Electron Irradiation of p-Type Germanium at 4.2°K*

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Degenerate p-type germanium samples ($p_0 \simeq 10^{18}$ cm^{-3}) have been irradiated at 4.2°K with 4.5-MeV electrons from a microwave linear accelerator. Measurements of electrical conductivity and Hall effect have been made during the irradiation and later infrared illumination and heating. Small changes occur during the irradiation and may be described by a carrier removal rate of 0.4 cm^{-1}. Under the same conditions n-type Ge has a removal rate 25 times larger. This result is also in contrast to the case of 1.1-MeV electron irradiation of p-type Ge, where the changes are immeasurably small. Subsequent illumination-induced changes lower the conductivity and may be represented as the sum of two components, each exponential in the time of illumination. Two processes may also be observed during the heating. One, occurring between 30 and 90°K, restores the conductivity; another, between 70 and 110°K, has the reverse effect. Observation of both of the annealing processes is related to the duration of prior illumination. From this information relationships between the annealing processes and the stages of illumination-induced change are deduced. A crude analysis of the annealing is attempted and possibilities for the mechanisms are discussed.

I. INTRODUCTION

PREVIOUS investigations have shown there to be startling differences in the behavior of the electrical characteristics of n- and p-type germanium during high-energy electron irradiation. MacKay and Klontz[1] reported that at 4.2°K the changes in p type during 1.1-MeV irradiation were immeasurably small. Changes occurring in n type on the other hand are quite easily measured. The difference in behavior between n and p type at 78°K is still considerable, a factor of about 4 or 5 at 1.1 MeV. The above authors have shown how,[2,3] by developing a model originally proposed by Wertheim[4] and themselves, differences between the damage in n and p type can be understood qualitatively.

Changes occurring during α-particle irradiation at 4.2°K and subsequent heating have been described by Gobeli.[5] Effects of illumination on p type following 1.0-MeV electron irradiation at 78°K have been reported by Brown *et al.*[6] The same effect has also been studied by Callcott[7] and by Flanagan.[8]

The present work was initiated parly to investigate whether the apparent resistance of p type towards damage extended to energies higher than 1.1 MeV. Experiments have been carried out at just one energy, 4.5 MeV. It will not be possible to outline definitive models for the defects which have been observed. Indeed, only the most tentative suggestions can be made for what they may be. The text will therefore be, in the main, a presentation of results with an attempt to classify them.

II. EXPERIMENTAL

The gross features of the liquid-helium cryostat used in this work have recently been described by the author in collaboration with colleagues in this laboratory.[9] In operation the arrangement of the cryostat is very similar to that described by MacKay and Klontz.[1] The tailpiece rests between the poles of a Hall magnet. The beam tube passes through an axial hole in one pole-piece. A 1-mil Mylar window on the sample compartment, containing low pressure helium as exchange gas, allows electrons and light to enter. The vacuum of the cryostat is common with that of the 4.5-MeV microwave linear accelerator which is the electron beam source. A Globar (silicon-carbide glower) is used as an infrared light source. Its light is condensed by a concave mirror and enters the vacuum system through a thick germanium filter. A mirror can be inserted into the system to direct the light along the beam tube and onto the sample.

The samples are rectangular parallelipipeds approximately 2 mm×6 mm×100 μ thick. They are prepared from crystal slices by grinding and etching. Their broad face is a 110 plane. Probes for the electrical measurements consist of 1 mil copper wires attached with Ceroseal solder. The 1 mil wires are then attached to 3 mil wires and the whole assembly is supported on a Micro-Mod plug[10] which mates with a socket in the sample compartment.

All measurements are made at 4.2°K with the beam off, using a semiautomatic measuring unit. The readings are taken from a digital voltmeter (self-balancing potentiometer) which at maximum sensitivity responds to 10^{-7} V.

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[2] J. W. MacKay and E. E. Klontz, *Radiation Damage in Solids*, (International Atomic Energy Agency, Vienna, 1963), Vol. III, p. 27.
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[7] T. A. Callcott, M. Sc. thesis, Purdue University, 1961 (unpublished).
[8] T. M. Flanagan (private communication).
[9] J. E. Whitehouse *et al.*, Rev. Sci. Instr. **36**, 768 (1965).
[10] A product of the Amphenol-Borg Electronics Corporation.

III. RESULTS

It was intended that the material to be used would be degenerate at 4.2°K, thus avoiding carrier "freeze-out." Accordingly germanium with about 10^{18} Ga atoms per cm^3 was chosen. This material showed very little change in its conductivity in cooling from room temperature down to 78°K and then to 4.2°K. A result of using such material is, of course, that the Hall effect is very small. We have made measurements with reproducible accuracy no worse than 0.25%. However this is too great for some of the changes to be clearly seen so we will for much of the time refer only to the conductivity changes.

A. Changes During Irradiation

Two samples have been irradiated, each a number of times. Each irradiation was taken to a total dose of about 2×10^{16} electrons cm^{-2}. Between experiments a sample was warmed to room temperature. It has been

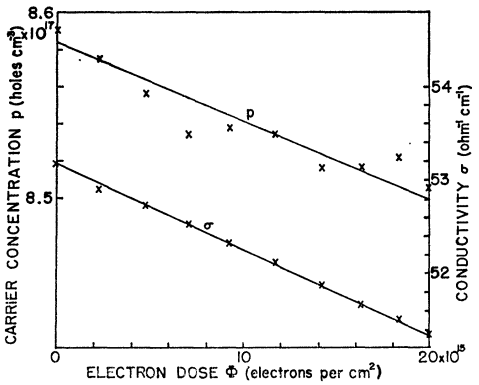

FIG. 1. The effect of 4.5-MeV electron irradiation on degenerate p-type germanium at 4.2°K.

possible to make fairly good Hall measurements during a number of the irradiations so that we may follow the carrier concentration as a function of the electron dose. We have taken for the approximate relationship of Hall coefficient to carrier concentration a single carrier formula with the ratio of Hall to drift mobility as unity. Carrier concentration versus electron dose for a typical case is shown in Fig. 1. The slope of the curve determines a "removal rate" of about 0.4 carriers per cm^3 removed per incident electron per cm^2. The accompanying conductivity change is also shown. There does not appear to be any effect of prior irradiation on the results.

For comparison an experiment on degenerate n-type ($n_0=3.2\times10^{17}$ cm^{-3}) was also conducted. The relation of carrier concentration to electron dose is essentially linear to a dose of 2×10^{16} cm^{-2} determining a removal rate of about 10 cm^{-1}. The ratio between n and p type in their removal rates measured during irradiation is therefore 25.

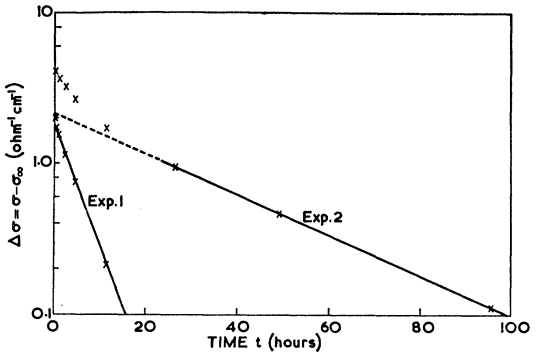

FIG. 2. The decrease in conductivity during infrared ($h\nu<E_G$) illumination after irradiation. σ_∞ is the estimated limiting conductivity for very long illumination times, it is chosen for the best fit of the data to straight lines on this plot. The lower line (Exp. 1) is obtained by subtracting Exp. 2 from the original data points.

B. Changes During Illumination

The change in the conductivity during subsequent illumination with infrared light ($h\nu<E_G$) is shown as a semilog plot for a typical case in Fig. 2. It will be seen that the change may be considered as the sum of two exponentials each contributing almost exactly one-half of the total change. We shall refer to these two components as Exp. 1 and Exp. 2, the faster and the slower, respectively.

C. Changes During Heating

Isochronal heating runs up to about 120°K have been conducted in a straightforward way following various periods of illumination. The temperature was held for 7 min at each point. The results are shown as cases (i) through (iii) in Fig. 3. A fourth, more detailed, experiment (case iv) is shown in Fig. 4.

In case (i) the heating followed prolonged illumina-

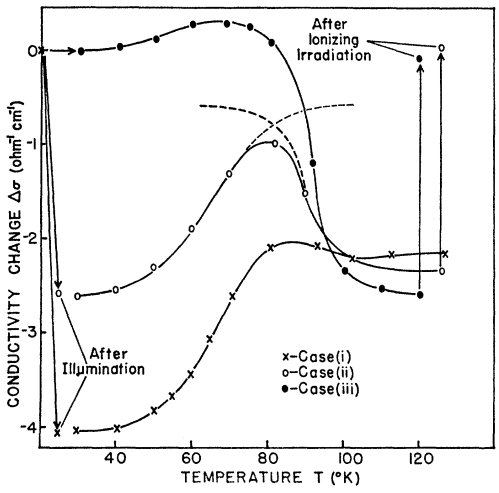

FIG. 3. Changes in conductivity due to heating after various periods of infrared illumination. The changes are measured with respect to the value immediately following the damaging irradiation

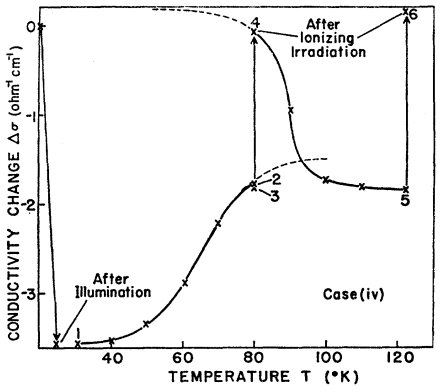

FIG. 4. The results of a composite experiment. A period of illumination and an ionizing irradiation were interposed following the 80°K point in an isochronal run started after prolonged illumination of the sample. The origin is chosen in the same way as for Fig. 3.

tion during which both exponentials 1 and 2 were driven essentially to completion. A process which restores about 50% of the illumination-induced change is observed. We shall refer to this as P1. In case (iii) the crystal was not illuminated before heating. Here a decrease in the conductivity occurs. We shall refer to this as P2. Case (ii) is the intermediate situation where prior illumination has removed most of Exp. 1 while leaving Exp. 2. Contributions from both P1 and P2 are evident. We attempt to show the magnitudes of the two processes in this case by means of a tentative graphical construction.

The composite experiment [case (iv)] proceeded initially as case (i). When it was considered that P1 would be complete an unsuccessful attempt was made to reverse the effect of P1 with illumination (point 3). Next, the sample was subject to a short electron irradiation, the major effect of which would be to create ionization. The conductivity was restored to a value the same as that immediately following the prolonged irradiation. Thereafter the experiment progressed in the same way as case (iii).

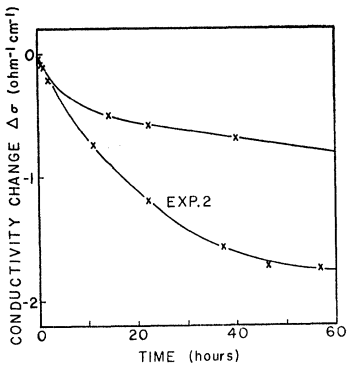

FIG. 5. The effect of illumination on conductivity after heating to 120°K. Exp. 2 (the longer lived component seen before heating) is shown for comparison. The changes are again referred to the immediate post-irradiation value of conductivity.

D. Further Changes

Following heating to 120°K an ionizing irradiation returns the conductivity to approximately the value it had immediately following the damaging irradiation. The effects which infrared illumination can then produce are shown in Fig. 5. For comparison Exp. 2 is shown on the same scale.

If the conductivity is again restored with an ionizing irradiation then a process which decreases conductivity is observed during an isochronal run (Fig. 6.). Two consecutive observations of this are shown together with a plot of P2 for the same sample.

IV. PRELIMINARY CONCLUSIONS

(a). During a damaging irradiation decreases in conductivity and carrier concentration occur, the rates of decrease depending linearly on the electron dose.

(b). Two processes Exp. 1 and Exp. 2 occur during subsequent illumination and contribute about equally to the induced change.

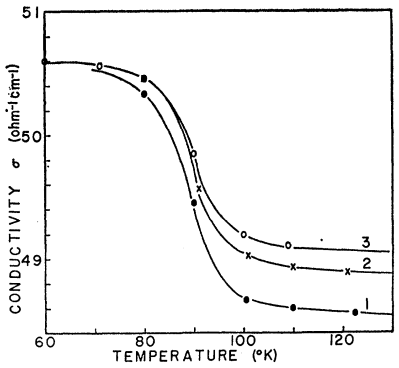

FIG. 6. Repeated observations of the effects of heating the same sample above 70°K. 1 is the first observation of P2 following a damaging irradiation. Between 1 and 2 the effect of illumination (Fig. 5) was investigated. 2 and 3 are then successive observations made by re-ionizing the sample with short electron irradiations.

(c). Two processes P1 and P2 also occur during heating.

(d). After heating to 120°K some of the defects may be further affected by illumination and heating, opposing changes can be produced by short (ionizing) irradiations. Since we are dealing with degenerate p type we conclude that these defects are temporary traps for minority carriers (electrons) and that they commute between possible charge states under the above stimuli. (We do not eliminate at this stage the possibility that simultaneous configurational changes may occur.)

The total change which can be effected by an ionizing irradiation will give an estimate of the number of trapping defects present.

(e). Process 1 is seen only following prior illumination. Its magnitudes in cases (i) and (ii) are approximately equal. Thus it grows only in relation to the Exp.

1 illumination-induced change. It does not grow further with Exp. 2.

(f). Process 2 is removed by prior illumination. In case (iii) P2 has a slightly greater magnitude than in cases (ii) and (iv). However in case (ii), Exp. 2 has already run down by about 25%. There would be a corresponding decrease in P2. In case (iv) heating to 80°K unavoidably removed some of P2 before observations on it could be made by re-ionizing and heating. With these qualifications in mind one can say that P2 disappears only in relation to Exp. 2. It is not affected by the faster Exp. 1.

(g). Therefore under the circumstances of our experiments it appears that light operates independently on the defects involved in P1 and P2. There is no exchange between P1 and P2.

(h). Following the completion of P1 and P2 illumination operates on whatever defects are present in a way distinctly different from the previous effect of illumination (Fig. 5). On this basis we conclude that the defects present have been changed by heating. We note, however, that the effect of heating the "converted" defects is the same, as judged from Fig. 6, as P2.

V. DISCUSSION

The observed changes fall into two categories: (i). those occurring directly as a result of a prolonged (mainly damaging) irradiation, and (ii). those further changes resulting from infrared illumination, heating, and short electron (mainly ionizing) irradiation. The latter effects do not occur for samples prior to their prolonged irradiation. Therefore we ascribe them, as we do the directly observed effects, to the introduction of defects by the irradiation. We observe that an ionizing irradiation will always return the conductivity to a value the same as that immediately following the damaging irradiation even though there may have been numerous intermediate treatments (illumination and heating). This strongly suggests that two types of defects are involved, some contributing immediately to conductivity changes, the others latent until the sample is illuminated or heated. There is possibly some interaction between the two types of defects as evidenced, for instance, by the initial increase in conductivity beyond the immediate post-irradiation value as seen for one case in Fig. 3.

We are without any information, other than their production rate, concerning the "directly observable defects." Discussion of their character must await higher temperature annealing studies than we have carried out. We shall concern ourselves for the rest of the discussion only with those defects which can be changed by illumination and heating up to 120°K. Initially, we bear in mind the apparent independence of P1 and P2 as mentioned in Sec. IV (g).

Consider first P1. The defects which undergo this change are observed electrically only after illumination. Process 1 then reverses the illumination-induced change. Without illumination the defects could still undergo a change but not show up in conductivity variations. That is, we suggest P1 occurs in case (iii) as in cases (i), (ii), and (iv), but goes unobserved.

The most obvious explanation for the decrease of conductivity during illumination is that minority carriers (electrons) are released from traps and annihilate holes. We have demonstrated (points 2 to 3, Fig. 4) that P1 is not simply the reverse of Exp. 1, that is, the temporary re-trapping of an electron by the same defect. Therefore we conclude that P1 involves atomic motion. It is possible that a new temporary electron trap is formed having a greater resistance to illumination-induced changes. If this were filled on formation then one would obtain the observed increase in conductivity. However the last condition makes this unlikely in degenerate p type. It is more probable that an empty state becomes degenerate with the valence band by the tight binding of a radiation-induced defect to a sink.

For reasons similar but reciprocal to the above, one can see how P2 could occur in all cases but go unobserved in case (i). When seen, the change during P2 is towards lower conductivity, as is the change during Exp. 2. If indeed a shedding of electrons occurs during illumination, allowing the defects to show contributions to the conductivity, then the same could occur during P2. This would allow the possibility of the defects involved in P2 having shed their electrons during illumination to show no further change on heating. The shedding of electrons during P2 could arise by the creation, in the forbidden gap, of occupied levels which lose their electrons to the valence band.

The behavior of the defects with respect to illumination following P1 and P2 is very similar to that reported by Callcott[7] for defects introduced at 78°K. We consider that the "converted" defects in the present work are the same as those reported to be produced at the higher temperature. Taking the rate equation

$$-\partial N/\partial t = N(N_S/N_L)\nu e^{-\epsilon/kT},$$

where N is the number of moving entities, N_S is the number of sinks, N_L is the effective number of sites for sinks, ν is the effective vibrational frequency and $e^{-\epsilon/kT}$ is the appropriate Boltzmann factor, we have made fairly crude analyses of our isochronal annealing data. In doing so we have assumed that whatever the factor relating the fractional conductivity change to the fractional change in the number of carriers, it remains the same throughout the annealing. We have therefore analyzed the conductivity data.

In the case of P1 we find that the best fit to the data is obtained by assuming that N_S remains constant, that is, first order kinetics. Then $\epsilon \simeq 0.025$ eV and $(N_S/N_L)\nu \simeq 10^{-1}$ sec^{-1}. If we were to assume ν to be the usual lattice frequency ($\sim 10^{13}$ sec^{-1}) and N_L to be the total density of lattice sites ($\sim 10^{23}$ cm^{-3}), then the number of sinks predicted would be 10^9 cm^{-3}. Dislocations in the

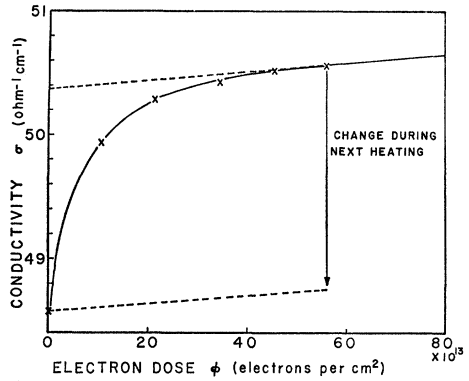

FIG. 7. The recovery of conductivity with small electron doses.

crystal could provide this number of sinks. By causing dislocation climb the precipitation of defects on the dislocations need not lower the number of sinks. Their number, although small, could remain constant throughout, as required for the observed order of kinetics.

For P2 on the other hand, a poor fit is obtained by assuming first-order kinetics. A better analysis results if we take a second-order rate equation, meaning that N and N_S remain equal. Calculation then yields $\epsilon \simeq 0.16$ eV and $\nu/N_L \simeq 10^{-10}$. The latter is consistent with the usual lattice frequency and atomic density. In this case we can estimate N (or N_s) from the conductivity change, to be between about 10^{15} and 10^{16} cm^{-3}. There are a number of defects and impurities, for instance oxygen, which might be present in this concentration and act as sinks. We have no grounds for choosing any particular one. Instead we consider other features of the behavior of the defects which suggest something more of the nature of P2.

Firstly we point out that in case (iv) (Fig. 4) the number of defects transformed by heating to 120°K is substantially less than in cases (ii) and (iii). In each case we estimate the number of these defects from the change produced by an ionizing irradiation following heating. The distinction in case (iv) is that it has received an intermediate ionizing irradiation. Secondly, we note the progressive decrease of the magnitudes of P2 for repeated observations as shown in Fig. 6. Lastly, we examine the recovery of the conductivity versus dose during a typical ionizing irradiation as shown in Fig. 7. For these short irradiations we may assume that no additional defects are created. We would therefore expect the number of ionized defects to increase with dose (ϕ) according to $(1-e^{-\alpha\phi})$, where α is the cross section for the process. One may easily verify that in fact the dashed line in Fig. 7 is the appropriate asymptote to a curve with the above form. We may explain the fact that the asymptote is not independent of electron dose by assuming that some other process is also reducing the number of defects observed. The above pieces of information are strong evidence that radiation annealing of the defects occurs. We would expect such a process to remove defects according to $(1-e^{-\beta\phi})$ where β is another cross section. If β were small, then for low doses the effect would be linear, going as $\beta\phi$. A second effect to which we wish to draw attention is the ability we have to "re-cycle" P2, as shown in Fig. 6.

With the above information in mind we can outline two possibilities for the nature of P2. Either (i). P2 is a diffusive reaction the effects of which are reversed for all of this type of defect by an opposing diffusive reaction which occurs during an ionizing irradiation. Some of the defects become trapped at sinks as they diffuse during the ionizing irradiation so that on next observing P2 it will be seen to have diminished in magnitude. Or (ii). P2 is an electronic change which is reversed by the ionizing irradiation. During subsequent heating to observe P2 some of defects diffuse to sites where they no longer act as temporary electron traps.

There are more problems with the second interpretation than with the first. If we assume that P2 is simply an electronic change, the question then arises as to when the electron traps are formed. We cannot eliminate the possiblity that P1 is their formation, although this would require that the traps are sometimes formed with a temporarily trapped electron [for instance case (ii)]. Problems also arise in trying to understand how an electronic process could manifest second-order kinetics. Besides the disappearance of defects which we assume in the second case might occur during heating *subsequent* to an ionizing irradiation, we know that some annealing actually takes place *during* the ionization (Fig. 7.) Our data are not sufficiently precise or extensive to decide whether both types of annealing occur. Neither can we conclusively resolve the other questions. However the results certainly point to a model in which opposing diffusive changes occur during ionization and heating.

A general, but imporant, result of the work is the contrast we can now see between the natures of the defects produced in n- and p-type germanium at low temperature. As illustration we show P1 in Fig. 8 together with the annealing in n type following 4.5-MeV electron irradiation. The latter is typical of very many observations[1] both at 4.5 MeV and lower energies, and

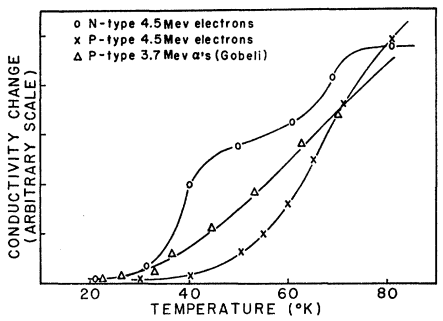

FIG. 8. A comparison between the recovery of conductivity in n- and p-type germanium following 4.5-MeV electron irradiation. The recovery following 3.7-MeV α-particle irradiation of p type (after Gobeli) is also shown.

also for materials of various initial resistivities. It has previously been asserted[5] that the annealing in n and p type is the same, at least after 3.7-MeV α-particle irradiation. While we agree that in this case n type shows the usual annealing stages at 35 and 65°K, we believe the extension of this statement to p type to have been unwarranted. Our criticism stems from the marked similarity of the annealing in p type following α-particle irradiation to that following electron irradiation, as may be seen in Fig. 8. It follows that differences between the defects in n and p types which we have observed must also obtain for those created by an α-particle irradiation. That is, in n type annealing occurs without prior modification of the defects and shows stages at 35 and 65°K, whereas in p type a single broad process occurs between 30 and 80°K and only after prior modification. The question arises as to how the defects created by α-particle irradiation arrived in a state apparently susceptible to P1. There is a slight possibility that light could have entered the cryostat used in the α-particle work. On the other hand α-particle irradiation may leave the defects in such a state.

Some very recent work has been reported by Vook[11] who studied changes in the thermal conductivity during 2.0-MeV electron irradiation and later annealing. Starting with high resistivity n-type germanium the large doses employed ($\sim 10^{18}$ electrons cm^{-2}) convert the material to p type. It is therefore an agreeable result that the initial low temperature annealing observed corresponds very well with that seen in the present work (P1) and also by Gobeli for p type. The annealing, which is very small in magnitude compared to later stages, does not require prior illumination to be observed. No problem of reconciling the two results need arise here, since the charge state of a defect may well affect the electrical and thermal conductivities in very different ways. Indeed, it has been the contention in the present work that electrons may be trapped at the defects and raise the electrical conductivity while Vook reviews arguments for the presence of charge localized at the defect increasing the phonon scattering and hence lowering the thermal conductivity. It would be interesting to know if P1 as observed in the thermal conductivity changes is quenched by illumination immediately following irradiation. The higher temperature annealing in Vook's work restores the thermal conductivity, the opposite effect to our observations between 80 and 120°K. In the absence of a detailed scheme for how the defects contribute to the changes in each case we cannot say that this actually represents a contradiction.

[11] Frederick L. Vook, Phys. Rev. 138, A1234 (1965).

VI. CONCLUSIONS

Changes in the electrical properties of degenerate p-type germanium occur during 4.5-MeV electron irradiation at 4.2°K. The magnitude of these changes is 25 times smaller than the effect in degenerate n type under the same conditions.

Defects are also produced which are apparently temporary electron traps. Two concurrent changes of these traps can be effected with infrared illumination. There is a relation between the duration of this illumination and the observation of subsequent thermal modification of the traps.

The effects of heat on the defects in p type is markedly different from the effects in n type both in the relation to prior illumination and also to the number of stages of annealing seen up to 120°K.

We conclude therefore that the defects annealable in this temperature range differ greatly between n-type and p-type germanium.

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