposed in this paper is even stronger in those conditions.

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