Fast Neutron Bombardment of p-Type Germanium

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Extensive studies of fast neutron bombardment effects in p-type Ge have been carried out. Analysis of the initial conductivity behavior indicates the introduction of three vacant states below the middle of the forbidden band: (1) an acceptor state 0.18 ev above the valence band, (2) an occupied (donor) state which acts as a hole trap with a depth of $\sim$0.07 ev, (3) a second low-lying donor which is a quite shallow hole trap. This distribution of energy levels is consistent with the Frenkel defect model of James and Lark-Horovitz. After prolonged bombardment or room temperature aging, the ionization energy of bombardment-produced acceptors moves to lower values, a behavior which has been attributed to a difference in annealing rate of interstitials and vacancies. The scattering mechanism for holes in bombarded specimens does not appear to be completely describable in terms of ionized impurity scattering. Moreover, the temperature dependence of hole mobility is quite different from electron mobility in bombarded specimens. Extensive bombardments in the range from $-165°$ to $-90°$C are described and complex relaxation effects observed on warming are discussed.

I. INTRODUCTION

THE effect of fast neutron bombardment of the semiconducting properties of n-type Ge was treated in some detail in a previous paper.[1] The behavior of electron concentration and mobility during exposure in the reactor at or near room temperature was described and studies of conductivity and photoconductivity during and after exposure at low temperatures were also discussed. It was shown that the localized states produced by bombardment in the room temperature range, which are responsible for the removal of conduction electrons, are consistent with the energy level model for Frenkel defects proposed by James and Lark-Horovitz.[2] It was further shown that the effect of irradiation on Hall mobility could not be explained simply on the basis of additional charge-center scattering and that low-temperature irradiation was accompanied by extensive photoconductivity which could be interpreted as arising from trapped minority carriers.

The present paper is concerned with fast-neutron bombarded p-type Ge: both originally p-type material and that converted to p-type by irradiation. The situation with regard to changes in carrier concentration is not so clear cut as in the case of n-type material because of the greater complexity of defect-produced energy levels below the middle of the forbidden band. Theory predicts[2] and experiment confirms[3] the presence of both occupied and vacant localized states above the valence band. Consequently, depending on the initial hole concentration, the conductivity may either increase or decrease with bombardment.

Extensive measurements of conductivity σ on specimens with a wide range of initial hole concentration p_0 during irradiation in both the room-temperature range and at $-78°$C have been obtained. These data, together with measurements of Hall coefficient and conductivity as a function of temperature after successive periods of exposure at room temperature, permit an extensive examination of the nature and position of the states associated with defects which lie below the middle of the forbidden band. Information concerning hole mobility in irradiated Ge is also presented. Finally, the results of low-temperature exposures in the range from $-165°$C to $-90°$C are discussed.

II. IMPLICATIONS OF THE MODEL OF JAMES AND LARK-HOROVITZ

It was shown previously[3] that both the magnitude and the sign of the initial rate of change of hole concentration $[dp/d(nvt)_f]_{t=0}$ are dependent on the initial hole concentration p_0 and the temperature of exposure T_e. This result is consistent with the proposed model of energy levels associated with Frenkel defects,[2] since both occupied and vacant localized states above the top of the valence band are predicted by this model. Consequently, the situation is characterized by two competing processes: production of holes by the vacant states (acceptors) and trapping of holes by the occupied states (deep-lying donors). Under conditions of thermal equilibrium, the effect of Frenkel defect introduction depends on the position of the initial Fermi level ζ^0 relative to the limiting value ζ^* which is determined solely by the positions of the defect energy levels and the temperature. According to the model, two occupied levels and one vacant level are expected. If it is assumed that all of the chemical acceptors are completely ionized, the law of electrical neutrality requires that

$$p = p_0 + N_1^- - N_2^+ - N_3^+, \qquad (1)$$

where N_1^- is the concentration of ionized acceptors and N_2^+ and N_3^+ are the concentration of holes in the deep and shallow hole traps, respectively. If it is assumed that the levels are discrete, the law of mass

[1] Cleland, Crawford, and Pigg, Phys. Rev. **98**, 1742 (1955).
[2] H. M. James and K. Lark-Horovitz, Z. Physik. Chem. **198**, 107 (1951).
[3] Cleland, Crawford, Lark-Horovitz, Pigg, and Young, Phys. Rev. **84**, 861 (1951).

action gives

$$N_1^- = NK_1/(p+K_1),$$
$$N_2^+ = Np/(p+K_2), \tag{2}$$
$$N_3^+ = Np/(p+K_3),$$

where $N_1=N_2=N_3=N$, the total Frenkel defect concentration, and the equilibrium constants are given by

$$K_i = \gamma_i C(T) e^{-\epsilon_i/kT}, \tag{3}$$

where

$$C(T) = (2\pi m_h kT/h^2)^{\frac{3}{2}},$$

ϵ_i is the energy of the level measured from the top of the valence band, and γ_i takes a value of either unity or four depending on whether the state occupied by the hole has a residual electronic spin or not.[4] Substitution of Eqs. (2) in Eq. (1) yields

$$p = p_0 + N\left[\frac{K_1}{p+K_1} - \frac{p}{p+K_2} - \frac{p}{p+K_3}\right], \tag{4}$$

a quartic equation in p. If

$$p_0 = p^* = 2C(T)\exp(-\zeta^*/kT), \tag{5}$$

where p^* is the limiting hole concentration for the temperature in question, p will remain invariant with defect introduction. Under these conditions Eq. (5) reduces to the cubic equation

$$p^{*3} + \tfrac{1}{2}(K_1+K_2+K_3)p^{*2} - \tfrac{1}{2}K_1K_2K_3 = 0. \tag{6}$$

Only the positive root of Eq. (6) is significant, which, to a good approximation, is given by

$$p^* = \left(\frac{K_1K_2K_3}{K_1+K_2+K_3}\right)^{\frac{1}{2}}. \tag{7}$$

Using Eqs. (5) and (7), Eq. (3) becomes

$$\zeta^* = \frac{\epsilon_1+\epsilon_2+\epsilon_3}{2} - \tfrac{1}{2}kT\ln\left[\frac{4(\gamma_1 e^{-\epsilon_1/kT}+\gamma_2 e^{-\epsilon_2/kT}+\gamma_3 e^{-\epsilon_3/kT})}{\gamma_1\gamma_2\gamma_3}\right]. \tag{8}$$

If ϵ_3 is significantly smaller than ϵ_2 and hence ϵ_1, Eq. (8) may be approximated by

$$\zeta^* = \tfrac{1}{2}(\epsilon_1+\epsilon_2) - \tfrac{1}{2}kT\ln(4/\gamma_1\gamma_2), \tag{9}$$

which is identical to the expression obtained for a single trapping level and a single acceptor. The temperature dependence of ζ^* enters through the logarithmic term of Eq. (9) which, in this approximation, is

$$d\zeta^*/dT = -\tfrac{1}{2}k\ln(4/\gamma_1\gamma_2). \tag{10}$$

From the nature of the levels below the middle of the band as suggested by the theory,[2] it can be shown, whatever the identification of levels in question with those available, that $\gamma_1\gamma_2=4$. Hence $d\zeta^*/dT=0$.

The value of ζ^* indicates only the midpoint between the acceptor and the deepest hole trap. It is possible in principle to determine ϵ_1 and ϵ_2 from initial rates of change of p during bombardment as a function of p_0, provided that the relation between the Frenkel defect concentration N and integrated flux is known. The derivative of Eq. (4) with respect to N evaluated at $N=0$ and $p=p_0$ gives for the initial rate of change

$$[dp/dN]_{N=0} = \frac{K_1}{p_0+K_1} - \frac{p_0}{p_0+K_2} - \frac{p_0}{p_0+K_3}. \tag{11}$$

Hence there are apparently three adjustable parameters which would seem to indicate that curve fitting with Eq. (11) may not be a sensitive test of the theory. In actual fact, however, the condition imposed by either Eq. (8) or Eq. (9) reduces the number of parameters to two. Furthermore, the contribution of the last term of Eq. (11) is negligible until ζ^0 lies within $\sim 2kT$ of ϵ_3. In order to test the theory rigorously, it is necessary to use the values of ϵ_1, ϵ_2, and ϵ_3 obtained by using Eq. (11) to reproduce a representative conductivity *vs* bombardment curve according to Eq. (4). The latter test is possible only if (1) the effect of bombardment on mobility is negligible compared to the effect on hole concentration, (2) there is no differential annealing of different types of defects during exposure and (3) appreciable photoconductivity is absent. In the following section we shall apply these relationships to the behavior of conductivity measured during bombardment at room and dry ice temperatures.

III. EFFECT OF BOMBARDMENT ON CONDUCTIVITY

A. Initial Rate of Change

The conductivity σ of a large number of single-crystal p-type samples with a wide range of hole concentrations has been measured during bombardment in the reactor in the room-temperature range. Under the assumption that the initial change of mobility is negligible compared to the effect on hole concentration, the initial change in hole concentration per incident fast neutron[5] $[dp/d(nvt)_f]_{t=0}$ was calculated from σ *vs* nvt curves, using the initial conductivity σ_0 and uncorrected values[6] of p_0 obtained from Hall coefficient measure-

[4] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), second edition, pp. 157–158. See also J. H. Crawford, Jr., and D. K. Holmes, Proc. Phys. Soc. (London) **A67**, 294 (1954). The necessity of using this statistical factor was pointed out to the authors by H. M. James.

[5] The flux unit is discussed in reference 1.

[6] Here, as elsewhere in the paper, hole concentrations were calculated from the customary relation $p=7.37\times10^{18}/R$, where R is the Hall coefficient. No attempt was made to correct the values for impurity scattering since recent work [F. J. Morin, Phys. Rev. **93**, 62 (1954)] has shown that the ratio of Hall to drift mobility μ_H/μ_d for holes not only does not have the proper magnitude but is marked by temperature dependence. Willardson, Harman, and Beer [Phys. Rev. **96**, 1512 (1954)] have shown that this discrepancy is produced by the complex nature of the valence band in Ge. Consequently, values of p given in this paper may be in error by as much as a factor of two.

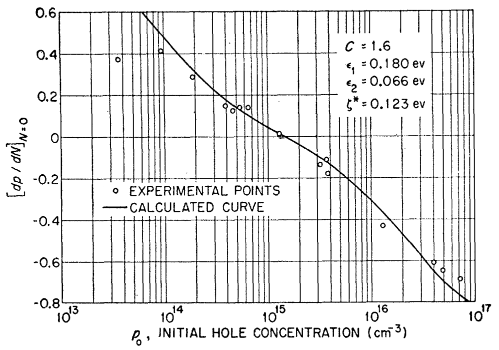

FIG. 1. The initial rate of change of hole concentration per Frenkel defect *vs* the initial hole concentration during bombardment at 195°K. The points are experimental and the solid curve is calculated from Eq. (11) assuming that C, the number of defects introduced per incident neutron, is 1.6.

ments. Values of p_0 and the exposure temperature for these specimens are listed in Table I. Although there is scatter in the data, it is apparent that $[dp/d(nvt)_f]_{t=0}$ changes from positive to negative with increasing p_0 at $p^*=(6.5\pm1.5)\times10^{16}$ cm^{-3}. The value of ζ^* at this temperature (~50°C) may be obtained from Eq. (5) provided m_h is known. Measurements of magnetic susceptibility[7] and cyclotron resonance[8] indicate that $m_h\simeq-0.3m_0$. With this value of m_h, $\zeta^*(323°\text{K})=0.120\pm0.006$ ev. Besides room-temperature exposures, a number of specimens have been irradiated at dry ice temperature. At -78°C, $p^*=(1.5\pm0.2)\times10^{15}$ cm^{-3} leading to $\zeta^*=0.123\pm0.003$ ev. Hence it appears that ζ^* is temperature independent within experimental error. This would indicate that the approximation leading to Eq. (9) is a good one.

Attempts have been made to evaluate ϵ_1, ϵ_2, and ϵ_3 by using Eq. (11) to fit the $[dp/d(nvt)_f]_{t=0}$ *vs* p_0 curve for the -78°C exposures. It has been shown[9] that ~3.2 electrons are removed per incident fast neutron in moderate to high-conductivity n-type material. Since two electron traps are expected per Frenkel defect,[2] this result indicates that the number of defects per incident neutron is approximately 1.6. The results of this analysis are shown in Fig. 1 where $[dp/dN]_{N=0}$ is plotted against $\log p_0$. The points are experimental and the solid curve was calculated from Eq. (11) by using $\epsilon_1=0.180$ ev, $\epsilon_2=0.066$ ev, and $\epsilon_3\simeq0$ and assuming $\gamma_1=4$ and $\gamma_2=1$. Considering expected experimental uncertainties, a reasonable fit to the data was obtained. Interchange of the values of γ_1 and γ_2 did not permit a good correlation even for a wide range of choice of energy parameters. These results strongly indicate that, provided the model is valid, ϵ_3 is quite small and, therefore, only one hole trap need be considered at this and higher temperatures. Furthermore, the required choice of values for γ_1 and γ_2 indicates that the acceptor can be identified with the doubly ionized interstitial atom. This calculation assumes that there has been no appreciable differential annealing between interstitials and vacancies in the initial range.

B. Conductivity *vs* Bombardment Curve

The energy parameters obtained above were used in Eq. (4) to calculate σ *vs* $(nvt)_f$ curves obtained at -78°C under the assumption that the mobility is unaffected by exposure. Although reasonable correspondence was obtained early in the exposure, the calculated and observed curves began to diverge as the bombardment proceeded. It is significant that the calculated curve predicts a lower value of σ after appreciable exposure than is actually observed for a p_0 either greater or less than p^*. If a decrease in mobility during exposure was solely responsible for the discrepancy, a deviation in the opposite direction would be expected. The greater observed values of σ may be due to either or both of two processes: (1) trapped minority carriers which produce an excess concentration of majority carriers, enhancing σ; and (2) a difference in annealing rate of the two types of defects which would alter the relative concentration of energy levels arising from each type and, thereby the distribution of energy levels. If the second process is responsible, the alteration of the distribution must occur in such a direction to cause p^* apparently to increase as bombardment progresses. Evidence for both of these processes will be discussed below in more detail.

The results of the foregoing analysis of the initial behavior of conductivity during bombardment reveals that the model proposed by James and Lark-Horovitz is consistent with observation. When applied to the behavior on prolonged bombardment, qualitative agreement is still obtained, but the data indicate that additional processes appear which require explanation. In this connection, it should be pointed out that similar

TABLE I. Initial rate of change of hole concentration during pile ambient temperature bombardment.

Sample	p_0 (cm^{-3})	T_e°C	$[dp/d(nvt)_f]_{t=0}$
1	4.2×10^{14}	20	0.70
2	1.7×10^{15}	30	0.77
3	3.5×10^{16}	53	0.08
4	4.0×10^{16}	55	0.20
5	5.7×10^{16}	62	0.037
6	7.2×10^{16}	49	-0.058
7	8.1×10^{16}	50	-0.10
8	1.5×10^{17}	62	-0.05
9	5.3×10^{17}	45	-0.80
10	7.0×10^{17}	32	-0.50
11	1.3×10^{19}	48	-2.2
12	1.5×10^{19}	48	-2.9

[7] D. K. Stevens and J. H. Crawford, Jr., Phys. Rev. **92**, 1065 (1953).
[8] Dresselhaus, Kip, and Kittel, Phys. Rev. **92**, 827 (1953); Dexter, Zeiger, Lax, and Rosenblum, Phys. Rev. **95**, 597 (1954).
[9] Cleland, Crawford, Lark-Horovitz, Pigg, and Young, Phys. Rev. **83**, 312 (1951).

studies carried out with 10-Mev deuterons[10] at a much higher rate of defect introduction show some interesting differences. The value of ζ^* obtained by fitting a σ *vs* bombardment curve at $-78°C$ was 0.089 ev, considerably smaller than the value obtained above from initial behavior. In addition, specimens with p_0 only slightly greater than the value of p^* obtained with fast neutrons, showed first a decrease in σ followed by an increase after additional deuteron bombardment. Although it is possible that the different results may be produced by differences in the effect of fast neutrons and charged particles, it is interesting to note that, considering the much higher rate of disordering by deuterons, these deviations are in the direction expected if process (2) described previously were operating.

IV. TEMPERATURE DEPENDENCE OF HOLE CONCENTRATION AFTER EXPOSURE

In general, the hole concentration before exposure is only slightly temperature dependent. Since, according to the model in question, ζ^* is essentially temperature independent and p^* is given by Eq. (5), p^* is expected to correspond to p_0 at some temperature T^* in an easily attainable temperature range (77°K to 300°K) over a wide range of p_0 values (10^{13} to 10^{17} cm^{-3}). Bombardment should cause an increase in p above T^* and a decrease in p below T^*. This result should be reflected in a rotation of the $\log R$ *vs* $1/T$ curve about a point $1/T^*$ approaching a slope of ζ^*/k.

Curves have been obtained after various exposures on a number of p-type specimens. Because of the induced radioactivity in the specimen and holder, it was usually necessary to wait appreciable periods (1 to 3 days) before handling was safe. Since room-temperature aging may occur during this waiting period, the curves do not necessarily represent conditions existing immediately on removal from the reactor. Typical log R *vs* $1/T$ curves after bombardment are compared with their original curves in Fig. 2 for three widely different values of p_0. The dashed curve in Fig. 2(a) was taken 3.5 days after an exposure to 1.6×10^{-17} fast neutrons cm^{-2} at 60°C on a specimen with $p_0=3.4\times10^{18}$ cm^{-3}, that in Fig. 2(b) was obtained 6 days after $(nvt)_f=5.8\times10^{16}$ cm^{-2} at 60°C with $p_0=7.0\times10^{16}$ cm^{-3}, and that in Fig. 2(c) 19 hr after $(nvt)_f=2.2\times10^{16}$ cm^{-2} at 60°C with $p_0=7.3\times10^{14}$ cm^{-3}. The solid curves are those taken before exposure.

The curve in Fig. 2(a) indicates that bombardment decreases the hole concentration over the whole temperature range. This behavior is borne out by the observed conductivity change during exposure. Further irradiation was found to produce an additional decrease in σ toward a limiting value. In the case of the curve in Fig. 2(b), the curve after exposure crosses the original curve indicating an increase in p above 250°K and a decrease in p at lower temperatures. The behavior in these two cases is qualitatively what is expected according to the model employed. In the case of small p_0, however, indications of Fig. 2(c) are that there is an increase in p over the whole temperature range despite the fact that the value of ζ^* indicates that the two curves should cross at $T^*=166°K$. Furthermore, the curvature after bombardment suggests a wide distribution of acceptor level energies that vary from an appreciable value at room temperature to a value near zero at liquid nitrogen temperature. These results indicate that, although there is qualitative agreement with the model at high values of p, there is a serious lack of agreement for small hole concentrations. The discrepancy cannot be reasonably explained by the initial introduction of an appreciable concentration of very shallow acceptors during bombardment since they would, to a large extent, mask the presence of hole traps indicated by studies of initial behavior (Sec. III A). Rather it is necessary to assume that the apparent low acceptor ionization energy results from some process which occurs during bombardment or during the aging period at room temperature. The same two processes appear probable which were mentioned in Sec. III B, namely, trapping of minority carriers or differential annealing of interstitials and vacancies. Evidence for these two processes will be treated in turn.

Although a more detailed discussion of minority carrier trapping will be deferred until later (Sec. VI), it is appropriate to say here than on closer examination

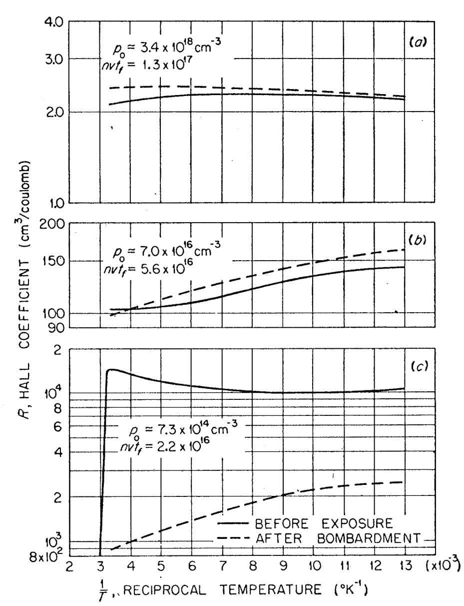

FIG. 2. Log Hall coefficient *vs* reciprocal temperature for three p-type specimens. The solid curves refer to the original behavior and the dashed curve was taken after exposure. The exposures $(nvt)_f$ and initial hole concentrations are indicated on the curves.

[10] Forster, Fan, and Lark-Horovitz, Purdue Progress Reports to Signal Corps, PRF-746, January 1, 1952 (unpublished), pp. 28–31. See also J. H. Forster, thesis, Purdue University, 1953 (unpublished).

it was found that at liquid nitrogen temperature, the Hall coefficient and resistivity of irradiated samples were extremely photosensitive. All of the data, however, were taken on specimens wrapped with several layers of linen tape and mounted in a narrow-necked Dewar, the mouth of which was plugged with glass wool. Consequently, the amount of ambient light incident on the specimen was quite small. It was impossible, however, to exclude the β and γ radiation which resulted from radioactive decay of the specimen, leads and holder. This radiation, though of relatively low intensity, is capable of producing electron-hole pairs. Consequently, measurements at low temperature taken shortly after removal from the pile undoubtedly include photoeffects. This process, however, cannot be solely responsible for the discrepancy, since after the activity in the specimen and its surroundings had essentially completely decayed, the difference between the observed and expected curve persisted.

The possible alteration of the distribution of energy levels was examined by following the progress of aging at and slightly above room temperature. The two specimens which were studied both showed a flattening of the log R *vs* $1/T$ curve while standing at room temperature. In one of these, the curve after exposure crossed the original one and it was difficult to decide whether the flattening of the curve was a result of uniform annealing of the vacancies or an alteration of the energy level distribution. The second specimen, however, gave a curve similar to that of Fig. 2(c), and its interpretation is less ambiguous. The results of the study are shown in Fig. 3. Curve I is the log R *vs* $1/T$ curve before bombardment, Curve II is that 10 hours after an $(nvt)_f$ of 2.6×10^{16} cm^{-2}, Curve III is that after an additional 96 hours, and Curve IV was obtained subsequently after warming to 140°C for 10 min. The curvature of Curve II is such that, if its trend continues, it will not intersect Curve I. R and ρ, measured during subsequent aging, showed a slow increase at room temperature and a slow decrease at 77°K. After 106 hours total aging the rate of change was very small and Curve III resulted. If both interstitials and vacancies were removed at the same rate, the curves after bombardment would be expected to approach the original one rather uniformly over the whole range. Comparison of Curves II and III, however, show that this is not the case. Instead, the decrease at low temperature and the increase at high temperature indicates that the distribution of acceptors is shifted toward lower ionization energy. In addition, since a rotation, instead of a general lowering, of Curve III occurs with respect to Curve II, the total concentration of acceptors apparently decreases during aging. On heating the specimen at 140°C for 10 min, it is evident from Curve IV that the process is accelerated and marked flattening of the curve occurs.

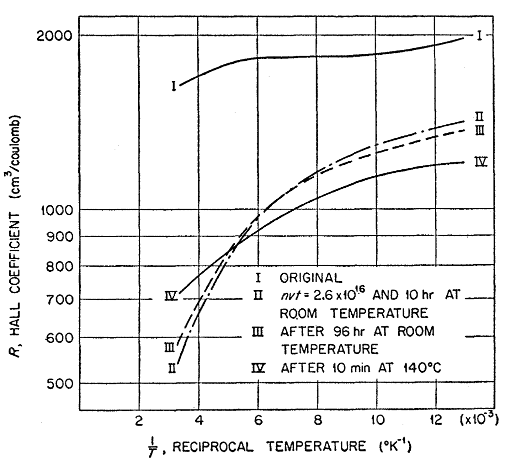

FIG. 3. Log Hall coefficient *vs* reciprocal temperature for a p-type specimen before and after bombardment and subsequent to annealing at room temperature and 140°C.

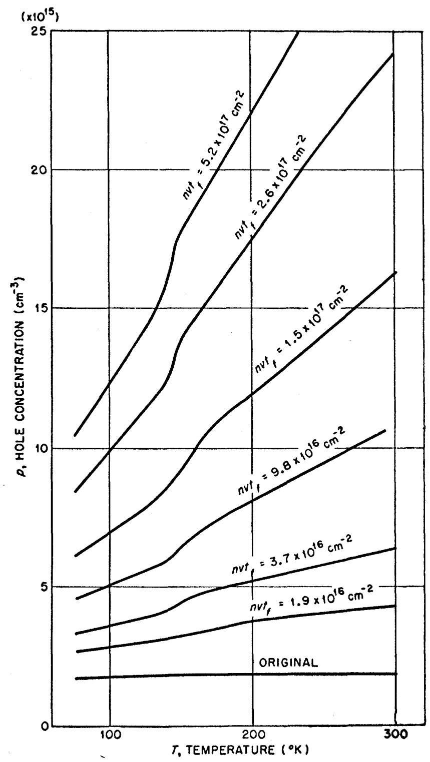

FIG. 4. Hole concentration *vs* temperature after successive exposures. The exposures are indicated on the curves.

In view of these observations it is not unreasonable to assume that similar annealing occurs during exposure as well. According to the model in question and indications of Sec. III A, a vacancy introduces two low-lying empty states which are filled by electrons from a doubly ionized interstitial. If an interstitial is removed by some process, such as clustering or trapping in the vicinity of a dislocation, two shallow acceptors are produced. Since a decrease in total acceptor concentration is also observed, recombination, to a smaller extent, of interstitials and vacancies must also be postulated. It is noteworthy that these assumptions require the interstitial atom to be the mobile component of the Frenkel defect. These considerations receive support from observations on low-temperature aging of irradiated n-type Ge[1] and quenching experiments of Mayburg.[11]

The temperature dependence of hole concentration[6] after successive periods of bombardment at $\sim 40°C$ was determined from Hall coefficient measurements on one p-type specimen ($p_0 = 1.8 \times 10^{15}$ cm^{-3}). Representative p *vs* T curves after various exposures are shown in Fig. 4. All of the curves after bombardment are characterized by a sigmoid involution, with its inflection point centered in the vicinity of 145°K, superimposed on an almost linear increase in p with T. The almost linear increase of p indicates a broad distribution of acceptor ionization energies, whereas the sigmoid step reveals the presence of a discrete level or closely grouped set of levels superimposed on the broad distribution. Although it is possible to obtain acceptable fits to these curves by using arbitrarily chosen acceptor distributions,[12] such fits require the use of at least four adjustable parameters. Consequently, little can be learned concerning the nature of the broad distribution by these means. Such calculations, however, do indicate that the discrete level or bump in the distribution lies in the vicinity of 0.10 ev above the band edge.[12]

In the case of an n-type specimen converted to p-type by bombardment, the resulting energy-level distribution may be examined without complications produced by holes initially present. Log R *vs* $1/T$ curves obtained after bombardment on an originally n-type specimen ($n_0 = 7.5 \times 10^{15}$ cm^{-3}) are shown in Fig. 5. Curve I was obtained after an $(nvt)_f = 1.0 \times 10^{16}$ cm^{-2}, Curve II after an $(nvt)_f = 2.2 \times 10^{16}$ cm^{-2}, Curve III after a 40-day anneal at room temperature, and Curve IV after annealing for 30 min at 150°C. Shortly after conversion to p-type, the slope of the log R *vs* $1/T$ curve (Curve I) is linear over most of the range with a slope corresponding to an acceptor ionization energy of ~ 0.08 ev. This level probably corresponds to the one producing the step in Fig. 4 and may presumably be identified with the deep trap determined from dry ice experiments (see Sec. III A). The curvature toward lower slope near 77°K indicates the presence of more shallow levels. After additional irradiation (Curve II) the shift of acceptor ionization toward lower values is quite evident. After the 40-day room-temperature anneal (Curve III), behavior is observed which is similar to that occurring in the case of initially p-type specimens (Fig. 3). After 40 days, however, the room-temperature aging process is essentially complete as is evidenced by the uniform decrease of p over the whole range which accompanies the 150°C annealing period (Curve IV).

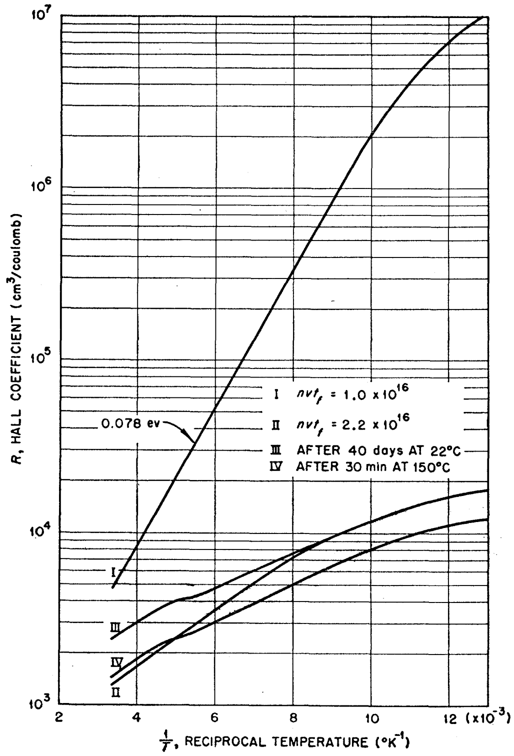

FIG. 5. Log Hall coefficient *vs* reciprocal temperature for an originally n-type specimen converted to p-type by bombardment, after two successive bombardments and subsequent anneals.

V. EFFECT OF BOMBARDMENT ON HOLE MOBILITY

Studies of n-type Ge[1] reveal that fast-neutron bombardment markedly decreases electron mobility. Moreover, the additional scattering was found to possess a greater temperature dependence than that predicted by the usual theories of ionized impurity scattering. Similar studies have been carried out on p-type Ge.

In Fig. 6 the mobility μ[13] is plotted against temperature for the specimen of Fig. 4 ($p_0 = 1.8 \times 10^{15}$ cm^{-3}) after several exposures. Values of $(nvt)_f$ for each exposure are indicated on the curves. The slope of the curve before irradiation is -2.1, in reasonable agreement with the reported temperature dependence for lattice scattering in p-type Ge.[14,15] Furthermore, the

[11] S. Mayburg, Phys. Rev. **95**, 38 (1954).

[12] The authors have employed with good results a uniform distribution extending from the edge to the center of the forbidden band with a superimposed discrete level centered ~ 0.10 ev above the band edge. In addition I. M. Katz (unpublished work) has obtained an excellent fit using a Gaussian distribution of levels of 0.24-ev half-width centered at the middle of the forbidden band with a superimposed discrete level at ~ 0.09 ev. These energy values were calculated assuming $m_h = m_0$; hence they are expected to be somewhat high.

[13] As used here, $\mu = R\sigma/r$, where the Hall parameter r is taken to be $3\pi/8$, the same value as that used in deriving p. Although the true value of r may be quite different from this (see reference 6), it is desirable to use the same value throughout, since r is thus effectively eliminated when $1/\mu$ is compared with p (Fig. 7).

[14] M. B. Prince, Phys. Rev. **92**, 681 (1953).

[15] F. J. Morin, Phys. Rev. **93**, 62 (1954).

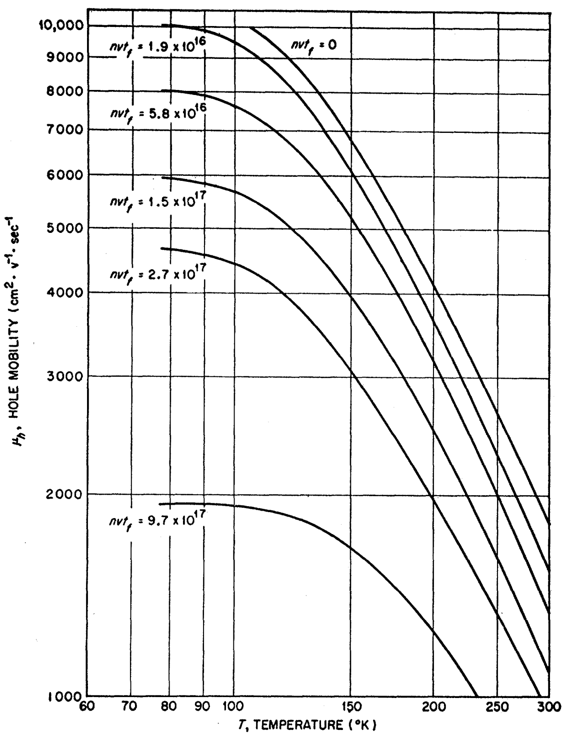

FIG. 6. Hole mobility *vs* temperature after successive exposures. The exposures are indicated on the curves.

initial curve shows the expected onset of the ionized impurity scattering at low temperatures, which is not sufficiently great at this concentration to produce a maximum in the curve in this temperature range (77° to 300°K). On bombardment μ decreases over the whole temperature range with a somewhat greater decrease occurring at low temperature. It is interesting to note that, even after appreciable bombardment, no discernable maximum is produced. If the additional, bombardment induced scattering were strictly of the charge-center type, a maximum which moves toward higher temperature with increasing defect introduction might be expected to appear. The lack of such a maximum may be taken as tentative evidence that the scattering associated with lattice damage of this type may not be amenable to treatment in terms of ionized impurity scattering.[16–18] It is noteworthy, however, that the excessively large temperature dependence of electron mobility observed in bombarded n-type Ge[1] is absent in p-type. Similar behavior to that shown in Fig. 6 was observed with a number of other specimens. In no case was a maximum observed which was not already present before exposure.

Since the curves of Fig. 6 indicate that μ at 77°K is limited predominantly by scattering processes other than lattice scattering, the reciprocal of this value $1/\mu_{77}$ is expected to be approximately proportional to the scattering probability of these processes at that temperature. The dependence of the scattering probability on defect concentration is shown in Fig. 7 where $1/\mu_{77}$ is plotted against the hole concentration at 77°K p_{77}. The convenient use of p_{77} as an index of disorder is possible because it increases approximately linearly with exposure. All points after the initial exposure fall on a straight line whose slope is 2.1×10^{20} in appropriate units. Since the same value of the Hall parameter was used in determining both μ and p, the correlation should be independent of its value.[13]

Although it was indicated in the foregoing that the scattering mechanism of the defects may not be of the ionized-impurity type, it can be shown that the data of Fig. 7 are not completely inconsistent with such a model. According to the Frenkel-defect energy-level model,[2] it is reasonable to expect the concentration of ionized scattering centers to be considerably larger than p_{77}. Moreover the model suggests that an appreciable fraction of these may be doubly rather than singly charged. For a mixture of scattering charges it is necessary to write the Conwell-Weisskopf formula[16] in a more general form.[19] In terms of the measure of

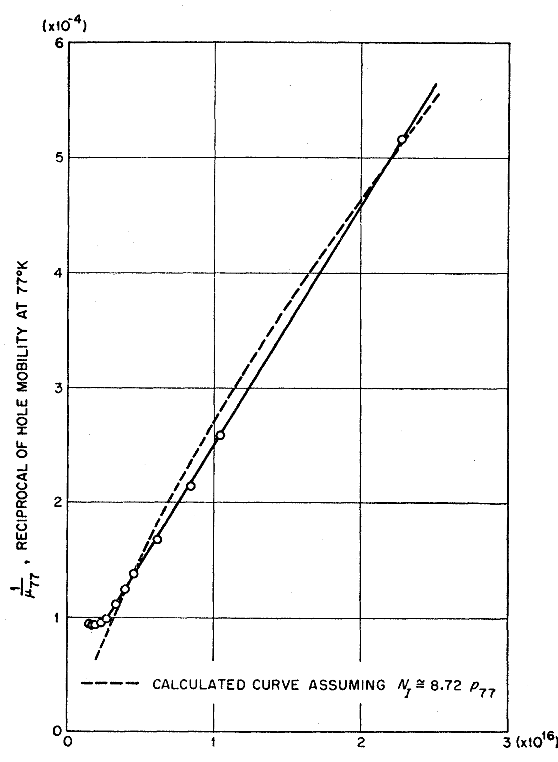

FIG. 7. The reciprocal of hole mobility *vs* hole concentration at 77°K in a p-type specimen after successive bombardments.

[16] E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950).
[17] H. Brooks, Phys. Rev. **83**, 879 (1951).
[18] P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).
[19] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 264.

scattering probability used here,

$$1/\mu = A\langle Z^2\rangle_{\text{Av}} N_I \ln\left[1+\frac{B}{\langle Z^2\rangle_{\text{Av}} N_I^{\frac{2}{3}}}\right], \qquad (12)$$

where $A=\pi^{\frac{3}{2}} m^{*\frac{1}{2}} e^3 2^{7/2} \kappa^2 (kT)^{\frac{3}{2}}$, and $B=(3kT/e^2)^2$. N_I is the total concentration of all ionized scatterers regardless of magnitude of charge, and $\langle Z^2\rangle_{\text{Av}}$ is the mean square of the charges,

$$\langle Z^2\rangle_{\text{Av}} = (\textstyle\sum_i z_i^2 N_i)/N_I, \qquad (13)$$

the subscript i referring to those ions of the same charge magnitude.

It was shown in the previous section that, presumably because of different annealing kinetics of the interstitials and vacancies, the energy level model begins to break down appreciable exposure. Consequently it is useless to attempt to evaluate $\langle Z^2\rangle_{\text{Av}}$ on the basis of the model. However, one can determine approximately the product $\langle Z^2\rangle_{\text{Av}} N_I = N_I'$ from experiment by setting $\langle Z^2\rangle_{\text{Av}} N_I^{\frac{2}{3}} = N_I'^{\frac{2}{3}}$ in the logarithmic term. This approximation would tend to make N_I' too small,[20] but since for a maximum charge of two units $\langle Z_1^2\rangle_{\text{Av}} < 4$, the error is probably less than a factor of 1.5. The ratio of N_I', the effective concentration of singly charged scatterers required to produce the observed scattering probability, to p_{77} was obtained by matching the experimenta curve of Fig. 7. The dashed curve shows the results obtained using $m^*=0.3m_0$ and $N_I'/p_{77}=8.72$. A reasonable agreement with regard to magnitude was obtained, but the calculated curve shows a distinct curvature which is not apparent in the experimental one.

In summary, we can only say that the nature of the scattering mechanism of bombardment-introduced defects is uncertain. Although certain features of the temperature and concentration dependence of the scattering probability are not consistent with charge-center scattering, the magnitude of the scattering probability is approximately that which would be expected if $\sim$9 singly ionized defects were introduced for each ionized acceptor at 77°K. The reason for the large disparity in behavior of electron mobility to that observed for holes in bombarded Ge is not clear. More extensive experimental information is required to answer this question.

VI. LOWT-EMPERATURE BOMBARDMENTS

As in the case of n-type Ge,[1] the conductivity of a number of p-type specimens has been measured during exposure in the low-temperature facility of the graphite

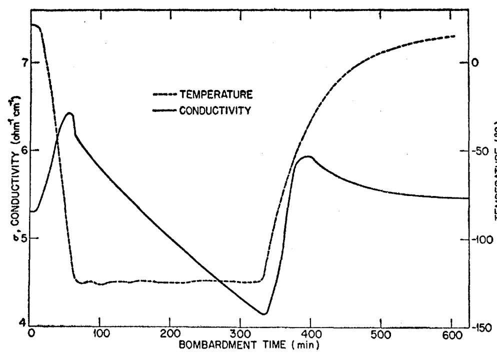

FIG. 8. Conductivity vs bombardment time for a p-type specimen during thermal cycling. The dashed curve is the temperature during bombardment.

reactor at temperatures in the range $-165°$ to $-90°$C. The variation of conductivity was also followed during various thermal cycles subsequent to exposure. The specimens investigated included those which were both originally p-type and those which had been converted to p-type by previous bombardment.

For all specimens investigated, σ decreases during bombardment at these temperatures. In this respect their behavior is consistent with the Frenkel-defect energy-level model[2] and the analysis of the critical rate of hole removal at higher temperatures. For the value of ζ^* obtained above, it can be shown from Eq. (5) that $p^* \leq 8\times 10^{14}$ cm^{-3} for this temperature range. Since in all specimens $p > p^*$ at their respective temperatures of exposure T_e, a decrease in σ with bombardment is expected. Moreover, though not entirely conclusive, the dependence of the initial rate of decrease of σ on T_e and the initial value of σ or p_0 also appears to be in qualitative agreement with the model, the initial rate of decrease of σ being greater the lower T_e and the larger σ_0. In contrast to the behavior of σ during bombardment at constant temperature, which is apparently consistent with the chosen model, the variation of σ with temperature, during thermal cycling either during or subsequent to bombardment after a period of exposure at constant temperature, cannot be explained entirely on this basis. Similar results to those described below have also been observed in deuteron-bombarded Ge.[21]

The curve for σ vs bombardment time obtained for a typical run is shown in Fig. 8. The temperature throughout the run is shown by the dashed curve. Initially, as the sample is cooled, σ increases because of the temperature dependence of hole mobility. In the constant-temperature range (-135°C for this run), σ decreases monotonically with bombardment. At higher exposure temperature, the curvature in the constant-temperature region is much more pronounced. When the sample of Fig. 8 is warmed, σ increases rapidly to a

[20] There is another factor which has the opposite effect. The Conwell-Weisskopf scattering formula does not include screening effects. These are apt to become important even in this concentration range when $N_I > p$, thus decreasing the screening and increasing the scattering power of the ions (see reference 18). The error involved in the above approximation is expected to be compensated to some extent by the neglect of screening.

[21] Forster, Fan, and Lark-Horovitz, Phys. Rev. **91**, 229 (1953); See also J. H. Forster, thesis, Purdue University, 1953 (unpublished).

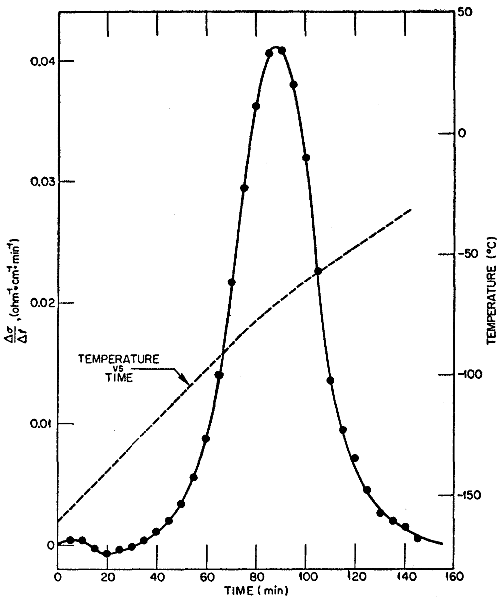

FIG. 9. The rate of conductivity change *vs* time after 640-min bombardment at -150°C. The dashed curve is the temperature.

maximum at -40°C and then decreases to a room-temperature value slightly higher than that at the start of the run. This increase in σ at room temperature is that expected to result from the same exposure period at room temperature. Similar behavior is observed if the warming is conducted after the reactor has been shut down.

Although the rapid increase in σ during warming may be due, all or in part, to thermal release of holes trapped in bombardment-produced defects, subsequent recooling of the specimen shows that all of the decrease in σ induced by low-temperature irradiation has annealed during the warming period. The rate of increase in σ during the heating cycle for a sample exposed for 640 min at -150°C is shown in Fig. 9; $\Delta\sigma/\Delta t$ is plotted as a function of time and the temperaperature during the cycle is indicated by the dashed curve. The curve shows a single maximum which is characteristic of a single-rate process. If the temperature dependence of mobility is suitably accounted for, the increase in σ during warming may be due to one or both of two processes: (1) the thermal release of holes from traps or (2) the annealing, by some mechanism, of the hole-trap defects which then release holes. Although recooling the specimen reveals that all of the decrease in σ, and hence the hole traps, has been removed during the heating cycle, the first process is by no means ruled out. A defect which behaves as a hole trap is stabilized by the approximate extent of the trapping energy when the trap is occupied. Consequently, it is possible that the annealing process takes place in two steps; the thermal release of holes from traps, followed by the annealing of those traps which have lost the stabilizing effect of the trapped hole. If such behavior is the case, the $\Delta\sigma/\Delta t$ *vs* time curve will not reflect the rate of annealing of hole-trap defects but, rather, the rate of thermal release of holes. This point will be considered in more detail in connection with pulse-annealing experiments which yield the necessary information for deciding between processes (1) and (2).

If specimens are irradiated for considerable periods at temperatures below -140°C, quite a different behavior of σ is observed during warming even though the form of the σ *vs* bombardment time curve is apparently the same as that obtained above this temperature. Initially, as the temperature begins to rise, there is a further sharp decrease in σ which persists until the temperature reaches ~-120°C. Above this temperature σ rapidly increases in the manner shown in Fig. 8. This initial decrease in σ is evident in the initial portion of the curve of Fig. 9 in which $\Delta\sigma/\Delta t$ is negative.

In order to investigate the relaxation effects during warming in greater detail, several pulse-annealing experiments were carried out. The procedure used is as follows: A specimen was irradiated for the desired time at constant temperature. The reactor was then shut down and the specimen was warmed in place. The temperature was pulsed to a desired value, held constant for the desired time, and then returned to the reference value. The process is then repeated, pulsing to successively higher temperatures. This annealing technique has the advantage that the effect of a known thermal treatment on the specimen can be examined at a constant temperature, thereby eliminating complications associated with the temperature dependence of carrier concentration and mobility. The results of one such experiment, performed simultaneously on two *p*-type specimens after they had been irradiated for 18 hours at ~-160°C, are shown in Fig. 10. The reference temperature during the run was -166°C. These curves indicated conclusively that σ is influenced by two distinct relaxation processes. After each pulse σ shows a definite decrease until -122°C is reached. After annealing at this temperature both specimens exhibit a σ which is lower than the initial value by more than an order of magnitude, the specimen with the lower initial σ showing the greater decrease. Pulsing to higher temperatures produces an irreversible increase which is characteristic of the annealing behavior of specimens irradiated above -140°C.

Inspection of Fig. 10 reveals that, besides the two irreversible processes, a reversible process, presumably thermal ionization of trapped holes, plays an important role in the σ *vs* t behavior during pulsing. The warm-up and cool-down behavior between pulses has been examined in detail. Typical logσ *vs* $1/T$ curves are shown in Fig. 11. After each pulse these curves are straight lines below -120°C and the slopes correspond to an apparent ionization energy of 0.10 ± 0.01 ev for both specimens. This value of hole-trap depth is somewhat higher than that determined for the deep trap

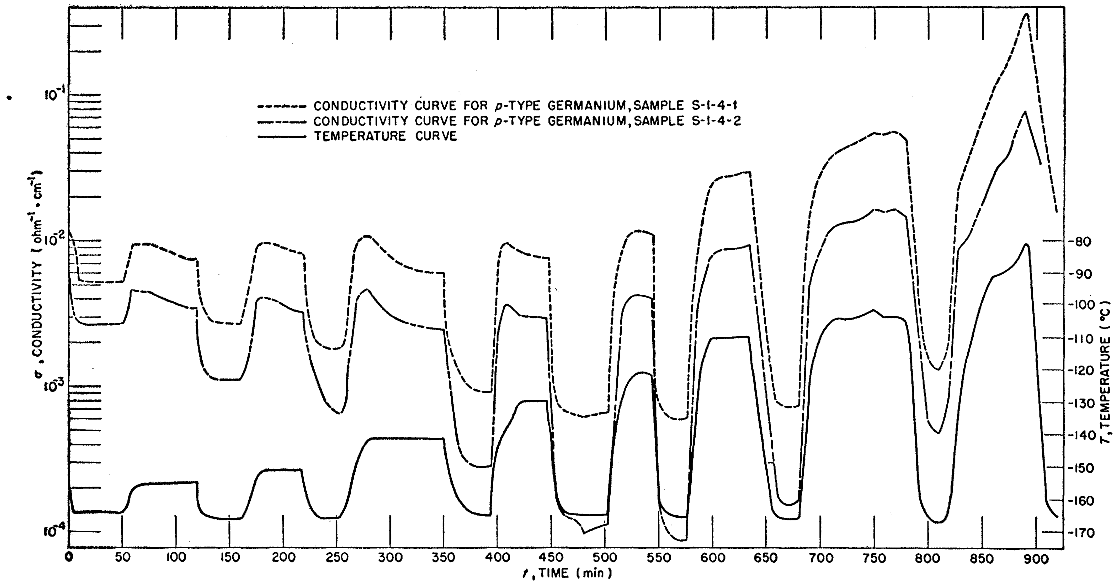

FIG. 10. Conductivity *vs* time during a pulse-annealing run on two p-type specimens after 18-hour bombardment at $-160°$C. The temperature during the run is indicated by the solid curve.

from fitting the initial slope *vs* p_0 curve at dry ice temperature (Fig. 1, Sec. III). These results indicate that the defects responsible for the traps are able to stabilize themselves by ~0.1 volt when they are occupied. In the temperature range under consideration this would correspond to appreciable stabilization. Returning to the question raised earlier in connection with the curve for $\Delta\sigma/\Delta t$ *vs* time (Fig. 9), in view of the possible stabilization effect and the evidence for the large reversible contribution to the pulse height, it would seem that the character of this curve is predominantly determined by the thermal release of trapped holes (process 1), at least in the low-temperature region covered by the pulse-annealing runs. Consequently, it is concluded that little can be learned concerning the annealing kinetics of hole-trap defects from curves of this sort.

We shall now examine the irreversible processes revealed by pulse annealing, considering first the higher temperature ($T>-120°$C) process. The irreversible increase in σ during warming is apparently quite similar to the process discussed in Sec. IV which occurs during prolonged room-temperature exposure or aging in the room-temperature range. The end result of both processes is a virtual removal of hole traps and a decrease in ionization energy of acceptors. The major difference in the two processes is the rate at which they occur. In the case of the low-temperature exposure, the relaxation is presumably inhibited by the low-thermal energy of the lattice and perhaps by the stabilization of hole traps as indicated above. Consequently, it is reasonable to expect that an appreciable amount of annealable disorder is stored during exposure at these temperatures. On warming, such a situation would produce rapid annealing over the temperature range in which the disorder becomes unstable. The nature of the relaxation process is not clearly understood. It is possible that the annealing or rearrangement of the disorder to a more stable configuration involves the removal of interstitials by the same mechanisms suggested above (Sec. IV). However, it is also possible that, although the effects of the process are similar to those at room temperature, the annealing mechanism is quite different. This is to be expected if, as has been suggested,[22] the disorder resulting from the collisions of fast neutrons with lattice atoms is highly localized in small regions and cannot be described by randomly distributed Frenkel defects. Such a configuration of disorder would be thermally unstable and would be expected to rearrange to one of greater stability as the thermal energy of the lattice increases. A careful study of the annealing kinetics of low temperature exposures is necessary to answer the questions posed here.

The effect of the irreversible process occurring below $-120°$C is essentially the opposite of the one just discussed in that a decrease rather than an increase in σ results. To explain this behavior it is necessary to postulate both the presence of minority-carrier traps and their removal by annealing at low temperature. There is convincing evidence that electron bombardment of p-type Ge at 78°K introduces electron traps.[23] Moreover, photoconductivity measurements as a function of temperature on p-type Ge bombarded at room

[22] Crawford, Cleland, Holmes, and Pigg, Phys. Rev. **91**, 243 (1953).

[23] Brown, Fletcher, and Wright, Phys. Rev. **96**, 834 (1954); Stoeckmann, Klontz, Fan, and Lark-Horovitz, Phys. Rev. **98**, 1535(A) (1955). Klontz, Pepper and Lark-Horovitz, Phys. Rev. **98**, 1535(A) (1955).

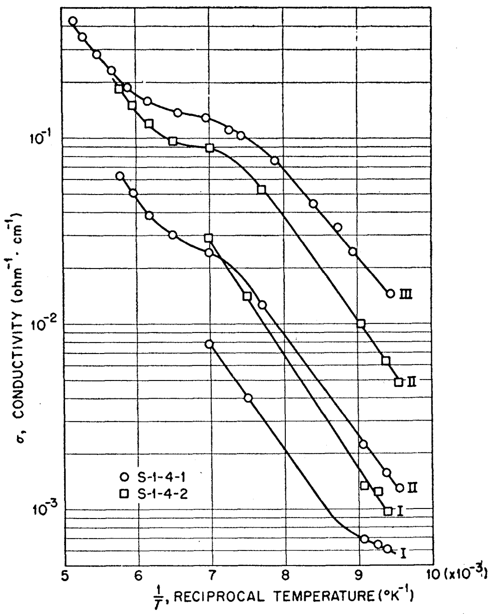

FIG. 11. Log conductivity *vs* reciprocal temperature. These curves are typical of those obtained after each pulse. Curves I, Curves II, and Curve III were obtained after the fourth, seventh, and eighth pulses respectively.

temperature with fast neutrons also indicates minority-carrier trapping.[24] Consequently, similar effects are expected in p-type Ge bombarded with fast neutrons at low temperature. Hence it is surprising that the curves of Fig. 11 indicate almost no temperature independent or nearly temperature independent component of σ at low temperature which would normally be expected to result from minority-carrier trapping under constant excitation (by γ radiation in the reactor). There is, however, a pronounced inflection in the $\log\sigma$ *vs* $1/T$ curves (Curves II and III) in the region of -120°C. Moreover, it is noted that the slopes of these curves are essentially the same both above and below the inflection which serves to off-set the curves toward lower values of σ at high temperatures. Minority-carrier trapping would indeed be expected to produce such behavior, provided that the concentration of hole traps were large compared to the total concentration of available holes.

This point can be illustrated as follows: Since an occupied hole trap is statistically equivalent to an acceptor, let us consider an acceptor level, equivalent to the level of hole traps, containing N states of which only $N_a{}^0$ are occupied by holes at $0°\mathrm{K}(N \gg N_a{}^0)$. In the absence of exciting radiation and at sufficiently low temperatures ($p \ll N_a{}^0$), the law of mass action gives approximately

$$p \simeq N_a{}^0 K_a / N, \tag{14}$$

where the equilibrium constant K_a has the same form as Eq. (3). It is evident from Eq. (14), that in this approximation p is proportional to N_a: If Δn_t electrons are trapped under constant exciting radiation, an equal concentration of excess holes is produced. Because of the large number of vacant states in the acceptor level, these holes do not necessarily remain free, but rather they go to increase N_a. Hence, approximately,

$$N_a \simeq N_a{}^0 + \Delta n_t, \tag{15}$$

and p increases proportionately. The inflection in the $\log\sigma$ *vs* $1/T$ curves is then caused by a transition from a condition of minority-carrier trap saturation at low temperature to one in which the traps are empty at high temperature.

Although the above explanation adequately accounts for the inflection in the $\log\sigma$ *vs* $1/T$ curves, the intensity of radiation is such that the traps are essentially saturated below -120°C. In order to account for the σ decrease on pulsing below this temperature, it is necessary to postulate the removal of electron traps by some annealing process. Analysis of the behavior of σ during the third pulse (Fig. 10) indicates a first order relaxation process. The nature of the defects responsible for these electron traps is uncertain but, whatever the origin, some electron traps remain in the crystal at temperatures well above those at which the hole traps anneal.[24]

To summarize, low-temperature bombardment of p-type Ge decreases the conductivity, presumably by removal of holes by defects in a manner apparently consistent with the Frenkel-defect energy-level model. On warming after irradiation below -140°C, two distinct relaxation processes are observed: (1) a further decrease in σ which is virtually complete at -120°C and which may be associated with minority-carrier trapping phenomena and (2) the rapid annealing of the decrease in σ produced by bombardment at low temperature. The second process is similar in effect to annealing which has been observed in the room-temperature range. Extensive annealing-kinetics investigations in this temperature range are necessary before these processes can be understood. Such studies are now underway.

VII. DISCUSSION OF RESULTS

The distribution of defect-connected energy levels in bombarded p-type Ge, as indicated by an analysis of the initial behavior of specimens bombarded at room temperature and 195°K, is consistent with the Frenkel-defect model of James and Lark-Horovitz.[2]

The results for both n-type[1] and p-type material are summarized schematically in Fig. 12. The density of states in arbitrary units is plotted against energy over the forbidden energy band. Although the analysis yields discrete values for the defect levels, they are represented as bands in the diagram primarily because perturbations produced by neighboring defects are expected to broaden a set of discrete levels into a band.

[24] Cleland, Crawford, and Pigg (unpublished).

The bands of levels shown in Fig. 12(a) are as follows: Band A which is centered ~0.2 ev below the conduction band, represents the shallow electron trap associated with the interstitial atom.[1] Band B is the second vacant level which, lying below the middle of the forbidden band, may either trap electrons or accept holes. This band, which lies 0.18 ev above the valence band, may be associated with either the interstitial or the vacancy, although the choice of γ's required to fit the 195°K data (Sec. III) indicates that the interstitial is responsible. Bands C and D are the low-lying occupied states which act as hole traps. These are presumably associated with the vacancy. Band C is placed ~0.07 ev above the valence band. Although there is no direct information concerning band D, its depth as a hole trap is known to be considerably less than that of band C. Hence it is arbitrarily placed at 0.02 ev above the valence band. The last two bands are shaded to indicate that they are normally occupied.

The situation just described is expected for equal concentrations of vacancies and interstitials. If, as is indicated by room temperature annealing, an appreciable concentration of interstitials and the electrons originally associated with them are removed by some process, the distribution is expected to change to that indicated in Fig. 12(b). The result of such a process is to transform band C and a part of band D into acceptor states. This transformation would explain the low acceptor ionization energy values of converted n-type material after prolonged exposure and room-temperature aging (Fig. 5). Moreover, the ionization energy of 0.08 ev shortly after conversion (Curve I, Fig. 5) and the level indicated by the curves of Fig. 4 would be identified with band C in a manner consistent with this hypothesis.

It is possible, though the evidence is much more tenuous, to interpret the results of low temperature (<-90°C) exposure in the same manner. The disappearance of the bombardment induced decrease in σ on warming would then be explained by a transition from the situation depicted in Fig. 12(a) to that in Fig. 12(b). In view of alternative possibilities, however, much additional support for this view is required before it can be taken as conclusive.

Because of the consistency of results for both n- and p-type material with the model of James and Lark-Horovitz, it is indeed tempting to conclude that lattice defects introduced by fast-neutron bombardment can be described in terms of randomly distributed Frenkel defects. However, as pointed out previously,[1] because of the localized fluctuation in defect density expected to result from bombardment, this view should not be taken as conclusively established. Careful annealing studies of disordered specimens should help clear up this question. Comparison of the results of fast-neutron bombardment and electron bombardment would also be helpful since electrons with energies near the threshold value for displacing atoms from their normal lattice sites would be more likely to introduce randomly distributed defects.[25,26]

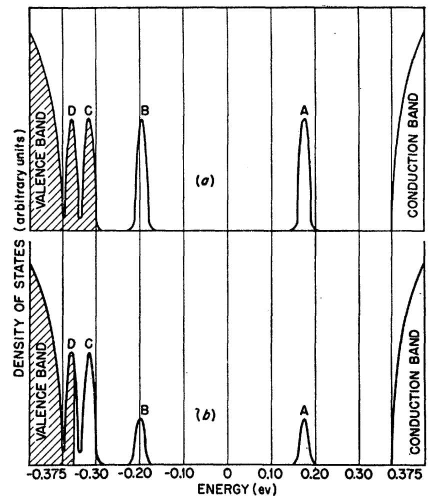

FIG. 12. A diagram of the distribution of energy levels produced by bombardment. Part (a) indicates the distribution expected for equal concentrations of interstitials and vacancies. Part (b) shows the effect expected to result from partial interstitial removal.

Another interesting point raised by these studies is the difference in the effect of bombardment on the mobility of holes as compared to that of electrons. Such a difference may well be associated with a nonrandom distribution of defects in that the charge density, and hence the electrostatic potential, associated with a disordered region may be a sensitive function of Fermi level. Such effects associated with dislocations in semiconductors have been recently considered by Read.[27] Consequently, a detailed study of the scattering process in Ge as well as annealing studies appears to be a valuable approach to a better understanding of the spatial distribution and detailed nature of bombardment-produced defects.

VIII. ACKNOWLEDGMENTS

We wish to thank Miss Louise Roth of Purdue University for furnishing the single crystals of Ge used in these experiments. In addition we are indebted to D. K. Holmes and H. C. Schweinler of this laboratory for many helpful discussions. The assistance of E. S. Schwartz in some of the measurements is gratefully acknowledged.

[25] E. E. Klontz and K. Lark-Horovitz, Phys. Rev. **86**, 643 (1952); see also E. E. Klontz, thesis, Purdue University, 1952 (unpublished).
[26] Brown, Fletcher, and Wright, Phys. Rev. **92**, 591 (1953).
[27] W. T. Read, Jr., Phil. Mag. **45**, 775 (1954); **45**, 1119 (1954); **46**, 111 (1955).