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The Mobility and Life of Injected Holes and Electrons in Germanium

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The mobilities of holes injected into *n*-type germanium and of electrons injected into *p*-type germanium have been determined by measuring transit times between emitter and collector in single crystal rods. Strong electric fields in addition to those due to injected current were employed so that spreading effects due to diffusion were reduced. The mobilities at 300°K are 1700 cm^2/volt-sec for holes and 3600 cm^2/volt-sec for electrons with an error of probably less than five percent. The value for electrons is about 20 percent higher than the best estimates obtained from the conventional interpretation of the Hall effect and the difference may be due to curved energy band surfaces in the Brillouin zone. Studies of rates of decay indicate that recombination of holes and electrons takes place largely on the surface of small samples with constants varying from 10^2 to $>10^4$ cm/sec for special treatments.

I. INTRODUCTION

As a result of new experimental techniques[1] developed in connection with the transistor[2] program, the speed with which holes and electrons drift in electric fields in germanium can now be measured with an accuracy sufficient to determine their mobilities to within a few percent. The basic phenomena which permit these new experiments to be performed are those of carrier injection[3] and collector action;[2] with the aid of the former, holes or electrons can be injected at a given place and time, and with the aid of the latter their arrival time at another point can be determined.

It should be emphasized that transit time measurements determine drift mobility in a very direct way. Hall effect measurements, which have previously been used to determine mobilities in semiconductors, are quite indirect. The relationship between Hall mobility, defined by the angle between current and electric vectors in unit magnetic field, and true mobility involves the detailed nature of the scattering processes and energy band shapes and only under special conditions does the ratio have the conventional value of $3\pi/8$. It now appears probable that a real deviation from the simple ratio $3\pi/8$ occurs for electrons in germanium and that this is associated with energy band shapes.[4]

II. SIMPLE CIRCUIT ARRANGEMENT FOR MOBILITY STUDIES

The essence of the technique described in this paper is incorporated in the circuit[5] shown in Fig. 1. A rod of *n*-type germanium, cut from a single crystal, is provided with rhodium-plated contracts at either end for good electrical contact. A battery is placed in series with these plated contacts so that a direct current I_B, called the sweeping current, flows downward in the crystal producing electric field in the same direction. Four phosphor bronze points are placed in contact with the germanium with the aid of a micromanipulator. A relay and a battery are placed in series with the point ϵ so that when the relay is closed a current I_ϵ flows from the point into the germanium making this point an emitter of positive holes. In series with the point C is placed a resistance R_1 and a battery, so that this point is biased negatively with respect to the germanium, as is a collector in a type A transistor. The other two points P_1 and P_2 are used as probes to measure the potential difference in the germanium crystal between the emitter and collector points. The input amplifier of a cathode-ray oscilloscope is connected across the resistance R_1. This resistance has a value which is small compared with the impedance of the collector point so that the voltage applied to the oscilloscope is proportional to the admittance of the point. At a certain instant of time a positive pulse of current is applied to the emitter point by closing the relay. Holes enter the crystal at this time and are swept down to the collector in the electric field produced by the combined

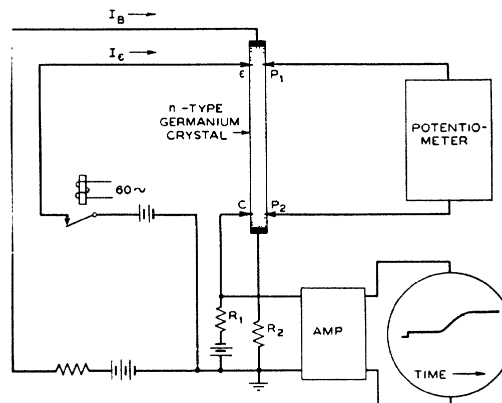

FIG. 1. Schematic diagram of simple circuit used to measure mobility of injected holes and electrons.

[1] Shockley, Pearson, and Haynes, Bell System Tech. J. **28**, 344 (1949).
[2] J. Bardeen and W. H. Brattain, Phys. Rev. **74**, 230 (1948); **75**, 1208 (1949).
[3] E. J. Ryder and W. Shockley, Phys. Rev. **75**, 310 (1947). J. N. Shive, Phys. Rev. **75**, 689 (1949). J. R. Haynes and W. Shockley, Phys. Rev. **75**, 691 (1949).
[4] Pearson, Haynes, and Shockley, Phys. Rev. **78**, 295 (1950).
[5] This circuit is drawn for the study of the behavior of injected holes in *n*-type germanium. It is equally well adapted to the study of injected electrons in *p*-type germanium. For this purpose it is only necessary to reverse the polarity of the batteries.

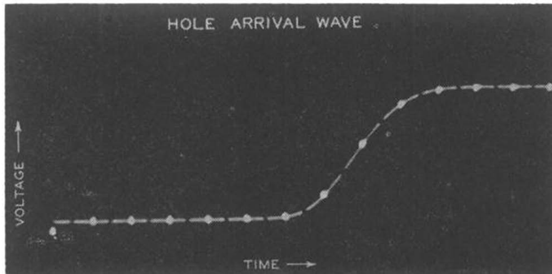

FIG. 2. Photograph of characteristic obtained on cathode-ray tube. Oscilloscope synchronized to start of hole injection.

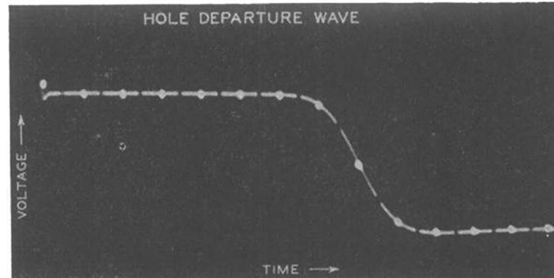

FIG. 3. Photograph of characteristic obtained on cathode-ray tube. Oscilloscope synchronized to stop of hole injection.

currents I_B and I_ϵ. When they arrive at the collector, they produce a measurable signal on the oscilloscope.

III. FORM OF SIGNAL OBTAINED AND TRANSIT TIME

A photograph of the signal obtained with the oscilloscope synchronized to the start of hole injection is shown in Fig. 2. The dots on the oscilloscope trace are 10 μsec marker intervals. A small initial rise can be observed. This rise is due to the added emitter current and is produced by the consequent increased voltage drop in the segment of the germanium crystal between the collector point and ground. After this initial rise, the signal remains constant for 60 μsec. During this time the injected holes are moving down the crystal from the emitter point, which was placed a centimeter away from the collector. When the holes arrive at the collector, the voltage applied to the oscilloscope rises slowly to a maximum at 120 μsec. This increase in voltage, which is made by the circuit to be proportional to the increase in collector current, has been shown to be also proportional to the hole density arriving at the collector point.[6]

The hole injection from the emitter point stops abruptly when the relay is opened. The photograph shown in Fig. 3 was obtained with the oscilloscope synchronized to this time. The initial short drop which occurs when the relay opens is analogous to the initial rise obtained at the start of hole injection and is due to the stop of emitter current. After this initial drop the signal remains nearly constant[7] for 60 μsec until the holes are swept past the collector when the signal voltage drops, reaching a minimum in 120 μsec. This drop in signal voltage owing to hole wave departure has been shown to be proportional to the hole density departing from the germanium is the immediate region of the collector point.[6]

The time required for the emitter current to rise to its maximum or fall to its minimum value when the relay was closed or opened was found by connecting the oscilloscope across R_2 instead of R_1 (Fig. 1). Although this time was shown to be a small fraction of a microsecond, the hole arrival and departure wave fronts are seen to be spread out over some 30 μsec. This "softening" of these waves has been found to be quantitatively that to be expected from random diffusion. When the emitter current is made sufficiently small so that the conductivity modulation can be neglected,[8] the shape of these characteristics[9] is given by the customary integral of the error function, such as is met with in heat flow problems, and diffusion takes place to equal degrees behind and ahead of the average portion of the wave fronts. For this reason the transit time required for the holes to pass from the emitter to the collector has been taken as the time at which the wave reaches half-maximum on arrival and half-minimum on departure.

IV. ELECTRIC FIELD ASSOCIATED WITH MEASURED TRANSIT TIME

The electric field in the germanium crystal during the time that the hole arrival characteristic was obtained (Fig. 2) was somewhat greater than that for the hole departure wave characteristic (Fig. 3), because the current flowing in the crystal was greater in the first case by an amount equal to the emitter current. In Sec. XI we shall show that, owing to conductivity modulation of the germanium, the electric field experienced by the wave front is never quite constant. Since, however, conductivity effects are minimized by using small values of the emitter current, the steady-state values of the electric field obtained with and without an emitter current are closely those experienced by the holes in the arrival and departure waves. These steady-state electric fields were determined by measuring the steady-state voltages between the probe points P_1 and P_2 with a potentiometer and dividing by the distance

[6] Shockley, Pearson, ann Haynes, Bell System Tech. J. **28**, 344 (1949).

[7] A slight decrease occurs because the transit time for holes in the crystal is progressively longer, owing to a lower electric field, since the emitter current has been removed. This results in a decreasing signal. As will be shown in Sec. VI, the signal amplitude decreases with transit time due to recombination of holes and electrons.

[8] The shape of these wave fronts when conductivity modulation is important has been investigated theoretically by C. Herring, Bell System Tech. J. **28**, 401 (1949).

[9] In cases where the diffusion spread is comparable to the mean life of the injected carriers correction must be made for wave front alteration due to recombination. The correction factor required is $\exp(t/\tau)$, where t is the transit time and τ is the mean life of the holes.

between them. This method of measuring the electric field involves, of course, the further assumption that the sample is homogeneous. The validity of this assumption is discussed in Secs. VIII and XI.

V. CALCULATION OF THE MOBILITY

Since we can measure the transit time from emitter to collector, the transit distance, and the electric field, we can calculate the mobility of the injected holes in this sample of n-type germanium.

The mobility of a charged particle moving in an electric field is by definition, $\mu = v/E$, where v is the velocity of the particle and E is the electric field intensity. The average velocity of the holes is equal to the distance of the emitter from the collector L, divided by the transit time t or $\mu = L/Et$. Since $E = V/L$, where V is the voltage between the emitter and collector, $\mu = L^2Vt$. Further, if t_1 is the transit time measured from the hole arrival wave, t_2 the transit time measured from the hole departure wave, V_1 the voltage between the probe points with current $I_\epsilon + I_B$, and V_2 the voltage with current I_B only, we may calculate two values of mobility, $\mu_1 = L^2/V_1t_1$ and $\mu_2 = L^2/V_2t_2$. As will be shown in Sec. XI, the true value of μ lies between μ_1 and μ_2, which approach each other as the emitter current is reduced.

VI. LIFETIME

In addition to having a uniform electric field it is necessary to have a long lifetime for the injected carriers (either holes or electrons), since otherwise no appreciable signal will arrive at the collector point.

The lifetime can be determined by measuring the amplitude of the signal arriving at the collector point as the distance between the emitter and collector points is changed keeping I_B and I_ϵ constant. This in effect changes the time which the carriers spend in the crystal before arriving at the collector.

Early measurements showed that injected holes in n-type germanium recombine with excess electrons so that, if N_0 is the original number of injected holes, there will exist after time t a number $N = N_0 \exp(-t/\tau)$, where τ is the lifetime of a positive hole.[10] Later experiments show that this exponential law is obeyed well for injected electrons in p-type germanium.

The measurement of the lifetime of the carriers using crystals of various cross section shows that the lifetime of either injected holes or electrons decreases as the cross-sectional dimensions are decreased in a manner which is consistent with the view that injected carriers are recombining both in the volume and on the surface of the germanium.[11] We may therefore write $1/\tau = (1/\tau_v) + (1/\tau_s)$, where τ is the measured lifetime, τ_v the lifetime of the carriers in the volume of the germanium, and τ_s the effective lifetime due to surface recombination only.

Using crystals of large cross-sectional dimensions (0.4 cm) made by the crystal-pulling technique of Teal and Little,[12] lifetimes of the carriers as long as 200 μsec are obtained with both n and p type germanium.[13] Even with these large samples the carriers may still be recombining largely on the surface, so that it can only be concluded that the lifetime of the injected carriers is at least 200 μsec in the bulk material and probably is considerably greater.[14] The volume recombination rate can be increased by heating the crystals to a high temperature (above 500°C) and quenching. It can also be increased by bombardment of the crystal with alpha-particles or deuterons.

The surface recombination has been investigated using crystals produced by the pulling technique. These crystals are cut into samples having cross-sectional dimensions of the order of a half-millimeter. With these dimensions the carriers diffuse to the surface so rapidly that surface recombination dominates the measured lifetime.

Measurements show that the surface recombination rate depends on surface treatment. Using a sandblasted surface on a sample with cross-sectional dimensions of $7.59\times10^{-2}\times4.71\times10^{-2}$ cm the measured lifetime was 4 μsec. This value agrees with that predicted by the formula (see Appendix) derived on the assumption that every carrier which arrives at the surface disappears immediately. This formula is

$$1/\tau = (1/\tau_v) + D\pi^2(B^{-2} + C^{-2}),$$

where D is the appropriate diffusion constant and $2B$ and $2C$ the width and thickness of the rod. With a smoothly etched surface the measured lifetime of the carriers may be increased to about 30 μsec, showing that the carriers do not recombine immediately on reaching the surface.

Surface recombination can also be altered by chemical treatment. Work in collaboration with R. D. Heidenreich has shown that a recombination rate as high as that achieved by sandblasting the surface can be obtained by simply heating the sample in tap water or distilled water containing zinc ions. On the other hand, placing the sample in a solution of SbOCl with a positive polarity on the crystal increases the life of the carriers to the order of 100 μsec. Reversing the polarity reduces the measured lifetime to a value as low as that produced by sandblasting.

Recombination at the surface may be expressed in terms of a quantity having the dimensions of a velocity, as if the carriers were disappearing by flowing

[10] A discussion of the results of early measurements of lifetime will be found in reference 3.

[11] Reference to the recombination of holes, electrons on the surface as well as the interior of germanium volume will be found in H. Suhl and W. Shockley, Phys. Rev. 75, 1617 (1949).

[12] G. K. Teal and J. B. Little, Phys. Rev. 78, 647 (1950).

[13] Nearly all crystals examined which have been grown by this method display these long volume lifetimes. Crystals produced by other methods exhibit volume lifetimes usually less than 200 μsec. In one case a volume lifetime as short as 5 μsec was observed.

[14] A possible explanation of these long lifetimes is given in reference 3.

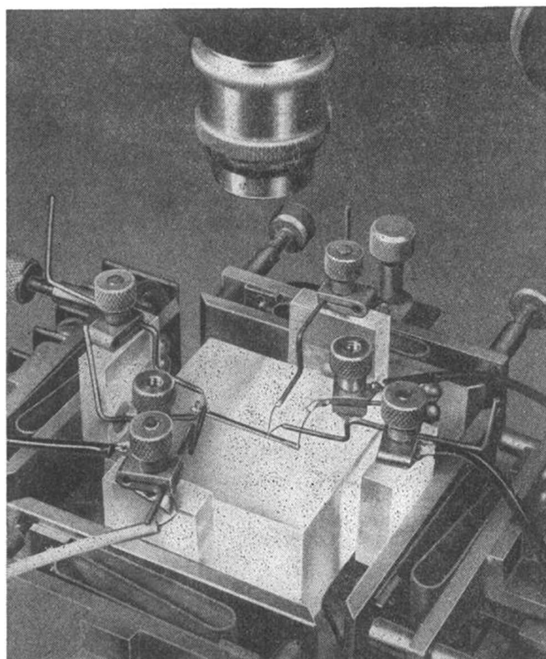

FIG. 4. Photograph of apparatus used to place metal points on germanium single crystal.

out of the surface. (See Appendix.) Values of this surface velocity have been obtained which range from 10^2 to $>10^4$ cm/sec, depending upon the kind of surface treatment.

VII. FABRICATION AND UNIFORMITY OF SAMPLES

Use has been made of this knowledge of surface recombination of injected carriers in the fabrication of the samples used for mobility measurement. Near the end electrodes it is desirable to have a short lifetime so that carriers injected from the electrodes do not enter the central portion of the sample and alter the resistivity. On the other hand, in the central portion of the crystal a long lifetime is desirable, not only so that the emitter may be placed at considerable distances from the collector, but also so that the shape of the signal received is negligibly affected by carrier recombination during the time of wave arrival and departure.

The cross-sectional dimensions of the samples were chosen to give sufficiently long lifetimes of the carriers in the central portion of the crystal without demanding the use of large currents to produce appropriate electric fields. Only single crystals were used, because of the uncertainty of the magnitude of the electric field in the neighborhood of grain boundaries.

In accordance with these considerations the samples were cut, ground, and polished into rectangular rods having dimensions of roughly $2.5\times0.05\times0.05$ cm. Approximately 0.2 cm of each end of the rod was then sandblasted and a section approximately 0.05 cm nearest each end was plated with rhodium. This left about 0.15 cm of sandblasted surface adjacent to each electrode to act as a recombination surface for carriers injected from the electrodes. The central portion of the rod was then etched for approximately one minute in CP-4 etch[15] and rinsed in methyl alcohol. Finally the rod was immersed in a solution of SbOCl with 1.5 volts positive potential on the rod for 5 minutes and again rinsed in methyl alcohol.[16]

The finished sample, mounted on a plastic block and surrounded by four micromanipulators, is shown in Fig. 4. The scale of the photograph can be judged from the microscope objective seen at the top and from the fact that the germanium crystal is 2.5 cm long. Four contact points, each controlled by a micromanipulator, may be seen contacting the sample. One of the points on the left was used as an emitter and one on the right was used as a collector, the other two being used as voltage probe points.

Only germanium crystals having a high degree of perfection were used. In order to make certain that the passage of the current I_B results in a uniform electric field all of the samples used have been probed to insure that in each the voltage drop is a nearly linear function of the distance along the crystal. Typical voltage distance plots are shown in Fig. 5 for four different samples, details of the individual specimens being given in the legend. It will be observed that some are n-type and some or p-type. One of the most satisfactory of the latter samples was produced by the addition of gallium to the melt from which the crystals are widthdrawn.

VIII. TEMPERATURE OF SAMPLES DURING MOBILITY MEASUREMENTS

Since the mobility is a function of temperature, it is important to know the temperature of the germanium crystal during mobility measurements. It has been

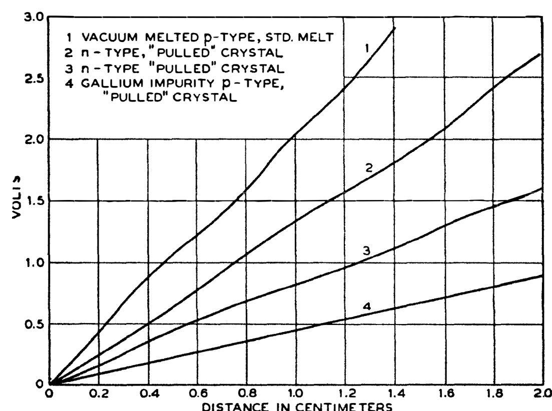

FIG. 5. Voltage as a function of distance along axes of typical samples for a current of 1.0 milliampere.

[15] The composition of CP-4 etch is as follows: 15 cc CH_3COOH, 25 cc concentrated HNO_3, 15 cc 48 percent HF, and 0.3 cc Br.

[16] This treatment was developed in collaboration with R. D. Heidenreich.

shown by Wilson[17] and more generally by Sietz[18] that, in the temperature range where the mobility is determined by lattice scattering in a nonpolar substance such as germanium or silicon, the mobility should vary at $T^{-\frac{3}{2}}$ for the nondegenerate case. This theoretical law has been confirmed by numerous observers including Pearson and Bardeen,[19] who found the predicted Hall coefficient variation with temperature in silicon, and by Pearson in his studies of germanium.[20] This work further shows that in both silicon and germanium the $T^{-\frac{3}{2}}$ law is not obeyed at low temperatures, since impurity scattering becomes important. However, Pearson's measurements of Hall coefficient and conductivity of the samples used in these drift mobility experiments show that the purity of these crystals is such that the law is closely obeyed for temperatures higher than 90°K. In correcting the measured values of drift mobility to a common temperature; therefore, it certainly seems fair to assume this law over the very limited range of from 295° to 310°K used.

The temperatures of the germanium samples during mobility measurements were determined by making use of the observation that a thermometer bulb coated with a thin coating of ceresin wax changed its luster abruptly at 51°C. The procedure used was to increase the current through a sample previously prepared with a thin coating of ceresin until the luster change occurred. It was then assumed that the temperature for lower values of current was proportional to the heat dissipated in the crystal, or that the increase in the temperature of the sample above ambient, $\Delta T = k(I_B)^2$. At the melting point of the wax (51°C) ΔT is known and I_B can be measured so that k, the proportionality constant, can be evaluated. In the measurements of drift mobility just described, the relay is closed for only half the time. The temperature of the sample under these conditions is

$$T = T_0 + \tfrac{1}{2}kI_B^2 + \tfrac{1}{2}k(I_\epsilon + I_B)^2,$$

where T_0 is the ambient temperature.

Although the error in these measurements may be as high as 10 percent, ΔT was never greater[21] than 10°C, so that the temperature of the sample was determined to within a degree Centigrade. This doubt of 1°C in the sample temperature corresponds to a maximum uncertainty of only 0.4 percent in the mobility due to this cause.

[17] H. A. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1936), p. 211.
[18] F. Sietz, Phys. Rev. **73**, 549 (1948).
[19] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).
[20] The justification of the use of the variation of mobility with temperature as determined by the measurement of the Hall coefficient and the conductivity supposes only that for a single sample the mobility so derived is proportional to the true mobility.
[21] In the measurements using pulse techniques (to be described later) ΔT never exceeded 3°C with an even lower uncertainty in temperature and mobility.

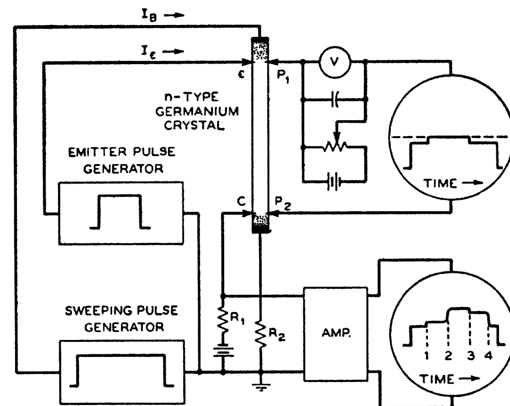

FIG. 6. Schematic diagram of circuit used to obtain more accurate measurements of mobility.

IX. DIFFUSION AND ELECTRIC FIELD DISPLACEMENT

It is desirable to make the electric field in the crystal as high as possible in order to minimize the ambiguity in transit time due to diffusion.

The relative effect of diffusion and applied voltage may be estimated from the following considerations. The distance which a hole (or electron) diffuses in time t is given by the usual diffusion formula, $l^2 = Dt = kT\mu t/e$, where D is the diffusion constant, k is Boltzman's constant, T is the absolute temperature, and e is the electronic charge. On the other hand, the distance that it travels in an electric field, $L = \mu Et$. If L is made equal to the distance from the emitter to the collector and V is the potential difference in the crystal between the position of the emitter and collector points, then $E = V/L$ and $L^2 = \mu Vt$. The ratio of these two distances is, therefore, $l/L = (kT/eV)^{\frac{1}{2}}$. Since the room temperature $kT/e = 1/40$ electron volt, $l/L = 1/6V^{\frac{1}{2}}$.

It is evident, therefore, that the voltage difference between the emitter and collector in the germanium crystal should be made as large as possible in order to obtain maximum accuracy in the determination of the carrier transit time. At the same time it is essential to avoid raising the temperature of the crystal much above ambient because of the difficulty of measuring the temperature rise accurately. Both of these criteria, however, may be met by pulsing I_B as well as I_ϵ so that the duty cycle of these currents is made a small fraction.

X. CIRCUIT FOR MORE ACCURATE DETERMINATION OF TRANSIT TIME

While the simple circuit shown in Fig. 1 gave results which could be repeated within fairly close limits and which are entirely consistent with those obtained using the pulse techniques (described below), the results obtained with the latter are much to be preferred, since the transit times of the carriers are determined with considerably greater accuracy.

The circuit used which takes advantage of these pulse techniques is shown schematically in Fig. 6. In this

circuit only two essential changes have been made from the circuit shown in the Fig. 1. (1) The batteries B_1 and B_2 have both been replaced by square wave pulse generators, and (2) the dc potentiometer has been replaced by a cathode-ray oscilloscope tube arrangement permitting the evaluation of differences of potentials which persist for only short periods of time.

The pulse generators utilize standard multi-vibrator circuits which give appropriate delays and wave shapes. The sweeping pulse generator which is used to supply the sweeping current I_B has a pulse repetition rate of 38/sec, and a constant voltage pulse duration of 200 μsec. The emitter pulse generator, which is used to supply the emitter current I_ϵ to the emitter point, has the same pulse repetition rate but is delayed 40 μsec behind the sweeping pulse and has a constant voltage duration of only 120 μsec. Both generators have a rise time of the order of 0.25 μsec.

The resulting sequence of events is as follows:

(1) The sweeping pulse generator initiates a constant voltage across the ends of the sample giving rise to nearly constant sweeping current, I_B.

(2) After a delay of 40 μsec the emitter pulse generator produces a constant voltage giving rise to a nearly constant emitter current, I_ϵ.

(3) The emitter pulse generator is turned off, and I_ϵ is reduced to a value very close to zero.

(4) After a delay of an additional 40 μsec the sweeping pulse generator is turned off, and the sweeping current is also reduced to a value close to zero.

The shape of the approximate resultant voltage gradient in the crystal is shown schematically on the cathode-ray tube potentiometer trace (upper right). The vertical deflecting plates of this tube are directly connected to two probe points through low capacitance leads. A variable potential source obtained with a battery and potentiometer is inserted in one of these leads. The value of this inserted potential was read directly on a voltmeter. The horizontal deflecting plates of this tube are connected to a linear time sweep which is synchronized to the sweeping pulse generator.

The procedure used in the measurement of the potential difference in the crystal between the emitter and collector points was as follows. With the voltmeter reading zero volts, the probe point P_1 was removed from the crystal and connected to P_2, which was placed opposite to the collector point as shown in the figure. This point was then "formed" [22] to lower its impedance. Under these conditions a nearly straight line trace down the center of the tube was obtained as indicated by the dotted line shown in Fig. 6. This zero potential line was traced carefully on the tube. The point P_1 was then placed opposite to the emitter point and also "formed." The measurement of the potential between P_1 and P_2 for any part of the characteristic was then found by simply bringing that part of the voltage characteristic to the zero potential line by adjusting the potentiometer. At the required instant of time, therefore, the deflecting plates of the cathode-ray tube are at the same voltage and the potential of P_1 differs from P_2 by an amount equal to that of the voltmeter reading.

The cathode-ray tube used was a Dumont 5X low capacitance and high sensitivity tube. Capacitance of both the leads and the inserted potential source were held to a minimum so that the time constant of the circuit was of the order of 0.5 μsec. This circuit is therefore capable of measuring the true potential difference in the germanium crystal at times of the order of a few microseconds after voltage changes in it occur.

The circuit used to measure the relative hole concentration at the collector point C as well as the current through the bridge is shown in the lower right of Fig. 6. It consists simply of a wide band amplifier and oscilloscope as before. When the amplifier was connected across R_1, as shown, the hole arrival and departure wave was displayed on the oscilloscope as indicated schematically. The four important parts of this characteristic are shown. The initial rise of this characteristic is due simply to the voltage produced between the collector point and ground by the sweeping current I_B introduced by the sweeping pulse generator. The emitter pulse starts at **1** and produces a further rise since additional current is introduced. At **2** the hole wave arrives, the wave front being now quite sharp due to the comparatively high voltage between the emitter and collector points. The emitter current is cut off at **3** giving a sharp drop in the characteristic. At **4** the characteristic due to hole wave departure, also quite sharp, is obtained. A short time later the sweeping pulse is removed and the characteristic returns to its initial voltage.

The time represented by the distance **1** to **2** is the transit time of the injected carriers with currents I_ϵ and I_B flowing and the time represented by the distance **3** to **4** is the transit time with I_B only.

The currents I_ϵ and I_B were measured by connecting the amplifier across R_2, instead of R_1, so that the voltage across this resistance as a function of time could be determined. The temperature of the sample during measurement was then computed as described in Sec. VIII.

XI. TECHNIQUES AND ERRORS

It is possible to measure the mobility to a high order of accuracy with this circuit, since the ambiguity in the transit time of the carriers is reduced to a negligible value. In a typical example the time required for the fastest carriers to arrive was 20 μsec, while the diffusion spread from 0.1 to 0.9 maximum was only 1.5 μsec. The error in the measurement of the time of arrival of the half-maximum in this case was less than 0.1 μsec as estimated using one microsecond marker intervals previously calibrated with standard frequencies. Con-

[22] J. Bardeen and W. H. Brattain, Phys. Rev. **75**, 1208 (1949); W. G. Pfann and J. H. Scaff, Phys. Rev. **76**, 452 (1949); and J. Bardeen and W. G. Pfann, Phys. Rev. **77**, 401 (1950).

sequently, the error in measuring the transit time was less than 0.5 percent.

The transit distance from emitter to collector was usually of the order of 1 cm. This distance was measured with a microscope equipped with an optical micrometer calibrated with standard scales. Measurements showed that readings could be repeated to well within 2×10^{-3} cm giving a maximum error of 0.2 percent in the measurement of L.

The voltage between the probe points could be repeated with differences of less than 0.1 volt. Since the absolute values of these voltages were always in the neighborhood of 20 volts, and were read on a calibrated voltmeter, errors due to the measurement of the potential difference were less than 0.5 percent.

Some ambiguity exists, however, in the electric field to be associated with the measured transit time. This is because, owing to conductivity modulation of the germanium by the injected carriers, the electric field is constantly changing during hole wave arrival and departure. The state of affairs is indicated by the characteristic obtained on the oscilloscope tube connected to the probe points P_1 and P_2. Such a characteristic typical of those obtained using large emitter currents is shown in the drawing of Fig. 7. The initial rise at A is produced by the start of the sweeping current I_B. After this initial rise the characteristic remains constant until an additional rise is produced by the start of emitter current I_ϵ at B. At this time carriers are injected into the germanium crystal with a resultant progressive decrease in the resistance of the crystal between the probe points P_1 and P_2. The currents in the crystal remain substantially constant, owing to the high impedance of the pulse generators, so that the voltage falls. This decrease in resistance and consequent decrease in the voltage between the probe points continues as the carrier wave advances until at F the wave front passes P_2. A semi-steady-state voltage and electric field between the emitter and collector then exists until the emitter current is removed at G. In consequence of this, the voltage drops abruptly. I_B is now the only current flowing in the crystal. The value of the voltage produced initially by this current is, however, less than that obtained at the start of the sweeping current, since the region between the probe points is now filled with injected carriers, and recovery is only complete when the last of the injected carriers in the departure wave flows past P_2 at H.

It is possible in principle to solve the equations for the leading and trailing edges of the carrier wave exactly, taking into account diffusion and conductivity modulation. This problem has not been dealt with completely theoretically at the present time although certain phases of it have been examined in considerable detail by Herring.[23] However, it is possible to eliminate the effects of conductivity modulation by suitable experimental conventions.

[23] C. Herring, Bell System Tech. J. 28, 401 (1949).

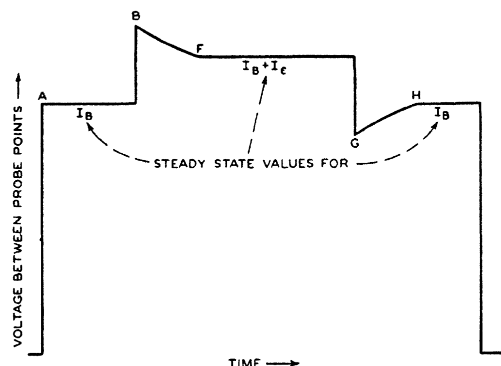

Fig. 7. Characteristic of voltage between emitter and collector points as a function of time, showing effects of conductivity modulation. (Emitter current large.)

The convention used has been to associate the transit time with the final or semi-steady-state value of the voltage obtained with the appropriate currents flowing in the crystal. For the transit time due to carrier wave arrival this voltage is F of Fig. 7. This value is obviously too low and the resultant electric field calculated by V/L will also be too low, leading to a mobility which is too high. On the other hand, by using this convention, the voltage associated with the transit time obtained from the carrier departure wave is H, a voltage which is obviously too high leading to a mobility which is too low. The true mobility, therefore, lies always between the value obtained using the transit time due to carrier wave arrival and that obtained with carrier wave departure. Since these effects, owing to carrier injection modulation of the crystal resistance, decrease as the injected currents decrease, the difference between the mobility calculated using carrier wave arrival and that obtained using carrier wave departure approaches zero as the injected current approaches zero, with assurance that the desired value always lies between the two.

A plot of the values of mobility so obtained is shown in Fig. 8. Here the apparent mobility for injected holes in n-type germanium is plotted as a function of the emitter current. While for large emitter currents the difference in the values obtained using the transit time and conventional voltage associated with hole wave

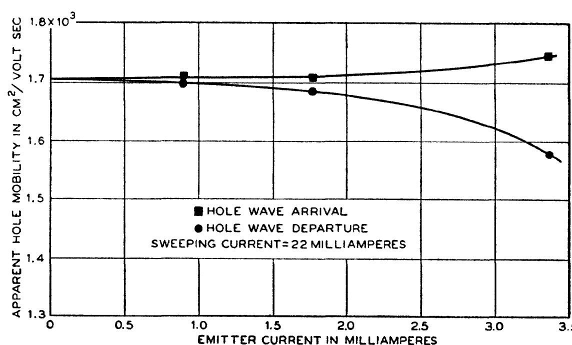

Fig. 8. Calculated mobility as a function of emitter current.

arrival and hole wave departure is large, the values approach each other as the emitter current is reduced. A value of mobility from which the conductivity effects are eliminated is obtained by extrapolating the two curves to zero emitter current. It is also apparent that for small emitter currents this extrapolated value of mobility is very close to the average value obtained using hole wave arrival and departure transit times.

Another source of error arises from the fact that in the immediate neighborhood of the emitter and collector points the electric fields are not uniform and differ from the average field used in computing the mobility. Also, the carriers are injected at a point and collected at a point, so that, in the vicinity of the emitter and collector, the paths of the carriers are curved. As a result of these local disturbances there will be end effects which should become progressively less important as the distance between the emitter and collector points is increased. The extent of these effects is shown in Fig. 9, in which we have plotted the average values of mobility obtained using small emitter currents, as a function of the spacing between the emitter and the collector points. As is seen, the end effects appear to be entirely negligible for spacings greater than a centimeter.

The measurements of mobility on a single sample were reproducible to within 0.6 percent, which is in agreement with the estimates of the errors involved in the measurement of transit time voltage, and spacing between the emitter and collector. However the values of the mobility obtained using different crystals of germanium had a spread more than 10 times as great. This indicates that by far the greatest error is introduced by the assumption that the electric field is everywhere uniform and equal to V/L. As is seen from Fig. 5 this is only approximately true. Since any deviation from linearity in these characteristics results in a calculated mobility which is too low by an amount which depends on the shape of the particular characteristic, an individual correction factor must be applied to each sample. This correction factor is found by dividing these characteristics in the section between the position of the collector and that of the emitter into a number of small segments l_i for each of which the field is substantially uniform and the voltage is V_i. Then the transit time for each segment is $t_i = l_i^2/V_i\mu$, so that

$$\mu\Delta t_i = \Sigma l_i^2/V_i.$$

Since $\Sigma t_i = t$, the total transit time, this value of μ can be expressed in terms of the uncorrected mobility, $\mu' = l^2/Vt$, as follows:

$$\mu = (\Sigma l_i^2/V_i)/t = [(\Sigma l_i^2/V_i)V/l^2]\mu'.$$

The correction factor, in square brackets, can be determined from voltage *versus* distance plots.

The application of this correction factor reduced the variation in the values of mobility obtained using different samples. A residual spread, however, of nearly six percent persisted. It is felt that this is due to deviations from a uniform field on a smaller scale, which are extremely difficult to measure experimentally.

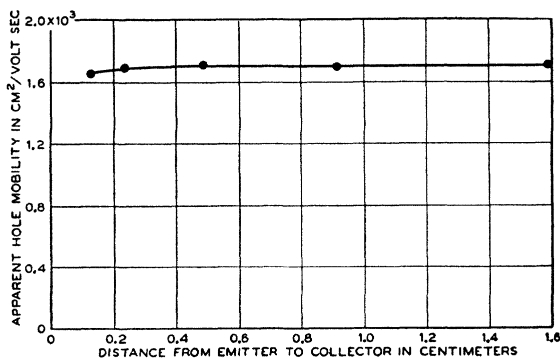

FIG. 9. Calculated mobility as a function of separation of emitter and collector points.

XII. RESULTS

The average value of the mobility of holes in germanium obtained using four different samples was 1700 cm^2/volt-sec. The average mobility of electrons using three samples of p-type germanium was 3600 cm^2/volt-sec. These values were obtained using samples of crystals grown in different ways and having values of specific resistance ranging from 1.5 to 6 ohm-cm. Too few samples have so far been examined to be certain of the accuracy of the results. However, the maximum spread of these values (obtained with n-type samples) was less than six percent. It is felt, therefore, that the average values have an error of less than five percent.

XIII. REVIEW OF METHODS OF MEASURING MOBILITY

As has been pointed out previously,[24] the values for the mobility determined in various ways need not necessarily agree. We can at present distinguish between four experimental methods of measuring mobility and three theoretical definitions, the latter being described as follows.

μ_m = *microscopic mobility*. This is the mobility of a charge carrier in the conduction band or valence-bond band and is the conventional concept.

μ_d = *drift mobility*. This is the drift velocity that a carrier would have in unit field allowing for trapping. For example, if an injected hole spent only half its time in the valence-bond band and the other half trapped on acceptors, μ_d would be $\frac{1}{2}\mu_m$.

μ_H = *Hall mobility* = $R\sigma$. For spherical energy surfaces in the Brillouin zone and degenerate statistics, as in a metal, theory predicts that $\mu_H = \mu_m$. For spherical energy surfaces, a mean free path independent of direction and energy, and a maxwellian distribution of velocities, $\mu_H = (3\pi/8)\mu_m$. If the energy surfaces are concave, theory predicts that $\mu_H = A(3\pi/8)\mu_m$, where A

[24] Pearson, Haynes, and Shockley, Phys. Rev. 78, 295 (1950).

may be less than unity or even negative. For negative values of A, we would have *anomalous electrons* and *anomalous holes*. An injected anomalous hole would move towards the negative terminal, yet a p-type sample conducting by such holes would give the Hall effect ordinarily attributed to electrons. Evidence that holes and electrons in germanium are not anomalous is furnished by the sign of the Suhl effects[25] and the consistency of the Hall effect with (1) motion of injected carriers, (2) sign of rectification, and (3) thermoelectric power and (4) valence of added impurities.

Experimentally, the Hall effect and the drift velocity should measure the quantities described by the preceding theoretical concepts for μ_H and μ_d. In addition, a *conductivity mobility* $\mu\sigma$ can be measured by adding known amounts of impurity which thus adds known numbers of carriers;[26] from these known numbers and the measured conductivity a mobility can also be determined. In germanium at room temperature, the fraction of the carriers trapped on donors and acceptors is negligible, and μ_d, μ_m, and μ_σ should all be equal. The sum of the drift mobility for electrons μ_{dn} and μ_{dp} for holes may also be determined from photo-conductivity experiments assuming 100 percent quantum efficiency. In this determination it is assumed that each photon absorbed creates one hole-electron pair which persists on the average for the lifetime of a hole which may be independently measured.[27] Since the quantum efficiency can be less than 100 percent, this measurement gives a lower limit for

$$\mu_{dn}+\mu_{dp}.$$

The values of mobility obtained in these ways are shown in the Table I. All of the values except that of μ_σ were obtained on the same samples. The Hall effect data, however, correspond to the normal carriers rather than the injected carriers. It is seen that the data in the last three columns, which should correspond to μ_d, are consistent within the experimental accuracy. There appears to be a real discrepancy, however, between the Hall effect data for electrons and the other data. It is proposed that this discrepancy is due to curvatures of the energy surface in the Brillouin zone as discussed above.

Further evidence for nonspherical surfaces is furnished by magnetoresistance effects in germanium.[28,29]

At lower temperatures, appreciable trapping of injected carriers may take place and deviations of μ_d from μ_m should occur. Observations of such effects may furnish a useful tool for investigation trap densities in germanium.

TABLE I. Mobilities in cm²/volt-sec in germanium at 300°K.

	$(8/3\pi)\mu_H$	μ_d	μ_σ	Photo-conductivity
Electrons	2600±300	3600±180	3350±400	——
Holes	1700+500−100	1700±90	——	——
Sum	4300+800−400	5300±270	——	≧5300±500

We are indebted to F. S. Goucher, W. L. Bond, R. D. Heidenreich, H. R. Moore, G. L. Pearson, G. K. Teal, and W. W. Van Roosbroeck for advice and help with the experiments and to J. Bardeen and F. Seitz for stimulating discussions of the theory and to W. C. Westphal who prepared the specimens and took many of the data.

APPENDIX A1. RECOMBINATION FORMULAS

We shall treat the case of holes injected into n-type germanium below; the formulas for electrons injected into p-type are obtained by a suitable change of subscripts.

A hole injected in a filament may recombine either in the interior or on the surface. These processes lead to a set of eigenfunctions for hole density p, as a function of y and z, the transverse dimensions. These functions satisfy the continuity equation in which τ_p is the body lifetime for holes and D_p is the diffusion constant;

$$\partial p/\partial t=-(p/\tau_p)+D_p[(\partial^2 p/\partial y^2)+(\partial^2 p/\partial z^2)].$$

The eigenfunctions must also satisfy the boundary conditions

$$sp=\mp D_p(\partial p/\partial y) \text{ at } y=\pm B,$$
$$sp=\mp D_p(\partial p/\partial z) \text{ at } z=\pm C,$$

where s is surface recombination velocity and B and C are half-widths of the filament.[30] The solution for p which decays most slowly is

$$p=\exp(-t/\tau)\cos(by)\cos(cx),$$

where in order to satisfy the boundary conditions,

$$bB\tan(bB)=sB/D_b,\quad cC\tan(cC)=sC/D_p.$$

Letting b_0 and c_0 represent the smallest solutions of these equations, we find that

$$1/\tau=(1/\tau_p)+D_p(b_0^2+c_0^2).$$

For the case in which sB/D_p and sC/D_p are $\gg 1$, $bB=\pi/2$ and

$$1/\tau=(1/\tau_p)+D_p(\pi/2)^2(B^{-2}+C^{-2}),$$

this being the formula found valid for sandblasted surfaces for which s is 10^4 cm/sec so that, for example,

$$sB/D_p>10^4\times(2.5\times10^{-2})/44>6$$

for a filament 0.5 mm square and $(1/\tau)-(1/\tau_p)$ is about $(3\ \mu\text{sec})^{-1}$. For a long lifetime surface, so that $sB/D_p\ll 1$, the value of b_0B is $(sB/D_p)^{\frac{1}{2}}$ and

$$(1/\tau)-(1/\tau_p)=(s/B)+(s/C),$$

which is $(60\ \mu\text{sec})^{-1}$ for $s=200$ cm/sec. For a filament of these dimensions, body lifetimes of 100 μsec or more contribute little to the recombination process.

The other eigenfunctions decay much more quickly and die out so rapidly that they need not be considered in analyzing lifetimes in filaments by the methods of this paper.

[25] H. Suhl and W. Shockley, Phys. Rev. 75, 1617 (1949).

[26] Pearson, Struthers, and Theuerer, Phys. Rev. 75, 344 (1949) and 77, 809 (1950).

[27] The data used are those of F. S. Goucher, Phys. Rev. 78, 646 (1950), who assumed drift mobilities of 1700 and 3600 and found 100 percent quantum efficiency. In this analysis we assume efficiencies ≤100 percent and deduce the sum of the mobilities.

[28] G. L. Pearson, Phys. Rev. 78, 646 (1950).

[29] H. Suhl, Phys. Rev. 78, 646 (1950).

[30] Additional details are given in W. Shockley, Bell System Tech. J. 28, 435 (1949), Appendix V.