and $\Gamma_{2'}$ solutions. A more detailed description of the work summarized here will be submitted to this journal.

The writer wishes to thank Dr. Harvey Winston of the Hughes Semiconductor Laboratory for helpful discussions of the symmetry properties of crystal wave functions and Dr. Frank Herman of the RCA Laboratories for information about his diamond and germanium calculations prior to their publication. This work was carried out while the writer was a member of the technical staff of the Semiconductor Laboratory of Hughes Aircraft Company and a holder of a Howard Hughes Fellowship.

PHYSICAL REVIEW VOLUME 98, NUMBER 6 JUNE 15, 1955

Fast-Neutron Bombardment of *n*-Type Ge

J. W. CLELAND, J. H. CRAWFORD, JR., AND J. C. PIGG
Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received January 20, 1955)

The effect of fast-neutron bombardment on the electrical properties of *n*-type Ge has been extensively studied by a variety of experiments. The initial rate of carrier removal, the shape of the bombardment curve, and the temperature dependence of electron concentration in bombarded specimens all indicate the production of two vacant states, one located below the middle of the forbidden energy band and the other located $\sim$0.2 ev below the conduction band. These two vacant states are consistent with predictions of the model of James and Lark-Horovitz. Studies of mobility reveal that the additional scattering associated with bombardment-induced lattice disorder is more complex than charged impurity scattering in that it exhibits a much greater temperature dependence and is markedly dependent on electron concentration. Low-temperature exposure and subsequent warming experiments indicate that appreciable photoconductivity associated with minority-carrier trapping results from fast-neutron bombardment. The important minority-carrier traps appear to anneal during warming below room temperature.

I. INTRODUCTION

THE electrical properties of diamond-lattice semiconductors are extremely sensitive to lattice-disordering effects which result from bombardment with high-energy particles. Lattice defects produced by fast-neutron bombardment introduce localized energy states into the forbidden energy band of Si,[1] Ge,[1–3] and InSb.[4] The predominant effect of bombardment of Ge is the introduction of vacant states which may either trap electrons in *n*-type or behave as acceptors in *p*-type material. In addition, convincing evidence has been obtained for the production of occupied states, which lie too low in the forbidden energy band to act as donors in *n*-type material but may act as shallow hole traps.[3] The results obtained on Ge by other investigators using a variety of fast particles (deuterons,[1,5] α particles,[1,6,7] and fast electrons[8,9]) are in qualitative accord with those obtained with fast neutrons.

James and Lark-Horovitz[10] have proposed a model for the energy levels associated with Frenkel defects, defects which are generally expected to result from bombardment. This model has been used successfully in explaining qualitatively not only the more important features of the behavior of bombarded Ge but in addition the behavior of bombarded Si, which is quite different from that of Ge.[1] With suitable modification, this model has also been applied with reasonable success to bombarded InSb.[4] Although the results of Ge bombarded in the room temperature range are in qualitative agreement with the model, such is not the case for irradiations carried out at temperatures below 200°K. Quite complex annealing behavior has been observed on warming the specimens after irradiation at low temperatures with both fast neutrons[11] and deuterons.[12]

In order to investigate the nature of fast-neutron bombardment effects in more detail, a wide variety of experiments have been carried out and the range of consideration of important parameters has been extended. Specimens of both *n*- and *p*-type material with a wide range of carrier concentration have been irradiated in the ORNL graphite reactor for varying

[1] For a review of the early work on Si and Ge see K. Lark-Horovitz, in *Semi-Conducting Materials*, edited by H. K. Henisch (Academic Press, Inc., New York, 1951), p. 47 ff.
[2] Cleland, Crawford, Lark-Horovitz, Pigg, and Young, Phys. Rev. **83**, 312 (1951).
[3] Cleland, Crawford, Lark-Horovitz, Pigg, and Young, Phys. Rev. **84**, 861 (1951).
[4] J. W. Cleland and J. H. Crawford, Jr., Phys. Rev. **93**, 894 (1954); **95**, 1177 (1954).
[5] J. H. Forster, thesis, Purdue University, 1953 (unpublished).
[6] W. H. Brattain and G. L. Pearson, Phys. Rev. **80**, 846 (1950).
[7] K. Lark-Horovitz, *The Present State of Physics* (American Association for the Advancement of Science, Washington, D. C., 1954), p. 57 ff.
[8] E. E. Klontz and K. Lark-Horovitz, Phys. Rev. **86**, 643 (1952); see also E. E. Klontz, thesis, Purdue University, 1952 (unpublished).
[9] Brown, Fletcher, and Wright, Phys. Rev. **92**, 591 (1953).
[10] H. M. James and K. Lark-Horovitz, Z. physik. Chem. **198**, 107 (1951).
[11] Crawford, Cleland, Holmes, and Pigg, Phys. Rev. **91**, 243 (1953).
[12] Forster, Fan, and Lark-Horovitz, Phys. Rev. **91**, 229 (1953).

periods of time at both pile ambient and low temperature ($\sim$35°C to as low as -160°C). Hall coefficient and conductivity have been measured as a function of temperature after successive periods of exposure for a number of specimens irradiated in the room-temperature range, and conductivity measurements during various heating cycles have been obtained during and after low-temperature irraidation. These data permit an extensive test of the James, Lark-Horovitz model of bombardment-produced energy levels and, in addition, they yield much other information of interest.

Because of the extensiveness and complexity of the data taken as a whole, it has been decided to present here only the results obtained on n-type Ge, reserving all information pertaining to p-type Ge for a subsequent publication. The purpose of both papers will be to correlate, insofar as possible, experimental results with existing ideas concerning the nature of bombardment lattice defects and to point out additional problems which as yet do not fit into the existing theoretical framework. The results of ambient bombardment will be analyzed quantitatively on the basis of the theory of James and Lark-Horovitz. In the present paper, since n-type Ge alone is considered, only the positions of those defect-states which lie above the middle of the forbidden energy band can be determined. The effect of bombardment on mobility is next considered and, finally, the results of low-temperature irradiation of n-type Ge will be discussed.

II. THE MODEL OF JAMES AND LARK-HOROVITZ

Earlier ideas concerning energy levels associated with lattice defects[1] were based on single ionization of lattice vacancies and interstitial atoms. Hence a vacancy was expected to behave as an acceptor or an electron trap whereas an interstitial atom was expected to behave as a donor or a hole trap. However, examination of the conductivity σ *vs* bombardment time curves for n-type Ge revealed that extrapolation of the initial linear slope to zero conductivity gave a value of exposure which is only about one-half of that required to produce the conductivity minimum or intrinsic behavior. This behavior would seem to indicate the presence of two electron trapping centers, of which one is rather shallow. It was on the basis of this observation that James and Lark-Horovitz considered the possibility of multiple ionization. They find that, in a lattice with as high a dielectric constant as that of Ge, one might indeed expect states corresponding to the first and second ionization energies of the interstitial atom to lie in the forbidden energy band. Similarly, the energy required to put as many as two electrons into a vacant site is expected to lie in the forbidden gap. When both the interstitial and vacancy are present simultaneously, the electrons arising from the interstitial atoms are redistributed among all of the localized states to positions of lowest energy. Hence, for Ge they find the following levels of localized states: (1) a shallow vacant level corresponding to the first ionization of the interstitial atom which is estimated to lie $\sim$0.05 ev below the bottom of the conduction band; (2) a deep vacant level below the middle of the conduction band which arises from either the second ionization of the interstitial or the second ionization of the vacancy; and (3) the two remaining levels, which are occupied and which lie near the top of the valence band. Because of the complex nature of the wave functions in the diamond lattice and because of the large perturbing effect of the defects, it is impossible to locate the levels any more precisely in the band scheme from theoretical considerations alone. It is evident, however, that, since their relative positions are sensitive to both dielectric constant and gap width, the situation might be expected to change markedly from one diamond lattice semiconductor to another.

Since in the present paper we are concerned with bombarded n-type Ge, only the vacant levels are of interest: One shallow level of electron traps which is only partly effective in removing electrons and a deep level which is completely effective. We assume that all chemical impurities are completely ionized (a good assumption for temperatures above 77°K for the usual doping agents) and that the intrinsic process is negligible over the whole range of consideration. The electron concentration is given by

$$n=n^0-N_s^- - N, \tag{1}$$

where n^0 is the initial electron concentration, N_s^- is the concentration of occupied shallow traps, and N is the concentration of deep traps (which is identically equal to the Frenkel defect concentration). From the law of mass action it can be shown that N_s^- is given by

$$N_s^-=nNK_s/(1+nK_s), \tag{2}$$

where the equilibrium constant for the shallow trapping process (trap+electron$\rightleftharpoons$occupied trap) is given by

$$K_s=\frac{h^2e^{\epsilon_s/kT}}{\gamma(2\pi m_e kT)^{\frac{3}{2}}}, \tag{3}$$

in which ϵ_s is the depth of the shallow traps, m_e is the appropriate effective mass, and γ is the ratio of the statistical weights of the reactants to that of the product.[13] For the case in question the shallow trap is identified with a singly ionized interstitial atom. Hence $\gamma=4$. Substitution of Eq. (2) in Eq. (1) yields a quadratic in n, the solution of which is

$$n=\frac{(n^0-2N)K_s-1+\{[(n^0-2N)K_s-1]^2+4K_s(n^0-N)\}^{\frac{1}{2}}}{2K_s}. \tag{4}$$

Equation (4) may be used to test the two-level model.

[13] J. H. Crawford, Jr., and D. K. Holmes, Proc. Phys. Soc. London, **A67**, 294 (1954).

TABLE I. Values of K_s and ϵ_s obtained from initial rates of change of n during bombardment calculated from the simple two-acceptor-level model.

Sample	$(dn/dN)_{N=0}$	n^0 cm^{-3}	Temperature °K	K_s $cm^3\times10^{16}$	ϵ_s ev
1	1.42	8.9×10^{14}	304	6.95	0.213
2	1.63	2.03×10^{15}	300	8.40	0.205
3	1.67	7.4×10^{15}	313	2.74	0.194
4	1.85	1.12×10^{16}	313	5.05	0.211
5	1.74	1.18×10^{16}	309	2.41	0.187
6	1.76	1.21×10^{16}	313	2.54	0.193
7	1.75	1.24×10^{16}	313	2.42	0.191
8	1.86	2.02×10^{16}	309	3.04	0.194
9	2.07	1.58×10^{16}	313	...	...
10	2.50	2.43×10^{17}	300	...	...
11	1.87	2.92×10^{14}	195	229.0	0.184
				Average	0.197

III. DEFECT STATES IN n-TYPE Ge

It is possible to determine K_s and hence ϵ_s by three independent approaches. These are: (1) the variation of the initial slope as a function of n^0 of the n *vs* bombardment curve, (2) the application of Eq. (4) to the bombardment curve over the entire n-type range, and (3) the temperature dependence of electron concentration in bombarded Ge. If the model is valid, each approach should yield the same value for ϵ_s. We shall consider each of these in turn.

A. Initial Slopes of Bombardment Curves

It is evident from Eq. (4) that the initial rate of change of n with Frenkel defect concentration is

$$[dn/dN]_{N=0} = -(1+2K_sn^0)/(1+K_sn^0). \qquad (5)$$

This rate is directly proportional to the initial change of conductivity σ per incident fast neutron, provided that the initial decrease in mobility is small compared to the initial rate of electron removal. If it is assumed that the defect concentration at the minimum of the σ *vs* $(nvt)_f$[14] curve is equal to the initial electron concentration,[15] $[dn/dN]_{N=0}$ is directly available from experiment and K_s may be determined from Eq. (5). ϵ_s may then be readily determined if m_e is known. For m_e we have used the indications of cyclotron resonance measurements of Lax and co-workers[16] which include the effect of spatial degeneracy of energy surfaces in K-space[17]:

$$m_e = [\omega_s^2 m_x m_y m_z]^{\frac{1}{3}} = 0.51 m_0; \quad \omega_s = 4.$$

[14] $(nvt)_f$ is defined as the weighted average integrated flux of those neutrons capable of displacing atoms. The absolute values may be in error by as much as a factor of two. Relatively, however, the scale used here is consistent with that used in references 1–4.

[15] This is not exactly true as was pointed out in reference 2, since the conductivity minimum does not correspond to the intrinsic condition ($p=n$) but rather to $p=bn$ where b is the ratio of electron mobility to hole mobility. For the present application, however, the assumption is a good approximation.

[16] Lax, Zeiger, Dexter, and Rosenblum, Phys. Rev. **93**, 1418(L) (1954).

[17] We are indebted to H. C. Schweinler for pointing out this relationship.

Using these values in Eq. (3) leads to

$$\epsilon_s = 8.63\times10^{-5}T[34.42+(\ln K_s)T^{\frac{3}{2}}]. \qquad (6)$$

The results of analysis of initial slopes of σ *vs* $(nvt)_f$ curves for a number of n-type samples exposed under a variety of conditions are listed in Table I. It is evident from the values of ϵ_s that reasonably consistent results are obtained using this model. Samples 9 and 10, which do not yield agreement, exhibit a very broad minimum in the σ *vs* $(nvt)_f$ curve and apparently have an inhomogeneous impurity distribution. If such is the case, the minimum would be displaced toward longer exposures and would no longer correspond to $N=n^0$. The data for sample 11 were obtained at -78°C and reasonable agreement is indicated even at this temperature.

B. Fitting the Bombardment Curve

Equation (4) has also been used to calculate a bombardment curve using K_s as the adjustable parameter. The calculated points are compared with the experimental curve in Fig. 1. For purposes of convenience the concentration of electrons during the bombardment is expressed relative to the initial concentration (n/n^0) and the exposure is given in terms of N/n^0 under the assumption that $N=n^0$ at the point of conversion to p-type (the conductivity

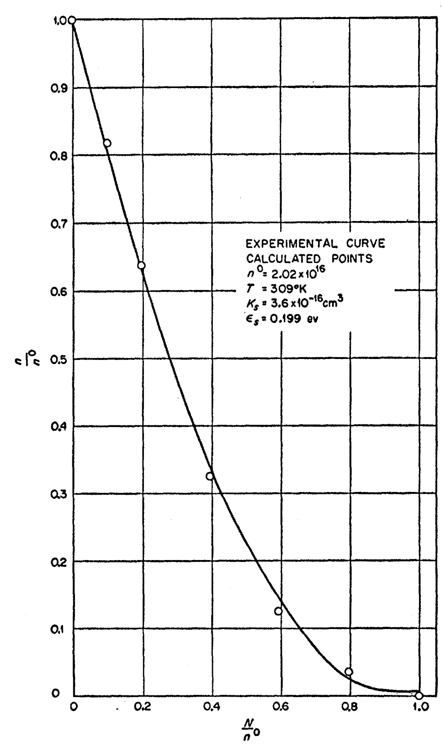

FIG. 1. Electron concentration *vs* defect concentration produced by bombardment of n-type germanium. For convenience the concentrations are expressed in units relative to the initial electron concentration. The points are calculated from Eq. (4) using the values of parameters shown on the figure.

minimum).[15] Since the electron concentration is inferred from the conductivity during irradiation using the initial value of mobility, it is inherently assumed that the mobility is unaffected by bombardment. As will be shown later this is not necessarily a good assumption since even at room temperature a considerable decrease in mobility may be expected for an exposure of this magnitude $[(nvt)_f=1\times10^{16}\text{ cm}^{-2}]$. However, for the initial half of the curve and at the end, this assumption is expected to be reasonably good. A rather good fit to the curve was obtained using $K_s=3.6\times10^{-6}$ cm^3 which corresponds to $\epsilon_s=0.199$ ev. This value is in good agreement with those listed in Table I.

C. Temperature Dependence of n

It is possible to test the model more stringently by using Eq. (4) to calculate the temperature dependence of electron concentration in a bombarded n-type sample. For $n>2N$, Eq. (4) predicts a transition with increasing temperature from a condition in which all the shallow traps are occupied to one in which these are completely empty. Since in the derivation of Eq. (4) the intrinsic process has been neglected and it is assumed that all chemical donors are completely ionized, n is temperature independent both above and below this transition region. When all shallow traps are filled, $n=n^0-2N$, a condition which readily permits fixing the value of N from experimental data.

Curves of log n vs $1/T$ for an n-type sample after various periods of irradiation at ~45°C and heat

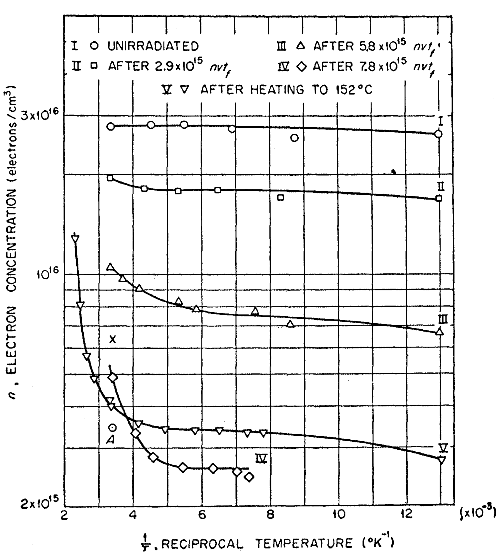

FIG. 2. Electron concentration in n-type Ge vs reciprocal temperature after various periods of exposure and subsequent treatment. The curves were obtained as follows: I on the original, II after $(nvt)_f=2.9\times10^{15}$ cm^{-2}, III after 5.8×10^{15} cm^{-2}, and IV after 7.8×10^{15} cm^{-2}. All exposures were carried out at ~45°C. Point A was obtained after standing at room temperature for one month subsequent to the final exposure and curve V was taken after heating to 152°C for ~10 min.

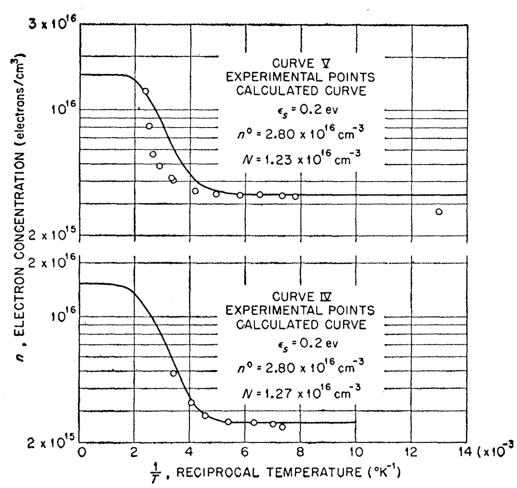

FIG. 3. Comparison of experiment with the two-level model. Equation (4) has been used to calculate Curves IV and V of Fig. 2 using 0.20 ev for the shallow trap depth. Values of N and n^0 inferred from experiment are indicated on the figure for the two curves.

treatment are shown in Fig. 2. The values of n were obtained from Hall coefficient measurements and corrected for impurity scattering by the method of Johnson and Lark-Horovitz[18] as modified by Fan.[5] Although there is evidence that the additional scattering resulting from bombardment may not be of a charge center type (see below), it is evident from Curve I and the low-temperature portions of the curves after bombardment that this method of correction yields the expected temperature dependence for n arising from chemical impurities. Curve I is that of the sample before bombardment; Curves II, III, and IV were taken after exposures of $(nvt)_f=2.9\times10^{15}$, 5.8×10^{15}, and 7.8×10^{15} cm^{-2}, respectively. The encircled point (point A) was measured after the specimen had stood at room temperature for one month subsequent to the final exposure and Curve V was taken during cooling after heating the specimen to 152°C for a short period of time (~10 min). In Fig. 3 the curves calculated from Eq. (4) by using $\epsilon_s=0.199$ ev are compared with the experimental points of Curves IV and V of Fig. 2. Curve IV yields excellent agreement with the model using $n^0=2.80\times10^{16}$ cm^{-13} and $N=1.27\times10^{16}$ cm^{-3}.

In the case of Curve V, however, with $N=1.23\times10^{16}$ cm^{-3} agreement is not so good since the model predicts a much more rapid initial rise of n with temperature in the transition range. At first glance it might appear that the heating has not only caused some annealing, increasing the low temperature value of n from 2.6×10^{15} to 3.4×10^{15} cm^{-3}, but has in addition increased the shallow trap depth. Closer examination, however, reveals that after standing for one month the electron concentration at room temperature decreased from 4.9×10^{15} to 3.5×10^{15} cm^{-3}. This change is in the opposite direction

[18] V. A. Johnson and K. Lark-Horovitz, Phys. Rev. 82, 977 (1951).

from that normally expected to accompany the annealing of lattice defects. Such a decrease cannot be explained as being caused by the introduction of Ga by nuclear transmutation[19] since the maximum Ga concentration expected for the exposure in question is only $\sim 2\times 10^{14}$ cm^{-3}. Consequently, it is probable that the apparent increase in shallow trap depth observed subsequent to heating actually resulted from some process which occurred during the one-month aging period at room temperature. One process which suggests itself is a clustering of defects, possibly interstitials. If such is the case, the shallow-trap concentration would no longer be equal to but rather less than the deep-trap concentration making Eq. (4) invalid. This hypothesis receives support from studies of the annealing kinetics of quenched-in lattice defects[20] and from current studies of room temperature aging of fast neutron bombarded Ge.[21]

In summary, it appears that the model suggested by James and Lark-Horovitz is justified experimentally when applied to n-type Ge irradiated at or near room temperature. Tests of the model using three different approaches all give consistent results and the shallow state appears to lie ~ 0.2 ev below the bottom of the conduction band. This value is greater by a factor of four than the theoretically predicted value (~ 0.05 ev). The Purdue group finds similar indications in deuteron bombarded n-type Ge.[7]

IV. MOBILITY IN BOMBARDED n-TYPE Ge

The Hall coefficient and resistivity measurements taken after successive exposures for several specimens permit an examination of the additional charge carrier scattering introduced by bombardment. In Fig. 4, the Hall mobility[22] μ_H of the sample of Figs. 2 and 3 is plotted as a function of temperature after each exposure. Curve I was obtained before bombardment, Curves II, III, IV, and V were taken after cumulative exposures of $(nvt)_f = 2.9\times 10^{15}$, 5.8×10^{15}, 7.2×10^{15} and 7.8×10^{15} cm^{-2}, respectively, and Curve VI was obtained after heating the specimen to 152°C for ~ 10 min subsequent to the total exposure and aging at room temperature for one month. The mobility is decreased by bombardment over the whole temperature range. After a total exposure of 7.8×10^{15} cm^{-2} μ_H is decreased by a factor of two at room temperature and by more than an order of magnitude at 77°K. The negative temperature coefficient, evident in Curve I, which is characteristic of charge carrier scattering by thermal vibrations of the lattice ($\mu_H \propto T^{-\frac{3}{2}}$) is rapidly removed by exposure and Curve V possesses approximately a T^2 dependence. This behavior indicates that irradiation introduces additional scattering centers which scatter carriers more effectively at low temperature. It is interesting to note that the combination of room-temperature aging and the short anneal subsequent to exposure markedly improved the mobility over the entire range and restored, to an appreciable extent, the lattice-scattering temperature dependence. This behavior, coupled with indications of the previous section that the same combination of conditions subsequent to exposure apparently increased the depth of the shallow electron traps, seems to indicate that low-temperature annealing produces more extensive healing or rearrangement of lattice disorder than was previously expected.

Figure 5 is a plot of μ_H *vs* T for a specimen with a large initial electron concentration ($n^0 \sim 7\times 10^{17}$ cm^{-3}) subjected to much heavier exposures. Curve I refers to the original specimen and Curves II, III, IV, V, and VI were obtained after fast neutron exposures of 7.2×10^{16}, 1.27×10^{17}, 1.61×10^{17}, 1.84×10^{17} and 2.01×10^{17} cm^{-2}, respectively. These curves exhibit the same qualitative behavior as those of Fig. 4, however, a considerably greater exposure was necessary for this specimen to remove lattice scattering behavior in the high-temperature range. In fact Curve II, which was obtained after an exposure about ten times as long as that of Curve V of Fig. 4, still shows a definite maximum, whereas Curve V shows almost no trace of the lattice-scattering process. This behavior seems to indicate that the charge carrier concentration is an important variable in the scattering process introduced by irradiation. Another important feature not apparent from Fig. 4 is that the temperature dependence of μ_H is enhanced by exposure. Whereas in curve V of Fig. 4 μ_H is apparently dependent on T^2 in the low-temperature region, Curves V and VI of Fig. 5 yield approximate $T^{3.2}$ and $T^{6.3}$ dependences, respectively. Hence a much more complex functional dependence of μ_H on T is indicated than a simple power law

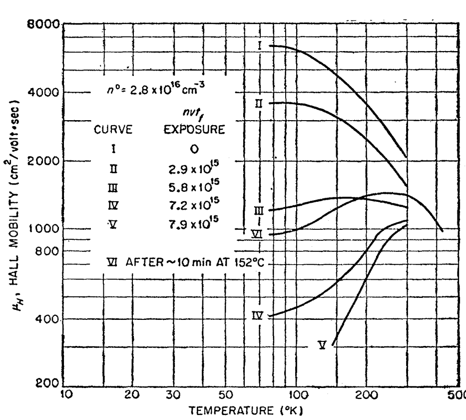

FIG. 4. Hall mobility *vs* temperature for the specimen of Fig. 2 after the indicated periods of exposure. Curve VI was obtained after standing for one month at room temperature and a short anneal at 152°C subsequent to the total exposure.

[19] Cleland, Lark-Horovitz, and Pigg, Phys. Rev. **78**, 814 (1950).
[20] S. Mayburg, Phys. Rev. **95**, 38 (1954).
[21] Cleland, Crawford, and Pigg (unpublished data).
[22] μ_H is defined as $\mu_H = R\sigma$ and is related to the true drift mobility μ by $\mu_H/\mu = r$, where r is the Hall parameter ($r = n_e eR$). In the case of spherical energy surfaces, for lattice scattering only, $r = 1.18$, whereas, for purely charge center scattering $r = 1.93$. [W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), pp. 278, 279].

($T^{\frac{3}{2}}$) which would be expected for charge-center scattering according to either the Conwell-Weisskopf theory[23] or the theory of Brooks[24] and Herring.[25]

Since as a general rule the extraneous scattering becomes predominant compared to lattice scattering at sufficiently low temperatures, $1/\mu_H$ at 77°K is expected to be approximately proportional to the scattering probability per unit time arising from charged impurities originally present and the additional scattering processes introduced by bombardment. Figure 6 shows the variation of $1/\mu_H$ at 77°K with exposure for three n-type specimens. Curve I refers to the specimen of Figs. 2, 3, and 4 in which $n^0=2.7\times10^{16}$ cm^{-3}, Curve II refers to a sample with $n^0=3.8\times10^{16}$ cm^{-3}, and Curve III was obtained on the sample of Fig. 5 ($n^0=7\times10^{17}$ cm^{-3}). In every case the scattering probability increases with exposure at much more than a linear rate. Furthermore, the rate of increase is greater the smaller the initial electron concentration.

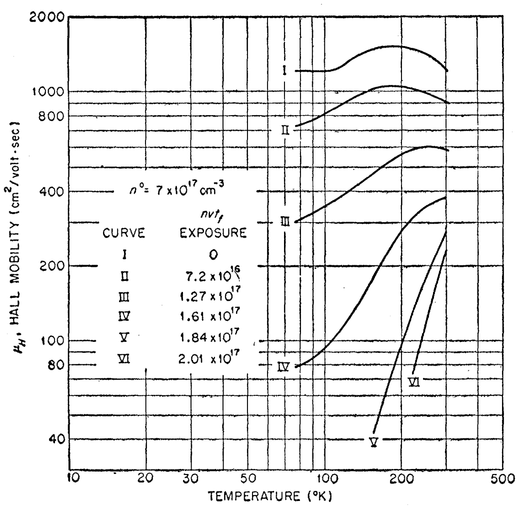

FIG. 5. Hall mobility *vs* temperature for n-type Ge after the indicated exposures, for a specimen with $n^0=7\times10^{17}$ cm^{-3}.

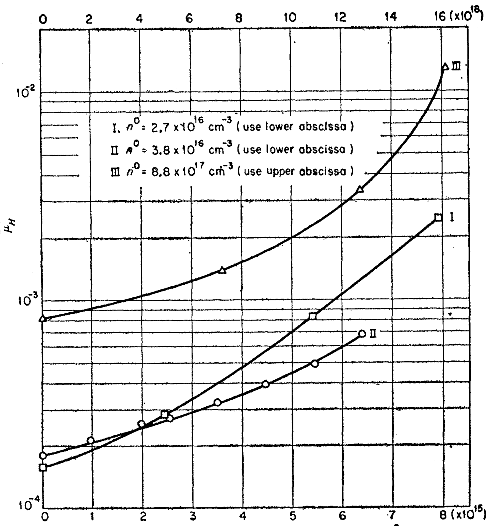

FIG. 6. Reciprocal of Hall mobility *vs* integrated fast-neutron flux for three n-type Ge specimens at 77°K. Note that the scale of the abscissa for Curve III is compressed by a factor of 20 relative to that of Curves I and II.

In order to make any definite statement concerning the nature of the scattering process or processes associated with the radiation-disarranged lattice, it is necessary to separate the effects of such from other known scattering mechanisms, i.e., scattering from lattice vibrations, charge centers, etc.[25] The information presently available is too scanty to warrant such a treatment. Consequently we shall only point out certain features for which any proposed scattering mechanism must account.

(1) There appears to be a large and apparently complex temperature dependence of μ_H which increases with bombardment (see Figs. 4 and 5). This behavior cannot be explained by the usual types of localized energy-dependent scattering mechanisms. Since the defects produced by bombardment are not expected to be completely randomly distributed, but to some extent localized in the region of the primary collision, it is reasonable to expect localized fluctuations in the defect concentration. These may give rise to small fluctuations in the electrostatic potential in the crystal and hence in the bottom of the conduction band. If such is the case, a complex dependence of scattering probability on the energy of the carrier would not be surprising.

(2) The rate of change of scattering probability with bombardment is sensitive to the electron concentration. Consequently, screening of localized charge fluctuations by charge carriers appears to be important.

(3) The scattering probability increases at a greater than linear rate (even greater than an exponential rate, see Fig. 6) with exposure. This behavior may also be related to the postulated fluctuations in defect concentration and to the extent of screening.

Studies of mobility in deuteron bombarded n-type Ge[5] seem to indicate that the decrease resulting from bombardment can be explained on the basis of charged scattering centers alone. This difference between deuteron and fast-neutron irradiated Ge may be due to a difference in the distribution of defects in the vicinity of the primary collision.

V. RESULTS OF LOW-TEMPERATURE BOMBARDMENT

Several n-type Ge samples have been irradiated in the low-temperature facility of the ORNL graphite reactor at temperatures below −100°C. The conductivity decreases with bombardment, indicating that electron removal by bombardment-produced acceptors is the predominant effect. The initial rates of electron removal,

[23] E. M. Conwell and V. F. Weisskopf, Phys. Rev. 77, 388 (1950).
[24] H. Brooks, Phys. Rev. 83, 879 (1951).
[25] P. P. Debye and E. M. Conwell, Phys. Rev. 93, 693 (1954).

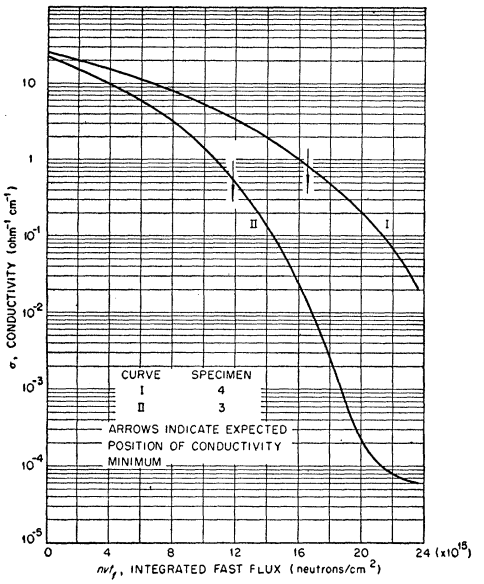

FIG. 7. Log conductivity *vs* integrated fast neutron flux for two specimens of n-type Ge (3 and 4 of Table II) exposed at 120°K. Curves I and II refer to specimens with $n^0 = 3.25 \times 10^{16}$ and 2.36×10^{16} cm^{-3} respectively. The arrows indicate the expected positions of the minima for a linear rate of introduction of Frenkel defects assuming the mobility to be unaffected by bombardment.

calculated under the assumption that the initial rate of decrease of μ_e is negligible,[26] are listed in Table II together with the initial electron concentrations n^0 and the temperatures of exposure T_e. The rate of removal is higher at these temperatures than at room temperature[2] by a factor of about 1.5. A portion of the enhanced rate of removal may be caused by the complete effectiveness of the shallow vacant states (see Sec. III). Inspection of Table I and Eq. (4), however, reveals that for the values of n^0 in question such a process can account for only 20 percent or less of the enhancement. It is uncertain whether the remaining 30 percent of the enhancement is because of an appreciable initial rate of decrease of μ_e with bombardment,[26] rendering the values of $[dn/d(nvt)_f]_{t=0}$ in Table II too large, or whether a portion of the acceptors introduced at low temperatures are unstable in the room temperature range.

Plots of log σ *vs* $(nvt)_f$ for Samples 3 and 4 of Table II are shown in Fig. 7. Sample 3 was bombarded to virtually the conductivity minimum, whereas Sample 4 was still definitely n-type after the exposure. Positions of the conductivity minima expected for a linear rate of defect introduction consistent with the values of $[dn/d(nvt)_f]$ of Table II are indicated by arrows. Since these do not correspond to the experimental positions of the minima, it appears that either the rate of defect introduction decreases with increasing exposure or the initial rate of change of mobility is comparable to the rate of electron removal.[26] Whatever the reason for this difference, the shape of the σ *vs* $(nvt)_f$ curve does not conform to expectation according to Eq. (4) in that it deviates from the expected linear behavior toward a less rapid decrease early in the bombardment. Consequently, it appears that the two-level vacant-state model is not adequate at these temperatures.

Even though the period of exposure covered by Fig. 7 is expected to produce a marked decrease in μ_e at these temperatures, the conductivity minimum approached by Sample 3 is several orders of magnitude higher than the intrinsic value calculated using the pre-bombardment value of μ_e. This seems to indicate that the intense ionizing radiation in the reactor excites an appreciable concentration of electron-hole pairs. This explanation is supported by the observation that immediately after reactor shut-down both specimens showed a further decrease of σ with time at constant temperature (114°K). The initial decrease was quite rapid, and was followed by a slower decay which was approximately exponential with a time constant of ~10 min. Hence the magnitude of σ reflects the expected variation of γ radiation intensity after reactor shut-down.[27] Since the concentration of excess electron-hole pairs is expected to be proportional to the exciting intensity, it is concluded that at least a portion of the excess conductivity is produced by photoelectric excitation.

In addition to the photoexcitation of electron-hole pairs, trapping of minority carriers will make an additional contribution to the photoconductivity.[28,29] Brown *et al.*[30] report that high energy electron bombardment at 78°K introduces minority carrier traps in appreciable concentrations into both n- and p-type Ge. There is convincing evidence that low-temperature fast neutron bombardment also introduces hole traps

TABLE II. Rates of removal of conduction electrons at low temperatures.

Sample	n^0(cm^{-3})	T_e(°C)	$[dn/d(nvt)_f]_{t=0}$
1	1.10×10^{18}	−157	−6.4
2	1.36×10^{17}	−157	−4.8
3	2.36×10^{16}	−153	−4.8
4	3.25×10^{16}	−153	−4.0
			Average = −5.0

[26] This assumption may not be a good one at low temperatures. If μ_e before exposure is limited entirely by charged impurity scattering and if the additional scattering introduced during the early stages of bombardment is of this type, the initial decrease of σ caused by a decrease in μ_e is expected to be approximately one-half that produced by electron removal according to the Conwell-Weisskopf theory (reference 23) and the two-level model used in Sec. III. For the samples of Table I the impurity scattering contribution to μ_e is appreciable at these temperatures.

[27] Immediately after shut-down, that portion of the γ-ray flux which arises from (n,γ) and fission reactions disappears. An additional rapid decrease results from the decay of short-lived activities. After this initial rapid decrease, the γ-ray intensity is expected to decay at a rather slow, uniform rate.

[28] J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953).

[29] H. Y. Fan, Phys. Rev. **92**, 1424 (1953).

[30] Brown, Fletcher, and Wright, Phys. Rev. **96**, 834 (1954).

into n-type Ge. After irradiation $[(nvt)_f=2.4\times10^{16}$ $cm^{-2}]$ and standing at 114°K for 40 min, Sample 4 was warmed in the reactor at a relatively uniform rate ($\sim$1°C min^{-1}) to 260°K and then recooled. The σ *vs* T curves are shown in Fig. 8, the solid and dashed curves referring to the warming and cooling operations, respectively. Two well-defined maxima falling at 134°K and 165°K are observed during warming. After the second maximum σ falls to a minimum value at $\sim$195°K and increases rapidly with further heating. The oscillatory behavior is interpreted as the successive escape of trapped holes (and their subsequent recombination with excess electrons) from two discrete trapping levels of different depth. It is assumed that at 114°K the γ-ray intensity is sufficient to saturate these traps and that the rate of heating is sufficiently low to preserve steady-state conditions. As the temperature is raised, a point is reached at which the rate of release of holes from traps becomes comparable to the rate of trapping and saturation is no longer possible. With further heating the traps empty rapidly, the transition from a filled to an empty condition occurring over a relatively narrow temperature range. Although it is possible in principle to calculate the trap depth ϵ_t from the position of the inflection point,[29] the situation is complicated in the present case by the strong and unknown temperature dependences of μ_e and n in the range of interest. Consequently, it is impossible to make a reliable estimate of the trap depths in question.

On cooling at about the same rate, one would expect the reappearance of the same maxima under steady-state conditions of excitation provided the traps are still present and the γ-ray intensity is unchanged. The cooling curve in Fig. 8 shows no such behavior and it is concluded that those traps which are responsible for the oscillatory behavior of the warming curve have annealed. This result is consistent with the findings on electron bombarded Ge.[30] That some sort of annealing has occurred during the temperature excursion is evident from the position of the cooling curve relative to the heating curve. The cooling curve lies appreciably above the warming curve at temperatures above 173°K. It crosses the warming curve at that point and attains a value at 113°K of only about one-half the value before heating. The increase in σ in the range above 173°K can be caused either by an improvement in μ_e which had been decreased by bombardment or by the annealing of a portion of the defects responsible for removing electrons, or more probably both. A decrease in σ after heating at the low temperature end of the curve is expected if the hole traps have annealed, since an important source of photo conductivity is thereby removed. It was possible to retrace the cooling curve at least as high as 200°K by subsequent warming.

The behavior attributed to trapping described in the aforementioned, was confirmed by the warming of an n-type sample in which σ was reduced from 52 to 2.3 ohm^{-1} cm^{-1} by bombardment at 116°K. Again two

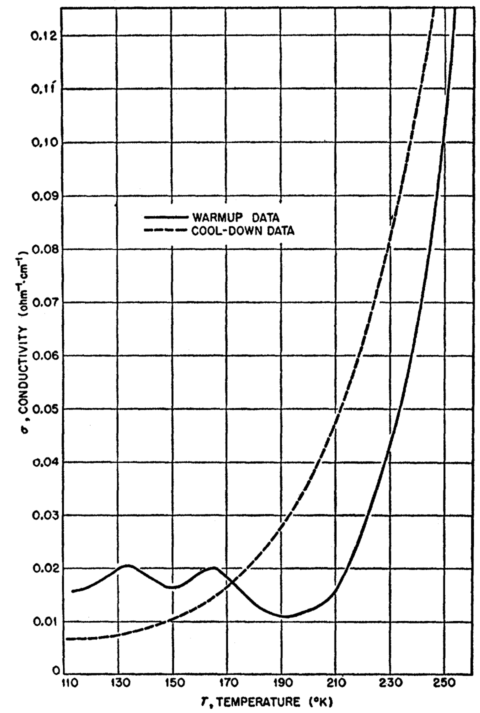

FIG. 8. Conductivity *vs* temperature for an n-type specimen of Ge obtained on warming and cooling after an exposure of $\sim3\times10^{16}$ neutrons cm^{-2} at 116($\pm$2)°K.

maxima in the σ *vs* T curve were observed during warming in the same temperature range. It is interesting to note in this connection that Sample 3, which was bombarded almost to the conductivity minimum and hence was essentially intrinsic, showed only a small indication of the first maximum and one at all of the second. Such behavior would be expected when the Fermi level lies deep in the forbidden band or near one of the trapping levels.[29]

VI. DISCUSSION

In the foregoing treatment the Frenkel-defect energy-level model of James and Lark-Horovitz[10] was extensively used as a basis for analyzing experimental data. This choice was considered reasonable because of the successful use of the model in explaining qualitatively the results obtained on bombarded Ge and Si. These studies indeed indicate that the predominant effect of fast neutron bombardment in the room temperature range is the introduction of two groups of vacant states, one shallow and one deep, which are consistent with the predictions of the model. Consequently, it is reasonable to conclude that disorder produced by bombardment at or near room temperature may be described as interstitial-vacancy pairs. The difference between the observed shallow-trap depth of $\sim$0.20 ev and the theoretically predicted depth (0.05 ev) is not considered serious in view of the approximations involved in the calculation of the latter.

It is also possible to explain in terms of the model in question the effect of room-temperature aging of irradiated *n*-type Ge. On standing for appreciable periods of time at room temperature, bombarded specimens exhibit a further decrease in electron concentration. This behavior can be understood if it is postulated that, in addition to the expected recombination of interstitials and vacancies there is an appreciable tendency at this temperature for the interstitials to be removed by some process such as clustering or migration to dislocations. Since removal of an interstitial also removes those electrons and localized states associated with it, the shallow trap is effectively replaced by one near the top of the valence band which is associated with the vacancy. It was pointed out that this hypothesis, which requires that the interstitial be the mobile component of the defect, is consistent with findings of Mayburg[20] and much additional support has been obtained from studies of the behavior of bombarded *p*-type Ge on room-temperature annealing.[31]

The results of exposure at low temperature ($<-100°C$) are not in accord with the model. The σ *vs* $(nvt)_f$ curves obtained at these temperatures exhibit a marked upward concavity in the range wherein a linear decrease is predicted by Eq. (4). This lack of agreement apparently indicates that the description of lattice disorder introduced at low temperature completely in terms of Frenkel defects is no longer valid. It seems reasonable to conclude that restriction of atomic motion by the lower thermal energy of the lattice leads to a more complex configuration of disorder. On warming this disorder of low thermal stability would be expected to rearrange to configurations of higher stability, e.g., isolated interstitials and vacancies. That some type of rearrangement takes place is indicated by the disappearance of minority-carrier traps during warming at temperatures below 260°K.

Although the work presented here and other information[31] on *p*-type Ge support strongly the Frenkel-defect model of energy levels, it is felt that this picture of fast-neutron-produced disorder should not be accepted without some reservation. In order for the model to be completely applicable, the interstitials and vacancies must be more or less randomly distributed throughout the lattice. As was pointed out earlier, one does not expect bombardment produced defects to be randomly distributed but rather to be localized to some extent in the region of the primary collision, with a resulting localized variation in carrier concentration. Because of the continuous neutron energy spectrum, any such fluctuation in defect density would itself be expected to vary widely both as to radial extent and absolute magnitude. Consequently, the nature of the effect on the over-all carrier concentration to be expected from the introduction of such a distribution of disorder is uncertain. The only manifestation which might be specifically attributed to such a situation is possibly the effect of bombardment on the electron mobility. As was postulated above, the large negative temperature dependence of the scattering probability and its marked dependence on electron concentration may result from localized fluctuations in the bottom of the conduction band. Additional experiments are necessary before the questions raised here can be answered unambiguously.

The nature of the annealable hole traps which produce photoconductivity during and subsequent to low-temperature ($<-100°C$) exposure is not at all clear. Since they disappear on warming, it is reasonable to conclude that they cannot be identified with those hole traps, stable at room temperature, which have been observed in *p*-type Ge.[3] The two groups of traps in question empty over a narrow temperature range. Therefore, they appear to have a discrete depth. We can only say that they are apparently associated with two definite types of composite defects. It should be pointed out that in addition to these there may be shallower traps which do not anneal and which become apparent at lower temperatures. Indications of these have been obtained at liquid nitrogen temperature on *n*-type specimens exposed at room temperature.[32] A more detailed study of minority-carrier trapping and associated photoconductivity in bombarded Ge is currently being carried out.

The authors are indebted to Miss Louise Roth of Purdue University who furnished the single crystal specimens of Ge used in these investigations. They also wish to thank D. K. Holmes and H. C. Schweinler of this laboratory for their discussions and critical comment. The assistance of E. S. Schwartz in some of the measurements is gratefully acknowledged.

[31] Cleland, Crawford, and Pigg (to be published).

[32] Cleland, Crawford, and Pigg (unpublished data).