Electron Bombardment Conductivity in Diamond*

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A study has been made of electron bombardment conductivity in diamond using primary electrons of energies up to 14,000 ev. An alternating field method is used which reduces or eliminates the effects of internal space charge fields. Data on internal yields as a function of crystal field are given for both electron and positive hole carriers. Internal yields as high as 600 have been attained. The experimental curves are fitted to a theoretical curve for the space charge free crystal from which are derived reasonable values for the number of electrons produced in the conduction band per incident primary electron, the probable life time of the conduction electrons and the crystal trap density. Experiments are described which lead to a hypothesis of space charge neutralization. A possible cause of the current fluctuations observed at high crystal fields is discussed.

1. INTRODUCTION

ALTHOUGH photoconductivity has been studied extensively, the similar process of bombardment conductivity, i.e., the rendering conductive of an insulator or semi-conductor by particle bombardment, has received scant attention until recently. Early work with alpha-particle bombardment[1-3] demonstrated disappointingly small induced currents per incident particle. However, the recently published work of Van Heerden[4] demonstrated the feasibility of detecting individual high energy particles in silver chloride crystals at low temperatures and has stimulated considerable interest in its use as a solid counter.[5-7]. Earlier attempts by D. E. Wooldridge to observe electron bombardment conductivity led to the use of alpha particles as a tool to select suitable solids and to the utilization of diamond as a solid counter at room temperature.[8-14] Thallium bromo-iodide,[15] cadmium sulfide[16] and zinc sulfide[17] have also been shown capable of high energy particle detection.

A problem closely related to the solid counter and also to external secondary emission is electron bombardment conductivity produced by relatively low energy electrons, i.e., excluding beta-conductivity. Here we can define an internal yield equal to the induced current traversing the solid as measured externally, divided by the bombarding current. Lenz[18] obtained a yield of 10^{-4} or less with a crystal of zinc sulfide and 20,000 ev bombarding energy. There is some doubt as to whether he actually observed bombardment conductivity or whether his results were caused by some other effect. Distad's[19] results on zinc sulfide with 900 ev electrons were greatly complicated by space charge effects and his yields were less than 10^{-5}. Bloembergen[20] attempted to measure bombardment conductivity in silver chloride by electrons of 500 ev energy and could detect no effect.

The work to be described is a study of electron bombardment conductivity in diamond. Although the results have a considerable bearing on its use as a solid counter, it is of more significance

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that a new method of investigating certain of the solid state properties of insulators and semi-conductors is described. The information so obtained may also be of considerable value in setting up theories of external secondary emission or of dielectric breakdown.

2. MATERIAL CONSIDERATIONS

To determine the type of material which would be best suited to demonstrate bombardment conductivity, let us consider the actual process in its simplest form. In Fig. 1, a beam of electrons bombards an insulator or semi-conductor through a thin electrode which is mounted directly on the surface of the material and to which a current indicating device, such as a galvanometer is connected. On the other face of the material is mounted a second electrode maintained at an elevated potential. According to available theories on the interaction of electrons with matter[21,22] most of the energy of the bombarding electrons will go into the excitation of a relatively large number of electrons in the solid if the bombarding energy is sufficiently high. In an insulator, this will result in the elevation of electrons from the filled band into the conduction band. The production of each of these "internal secondary" electrons will involve the creation of a positive hole in the filled band which may also be mobile. Although the internal secondaries will actually be produced throughout the range of the bombarding primaries, let us assume for clarity that they are all produced at the end of the primary range at the distance from the surface represented by the dotted line in Fig. 1. Through collisions with the lattice, the internally produced electrons and positive holes will rapidly come into thermal equilibrium with the lattice. However, superimposed on their random thermal motion will be a drift velocity induced by the electric field, the electrons moving towards the right and the positive holes to the left with the field polarity shown. This movement of charge within the material will induce a charge in the external circuit as discussed by Shockley.[23] If an electron travels a distance x through the crystal, the charge measured by the galvanometer or electrometer will be ex/l where l is the distance between the electrodes and e the electronic charge. The galvanometer will measure a current, caused by the charge displacement, even if no charge flows from the crystal to the electrode, i.e., if all the electrons are trapped in the crystal. These considerations also apply, of course, to the positive holes. Assume that an electron remains in the conduction band for a length of time T before being trapped and that T is independent of the applied field F. Then the range ω_- is given by

$$\omega_- = (vT)_- F,$$

where v is the mobility (velocity of drift in unit field) of an electron in the conduction band. Here v and T are appropriate to an electron. The range ω_+ for positive holes is defined similarly with suitable values of v and T. Thus, the charge observed in the external circuit is proportional to the total range of all the conducting electrons and positive holes in the material. Or, more precisely,

$$Q_{\text{obs}} = e/l(\sum \omega_- + \sum \omega_+). \tag{1}$$

To make Q_{obs} large, we wish l small and ω_- and ω_+ large. This implies that the material should be one in which v and T are large. T is inversely proportional to the density of electron traps in the material and thus we would wish to minimize the number of traps. These traps may be caused by lattice defects, such as vacant lattice points, interstitial ions, domain boundaries, crystal boundaries, or by impurities. These considerations should enable us to list certain

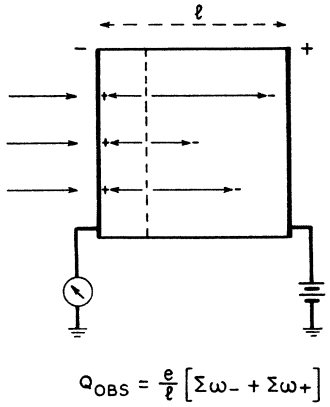

FIG. 1. Illustration of principle of bombardment induced conductivity.

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desirable properties for a material which is suitable for bombardment conductivity.

1. It should be a sufficiently good insulator to permit the application of an adequate field across it during the time that the action is to be observed.
2. It should have relatively few traps for electrons or positive holes. This suggests the use of a single flawless crystal with a high degree of lattice regularity and stability and high chemical purity.
3. Further to reduce the trap density, it should be possible to anneal the crystal thoroughly without distorting the crystal structure.
4. It should have a high electron mobility and, if possible, also a high mobility for positive holes. This also suggests that it would be advantageous to make measurements at low temperatures since, in general, the mobility varies in an inverse manner with the temperature.
5. A large number of internal secondaries should be produced per incident primary electron. Thus the primary energy should be high although not so high that the primary electron would traverse the crystal completely and still retain much energy. Data are not available on the variation of the number of internal secondaries produced for a given primary energy as a function of the forbidden energy gap width.
6. The simple picture presented above does not take into account the internal space charge or polarization effects set up by the trapped electrons and positive holes. A large dielectric constant would tend to reduce the effect of such trapped charges on the internal field. Thus a high dielectric constant would appear to be desirable. It is also possible that this would tend to reduce recombination of electrons and positive holes immediately after they are produced.

At the present time we believe that these are desirable properties for a bombardment conductive material. They are probably not the necessary or sufficient conditions governing the process. It will be observed that diamond fulfills conditions 1, 2, and 6 quite well. Although experimental measurements have not been made of the electron or positive hole mobilities, from theoretical considerations they are expected to be high, thus satisfying condition 4. In part, these were the reasons which led to the original choice of diamond for experiments with alpha-particle bombardment. The fact that these experiments were successful was adequate justification for its use in electron bombardment.

3. THEORY

3.1 Theory for a Space-Charge Free Crystal

Consider the crystal shown in Fig. 1. If the width of the bombarding beam of electrons is large compared with the thickness of the crystal, we can neglect edge effects and consider merely the one dimensional case. We assume that the primary bombarding electrons create a certain number of positive holes in the uppermost filled band and an equal number of electrons in the conduction band of the crystal. We wish to determine the way in which the current in the measuring circuit varies with the field applied across the crystal. In essence, this is the problem which was solved by Hecht[24] for photo-conductivity. However, we must consider the assumptions involved carefully. These are as follows:

A. The traps are distributed homogeneously throughout the crystal.
B. The effects of the space charge fields set up by trapped charges are negligible.
C. The interaction between positive holes and the corresponding free electrons is negligible.
D. The drift velocity of the mobile charge carriers as a result of the applied field is small compared with their thermal velocity.
E. A charge which is trapped either remains trapped throughout the time interval under consideration or is again released in a time which is short compared with the time resolution of the measuring circuit.
F. At any time in any region of the crystal, the number of trapped charges is small compared with the number of available traps, i.e., we do not approach trap saturation.

The extent of the restrictions imposed by these assumptions will be considered later when the experimental results are compared with the theory.

Let us consider first the current contributed only by the free electrons. Assumption *D* implies that the concepts of charge mobility apply and, with assumption *A*, that the probable time which a free electron spends in the conduction band of an infinite crystal is T which is independent of the applied field F. Then the probable range of an electron in an infinite crystal is given by

$$\omega = vFT,$$

where v is the mobility or the drift velocity in a unit field, and is related to τ, the time between collisions with the lattice, by

$$v \sim (e/m)\tau.$$

The subscripts identifying these quantities with free electrons have been omitted for clarity.

[24] K. Hecht, Zeits. f. Physik. **77**, 235 (1932).

These assumptions lead to the mean distance $\bar{x}$ traveled by an electron in a finite crystal[25]

$$\bar{x}=\omega(1-e^{-x_0/\omega}), \tag{2}$$

where x_0 is the distance from the point of origin of the free electrons to the anode. The charge measured externally equals the charge released in the crystal multiplied by $\bar{x}/l$, where l is the total distance between the crystal electrodes. Thus the ratio of the charge observed to the charge released is given by

$$\psi_1=\omega/l(1-e^{-x_0/\omega}). \tag{3}$$

So far we have considered only the contribution of the electrons to the observed charge. If we assign suitable values of mobility v_+ and probable time before trapping T_+ to the positive holes, we obtain a probable range for them of $\omega_+=v_+T_+F$. The calculation of their contribution to the observed charge is exactly analogous to that for electrons except that they are traveling in the opposite direction so that we must replace x_0 by $l-x_0$ and the ratio of the total observed charge to released charge is

$$\psi=\frac{\omega}{l}(1-e^{-x_0/\omega})+\frac{\omega_+}{l}(1-e^{-(l-x_0)/\omega_+}). \tag{4}$$

Although Bethe's[21] equations for the rate of energy loss by electrons to matter are not integrable down to low energies, they should enable us to make an estimate of the depth of penetration of the bombarding electrons. In the experiments which are to be described later, the energy of the bombarding electrons does not exceed 14 kv. Assuming a density[26] for diamond of 3.5, Bethe's equations give a range of about 3×10^{-4} cm for 14-kv electrons. The average distance from the bombarded surface at which a positive hole is produced is probably about 60 percent of this, i.e., mean value of $l-x_0=2\times10^{-4}$ cm. The value of l in all of these experiments is $l=4.5\times10^{-2}$ cm. If the crystal field has the polarity shown in Fig. 1, and is of a sufficiently high value, the positive holes can contribute less than 1 percent to the observed current. For low field strengths where ω is of the same order of magnitude as the depth of penetration of the primaries, the ratio between the portion of the observed current contributed by positive holes to that contributed by electrons is approximately ω_+/ω. In the present work, this means that appreciable errors could occur resulting from the neglect of the positive hole current only at yields which are so low that other effects mask this discrepancy. Hence Eq. (3) has been used throughout.

If the field across the crystal is reversed in direction, the terms "electrons" and "positive holes" should be interchanged and the argument proceeds as before. Again we arrive at Eq. (3) interchanging ω and ω_+.

We must now throw Eq. (3) into a form which is more suitable for comparison with the experimental results. Let the primary bombarding current be i_p and the number of internal conduction electrons produced per unit time be Ni_p. Some of these electrons may recombine with positive holes so let the total number of electrons available for conductivity per unit time be βNi_p. β cannot exceed unity and may be less than unity at low field strengths. We also assume that $x_0\simeq l$. Thus the yield for any given field strength is

$$\delta=\frac{\beta Ni_p}{i_p}\cdot\frac{\bar{x}}{l}=\beta N\frac{\omega}{l}(1-e^{-l/\omega}), \tag{5}$$

where the yield δ is defined as the current passing through the crystal at any instant divided by the bombarding current.

This can be normalized to the expression

$$\Delta=\Omega(1-\exp(-\Omega^{-1})), \tag{6}$$

where

$$\Delta=\delta/\beta N=\delta/\delta_\infty,$$

δ_∞ = the yield at infinite field strength

$$\Omega=\omega/l=vTF/l.$$

A plot of Eq. (6) is given by the solid line in Fig. 10.

3.2 Dissipation and/or Neutralization of Space Charge

Although some of the concepts presented in this section were arrived at as a result of the experiments which are later described, the experi-

[25] A derivation of this equation is given on page 122 of Mott and Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1940).

[26] Robertson, Fox and Martin, Phil. Trans. Roy. Soc. **232(a)**, 463 (1934).

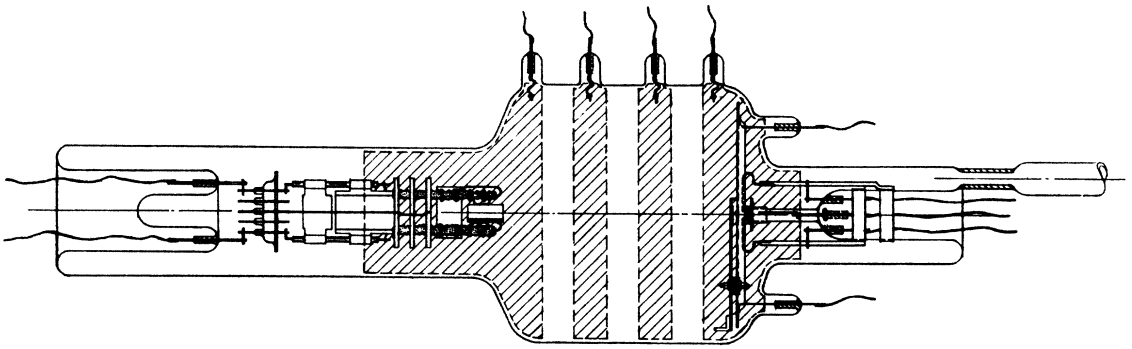

FIG. 2. The experimental tube.

mental procedures will be more readily comprehended if the ideas are discussed at this point.

In the previous section it was shown that for $\Delta<1$, many of the conduction electrons (or positive holes) are trapped in the body of the crystal. These trapped charges set up a space-charge field which opposes the applied field. If the applied field remains fixed and the bombardment is continued, the internal space-charge field will continue to build up until an equilibrium is established which is a function of the rate of arrival of electrons, the applied field and the rate at which electrons are released from traps by thermal agitation, fluorescent radiation or recombination with positive holes. Thus a stationary state can be set up in which the current flowing through the crystal will be a function of all of these parameters and will be less than the corresponding current for an idealized space charge free crystal. To overcome this difficulty the rate of release of trapped electrons could be increased by heat or light although this is not always feasible nor desirable; or the probable range may be increased by filling up the majority of the available traps. However, a rough calculation indicates that with reasonable trap densities ($\sim 10^{16}/\text{cm}^3$), it does not appear possible to set up a steady state by filling all of the available traps as the internal space-charge fields would then probably be too intense, although it may be possible to increase the probable range somewhat by filling up all the traps in a narrow region.

At this point it is observed that conditions similar to those existing in a space-charge free crystal may be obtained by neutralizing the space charge rather than eliminating it. In diamond, the positive holes are expected to have a mobility which is roughly of the same order of magnitude as that of conduction electrons. If an alternating field is applied across the crystal, with the connections shown in Fig. 1, and primary bombardment takes place during some part of both the positive and negative half-cycles of the applied field, the following action takes place: During the positive half-cycle, internally produced electrons travel through the body of the crystal. Some of these are trapped thus setting up a negative space charge field which opposes the applied field. During the negative half-cycle, however, positive holes, resulting from the primary bombardment, travel through the body of the crystal under the influence of the applied field which is now augmented by the previously created negative space-charge field. Some of these positive holes may recombine with the trapped electrons and some may themselves be trapped. In either case the net result is a reduction of the negative space charge field and if the relative bombardment during the positive and negative half-cycles of the applied field is properly adjusted, it should be possible to neutralize the crystal completely before the onset of the next pulse of current to be studied. This is the hypothesis of space-charge neutralization and it will later be shown that the experimental results can be explained on this basis.

It will be observed that the mere fact that an optimum electron range can be achieved by adjustment of the relative bombardment during the positive and negative half-cycles, does not necessarily mean that complete neutralization

has been attained. Undoubtedly the positive holes are not trapped in exactly the same regions as the electrons, as a result of differences in their relative ranges. Thus the crystal as a whole may be made neutral but space-charge fields may still exist within the crystal. It is possible that the use of the d.c. bias field together with the a.c. field may further improve this situation.

4. EXPERIMENTAL METHOD

4.1 Experimental Tube

Although the experimental arrangement delineated in Fig. 1 is operable in principle, the action would be so complicated by the effects of internal space charge that the results would be most difficult to interpret. Much of the effort in this investigation has been devoted towards the development of techniques which would separate the various processes involved into component actions which individually are amenable to interpretation and analysis. The most successful technique was a pulsed method by which all the results presented here were obtained. All these measurements have been made with one diamond and with the primary beam striking the same area of the diamond although electron bombardment conductivity has been observed on other diamond crystals. This procedure helps to eliminate variations in response caused by inhomogeneous trap distribution in the crystal.[14] Although the results obtained represent only the behavior of this particular spot on this particular crystal, at least they are self-consistent and probably qualitatively characteristic of the performance to be expected from other crystals.

Figure 2 shows the experimental tube used throughout this investigation which was designed by J. A. Burton. On the left-hand side is mounted a conventional high voltage electron gun. A series of three accelerating rings follows. The right-hand side of the tube is practically closed off by a metal diaphragm, in the center of which is a 0.75-mm diameter hole. In front of this is a magnetically controlled shutter on which is mounted an alpha-particle source. With the shutter properly oriented, the alpha-particles can pass through the hole in the diaphragm and bombard the diamond crystal for test purposes. The crystal, mounted 1.6 mm behind the diaphragm hole, is approximately 6.3 mm in diameter and 0.45 mm in thickness. The two major faces are coated with an evaporated gold layer deposited to give a weight per square inch of 4 mg. This corresponds roughly to a thickness of about 2.5×10^{-4} mm. The actual thickness after evacuation was probably less than this because of migration during heat treatment. In addition, the front or bombarded electrode is divided by a 0.05 mm gap which is lined up behind the hole in the diaphragm. The diamond is held in place by two spring contacts on the front face which press it against the rear backing plate. This particular diamond was colorless and, by purely visual observations, apparently flawless. Before the electrodes were evaporated on, ultraviolet transmission measurements were made and it was shown to become opaque at 2300A. According to the nomenclature of Robertson, Fox and Martin,[26] this would correspond to a Type II diamond.

The outgassing schedule was quite conventional since the principal requirement placed on the vacuum conditions was that ionization be negligible as evidenced by cathode deterioration or electric breakdown.

4.2 Method of Measurement

After a general survey had been made by other methods, it was felt to be desirable to attempt to separate the effects caused by mere trapping of electrons in the crystal from those caused by the internal space charge set up by

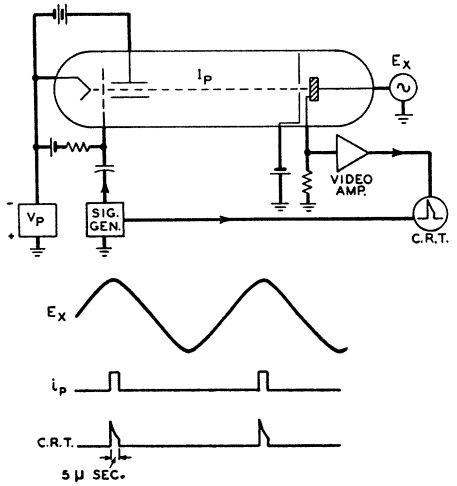

FIG. 3. Experimental schematic and time relationships.

those electrons. A schematic drawing of the method adopted is shown in Fig. 3. Intensity modulation is used on the electron beam and the beam is always so oriented as to strike the crystal. A short pulse (~5 μsec.) of primary current is produced. Simultaneously a high speed sweep is applied to the oscilloscope so that the details of the conductivity current through the crystal, resulting from the primary current bombardment, can be examined. As discussed in Section 3.2, there are substantial advantages in periodically reversing the crystal field rather than using a d.c. field. For convenience a sinusoidal 60-cycle field has been used in general as this frequency is greatly attenuated by the amplifier and thus no bucking circuit is required to prevent the amplification of the crystal voltage developed across the amplifier input by the finite impedance of the unbombarded crystal. In general, the pulse recurrence frequency is also 60 cycles with variable phase so that it can occur at any desired phase of the crystal field.

The video amplifier used throughout this investigation had an overall maximum gain of 113 db, and the high frequency amplitude response, which was shaped to follow a Gaussian, was 6 db down at 18 mc. All input current magnitude measurements were made by adjusting a calibrated attenuator to give a constant deflection on the oscilloscope. This procedure eliminated any deleterious effects resulting from non-linearity of the output amplifier.

The pulser followed the customary design for double thyratron pulsers. It gave a flat-topped pulse of variable length with a rise time of approximately 0.02 μsec. and variable amplitude up to 75 volts. The sweep circuit gave a calibrated sweep speed of from 0.3 μsec./inch to 10 μsec./inch.

In measurement, the amplifier gain was set so that the current in the primary beam, measured with zero voltage across the crystal, gave a certain scope deflection $=P_0$ in the negative direction. With a positive voltage on the crystal, the main contribution is due to electrons giving a pulse in the positive direction of say height $=P^+$. Then the "positive" yield

$$\delta_i^+ = \frac{P_+ + P_0}{P_0} - \frac{P_+}{P_0} + 1.$$

Similarly the "negative" yield caused primarily by positive holes traversing the crystal when a negative voltage is applied to its back face is given by

$$\delta_i^- = (P_-/P_0) - 1,$$

the observed conductivity pulse being in the negative direction.

In addition to the definitions of δ_i^+ and δ_i^-, the following symbols are used:

I_p = unvarying primary beam current on which the pulse current is superimposed.
i_p = primary beam current during the pulse.
i_x = instantaneous value of effective current flow through the crystal.
$\delta_i = i_x/i_p$.
V_p = energy in electron volts of bombarding electrons when they strike the diamond crystal.
V_D = potential of the diaphragm relative to the bombarded face of the crystal.
E_x = voltage applied across the crystal relative to the bombarded face at the instant of the primary pulse.
fE_x = frequency of voltage E_x.
f_r = pulse recurrence frequency of primary bombardment.
PL = pulse length of primary beam pulse.

5. EXPERIMENTAL RESULTS

5.1 External Secondary Emission from Bombarded Face

As stated in Section 4.1, the surface structure of the bombarded face is not known too well owing to the effects of the heat treatment. Probably the primary beam strikes a relatively thick gold layer in the center of which lies the 0.05-mm gap which is covered by an extremely thin gold layer which has migrated across the gap. In addition, the surface is covered with a layer of adsorbed gas since the heat treatment was certainly not adequate to produce a clean surface. To safeguard against possible spurious effects in the EBC measurements, it was necessary to make a rough measurement of the external secondary emission from the bombarded surface. Using the method shown in Fig. 3 but with both electrodes connected to the amplifier, i.e., no voltage across the crystal, the current to the target was measured as a function of diaphragm voltage V_D. With $V_D = -130$ volts practically all of the secondaries are prevented from leaving the target thus giving a measurement of i_p. With $V_D = +130$ volts, all of the secondaries are

drawn away from the target surface thus giving a measurement of $i_p - i_s$. Figure 4 shows the δ/V_p curves obtained from these data for 3 kv $< V_p \leq 15$ kv, where δ is the external or secondary emission yield.

If i_m is the current measured by the amplifier,

$$\frac{di_m}{dV_D} \sim 0 \text{ for } \begin{matrix} (-130 \lesssim V_D \lesssim -20) \\ (+130 \gtrsim V_D \gtrsim +50) \end{matrix}$$

volts over most of the range in V_p so that it is reasonable to assume that space charge effects were negligible and that most of the slow secondaries were suppressed when V_D was negative. However, one source of error lies in the impossibility of suppressing the elastically and inelastically scattered primaries. This affects the primary current measurement and is also important in determining the internal yield. From geometrical considerations, we can estimate roughly that the observed external yield should be decreased by 13 percent for $V_p = 3$ kv and by 7 percent for $V_p = 15$ kv if we take account of the reflected primaries and the tertiaries which they produce on the diaphragm.

It is interesting to see how this action affects the measurement of the internal yield in bombardment conductivity. All measurements are made with $V_D = -40$ volts thus suppressing most of the external secondary emission. The scattered primaries, if they lose energy, probably lose it in the gold electrode and it is unlikely that the internal secondaries produced ever reach the diamond lattice. Thus the scattered primaries do not contribute to bombardment conductivity and they are not measured in the primary current so that, as such, they can be neglected without error. However, the tertiaries which they produce on the diaphragm are collected by the crystal and measured as part of the primary current although they do not have sufficient energy to penetrate the electrode and produce any contribution to the induced conductivity. Consequently, we can estimate that the internal yield for 15-kv electrons should be increased by 5 percent and for 3-kv electrons should be increased by 9 percent corresponding to the percentages by which the primary current is increased by the addition of the tertiaries. This correction has not been applied to the results since it is felt that the accuracy of measurement is not sufficient to warrant a correction of this magnitude.

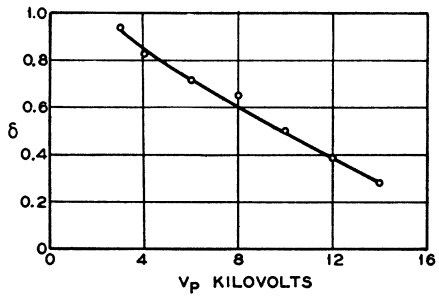

FIG. 4. External secondary electron emission from gold electrode.

5.2 Internal Yield in the "Space-Charge Free" Crystal

Using the pulsed method as shown in Fig. 3, it has been found experimentally that the largest yields at low field strengths across the crystal are obtained with an alternating voltage field in conjunction with primary bombardment during all or some part of both the positive and negative half-cycles of the field. It was concluded in Section 3.2 that this process produces a neutralization of the space-charge fields in the crystal so that, if the relative amounts of primary current bombarding the crystal during the positive and negative half-cycles of the field are properly adjusted, the internal conduction electrons produced by the first primary electrons in the pulse under consideration, enter an essentially space charge free crystal. The data which lead to this hypothesis will be considered later in Section 5.7; for the purposes of this section it is sufficient to assume that all measurements have been made with a space-charge neutralized crystal as defined by this procedure. The primary current pulse to be studied is locked in phase to the a.c. field applied across the crystal and may occur at the peak of either the positive or negative half-cycles. This pulse is superimposed on a much smaller steady primary current whose magnitude is adjusted for each value of V_p so as to give the maximum yield at low field strengths. At present this is purely an empirical adjustment.

Figure 5 shows sketches of some typical wave forms of the induced current obtained by this

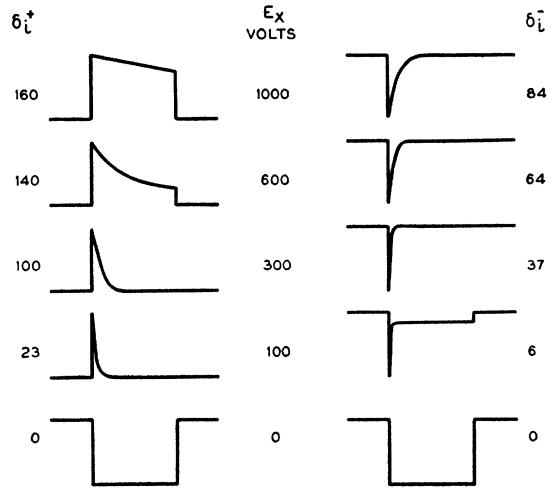

FIG. 5. Variation of observed pulse shapes with crystal voltage $E_x \cdot V_p = 10$ kv, $i_p = 0.5$ μamp., pulse length = 5 μsec.

method. In all cases the amplifier gain has been adjusted to give the same maximum excursion on the CR tube. The left-hand column shows the behavior of electrons traversing the crystal under various peak field strengths E_x. Unless otherwise stated, the primary pulse current in all of the experiments has been 0.5 μamp. Although the absolute error in this figure may be as high as 20 percent, the relative error in reproducing it is probably of the order of 5 percent. It will be observed that at low field strengths the current through the crystal falls off rapidly after the initial peak. Presumably, this is due to the formation of an internal space charge or polarization which is set up by conduction electrons which have been trapped as they traverse the crystal. With $E_x = 1000$ volts, corresponding to an applied field of 22,000 volts per cm, the rate of decay of the induced current is small in these experiments. Although the current flowing through the crystal is much larger in this case, the applied field is sufficiently great to overcome the influence of the internal space charge to a high degree.

The right-hand column of Fig. 5 shows the variation of the negative yield taken under conditions identical with those prevailing for the positive yield except that here the primary current pulse occurs at the peak of the negative half-cycle of the applied field. In this case the induced current is due to positive holes traversing the crystal. The space charge effects are here much more severe. At the highest field strength used the current has fallen to half its peak value in less than 0.5 μsec. This difference in the rates at which electron and positive hole space charges form may be due to differences in mobility, trap density or trapping cross section, or a combination of the three.

If we assume that the crystal is electrically neutral at a time immediately preceding the primary current pulse, the size of the initial induced current pulse should be a measure of the conductivity to be expected from a space charge free crystal. Consequently, we can define the peak yield as the maximum current traveling through the crystal during a pulse, divided by the bombarding current. Figure 6 shows the peak positive yield (electrons as charge carriers) so obtained as a function of applied field for different values of primary electron energy V_p. The value of V_p does not take into account the amount of energy which the primaries lose in traversing the gold electrode on the bombarded face. The values of yield are not corrected for the effect of tertiaries on the primary current measurement as discussed in Section 5.1. The data in Fig. 6 were obtained with a 60-cycle applied field, i.e., $f_r = f_{E_x} = 60^{\sim}$, $i_p = 5 \times 10^{-7}$ amp., $V_D = -40$ volts, $PL = 10$ μsec. The steady component of primary current, I_p, was readjusted to give optimum neutralization for each value of V_p and ranged from 10^{-8} amp. for low V_p to less than 10^{-11} amp. for high V_p. For the values of f_r and PL used, the bombarding current during the pulse delivered a charge which would be equivalent to a steady current throughout the cycle of 3×10^{-10} amp. It should be observed that the peak positive yield for $V_p = 14$ kv is about 600, which is many orders of magnitude greater than values which have previously been reported for bombardment conductivity.*

Figure 7 shows the variation of the peak negative yield (positive holes as charge carriers) observed under conditions identical with those described above for the peak positive yield. In particular, for a given value of V_p, the value of

* Subsequent to the preparation of this paper, L. Pensak (Bull. Am. Phys. Soc. **23**, No. 3, 47 (1948)) reported yields in excess of 100 from thin films of silica; and E. S. Rittner (Phys. Rev. **73**, 1212 (1948) reported a yield of 123 for selenium bombarded with 2000 ev electrons.

I_p is the same for δ_i^+ and δ_i^-. In other words the conditions of space charge neutralization which give the highest values of δ_i^+ appear to be the same as those for highest δ_i^- in the low field strength region. The variation of δ_i^- with E_x is similar to that for δ_i^+ but, in general, for a given E_x and V_p, δ_i^- is less than δ_i^+ by a factor which ranges from 2 to 5. Again, this suggests that the positive holes have a smaller range than the electrons. We would expect that as the applied field is increased indefinitely, δ_i^+ and δ_i^- should both approach the same limiting value, neglecting the possibility of ionization by the internally produced charge carriers.

5.3 Rate of Space-Charge Development

A study of the pulse shapes described in the previous section can also give information about the rate of formation of the internal space charge. Of course, the evidence is indirect since we can observe only the variation of the induced current, i.e., the effect of the space charge on the current traversing the crystal. To date, these wave forms have not been analyzed in detail. Visual observation suggests that the rate of decay in most cases resembles an exponential curve. Some rough measurements of τ, the time required for the induced current to fall to one-half of its peak value, were recorded at the same time that the data discussed in the previous section were obtained. For electron carriers, τ is less than 0.1 μsec. for low crystal fields and increases to more than 10 μsec. for the highest fields which were applied; it varies in an inverse manner with bombarding energy. For positive hole carriers, τ behaves in a similar manner although, for a given field and bombarding energy, it is very much less than for electron carriers. It has been observed that the decay time is a marked function of the degree of space-charge neutralization, the condition of optimum neutralization producing a minimum decay time. Since it is unlikely that complete neutralization has been achieved in these experiments, it is quite possible that these values of τ are too large to be consistent with the assumption of an initially space-charge free crystal.

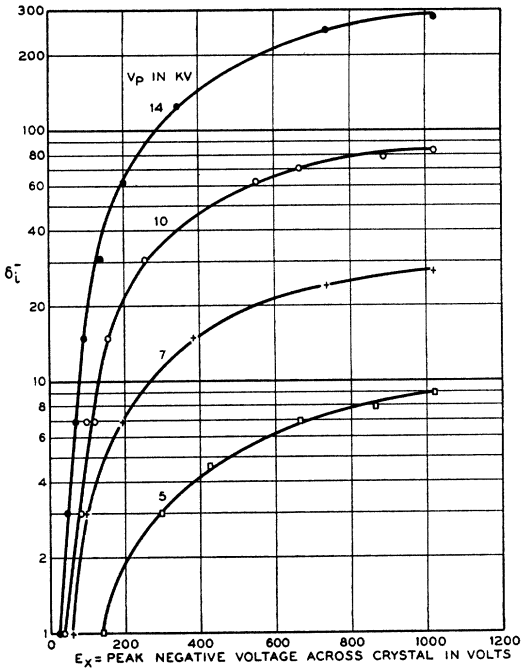

FIG. 7. Peak negative yield for space-charge neutralized crystal.

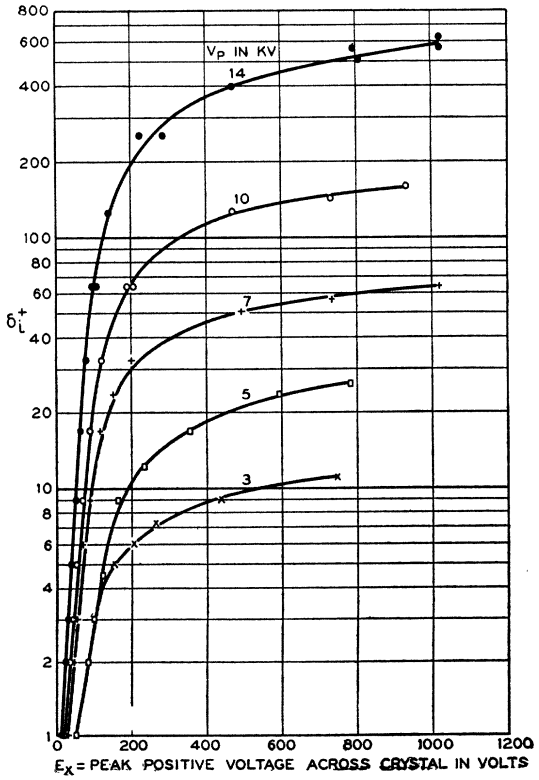

FIG. 6. Peak positive yield for space-charge neutralized crystal.

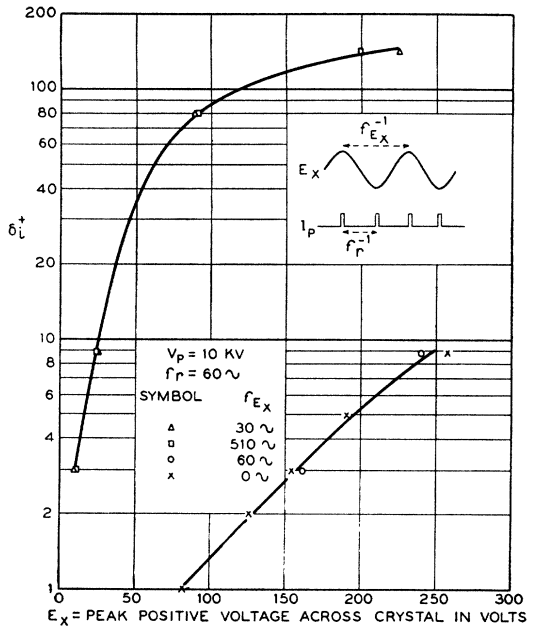

FIG. 8. Effect of space-charge neutralization on peak positive yield.

5.4 D.C. Field Applied Across the Crystal

One aspect of this investigation, which led to the hypothesis of space charge neutralization, was the variation of the internal yield with the strength of a d.c. field applied across the crystal. The experiments were carried out in exactly the same manner as in the pulsed method in Section 5.2, with the substitution of a d.c. potential source in place of the 60-cycle source which previously supplied the crystal field. The pulse recurrence frequency $f_r=60$ cycles, pulse length $PL=10$ μsec., $i_p=0.5$ μamp. Certain general characteristics were immediately apparent. The induced current resulting from electrons requires some time to reach an equilibrium value following a change in applied field. Any rapid change in this field produces a sudden increase in induced current which, within a second or so, decays to the equilibrium value corresponding to the new value of the field. The positive yield is not very reproducible and depends to some extent on the previous history.

The behavior of the induced current as a result of positive holes is most interesting. It too exhibits a sudden increase with any change in E_x and the equilibrium yield is very low. For all values of V_p up to 14 kv and applied field up to 20,000 V/cm, the equilibrium value of δ_i^- was less than unity. This value was normally attained at low field strengths and then remained constant up to the highest field strengths used.

The crosses in Fig. 8 show a typical variation of δ_i^+ with a d.c. field E_x for $V_p=10$ kv. In general, the induced current did not decay appreciably with time during the pulse duration. Irrespective of the value of V_p, the induced current broke into severe oscillations or fluctuations somewhere in the region of $500<E_x<700$ volts rendering the measurement of δ_i^+ above this value of E_x impossible. These fluctuations, once started, continued until the applied field was reduced considerably. If E_x was then increased, the yield curve could again be reproduced with the induced current breaking into oscillation at approximately the same value of E_x as before. The oscillations did not necessarily occur immediately after E_x was increased to the critical value. With E_x constant at this value, as much as ten seconds might elapse before the oscillations started. Another feature was observed particularly for $V_p=14$ kv. At a steady field strength slightly less than the critical value, δ_i^+ suddenly increased spontaneously by about 50 percent. In this region, $\delta_i^+\sim 200$. This effect was not always reproducible and certainly the yield exhibited a hysteresis-like behavior as E_x was varied around this value.

These experiments indicate that large space charge fields can be set up in the crystal by trapped charges. Moreover at sufficiently high applied fields, sizable positive yields are obtained which do not decay with time. In this case a dynamic equilibrium is established in which the build-up of space charge is balanced by its decay as discussed in Section 3.2. The crystal is well shielded from ambient light so the decay is probably caused by the re-emission of trapped electrons into the conduction band by thermal agitation or by recombination with positive holes. The "inertia" effects indicate that if the equilibrium is suddenly upset, some time elapses before a new equilibrium can be established. It is possible that voltage polarization effects associated with impurity migration or surface charges are further complicating the process. Here the motion of positive holes is much more affected

by space charge than that of electrons and to a greater degree than in the experiments described in Section 5.2.

5.5 Effect of A.C. Field Alone on Yield

It is of interest to see if the mere application of an a.c. field across the crystal can affect the build-up of internal space charge appreciably. The pulsed method was used in such a way that the primary current pulse could occur only at the peak of the positive half-cycle of the 60-cycle field and there was no bombardment during any other portion of the field cycle, i.e., $I_p=0$. The circles in Fig. 8 show that the plot of δ_i^+ against E_x is very nearly the same as that shown by the crosses for a steady field. A few measurements with a field frequency of $f_{E_x}=480$ cycles and recurrence frequency $f_r=60$ cycles gave substantially the same result. Moreover, the same "inertia" effects were observed and the negative yield behaved as it did with a steady field in that $\delta_i^- \gg 1$ for any value of E_x.

The general action does not appear to be appreciably different with an a.c. field from that obtained with a steady field under the conditions of the experiment. From this we may conclude that a mere reversal of the 60-cycle applied field alone does not affect the growth or decay of the internal space-charge fields appreciably, i.e., the trapped electrons cannot be released solely by virtue of the influence of the field reversal.

5.6 The Effect of Pulse Bombardment During the Positive and Negative Half-Cycles of an A.C. Field

The experiment just described in Section 5.5 was repeated with the one difference that the frequency of the a.c. field was reduced to one-half the pulse recurrence frequency. In this the primary current pulse occurred first at the peak of the positive half-cycle of the field applied to the crystal and then at the peak of the negative half-cycle. The triangles in Fig. 8 show the δ_i^+/E_x curve so obtained. The same curve was repeated for all f_{E_x} for which $(f_{E_x})(f_r)^{-1}=n+\frac{1}{2}$ up to $n=8$, the highest value used. This curve and a similar one for δ_i^- are in general agreement with the data presented in Section 5.2. Moreover, the "inertia" and instability obtained with a d.c. field are now not evident.

5.7 The Effect of a Continual Bombardment in Conjunction with Pulse Bombardment and an A.C. Field

Another way in which bombardment during both positive and negative half-cycles of the a.c. field can be obtained is simply to maintain a constant primary beam current I_p and periodically superimpose a primary pulse i_p phased with the field; i.e., $f_r=f_{E_x}$. This is the method used in Section 5.2 to obtain the values of the peak yield for the "space-charge free" crystal. In this case, the pulse can be considered merely as a probe which samples the field conditions in the crystal periodically. However, in all the cases studied, the pulse had an appreciable effect on the internal fields so that in that sense, it was not an ideal probe.

Figure 9 shows the variation of the peak positive yield with applied field for various values of steady primary current I_p and $V_p=10$ kv. In all cases the primary current delivered during the pulse is a constant, $i_p=5\times10^{-7}$ amp. Clearly, there is a certain value of $I_p\sim3\times10^{-11}$ amp. which gives the maximum yield at low field strengths under these particular experimental conditions. Actually if the adjustment of I_p is done empirically to give the highest yield

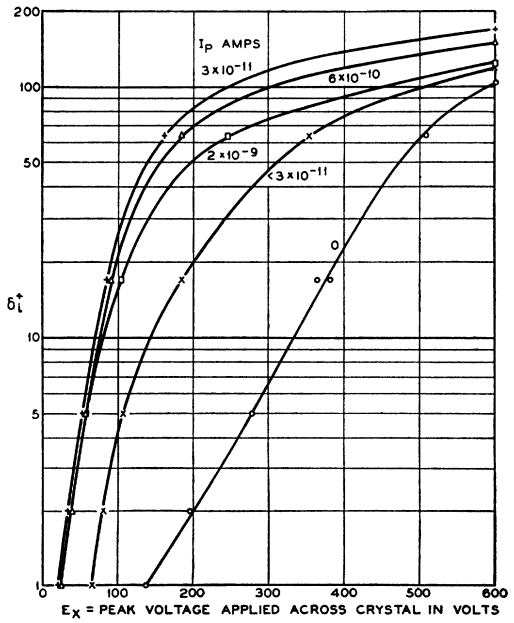

FIG. 9. Peak positive yield as a function of various values of superimposed steady bombarding current.

rather than in fixed steps as was done here, the optimum δ_i^+/E_x curve more nearly approximates the results obtained in Section 5.6 using double pulsing. If δ_i^- is examined as a function of I_p, it also increases as I_p is decreased until an optimum is attained. The value of I_p for optimum δ_i^- appears to be the same as the value for optimum δ_i^+. However, as I_p is further reduced, δ_i^- very quickly develops severe "inertia" effects and drops to the order of unity. The behavior of both δ_i^+ and δ_i^- for other values of V_p is quite similar to that for $V_p=10$ kv.

The different methods described in this and the previous section both achieve approximately the same result. In neither case are "inertia" effects observed, which suggests that here we do not have an equilibrium set-up such as considered for a d.c. crystal field in Section 5.4. In all, the behavior is adequately described by the hypothesis of space-charge neutralization propounded in Section 3.2. It should be observed that the criterion for optimum neutralization is solely that the relative bombardment during the positive and negative half-cycles of the crystal field should be such as to produce the maximum yield at low field strengths. Since a d.c. bias field was not used here, there is no assurance that the neutralization was homogeneous. Consequently the results presented in Section 5.2 for the yield in a "space-charge free" crystal should be considered with caution.

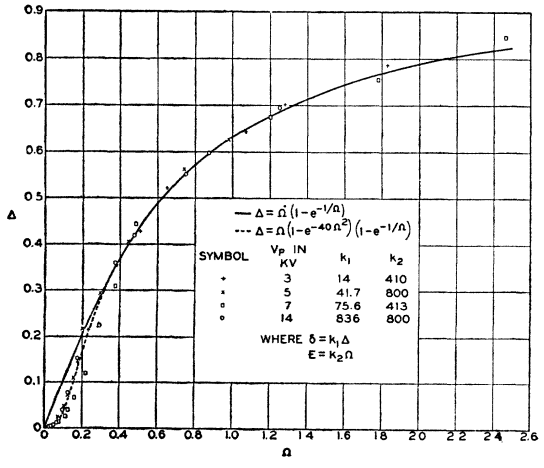

FIG. 10. Comparison of theoretical yield curve with experimental results.

5.8 Comparison of Theoretical and Experimental Yield Curves for the "Space-Charge Free" Crystal

We are now in a position to make a comparison between the theoretical yield curve derived in Section 3.1 and the curves for the peak yield obtained experimentally in Section 5.2. However, the assumptions involved in the theoretical development should first be examined in the light of the experimental evidence.

Although Ahearn's experiments[14] with alpha-particle bombardment have demonstrated that the trap distribution in diamond is far from homogeneous, it is probable that the electron beam diameter (0.75 mm) is sufficiently large to cover many regions of different trap densities and thus we can take an average trap density which is equivalent to a homogeneous distribution. By considering only the peak yield for a neutralized crystal, the neglect of the effects of internal space-charge fields is probably valid except for low field strengths where the decay time is of the order of the amplifier resolution time. The neglect of the interaction between positive holes and the corresponding free electrons is justifiable at these current densities and field strengths. However, this might not be true if high current densities were involved. Using the best available value for the mobility of a conduction electron in diamond ($v=156$ cm^2/volt/sec.,[27] the drift velocity is less than the thermal velocity almost up to the highest field strengths used.

The solid line in Fig. 10 is a plot of Δ against Ω as given by Eq. (6). We can relate our experimental results for the peak yield in a supposedly space-charge free crystal to this curve by suitable scaling factors applied to the ordinates and abscissae. Let the observed yield $\delta=k_1\Delta$ and the corresponding voltage applied across the crystal $E=k_2\Omega$. The experimental data on the peak positive yield as shown in Fig. 6, have been so treated and the results are shown by the experimental points in Fig. 10. The fit, for each value of V_p, was made at two points; no attempt was made to use a least-squares method. In view of the roughness of the data and the method of curve fitting, it is gratifying that the agreement

[27] F. Seitz, Phys. Rev. **73**, 549 (1948).

between experiment and theory is quite good over most of the range of Δ.

In all cases, the experimental curve falls below the theoretical curve for low values of Δ. In this region, the experimental points may be approximated by the dotted curve given empirically by

$$\Delta=\Omega[1-\exp(-40\Omega^2)][1-\exp(-\Omega^{-1})].$$

This discrepancy may be due to the neglect of interaction between positive holes and free electrons. From this we should expect some recombination at sufficiently low field strengths, thus reducing the number of free electrons available for conduction. However, a calculation by R. R. Newton[28] suggests that this effect is negligibly small at the current densities used. It appears that this discrepancy is entirely due to the experimental set-up. In all cases where Ω was small, τ, the time required for the observed induced current to fall to half-value, was of the order of 0.1 μsec. or less. This is approaching the resolution time of the amplifier and it is probable that in these cases the space-charge fields developed so quickly that the induced current was appreciably reduced from its peak value before the amplifier could respond fully. Since the decay times for negative yields caused by the transit of positive holes were much less than those for positive yields, this effect should be much more severe. For this reason, no attempt was made to correlate the experimental data for negative yields with the theoretical curve.

The scaling factors employed to fit the experimental points to the theoretical curve in Fig. 10 provide certain additional information. Since $\Delta=\delta/\delta_\infty$, we see that $\delta_\infty=k_1$. We would expect that k_1 should be proportional to V_p; this is not found to be true. Rather, k_1 increases much more rapidly than does V_p. This is probably caused by the loss in energy of the primary electrons in traversing the gold electrode. The energy so lost is a function of the primary energy particularly since the electrode is probably not of uniform thickness (Section 4.1). Thus we can only conclude that the values of $k_1=\delta_\infty$ are too small, the error being smallest for large V_p. For $V_p=14$ kv, $\delta_\infty=836$ which corresponds to 16.7 ev of the primary electron's energy being required to produce one internal secondary. If this were corrected for the energy loss in traversing the electrode, it would probably be close to the value of 10 ev/electron found by A. J. Ahearn for alpha-particle bombardment of diamond.[14]

The values of the abscissa scaling factors k_2 are also useful. Since $\Omega=vTE/l^2$, we see that $k_2^{-1}=vTl^{-2}$. As none of the factors in k_2 depend on the current traversing the crystal, we should expect that k_2 would be a constant independent of V_p. Actually, k_2 varies irregularly from 410 volts^{-1} to 800 volts^{-1}. It is believed that this variation is caused by imperfect space-charge neutralization of the crystal between primary pulses. Since the degree of neurtalization was adjusted empirically for each different value of V_p, it is probable that variations should exist between the various sets of measurements. In any case, the values of the product vT range from 3.1×10^{-6} to 6.1×10^{-6} cm^2/volt. As the space-charge neutralization is improved, the yield at low applied fields increases, i.e., vT apparently increases. Thus we are justified in assuming that the larger value of vT is more nearly appropriate to the case of the space-charge free crystal. Unfortunately, we have no experimental evidence which yields values of either v or T independently. However, Seitz[27] has recently computed the mobility of free electrons in diamond at room temperature and arrives at a value of $v=156$ cm^2/volt/sec. Using it, we see that $T=3.9\times10^{-8}$ second.

The density of traps in a homogeneous crystal is related to the free electron lifetime by the expression,

$$N_t=1/T\sigma u, \tag{7}$$

where N_t = density of traps, σ = area of trapping cross section, u = thermal velocity of a free electron $\sim1.2\times10^7$ cm/sec.

Although we have no direct experimental evidence for a value for σ, we can assume that $10^{-16}>\sigma>10^{-17}$ cm^2, as determined from phosphor studies on ZnS. With these values we find that the density of effective traps lies between 2.1×10^{16}/cm^3 and 2.1×10^{17}/cm^3. These values, which correspond to concentrations of between one to ten traps per 10^7 atoms, appear to be entirely reasonable, thus lending confirmation to the validity of the foregoing theory.

[28] Private communication.

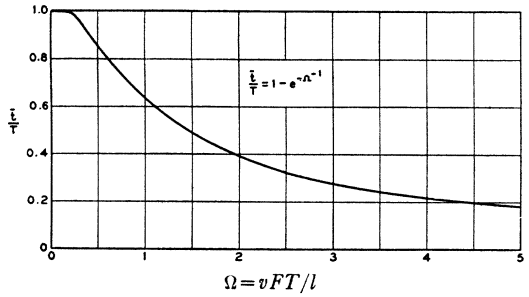

FIG. 11. Theoretical variation of probable "transit" time with electron range.

5.9 Average Electron Transit Time

The transit time of a primary electron is here defined as the time elapsing between the entrance of the primary into the crystal and its arrival at the end of its ionization range. A 14-kv primary traveling with a velocity of 7×10^9 cm/sec. is "stopped" in about 3×10^{-4} cm and thus has a transit time of less than 10^{-13} sec. which is probably negligible.

Of more interest is the transit time of the internal secondary electrons which is defined here as the total time that they are mobile. Equation (2) gives the mean range of all conduction electrons. These are assumed to move in the direction of the field with a drift velocity vF so that the average time in motion or transit time $\bar{t}$ is given by

$$\bar{t}/T=1-\exp(-\Omega^{-1}). \tag{8}$$

Figure 11 shows a plot of this function. For low field strengths, the transit time is simply equal to T. It decreases as the field strength increases since an increasing number of electrons are collected on the anode and thus do not spend the full time T in the conduction band. When the yield has reached 90 percent of δ_∞, the transit time has decreased to $0.19T$. The ordinate scale is established by the value $T=3.9\times10^{-8}$ second determined in Section 5.8. From this we can conclude that frequencies of the applied field of the order of 10^8 cycles can be used before adverse transit time effects will be encountered.

5.10 Internal Current Fluctuations

In Section 5.4 there is a discussion of the development of large fluctuations in the induced current for d.c. fields of about 10,000 volts/cm. It should also be noted that small fluctuations have occasionally been observed at field strengths of around 20,000 volts/cm using an a.c. field in conjunction with space-charge neutralization. No extensive measurements have been made of the phenomenon. However, a tentative hypothesis has been considered. Fröhlich[29] has recently published an extension of his theories of dielectric breakdown in which he shows that, if the interaction between free electrons in the conduction band is negligible, an electron which exceeds a certain energy will tend to gain energy from the field more rapidly than it can lose it to the lattice and thus will continue to gain energy indefinitely until it can produce ionization. Very roughly, such a process should become feasible when the electron acquires energy amounting to about kT from the field during the interval between two large angle collisions. Although Fröhlich's theory is developed for ionic crystals, this criterion is probably applicable to a nonpolar crystal by using a suitable value of the mobility. The relation between the mobility v and the relaxation time τ is roughly equivalent to the statement that v is the velocity which an electron, starting from rest, would acquire in τ seconds under the influence of a unit field. Thus the energy which an electron acquires between collisions resulting from interaction with a field F is approximately

$$\epsilon=\tfrac{1}{2}m(vF)^2. \tag{9}$$

The critical field strength is determined by equating ϵ to kT and is equal to

$$F_c=1/v(2kT/m)^{\frac{1}{2}}. \tag{10}$$

If we assume Seitz' value of $v=156$ cm^2/volt/sec., $m=$normal electronic mass, and room temperature, we find that $F_c=6.1\times10^4$ volts/cm. This is somewhat higher than the field strengths which have been applied during the experiments. However, we have not taken into account the effect of the internal space-charge fields. Even when space-charge neutralization was used, it is unlikely that the neutralization was completely homogeneous and thus, in some part of the crystal, the actual field must have exceeded the applied field. This effect should be much more pronounced when a d.c. field is used as much

[29] H. Fröhlich, Proc. Roy. Soc. (A) **188**, 532 (1947).

more intense space-charge fields can then be built up. Any electron which has passed through the region where the majority of the trapped electrons occur would then encounter a strongly accelerating field considerably in excess of the applied field. As a result of energy fluctuations, a certain number of these electrons may exceed the critical energy value and then may be accelerated to ionizing energies. It is significant that experimentally, the fluctuation currents are more pronounced and occur at lower applied fields when large space-charge fields are allowed to develop. The sudden increase in yield occasionally observed in this case just before the critical field strength is reached would then be interpreted as caused by the temporary establishment of the right field distribution to produce a non-fluctuating enhancement of the induced current by "tertiary" production by the conduction electrons. In general, such a condition is expected to be a very critical function of crystal field.

Considering the effects of inhomogeneous trap distributions, it is probable that it will be undesirable to exceed this critical field strength in bombardment conductivity studies in general. The product vF is then bounded above and, since the figure of merit of a bombardment conductive material is the range $\omega = vFT$, improved performance could only be obtained by increasing T, i.e., reducing the probability that an electron may be trapped in a given time interval. This limitation of the product vF is probably not applicable to thin film targets since there a conduction electron may never gain sufficient energy to produce tertiaries even in very high fields.

This hypothesis, if correct, leads to the possibility of making a quantitative study by a new method of the factors which lead to dielectric breakdown. The use of a non-polar material may have some advantages over the polar materials which have been so extensively studied heretofore.

I wish to express my thanks to my colleagues at the Bell Telephone Laboratories who have contributed much to this work. In particular, I am grateful to A. J. Ahearn who performed a preliminary investigation of the diamond crystal by alpha-bombardment, and to J. B. Johnson and A. H. White for many illuminating discussions.