

have used the fact that

$$\sum_{n=1}^N \cos^2\left(\theta + \frac{2\pi n}{N}\right) = \frac{1}{2}N.$$

The acoustic and optical branches are given by

$$M\omega_{ac}^2 = k - 2f_1(0) - 2 \sum_m f_1(m) + \frac{1}{4} \sum A_m N_m d_m^2 Q^2 \quad (\text{A12})$$

and

$$M\omega_{op}^2 = k - 2f_1(0) - 2 \sum_m f_1(m) + 2 \sum_u A_u N_u - \frac{1}{4} Q^2 \left(\sum_u A_u N_u d_u^2 - \sum_l A_l N_l d_l^2 \right). \quad (\text{A13})$$

The amplitudes for $Q=0$ are in the ratio $W_s(0)/W_o(0) = \pm 1$ for ω_{ac} and ω_{op} , respectively, as required. That is,

the acoustic mode for $Q=0$ is equivalent to the entire layer always moving parallel to itself, while the optical mode at $Q=0$ corresponds to the s and s^* ions moving in opposite phase. The acoustic mode is the one we are interested in, and it has the membranelike feature referred to in the text. The expression (A12) for the acoustic mode shows that any error in the summation $\sum A_l \cos(\mathbf{Q} \cdot \mathbf{R}_l)$ shows up only in the Q -dependent part. The sum multiplying Q^2 is divergent if all the m terms are to be taken into account. However, the expansion of $\cos(\mathbf{Q} \cdot \mathbf{R}_l) = 1 - \frac{1}{2}(\mathbf{Q} \cdot \mathbf{R}_l)^2$ ceases to be valid for large l . We decide to cut off the series at a certain R_l and approximate the remaining by the Bessel integral in which the Q dependence is not very strong if Q is of the order of the reciprocal of the upper limit of the integral. The calculation of the parameter μ appearing in Eq. (33) is straightforward if a van der Waals interaction is assumed for the carbon-carbon interactions in the two layers in addition to the image-force interactions.

Radiation Effects in Tellurium-Doped Germanium†

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Ambient-temperature irradiation of Te-doped n -type Ge by 1.7-MeV electrons, ^{60}Co photons, thermal neutrons, and fast neutrons decreased the carrier concentration, presumably by removing conduction electrons into deep-lying radiation-induced acceptor states. There was no evidence for the shallow acceptor state 0.2 eV below the conduction-band characteristic of irradiated Ge doped with As or Sb. Vacuum annealing at 450°C for 16–20 h has been shown to restore the carrier concentration and mobility of As- or Sb-doped Ge to pre-irradiation values; however, comparable annealing reduced the apparent concentration of Te double donors after fast-neutron irradiation. The loss of Te double-donor action can be postulated as field-assisted migration of a composite Te-vacancy imperfection. The electric field in the space-charge zone surrounding a fast-neutron-induced disordered region is thought to be sufficiently large to sweep the Te-vacancy complexes (assumed to be positive) into the disordered region where they aggregate and become electrically inactive.

IT is well established that the type of lattice defect introduced in germanium or silicon by radiation depends critically on the type and energy of the incident bombarding particle. The basic structural defects produced by irradiation are usually defined as point or composite defects. The term “Frenkel-type defects” is used to denote interstitial-vacancy combinations, whereas the term “composite defects” refers to more complicated structures, such as defect clusters or disordered regions. The change in electronic properties as a consequence of irradiation also depends on the initial carrier concentration, the type of chemical dopant, and the initial concentration of other lattice

defects. The subsequent annealing of radiation-induced defects is also influenced by these same parameters.

Monoenergetic electron irradiation experiments¹ have indicated that the threshold energy required for the formation of a stable lattice defect (Frenkel-type defect) is ~ 13 eV in Ge, which corresponds to an incident electron energy of about 0.4 MeV. The photons from a ^{60}Co γ source have an average energy of 1.25 MeV and produce Compton electrons with a maximum energy of about 1.0 MeV in Ge. These Compton electrons also produce Frenkel-type defects in Ge,² and the temperature dependence of carrier concentration after irradi-

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¹ E. E. Klontz, *Phys. Rev.* **86**, 643 (1952); W. L. Brown and W. M. Augustyniak, *J. Appl. Phys.* **30**, 1300 (1959); J. J. Loferski and P. Rappaport, *ibid.* **30**, 1296 (1959).

² J. W. Cleland, J. H. Crawford, Jr., and D. K. Holmes, *Phys. Rev.* **102**, 722 (1956).

ation of As- or Sb-doped Ge reveals the presence of a deep and shallow-lying acceptor state. Continued irradiation and an analysis of the slope of the curve of carrier concentration versus temperature places the shallow state at ~ 0.2 eV below the conduction band and the deep state at ~ 0.26 eV above the valence band. Annealing at 100°C virtually erases the shallow state³ and a vacuum anneal at $\sim 450^\circ\text{C}$ for 16–24 h removes all evidence of radiation-induced defects.^{2,3} Recent studies⁴ have revealed that interstitials and vacancies in Ge are highly mobile at room temperature, hence it is likely that the simple model of Frenkel-type defects is inadequate.

The kinetic energy of recoil of a Ge atom resulting from thermal neutron absorption and capture γ -ray emission has been estimated⁵ as ~ 180 eV, and the recoiling atom can introduce additional Frenkel-type defects.⁶ The position of the defect acceptor states after irradiation of As- or Sb-doped Ge is identical to those observed with ^{60}Co photons.⁶ Moderate energy electrons⁷ (0.5–6.0 MeV) and reactor spectrum neutrons⁸ have been shown to produce Frenkel-type defects with similar acceptor state ionization energies; however, 50-MeV electrons⁸ and fast neutrons with energies greater than ~ 0.7 MeV⁹ have been shown to introduce Frenkel-type and other low-lying defect acceptor states in Ge, and these low-lying states have been attributed to disordered regions or defect clusters.^{3,9} Again, vacuum annealing at 450°C for 16–24 h removes these radiation-induced defects and restores the sample to its original carrier concentration and mobility.^{3,6–9}

The purpose of these present experiments was to study the effect of radiation on the electrical properties of *n*-type Te-doped Ge and to ascertain if the presence of this particular impurity had any effect on the introduction or annealing behavior of radiation-induced defects, as reflected by changes in the 0.2-eV acceptor level position.

EXPERIMENT

Tellurium behaves as a double donor¹⁰ in Ge, with energy levels at 0.11 and 0.30 eV below the conduction

³ J. H. Crawford, Jr., and J. W. Cleland, *J. Appl. Phys.* **30**, 1204 (1959).

⁴ R. E. Whan, *Phys. Rev.* **140**, A690 (1965); A. Hiraki, J. W. Cleland, and J. H. Crawford, Jr., in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Publishing Corp., New York, 1968), p. 224; *Phys. Rev.* **177**, 1203 (1969).

⁵ H. C. Schweinler, *J. Appl. Phys.* **30**, 1125 (1959).

⁶ J. W. Cleland, *Radiation Damage in Solids* (Academic Press Inc., New York, 1962), p. 384; J. H. Crawford, Jr., and J. W. Cleland, *Radioisotopes in the Physical Sciences and Industry* (International Atomic Energy Agency, Vienna, 1962), Vol. 1, p. 269.

⁷ H. Y. Fan and K. Lark-Horovitz, in Proceedings of the International Conference on Semiconductors, Garmisch, Partenkirchen, 1956 (unpublished); W. L. Brown, W. M. Augustyniak, and T. R. Waite, *J. Appl. Phys.* **30**, 1258 (1959).

⁸ A. H. Kalma, J. C. Corelli, and J. W. Cleland, *J. Appl. Phys.* **37**, 3913 (1966).

⁹ J. W. Cleland, R. F. Bass, and J. H. Crawford, Jr., in *Radiation Damage in Semiconductors* (Dunod Cie., Paris, 1964), p. 401.

¹⁰ W. W. Tyler, *Advances in Semiconductor Science* (Pergamon Press, Inc., New York, 1959), p. 59.

band. Te is difficult to introduce because of a high vapor pressure in the melt; however, both melt-doped and diffused material have been studied and the following values were determined¹⁰: maximum solubility, 2×10^{15} cm^{-3} ; distribution coefficient, 10^{-6} ; diffusivity (920°C), 10^{-11} $\text{cm}^2 \text{sec}^{-1}$. High-purity *n*-type Te-doped single crystals of Ge were grown in a sealed horizontal leveling operation from pure zone-refined Ge with no other dopant except Te.¹¹ Bridge-type samples were cut from 0.5- to 1.0-mm slices for Hall coefficient and resistivity measurements. The magnetic field strength for Hall coefficient measurements was 4000 G. Specimens were exposed at or near room temperature to a variety of radiations.

RESULTS

Figure 1, which is a graph of the log Hall coefficient and resistivity versus reciprocal temperature, shows typical data (curves I) for one of the ingots. The initial electron concentration was $\sim 3.9 \times 10^{13}$ cm^{-3} at 77°K and the difference in carrier concentration between 77 and 200°K indicates the presence of $\sim 1.15 \times 10^{14}$ Te-donor atoms cm^{-3} . Similar curves obtained for another ingot indicated the presence of $\sim 3.7 \times 10^{14}$ Te-donor atoms cm^{-3} .

The sample of Fig. 1 was irradiated at $\sim 295^\circ\text{K}$ with 1.7-MeV electrons to a fluence of 4.7×10^{14} cm^{-2} (curves

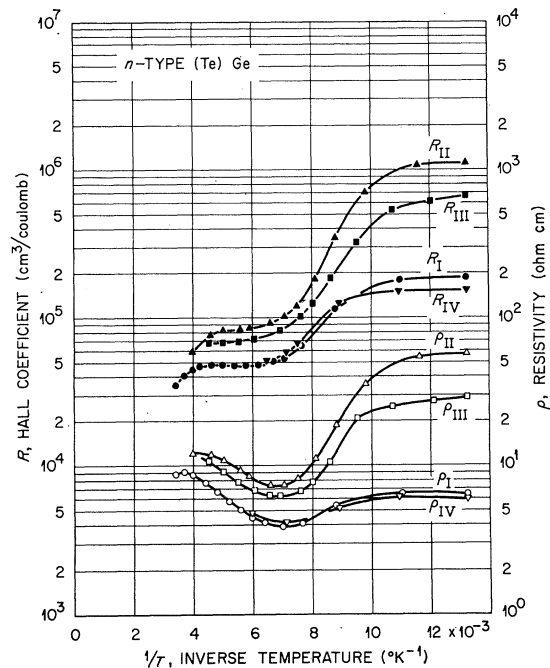


FIG. 1. Hall coefficient and resistivity versus reciprocal temperature for *n*-type Te-doped Ge before irradiation (curves I), after 1.7-MeV electron irradiation (curves II), after annealing at 105°C (curves III), and 450°C (curves IV).

¹¹ These crystals grown by the Linde Division, Parma Research Center, Union Carbide Corp. We are indebted to R. D. Westbrook for the careful preparation of these crystals.

II). The electron beam was limited to $0.25 \mu\text{a cm}^{-2}$. The apparent rate of removal of conduction electrons was ~ 0.14 per incident electron, as determined at 77°K , where this value agrees quite closely with the apparent removal rate in P-, As-, or Sb-doped Ge of comparable initial carrier concentration irradiated in a similar manner.¹² However, there was no evidence of the acceptor state 0.2 eV below the conduction-band characteristic of radiation defects in As- or Sb-doped Ge^{2,3,6} in the data of curves II of Fig. 1, or from similar experiments in which all conduction electrons were removed and conversion to essentially intrinsic conditions was achieved.

Curves III of Fig. 1 were obtained after annealing at 105°C for 16 h, and the data reveal a partial removal of radiation-induced defects, but nothing that can be attributed to the removal of one shallow acceptor state or its replacement by a deeper set of states,³ which is the behavior observed in *n*-type Ge doped with As or Sb. Curves IV were obtained after annealing at 450°C for 16 h in vacuum, and it is evident that virtually all of the radiation-induced defects were removed, with no apparent effect on the initial Te-donor concentration. Extended irradiations and anneals showed that the creation and removal of Frenkel-type defects had no significant effect on the Te-donor concentration.

The results of a series of experiments involving irradiation with ^{60}Co photons were almost identical with those obtained with 1.7-MeV electrons. An irradiation with 4.0×10^{17} photons cm^{-2} removed $\sim 2 \times 10^{14}$ conduction electrons cm^{-3} , as determined at both 77 and 200°K . The apparent rate of removal of conduction electrons was $\sim 5 \times 10^{-4}$ per incident photon, which agrees quite closely with the apparent removal rate in As- or Sb-doped Ge of comparable initial carrier concentration irradiated in a similar manner.^{2,3} Once again there was no evidence of the defect acceptor state in the upper half of the gap, and annealing at $\sim 100^\circ\text{C}$ did not cause any transformation of shallow states into deeper states. Annealing at 450°C for 16 h vacuum removed all of the radiation-induced defects, and extended irradiations and anneals showed that the creation and removal of Frenkel-type defects had no apparent effect on the Te-donor concentration.

The results of a series of experiments involving irradiation with thermal energy neutrons¹³ were also quite similar to those obtained with 1.7-MeV electrons and with ^{60}Co photons. The kinetic energy of recoil in the (n,γ) process is sufficient to introduce Frenkel-type defects; however, a series of irradiations and anneals showed that the creation and removal of such Frenkel-

¹² J. W. Cleland and W. S. Paciasas, IEEE Trans. Nucl. Sci. (to be published).

¹³ The *N* or *S* holes in the D_2O tank attached to the Bulk Shielding Reactor have a thermal neutron flux at a 2-MW power level of $1.5 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$, and a fast flux of only $7 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$ as determined with *S* or *N* detectors. The thermal/epithermal ratio as determined by the ratio of activation of bare gold to cadmium covered gold is 1700.

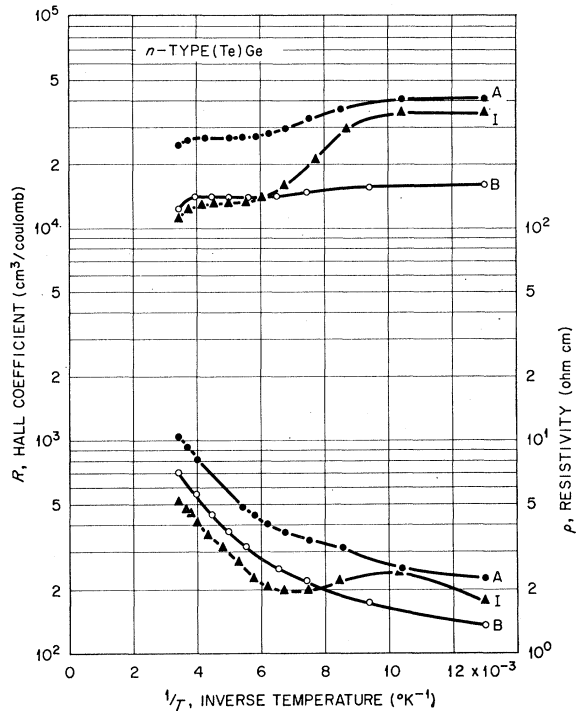


Fig. 2. Hall coefficient and resistivity versus reciprocal temperature for two identical samples of *n*-type Te-doped Ge before irradiation (curves I) and after two different total reactor doses and subsequent annealing (curves A and B). Hall coefficient curves on top of figure.

type defects had no apparent effect on the initial Te-donor concentration. The subsequent introduction of ^{75}As donors and ^{71}Ga acceptors as a consequence of transmutations was also observed, and there was no evidence of any interaction between these chemical impurities and the original Te donors.

Figure 2 shows typical Hall-coefficient and resistivity data (curves I) for two specimens that each contained $\sim 3.7 \times 10^{14}$ Te-donor atoms cm^{-3} . Both samples were irradiated in the pneumatic facility of the Low Intensity Test Reactor at Oak Ridge National Laboratory (ORNL), were vacuum annealed for 16 h at 450°C to remove (n,γ) and fast neutron-induced lattice defects, and were remeasured ~ 40 h after irradiation. Sample A received $\sim 4.7 \times 10^{15} nvt_{\text{fast}}$ and $\sim 4.7 \times 10^{15} nvt_{\text{thermal}}$, which would be expected to introduce $\sim 6 \times 10^{13}$ As atoms cm^{-3} by radioactive decay at the time of measurement, whereas sample B received $\sim 2.8 \times 10^{16} nvt_{\text{fast}}$ and $\sim 2.8 \times 10^{16} nvt_{\text{thermal}}$, which would be expected to introduce $\sim 3.6 \times 10^{14}$ As atoms cm^{-3} . The difference in the apparent carrier concentration between samples A and B after irradiation at the time of measurement was $\sim 3 \times 10^{14} \text{ cm}^{-3}$, which is exactly the amount that would be expected from the difference in the donor-type As-atom concentration due to radioactive decay; however, it is also apparent that the 450°C anneal served to remove or compensate most of the initial Te-donor atoms initially present. The apparent Te-donor con-

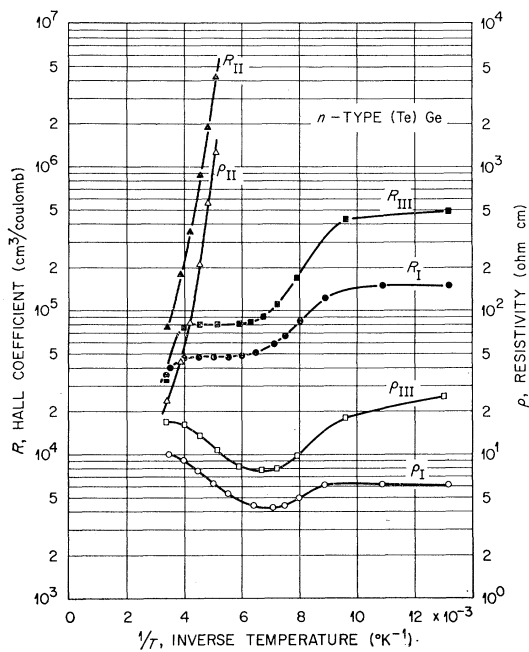


FIG. 3. Hall coefficient and resistivity versus reciprocal temperature for *n*-type Te-doped Ge before irradiation (curves I), after fast-neutron irradiation (curves II), and after annealing at 450°C (curves III).

centration, as determined at 77 and 200°K, was $\sim 3.7 \times 10^{14} \text{ cm}^{-3}$ for both samples before irradiation; however, this had been reduced to ~ 1.0 and $0.7 \times 10^{14} \text{ cm}^{-3}$ for the two samples, respectively, after irradiation and annealing. Therefore, either as a result of irradiation, anneal, or a combination of the two, some process has occurred which has destroyed the ability of $\sim 75\%$ of the Te atoms initially present to act as double donors.

Figure 3, in which the log Hall coefficient and resistivity are plotted versus reciprocal temperature, shows typical data (curves I) for a specimen with an initial electron concentration of $\sim 4.7 \times 10^{13} \text{ cm}^{-3}$ at 77°K, and the difference in carrier concentration between 77 and 200°K indicates the presence of $\sim 1.1 \times 10^{14}$ Te-donor atoms cm^{-3} . This sample was shielded against thermal neutrons with Cd foil and irradiated in a poolside facility of the Bulk Shielding Reactor at ORNL to an estimated fluence of $\sim 3 \times 10^{13} nvt_{\text{fast}}$ (> 1 MeV) neutrons. Although the sample was still *n* type after the irradiation (curves II), these data cannot be used to obtain an apparent removal rate of conduction electrons because the slopes of the curves are close to the intrinsic value. The sample was then vacuum annealed for 16 h at 450°C (curves III), and it is again evident that the irradiation or annealing has served to remove or compensate some of the initial Te donors. A comparison of the difference in carrier concentration at 77 and 200°K after irradiation and annealing indicates the presence of

$\sim 0.77 \times 10^{14}$ as compared to $\sim 1.1 \times 10^{14}$ Te-donor atoms cm^{-3} present initially; hence an irradiation with $\sim 3 \times 10^{13} nvt_{\text{fast}}$ (> 1 MeV) neutrons, followed by anneal, decreased the effective Te concentration by $\sim 3.3 \times 10^{13}$ Te-donor atoms cm^{-3} .

DISCUSSION

There are two experimental observations of interest resulting from this study: (a) the loss of Te donors which results from fast-neutron bombardment followed by a 450°C vacuum anneal and (b) the absence of the net acceptor state located ~ 0.2 eV below the conduction band which is characteristic of irradiated *n*-type Ge doped with As or Sb.

We believe that the loss of Te double donors which results from fast-neutron bombardment and anneal is connected in some way with the disordered regions and their associated space-charge zones characteristic of fast neutron damage in Ge.^{3,14} This conclusion is perhaps obvious since no such loss occurs if comparable radiation-induced changes in carrier concentration are produced by particles whose energies are insufficient to cause disordered regions. On the other hand, since fast-neutron bombardment and anneal has no detectable effect upon the concentration of As or Sb single donors in Ge, the apparent loss of Te concentration must also in some way be related to the fact that Te acts as a double donor.

The following mechanism is proposed to account for the loss of Te double donors: (a) During irradiation the Te impurity atoms capture migrating Ge vacancies which are apparently quite mobile at room temperature. In contrast to the corresponding composite imperfections formed between mobile vacancies and single donors, which are expected to be electrically neutral at room temperature, we expect the Te-vacancy complex to bear a single positive charge at and above room temperature. The presence of the vacancy in the complex gives mobility to this center since it is known that similar complexes in silicon (*E* centers) migrate as a unit by the alternate interchange of positions by the components and motion of the vacancy around the impurity atom.¹⁵ (b) Those Te-vacancy complexes which find themselves within or which migrate into the space-charge zone surrounding disordered regions will experience a strong electric field ($\sim 5 \times 10^4$ V/cm) which will tend to sweep them into the disordered region. This field exists because the heavily damaged region ($\sim 10^{-6}$ cm in radius) acts like a *p*-type island in the *n*-type matrix.^{3,14} Consequently the space-charge zone is simply the consequence of the *p-n* junction and extends $\sim 10^{-5}$ cm from the center of the damaged region.^{3,14} (c) Because of the field-assisted migration of the Te-vacancy complexes, there will be a tendency

¹⁴ B. R. Gossick, *J. Appl. Phys.* **30**, 1214 (1959).

¹⁵ M. Hirata, H. Saito, and J. H. Crawford, Jr., *J. Appl. Phys.* **38**, 2433 (1967).

for Te to concentrate in the disordered regions. Here several Te atoms can come together to form a stable aggregate or precipitate which is electrically inactive.

Let us now consider some of the quantitative aspects of the problem. In one experiment (Fig. 3) a fast-neutron fluence of $3 \times 10^{13} \text{ cm}^{-2}$ reduced the Te-donor concentration from ~ 1.1 to $0.77 \times 10^{14} \text{ cm}^{-3}$, which amounts to a 30% reduction. If we make the naive assumption that the affected Te impurity all fell within space-charge zones, the fraction of the crystal volume occupied by space charge was also 30%. Hence the average volume of a zone around a disordered region is

$$\bar{v}_{sc} = V/N_L \sigma_s F_f, \quad (1)$$

where V is the total (fractional) volume affected, N_L is the concentration of lattice sites ($4.45 \times 10^{22} \text{ cm}^{-3}$), σ_s is the fast-neutron scattering cross section of Ge ($\sim 4 \times 10^{-24} \text{ cm}^2$), and F_f is the fast-neutron fluence. Using the appropriate values in Eq. (1) gives for \bar{v}_{sc} $5.5 \times 10^{-14} \text{ cm}^3$ which corresponds to an average radius of $2.3 \times 10^{-5} \text{ cm}$. This is only slightly larger than the size of the space-charge zone estimated from a variety of property measurements and observed by Bertolotti and co-workers¹⁶ by means of electron-microscope replication techniques ($\sim 1.5 \times 10^{-5} \text{ cm}$).

In view of the fact that some migrating complexes will wander across the boundary of the space-charge zones and that this will have the effect of increasing the apparent size of the space-charge zones, we consider this to be excellent agreement.

In another experiment (Fig. 2) the fast-neutron fluence was a factor of $\sim 10^2$ to 10^3 larger, hence one would anticipate a considerable overlapping of the space-charge zones, with a consequent reduction in the electric field intensity and field-assisted migration to disordered regions. However, $\sim 75\%$ of the Te atoms were no longer evident as double donors after fast-neutron irradiation and vacuum anneal, in spite of the fact that all of the donor-type ⁷⁵As was observed.

The average number of Te atoms swept into a disordered region may also be estimated. The number of neutron collisions and hence the number of disordered

regions is simply

$$N_d = N_L \sigma_s F_f, \quad (2)$$

which yields $\sim 5 \times 10^{12} \text{ cm}^{-3}$ for the sample of Fig. 3. Since the loss in Te-donor concentration was $3.3 \times 10^{13} \text{ cm}^{-3}$, some six Te-vacancy complexes on the average were swept into a disordered region. For a typical disordered region this corresponds to a very high Te concentration ($> 10^{18} \text{ cm}^{-3}$), a value well in excess of the expected solubility, so that stable aggregate formation is not unreasonable.

We next consider the absence of a net acceptor state in the upper half of the gap in irradiated Te-doped Ge. It is generally agreed that the 0.2-eV state is associated with a vacancy-donor complex¹⁷ in irradiated *n*-type Ge doped with As or Sb. This defect is analogous to the *E* center which has been extensively studied in *n*-type Si.¹⁸ As postulated above in order for our interpretation of the fast-neutron irradiations to hold, the Te double donors must capture mobile vacancies to form a charged donor-vacancy complex. In view of the anticipated charge difference, it is perhaps not surprising that the energy levels are also different. The charged donor-vacancy state, if it exists, must lie either much closer to the conduction band or in the lower half of the band gap.

SUMMARY

The loss of Te double donors in Ge which has been irradiated with fast neutrons and subsequently annealed at a temperature normally adequate to remove all traces of radiation damage appears to be explicable on the basis of field-assisted migration of composite imperfections comprised of the Te and a vacancy. The electric field in the space-charge zone surrounding heavily disordered *p*-type regions is sufficiently large and in the proper direction to sweep the Te-vacancy complexes (postulated to be positive) into the disordered regions where they aggregate and become electrically inactive. Evidently, this composite defect has an energy-level structure different from the analogous one observed in material doped with As or Sb, since the net acceptor state 0.2 eV below the conduction band is not observed.

¹⁷ A. Hiraki, J. W. Cleland, and J. H. Crawford, Jr., *Phys. Rev.* **177**, 1203 (1969).

¹⁸ G. D. Watkins, in *Proceedings of Seventh International Conference in the Physics of Semiconductors* (Dunod Cie., Paris, 1965), Vol. 3, p. 97.

¹⁶ For a review of relevant work see M. Bertolotti, in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Publishing Corp., New York, 1968), p. 311.