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The Effect of Fast Neutron Bombardment on the Electrical Properties of Germanium

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Lattice disorder in bulk Ge produced by collisions of fast neutrons with lattice atoms introduces a net excess of electron traps or acceptor states, which appear to have an energy distribution in the forbidden band. Bombardment of N-type Ge causes the conductivity to decrease, initially at a uniform rate, to a minimum value and then to increase. Examination of the data shows that initially about 3.2 conduction electrons are removed per incident fast neutron. The minimum value of the conductivity is higher than the value calculated assuming complete homogeneity and thermal equilibrium. Hall effect measurements prove that after the minimum is passed the material has been converted to P-type by fast neutron bombardment. The conductivity of P-type Ge increases with bombardment. The rate of increase decreases monotonically indicating an approach to saturation. The initial rate of carrier introduction in P-type Ge appears to be temperature dependent, being greater at higher temperatures (∼0.8 carrier per incident neutron at 30°C), and smaller than the rate of carrier removal for N-type Ge which is apparently temperature independent in the temperature range investigated (−79°C to 45°C). The effect of lattice disordering on the electrical properties of Ge may be removed by careful vacuum annealing at 450°C while a portion of this effect readily anneals at room temperature.

I. INTRODUCTION

THE effect of high energy nucleon bombardment on the electrical properties of Ge and Si was first investigated by Lark-Horovitz and co-workers[1] using 10-Mev deuterons and 20-Mev alpha-particles from the Purdue cyclotron. They also investigated the effects of neutrons from the Be−D reaction and alpha-particles from a polonium source. The Purdue group in collaboration with Johnson and Siegel[2] investigated the effect of fast neutrons by irradiating bulk Ge and Ge-diodes in the Oak Ridge nuclear reactor. This work has been extended by the authors, and the present paper is intended to summarize the results of investigations to date on the effect of fast neutrons on the ohmic properties of bulk Ge. More recently Brattain and Pearson[3] have also studied the effect of alpha-particles from a polonium source.

When P-type Ge is bombarded with high energy nucleons the conductivity increases monotonically with bombardment. The conductivity of N-type Ge, on the other hand, first decreases, passes through a minimum and then increases with further bombardment. Hall coefficient measurements prove that the bombarded N-type material has been converted to P-type. The only difference between the effects of charged particles and neutrons is in the distribution of the effect in a massive target. The bombardment effects induced by charged particles are limited to their range in the material (about 0.2 mm for 10-Mev deuterons,[1] and only, 0.019 mm for 5.3-Mev polonium alpha-particles).[3] In order to achieve complete penetration with charged particles, samples thinner than the effective range must be used, and even then, because of range-energy relationships, the effect is not uniform throughout the thickness of the target. On the other hand, because of their relatively large mean free path, fast neutrons produce effects which are uniformly distributed throughout a bulk target of relatively large dimensions. The advantages of the use of fast neutrons in a study of the effect of nucleon bombardment on the electrical properties of Ge are therefore obvious. It should be mentioned, however, that there are disadvantages associated with irradiations in a nuclear reactor. Here one is dealing with a wide neutron energy spectrum, i.e., from thermal energies up to the Mev range, and high intensity β- and γ-radiation as well. Thus the effect of nuclear reactions induced by thermal neutrons must be considered as must also the effect of β- and γ-radiations.

The bombardment produced change in the properties of Ge is much too large to be explained on the basis of impurities introduced by nuclear reactions. The number of impurity atoms produced by transmutations with charged particles is extremely small although this does play an important part in the case of pile bombardment.[4] Lattice disordering and lattice displacements are caused by elastic collisions of the bombarding particles with lattice atoms and by secondary collisions of struck atoms or "knock-ons" with those of the lattice. This disordering process produces a net excess concentration of electron traps or acceptors. Hole traps may also be produced but in the case of Ge these are not nearly so efficient as the electron traps, else either P- or N-type Ge would tend toward an intrinsic semiconductor with bombardment.[4a] These traps or acceptors neutralize

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[1] Lark-Horovitz, Bleuler, Davis, and Tendam, Phys. Rev. **73**, 1256 (1948). See also Purdue Progress Reports to Signal Corps. Nov. 1947 to present (unpublished).

[2] Davis, Johnson, Lark-Horovitz, and Siegel, Phys. Rev. **74**, 1255 (1948): W. E. Johnson and K. Lark-Horovitz, Phys. Rev. **76**, 442 (1949). See also Davis, Johnson, Lark-Horovitz, and Siegel, AECD Report 2054, June 1948 (unpublished).

[3] N. H. Brattain and G. L. Pearson, Phys. Rev. **80**, 846 (1950).

[4] Cleland, Lark-Horovitz, and Pigg, Phys. Rev. **78**, 814 (1950).

[4a] In the case of bombardment of Si the effect of both electron and hole traps is equally important in contrast with the case of Ge. The conductivity of both N-type and P-type silicon decreases with bombardment and each appears to approach a limiting

donors in N-type Ge thus decreasing the current carrier concentration, and in the case of P-type Ge, if they are sufficiently deep lying, they may augment the concentration of positive carriers in the filled band. All of the electrical effects of lattice disordering may be removed by annealing the crystals at about 450°C.

The behavior accompanying bombardment is analogous in many ways to that observed with appropriate heat treatment. If N-type Ge is quenched from temperatures near the melting point ($\sim 800°C$), P-type Ge is produced.[5] This conversion of type is presumably due to "frozen-in" Frenkel type lattice defects which act as acceptors. By annealing at 450°C and cooling slowly the original N-type character is restored.

II. THEORETICAL DISCUSSION

When high energy particles are stopped by crystalline solids the primary particle loses its energy by two types of interactions with the lattice: (1) elastic energy losses by direct momentum transfer to atomic cores, thereby producing displaced atoms, and (2) inelastic energy losses in which electrons are excited by charge interaction. The latter type, of course, applies only to the interaction of charged particles. The struck atom (secondary particle or "knock-on") in turn also loses its energy in a similar manner until all of the energy imparted to the lattice by the primary particle is either dissipated or stored. The inelastic energy losses appear exclusively as heat in conductors but in the case of insulators some of this energy may be stored by trapped electrons (F-centers, etc.). Most of the elastic energy losses, however, are stored by the lattice in the form of displaced atoms. Seitz[6] has treated this problem theoretically and has calculated the number of displaced atoms to be expected from the interaction of various particles of specified energy with a number of materials.

In order to understand the behavior of the conductivity of Ge during fast particle bombardment one must know the effect of these displaced atoms on both the concentration of current carriers and on their mobility. We shall assume that the lattice disorder may be resolved more or less distinctly into two classes: (1) lattice vacancies and interstitial atoms in regions of small amounts of disorder and (2) complexes or clusters of disorder of the type considered by Vand[7] in regions of concentrated damage. In view of the similarity in the behavior of Ge and Si on quenching from high temperature[5] to that observed on particle bombardment, one would expect the first class of disorder to produce hole and electron traps or donors and acceptors. Such centers of disorder will have associated with them localized charges which will scatter carriers, thereby decreasing the mobility. The role of the second class is not so clear. These may also be able to produce carriers. Also, certainly, damage centers of this type will scatter conduction electrons and holes.

The introduction of vacant states[7a] deep in the forbidden band of an N-type semiconductor will cause the Fermi level ζ (electronic chemical potential) to be lowered toward the filled band. If these traps are distributed in energy, as experiment seems to indicate, initially they will all remove electrons from the conduction band and, of course, the original donor level. After nearly all of the electrons are removed, further introduction will cause a redistribution of the trapped electrons to vacant states of lower energy, until essentially all of the electrons occupy the lower-lying states. Only after this redistribution has taken place can the low-lying vacant states begin to act as acceptors, causing the material to become P-type. Consequently, a constant rate of introduction of a distribution of low-lying vacant states may be visualized as causing (1) a rapid lowering of ζ toward the center of the forbidden band corresponding to the initial removal of electrons from the conduction band, (2) a gradual lowering of ζ across the center of the forbidden band corresponding to the redistribution of electrons to traps of lower energy and transition to P-type, and (3) a rapid, though not so precipitous as in (1), depression of ζ toward some limiting position near the top of the filled band. Actual calculations of this type have been carried out for the case in which acceptors of a single energy are added.[8]

Addition of acceptors to P-type Ge has the same effect as phase (3) above in the case of N-type Ge. High resistivity P-type Ge is readily affected, since in this situation ζ is well above the top of the filled band. In low resistivity P-type Ge, however, the Fermi level may already lie below the limiting position mentioned above. If such is the case, the only effect produced by bombardment on the conductivity will be through a decrease in the mobility. It should be emphasized that the increase in hole concentration in P-type Ge is less than the decrease in electron concentration for a given period of irradiation. This is expected since only that portion of acceptors which are thermally ionized are effective in increasing the hole concentration.

With regard to mobility any departure from the periodic potential of the lattice will tend to shorten the mean free path of a carrier because of additional scattering. The effect of localized charge in the lattice has

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value. A report concerning the behavior of reactor irradiated silicon will be forthcoming in the near future.

[5] K. Lark-Horovitz, NDRC Report 14–585, covering the period from March, 1942, to November, 1945, p. 24 (unpublished). For more recent developments see W. E. Taylor, doctoral thesis, published as a special report to Signal Corps, Purdue University, June, 1950, and J. Metal Tech. (to be published).

[6] F. Seitz, Disc. Faraday Soc. No. **5**, 271 (1949).

[7] V. Vand, Proc. Phys. Soc. (London) **55**, 222 (1943).

[7a] The probability of the existence of hole traps or donors has been noted previously. These are not considered in the above discussion, since in Ge they presumably lie near the top of the filled band and, therefore, are not effective in releasing electrons or trapping holes. However, if these hole traps lie above acceptors, their net effect will be to increase the ionization energy of available holes. For an account of the effect of hole traps on the energy distribution in semiconductors see reference 8.

[8] K. Lark-Horovitz, Appendix II, (Lehman) International Conference on Semiconductors, Reading, 1950; See also G. Lehman, Phys. Rev. **81**, 321 (1951).

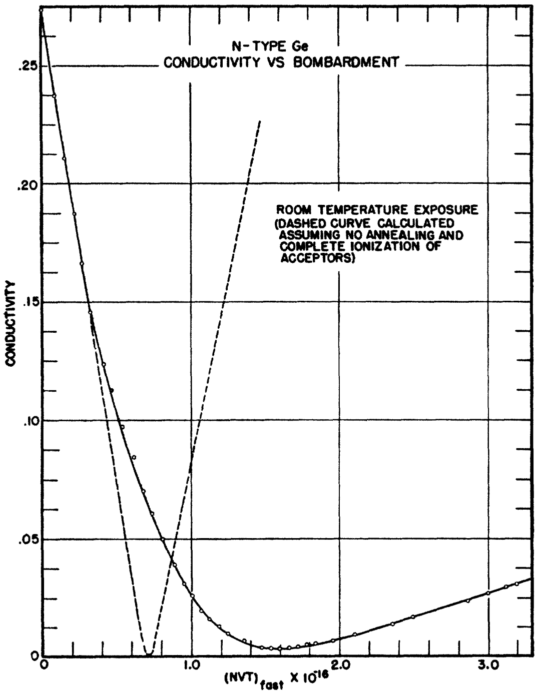

FIG. 1. Conductivity of N-type Ge *vs* integrated fast neutron flux bombarded at room temperature. The dashed line indicates the expected behavior in the absence of annealing, variation in mobility, and complete ionization of introduced acceptors.

been extensively investigated both theoretically[9] and experimentally.[10] Also a treatment of neutral scattering has been reported[11] more recently. Except for high concentrations of scattering centers, impurity and defect scattering is usually subordinate to scattering from lattice vibrations at moderate temperatures, the former being more important at low temperatures. Consequently, no effect on mobility is expected until the concentration of bombardment introduced defects becomes comparable to or greater than the initial impurity concentration at the exposure temperatures used in these experiments.

The minimum conductivity observed during conversion of N-type Ge to P-type by fast particle bombardment may be examined from the simple model of semiconductors. The general equation for the conductivity of a semiconductor capable of exhibiting intrinsic behavior is

$$\sigma = e\mu_e n_e + e\mu_h n_h, \tag{1}$$

where e is the electronic charge, μ is the mobility, n the carrier concentration and the subscripts refer to the type of carrier. For carrier concentrations considered here classical statistics are valid. Thus for *thermal equilibrium* the carriers obey the relation

$$n_e n_h = \kappa(T) = 4h^{-6}(2\pi \bar{m}^* kT)^3 \exp(-\Delta\epsilon_g/kT), \tag{2}$$

where $\bar{m}^*$ is the geometric mean of the effective masses of the carriers and $\Delta\epsilon_g$ is the energy gap between the highest filled band and the conduction band. The best value of $\kappa(T)$ obtained from measured properties of Ge in the intrinsic range is given by[12]

$$\kappa(T) = 5.15 \times 10^{31} T^3 e^{-8630/T}.$$

By using Eq. (2) to write Eq. (1) in terms of only one carrier concentration and minimizing the conductivity with respect to this carrier one finds that the carrier concentrations at the minimum are

$$\begin{aligned} n_e &= (\kappa/c)^{\frac{1}{2}}, \\ n_h &= (\kappa c)^{\frac{1}{2}}, \end{aligned} \tag{3}$$

where c is the ratio of electron mobility to hole mobility. Substituting these values into Eq. (1) gives for the minimum conductivity

$$\sigma_{\min} = 2e\mu_e(\kappa/c)^{\frac{1}{2}}. \tag{4}$$

It is evident from Eq. (3) that the conductivity minimum lies at the intrinsic concentration ($n_e = n_h$) only if $c = 1$. For Ge, $c \sim 1.5$. Therefore, the material has already become P-type before the minimum is reached. The general expression for the Hall coefficient is given by

$$R = (3\pi/8e)(n_h\mu_h^2 - n_e\mu_e^2)/(n_h\mu_h + n_e\mu_e)^2. \tag{5}$$

Substitution in Eq. (5) of the carrier concentrations from Eq. (3) gives

$$R_{\min} = (3\pi/32e)(1-c)/(\kappa c)^{\frac{1}{2}}. \tag{6}$$

Hence it is evident that the Hall coefficient is negative even though at the conductivity minimum the material is P-type. Similar examination of the thermoelectric power[13] shows that the Seebeck coefficient is given by

$$\theta_{\min} = -(k/5e)\ln c \tag{7}$$

which is also negative even though the material is P-type.

III. THE EFFECT OF FAST NEUTRONS ON N-TYPE Ge

A typical room temperature conductivity *vs* bombardment curve for N-type Ge is shown in Fig. 1. The measurements were taken in-pile during bombardment. Initially the slope is quite linear, the conductivity decreasing at a constant rate with bombardment. As the minimum is approached the slope becomes less and less negative producing a wide, flat minimum. After the minimum the conductivity increases much more slowly than the initial rate of decrease. By assuming that annealing of lattice disorder and changes in the electron mobility are negligible during the initial part of the

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[9] E. Conwell and V. F. Weisskopf, Phys. Rev. **69**, 258 (1946); **77**, 388 (1950).

[10] V. A. Johnson and K. Lark-Horovitz, Phys. Rev. **69**, 258 (1946).

[11] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949); C. Erginsoy, Phys. Rev. **78**, 1013 (1950).

[12] V. A. Johnson and H. Y. Fan, Phys. Rev. **79**, 899 (1950).

[13] K. Lark-Horovitz, Appendix I, (Johnson and Lark-Horovitz) International Conference on semiconductors, Reading, 1950.

bombardment, the average net number of electron traps produced per incident neutron K for the fast neutron spectrum which exists in the Oak Ridge reactor may be calculated from the initial linear portion of the curve. The initial mobility of the samples is known from Hall coefficient and resistivity measurements and K is readily calculated by means of the relation

$$K = dn_e/d(nvt)_{\text{fast}} = (1/e\mu_e)d\sigma/d(nvt)_{\text{fast}}. \qquad (8)$$

The results of these calculations have been reported previously for a number of N-type samples.[14] The average value of K, revised slightly in the light of additional data, is 3.2. Assuming a scattering cross section of 1×10^{-24} cm^2 one finds the number of traps produced per scattered neutron to be 81. This value is in reasonable agreement with the calculations of G. E. Evans[15] from particle interaction theory who finds that 135 displaced atoms should be produced per scattered neutron using the energy distribution in the Oak Ridge Reactor. This agreement, however, depends on the choice of the scattering cross section. These measurements seem to indicate that K is independent of temperature and initial impurity concentration.

The dashed curve in Fig. 1 was calculated on the assumptions that (1) all acceptors introduced by bombardment lie on the top of the filled band thus being equally effective in removing electrons or producing holes, (2) no annealing takes place, and (3) the mobility of the carriers is unaffected by bombardment. It is interesting to note that this has the same form as a simple conductiometric titration curve. The minimum value was calculated from Eq. (2). The early observed departure from linearity is readily explained on the basis of the aforementioned redistribution of trapped electrons seeking lower energy traps as these become available. Also any annealing of lattice disorder at room temperature, which is known to be appreciable from various indications to be discussed below, will cause the rate of electron removal to decrease with bombardment.

The minimum value of the conductivity of a homogeneous semiconductor in thermal equilibrium may be calculated directly from Eq. (4) by using the appropriate values of μ and κ. In a previous publication[16] it was pointed out that the observed value of $\sigma_{\min}$ was higher by a factor of 2 to 3 than the calculated value. This discrepancy was attributed to slight inhomogeneities in the impurity distribution throughout the sample. It should be stated, however, that the same effect could be caused by the photoelectric production of carriers by high intensity β- and γ-radiation. Experiments are underway to determine the influence of high intensity ionizing radiation on the electrical conductivity of Ge. As yet we have been able to determine no observable effect due to 1.3-Mev radiation even in high resistivity Ge (~5 ohm cm) though samples containing a rectifying potential barrier show large conductivity increases at liquid nitrogen temperature.

After the minimum is passed the conductivity increases at a rate much lower than the initial rate of decrease. The reduction in rate is due to two causes: (1) annealing of lattice defects and (2) only those acceptors which are ionized are effective in increasing the hole concentration. In this connection it is instructive to examine the ratio of slopes of the two legs of the conductivity *vs* bombardment curve. In Table I the ratios of the initial slopes to those after conversion to P-type for a number of N-type samples bombarded at room temperature are listed, together with the initial electron concentration $n_e^{\,o}$ which, because of exhaustion,[17] is essentially equal to the original donor concentration. The slope ratio for $n_e^{\,o}<10^{13}$ (P-type Ge) was obtained from the mean value of the original N-type slope and that of P-type material at room temperature.[18] From these data it is evident that the ratio of slopes increases with increasing initial electron concentration. Since it has been shown previously[14] that the initial rate of change of conductivity for N-type Ge under bombardment at temperatures in the exhaustion range is constant, the variation of the ratio is due to the dependence of the slope after conversion to P-type on the initial electron concentration of the N-type material.

The dependence of the conductivity *vs* bombardment slope after conversion may be caused by either the variation of disorder-annealing rate with the amount of disorder at the minimum, of which $n_e^{\,o}$ is an index, or the variation of the number of ionized acceptors introduced at the minimum which are occupied by electrons from the conduction band and donor levels. This latter effect is analogous to the common ion effect of

TABLE I. The ratios of the initial slope to that after the conductivity minimum obtained from the room temperature conductivity *vs* bombardment curves of N-type Ge. Also listed is the original electron concentration $n_e^{\,o}$. The P-type value above is the ratio of the slope of an N-type sample which is constant from sample to sample to that of a P-type sample at 30°C.

Sample	Slope ratio	$n_e^{\,o}$
1	7.2	4.2×10^{14}
2	8.0	5.1×10^{14}
3	10.0	1.3×10^{15}
4	12.9	2.5×10^{15}
5	21.0	1.0×10^{16}
6	21.4	2.8×10^{16}
7	24.3	5.5×10^{16}
P-type value	~6.5	$<10^{13}$

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[14] J. H. Crawford, Jr., and K. Lark-Horovitz, Phys. Rev. **78**, 815 (1950).

[15] G. E. Evans, (to be published).

[16] J. H. Crawford, Jr. and K. Lark-Horovitz, Phys. Rev. **79**, 889 (1950).

[17] The exhaustion region is that region in temperature at which essentially all of the impurity atoms are ionized.

[18] Since it has been shown that the initial N-type conductivity slope is constant from sample to sample except for mobility variations [Eq. (8)] the ratio of this value to the room temperature value for a P-type sample should be an index of the slope ratio as defined above for $n_e^{\,o}<10^{13}$.

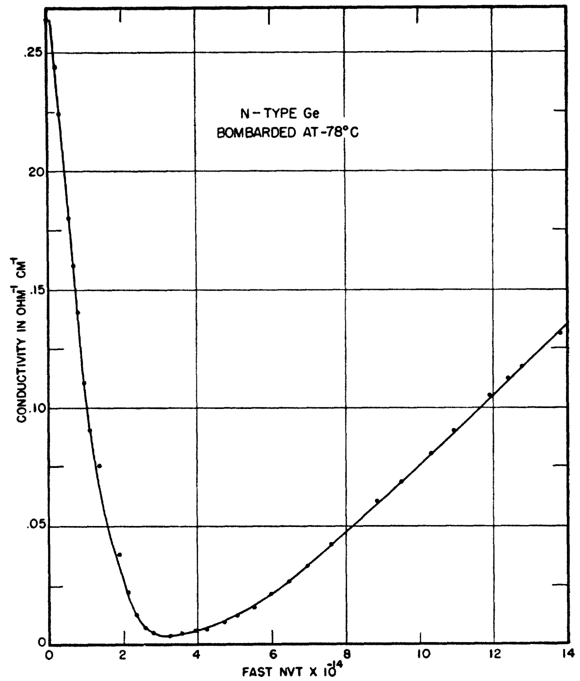

FIG. 2. Conductivity of N-type Ge *vs* integrated fast neutron flux bombarded at dry ice temperature.

solution chemistry. There is not sufficient evidence at the present time to make a clear choice. Both, quite probably, are in some manner responsible for the dependence of the slope ratio on the initial electron concentration of the N-type material. Examination of the data in Table I indicates that apparently $\ln n_e^0$ is approximately proportional to the slope ratio. An elementary examination of the two explanations offered above, however, indicates that in both cases one would expect an approximately linear dependence between the ratio and n_e^0. It is encouraging to note that the ratio approaches the value 6.5 obtained for originally P-type material. A more elaborate treatment on the basis of more accurate data is necessary to explain this behavior quantitatively.

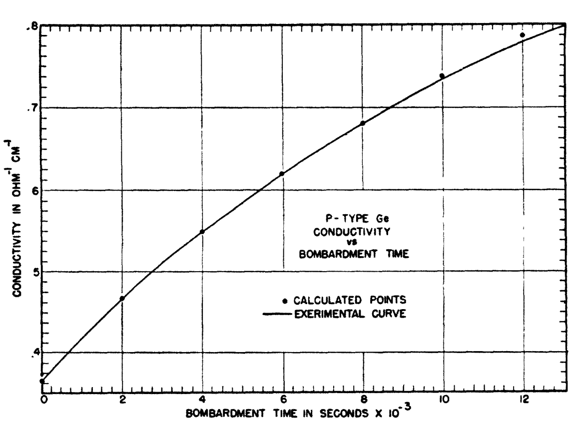

FIG. 3. Conductivity of P-type Ge *vs* integrated fast neutron flux bombarded at room temperature. Dots represent the points calculated from Eq. (6).

In order to minimize annealing during bombardment several N-type Ge samples were exposed at dry-ice temperature and the conductivity measured during bombardment. The conductivity *vs* bombardment curve for one such sample is shown in Fig. 2. The behavior of the conductivity is qualitatively the same as at room temperature. The initial rate of removal of electrons is the same as that measured at higher temperatures within experimental error. The conductivity minimum occurs at a lower value than that observed at room temperature which is expected from the temperature dependence of κ in Eq. (4), though the observed value is higher by two orders of magnitude than the calculated value (3×10^{-3} ohm^{-1} cm^{-1} observed compared to 8×10^{-6} ohm^{-1} cm^{-1} calculated). The ratio of the initial rate of conductivity change to that after conversion is 12.5 and the initial donor concentration, as determined from the room temperature Hall constant, is $\sim4\times10^{14}$. Comparison of these values with those of Table I shows that, for samples of comparable impurity concentration (samples 1 and 2), the rate of increase of carrier concentration is larger for higher temperatures. The temperature dependence of the rate of increase of holes will be considered further in connection with P-type Ge bombardment.

IV. THE EFFECT OF FAST NEUTRONS ON P-TYPE Ge

A typical conductivity *vs* bombardment curve for P-type Ge at room temperature is shown in Fig. 3. The conductivity increases monotonically with bombardment and the initial slope is linear. As in the case of N-type Ge the number of carriers introduced per incident fast neutron may be calculated from the initial slope and the initial mobility under the same assumptions used in the N-type analysis. These calculations have also been previously reported,[16] and are reproduced with additional data in Table II. The value at 30°C is about 0.8 hole per incident fast neutron. Thus only about one out of four traps produced by bombardment is effective in increasing the hole concentration at this temperature. The high temperature rates (0°C to 30°C) appear to be essentially independent of initial carrier concentration but are evidently temperature dependent. It should be noted, however, that dependence on initial carrier concentration could be masked by a larger effect of temperature.

Further examination of the P-type Ge bombardment curve shows that the slope falls off with increasing bombardment indicating that the conductivity tends toward saturation. This may be explained, at least in part, on the basis of annealing of lattice defects and is borne out by the decay of the conductivity increase during pile shut down. In fact, by assuming only one annealing process with a single activation energy, the above curve may be fitted rather well by the familiar first-order build-up equation

$$\sigma=\sigma_0+(A/k')(1-e^{-k't}), \qquad (9)$$

where k' is the rate constant and A is a constant determined by the initial slope. The calculated points for $k'=6.2\times10^{-5}$ sec^{-1} are shown in Fig. 3. This result, however, is not very definitive since the value of k' depends on A. Because of pile power and temperature changes during start-up, the value of A is not sufficiently accurate for a refined determination of the rate constant. Attempts were made to calculate the curve using a simple second-order build-up equation

$$\sigma=\sigma_0+(A'/k'^{\frac{1}{2}})\tanh[(A''k')^{\frac{1}{2}}t], \qquad (10)$$

but no acceptable fit could be obtained. Similar analyses have been carried out by Brattain and Pearson[2] on Ge bombarded with polonium alpha-particles. Both build-up and decay curves were fitted with first-order equations and the rate constant thus obtained was $k=1.5\times10^{-5}$ sec^{-1}. These authors found that about 75 percent of the carriers introduced by bombardment was annealable at room temperature.

There is evidence that the annealing mechanism is much too complicated to be explained on such a simple basis as is discussed above. Preliminary experiments on the rate of annealing of Ge exposed at dry ice temperatures as well as examination of heat treatment data indicate that, quite probably, the annealing of lattice disorder involves multiple rate processes of different activation energies. There is even the possibility that there is a continuous spectrum of activation energies. A program intended to investigate this problem is now under way.

Two P-type samples were bombarded at dry ice temperature in order to decrease the effect of annealing. The conductivity *vs* bombardment curve of the higher resistivity sample is shown in Fig. 4, and the pertinent data for the two samples are summarized in Table II. The initial slopes for these samples indicate quite definitely that they are dependent on the initial carrier concentrations. The slope, in fact, seems to be dependent on the hole concentration at any point during the bombardment. This is borne out by the observation that, if one adjusts the $(nvt)_{\text{fast}}$ scale of the low resistivity sample so that its initial conductivity falls on the curve for the high resistivity sample (shown in Fig. 4), the curves coincide. This is indicated in Fig. 4 by two vertical marks on the curve between which the curves are coincident. Departure above the upper mark is due to temperature variation which sets in at this point.

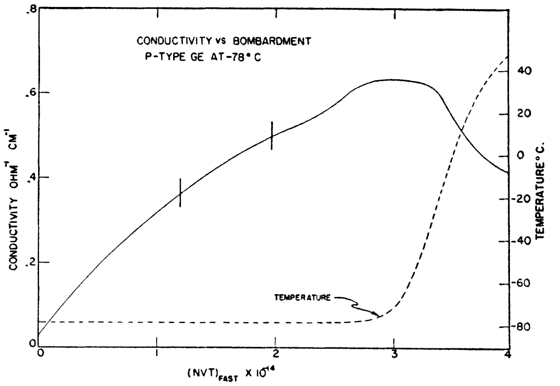

FIG. 4. Conductivity of P-type Ge *vs* integrated fast neutron flux bombarded at dry ice temperature. The dashed line represents temperature. The vertical lines on the curve represent the range of coincidence with the curve of another sample (see text).

During the low temperature bombardment discussed above, the conductivity was followed until all of the dry ice sublimed and the temperature rose toward pile ambient. The interesting behavior shown in Fig. 4 was observed. When the temperature (indicated by a dashed line) begins to rise the curve goes through an inflection and the rate of change of conductivity with bombardment begins to increase. The conductivity then reaches a maximum value with further temperature increase and then decreases. This behavior can be readily explained on the basis of simple semiconductor theory. The accelerated increase in conductivity when the temperature begins to rise is due to an increase in hole concentration. The decrease of conductivity at higher temperatures is caused by the decrease in lattice mobility with increasing temperature, which becomes predominant over the effect of increasing carrier concentration. It is also quite possible that an increased annealing rate caused by the temperature rise could anneal out a fraction of accumulated disorder at the high temperature, thus further decreasing the conductivity. This latter point, however, cannot be substantiated on the basis of existing data.

Perhaps the most interesting information to be obtained from the low temperature bombardment experiments is that even for very low annealing rates there is appreciable curvature in the P-type Ge conductivity *vs* bombardment curve. This curvature is presumably due to the nonlinear dependence of the carrier concentration on acceptor concentration. In view of this behavior the validity of such a simple rate analysis of the build-up behavior of the conductivity during bombardment of P-type Ge is even less certain.

TABLE II. The rate of increase in hole concentration per incident neutron for P-type material at various temperatures. Also listed is the original hole concentration at 27°C.

Sample (P-type Ge)	Temperature of exposure	Increase in hole concentration per incident neutron	Original hole concentration at 27°C (cm^{-3})
1	30°C	0.77	1.7×10^{15}
2	20°C	0.70	4.2×10^{14}
3	0°C	0.61	2.5×10^{14}
4	−78°C	0.20	4.6×10^{14}
5	−78°C	0.48	4.9×10^{13}

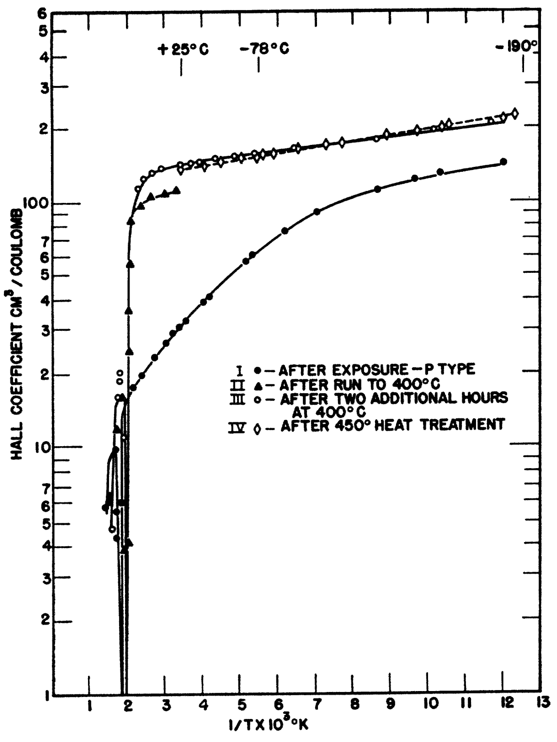

FIG. 5. Log Hall coefficient *vs* reciprocal of absolute temperature of P-type Ge after long bombardment showing effect of various heat treatments.

V. THE ENERGY DISTRIBUTION OF BOMBARDMENT INTRODUCED ACCEPTORS

In order to study the energy distribution of acceptors produced by bombardment, measurements of the Hall coefficient R as a function of temperature on bombarded material are necessary. Because of the appreciable rate of annealing at moderate and high temperatures and because of the long "radioactivity cooling" period required before the samples can be handled, little can be learned concerning the energy distribution in this temperature range except for those acceptors which anneal at higher temperatures.

Figure 5 gives the $\log R$ *vs* $1/T$ curve for a sample which had been stored at room temperature for several months after a long bombardment. Curve I was taken before any heat treatment, curve II after being heated to 400°C, curve III after 2 additional hours at 400°C and curve IV after 24 hours at 450°C. Further heat treatment produced no detectable change. Since a single ionization energy[19] in the impurity range would yield a constant slope, the curvature of curve I obviously indicates a wide distribution of ionization energies. It is interesting to note that nearly all of the effect of lattice disorder can be removed by merely heating to 400°C.

Additional information may be gained by exposing a sample at dry ice temperature and storing it in dry ice during the "cooling" period. By keeping the sample at this temperature and by first taking measurements at the low temperature, annealing of lattice disorder may be minimized. The results of two such exposures on the same sample are shown in Fig. 6. Hall coefficient curves are shown after various treatments. The sample was originally a high resistivity N-type Ge plate. The conductivity was followed during the bombardment and the sample was removed from the pile as near the conductivity minimum as possible in order to trap most of the conduction electrons. Curve I is the initial measurement before the first exposure. Unfortunately one of the Hall probes was detached during bombardment and had to be resoldered. This caused an uncertain amount of annealing and, therefore, curve II, taken after exposure, is not entirely representative. Curve III was taken after the sample was heated to 150°C and curve IV was taken after a full anneal.

After the second exposure the Hall coefficient had a positive sign indicating that the material had been converted to P-type [see Eq. (5)]. Because of rectification due to inhomogenities in impurity distribution which, though unimportant in the original, produce rectifying P-N potential barriers[20] at the conductivity minimum, reliable Hall coefficient measurements could not be made. The sample was briefly warmed to room temperature and recooled. By this action sufficient annealing took place to cause the sample to revert to N-type and to reduce the low temperature rectification. Curve VI was taken on this material.

Apparent ionization energies calculated from the low temperature slopes of curve II and VI are respectively 0.14 and 0.31 ev. These ionization energies are only apparent since they represent the effective energy of electrons in a distribution of traps. Presumably curvature like that in curve II, Fig. 5 would appear if the measurements could have been extended to lower temperature. Noting that the sample in curve II has had more heat treatment than in curve VI, this seems to indicate that annealing of lattice disorder in N-type Ge near the minimum tends to decrease the apparent activation energy. If one assumes that these bombardment produced acceptors are distributed in energy, uniform annealing will have the effect of promoting electrons to the more shallow traps. As the annealing progresses the concentration of electrons associated with the original donors increases and the ionization energy tends to revert to that of the original sample even though there is a considerable concentration of acceptors yet remaining. This is the case for curve III.

VI. SUMMARY AND CONCLUSIONS

Fast neutron bombardment of Ge introduces into the forbidden energy band a distribution of electron

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[19] The term "ionization energy" is preferred instead of the more frequently used "activation energy" since the latter has special application in rate process theory.

[20] Orman, Fan, Goldsmith, and Lark-Horovitz, Phys. Rev. **78**, 645 (1950).

traps. These traps are associated with lattice defects, presumably lattice vacancies, caused by the bombardment. Hole traps may also be produced, but, if these are present in Ge, they lie so near the top of the filled band that they have no observable effect on the electron concentration. The introduced traps remove electrons from N-type Ge initially at a uniform rate (3.2 electrons removed per incident fast neutron of the energy spectrum considered here). As intrinsic behavior is approached the trapped electrons are redistributed moving to traps of lower energy, until a sufficient concentration of low energy traps is introduced to contain all of the impurity electrons. Further bombardment causes a transition to P-type material and the low-lying traps behave as acceptors. Experimental evidence indicates that at room temperature one out of about four of the introduced traps are sufficiently deep lying to produce positive carriers. The conductivity *vs* bombardment curve resembles a conductiometric titration curve between a strong and weak electrolyte. Bombardment of P-type Ge causes a monotonic increase in conductivity with concave downward curvature indicating an approach to saturation, provided the Fermi level does not lie so deep as to be insensitive to additional acceptors of finite ionization energy.

Bombardment-produced disorder, like disorder produced by quenching, can be annealed out by proper heat treatment. All of the effects on electrical properties of Ge can be removed by a vacuum anneal at 450°C. Considerable annealing at room temperature is also observed. A simplified analysis of the P-type bombardment curve indicates that recombination of defects takes place through a first-order process, but other evidence seems to indicate that the annealing kinetics are too complicated to be fruitfully treated by such a naive approach.

The purpose of the investigations reported here is twofold: (1) the use of the fast neutron bombardment technique to investigate the effect of lattice disorder on the energy level scheme of Ge, and (2) the use of semiconductors whose properties are sensitive to small amounts of disorder to investigate the fundamental nature of radiation damage. The results of these experiments indicate that further thorough study of the energy distribution of electron traps produced by bombardment and the kinetics of annealing of the lattice disorder should be of considerable value in elucidating both aspects of the problem. Experiments designed to accomplish these ends are now under way.

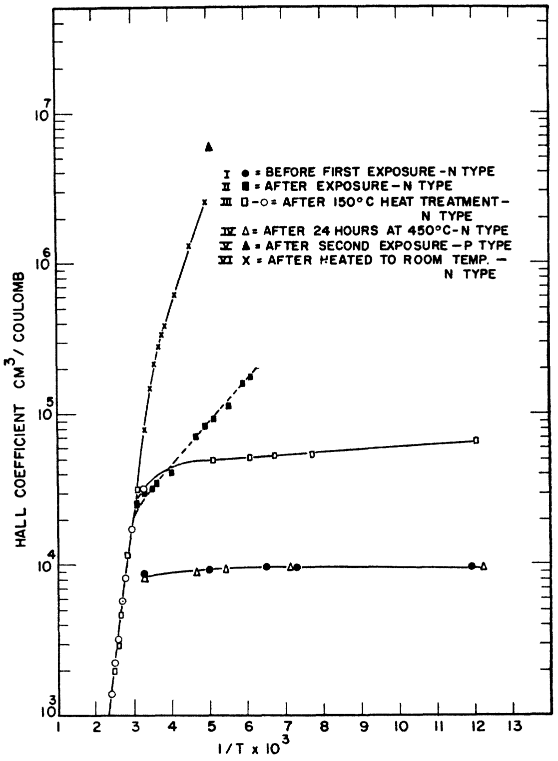

FIG. 6. Log Hall coefficient *vs* reciprocal of absolute temperature of N-type Ge exposed to minimum conductivity at dry ice temperature after various heat treatments.