Recombination of Electrons and Donors in n-Type Germanium*†‡

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This paper describes a study of the recombination of electrons and donors in n-type germanium at helium temperatures. The excess electron density is obtained by means of low-temperature breakdown. Experimental results indicate that the recombination probability varies approximately with the inverse of the square of the temperature. Recombination light was detected. The origin of the disagreement of the present measurements with those published by S. H. Koenig is discussed, and evidence is given to explain the discrepancies between the two measurements. The magnitude of the recombination cross section appears to depend on the binding energy of the electrons to the donor impurities, but large errors that are present in the determination of N_A are responsible for a large uncertainty in the absolute magnitude of the cross section. The cross sections vary from 10^{-12} to 10^{-11} cm^2.

I. INTRODUCTION

WHEN a sufficiently large electric field (≈ 5 v/cm) is applied to a sample of germanium at liquid helium temperatures, the density of electrons in the conduction band increases rapidly for small changes in electric field. The rate of change of the electron density is determined by the interplay of electron-production and electron-loss mechanisms. The mechanism responsible for the increase in the free electron density is impact ionization of electrons bound to donor impurities. The recombination of electrons with donors is responsible for the electron loss mechanism.

Many workers have observed the above-mentioned increase of the electron density.[1–6] In particular, Sclar and Burstein[3] proposed an equation to describe the change in the electron density as a function of time, for a constant electric field.

By showing that the "breakdown" field was independent of sample size, Sclar and Burstein[3] established that diffusion of the electrons to the surface of the crystal was not the mechanism responsible for electron loss. Two additional mechanisms could determine the rate of loss of electrons in the bulk of the crystal: direct electron donor recombination with or without the emission of light, and impact recombination in which two electrons collide with a donor—one of them recombines, and the other is responsible for the removal of the momentum of the recombining electron. This last mechanism is, according to Moss,[7] responsible for the recombination of photocarriers in PbS; these measurements were made by means of the photoelectromagnetic effect. We shall show that impact recombination is unimportant in germanium of high purity.

Many workers have attempted calculations of first-order processes that could be responsible for the direct electron donor recombination. Sclar and Burstein[8] calculate the probability of recombination of an electron with a donor with the emission of light. Their calculation is based on scaling the classical result for the hydrogen atom to a hydrogen-like model of the ground state of the donor. The calculation predicts a recombination probability α whose dependence on temperature is proportional to $T^{-\frac{3}{2}}$.

Gummel and Lax[9,10] calculate a cross section for recombination with the emission of one phonon; the dependence of the corresponding cross section is proportional to T^{-1}. Both of the cross sections predicted by these calculations are much smaller than those found experimentally. Lax[11,12] used a semiclassical model similar to the Thomson[13] scattering in a gas, by means of which an electron is initially captured in a highly excited state of the donor by the emission of a phonon. After that, the electron can either absorb a phonon and be excited back into the conduction band or emit a phonon falling into a more tightly bound donor state; this process repeats itself, and the electron slowly diffuses into the ground state. When the binding energy of the electron is of the order of kT its final capture is practically assured, and the remaining steps may take place with a mechanism that has a much smaller

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[2] E. J. Ryder, I. M. Ross, and D. A. Kleinman, Phys. Rev. 95, 1342 (1954).
[3] N. Sclar, E. Burstein, W. J. Turner, and J. W. Davisson, Phys. Rev. 91, 215(A) (1953); also N. Sclar and E. Burstein, J. Phys. and Chem. Solids 2, 1 (1957).
[4] E. Burstein, J. W. Davisson, W. J. Turner, E. E. Bell, and H. G. Lipson, Phys. Rev. 93, 65 (1954).
[5] F. J. Darnell and S. A. Friedberg, Phys. Rev. 98, 1178, 1860 (1955).
[6] S. H. Koenig and G. R. Gunther-Mohr, J. Phys. Chem. Solids 2, 268 (1957).

[7] T. S. Moss, Proc. Phys. Soc. (London) B66, 993 (1953).
[8] N. Sclar and E. Burstein, Phys. Rev. 98, 1757 (1955).
[9] H. Gummel and M. Lax, Phys. Rev. 97, 1469 (1955).
[10] H. Gummel and M. Lax, Ann. Phys. 2, 28 (1957).
[11] M. Lax, J. Phys. Chem. Solids 8, (1959).
[12] M. Lax, Phys. Rev. 119, 1502 (1960).
[13] J. J. Thomson, Phil. Mag. 47, 337 (1954).

probability than the interaction with phonons; e.g., emission of light. The predicted cross section is proportional to T^{-4} and should be independent of the ground state of the electron in the donor when its energy is larger than kT. This, in general, will imply that this cross section is independent of the type of impurity.

Our experimental result gives a cross section that depends on temperature approximately as $T^{-2.5}$; the cross section also depends on the binding energy of the ground state of the donor impurity. Recombination light was detected.

The magnitude of the recombination cross section and its temperature dependence disagree with those determined by Koenig.[14] The disagreement can be explained with the assumption that there has been some Joule heating of the lattice and that at the lowest temperatures this is the predominant factor in the measured rate of disappearance of free electrons. We believe that such an assumption is confirmed by the more recent measurements of Koenig[12] on a new sample with the same characteristics as that reported in reference 14 and by our measurements on the sample used by Koenig.

Weinreich *et al.*[15] measuring the acoustoelectric effect were able to measure the intervalley scattering down to temperatures of approximately 20°K. The mechanism proposed by Weinreich *et al.* to explain the observed intervalley scattering is that an electron is trapped into one state of a donor corresponding to one of the valleys, is transferred to the level that is degenerate with the first and corresponds to another valley and is re-emitted from there into the conduction band. Extrapolating their results from 20°K to 10°K, Weinreich *et al.* found a recombination probability 30 times larger than that determined by Koenig; from this they concluded that the measured trapping probability can be explained by trapping into a highly excited state of the impurity. If we extrapolate our results on As-doped germanium at 4.2°K to 10°K and compare them with the corresponding extrapolation of Weinreich, the disagreement between them is only of the order of a factor of 2, which is excellent, in view of the many extrapolations involved.

Our measurements consisted of the measurement of the Q of a microwave cavity at different times after the pulsed dc breakdown field is removed. The procedure is repeated periodically, and, by varying the delay time between the measuring microwave pulse and the time that the breakdown field is removed, the sample conductivity can be measured as a function of time. The recombination is bimolecular, and from the shape of the electron-loss vs time curve the recombination time constant can be determined. If the electron mobility is known, the density of compensating impurities in very pure samples can be measured with a fair degree of accuracy.

II. NONEQUILIBRIUM STATES

Our measurements were made on a sample whose carrier density is not that corresponding to thermal equilibrium with its surroundings; its electron density is much larger than that corresponding to the lattice temperature and will decay to the equilibrium density at the lattice temperature in a time determined by the recombination mechanism. The average electron *energy* will decay to the lattice temperature in a time generally different from the former decay time for electron *density*.

Decay of the Electron Energy

There are two processes (both of which tend to redistribute the electron energy) that go on at the same time during the "afterglow of our discharge": The redistribution of the energy among the electrons themselves—so that a Maxwellian distribution whose temperature T_e is not generally equal to the lattice temperature T_L is produced, and processes in which the electron distribution loses energy to the lattice. The time constant associated with the former process is of the order of the inverse of the plasma frequency[16] $\omega_p = (4\pi n e^2/K m^*)^{\frac{1}{2}}$. We shall approximate this time constant by ω_p^{-1}; for electron densities of the order of 10^{12}/cc, $\omega_p \approx 10^{11}$ sec^{-1}.

The latter mechanism, which determines the decay of the electron temperature towards the lattice temperature, is usually longer than ω_p^{-1} and therefore determines the shortest significant time of our measurements. Gilardini and Brown[17] made a calculation of the time necessary for an electron in a gas, subject to an rf field E and angular frequency ω, to gain energy until it reaches equilibrium at an energy $\mathfrak{U} = kT_e = M(eE/2m^*\omega)^2$. This time interval is very sensitive to the mechanism responsible for the energy loss of an electron in each collision. We shall call M the mass of the particle with which the electron collides, m^* the effective mass of the electron, ν_m the collision frequency proportional to the hth power of the velocity, and T_L the lattice temperature corresponding to an energy U. The problem of the decay of the electron energy from an energy $\mathfrak{U}$ to an energy U is similar to the converse case of heating, so that we can use the results of Gilardini and Brown shown in Fig. 1. As will be seen, the corresponding times are generally much longer than ω_p^{-1}. The time scale is measured in units of $[(2m^*/M)\nu_m]^{-1}$, ν_m being the collision frequency for momentum transfer and in general a function of T_L and T_e. In the case of a semiconductor, as well as in a gas, it is important to know which transfer mechanism

[14] S. H. Koenig, Phys. Rev. **110**, 988 (1958).
[15] G. Weinreich, T. M. Sanders, Jr., and H. G. White, Phys. Rev. **114**, 33 (1959).

[16] D. Pines, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. I, p. 378.
[17] A. Gilardini and S. C. Brown, Phys. Rev. **105**, 31 (1957).

will be more effective in producing the required energy loss (or energy gain).

Collisions with ionized impurities, considered as ions in a gas, are not the most important mechanism for transfer of energy because m^*/M will be very small (of the order of 10^{-5}), and the time constants for the loss of energy will be exceedingly long. Collisions with acoustical phonons will, on the contrary, be very effective in disposing of the excess energy. Shockley[18] has shown, in connection with the problem of hot electrons, that, in an electron phonon collision, the phonon could be considered as having a mass kT_L/c^2, where T_L is the lattice temperature, and c is the velocity of sound. Thus $M/2m^*$ reduces to very reasonable values at helium temperatures: ≈ 35 for transverse phonons and ≈ 12 for longitudinal ones (at $T_L = 4°K$).

For longitudinal phonons the theory of hot electrons gives $h = 1$ $(v_m \propto T_e^{\frac{1}{2}} T_L)$, so that for $T_e/T_L \approx 3.5$, approximately 20 collision times are sufficient for the electron temperature to come within 1% of the lattice temperature. The times involved are of the order of 10^{-9} sec.

The Rate Equation

The change in carrier density as a function of time can be described by the following rate equation proposed by Sclar and Burstein.[3]

$$dn/dt = -\alpha n(n+N_A) + \beta(N_D - N_A - n)$$
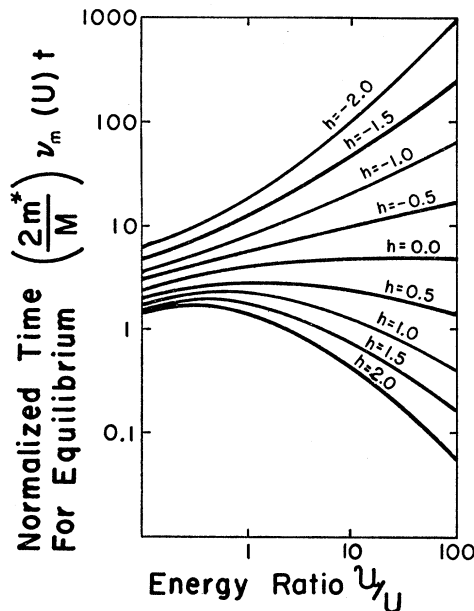$$+ \gamma n(N_D - N_A - n) - \delta n^2(n+N_A). \quad (1)$$

Fig. 1. Time necessary for an electron gas to reach an energy $0.99(\mathfrak{U}+U)$ starting from the "gas" energy U. $\mathfrak{U}$ is the energy due to the interaction with an applied rf field. The time is measured in units of $M/2m(1/\nu_m)$, where ν_m is the collision frequency for momentum transfer assumed proportional to (velocity)^h. [From A. L. Gilardini and S. C. Brown, Phys. Rev. **105**, 31 (1957).]

[18] W. Shockley, Bell System Tech. J. **30**, 990 (1951).

The first term, whose coefficient is α, describes the direct recombination of one of the n electrons that are in the conduction band with one of the $(N_A + n)$ ionized donors; α can be expressed in terms of the recombination cross section σ_r and the carrier velocity v:

$$\alpha = \langle \sigma_r v \rangle, \quad (2)$$

the average being taken over the electron distribution function. The term whose coefficient is β describes the thermal ionization of the $(N_D - N_A - n)$ nonionized donors. The term in γ is due to impact ionization of the impurities by electrons accelerated by the applied electric field; γ is zero in the absence of an electric field and is very sensitive to the exact form of the high-energy tail of the electron distribution function. (This subject will be taken up in more detail in a forthcoming paper.) The term in δ describes impact recombination; it will be shown to be negligible.

Contrary to the case of low-pressure breakdown in gases, diffusion has been completely neglected in Eq. (1). Sclar and Burstein[3] have shown that the "breakdown field" is independent of the sample dimensions. Confirming this, we found that the rate of loss of carriers is independent of the cross-sectional dimensions of the sample.

At thermal equilibrium, in the absence of an applied electric field, the terms in α and β are tied by a simple relation obtained by writing $n = n_\infty$, $dn/dt = \gamma = \delta = 0$, and using the condition of detailed balance

$$\frac{\beta}{\alpha} = \frac{n_\infty(n_\infty + N_A)}{N_D - N_A - n_\infty} = 2\left(\frac{2\pi}{h^2}kT\right)^{\frac{3}{2}} (m_1 m_2 m_3)^{\frac{1}{2}}$$

$$\times \exp\left(-\frac{\epsilon}{kT}\right), \quad (3)$$

where ϵ is the binding energy of the electrons into the donor levels, and the other symbols have their customary meaning. This formula is the usual expression that is used to describe the density of carriers in the conduction band in an extrinsic semiconductor.

If the term that is proportional to α is the most important term in Eq. (1), its solution for short times when $n \gg N_A$ is

$$n - n_\infty \propto 1/t.$$

If impact recombination, described by the term in δ, were predominant, a faster recombination, proportional to t^{-2}, would be expected.

If we assume γ and δ to be zero ($\gamma \equiv 0$ when no electric field is applied), Eq. (1) can be easily solved (α and β are independent of density).

$$n - n_\infty = \frac{1}{\alpha}\left[\frac{\alpha(N_A + 2n_\infty) - \beta}{\{[\alpha(N_A + 2n_\infty) - \beta]/\alpha n_0 + 1\}e^{t/\tau} - 1}\right], \quad (4)$$

where n_∞ is the equilibrium density in the absence of any applied field and is given by Eq. (3); n_0 is the initial

density, at the moment the breakdown field is removed; and τ is the main parameter measured experimentally and is

$$\tau^{-1} = \alpha(N_A + 2n_\infty) + \beta. \qquad (5)$$

In our case, from Eq. (3), for $n_\infty \ll N_A$, we have $\alpha N_A \gg \beta$. Accordingly Eqs. (4) and (5) can be simplified, and we obtain

$$n - n_\infty \approx \frac{N_A}{(N_A/n_0 + 1)e^{t/\tau} - 1}, \qquad (4a)$$

$$\tau^{-1} \approx \alpha N_A. \qquad (5a)$$

For large times, when $t \gg \tau$, corresponding to $n \ll N_A$, the recombination becomes exponential, and we have

$$n - n_\infty \approx \frac{N_A}{N_A/n_0 + 1}e^{-t/\tau} \qquad (4b)$$

if, additionally, $N_A \ll n_0$, $n - n_\infty \sim N_A \exp(-t/\tau)$.

By extrapolating this exponential to $t = 0$, the value of $N_A/[(N_A/n_0) + 1] \approx N_A$, the compensation, can be determined. If τ and N_A are known, α and σ_r can be calculated. To simplify the calculation of σ, we shall assume $\langle \sigma_r v \rangle \approx \langle \sigma_r \rangle (\langle v^2 \rangle)^{\frac{1}{2}}$.

III. DESCRIPTION OF THE MEASUREMENT METHOD

Our measurements are based on the knowledge of the Q of a microwave cavity as a function of time. The sample is mounted on the axis of a cylindrical re-entrant microwave cavity. The electron density in the sample is increased periodically by means of breakdown produced by a short (≈ 2 μsec) dc pulse applied across it. The cavity is filled with liquid helium to ensure good thermal contact with the sample. The applied fields are approximately 15 v/cm for the BTL samples and of the order of 50 v/cm for sample LL 2, so that breakdown is obtained after times of the order of 1 μsec. The breakdown field is removed approximately 0.5 μsec after breakdown is observed. A microwave pulse, whose frequency is equal to the resonant frequency of the cavity, is incident on the cavity, and the corresponding impedance at resonance is measured by determining the voltage-standing wave ratio in the line it terminates. This is proportional to the loaded Q of the cavity, Q_L, determined by the losses in the line and in the cavity. By varying the instant at which the microwave pulse is incident on the cavity, the variation of the cavity impedance can be followed as a function of time. The measurements of time intervals are accurate within 10^{-8} sec; the impedance measurements have an accuracy shown by the experimental data.

Denoting by Q_W, the Q of the cavity when no losses are due to the sample, by Q_S the Q of the cavity when losses are due only to the sample, and by Q the measured Q, we have $1/Q = 1/Q_S + 1/Q_W$ or $Q_W/Q_S = (Q_W/Q) - 1$.

The value of Q_W is determined by measuring the Q of the cavity when the sample is not broken down; the ratio of the cavity admittances at resonances, measured with the sample broken down and measured with the sample not broken down is thus Q/Q_W.

Bethe and Schwinger[19] calculated the frequency shift and the change in Q experienced by a microwave cavity when a sample is introduced into it. If the sample parameters are its dimensions, the dielectric constant K, and the complex conductivity $\sigma = \sigma_r + j\sigma_j$, then

$$\frac{\Delta\lambda}{\lambda} = \frac{1}{2}\left\{K - 1 + \frac{\sigma_j}{\omega\epsilon_0}\right\} \int_{\text{sample}} E^2 dv \Big/ \int_{\text{cavity}} E^2 dv, \qquad (6)$$

and

$$\Delta\left(\frac{1}{Q}\right) = \frac{\sigma_r}{\epsilon_0\omega} \int_{\text{sample}} E^2 dv \Big/ \int_{\text{cavity}} E^2 dv, \qquad (7)$$

where E is the electric field in the cavity.

When we have a lossless sample, as is the case of germanium at low temperatures, the measured frequency shift produced by the dielectric constant K allows us to calculate the ratio of the preceding integrals; hence, with a broken-down sample if Q_W is known, the conductivity can be calculated.

To obtain a good time resolution for a given Q, it would be ideal to work at the highest available frequency; the time constant Q_L/ω which is due to the rise-time of the resonant circuit representing the cavity could then be neglected when compared with the times associated with the conductivity changes. When very high frequencies are used, the imaginary part of the conductivity of the sample can become appreciable compared with the real part: $\sigma_j/\sigma_r = \omega/\nu_m$ (for an energy-independent collision frequency). When $\sigma_j/\sigma_r > 1$, a nonnegligible frequency shift accompanies the change in Q; taking it into account in fast transient measurements is a major difficulty. As a convenient compromise we choose $\lambda \approx 11$ cm. Experimentally (by means of continuous-wave measurements), it was verified that at this frequency the changes in the resonant frequency of the cavity resulting from the changes in electron density, could not be detected, being completely swamped by the changes in Q.

The microwave measuring power was sufficiently small (≈ 1 μwatt) to have a nonmeasurable effect on the sample conductivity. This was ascertained by measuring the impedance of the cavity when the microwave power was doubled and verifying that, within experimental error, the impedance of the cavity remained unchanged. During these tests the microwave power was continuously applied so that an eventual heating of the sample would have been much larger than that produced by the short measuring pulses used in the transient measurements. A block diagram of the circuit is given in Fig. 2.

[19] H. A. Bethe and J. Schwinger, National Defense Research Committee Report D 1-117, 1943 (unpublished).
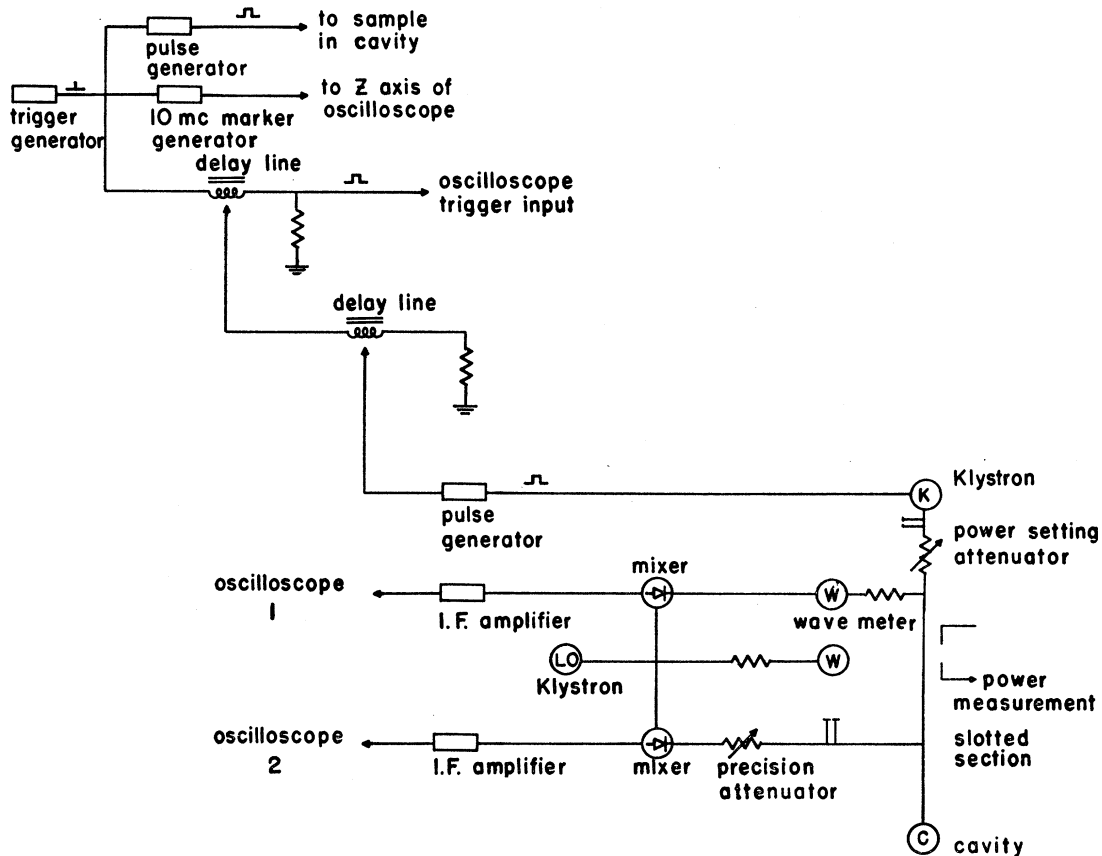
FIG. 2. Block diagram of the experimental apparatus used for measuring the very fast changes in conductivity.

A final problem must be solved before we can calculate the electron density from the observed conductivity: the electron mobility must be determined. Arbitrarily, we chose a mobility $\mu = 10^5$ cm²/v-sec; we refer the reader to Sec. IV for a justification of our choice.

Recombination light was detected by means of a far infrared photocell that consisted of a block of Sb-doped germanium whose impurity density was approximately 10^{16}/cc. Along the axis of this block, a hole was bored, and the sample under study was fitted into it in such a way that it would not have electrical contact with the photocell (Fig. 3). Both samples were housed in a light-proof casing and put into the liquid-helium Dewar.

By means of a constant field applied to the sample, breakdown was produced. Simultaneously, the conductivity of our "detecting block" was monitored so that any changes in its conductivity could be detected. These changes were detected with the help of a capacitively coupled amplifier and an oscilloscope. We chose to apply to our sample a voltage that would produce intermittent breakdown, and this effectively modulated the light output. In this manner, we avoid the unavoidable long time constants that are connected with

the high impedance of the detector (the modulation being at a relatively low frequency), as well as the pickup problems that are present when pulse techniques are used.

It is expected, in view of the high density of impurities in the detecting crystal, that the binding energies of the electrons to the donors will be somewhat smaller than in purer samples. This is evidenced by the fact that impurity band conduction is dominant at 4.2°K, as should be expected when there is an appreci-
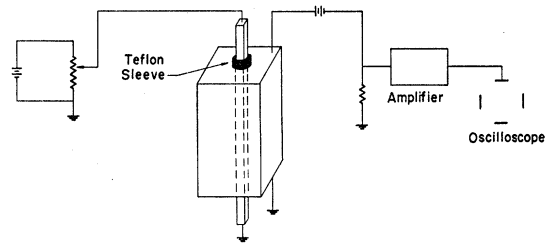

FIG. 3. Diagram of the experimental setup for detecting the emission of light during breakdown. The sample under study is mounted in the hole on the axis of the large germanium parallelepiped $(N_D - N_A \approx 10^{16}$ antimony atoms/cc). Both samples were mounted in a light-proof case that was lowered into the helium Dewar.

TABLE I. Characteristics of the samples used in the experiment.

Sample	Dimensions mm^3	Doping element	Photoconductive lifetime	Room temp. resistivity	Evaluations of N_A by originating laboratory
BTL-1[a]	1.98×2.03×22.6	Sb	>1000 μsec	31.7 ohm-cm	between 1 and 10% N_D
BTL-2[a]	0.88×0.8×18	Sb	>1000 μsec	31.7 ohm-cm	between 1 and 10% N_D
LL-2	1.4 ×1.4×16.5	As	2310 μsec	35 ohm-cm	unknown
n WLB-28-6	1.75×1.46×6.96	Sb	unknown	$N_D \approx 2 \times 10^{13}$/cc[b]	5×10^{12}/cc

[a] The etch pit count on the BTL samples was of the order of 100/mm^2 on the smaller face of the parallelepiped that constituted the samples. No similar data are known for the other samples.
[b] From reference 14.

able overlap of the electron wave functions corresponding to neighboring donors.

Our samples had different origins. The BTL samples were obtained from Bell Telephone Laboratories, Murray Hill, New Jersey, by courtesy of L. J. Varnerin, Jr. These samples are supposed to have between 1% and 10% minority impurities; the major impurity is Sb. Sample LL-2 came from Lincoln Laboratory, Massachusetts Institute of Technology, by courtesy of P. L. Moody. The major impurity is As; its compensation was unknown. Sample n-WLB 28-6 was obtained from S. H. Koenig of Watson Laboratories, International Business Machine Corporation, and is the same as that used for the measurements given in reference 14. The characteristics of the samples used in the experiment are shown in Table I.
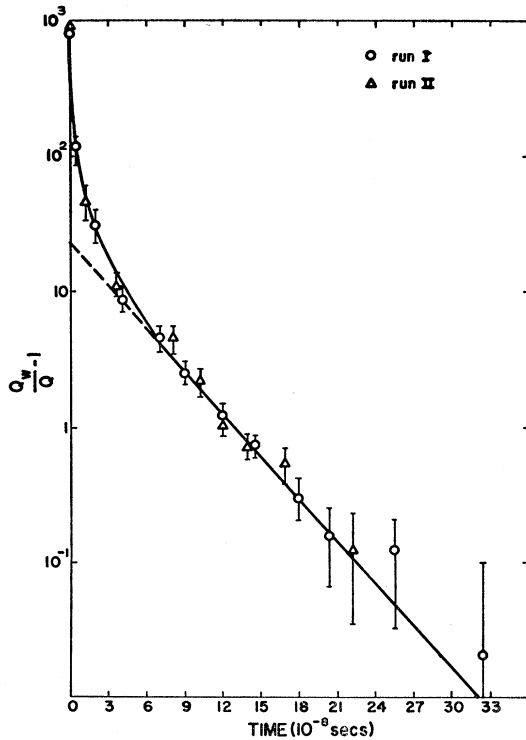

FIG. 4. Variation of the microwave losses in sample BTL-1 as a function of time after the breakdown field is removed. $(Q_W/Q)-1$ is proportional to the sample conductivity. The full line is obtained by fitting a curve solution of Eq. (1); $B=1.05$; temperature, 4.2°K.

IV. EXPERIMENTAL RESULTS

Using the microwave pulse technique described above, we measured the conductivity of sample BTL-1 as a function of the time interval from the instant the breakdown field had been removed. Figure 4 shows the results at 4.2°K. The solid line is drawn according to what would be expected from the solution of Eq. (1)

$$Q_W/Q - 1 = (A/B \exp t/\tau - 1).$$

Here, τ is measured directly from the slope of the straight line, and B is approximately obtained from the ratio of $[(Q_W/Q)-1]$ at $n=n_0$ and the extrapolation of the exponential towards $t=0$. For samples with a very small compensation, small changes in B around 1 will produce large changes in the theoretical curves. In the case of sample BTL-1 for a breakdown field of 14 v/cm, B is 1.05, and $N_A/(N_D-N_A) \approx 1.2\%$. The difference obtained for LL-2, which is more heavily doped (as is also evaluated from the breakdown characteristics) is clearly seen in Fig. 5; here the coefficient B has a value of 1.2. The values of N_A of Table II were calculated from the conductivity that corresponds to the extrapolation towards time $t=0$ of the exponential portion of the decay of the electron density. For this evaluation of N_A we assumed $\mu = 10^5$ cm^2/v-sec.

This choice of mobility can be justified. An upper limit for the mobility should be evaluated as being equal to that of pure ionized impurity scattering; for BTL-1 this is $\mu \approx 4 \times 10^5$ cm^2/v-sec. Another evaluation can be obtained from the data of Debye and Conwell[20] (on a sample similar to ours) measured at 11°K if it is extrapolated to 4.2°K and pure ionized impurity scattering is assumed. Finally, the results of cyclotron resonance of the Lincoln group[21] indicate that $\tau \approx 10^{-10}$ sec at 4.2°K. It is well known that the collision time measured by cyclotron resonance appears to be longer than the collision time computed from pure ionized impurity scattering; cyclotron resonance appears to discriminate against point imperfections. At these low temperatures and with the low density of compensating impurities present, scattering connected with im-

[20] P. Debye and E. Conwell, Phys. Rev. 93, 693 (1954).
[21] H. J. Zeiger, C. J. Rauch, and M. E. Behrndt, J. Phys. Chem. Solids 8, 496 (1959).

TABLE II. Recombination coefficients as a function of temperature.

T	τ_{rec}(sec)	τ_{tail}(sec)	α(cm³/sec)	σ_r(cm²)	β/α(cm⁻³)
		(a) Sample BTL-1			
4.2	$4.3\pm0.4\times10^{-8}$	$41\pm4\times10^{-8}$	5.1×10^{-5}	1.85×10^{-11}	2.3×10^{5}
3.42	$3.3\pm0.3\times10^{-8}$	$45\pm4\times10^{-8}$	6.6×10^{-5}	2.63×10^{-11}	3.82×10^{3}
2.96	$2.3\pm0.3\times10^{-8}$	$35\pm4\times10^{-8}$	9.45×10^{-5}	4.12×10^{-11}	24.7
	$N_A\approx4.6\times10^{11}$/cc			$N_D-N_A\approx3.8\times10^{13}$/cc	
		(b) Sample LL-2			
4.2	$5.6\pm0.3\times10^{-8}$	27×10^{-8}	5.1×10^{-6}	1.85×10^{-12}	5.7×10^{2}
3.48	$5.1\pm0.5\times10^{-8}$	$\cdots$	5.6×10^{-6}	2.24×10^{-12}	0.77
3.05	$3.0\pm0.6\times10^{-8}$	$\cdots$	9.5×10^{-6}	4.05×10^{-12}	7×10^{-4}
2.13	$2.5\pm0.3\times10^{-8}$	$\cdots$	11.6×10^{-6}	5.9×10^{-12}	3.28×10^{-13}
	$N_A\approx3.5\times10^{12}$/cc			$N_D-N_A\approx4.2\times10^{13}$/cc	

purities like H, N, and O, that are present in large quantities should become important.[22]

In this work it was noticed that for sample BTL-1 the conductivity corresponding to an electron density $N_A/[1+(N_A/n_0)]$ does not appear to depend on temperature in the range measured. The dependence of such conductivity in sample LL-2 is also very small.

These experimental results and the order-of magnitude calculations of previous workers lead us to conclude that the errors associated with this arbitrary choice of the mobility should not be greater than a factor of 3.

If the breakdown field is increased in either value or duration, a larger time constant appears in the ultimate decay of the density. This was attributed to Joule heating of the sample. In Fig. 6 the decay of the density in the low-field case is compared with the decay in the case of a higher breakdown field. If the long tail appearing in the curve of the higher breakdown field is extrapolated towards time $t=0$ and the corresponding

values are subtracted from the experimental data, the newly calculated points fall on the curve of the lower breakdown field. This slower decay process is probably never absent; experimentally, we can only minimize its importance by decreasing the applied breakdown field and the time during which the sample is "broken down." This time constant is very clear for an applied field of 43 v/cm; it is, however, probably responsible for the departure from a pure exponential of the last two points of Fig. 4, even though the field is only 14 v/cm.
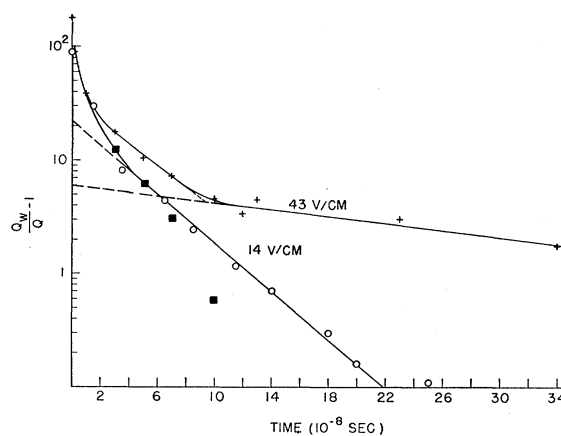
FIG. 6. Thermal effects appear if the power input during breakdown is increased (sample BTL-1 at 4.2°K). The longer time constant is attributed to Joule heating. The decay corresponding to pure recombination (and a lower breakdown field) can be obtained if the effect of heating is subtracted 229.

The long time constant is temperature-independent (for temperatures below 4.2°K) and does not depend upon the value of the breakdown field; the breakdown field determines only the intercept of the extrapolation of this exponential with the ordinate axis. To explore the origin of this tail, measurements were made on sample BTL-2 with dimensions approximately half those of BTL-1 but originating from the same ingot (Fig. 7). The low-field time constant of BTL-2 is not changed as compared with that of BTL-1, but the high-field time constant is nearly halved. This is what
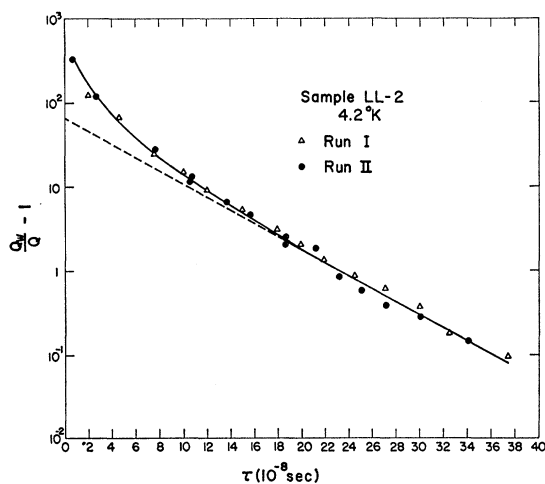
FIG. 5. Variation of the microwave losses in sample As LL-2 as a function of the time after the breakdown pulse is removed. The full line is a solution of Eq. (1); $B=1.2$; temperature, 4.2°K.

[22] H. A. Papazian and S. P. Wolsky, J. Appl. Phys. 27, 1561 (1956); J. H. Crawford, H. C. Schwenler, and D. K. Stevens, J. Appl. Phys. 22, 838 (1956).
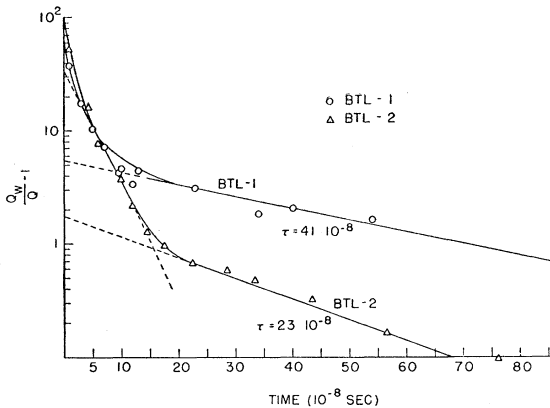
FIG. 7. Variation of conductivity after the breakdown field was removed. Both samples were cut from the same ingot; BTL-2 has cross-sectional dimensions nearly half of those of BTL-1. The fast decay is not influenced by sample size; the longer time constant is approximately halved, as expected from theory.

would be expected if the long time constant is due to heating and the phonon mean-free path is limited by sample size.

Similar measurements were made at lower temperatures. At temperatures between 4.2°K and the λ point of helium, the importance of heating was often appreciable, and the recombination time constants had to be obtained by subtracting the thermal effect. The results are shown in Table II and in Figs. 8 and 9. The best measurements are those at 4.2°K, where the error is smaller than 10%. At lower temperatures the errors increase somewhat, but they remain of the same order of magnitude.

Measurements on sample n-WLB-28-6 should be considered separately. This sample was shorter than the others, so that it could not completely fill the gap in the re-entrant cavity used for the measurements.
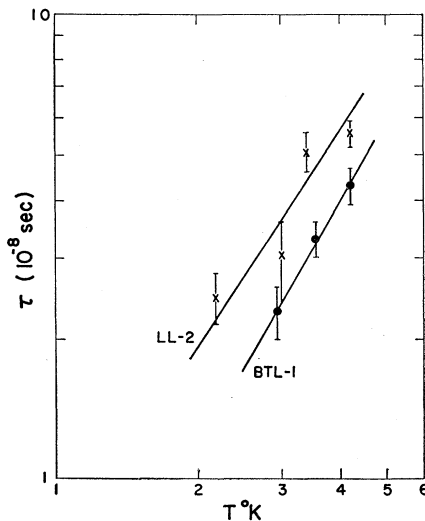

FIG. 8. Variation of the time constants for recombination as a function of temperature.

As a result the leads necessary to produce dc breakdown penetrate into the cavity, producing an appreciable distortion of the rf field, and our method for calculating the integrals appearing in Eq. (6) is not very reliable, particularly when the sample is broken down. Two elements are responsible for the decrease of our sensitivity: the penetration of the leads (which make the dc contact to the sample) and the decrease of nearly 4 in the sample volume. Consequently, the changes in the value of $(Q_W/Q)-1$ could not be followed over such a large range as in the other samples. The results are shown in Fig. 10. The corresponding time constant is
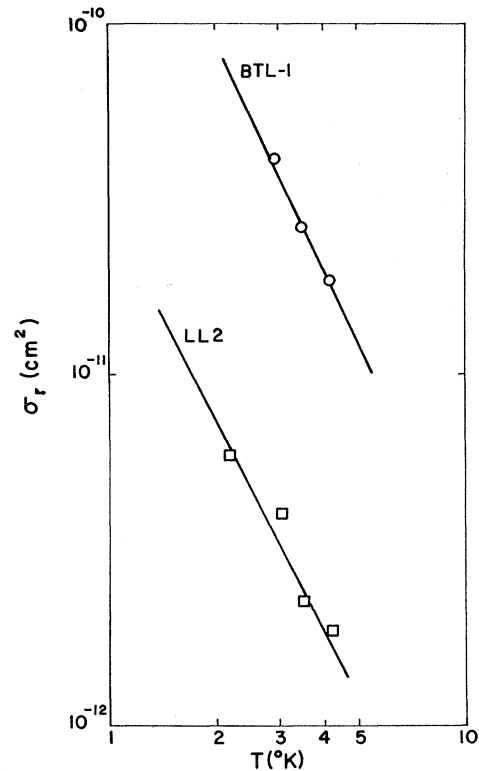

FIG. 9. Variation of the recombination cross section with temperature. $\sigma_r = 1/\tau \langle v^2 \rangle^{\frac{1}{2}} N_A$; N_A is calculated from the measured conductivity corresponding to the extrapolation of the exponential of Fig. 4 towards $t=0$.

3.4×10^{-8} sec, approximately three times smaller than the result of Koenig[14] on the same sample.

From our data on n-WLB-28-6 it was impossible to tell whether heating increased the apparent time constant. To obtain breakdown in a time of the order of microseconds larger fields had to be applied to this sample than to BTL-1. It was also not possible to observe the nonexponential portion of the recombination. This could be ascribed either to the fact that when the breakdown field is sufficiently low and there is no appreciable heating, then $n_0 < N_A$, or to the fact that the perturbation from both the wires and the sample produces changes in the field configuration of the cavity (mode jumping). We shall compare our result on this

sample with those of Koenig and try to explain the corresponding discrepancies, assuming that they are due to heating.

Light emitted during the breakdown of BTL-1 was detected. The signal observed was in the form of a large increase of noise when the value of the dc field was such that intermittent breakdown was produced. If the dc field applied to BTL-1 was increased, the detected signal decreased, as is to be expected if the sample's temperature is slightly increased by ohmic heating. The spectral distribution of the light was not measured, but since it is ascribed to recombination light, its energy cannot be much smaller than the binding energy of Sb donors in germanium. Its lower limit
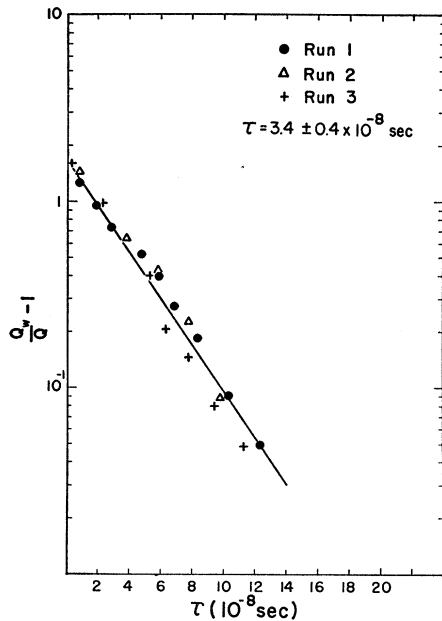

FIG. 10. Variation of the conductivity as a function of time after the removal of the breakdown pulse. Sample n WLB-28-6; temperature 4.2°K. Field applied during breakdown: run 1, 77 v/cm during 0.9 μsec; run 2, 77 v/cm during 1.8 μsec; run 3, 71 v/cm during 2 μsec.

should be that corresponding to the transition between the impurity band and the conduction band of our detector.

Recently, Koenig[23] confirmed this observation. He furthermore observed that the signal detected and attributed to light is larger when the broken-down sample was antimony-doped germanium and the detector was arsenic-doped germanium, rather than vice versa, as would be expected from energy considerations.

V. DISCUSSION OF RESULTS

We shall first discuss the rate of change of density resulting from thermal effects and explain the reasons

that lead us to attribute to them the longer observed time constant shown in Fig. 6. Assume that during breakdown the temperature of part of our sample is slightly changed by Joule heating. Differentiating Eq. (2) with $n \ll N_A$, we have

$$\frac{1}{n}\frac{dn}{dt} \approx \frac{\epsilon}{kT}\left(\frac{1}{T}\frac{dT}{dt}\right).$$

For small changes of temperature, T/ϵ can be considered nearly constant, and the rate of change of the logarithm of the density will be approximately proportional to that of the logarithm of the temperature: $1/\tau_T$. Classically, τ_T is determined by the specific heat of the sample, its thermal conductivity, and the sample dimensions.

If we wish to use phonons to describe the transport of thermal energy we should introduce the idea of phonon mean-free path λ as suggested by Casimir.[24] The random-walk problem applied to this case allows us to compute the number of collisions that a particle whose mean-free path is λ experiences before diffusing out the sample: $N_C = 3\Lambda^2/\lambda$ where Λ is the diffusion length of the sample. In the case of a parallelepiped

$$\Lambda^{-2} = \frac{\pi^2}{4}\left(\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)$$

a, b, and c are equal to one-half the sample dimensions.

The time between successive collisions is λ/v, so that the average time necessary for particles to diffuse out of the sample is

$$\tau_T = N_C\lambda/v = 3\Lambda^2/\lambda v.$$

It is well known that at very low temperatures the phonon mean-free path will be limited by sample dimensions; λ should then be taken as of the order of the smallest sample dimension. This is borne out, in the case of germanium, by the measurement of thermoelectric power at very low temperatures,[25,26] and in a more direct fashion by the measurements of the thermal conductivity below 10°K made by Geballe and Hull.[27] Accordingly, this will mean that τ_T varies proportionally to sample dimensions, and not proportionally to the square of sample dimensions, as expected from the usual diffusion theory. This fact is verified experimentally by the halving of the time constant measured on sample BTL-2 as compared with that on BTL-1. In the case of an isotropic distribution of phonons, the time constant can be calculated from the preceding formula by using an average of the velocities of longitudinal and transverse phonons in the different direc-

[23] S. H. Koenig and R. D. Brown, III, Phys. Rev. Letters 4, 190 (1960).

[24] A. B. Casimir, Physica 5, 495 (1938).
[25] A. P. R. Frederickse, Phys. Rev. 92, 248 (1953).
[26] T. H. Geballe and G. W. Hull, Phys. Rev. 94, 1134 (1954).
[27] T. H. Geballe and G. W. Hull, in Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry, Madison, Wisconsin, 1957, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 380.

tions. The result, calculated with $v=3.0\times10^5$ cm/sec, $\tau_T=2\times10^{-7}$ sec, is in reasonable agreement with the experimental result (4.1×10^{-7} sec).

If the phonon distribution is not isotropic and/or there is not equipartition of energy between the longitudinal and transverse modes (as is expected in the case of breakdown pulses of very short duration), τ_T should be different from the calculated value. The fact that our phonons are largely produced by electrons with a net drift velocity along the axis of the sample tends to produce a phonon beam directed in the same direction as the electron drift velocity and consequently leads to an increase of the time constant that is necessary for the decay of the phonon density. On the other hand, our electrons mainly produce longitudinal phonons whose propagation velocity is somewhat greater than the previously assumed average velocity. This consideration tends to decrease our estimate of τ_T. The fact that the calculated thermal-decay time constant is shorter than the experimental value tends to support the idea that the phonon distribution has been changed.

Two other observations support this interpretation of the origin of the longer time constant: its independence of the electric field and temperature in the range covered. This is in contrast with the electric field dependence of the intercept of the thermal exponential with the ordinate axis. (This intercept is proportional to the density of high energy ($\approx1\times10^{-3}$ ev) phonons achieved during breakdown.) Both of these properties are to be expected. When λ is limited by sample size, the only term in τ_T that presents a variation with temperature is the sound velocity, v. This variation is expected to be very small and was not detected with our type of measurements. For the same reason, τ_T is independent of the applied field as long as the effects of the anisotropy and nonequipartition of energy of the phonon distribution do not change very much. The variation of the initial phonon density distribution with electric field is also to be expected. The density of the energetic phonons that can produce electrons is related to the electric field applied to the sample. Summing up, it can be said that the long observed time constant can be attributed to a variation of n_∞ with time; this variation is due to a variation of the lattice temperature T_L.

We can now draw some conclusions on the recombination of electrons and donors. As we stated in the introduction, there are, basically, three different calculations for the recombination cross section. Sclar and Burstein[8] calculate the recombination probability for a radiative transition by scaling the well-known result for the hydrogen atom. Their result predicts a recombination probability proportional to $T_e^{-\frac{1}{2}}\epsilon$, where ϵ is the ionization energy of the donor level. The same criticism that is important for the case of hydrogen atoms can be applied here[28]: No provision is made for

an easy way to dispose of the momentum of the incident electron that must be given to the crystal as a whole. Gummel and Lax[9,10] calculated the recombination probability characterized by the emission of a single acoustical phonon. They predict a recombination probability proportional to $q_0^{-4}T^{-\frac{1}{2}}\epsilon^5$, where q_0 is the momentum of the emitted phonon whose energy is equal to the binding energy of the electron.

Finally, Lax[11,12] proposed a theory in which the electron decays from the conduction band into the ground state of the impurity through its excited levels. The temperature dependence of the recombination probability should be $T^{-7/2}$ and should be independent of the binding energy of the electron to the impurity. The measurements of Koenig[14] were interpreted by Lax as confirming this theoretical calculation; the flattening of the measured time constants toward the low-temperature end of the range of measurements (Fig. 11) was attributed to the overlap of the excited levels of different impurities at which the electron recombines: This would effectively decrease the number of recombination centers.

At 4.2°K we again measured the recombination time constant of sample n WLB-28-6 used by Koenig,[14] obtaining the point shown by a black triangle on Fig. 11. The discrepancy between our measurement and Koenig's can be explained in terms of heating. The temperature-independent value of the time constant represented by the broken straight line is obtained by means of the previous theory of thermal decay. When the temperature is increased, in the presence of important thermal effects, the measured time constant should vary continuously from pure thermal decay to pure recombination. As we saw previously (Fig. 6),
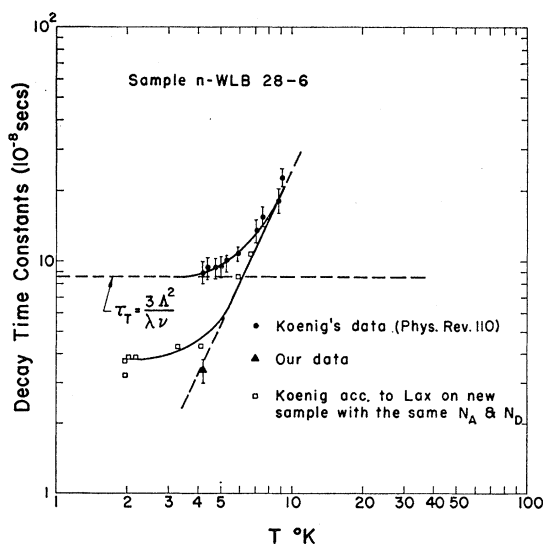

FIG. 11. Variation of the measured time constants for the decay of the conductivity as a function of temperature. Sample n WLB-28-6 and the equivalent one reported in reference 12. The microwave measurement of the time constant clearly lies on the tangent to the high temperature, measurements of Koenig.

[28] R. G. Fowler, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 22, p. 230.

if the decay of the density is not followed for a few orders of magnitude it is not possible to recognize the existence of heating, and the recombination time constant will appear longer than in the absence of heating.

Koenig's measurements,[14] in which the variation of the sample resistance was displayed on an oscilloscope, have the characteristic of having a relatively small range over which the sample's resistivity could be accurately followed. In that type of measurement, a greater weight is given to the long times, when heating is expected to be more important if $\tau_T > \tau$. This condition is found at the lowest temperatures.

More recent measurements by Koenig, as reported by Lax,[12] on a sample having the same impurity concentrations as n WLB 28–6 tend to confirm this view; they are shown by squares on Fig. 11. Some of these measurements, as well as our own, on n WLB 28–6, fall on a straight line tangent to the high-temperature measurements given in reference 14. The slope of this line is approximately 2, as is expected from our measurements.

If we take our result for the value of the time constant for recombination at 4.2°K, and take the value $5.10^{12}/$ cm^3 quoted by Koenig[14] for the value of the compensation, there is a large disagreement in the value of the cross section for recombination for BTL-1 and n WLB 28–6. This discrepancy can be very much decreased if we calculate the compensation with the Brooks-Herring formula for ionized impurity scattering corresponding to the mobility measured by Koenig[29] (7.5×10^5 cm^2/v-sec at 4.2°K).

To explain the observed magnitudes of the cross sections, their dependence on the binding energy of the donor ground state, and their lattice temperature, we propose a mechanism by means of which an electron is initially trapped in a highly excited state[30] and then decays radiatively to the ground state.

Assume that a low-energy electron initially emits a phonon being captured into a p state of the impurity whose energy is of the order of kT below the edge of the conduction band.[11,12,30] From this bound state the electron can either be scattered back into the conduction band, into a neighboring bound state with approximately the same binding energy, or it can decay into the ground state. If the electron is scattered into another highly excited bound p state, we have again the same possibilities, if it is instead a state with some other angular momentum the probability of radiative transition to the ground state decreases very much and only phonon induced transitions to other excited states or the continuum are possible. Finally if the electron gains an energy of the order of kT it will be excited into the conduction band and the process can repeat itself.

For the sake of simplicity in such a qualitative calculation we treat in the same way all electrons excited out of the p state. We shall call α_{pn} the probability that the electron in the excited state scattered by a phonon, and α_{pt} will be the probability that an electron will make a radiative transition to the ground state.

The cross section for the capture of the electron in the excited state σ_e will be estimated to be equal to the geometrical cross section of the corresponding classical orbit:

$$\frac{e^2}{Kr_0} = kT; \quad \sigma_e = \pi r_0^2 = \frac{\pi}{K^2}\left(\frac{e^2}{kT}\right)^2 \approx 2 \times 10^{-9} \text{ cm}^2$$

at 4.2°K.

The total recombination cross section will be

$$\sigma_r = \sigma_e \frac{\alpha_{pt}}{\alpha_{pt} + \alpha_{pn}} \approx \sigma_e \frac{\alpha_{pt}}{\alpha_{pn}}.$$

α_{pn} can be estimated from conductivity measurements,[21,31] $\alpha_{pn} \approx 10^{10}$; α_{pt} can be evaluated from a calculation similar to the calculation used for the transition between bound states in a hydrogen atom[32]:

$$\alpha_{pt} = \frac{e^2 \nu^3}{h}\left(\frac{n}{c}\right)^3 \cos^2\theta |x|_{ab}^2,$$

where n is the index of refraction of germanium and x_{ab}, is the matrix element of the coordinate x.

An order of magnitude of $|x|_{ab}$ can be obtained by substituting it by a, the Bohr radius of the electron in the ground state of the impurity:

$$\alpha_{pt} = (n^3)\left(\frac{e^2}{c^3}\right)\nu^3 a^2 \approx n^3 \left(\frac{1}{137}\right)\left(\frac{\nu a}{c}\right)^2 \frac{\nu}{K^2}$$

$$\approx \frac{\nu n^3}{(137)^3 K^2} \approx 10^{-7}\nu.$$

In our case $\nu \approx 3 \times 10^{12}$ cps, so that $\alpha_{pt} \approx 3 \times 10^5$, and at 4.2°K $\sigma_r \approx \sigma_e(\alpha_{pt}/\alpha_{pn}) \approx 6 \times 10^{-14}$ cm^2.

This order-of-magnitude calculation should be considered a lower limit of σ_e. The quantity α_{pt} might be increased by the contribution of states other than the p states considered in this "hydrogen-like" model—from both the effect of the ellipsoidal effective mass and the valley orbit interaction. The value of σ_r could also be appreciably increased by the fact that when we take α_{pn} equal to the inverse of the conductivity mean free time for phonon scattering, we overestimate it. Such a choice of α_{pn} would not have a "minimum exchanged energy" as is necessary for changing the state of the electron. This calculation allows for the possibility of

[29] W. Schillinger (private communication, April, 1959).

[30] The large cross sections obtainable if an electron is trapped in an excited state were pointed out to us by A. Rose, March, 1959.

[31] F. Morin and J. P. Maita, Phys. Rev. 34, 1525 (1954).

[32] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1954), 3rd ed., p. 178.

some dependence of the recombination cross section on binding energy, as well as the emission of light as observed by us and by Koenig and Brown.[23]

Ranges of 7.5- to 52-kev H_2^+, D_2^+, He^+, and Ne^+ Ions in Quartz*

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Experimental values of penetration depths of positive ions in quartz obtained from measurements of reflection coefficient versus wavelength are compared with theoretical predictions. Measurements of the change in refractive index of quartz as a function of the energy dissipated per unit volume are shown to give experimental values for the ratio of energy loss due to displacement collisions per unit thickness to the energy loss due to ionization per unit thickness. The energy loss due to displacement collisions per unit thickness agrees with theoretical predictions. From the experimental values of energy loss due to ionization, it is found that the cross sections for scattering of valence electrons by the field of the incident atoms are an order of magnitude larger than the geometric cross sections.

I. INTRODUCTION

THE penetration in solids of atoms with energies below 50 kev is of current interest in connection with investigation of radiation effects in solids. Most of the information available[1,2] deals with energies above 50 kev and contains very little concerning the penetration of medium weight low-energy atoms such as are formed in solids by fast neutron bombardments. Experimental determination of the ranges of the low-energy atoms of interest here are hampered by the very small penetration distances (10^{-5} cm) involved. However, a variety of techniques have been successfully employed to obtain range information at these low energies.[3-7] In this paper, some recent determinations of ion ranges in quartz[8] are compared with the theoretical predictions.

The theoretical analysis of low-energy atom penetration is limited to approximate methods which are valid over only small energy regions. In general the atoms lose energy both by ionizing atoms of the stopping material and also by making elastic collisions with atoms of the stopping material. The general framework of the theory of penetration of energetic particles is presented by Bohr.[9] More specific discussions of the penetration of low-energy atoms are given by Nielsen[7] and by Seitz and Koehler.[10]

2. THEORY

a. Energy Loss by Elastic Collisions

Following the treatment outlined by Seitz and Koehler,[10] the collision problem can be treated classically as long as

$$b/\lambda \gg 1, \tag{1}$$

where $\lambda = \hbar/\mu V$ and where $b = Z_1 Z_2 e^2 / \frac{1}{2}\mu V^2$ is the classical distance of closest approach in pure Coulomb scattering. Z_1 is the atomic number of the incident atom, V its velocity, and e is the electronic charge. Z_2 is the atomic number of the stationary atom. M_1 and M_2 are the atomic masses of the incident and stationary atoms, respectively, and $\mu = M_1 M_2 / (M_1 + M_2)$ is the reduced mass of the system. In all the cases of interest here, the classical approximation is justified.

* Supported by the U. S. Atomic Energy Commission.
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[2] S. K. Allison and S. D. Warshaw, Revs. Modern Phys. **25**, 779 (1953).
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[4] J. Koch, Nature **164**, 19 (1949).
[5] R. A. Schmitt and R. A. Sharp, Phys. Rev. Letters **1**, 445 (1958).
[6] U. F. Gianola, J. Appl. Phys. **28**, 868 (1957).
[7] K. O. Nielsen, *Electromagnetically Enriched Isotopes and Mass Spectrometry*, edited by M. L. Smith (Academic Press Inc., New York, 1956), p. 68.
[8] R. L. Hines and R. A. Arndt, Phys. Rev. **119**, 623 (1960).

[9] N. Bohr, Kgl. Danske Videnskab. Selskab. Biol. Medd. **18**, No. 8 (1948).
[10] F. Seitz and J. S. Koehler, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 305.