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Effect of Compensation on Breakdown Fields in Homogeneous Semiconductors

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Using Bloch and hydrogen-like functions, the impact-ionization coefficient has been calculated for processes in which an electron in a band collides with an electron on an impurity so as to ionize it. The problem is solved in the zero-order approximation, which is valid for trap depths large compared to kT_e. Estimates of impact-ionization cross sections obtained this way are in good agreement with exact numerical calculatoins for the range relevant to this paper. The theory is applied to study the effect of doping on breakdown electric fields in bulk materials at low temperatures. Comparison with experimental work done by Lambert on p-type germanium yields satisfactory agreement with the theory. Graphs of the impact-ionization coefficient as a function of electron temperature have also been obtained for several trap depths. Finally, we present a framework for predicting breakdown fields if donor and acceptor concentrations are known.

1. INTRODUCTION

A THEORY of Auger recombination into hydrogen-like traps has recently been developed and found to be in broad agreement with the sparse experimental facts available.[1–3] It is, therefore, important to extend the theory to situations for which more experimental information is at hand. This is attempted in this paper by considering impact ionization from shallow traps at low temperatures.[4–7] Other work not considered here has also been done in this field.[8–14] This brings within the range of the theory the dependence of the electric breakdown field in bulk materials on compensation ratio.

The theory is based on one-electron functions, perturbation theory, and parabolic bands, with the extrema at $k=0$, noninteracting impurities, and nondegeneracy (see Secs. 2 and 3). The electric field is assumed to enter through a displaced Boltzmann-like distribution function [see Eq. (3.9)]. This simplification makes the problem tractable and seems justified by the satisfactory agreement with experiment which is obtained (see Sec. 5).

The main results are the following: (a) An expression has been obtained for the probability $P_{\mathbf{k}}$ per unit time that an electron of wave vector $\mathbf{k}$ in the conduction band will ionize a hydrogen-like center by exciting an electron from the ground state or from an excited state into the continuous levels [Eq. (3.8) and Fig. 2]. Associated results have also been obtained for the probability per unit time $P(\mathbf{k},\gamma)$ of an electron in state $\mathbf{k}$ being scattered through an angle γ as a result of the impact ionization (Figs. 3 and 4). (b) The value of $P_{\mathbf{k}}$, integrated over the distribution function, is called the impact ionization coefficient and is denoted by X_1 and X_4 (Fig. 1). Earlier theoretical work on these coefficients has been done by Yamashita,[6] who took the cross section as independent of $\mathbf{k}$, and in Ref. 1, where only the case of thermal equilibrium (no electric field) was considered. This latter work is here extended to include the effect on X_1 and X_4 of the electric field and the electron temperature [Eq. (3.10) and Fig. 5]. (c) This work has been used to explain four curves of breakdown field as a function of compensation [Figs. 6 and 7]. Each curve has been fitted by assigning an appropriate value to one adjustable parameter [A in Eq. (4.3)].

We believe these results to be an improvement on earlier work comparing theoretical and experimental breakdown fields as a function of compensation (Ref. 7, Fig. 11; Ref. 15, Fig. 2). This work dealt with high-purity n-type material (impurity content $N_D+N_A<10^{13}$ cm^{-3}), and the impact ionization cross section was taken to be independent of $\mathbf{k}$ in both cases. The electron distribution functions were taken to be proportional to $\exp[-(bE/kT)^2]$, where b is a function of the applied field in Ref. 7, and proportional to $\exp[-(E/kT_e)^{5/2}]$ in Ref. 15. The latter expression was justified by assuming the electron-acoustic phonon interaction to dominate. The present treatment of $P_{\mathbf{k}}$ is

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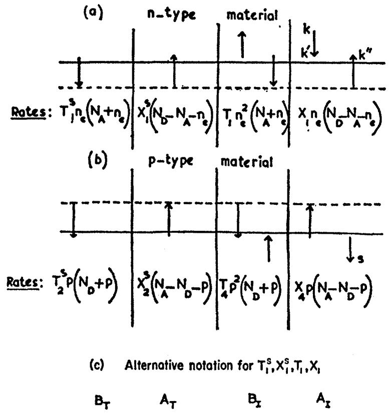

FIG. 1. Processes assumed to affect electric breakdown.

superior, and there is improved agreement with experiment. As to the use of the drifted Maxwellian distribution here, it can be regarded only as a rough approximation, but it seems a reasonable choice for higher impurity concentrations, where a number of different scattering mechanisms are in play.

2. OUTLINE OF THE CALCULATION

The calculation of the probability of an impact ionization in a time t after the perturbation has been switched on is based on the well-known result

$$T=\frac{2t^2}{\hbar^2}|U|^2\frac{1-\cos x}{x^2}, \tag{2.1}$$

where x is $(t/\hbar)$ times the change of energy in the transition. The conceptual background is here the same as discussed in Ref. 1, i.e., the wave functions are taken to be determinants of one-electron functions, and the perturbation U is the screened Coulomb interaction between the electrons in the conduction band. After summing over all spin assignments to states $\mathbf{k}$, $\mathbf{k}'$, $\mathbf{k}''$ (see Fig. 1) the matrix element has the form

$$|U|^2=2(|M_D|^2+|M_E|^2+|M_D-M_E|^2). \tag{2.2}$$

With the notation of Fig. 1,

$$M_D=\int\phi^*(\mathbf{k}',\mathbf{r}_1)\phi^*(\mathbf{k}'',\mathbf{r}_2)\frac{e^2\exp(-\lambda r_{12})}{\epsilon r_{12}}\times\phi(\mathbf{k},\mathbf{r}_1)\phi_d(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2,$$

and M_E is the corresponding exchange term. The effective dielectric constant has been denoted by ϵ, the ϕ's are Bloch functions, and ϕ_d is a superposition of Bloch-type functions;

$$\phi(\mathbf{k},\mathbf{r})=u(\mathbf{k},\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}},\quad \phi_d(\mathbf{r})=\sum_{\text{all }\mathbf{k}}v(\mathbf{k},\mathbf{r})G_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{2.3}$$

where u and v have lattice periodicity and $G_{\mathbf{k}}$ will be taken to be a Fourier coefficient of a hydrogen-like wave function for some specified quantum numbers n and l (m is taken to be zero). As in Ref. 1, it is found that approximately

$$M_D=\frac{4\pi e^2F''}{\epsilon V^{1/2}(\lambda^2+|\mathbf{k}-\mathbf{k}'|^2)}G_{-\mathbf{k}+\mathbf{k}'+\mathbf{k}''}, \tag{2.4}$$

where

$$F''\equiv V^{-1/2}\left\{\int_V u^*(\mathbf{k}',\mathbf{r})u(\mathbf{k},\mathbf{r})d\mathbf{r}\right\}\times\left\{\int_V u^*(\mathbf{k}'',\mathbf{r})v(-\mathbf{k}+\mathbf{k}'+\mathbf{k}'',\mathbf{r})d\mathbf{r}\right\}. \tag{2.5}$$

One may suppose that for the contribution to the probability T due to $|M_E|^2$, the final states $\mathbf{k}'$ and $\mathbf{k}''$ in Fig. 1 are interchanged. In all transition rates discussed here, these states are summed over so that the contribution due to $|M_E|^2$ is equal to that due to $|M_D|^2$. The contribution due to the third term in (2.2) is known to be usually small from the dotted graphs in Fig. 5 of Ref. 1. It will therefore be neglected, as will the effect of λ^2 in (2.4).

Although something is known about the first factor in (2.5),[16] very little is known about the second factor. The factor F'' is therefore retained in the theory; it is, however, put equal to unity for the numerical work leading to Figs. 6 to 8. In this way the method employed is broadly equivalent to the use of the Born approximation, at least when the impurity is ionized from its ground state. Our procedure is not quite equivalent to the effective-mass approximation. If the latter were used, the function v in (2.3) would be independent of $\mathbf{k}$, and an overlap integral would result which could not justifiably be replaced by unity.[2]

One might hope to improve this procedure by appeal to quantum-mechanical treatments of the ionization of hydrogen atoms by electron impact. Unfortunately, this is not yet a well-understood problem, at least for the low electron energies of interest here.[17] Neither quantum-mechanical methods alternative to the Born approximation,[18] nor classical procedures,[19,20] appear to give results much superior to those obtained by the Born approximation.

For a given trap state (n,l) and given wave vector $\mathbf{k}$ of the energetic electron, one can now obtain the impact ionization probability per unit time $P_{\mathbf{k}}$ by summing (2.1) with

$$|U|^2=4|M_D|^2 \tag{2.6}$$

over all $\mathbf{k}'$ and $\mathbf{k}''$, and multiplying by the number n_tV

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of occupied states (n,l). The simplifying feature here is that for a nondegenerate band the probability factors for states $\mathbf{k}'$ and $\mathbf{k}''$ to be empty can be taken as unity. Hence,

$$P_{\mathbf{k}}=\frac{2t}{\hbar^2}\left(\frac{V}{8\pi^3}\right)^2 n_t V\int 4|M_D|^2\frac{1-\cos x}{x^2}d\mathbf{k}'d\mathbf{k}''. \quad (2.7)$$

Also of interest is the impact ionization probability per unit time P, obtained by integrating $P_{\mathbf{k}}$ over the occupation probability of the states $\mathbf{k}$ of given spin in the conduction band. This distribution function $\theta(\mathbf{k},\mathbf{F})$ will in general be dependent on the applied electric field $\mathbf{F}$, and hence one obtains P as a function of $\mathbf{F}$;

$$P=\frac{V}{8\pi^3}\int P_{\mathbf{k}}\theta(\mathbf{k},\mathbf{F})d\mathbf{k}=X_1 n_e n_t V. \quad (2.8)$$

Here n_e and n_t are the conduction-electron concentration and the trapped-electron concentration, respectively. Equation (2.8) introduces the quantity X_1, conventionally called the impact-ionization coefficient. It was denoted by X_1 in Refs. 1 and 21 and by A_I in Refs. 4 and 5. The alternative notations and the processes of interest in this paper are shown in Fig. 1.

Equation (2.8) has been evaluated analytically by us, for each of the terms in Eq. (2.2). Expressions have also been obtained for degenerate semiconductors and for a nonparabolic band structure. These results will be reported in due course.

3. IMPACT IONIZATION FOR A BOLTZMANN-LIKE DISTRIBUTION

The use of (2.7) together with (2.4) requires knowledge of the Fourier coefficient G_κ of the hydrogen-like wave function $G(\mathbf{r})$ for specified quantum numbers n and l. This is given by

$$G_\kappa^*\equiv\frac{1}{V}\int_V G(\mathbf{r})e^{i\boldsymbol{\kappa}\cdot\mathbf{r}}d\mathbf{r} \quad (3.1)$$

$$=\frac{i^l 2^{2l+3}\sqrt{\pi}}{\alpha^{3/2}V}n^2 l!\left[\frac{(2l+1)(n-l-1)!}{(n+l)!}\right]^{1/2} \times\frac{c^l}{(1+c^2)^{l+2}}C_{n-l-1}{}^{l+1}\left(\frac{c^2-1}{c^2+1}\right), \quad (3.2)$$

where C is a Gegenbauer polynomial[22] defined by

$$(1-2xt+t^2)^{-\nu}=\sum_{j=0}^{\infty} C_j{}^\nu(x)t^j$$

$$|t|<|x\pm[(x^2-1)]^{1/2}|,$$

and $$c\equiv\kappa n/\alpha. \quad (3.3)$$

The parameter α will be related to the depth E_t of the state (n,l) below the conduction band through

$$\hbar^2 k_0^2/2m_e\equiv\hbar^2\alpha^2/2m_e n^2=E_t \quad (n=1,2,\cdots). \quad (3.4)$$

In a consistent application of the hydrogen model the donor spectrum is fixed by

$$\alpha=e^2 m_e/\epsilon\hbar^2, \quad (3.5)$$

an equation not used here. Equation (3.2) is a more convenient form of $G_{\mathbf{k}}$ than that used in Ref. 1.

Since $\boldsymbol{\kappa}=-\mathbf{k}+\mathbf{k}'+\mathbf{k}''$ in (2.4), it follows from (3.3) and (3.4) that

$$c^2=\kappa^2/k_0^2=|\mathbf{k}-\mathbf{k}'-\mathbf{k}''|^2/k_0^2. \quad (3.6)$$

The main contribution to the integral in (2.7) comes from the smallest admissible k values, i.e., $k\sim k_0$. Since $k^2-k'^2=k_0^2+k''^2$ (energy conservation), one may then neglect k' and k'' compared with k and k_0 in $|M_D|$.

This is the *zero-order approximation* of Ref. 1 and is adopted in Sec. 4 and 5 and in this section where stated. It implies that $c^2=1$, so that one can use the result

$$\begin{aligned} C_{n-l-1}{}^{l+1}(0)&= 0 \quad (n-l \text{ even})\\ &= (-1)^{(n-l-1)/2}\left(\frac{n+l-1}{2}\right)!\Big/ l!\left(\frac{n-l-1}{2}\right)! \quad (n-l \text{ odd}). \end{aligned} \quad (3.7)$$

This shows that impact ionization from certain hydrogenic levels does not occur in zero order (see the remarks about T_1 in Ref. 1.) In zero order, and apart from the overlap integral (2.5), the integrand in (2.7) is thus seen to depend on k' and k'' only through x. The overlap integral is taken out of the integral with k' and k'' replaced by zero. It is then denoted by $|F_0|^2$.

Another interpretation of the zero-order approximation is possible for the case when $n-l$ is odd. Then[23]

$$\max_{-\infty\leqslant c^2\leqslant\infty}\left|C_{n-l-1}{}^{l+1}\left(\frac{c^2-1}{c^2+1}\right)\right|=C_{n-l-1}{}^{l+1}(0).$$

Thus the approximation consists of (a) replacing the

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Gegenbauer polynomial by its maximum value, (b) replacing $|\mathbf{k}-\mathbf{k}'|^2$ by $|\mathbf{k}|^2$ in (2.4) and c^2 by 1 in (3.2), and (c) replacing the overlap integral $|F''|$ by $|F_0|$ before the integral in (2.7) is carried out.

The integration in (2.7) is now straightforward and yields

$$P_{\mathbf{k}}=\frac{(2l+1)(n-l-1)!}{(n+l)!}\left\{\frac{[\frac{1}{2}(l+n-1)]!}{[\frac{1}{2}(n-l-1)]!}\right\}^2 \times 2^{2l+3}n\pi\frac{m_e e^4 n_t}{\hbar^3\epsilon^2 k_0{}^3}\left[\frac{k^2}{k_0{}^2}-1\right]^2|F_0|^2(k\geqslant k_0). \quad (3.8)$$

The zero-order approximation restricts the validity of this result for $n=1$, $l=0$ to $(k/k_0)^2\leqslant 1.21$. The error does not then exceed 13%, as has been found by numerical integration. This also shows that for $2k_0{}^2<k^2<16k_0{}^2$, $P_{\mathbf{k}}$ increases linearly with $(k-k_0)^2/kk_0$, a result not used in the sequel.

Figure 2, obtained with the aid of a digital computer, shows the behavior of the corresponding cross section

$$\sigma_k=(m_e/n_e\hbar k)P_{\mathbf{k}}$$

in terms of the unit

$$\sigma_1=(m_e/n_e\hbar k_0)\times 10^4/\tau\sim 2\times 10^{-9}\ \text{cm}^2.$$

This value is based on $m_e/m=0.2$, $\epsilon=16$, $n_t=10^{16}$ cm^{-3},

$$|F_0|=1,\quad E_t=0.01\ \text{eV},\quad n_e=10^{13}\ \text{cm}^{-3},$$

$$\tau\equiv 3.9\times 10^3\left(\frac{m_e}{2}\right)^{1/2}\frac{\epsilon^2 E_t{}^{3/2}}{e^4 n_t|F_0|^2}\ \text{sec}\sim 3.63\times 10^{-8}\ \text{sec}.$$

The figure shows that the zero-order approximation is very good up to $(k/k_0)^2=2$, and this range dominates when one integrates over a Boltzmann-like distribution.

If in (2.7) one had not integrated over the angle γ (say) between $\mathbf{k}$ and $\mathbf{k}'$, one would have obtained the probability $P(\mathbf{k},\gamma)$ per unit time that an electron in state $\mathbf{k}$ is scattered through the angle γ as a result of ionizing a trap. For a relatively slow electron, $k/k_0\sim 1.01$, one would then expect a certain amount of back scattering (see Fig. 3). For a faster electron $(k\sim 4k_0)$ however, it is found that forward scattering completely dominates (Fig. 4). The results of Figs. 3 and 4 were computed numerically. In the zero-order approximation vector $\mathbf{k}'$ would be replaced by a null vector, so that $P(\mathbf{k},\gamma)$ would be independent of γ in this approximation.

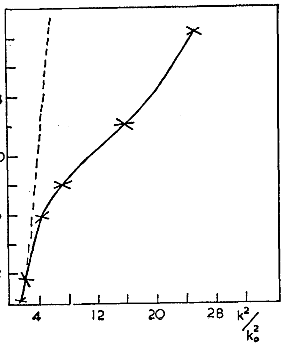


FIG. 2. The cross-section σ_k for impact ionization (due to an electron initially in state $\mathbf{k}$) of a hydrogen-like state $n=1$, $l=0$, plotted against $k^2/k_0{}^2$. The result in the zero-order approximation is shown dotted. σ_1 has been taken as 2×10^{-9} cm^2.

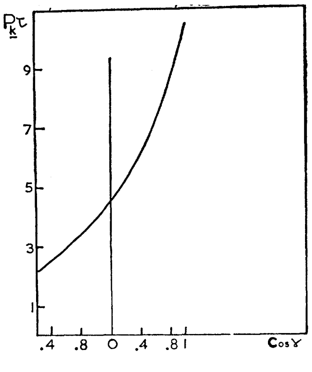


FIG. 3. The probability per unit time $P(\mathbf{k},\gamma)$ as in Fig. 2, for an initial electron energy of $16E_t$. A logarithmic scale has to be used because of the strong forward scattering.

In order to obtain analytical results for the average of the probabilities discussed so far, the distribution function $\theta(\mathbf{k},\mathbf{F})$ of Eq. (2.8) for the electrons in the band must be taken in the simplest possible form. This is usually done in similar problems. We here adopt a displaced Boltzmann-type distribution with an effective-electron temperature

$$\theta(\mathbf{k},\mathbf{F})=8(\pi\sigma)^{3/2}n_e e^{-\sigma(\mathbf{k}-\mathbf{k}_d)^2}, \quad (3.9)$$

where

$$\sigma\equiv\hbar^2/2m_e k_B T_e,\quad \mathbf{k}_d\equiv(m_e/\hbar)\mu\mathbf{F}.$$

Here k_B is Boltzmann's constant and μ is the drift mobility. Equation (3.9) presupposes a sufficiently small applied electric field. Using (3.8) and (3.9) in (2.8), one finds for the impact ionization probability per unit time P and the impact ionization coefficient X_1

$$P=D[I(+)-I(-)],\quad X_1=P/n_t n_e V, \quad (3.10)$$

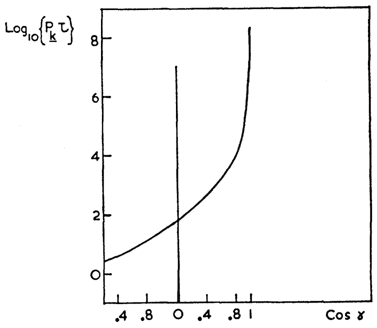
where

$$I(+)\equiv\left[\frac{k_d(k_d-k_0)(k_d+k_0)^2}{2\sigma}+\frac{1}{\sigma^3}+\frac{9k_d{}^2+7k_0k_d}{4\sigma^2}\right]\times\exp[-\sigma(k_0-k_d)^2]+\left[\frac{15k_d}{4\sigma^{5/2}}+\frac{5k_d{}^3-3k_0{}^2k_d}{\sigma^{3/2}}+\frac{k_d(k_d{}^2-k_0{}^2)^2}{\sigma^{1/2}}\right]\times\int_{\sigma^{1/2}(k_0-k_d)}^{\infty}e^{-x^2}dx, \quad (3.11)$$

$$D\equiv\frac{(2l+1)(n-l-1)!}{(n+l)!}\left\{\frac{[\frac{1}{2}(l+n-1)]!}{[\frac{1}{2}(n-l-1)]!}\right\}^2\times 2^{2l+3}\pi^{1/2}\sigma^{1/2}\frac{m_e e^4 V n_t n_e n}{\epsilon^2\hbar^3 k_0{}^7 k_d}|F_0|^2 \quad (3.12)$$

and $I(-)$ is obtained from $I(+)$ by replacing each k_d by $-k_d$.

FIG. 4. The probability per unit time $P(\mathbf{k},\gamma)$ of an electron in state $\mathbf{k}$ being scattered through an angle γ as a result of impact ionizing an electron from a state $n=1$, $l=0$, γ being the angle between $\mathbf{k}$ and $\mathbf{k}'$. The initial electron kinetic energy is assumed to be $1.02E_t$. τ has been taken as 3.63×10^{-8} sec.



The expression (3.10) for X_1 can be written for zero applied field ($k_d=0$)

$$X_1=\langle X_1\rangle_{\text{eq}}\exp(-E_t/k_BT),$$

where $\langle X_1\rangle_{\text{eq}}$ is an average impact ionization coefficient for carriers with sufficient energy to ionize a trap. Using the values given in Ref. 7, i.e., $m_e/m=0.25$, $\epsilon=16$, $E_t=0.012$ eV, and $T=6$°K, (3.10) yields

$$\langle X_1\rangle_{\text{eq}}/|F_0|^2\approx5\times10^{-7}\ \text{cm}^3/\text{sec}.$$

This compares well with the semi-empirical estimate of 10^{-7} cm^3/sec given by Ref. 7.

Equation (3.10) can also be used as an expression for X_4 if $n_t=N_D-N_A-n_e$ is replaced by N_A-N_D-p, m_e by m_h, n_e by p, and E_t is interpreted as the energy gap between the acceptor levels and the top of the valence band. This modification is needed in Sec. 5 in order to compare our results with experiment. It is, therefore, convenient to observe here that for given Fermi level and for given drift velocity $\mu\mathbf{F}$, the impact-ionization coefficient must be expected to rise with the electron temperature T_e in the valence band. The reason is that, under these conditions, the probability of finding a hole at energies greater than k_BT_e below the valence band edge is increased. The important state to consider for this purpose is state s (Fig. 1) near which the threshold for impact ionization occurs. The chance of finding a hole there is increased by raising the temperature. Calculated curves are shown in Fig. 5.

4. SOME AUXILIARY RELATIONS

The impact-ionization coefficient calculated in Sec. 3 involves the electron temperature T_e, the applied field F, and the mobility μ. The inter-relationships between these quantities have been investigated by other workers to some extent. The results which have been found must now be introduced into the above theory and are summarized in Table I. In Sec. 5 it will be shown how the preceding theory can, together with these relations, explain the dependence of breakdown electric field on compensation ratio.

TABLE I. Relationships adopted in this paper (valid for p-type Ge near breakdown and at $T=4.2$°K lattice temperature).

(F_B is measured in V/cm).

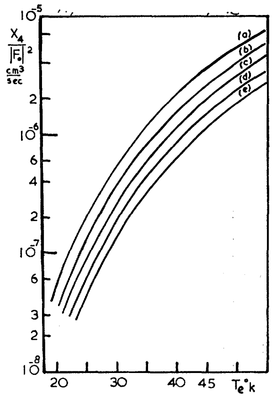
μ (cm^2/V sec)	$10^6/F_B$	(4.1)
$T_2{}^S$ (cm^3/sec)	$1.7\times10^{-5}/T_e$	(4.2)
T_e (°K)	$A\sqrt{F_B}$	(4.3)

Since the bulk of the comparison with experiment is concerned with p-type Ge, the critical drift velocity of 10^6 cm/sec inferred from experiments (Table 2 in Ref. 5) was used. The resulting relationship (4.1) for the mobility has been confirmed by other workers (Fig. 9 of Ref. 24 and also Ref. 25).

The equation for the recombination coefficient $T_2{}^s$ is based on a semitheoretical estimate [Eq. (31) of Ref. 6]. This should also hold away from the breakdown condition. On the basis of a phonon cascade model for a capture process via excited states of centers, one can understand the relationship (4.2) qualitatively as follows. It is a property of the cascade processes that the recombining particle (electron or hole) must come to within a critical distance d of the center in order to recombine. This distance d is often inversely proportional to T_e, or at any rate decreases as the temperature rises. This effect is believed to be responsible for the drop in certain capture cross sections with rise in temperature.[26]

The adopted relation between the electron temperature and electric field is again semiempirical. It was found by Yamashita [Eq. (15) of Ref. 6] that when $T_e/T\geqslant5$ and $\mu\propto1/F$ one may expect $\mu F^2\propto T_e{}^{3/2}$. However, his theory did not give a good account of experimental results for a majority impurity concentration in excess of 10^{14} cm^{-3}. A stronger dependence on electron temperature seemed to be indicated. We therefore adopt $\mu F^2\propto T_e{}^2$ at or away from the breakdown condition. Since $\mu\propto1/F$ near breakdown, one therefore arrives at the stated relationship. The coefficient A is regarded as an adjustable parameter. Since four curves

FIG. 5. The impact ionization coefficient $X_4/|F_0|^2$ as a function of electron temperature in zero order for hydrogen-like states $n=1$, $l=0$ according to Eq. (3.10). Values assumed are drift velocity $v_d=10^6$ cm/sec, $m_h/m=0.2$, and $\epsilon=16$. Trap depths E_t: (a) 0.0095 eV, (b) 0.0100 eV, (c) 0.0105 eV, (d) 0.0110 eV, (e) 0.0115 eV.



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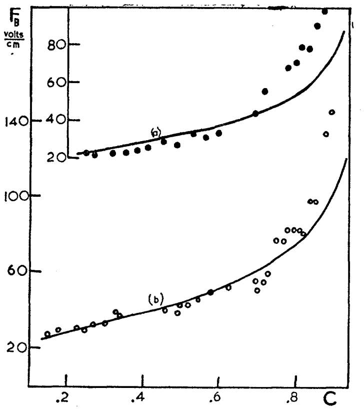

FIG. 6. Theoretical breakdown field as a function of compensation ratio for p-type Ge using Eqs. (3.10) and (5.3). The values $n=1$, $l=0$, $\epsilon=16$, $m_h=0.2m$, $E_t=0.01$ eV, and $|F_0|=1$ have been assumed. The experimental results are shown as dots: (a) Fig. 5 of Ref. 4, (b) Fig. 7 of Ref. 4.

are fitted, four empirical values of A are found (see Sec. 5).

5. COMPARISON WITH EXPERIMENT

The breakdown criterion is based on the following equation for the kinetics of the hole concentration:

$$dp/dt=X_2^s(N_A-N_D-p)+p[X_4(N_A-N_D-p)-T_2^s(N_D+p)]-p^2T_4(N_D+p)\,; \quad (5.1)$$

(see Fig. 1). Assuming p to be small enough because of the low temperature, one finds that in the steady state

$$p=\frac{X_2^s}{[C/(1-C)]T_2^s-X_4}\quad\left(C\equiv\frac{N_D}{N_A}\right). \quad (5.2)$$

It is usual to assume that at breakdown (see Appendix)

$$X_4(F_B,T_e)=[C/(1-C)]T_2^s(F_B,T_e). \quad (5.3)$$

This equation states essentially that the rates due to the processes T_2^s and X_4 (see Fig. 1) are equal, provided only that the hole concentration is small enough. This latter condition holds in the cases considered here (see Appendix). Because the theory of X_4 involves the field only through the product of μF, Eq. (4.1) implies that the breakdown field is involved only implicitly (through T_e) in (5.3). The choice of a T_e value now yields a value of X_4 by virtue of (4.1) and the theory of Sec. 3. It also yields a value of T_2^s by Eq. (4.2). Equation (5.3) therefore gives the value C corresponding to T_e, and (4.3) gives the corresponding breakdown field, A being the adjustable constant whose inferred values are shown in Fig. 8. This procedure yields good agreement with the experimental results of Lambert on indium and antimony doped p-type Ge, as shown in Figs. 6 and 7. Figure 8 shows that $T_e/\sqrt{F_B}$ increases as the majority impurity concentration is decreased. This relationship can be used in the prediction of breakdown fields (for the situations envisaged here) from the majority impurity concentration, the compensation ratio, and other physical constants of the material. This is illustrated in Fig. 9.

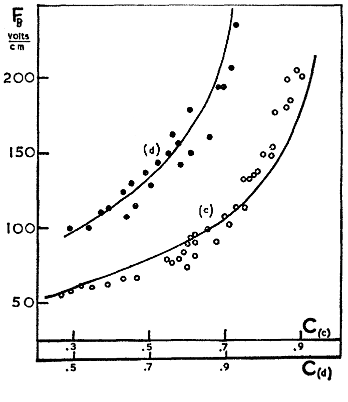

FIG. 7. Same as Fig. 6. (c) Fig. 8 of Ref. 4, (d) Fig. 9 of Ref. 4.

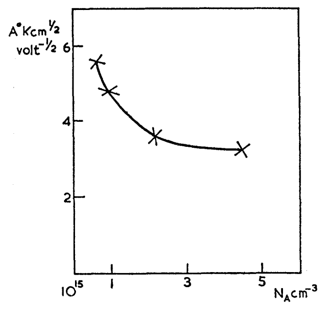

FIG. 8. The inferred values of $A\equiv T_e/\sqrt{F_B}$ as a function of majority impurity concentration. The minority impurity concentration can have any value up to $C\sim0.9$.

A broad over-all picture of the breakdown depends on the following points:

(a) X_2^s depends largely on lattice temperature, but little on the applied field, because an electron is always available in the valence band.

(b) T_2^s decreases with increase of applied field (Sec. 4).

(c) X_4 increases with increase of applied field (Fig. 5 and Sec. 3).

Well before breakdown $X_4\ll T_2^s$, so that according to Eq. (5.2) the hole concentration increases roughly according to

$$p=[(1-C)/C]X_2^s/T_2^s.$$

As the field is increased, X_4 comes into play and Eq. (5.2) shows that the rate of increase of hole concentration with field is accelerated. Eventually, the Eq. (5.3) is approximately satisfied and breakdown occurs. In the cases considered here $p\ll N_A-N_D$ even at breakdown.

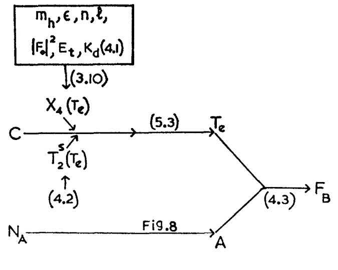

FIG. 9. A schematic diagram illustrating the application of the theory.

APPENDIX

Discussion of Eq. (5.3)

In the usual derivations, one obtains (5.2) having neglected terms in p^2. One then sets the denominator of (5.2) equal to a small quantity without investigating if the maximum permitted value for p is being exceeded. A more careful discussion can be based on the kinetic equation in the form

$$dp/dt=(T_2{}^s+T_4p)[\gamma(N_A-N_D-p)-(N_D+p)]p\,, \quad \text{(A1)}$$

where

$$\gamma\equiv(X_4+X_2{}^s/p)/(T_2{}^s+T_4p) \quad \text{(A2)}$$

is usually taken to be independent of p near breakdown:

$$\gamma\approx X_4/T_2{}^s\,.$$

In a steady state,

$$\frac{p}{N_A-N_D}=\frac{1}{1+\gamma}\left[\gamma-\frac{N_D}{N_A-N_D}\right]. \quad \text{(A3)}$$

Approximate and simplified relations can be obtained in three steps:

(1) Breakdown usually occurs for $p\ll N_A-N_D\sim10^{15}$ cm^{-3}. This is shown to be true by using Fig. 12 of Ref. 4 and the current density relation $J=pe\mu F$ giving

$$10^9\leqslant p\leqslant10^{12}\text{ cm}^{-3}. \quad \text{(A4)}$$

(2) From relation (4.2), $T_2{}^s\sim10^{-7}$ cm^3/sec, while $T_4\leqslant10^{-24}$ cm^6/sec (Figs. 2 to 6 of Ref. 1) at low temperatures and if excited states can be neglected. Thus $T_2{}^s\gg T_4p$; hence (A3) simplifies to

$$[N_D/(N_A-N_D)]T_2{}^s\approx X_4+X_2{}^s/p\,. \quad \text{(A5)}$$

(3) From p. 1685 of Ref. 7, $X_2{}^s\sim10^{-2}$ sec^{-1}, so that, using Fig. 5, $X_2{}^s/p$ can be neglected in comparison with the other terms, thereby reducing (A5) to (5.3).

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Extrinsic Recombination Radiation from Natural Diamond: Exciton Luminescence Associated with the *N*9 Center

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A luminescence system with no-phonon lines at 5.251 and 5.261 eV (at 100°K), observed in the edge luminescence spectra of natural diamonds containing relatively low concentrations of nitrogen in "platelet" form, has been identified with the so-called *N*9 center which is responsible for a well-known impurity-absorption feature. Evidence is presented supporting a recent identification of this absorption system with the creation of an indirect exciton bound to nearest-neighbor donor-acceptor pairs involving substitutional nitrogen donors and aluminium acceptors. The donor-acceptor pair behaves like a modified donor with reduced ionization energy, since the ratio of the ionization energies of the isolated donor and acceptor is approximately 10:1 and the donor binding energy is larger than the donor-acceptor interaction energy. The *N*9 absorption/luminescence system is only observed when the modified donor is neutral in the unexcited crystal. Comparison of the *N*9 absorption and luminescence spectra provides an unambiguous identification of the phonon replicas and of the principal no-phonon excited electronic states in the absorption spectrum. The one-phonon replicas have been studied in detail and are compared with those observed in a system involving excitons which are relatively weakly bound at neutral isolated aluminium acceptors in *p*-type semiconducting diamond. For both systems the exciton-phonon coupling is a maximum for the optical phonons of wave vector $\mathbf{k}_c$ which conserve momentum in the intrinsic indirect transitions. The breadth and shape of the *N*9 optical-phonon replicas indicate, however, that coupling occurs for phonons with wave vectors distributed throughout at least the outer half of the reduced zone, whereas the replicas for the less tightly bound acceptor-exciton complex indicate that the coupling is negligible other than to phonons with wave vector relatively close to $\mathbf{k}_c$.

I. INTRODUCTION

THE *N*9 system was first observed as an absorption center in natural diamonds some thirty years ago[1] and has since been investigated in absorption and luminescence excitation spectra by a number of workers.[1–6] This system has been shown to contain two strong sharp no-phonon lines at photon energies of 5.25 and 5.26 eV, a weaker line at 5.28 eV, and associated struc-

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