Stored-Energy Release in Electron-Irradiated Germanium*†

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Stored-energy release measurements have been made on heavily doped n- and p-type specimens of germanium following irradiation at 15°K by 1.0-MeV electrons. A novel feature of the technique is the use of a portion of the specimen as one element of a germanium-copper thermocouple to detect small tenperature differences arising from stored-energy release. The experimental results indicate that there are several annealing stages in the temperature range from 20 to 80°K in which stored energy is released in n-type germanium. This is interpreted to mean that the annealing involves recombination of vacancies and interstitials. No measurable release of energy is observed in p-type germanium over the above temperature range. Comparing the energy release to previous measurements of electrical properties indicates that the return of one electron to the conduction band in n-type germanium is accompanied by the release of 5.5±1.5 eV in thermal energy for annealing stages between 30 and 60°K, and 3.7±1.8 eV for stages between 60 and 80°K.

I. INTRODUCTION

THE behavior of germanium irradiated at very low temperatures is different for n-type material than it is for p-type. Electrical measurements[1,2] indicate that 1.0-MeV electron irradiation produces relatively large changes in n-type material while p-type material is scarcely affected. Isochronal annealing reveals recovery stages in n-type material centered at 35 and 65°K. Annealing of p-type material produces no changes in properties in these temperature ranges but, between 100 and 120°K, changes occur which indicate that some defects are introduced by low-temperature irradiation.[3]

The annealing stages in n-type germanium at 35 and 65°K have both been attributed to recombination of vacancies and interstitials.[1,2] Our primary motivation in undertaking the measurement of the stored energy released during annealing is to determine whether this interpretation is correct. If vacancy-interstitial recombination does occur, we would expect an energy release of several eV per annihilated pair which can be detected by sensitive calorimetric measurements. If the annealing involves only a modification of defect structure, such as association of defects, we would expect a very much smaller change in lattice energy. Thus measurement of stored energy release may provide a definitive answer to the question of annealing mechanism.

Measurements of stored-energy release following irradiation have been reported for other materials. Two different techniques have been used.[4–7] The first[5,6] employs a differential temperature measurement between an irradiated specimen and a control specimen. The self-warming of the irradiated specimen, resulting from energy release, is detected as a temperature difference between the two specimens as they are heated together through the temperature range of interest. The second method[4,7] compares the temperature, as a function of time for a single specimen, before and after irradiation, under conditions of controlled power input.

We have chosen to use the second method and to take advantage of the very large thermoelectric power of germanium itself to measure the stored energy release. This method requires more precise control of power input than does the differential method. However, it has the advantage that the specimen is in good thermal contact with its surroundings, thus reducing the effects of variations in undesired heat paths. It does not require the very difficult matching of sample pairs, or balancing of heat input to the pairs.

In this paper we report the measurement of stored-energy release over the temperature range from 20 to 80°K following irradiation at 1.0 MeV by 10^{17} electrons per cm^2 for heavily doped n- and p-type germanium.

II. EXPERIMENTAL APPARATUS

The basic cryostat used in this work is similar to one that has been previously described.[1] It is a modified liquid helium storage vessel with a 5-liter capacity. The tail piece of this apparatus is shown in Fig. 1. It consists of three concentric cylinders (cross-hatched) which progress downward in temperature from outside to inside: room temperature, liquid-nitrogen temperature (S), and helium temperature (A). A chamber (Q) is formed at the lower end of the inner cylinder by a disk soldered into its interior. A thin-walled stainless-steel tube (T) passes through this disk to connect the chamber to gas-filling and pumping connections at the top of the cryostat. The specimen holder is a copper

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[1] J. W. MacKay and E. E. Klontz, J. Appl. Phys. **30**, 1269 (1959).

[2] E. E. Klontz and J. W. MacKay, J. Phys. Soc. Japan **18**, Suppl. III, 216 (1963).

[3] T. M. Flanagan and E. E. Klontz, Phys. Rev. **167**, 789 (1968).

[4] T. H. Blewitt, R. R. Coltman, and C. E. Klabunde, Phys. Rev. Letters **3**, 132 (1959).

[5] C. J. Meechan and A. Sosin, Phys. Rev. **113**, 422 (1959).

[6] A. V. Granato and T. G. Nilan, Phys. Rev. Letters **6**, 171 (1961).

[7] T. H. Blewitt, R. R. Coltman, and C. E. Klabunde, J. Phys. Soc. Japan **18**, Suppl. III, 288 (1963).

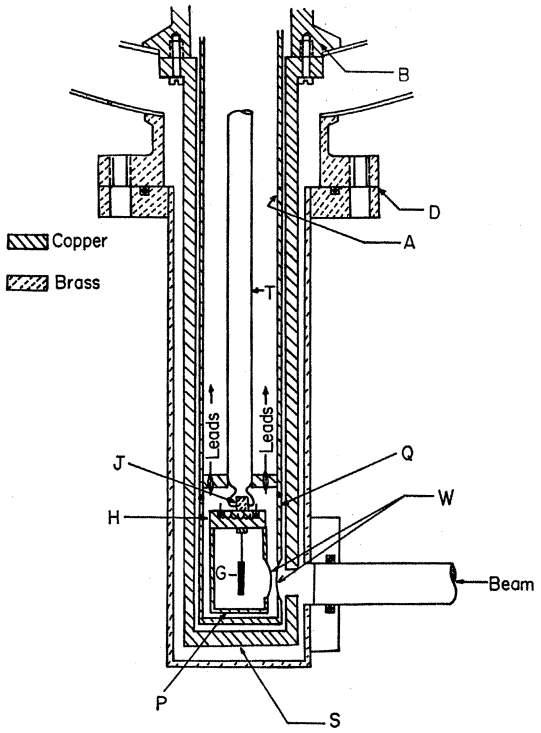

FIG. 1. Liquid-helium cryostat tail piece.

block (H) which is suspended by thin stainless steel strips and a glass-metal electrical insulator (J) from the above-mentioned disk. This specimen block has a heater sealed in its interior. A thermal shield, in the form of a copper cylinder (P) closed at the bottom, is connected to the specimen block to provide an enclosure of essentially uniform temperature for the specimen. When the cryostat is in use, the space in the inner cylinder above the sample chamber is filled with liquid helium. During irradiation the sample chamber contains helium gas at low pressure to provide efficient heat transfer, and maintain the specimen temperature at the desired value. For annealing studies the helium exchange gas is pumped out of the chamber, isolating the sample block from the liquid helium (except for the heat flow through the glass insulator and stainless steel supporting strips). The thermal shield surrounding the specimen has pumping ports near the top so that the space surrounding the specimen has the same exchange gas pressure as the rest of the chamber.

The electron beam enters the cryostat through a $\frac{1}{2}$-in.-diam tube that is connected directly to the output port of the Van de Graaf accelerator. The beam area is defined by an aperture in the liquid-nitrogen shield. The beam enters the lower chamber through an aluminum window 0.001 in. thick, then passes through a 0.0001-in. copper window (W) on the specimen heat shield. After passing through the specimen, the beam is stopped in the heat shield and its charge is collected on a capacitor.

The details of the mounting block and specimen geometry are shown schematically in Fig. 2. The specimen is cut from a single-crystal ingot. After a slice from the ingot is ground to a thickness of about 150 μ, a sample and continuous zig-zag bridge of the shape shown in Fig. 2 is cut by means of an ultrasonic cutter. The sample is then etched in CP-4 to a final thickness of approximately 100 μ. A system of thermocouples (copper-constantan) attached at the two ends of the bridge provide the means of calibrating a copper-germanium couple, formed by the bridge and two copper wires. This copper-germanium couple is the primary generator of experimental information in this experiment. All of the wires are 0.001 in. in diameter and have lengths of about 2 ft before they are wound into coils. All electrical leads are placed in thermal contact with the mounting block using G.E. 7031 varnish, before they exit from the chamber.

A heater coil of constantan wire is sealed in the interior of the sample mounting block. Before sealing,

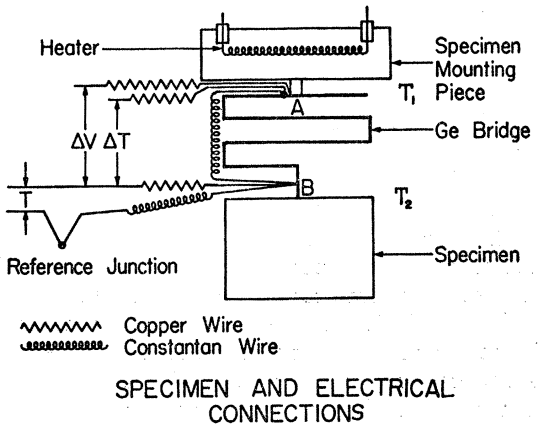

FIG. 2. Schematic view of specimen, mounting block, heater, and thermocouples.

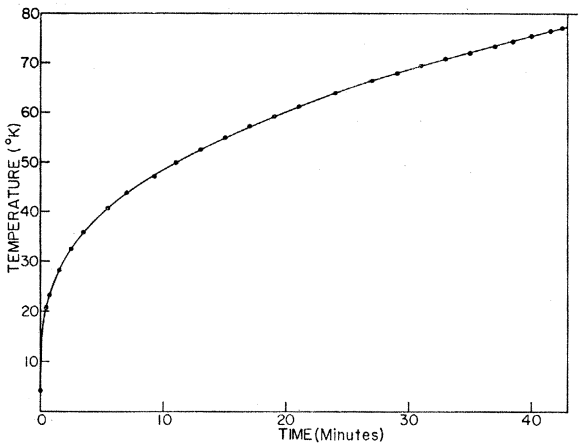

FIG. 3. Temperature as a function of time for heating runs on n-type specimen.

the heater compartment was filled with helium gas at low pressure, to assure good heat transfer at low temperatures. During heating runs, the heater current is supplied by a storage battery. The terminal voltage of the battery is carefully adjusted to a predetermined value by shunt resistances. The current to the heater is programmed as a function of time by a helipot in series with the heater. The helipot is driven by a synchronous motor.

All electrical measurements were made with a digital voltmeter.

III. ANALYSIS OF DATA

If the mounting block in Fig. 2 is heated so that its temperature T_1 rises at a predetermined, reproducible rate dT_1/dt, heat will flow through the bridge (and other paths) to the specimen which has heat capacity $C(T)$. In a warming run, in which no stored energy is released in the specimen, the specimen temperature T_2 will lag behind that of the block by an amount ΔT

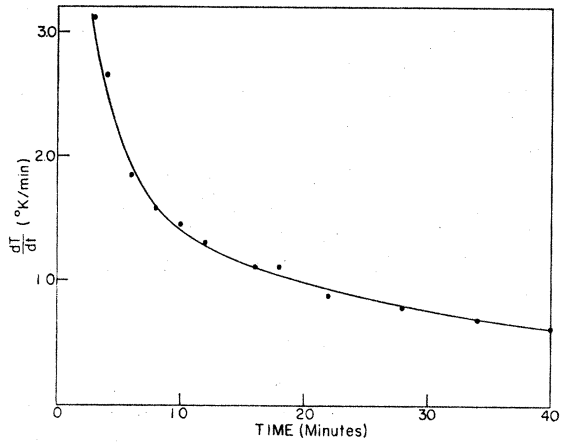

FIG. 4. Heating rate for n-type specimen.

determined by the thermal conductance K of the heat paths between the block and the specimen and the heat capacity C. In a second warming run following irradiation, in which T_1 is programmed in time identically to the first run, if energy is released in the specimen in certain temperature ranges, the specimen will be self-heated by the energy release, and ΔT will be reduced in these ranges. The difference in $\Delta T(t)$ between these two runs is a measure of the stored-energy release.

For a warming run in which energy release does not occur we may write a heat-balance equation

$$C dT_2/dt = K\Delta T. \tag{1}$$

For a second run, in which there is stored energy released,

$$C dT_2'/dt = K\Delta T' + dE/dt, \tag{2}$$

where dE/dt is the rate of energy release at temperature T_2'. In writing these equations, we have assumed that

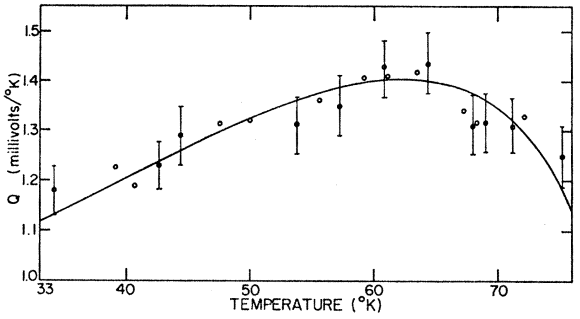

FIG. 5. Thermoelectric power for n-type Ge specimen.

the thermal conductance of the specimen is so large that it has uniform temperature.

Both C and K are functions of temperature. The value of C at any time should correspond to the sample temperature T_2 in Eq. (1) and T_2' in Eq. (2). However, in the experiment $T_2'-T_2$ never exceeds 0.01°K, and we are justified in taking C at any time to be the value corresponding to T_2. Similarly we will assume that the value of K may be taken to be the same in both equations at a given time t.

Define $\delta T = T_2'-T_2 = \Delta T - \Delta T'$. Subtracting Eq. (2) from Eq. (1), we obtain

$$dE/dt = K\delta T + Cd(\delta T)/dt. \tag{3}$$

From (1) we may obtain K in terms of C and the quantities ΔT and dT/dt, which may be determined in a warming run:

$$K = \frac{C}{\Delta T}\frac{dT_2}{dt}.$$

Equation (3) then becomes

$$\frac{dE}{dt} = C\left[\frac{dT_2}{dt}\frac{\delta T}{\Delta T} + \frac{d(\delta T)}{dt}\right]. \tag{4}$$

ΔT is determined by measuring ΔV, the output of the copper-germanium thermocouple. $\Delta T = Q\Delta V$, where Q is

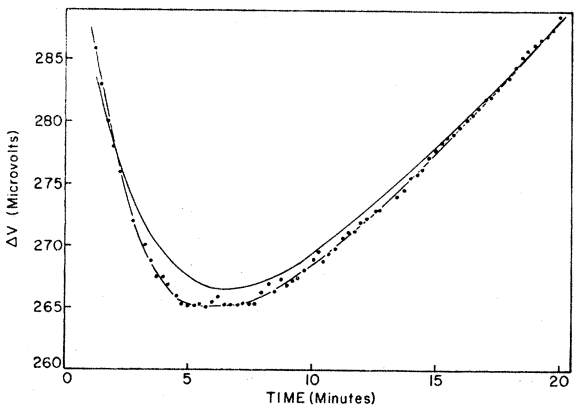

FIG. 6. Output of germanium-copper thermocouple during heating run. Lower curve—irradiated specimen. Upper curve—before irradiation.

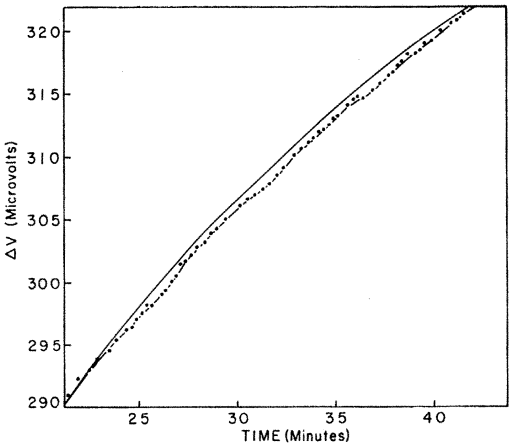

FIG. 7. Continuation of heating run shown in Fig. 6.

the thermoelectric power. Similarly, $\delta T=Q(\Delta V-\Delta V')=Q\delta V$. The stored-energy release rate may now be written:

$$\frac{dE}{dt}=C\left[\frac{dT_2}{dt}\frac{\delta V}{\Delta V}+\frac{d(Q\delta V)}{dt}\right]. \quad (5)$$

Using Eq. (5), we can determine the rate of energy release as a function of time. T_2, dT_2/dt, and ΔV are measured as functions of time in a warming run before the specimen is irradiated and, for comparison, again after the specimen has been annealed. δV is obtained by measuring $\Delta V'$ as a function of time during a warming run after the specimen has been irradiated. Q is determined by comparing the output of the germanium-copper thermocouple to that of a copper-constantan couple over the temperature range of interest. The values of specimen heat capacity, C, are obtained by multiplying previously measured values of the specific heat of germanium[8] by the measured mass of the specimen.

The first term on the right of Eq. (5) is the dominant contributor. The second term makes a significant contribution only at the beginning or end of an annealing stage when δV is very small but changing rapidly.

IV. EXPERIMENTAL RESULTS

A. *n* Type

We present in detail the results for an antimony-doped n-type specimen with a room-temperature resistivity of 0.02 Ω cm before irradiation. The specimen was irradiated at a temperature of 15°K to a total flux of 10^{17} electrons per cm^2. The incident electron energy was 1.0 MeV.

Figure 3 shows the programmed specimen temperature, and Fig. 4 is the heating rate dT/dt as a function of time.

Figure 5 persents the thermoelectric power, as a function of temperature, for the material in the bridge of this specimen. The measured values match, within experimental error, the values for similar material reported by Goff and Pearlman.[9]

Figures 6 and 7 show the output of the germanium-copper thermocouple as a function of time for a heating run before irradiation and a run following irradiation. The lower curves in Figs. 6 and 7 correspond to the behavior after irradiation. The thermocouple output is smaller in certain regions than for the preirradiation run, indicating the release of stored energy in these regions.

Figure 8 shows the release of stored energy as a function of time as calculated using Eq. (5). This is converted to stored-energy release as a function of temperature in Fig. 9. Here we have plotted $(dE/dt)/(dT/dt)$ versus T.

Figure 9 indicates that there are annealing stages in n-type germanium, that involve vacancy-interstitial recombination, in the temperature range between 30 and 80°K. The most prominent stage is centered at 38°K. There appear to be three other stages between 42 and 55°K that are not completely resolved. A second group of what appear to be unresolved peaks is seen between 63 and 80°K.

A second n-type sample was run, with very similar results, particularly in the temperature range below 60°K. The positions of the peaks above 60°K were not the same, indicating that our results in this temperature range are less reliable than in the lower temperature range.

B. *p* Type

An indium-doped p-type specimen with a room-temperature resistivity of 0.025 Ω cm was run under similar conditions to the n-type specimen described above. For this specimen, in Figs. 10 and 11, we show only the plot of the germanium-copper thermocouple output as a function of time for three warming runs; before irradiation, after irradiation, and a third run following the after-irradiation run. The after-irradiation run falls between the other two, indicating that there

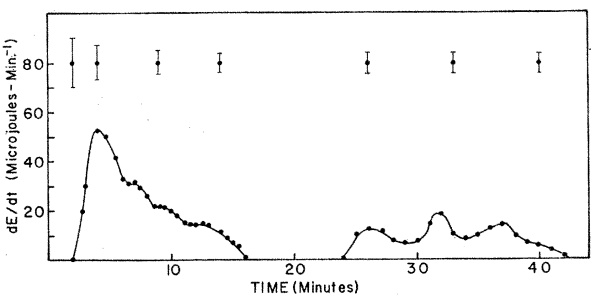

FIG. 8. Stored energy release for n-type specimen as a function of time.

[8] P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Phil. Mag. 4, 273 (1959).

[9] J. F. Goff and N. Pearlman, Phys. Rev. 140, A2151 (1965).

is no measurable release of stored energy over the temperature range between 20 and 80°K.

C. Experimental Errors

The major uncertainty in the experimental results arises from the necessity of obtaining a small difference between two relatively large signals ΔV and $\Delta V'$. These two signals are measured at different times under supposedly identical experimental conditions. Reproducibility of warming runs (see Figs. 10 and 11) is the criterion for judging the validity of the experiments.

We estimate that the uncertainty in reproducibility between different warming runs introduces a probable error of $e_1=\pm 0.4$ μV in δV. This error introduces a systematic shift in the values of dE/dt as calculated from Eq. (5), i.e., the curves plotted in Figs. 8 and 9 may be shifted up or down by failure to exactly reproduce experimental conditions. The error bars shown above the curves in these figures indicate the range of uncertainty due to the error e_1.

There is also a random error, or noise, in the measurement of each value of ΔV within a given warming run. This noise is estimated to produce an uncertainty in δV of $e_2=\pm 0.2$ μV. This corresponds to an uncertainty in the individual points, relative to each other, of half the range shown by the error bars in Figs. 8 and 9. The uncertainty due to the noise is sufficient to deter any attempt to resolve the experimental curves into a sequence of overlapping annealing peaks.

In the next section we will be interested in the integrated energy E that is released over different temperature ranges. In calculating the area under the curve in Fig. 8, the contribution of the noise, e_2, to the uncertainty in E will tend to average out. That due to e_1 will not. The ratio of the contribution due to e_2 to that of e_1 should be of the order of $e_2/e_1\sqrt{n}$, where n is the number of points defining the curve over the range of integration. This ratio is of the order of 0.1 and we may neglect the contribution of e_2. Errors due to other quantities in Eq. (5) are, at most, a few percent.

On the basis of the above discussion, the energy release in the range 30 to 60°K is $(2.2\pm 0.4)\times 10^{17}$ eV cm^{-3}. In the range 60 to 80°K, the integrated energy release is $(1.1\pm 0.5)\times 10^{17}$ eV cm^{-3}.

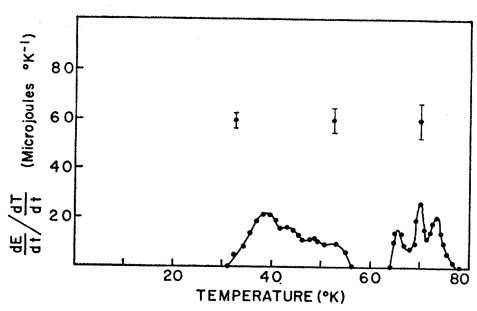

FIG. 9. Stored energy release per degree as a function of temperature during heating of n-type specimen.

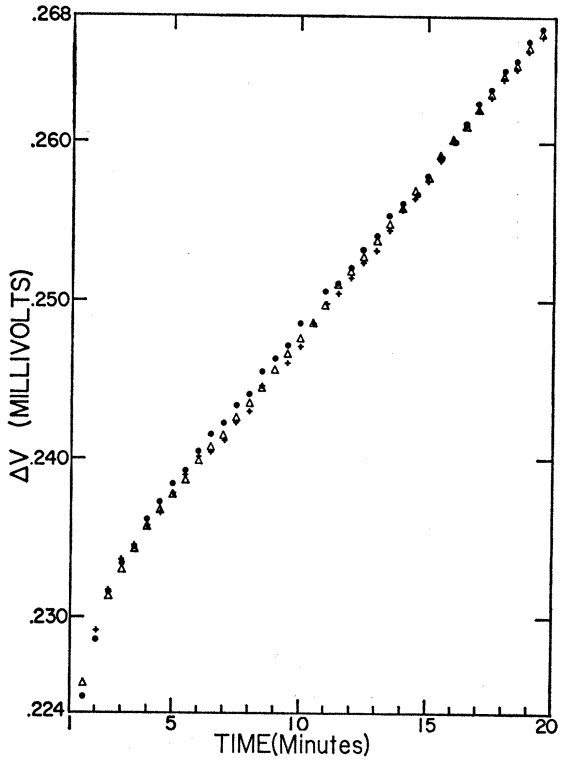

FIG. 10. Output of germanium-copper thermocouple for p-type specimen during heating runs. Dots: before irradiation. Triangles: following irradiation. Crosses: run taken after specimen has been warmed to 80°K.

V. DISCUSSION

Our results indicate that annealing stages in n-type germanium below 80°K involve vacancy-interstitial recombination. They also indicate that the behavior of defects in p-type Ge is indeed different from that in n type. There is no measurable release of stored energy in p type just as there is no measurable change in electrical properties, up to 80°K.

The magnitude of the stored energy released per defect pair is of interest. This energy is derived from the increase of lattice potential energy that results when a Frenkel pair is produced. Theoretical calculations have been made of the formation energy of single vacancies[10–12] and of single interstitials.[10] The sum of these two energies should give a value to be compared with the measured stored energy release. The calculated values of the vacancy formation energy range from 1.6 to 2.5 eV. Bennemann[10] finds a value of 0.93 eV for the formation energy of an interstitial in germanium. Thus the stored energy of a Frenkel pair is expected to be about 3.0 ± 0.5 eV.

Using previously published data on the electrical properties,[2] we can estimate the stored energy released per electron returned to the conduction band on anneal-

[10] K. H. Bennemann, Phys. Rev. 137, A1497 (1965).
[11] R. A. Swalin, J. Phys. Chem. Solids 18, 290 (1961).
[12] A. Scholz and A. Seeger, Phys. Status Solidi 3, 42 (1963).

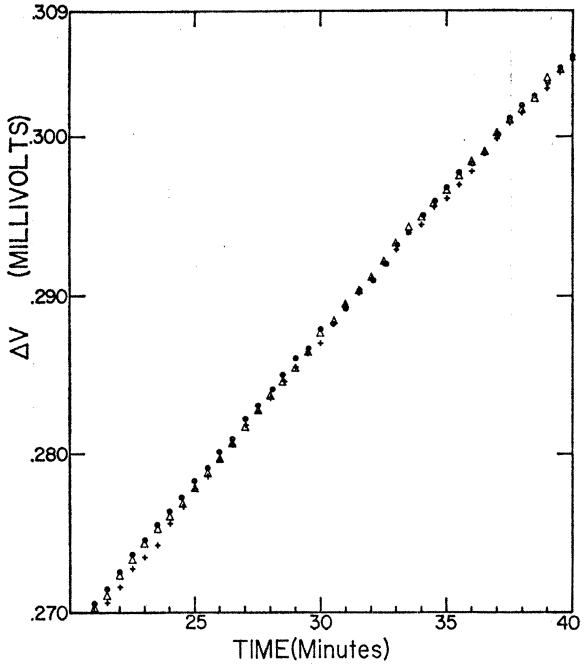

FIG. 11. Continuation of heating run shown in Fig. 10.

ing. Irradiation at 1.0 MeV by 10^{17} electrons cm^{-2} should remove 2×10^{17} carriers cm^{-3} in our specimens.[2] Annealing studies on the electrical properties[2] indicate that $(4.0\pm0.8)\times10^{16}$ of these carriers would be returned by annealing up to 60°K. The integrated energy release up to 60°K in Fig. 8 is $(2.2\pm0.4)\times10^{17}$ eV cm^{-3}. Thus we estimate the energy release per carrier recovered to be 5.5 ± 1.5 eV.

The integrated stored energy release in the peaks between 60 and 80°K is (1.1 ± 0.5) 10^{17} eV cm^{-3}. The number of carriers returned in the same temperature range on annealing is estimated[2] to be (3.0 ± 0.6) 10^{16} cm^{-3}. The energy release per carrier recovered is then 3.7 ± 1.8 eV.

How these numbers are related to the energy released per vacancy-interstitial recombination is not so clear. If each pair returns one electron to the band, then the energy released per electron recovered should equal the energy release per annihilation. However it is possible that two electrons are recovered per annihilation, in at least some of the stages, and of course it is possible that there are stages in which no electrons are recovered. Indeed, Callcott[13] has shown, for lightly irradiated n-type germanium, that the defects involved in the 65°K annealing stage do return two electrons each on annealing. However, heavily irradiated germanium has a much more complicated annealing spectrum. Defects appear to be modified[2] by prolonged irradiation and it is quite possible that most stages in heavily irradiated material involve the return of only one electron per Frenkel pair. The apparent difference in energy per electron for the stages above 60°K and the stages below 60°K may be due to a difference in the number of electrons per pair. However, the uncertainty in the experimental results is so great that the difference may not be real.

To indicate how different numbers of electrons could be associated with different annealing stages, consider the following possibilities. Suppose, as Watkins[14] has shown for silicon, that the vacancy is a double acceptor and that the divacancy is also a double acceptor. Then, if the interstitial is held somewhere in the lattice in a neutral charge state, annihilation of a single vacancy by an interstitial will result in two electrons returned to the conduction band. Annihilation of one of the vacancies of a divacancy will give no change in electron concentration. Annihilation of both components of a divacancy will average out to one electron returned per annihilation. If, in addition, the interstitial can find sites in which its charge state is $+1$, annihilation of vacancies by such interstitials would return one less electron in each of the cases cited above.

In view of the multiplicity of annealing peaks, which probably results from different initial defect configurations, there appears to be no way at present to make a valid comparison of our experimental results to theory. The best we can say is that the results are not incompatible with the theoretical calculations.

ACKNOWLEDGMENTS

The authors are indebted to Miss L. Roth for growing the single-crystal germanium used in these experiments and to J. R. Raby for technical assistance with the experimental equipment.

[13] T. A. Callcott and J. W. MacKay, Phys. Rev. **161**, 698 (1967).

[14] G. D. Watkins, in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Press, Inc., New York, 1968), p. 67.