Space Charge Effects in Bombardment Conductivity through Diamond

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Electrons excited to the conduction band of an insulator under electron bombardment are, in general, not able to leave the insulator, but become trapped at imperfections in the crystal lattice. The trapped electrons give rise to a space charge which modifies the motion of electrons excited to the conduction band subsequent to the trapping. In this way, the current through the crystal becomes a function of time.

In this paper, a tentative theory of such space charge effects is presented and compared with experiment. Agreement with the data which exist at present is reasonably good. Some predictions and suggestions for future experiments, which arise as consequences of the theory, are made.

I. INTRODUCTION

WHEN certain insulating crystals are bombarded with electrons of medium energy (~10 kv), some of the electrons in filled bands of the crystal may be raised to the conduction band, and the crystal may then show conductivity under an applied electric field. This phenomenon, which we shall call electron bombardment conductivity, or, more briefly, bombardment conductivity, is similar in many respects to the effects involved in crystal counters. Crystal counters which depend upon induced conductivity rather than upon observation of scintillations[1] have been made from various materials: silver chloride at liquid air temperature,[2] diamond,[3] zinc sulfide,[4] a mixture of thallous halides,[5] and cadmium sulfide.[6] In the work with electron bombardment, however, what is sought is the response to a beam of particles rather than response to isolated particles. Hence, the situation is perhaps more analogous to the photo-conductivity of an insulator when illuminated in its fundamental absorption band.[7]

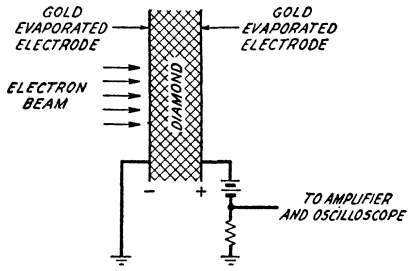

FIG. 1. Experimental arrangement for observing bombardment conductivity.

Bombardment conductivity has been observed by Dr. K. G. McKay in diamond.[8] The experimental arrangement which he used is shown in Fig. 1. The diamond used was in the form of a plate about 0.05 cm thick, with gold electrodes evaporated onto the faces. A collimated electron beam of variable energy, and of diameter $\frac{1}{32}''$ (~0.08 cm) impinged upon one face, which we shall call the front face of the diamond. The geometry of the system is a fair approximation to infinite plane-parallel geometry.

The impinging electrons penetrate the diamond and produce ionization; the ionization range is about 3×10^{-4} cm, which is less than 1 percent of the thickness of the diamond. With the voltage as shown, the positive holes left by the ionization travel to the front face, and can make no appreciable contribution to the observed current. The observed current is that carried by the electrons which travel toward the back face. Experiments were also performed in which the

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[1] R. J. Moon, Phys. Rev. **73**, 1210 (1948).

[2] P. J. Van Heerden, *The Crystal Counter* (thesis) (Utrecht, 1945); R. Hofstadter, Phys. Rev. **72**, 747 (1947); R Hofstadter, J. C. D. Milton, and S. L. Ridgway, Phys. Rev. **72**, 977 (1947).

[3] D. E. Wooldridge, A. J. Ahearn, and J. A. Burton, Phys. Rev. **71**, 913 (1947); L. F. Curtiss and B. W. Brown, Phys. Rev. **72**, 643 (1947); W. Jentschke, Phys. Rev. **73**, 77 (1947); G. Stetter, Verh. d. D. Phys. Ges. **22**, 13 (1941).

[4] A. J. Ahearn, Phys. Rev. **73**, 524 (1948).

[5] R. Hofstadter, Phys. Rev. **72**, 1120 (1947).

[6] R. Frerichs, Phys. Rev. **72**, 594 (1947).

[7] See J. H. De Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, London, 1935), p. 305.

[8] Reported verbally at the symposium of Division of Electron Physics, New York, Jan. 31, 1948, Phys. Rev. **73**, 1238 (1948).

back face was negative, so that the current is carried by positive holes.

We shall assume that there are no qualitative differences in behavior between electrons and positive holes, although their characteristic parameters (mobility, etc.) may have different values. Our discussion will then hold equally well for either type of current carrier; for convenience, however, we shall always speak of electrons as carriers, so that we are referring to the voltage arrangement of Fig. 1.

The diamond used is not a perfect crystal, but contains flaws or impurities which can act as electron traps. Thus some of the electrons which start across are trapped in the interior of the crystal, giving rise to a space charge which impedes the further flow of electrons. The current through the crystal will, as a consequence, vary with time; the purpose of this paper is to study this time variation.

In order to observe the time variation of the current, McKay pulsed the bombarding electron beam, using pulses lasting for the order of 10^{-6} sec., and repeated 60 times per second. Between pulses, he subjected the crystal to a treatment designed to neutralize the space charge deposited during the preceding pulse, so that the beginning of each pulse would find the crystal free of space charge.

Typical curves for the variation of current during a pulse are shown in Fig. 2. For a particular voltage, at some high current density, the curve is everywhere concave upward. With the same voltage, if the current density is lowered sufficiently, the curve is at first concave downward, and then becomes and remains concave upward. We believe that qualitatively different mechanisms are responsible for the different portions of the curve at low current densities, and that both portions are actually present in all the curves. At high current densities, however, the first portion is of such short duration that it is lost in the finite rise time of the pulse and the finite response of the amplifier.

As we mentioned before, the ionization range of the bombarding electrons is about 3×10^{-4} cm. Within the layer extending to this depth from the front face, which we shall call the plasma layer, both positive holes and electrons are to be found. We therefore expect different behavior in

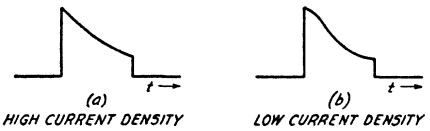

FIG. 2. Typical current-time curves.

this plasma layer from the rest of the diamond, in which only electrons are to be found. In the next section we shall discuss the plasma layer; the remainder of the paper will deal with the part of the diamond between the plasma layer and the back face. At the end of the next section, we shall be in a position to discuss the differences between the two portions of the curves in Fig. 2.

II. THE PLASMA LAYER

Each impinging electron penetrates the diamond a certain distance before losing its ability to produce ions, and, in this distance, produces on the average a number of electrons which we shall denote by δ_∞. If an infinite field were applied to the crystal, all of these electrons would be collected by the electrodes. Hence we call δ_∞ the yield for infinite field strength. We shall assume that the points of origin on these δ_∞ electrons are distributed uniformly along the ionizing range of the impinging electron.

Within the plasma layer are high concentrations of electrons and positive holes. This situation is comparable to that which exists when the diamond is illuminated in its fundamental ultraviolet band, when little or no photo-conductivity exists, presumably because most of the photo-electrons recombine with the holes.[7] Our first question is then: How many electrons escape from the plasma layer to enter the main body of the diamond?

We expect the number of recombinations of electrons and holes per cm^3 per second to be of the form:

$$Kn_+n_-, \tag{1}$$

where n_+ and n_- are the volume densities of holes and electrons, respectively, and K is a constant. K can be estimated to order of magnitude; if we neglect the velocity of the holes compared with that of the electrons and let v be the average velocity of an electron in its Brownian path, and σ the cross section for recombination:

$$K=v\sigma.$$

The electrons in question have just been knocked into the conduction band by the impinging electron, and probably have more than thermal velocity. If we assume that they have 0.5 ev of kinetic energy, and that $\sigma = 10^{-15}$ cm^2, we get $K = 6 \times 10^{-8}$.

We now wish to show that recombination is negligible unless the field is quite low, probably of the order of 20 volt/cm or less. With one of the largest bombarding currents and the highest δ_∞ which McKay has used, the number of electrons and holes created per sec. per cm^2 cross section of the plasma layer is 6×10^{16}. The lowest field used is about 2000 volts per cm; if the mobility of holes is 30 cm/sec. per volt/cm, the longest time required for a hole to traverse the plasma layer is

$$3 \times 10^{-4}/(30 \times 2000) = 5 \times 10^{-9} \text{ sec.}$$

After this length of time, the number of holes and electrons which have been created per cm^2 of plasma is

$$6 \times 10^{16} \times 5 \times 10^{-9} = 3 \times 10^{8},$$

and the density is certainly not greater than 10^{12} electrons or holes per cm^3 of plasma. The number of recombinations per cm^3 per sec., according to Eq. (1), is not greater than

$$Kn_+n_- = 6 \times 10^{-8} \times 10^{24} = 6 \times 10^{16}.$$

In 5×10^{-9} sec. then, per cm^2 cross section of plasma layer, we would have

$$6 \times 10^{16} \times 5 \times 10^{-9} \times 3 \times 10^{-4} = 9 \times 10^{4}$$

recombinations. Since, in the same time and the same volume, 3×10^8 electrons and holes have been created, the reader can readily convince himself that recombination is negligible under the conditions assumed, and is probably not important unless the field in the plasma falls below the order of 20 volts/cm.

We now wish to discuss the time and space variation of the densities of holes and electrons within the plasma. Let i_0 = bombarding current density in electrons/cm^2/sec., let l = thickness of the plasma layer, and let v_+ and v_- be the mobilities of holes and electrons, respectively. Then the equations of continuity for holes and electrons read

$$(\partial n_-/\partial t) = -v_-F(\partial n_-/\partial x) + (i_0\delta_\infty/l) - Kn_+n_-, \quad (2)$$

$$(\partial n_+/\partial t) = v_+F(\partial n_+/\partial x) + (i_0\delta_\infty/l) - Kn_+n_-. \quad (3)$$

The x coordinate is taken to be zero at the front face, and increases as we go into the crystal, while the field F is taken positive if in the direction of decreasing x. In Eqs. (2) and (3), the first term on the right in each represents the transport, the second the creation by the bombarding electrons, and the third the loss by recombination. We neglect trapping of holes or electrons within the plasma layer. Equations (2) and (3) are subject to the conditions that $n_+ = n_- = 0$ at $t = 0$ for all x, and that $n_+ = 0$, $x = l$, $n_- = 0$, $x = 0$, for all t.

We shall first assume that F does not change appreciably across the plasma layer. Unless the field F is quite small, the recombination is negligible, and Eqs. (2) and (3) are independent. The solutions for n_+ and n_- are similar; that for n_+ can be readily verified to be

$$n_+ = (i_0\delta_\infty/l)[t - \max.(t + (x-l)/v_+F, 0)]. \quad (4)$$

By the symbol max.(A, B), we mean the larger of A or B. At any position x, this becomes independent of t when $t = (l-x)/v_+F$. For $t \geq l/v_+F$, n_+ is everywhere independent of t, and is given by

$$n_+ = (i_0\delta_\infty/l)(l-x)/v_+F. \quad (5)$$

We now verify that the change in F across the plasma layer is small. If ΔF is the change in F, ϵ the electronic charge, and κ the dielectric constant, we have, neglecting the electrons in the plasma,

$$\Delta F = (4\pi\epsilon/\kappa)(i_0\delta_\infty/2v_+F)l.$$

Using the figures we used to estimate the recombination, $\Delta F/F = 2$ percent, or the field varies from its average value by about 1 percent. If the electrons are included in the computation, the result is multiplied by $1 - 2(v_+/v_-)$, as may be readily verified.

We should also make some statements about the possibility of electrons being trapped in the plasma layer. Using material to be presented in the next several sections, we can conclude that trapping in the plasma layer is negligible unless the field in the plasma falls below about 25 volts/cm.

The solution of Eqs. (2) and (3), when recombination, trapping, and variation of F are included, is a more formidable task which we shall

not undertake here. From the calculations which we have just made, however, we can draw two conclusions: (a) Unless the field is below, say, 200 volts/cm, the field across the plasma is fairly constant, and the charge contained in the plasma can be neglected in computing the space charge effects. (b) Unless the field in the plasma is below, say, 25 volts/cm, all of the electrons liberated by the bombarding electrons escape from the plasma layer into the main portion of the crystal. If the field is lower than this value, electrons may be lost either by recombination or trapping.

The significance of these conclusions is that, during the early part of the bombardment, when the field is 2000 volts/cm or higher, we can neglect the plasma and the positive holes, and assume that all of the electrons leave the plasma and start across the crystal. Some or all of these electrons are trapped in the crystal; their space charge lowers the field at the front face, so that electrons can be trapped more readily, and so on. This period of operation corresponds to the first portion of the curves in Fig. 2. Unless the trapped electrons are released too quickly, at some time the field at the front face must become nearly zero. When this occurs, the number of electrons leaving the plasma layer is substantially reduced. The current now falls to a steady value which is determined by this consideration: The field in the plasma layer is held by the trapped electrons (i.e., trapped in the main part of the crystal) at such a value that the number of electrons leaving the plasma layer just balances the number of electrons lost from the crystal by thermal release from traps and subsequent drift out of the crystal.

Qualitatively, this picture leads to a negative second time derivative of the current (current curve concave downward) as long as all electrons leave the plasma, at least for small thermal release rates. That is, a trapping of electrons, which means a decrease in current, so alters the field conditions that trapping, and hence the decrease in current, becomes more rapid. We shall give a semiquantitative discussion of this point in Section VI.

If the thermal release rate is large, a different condition of equilibrium from that just discussed may obtain. This condition will be discussed in Section VII. If this condition can be achieved, it affords a method of obtaining information about the plasma layer, which is at present inaccessible to study.

The point of inflection of the curve in Fig. 2 must then occur near the time when the field in the plasma layer becomes small. We can readily estimate the time at which this occurs, as follows: Until the point of inflection is reached, almost all of the electrons freed by the ionization leave the plasma, but are trapped in the body of the diamond. Hence, at time t, the number of electrons trapped per unit cross section of the diamond is approximately

$$i_0\delta_\infty t.$$

The change ΔF in F as we traverse the crystal is

$$\Delta F=(4\pi\epsilon/\kappa)i_0\delta_\infty t.$$

Since the voltage across the diamond is held constant, the average field must always equal the originally applied field F_0. Hence, if the field at the front face is to be approximately zero, ΔF approximately equals $2F_0$, and the time t at which the point of inflection occurs is approximately

$$t=2\kappa F_0/4\pi\epsilon i_0\delta_\infty. \tag{6}$$

Equation (6) was derived before any curves were observed which showed a point of inflection. Using this equation, conditions under which a point of inflection should be observable were computed, and the points of inflection were then discovered. Figure 3 shows the agreement between the observed values of t at the inflection point, and the values predicted by Eq. (6). The agreement is good only to order of magnitude, and the observed values are always greater than the predicted ones.

In the derivation of Eq. (6), we neglected the electrons which are released thermally from traps, and also those which cross the crystal without being trapped. In Section VI, we give a computation which includes these electrons. The results of these calculations are also shown in Fig. 3. The curves labeled $B(1-f)=0$ include the electrons which are not trapped, and the curves $B(1-f)=0.03\times10^6$ include, in addition, those released thermally, with a particular assumption about the thermal release rate. These latter curves are discussed in Section VI.

The hypothesis underlying Eq. (6) is in line with another observation. If we consider what should happen to the shape of the pulse as we vary the amount of space charge neutralization, we see that, if negative charge is left in the crystal, the field in the plasma layer is already small at the beginning of the pulse, and the entire pulse should be concave upward. The portion which is concave downward should not appear until the space charge neutralization is almost complete. This is the observed behavior.

III. TYPES OF TRAPS, THE TRAPPING LAW

Experiments which have been performed indicate that there is more than one type of electron trap in a diamond. Dr. A. J. Ahearn has performed some interesting experiments in this connection, which we shall describe briefly.

Ahearn was studying the properties of diamond as a counter of α-rays.[3] He first determined the counting efficiency of a particular diamond as a function of the electric field applied to it, when the bombardment lasts too short a time for space charge to be significant, for conduction either by holes or electrons. He then bombarded this diamond with α-particles at the rate of 500 per min., over a circle of 0.06-in. diameter, with 4000 volts per cm applied to the crystal in such a direction that electrons conduct, for one minute, and then removed the applied field. The space charge field then became the dominant field; it is in a direction such as to make the crystal conduct by means of holes. The counting rate immediately after removal of the applied field corresponded to a field of 320 volts per cm. When the bombardment time was increased to 2 min., the initial counting rate under the space charge field corresponded to 480 volts per cm.

As we shall show in the next section, most electrons released by the α-particles are trapped in the diamond. Assuming 5×10^5 ion pairs per α-particle, we find that, after 1-min. bombardment, there have been approximately 1.4×10^{10} electrons per cm^2 cross section trapped in the diamond. To produce a field of 320 volts per cm, however, requires only 1.8×10^9 electrons per cm^2. Hence we compute that a fraction,

$$1.8\times10^9/1.4\times10^{10}=13 \text{ percent},$$

remain trapped for the order of a minute. Similarly, when the bombardment with applied field continued for 2 min., about 10 percent were still trapped at the end of the bombardment.

We conclude, then, that of all the traps in the diamond, about 10 percent are deep enough that the half-life for thermal release is of the order of a minute. This measurement was made on only one diamond. Most of the other traps must be substantially shallower than this 10 percent.

It is of some interest at this point to estimate what depth of trap, expressed in volts, is actually required to produce the observed lifetime, and to see if the depth agrees with a reasonable mechanism for producing traps.

Mott and Gurney[9] give an approximate relation between the half-life and trap depth,

$$B/\sigma=2\pi m(kT)^2h^{-3}(6\pi)^{\frac{1}{2}}\exp(-E/kT), \quad (7)$$

in which B is the probability per second that an electron escapes from the trap, σ is the capture cross section of the trap for thermal electrons, and E the depth of the trap (below the conduction band). With $B\sim10^{-2}$ (half-life of 100 sec.), $\sigma\sim10^{-16}$ cm^2, we get $E=0.75$ ev. On the other hand, if $B=10^6$ (half-life of 1 μsec.), $E=0.25$ ev. Hence, we need assume only that the traps with which we are dealing lie at depths between one-fourth and three-fourths of a volt.

Regarding mechanisms, an obvious suggestion is that a foreign singly charged ion is placed at one of the many normally unoccupied lattice sites in the crystal. An electron could be caught in the field of this ion. The presence of such a foreign ion is not in itself sufficient to produce a trap, because, in an otherwise normal lattice, the ion would have to be neutralized. Dr. C. Herring has suggested to the author that a trap could be produced if the diamond contained both an interstitial foreign atom, and a trivalent atom in place of one of the carbons. Such a configuration would be electrically neutral; there would, however, be an unpaired electron on one carbon atom. Either of two things could conceivably occur: A valence electron from the foreign atom could pair off with the excess electron from a carbon, leaving the atom ionized, or the foreign atom could remain neutral, but an electron

[9] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 108.

could be trapped by forming a bond between the trivalent atom and the unsaturated carbon. For the latter process, the foreign atom is not necessary. No calculations have been made of the trap depths to be expected from such a model, but depths of the order of 1/2 volt do not seem unreasonable. A hydrogenic trap in a medium of dielectric constant = 5 has a depth of 13.5/25 $\approx 1/2$ volt. If the shallow traps are produced by interstitial alkali atoms or trivalent substituted atoms, deeper traps could be produced by divalent atoms at interstitial and lattice positions.

For later work, we wish to know a function $G(x, x')$, which is defined by saying that $G(x, x')dx$ is to be the probability that an electron set free at a depth x' in the crystal will be trapped at a depth between x and $x+dx$. We assume that the lines of force are straight, although not necessarily of uniform density, and that x is measured in the direction of drift of electrons. For reasons discussed by Mott and Gurney,[10] the probability that an electron has not been trapped depends on the time since it was released, and this probability is

$$\exp(-t/T),$$

where T is a constant which depends upon the density of traps and their capture cross section. This implies that the drift velocity of electrons is less than their thermal velocity. If the electron is traveling in a field which is a function of position, t is clearly given by

$$t=\int_{x'}^{x} dx/vF.$$

Hence the probability that an electron is still free after traveling from x' to x is

$$\exp\left(-\int_{x'}^{x} dx/vTF\right).$$

The function $G(x, x')$ is the negative derivative of this quantity with respect to x, or

$$G(x, x') = (vTF)^{-1} \exp\left(-\int_{x'}^{x} dx/vTF\right). \quad (8)$$

Equation (8) assumes $x \geq x'$. If $x < x'$, $G(x, x') = 0$.

[10] See reference 9, p. 122.

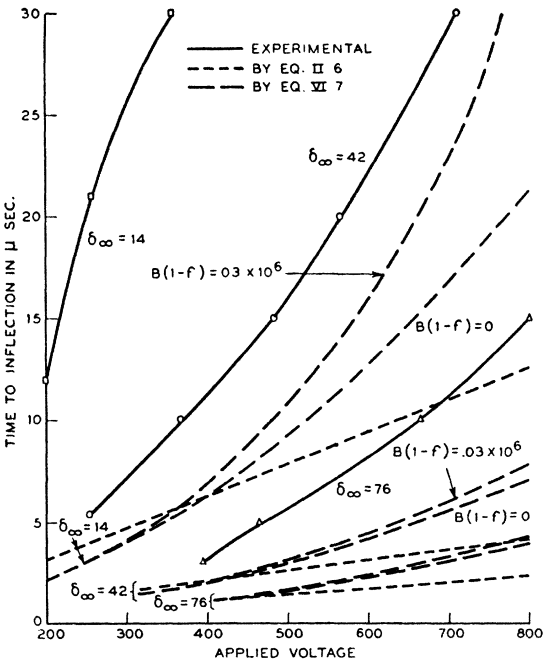

FIG. 3. Time to inflection *vs.* applied voltage.

$G(x, x')$ gives the probability of capture into some trap. The probability of capture into some particular type of trap is $G(x, x')$ times the relative number of traps of this type.

IV. EXPERIMENTAL DETERMINATION OF THE TRAPPING CONSTANT T

The trapping function $G(x, x')$ contains the unknown constant, T, which is to be interpreted as the mean life of an electron in the conduction band. McKay has measured T for the diamond which he is studying; we shall review his method briefly.

McKay defines a quantity δ, called the yield, which is the ratio of the current carried by conduction electrons to the bombarding current, when measured in a crystal free of space charge. δ should be given by the following formula, which was first derived by Hecht[11] in connection with photo-conductivity, and whose application to the present problem will be examined critically by McKay in his forthcoming paper:

$$(\delta/\delta_\infty) = (vTF/l)[1-\exp(-l/vTF)]. \quad (9)$$

l is the thickness of the crystal. In applying this

[11] K. Hecht, Zeits. f. Physik 77, 235 (1932). Also, see Mott and Gurney, reference 9, p. 122.

formula, δ is plotted as a function of F for a particular bombarding energy (constant δ_∞), and values of δ_∞ and vT are chosen so that Eq. (9) fits the experimental data as closely as possible. The same procedure is followed at different bombarding energies. In this way, δ_∞ is determined as a function of the energy of the bombarding electrons. If formula (9) applies, the value of vT necessary to fit the experimental data should be the same for all bombarding energies. McKay found that he could fit all the curves with vT varying by no more than a factor of two.

For the diamond used, he found $vT \sim 6\times10^{-6}$ cm^2/volt. Using $v=100$ cm^2/volt sec., this gives $T=6\times10^{-8}$ sec. Assuming that the electrons have thermal velocity, and that the traps have a capture cross section of 10^{-16} cm^2, this gives a trap density of 1.7×10^{16} per cm^3, which is reasonable.

V. THE SPACE CHARGE EQUATIONS

We are now in a position to set up the equations governing the accumulation of space charge in the diamond, and the current through it. We assume infinite plane-parallel geometry, so that we need only one space coordinate x. We take the origin of x to be at the boundary between the plasma layer and the rest of the crystal, and increasing as we go to the back face, which lies at $x=L$. As in Section III, we take the field F to be positive if it points in the negative x direction. We let n_s=density of electrons in shallow traps, with a probability B of thermal release per second, and let n_d=density of electrons in deep traps, with negligible probability of release. Let f be the ratio of the density of deep traps to the total trap density, and let j_0=number of electrons leaving the plasma layer per cm^2 per sec. At equilibrium, j_0 is also the current measured externally.

We saw in the last section that the mean life T of an electron in the conduction band is about 6×10^{-8} sec. Since this is somewhat smaller than the times of observation, we make the crude but simplifying assumption that the elapsed time between the release and the trapping of an electron is negligible.

Consider now the quantities $(\partial/\partial t)n_s(x,t)dxdt$ and $(\partial/\partial t)n_d(x,t)dxdt$, which are the changes in time dt of the numbers of electrons in shallow and deep traps, respectively, contained in the distance dx at x. These quantities consist of three parts:

(a) Loss by thermal agitation. This equals $-Bn_s(x,t)dxdt$ for shallow traps, and zero for deep traps.

(b) Capture in dx of electrons released elsewhere by thermal agitation. In time dt, $Bn_s(x',t)dtdx'$ electrons are released from the interval dx'. Of these, $G(x,x')dx$ are captured in dx. Hence, the total number of such electrons caught in dx in time dt is

$$Bdxdt\int_0^x G(x,x')n_s(x',t)dx'. \tag{10}$$

The contribution by this mechanism for shallow traps is $(1-f)$ times expression (10), and for deep traps is f times (10).

(c) Trapping of electrons entering from the plasma layer. In time dt, j_0dt electrons enter the crystal, and the fraction trapped in dx is $G(x,0)dx$. Hence, the contribution for shallow traps from this source is $(1-f)j_0G(x,0)dxdt$, and for deep traps is $fj_0G(x,0)dxdt$.

If we equate $(\partial/\partial t)n_s(x,t)dxdt$ and $(\partial/\partial t)\times n_d(x,t)dxdt$ to the sum of contributions 1, 2, and 3, and divide through by $dxdt$, we get the pair of integral-differential equations:

$$(\partial/\partial t)n_s(x,t) = -Bn_s(x,t)+(1-f)B\times\int_0^x G(x,x')n_s(x',t)dx' +(1-f)j_0G(x,0); \tag{11}$$

$$(\partial/\partial t)n_d(x,t) = fB\int_0^x G(x,x')n_s(x',t)dx' +fj_0G(x,0). \tag{12}$$

The function $G(x,x')$ is defined by Eq. (8), and involves, in addition to x and x', the field strength F at all points between x' and x. In addition to Eqs. (11) and (12), the quantities F, n_s, and n_d are further related by Poisson's equation:

$$\partial F/\partial x = (4\pi\epsilon/\kappa)(n_s+n_d). \tag{13}$$

Poisson's equation is subject to the restriction that the potential difference across the diamond

is fixed:

$$\int_0^L F dx = F_0 L, \tag{14}$$

where F_0 is the applied field. In other words, the mean value of the field is constant in time. The whole system of Eqs. (11) through (14) is subject to the initial conditions:

$$n_s(x, 0) = n_d(x, 0) = 0. \tag{15}$$

From $n_s(x, t)$ and $n_d(x, t)$, we wish to determine the current density $j(t)$ through the diamond. To do this, we observe that, in time dt, $j_0 dt$ electrons/cm^2 start across the crystal. Letting $n = n_s + n_d$, the number of electrons/cm^2 which travel the distance dx from x to $x+dx$ is

$$j_0 dt - dt \int_0^x (\partial/\partial t) n(y, t) dy.$$

Their contribution to the charge transferred in time dt is dx/L times this, so that the externally measured current density j is

$$j = \int_0^L \left[j_0 dt - dt \int_0^x (\partial/\partial t) n(y, t) dy \right] dx/L dt.$$

Canceling dt and reversing the order of integration gives

$$j = j_0 - L^{-1} \int_0^L (\partial/\partial t) n(x, t)(L-x) dx, \tag{16}$$

in electronic charges/cm^2/sec.

The system of equations which we have just derived holds for either portion of the current curves shown in Fig. 2. From the viewpoint of these equations, the difference between the two portions of the curves arises from the behavior of j_0, the current density. During the first portion of the curve, when the field in the plasma layer is high, j_0 is a constant and equals $i_0 \delta_\infty$. When the field in the plasma layer becomes small, j_0 becomes dependent on the strength of this field. In principle, we could calculate the dependence of j_0 on field by solving for conditions in the plasma layer, but, in view of the diversity of possible mechanisms and the mathematical difficulties of solution, it is unlikely that the results would be reliable.

VI. THE CURRENT FOR HIGH FIELDS IN THE PLASMA

This section deals with the current through the crystal during the first portion of the curves shown in Fig. 2, which, on the basis of our present picture, means that the current j_0 is constant and equal to $i_0 \delta_\infty$, the total number of electrons released by the impinging electrons.

Even with the assumption of constant j_0, the system of equations developed in the last section is too complicated to admit simple solutions. We can, however, develop approximate solutions good for small t by assuming analytic solutions and using power series methods. The procedure is quite straightforward.

We assume that the densities of electrons in shallow and in deep traps can be written in the form:

$$n_s(x, t) = \sum_{i=1}^{\infty} a_i(x) t^i, \quad n_d(x, t) = \sum_{i=1}^{\infty} b_i(x) t^i. \tag{17}$$

The summations start at $i=1$ rather than at $i=0$ because both densities are initially zero, by (15). Substituting (17) into (13) and using (14), we find that $F(x, t)$ can be written as

$$F(x, t) = F_0 (1 + \sum_1^{\infty} f_i(x) t^i), \tag{18a}$$

where

$$f_i(x) = (4\pi\epsilon/\kappa F_0) \left(\int_0^x [a_i(y) + b_i(y)] dy - \int_0^L L^{-1} dx \int_0^x [a_i(y) + b_i(y)] dy \right). \tag{18b}$$

$F(x, t)$ occurs only as the reciprocal, so we must divide (18a) into unity. Upon doing so, we may write $F^{-1}(x, t)$ as

$$F^{-1}(x, t) = F_0^{-1} (1 + \sum_1^{\infty} f_i^{(-1)}(x) t^i), \tag{19}$$

where $f_1^{(-1)}(x) = -f_1(x)$, $f_2^{(-1)}(x) = f_1^2(x) - f_2(x)$, etc. It is next convenient to write $G(x, x')$ as a power series in t:

$$G(x, x') = (vTF_0)^{-1} \exp[-(x-x')/vTF_0] \times (1 + \sum_1^{\infty} g_i(x, x') t^i). \tag{20}$$

The $g_i(x, x')$ are evaluated by substituting series

(19) into Eq. (8), and expanding the resulting exponential. The first two of the $g_i(x, x')$ are:

$$g_1(x, x') = f_1^{(-1)}(x) - (vTF_0)^{-1}\int_{x'}^{x} f_1^{(-1)}(y)dy;$$

$$g_2(x, x') = f_2^{(-1)}(x) - (vTF_0)^{-1}\int_{x'}^{x} f_2^{(-1)}(y)dy + \tfrac{1}{2}(vTF_0)^{-2}\left[\int_{x'}^{x} f_1^{(-1)}(y)dy\right]^2 - (vTF_0)^{-1}f_1^{(-1)}(x)\int_{x'}^{x} f_1^{(-1)}(y)dy.$$

We have thus developed the function $G(x, x')$ as a power series whose coefficients are related in a known manner to the coefficients in series (17). Substituting, then, series (17) and (20) into Eqs. (11) and (12) gives us a recurrence relation for the coefficients $a_i(x)$ and $b_i(x)$. The series whose coefficients are thus obtained satisfies formally Eqs. (11) through (15). The first few coefficients are:

$$a_1(x) = (1-f)j_0(vTF_0)^{-1}\exp(-x/vTF_0),$$

$$b_1(x) = fj_0(vTF_0)^{-1}\exp(-x/vTF_0),$$

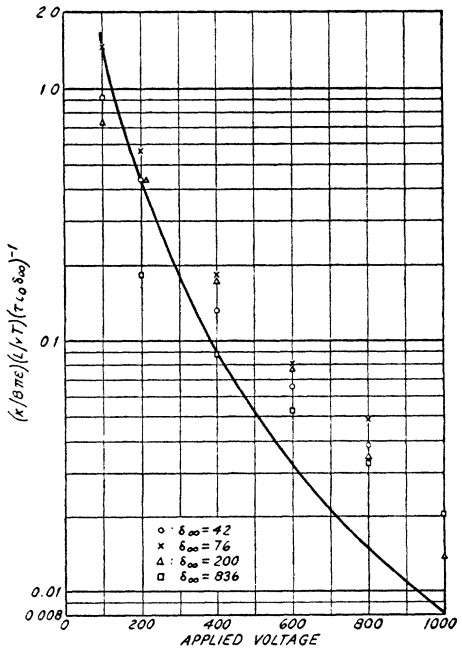

FIG. 4. Reduced half-life *vs.* applied voltage.

$$a_2(x) = -\tfrac{1}{2}Ba_1(x) + \tfrac{1}{2}(1-f)B(vTF_0)^{-1}\times\exp(-x/vTF_0)\times\int_0^x \exp(x'/vTF_0)a_1(x')dx' + \tfrac{1}{2}(1-f)j_0(vTF_0)^{-1}\times\exp(-x/vTF_0)g_1(x, 0),$$

$$b_2(x) = \tfrac{1}{2}fB(vTF_0)^{-1}\exp(-x/vTF_0)\times\int_0^x \exp(x'/vTF_0)a_1(x')dx' + \tfrac{1}{2}fj_0(vTF_0)^{-1}\exp(-x/vTF_0)g_1(x, 0).$$

Finally, the current j can be expanded in a series of the form

$$j = \sum_0^\infty J_i t^i. \tag{21}$$

The coefficients J_i are obtained in an obvious manner by substituting series (17) into Eq. (16). The first two of these coefficients are:

$$J_0 = j_0\lambda^{-1}(1-e^{-\lambda}),$$

$$J_1 = B(1-f)j_0[\lambda^{-1}(1-e^{-\lambda}) - e^{-\lambda}] - (4\pi\epsilon/\kappa)\times(j_0^2vT/L)[\tfrac{1}{2}(1-e^{-2\lambda}) - \lambda^{-1}(1-e^{-\lambda})^2], \tag{22}$$

where $\lambda = L/vTF_0$. Both quantities in square brackets, for a given diamond, are functions only of the applied field, and are further non-negative.

We are also interested in computing $F(0, t)$, the electric field in the plasma layer. The reader can readily verify that it is given by

$$F(0, t) = F_0 - (4\pi\epsilon/\kappa)(j_0 - J_0)t + (2\pi\epsilon/\kappa)J_1t^2 + \cdots. \tag{23}$$

By equating this to zero, we should obtain the time at which $F(0, t)$ becomes zero more accurately than we do from Eq. (6). We note from inspection of J_1 that the effect of thermal release of trapped electrons ($B>0$) is to increase this time, and, in fact, that if B is large enough, the field does not become zero in any time for which $F(0, t)$ is given accurately by three terms. However, if the initial derivative of the current is negative ($J_1<0$), we see that Eq. (23) has a root which is of the same order as that given by Eq. (6).

We can now get a rough comparison with

experiment by the use of Eqs. (22). If the current continued to decrease at its initial rate, we readily find that the time τ at which the current would have fallen to half of its initial value is found from

$$\tau^{-1} = -2J_1/J_0. \tag{24}$$

Values of τ have been estimated by McKay, from oscilloscope traces.

If we neglect B, we see that τ^{-1} is given by

$$\tau^{-1} = (8\pi\epsilon/\kappa) i_0\delta_\infty (vT/L) \times [e^{-\lambda} - 1 + \tfrac{1}{2}\lambda(1+e^{-\lambda})] \tag{25}$$

from Eqs. (22). In other words, the quantity $(\kappa/8\pi\epsilon)(L/vT)(\tau i_0\delta_\infty)^{-1}$ should depend only upon λ, which in turn depends only on field strength for a particular diamond, and should not depend upon the energy of the bombarding electrons. This is tested in Fig. 4, in which the quantity in square brackets is plotted against applied voltage. If $vT = 5\times10^{-6}$ cm^2/volt, and $L = 0.05$ cm, the relation between λ and V is $\lambda V = 500$ volts. The experimental values of $(\kappa/8\pi\epsilon)(L/vT)(\tau i_0\delta_\infty)^{-1}$ are also plotted for several values of the bombarding energy. The agreement is perhaps as good as could be expected, but it should be pointed out that for no values of the bombarding energy do the experimental values change as rapidly with V as is predicted.

An attempt was made to estimate a value for $B(1-f)$ by making the experimental points in Fig. 4 fit the theoretical curve as closely as possible. The required values of $B(1-f)$ turned out to be negative, and also to be roughly proportional to δ_∞, indicating a systematic discrepancy between experiment and the present theory.

We can, however, set an upper limit to $B(1-f)$ from the fact that the initial derivative of the current is negative in every situation which has yet been observed. If we compute the value of $B(1-f)$ in Eq. (22) which makes $J_1 = 0$, for various experimental conditions, we find that the smallest such value is 0.014×10^6 sec.$^{-1}$, or, in other words, the mean life for release of electrons from shallow traps by thermal agitation is of the order of 70 μsec. or greater.

Finally, we have also plotted in Fig. 3 the values of t at which $F(0, t)$ becomes zero, using Eq. (23), with $B(1-f) = 0$ and $B(1-f) = 0.03 \times 10^6$, using $j_0 = i_0\delta_\infty$. Since $B(1-f) < 0.014\times10^6$, the effect of thermal release upon this time is seen to be small. Most of the difference between Eqs. (6) and (23) does not come from the term quadratic in t, but from the fact that we have estimated the coefficient of t more accurately in (23) than in (6). The coefficient in (23) allows for electrons which cross the crystal without being trapped.

We mentioned in Section II that, if our theory is correct, it must lead to a negative second derivative for the current as long as the current density j_0 leaving the plasma is constant. To calculate the second derivative by extending the power series attack seems quite laborious and not justified at present. The following argument suggests strongly, however, that the second derivative is indeed negative, at least for small thermal release rates:

The current, according to Eq. (16), depends upon $\partial n/\partial t$, weighted by the factor $L-x$, and integrated over all x. Because of the weighting factor, what happens at the front face ($x=0$) is more important than what happens at the back ($x=L$). Accordingly, if $\partial^3 n/\partial t^3 > 0$ at $x=0$, we may expect that $\partial^2 j/\partial t^2 < 0$.

Neglecting thermal release, and adding Eqs. (11) and (12), we have

$$(\partial/\partial t) n(0, t) = j_0/vTF(0, t).$$

Differentiating twice with respect to t,

$$(\partial^3/\partial t^3) n(0, t) = (2j_0/vTF^3(0, t))(\partial F(0, t)/\partial t)^2 - (j_0/vTF^2(0, t))(\partial^2 F(0, t)/\partial t^2).$$

The first term of this is positive, since $F(0, t)$ is positive. By Eq. (23), $\partial^2 F(0, t)/\partial t^2 \approx (4\pi\epsilon/\kappa) J_1$ for small t, and is therefore negative whenever the initial derivative of the current is. Hence the second term above is also positive, and the second derivative of the current is probably negative for small t.

VII. CONDITIONS AFTER A LONG TIME

We are not in any position to discuss the approach of the current to equilibrium, having discovered no way to solve the necessary equations except numerically. Accordingly, we proceed at once to discuss equilibrium conditions.

Unless the fraction of traps which are deep is fairly large, we expect the crystal to approach

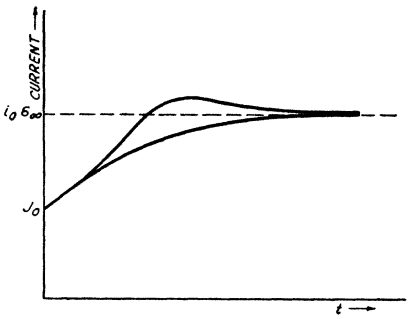

FIG. 5. Possible forms of the current if the thermal release rate is large. The current might also oscillate about the value $i_0\delta\infty$.

in a fraction of a second a condition in which the loss of entering electrons by trapping is just balanced by thermal release from shallow traps. As the time increases, the number of electrons in deep traps increases, and finally becomes the dominating factor. On a time scale such that this effect is important, the electrons in shallow traps are released in negligible times, so that we may say that the final equilibrium is the balance between capture in and release from deep traps. We shall discuss only the first situation in which the deeply trapped electrons are negligible. That is, we assume that the behavior of all trapped electrons can be represented adequately by ascribing to them a probability $B(1-f)$ of release per second.

We take, then, Eq. (11), with $n_s=n$, and with $\partial/\partial t=0$. Solving Eq. (11) for j_0 under these conditions, using γ for the equivalent release rate $B(1-f)$, gives

$$j_0=\gamma vTF(x)n(x)\exp\left(\int_0^x dy/vTF(y)\right)$$
$$-\gamma\int_0^x n(x')\exp\left(\int_0^{x'} dy/vTF(y)\right)dx'.$$

Differentiating with respect to x shows that

$$(dF/dx)n+F(dn/dx)=0,$$

whence the product of F and n is a constant, which we write in the form $C/\gamma vT$:

$$F(x)n(x)=C/\gamma vT. \tag{26}$$

Inserting this back into the equation for j_0, we find that $C=j_0$.

Using Eqs. (13) and (14), and performing the necessary manipulations, we finally obtain

$$F_0L=\gamma(\kappa/12\pi\epsilon)(vT/j_0)([F^2(0)+(8\pi\epsilon/\kappa)$$
$$\times(j_0/\gamma vT)L]^{\frac{3}{2}}-F^3(0)). \tag{27}$$

When j_0 is known as a function of $F(0)$, this can be solved numerically for $F(0)$, and other quantities of interest can be found by using the relations in Section V. For example, F can be computed as a function of x from Eq. (13), into which $n(x)$ is substituted from Eq. (26). $n(x)$ can then be computed by coming back to Eq. (26).

There are two general methods by which equilibrium may be attained, depending upon the size of γ. The first is the one which we discussed in Section II, in which $F(0)$ falls almost to zero, and j_0 becomes much smaller than $i_0\delta_\infty$. This is the only behavior which has yet been observed.

We see from Eq. (23), however, that if $J_1>0$ and is sufficiently large, $F(0,t)$ not only does not fall to zero, but begins to increase after a short period of decreasing. As long as deeply trapped electrons are negligible then, it seems unlikely that $F(0,t)$ will fall to zero at any later time. Therefore, j_0 always remains substantially equal to $i_0\delta_\infty$, and, since j_0 is the equilibrium current, there should be a second type of equilibrium in which the equilibrium current must equal $i_0\delta_\infty$. Further, the initial current must equal $i_0\delta_\infty\lambda^{-1}(1-e^{-\lambda})$, by Eq. (22), and hence the equilibrium current will be larger than the initial current.[12]

If this happens, the current *vs.* time curve must be like one of the forms sketched in Fig. 5. We cannot yet say which form it will follow; we can only say that, from conservation of charge,

$$\int_0^t jdt=i_0\delta_\infty t-\int_0^L n(x)dx, \tag{28}$$

for a value of t such that equilibrium is attained. $n(x)$ is evaluated by using Eq. (26).

VIII. TRAPPING AT THE ELECTRODES

A possibility which we have not yet discussed is that the space charge effects which cause the

[12] Compare with the discussion by F. Seitz in *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 569.

current through the diamond to vary with time come from electrons (and/or holes) trapped at the boundary between the crystal and the electrode, rather than within the diamond. If the contact between the diamond and the electrode is not intimate, trapping at the surfaces may well be a dominant factor. With the gold-evaporated electrodes which have been used in all of the experiments witnessed by the author, we believe that surface trapping is unimportant compared with trapping in the volume. This conclusion is supported by at least two considerations:

(a) Enormous surface charges, or, alternatively, enormous times, would be required to produce appreciable space charge. If the field in the diamond is reduced to zero, all of the potential drop (called F_0L in the previous sections) is across the gap between the electrodes and the diamond. Calling the width of this gap D, the field E in the gap is $E=F_0L/D$. Assuming that all electrons released by the bombardment are trapped at the surface, the surface density of charge is $i_0\delta_\infty t$ electrons/cm^2, which must be equated to $E/4\pi\epsilon$. Hence:

$$t=F_0L/4\pi\epsilon D i_0\delta_\infty. \tag{29}$$

Taking typical values such as were used in Section II ($F_0=10$ e.s.u./cm, $L=0.05$ cm, $i_0\delta_\infty=6\times10^{16}$ electrons/cm^2/sec.), with D as large as 10^{-6} cm, gives $t\approx10^{-3}$ sec. In 1 μsec., which is of the order of the observed half-lives, space charge would change the field in the diamond by only about 0.1 percent.

(b) The hypothesis of surface trapping is incompatible with the conclusion reached in Section II, namely, that all the liberated electrons leave the plasma layer unless the field there is below 200 volts/cm. For, combining Section II with surface trapping would mean that the current would stay constant until the field in the plasma becomes small, and then would fall rapidly to a steady-state value. Further, the yield *vs.* voltage curves would not agree with Eq. (9), as they do, but would saturate at a quite low voltage.

Should occasion arise, one can construct a theory based on surface trapping as follows: The measured curve of initial yield *vs.* voltage is to be interpreted as giving the variation of j_0, the current leaving the plasma, with field at the front face. That is, the curve gives

$$j_0=j_0(F). \tag{30}$$

F is no longer a function of x.

If a surface charge of density σ is collected on one or both faces of the crystal, F and σ are related at any time by an equation of the form

$$F=aF_0-b\sigma, \tag{31}$$

where a and b are constants, and F_0 is the applied field. σ and j_0 are further related; if release of trapped charge is negligible, for example,

$$\sigma=\int_0^t j_0 dt. \tag{32}$$

Differentiating (31) and substituting for σ from (32), we get

$$dF/dt=(dF/dj_0)(dj_0/dt)=bj_0. \tag{33}$$

In view of (30), this can be integrated at once to give j_0 as a function of t.

IX. CONCLUSIONS AND SUGGESTIONS

There is at least qualitative agreement between the experimental results of McKay and the theory presented in the present paper. In assessing the success of the theory, it should be borne in mind that the theory contains no adjustable constants. All constants occurring are measured by methods independent of a space charge hypothesis. The theory was able to predict one result which was later confirmed experimentally, and it yields reasonable values for two independently measured physical quantities, namely, the initial slope and the time of inflection.

The calculations of Section II, which led to the conclusion that recombination and trapping in the plasma layer are negligible except at low fields, were based on certain assumptions about mobilities and cross sections. If these quantities, when measured, should be found to differ substantially from the assumed values, it might be necessary to revise the entire theory.

The postulation of the second type of equilibrium suggests an interesting experiment. The quantity γ depends exponentially upon temperature, so, by increasing the temperature, it may

be possible to achieve this type of equilibrium. This gives us first, a method of measuring δ_∞ which does not depend upon having an initially space charge free crystal. Second, by applying low fields to the crystal, we can measure directly the dependence of j_0 (at equilibrium) upon field strength. This same dependence may not hold, of course, for the ordinary temperatures at which the crystal is usually operated, but the information should none the less be theoretically valuable.

Finally, at ordinary temperatures, j_0 can be measured as a function of F_0, and the results used in Eq. (27) to determine j_0 as a function of $F(0)$. This is not a direct measure of $F(0)$, however, and should preferably be supplemented by other measurements.

We have emphasized the determination of j_0 as a function of $F(0)$ because it seems to us a good way of getting some information as to what goes on inside the plasma layer.

We are considerably indebted to various of our colleagues, particularly to Dr. R. W. Hamming, for a discussion of mathematical methods, and to Drs. McKay and Ahearn for extensive discussions of their experiments, and the bearing of the present theory upon them.

The data which we used in preparing Figs. 3 and 4 are from McKay's preliminary data, and are being carefully checked by him for later publication. It is thought that these data, although preliminary, are nearly enough correct so that use of the final data will not appreciably alter the theory or the conclusions drawn from it.

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Absolute Voltage Determination of Three Nuclear Reactions

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A large electrostatic analyzer was used in conjunction with the Wisconsin electrostatic generator for an absolute voltage determination of the $Li^7(pn)Be^7$ threshold, an $Al^{27}(p\gamma)Si^{28}$ resonance, and a $F^{19}(p\alpha', \gamma)O^{16}$ resonance. Using absolute volts the values found are 1.882 Mev, 0.9933 Mev, and 0.8735 Mev, respectively. The uncertainties in the measurements appear to be about ± 0.1 percent.

INTRODUCTION

AN absolute measurement of the proton energy at the Li($p\gamma$) resonance was carried out by Hafstad *et al.*[1], using a calibrated resistor stack made up of I.R.C. metalized resistors. Parkinson *et al.*[2] checked this measurement and agree on a value of 0.440 Mev for the resonance energy with an estimated error of about two percent. Based on this determination, work at a number of laboratories lead to a number of secondary fixed points (i.e., F($p\gamma$) at 0.862 Mev and Li(pn) at 1.856 Mev), which are used widely as reference voltages. Recently Tangen[3] has measured the Li($p\gamma$) resonance by the method used in reference (1) and has obtained 0.440 Mev with an estimated uncertainty of $\frac{1}{2}$ percent.

If one attempts to establish absolute voltage values above 1 Mv, the resistor method becomes difficult. In this case some form of electrostatic analyzer can be used to scale down the voltage to be measured by a factor of about 100. Hanson and Benedict[4] used an electrostatic analyzer, calibrated by an electron beam, to determine the following reaction energies: Li(pn) at 1.883 Mev, Be(pn) at 2.058 Mev, F($p\gamma$) at 0.877 Mev, and Li($p\gamma$) at 0.4465 Mev. An absolute calibration by direct calculation from the geometry was also

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