

## Radiation-Induced Recombination and Trapping Centers in Germanium. II. Annealing in Gamma-Irradiated, Antimony-, and Arsenic-Doped Material\*

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(Received December 26, 1961)

An investigation has been made of the annealing properties of radiation-induced recombination centers in germanium. The annealing behavior of antimony-doped germanium is grossly different from that of arsenic-doped material. The experimental observations are explained on the following basis: The recombination level at 0.36 eV above the valence band belongs to the vacancy. In antimony-doped material the vacancy disappears by association with an antimony atom. This process does not occur in arsenic-doped material, and higher temperatures are required to produce annealing. It is thought that a trapping level, present only in arsenic-doped material, located 0.10 eV above the valence band might be due to an arsenic-interstitial pair.

### INTRODUCTION

ANNEALING experiments have played an important role in our present understanding of radiation damage. It is hoped through the studies herein reported to resolve some of the questions which remain concerning radiation-induced defects, especially as they act as centers for the recombination of excess carriers in germanium. An analysis of the recombination behavior associated with radiation-induced defects has been given in an earlier paper.<sup>1</sup>

One naturally expects a difference in the nature of radiation damage, depending upon the nature and energy of the bombarding particle. This difference has been demonstrated quite strikingly in the case of

minority-carrier-lifetime measurements in germanium, where the recombination behavior is dependent upon whether the bombarding particles are Co<sup>60</sup> gamma rays, fission neutrons, or 14-Mev neutrons.<sup>1</sup> A brief study has been made to ascertain the nature of the dependence of annealing behavior on the type of bombarding particles and it was shown that, indeed, there is a strong dependence.<sup>2,3</sup> However, it is not the purpose of this work to study in any detail these differences, rather, the case in which the simplest type of damage is expected, irradiation by Co<sup>60</sup> gamma rays, has been singled out in hopes that there might be a better chance of understanding the observations.

A number of studies of annealing behavior have been made. One such study is especially significant to this work, namely the work of Brown, Augustyniak, and Waite on electron-irradiated germanium.<sup>4</sup> These authors found that the chemical nature of the doping agent, present in quantities of approximately  $10^{15}$  cm<sup>-3</sup>, had gross effects upon the annealing behavior. These results indicate that previous analyses<sup>5,6</sup> made on the basis of annihilation of interstitials with their parent vacancies are invalid. In contrast to the present work, Brown, Augustyniak, and Waite primarily used conductivity as an indication of the amount of damage present. They used electrons with energies of the order of a million-electron volts, which would be expected to produce damage similar to that produced by Co<sup>60</sup> gamma rays. However, their defect concentrations were much larger than those required for annealing studies based on recombination behavior. A brief study of the near-room-temperature annealing of 15 ohm-cm, *n*-type germanium irradiated with Co<sup>60</sup> gamma rays also has

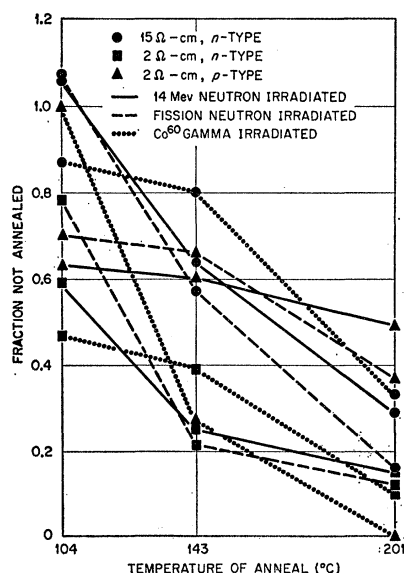


FIG. 1. Fraction of damage remaining following successive 4-hr anneals.

\* This paper is taken in large part from the thesis of O. L. Curtis, Jr., submitted to the Graduate Council of the University of Tennessee in partial fulfillment of the requirements for the Ph.D. degree.

† Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

<sup>1</sup> O. L. Curtis, Jr., and J. H. Crawford, Jr., *Phys. Rev.* **124**, 1731 (1961).

<sup>2</sup> O. L. Curtis, Jr., and J. H. Crawford, Jr., *Bull. Am. Phys. Soc.* **5**, 196 (1960).

<sup>3</sup> O. L. Curtis, Jr., thesis, submitted to the Graduate Council of the University of Tennessee in partial fulfillment of the requirements for the Ph.D. degree (unpublished).

<sup>4</sup> W. L. Brown, W. M. Augustyniak, and T. R. Waite, *J. Appl. Phys.* **30**, 1258 (1959).

<sup>5</sup> W. L. Brown, R. C. Fletcher, and K. A. Wright, *Phys. Rev.* **92**, 591 (1953).

<sup>6</sup> T. R. Waite, *Phys. Rev.* **107**, 463, 471 (1957).

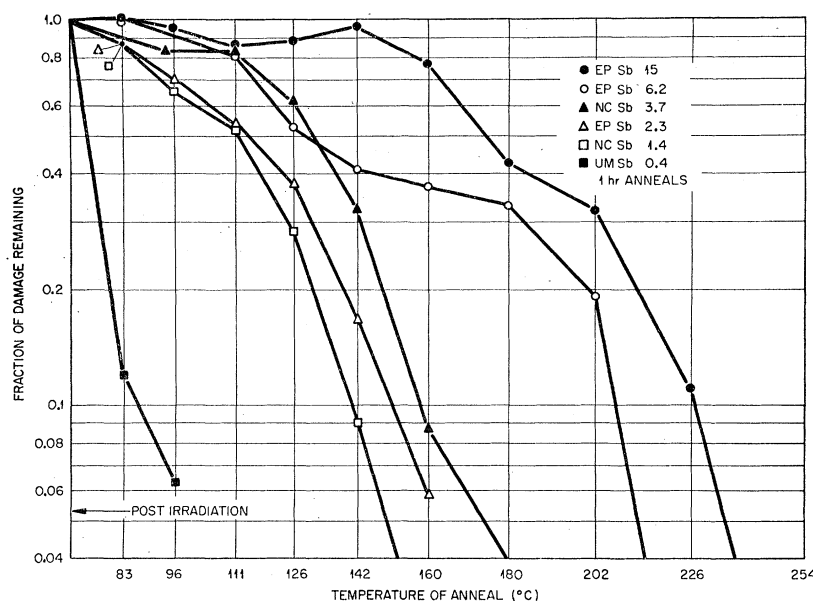


Fig. 2. Fraction of damage remaining following successive 1-hr anneals, antimony-doped germanium.

been made.<sup>7</sup> However, the results were analyzed in terms of direct recombination of vacancy-interstitial pairs, which Brown, Augustyniak, and Waite have shown do not occur in this temperature range. Annealing studies, also very brief, have been made on high-resistivity germanium irradiated with 14-Mev neutrons.<sup>8</sup>

#### EXPERIMENTAL PROCEDURE

This method of lifetime measurement utilized the exponential decay of excess carriers following injection by a light pulse. For details of the experimental procedure, the reader is referred elsewhere.<sup>3,9</sup>

Most of the annealing was carried out in a silicone-oil bath. A mercury-to-wire temperature controller was capable of maintaining the temperature to  $\pm 0.1^\circ\text{C}$ . The temperatures were measured with a copper-Constantan thermocouple or a mercury thermometer. The estimated accuracy of annealing temperatures was  $\pm 0.5^\circ\text{C}$ . The time required for the specimens to attain temperature equilibrium after being placed in the oil was observed. From this the estimated accuracy of time of anneal was  $\pm 1$  min. The silicone oil used in the oil bath was nominally stable to about  $250^\circ\text{C}$ . Therefore, for higher temperatures it was necessary to use a salt bath.<sup>10</sup> The accuracy of temperature measurements using the salt bath was estimated to be about  $\pm 1^\circ\text{C}$ . It was necessary to seal the specimens in an evacuated

Pyrex tube, thus lessening the thermal contact with the bath. However, the error in annealing time was estimated to be only about  $\pm 3$  min in this case. For the first series of measurements, which were performed to determine the nature of the annealing behavior for different types of radiation and sample characteristics, the anneals were carried out in a vacuum oven. In this case the temperature control was rather poor, and the error in the temperature of anneal may have been of the order of  $\pm 5^\circ\text{C}$ . These were all 4-hr anneals, with an estimated inaccuracy in the time determination, due to the slow response of the oven of  $\pm \frac{1}{2}$  hr.

The gamma irradiations were carried out in a  $\text{Co}^{60}$  source of approximately 1500 C, providing approximately  $2 \times 10^6$  r/hr or  $3 \times 10^{15}$  gammas/cm<sup>2</sup>/hr at the sample. The temperature of irradiation was about  $35^\circ\text{C}$ . The fission neutrons were obtained from a low-flux facility of the Oak Ridge graphite reactor. The temperature of irradiation was about  $28^\circ\text{C}$ .

#### RESULTS

##### I. Exploratory Measurements

Preliminary to making a detailed study of annealing behavior, a survey-type experiment was made in order to provide a general idea of the behavior to be expected.<sup>2</sup> Three types of irradiating particles were used: 14-Mev monoenergetic neutrons, fission neutrons, and  $\text{Co}^{60}$  gamma rays. In each case three types of specimens were used: 2 ohm-cm *p*-type, 2 ohm-cm *n*-type, and 15 ohm-cm *n*-type. Figure 1 summarizes the results of these measurements. In this figure the fraction of damage remaining,<sup>11</sup> as determined from the room-

<sup>7</sup> T. Asada, H. Saito, K. Omura, T. Oku, and M. Oka, J. Phys. Soc. Japan **15**, 93 (1960).

<sup>8</sup> R. F. Konoplev, T. V. Mashovets, and S. M. Ryvkin, Suppl. Fiz. Tverdogo Tela **2**, 11 (1950).

<sup>9</sup> O. L. Curtis, Jr., and J. H. Crawford, Jr., General Discussion of the Faraday Society, Saclay, France, April 11-12, 1961 (unpublished).

<sup>10</sup> This salt bath and the associated control equipment were kindly furnished by M. S. Wechsler and R. H. Kernohan of the Solid State Division, Oak Ridge National Laboratory.

<sup>11</sup> The fraction of damage remaining in the crystal was taken to be  $f = (1/\tau - 1/\tau_0)(1/\tau_i - 1/\tau_0)^{-1}$ , where  $\tau_0$  is the pre-irradiation lifetime,  $\tau_i$  is the post-irradiation lifetime, and  $\tau$  is the lifetime following anneal.

temperature-lifetime values, is plotted as a function of the annealing temperature. Three temperatures were used: 104, 143, and 201°C. The type and resistivity of the material are indicated by the symbols used for the points; the type of irradiation by solid, dashed, and dotted lines. The *n*-type samples were antimony doped; the *p*-type samples were indium doped.

Several conclusions can be drawn immediately from this plot. The annealing behavior depends markedly both on the type of irradiation and the properties of the material. Two ohm-cm *n*-type material annealed more readily than 15 ohm-cm *n*-type material regardless of the irradiation used. (The 15 ohm-cm value is nominal. Although the three specimens were from the same ingot, the values ranged from 11 to 15 ohm-cm.) The most striking difference between types of irradiation was demonstrated by the *p*-type material. Here, throughout the annealing range, the annealing behavior for material irradiated by Co<sup>60</sup> gamma rays was quite different from the two specimens irradiated by neutrons.

## II. Detailed Measurements for Gamma Irradiation

Since the nature of gamma-ray-induced damage is expected to be simpler than for the case of neutron bombardment and since the recombination process is better understood in *n*- than in *p*-type material, emphasis has been placed on *n*-type germanium irradiated with Co<sup>60</sup> gamma rays. Isochronal anneals were performed on antimony-doped samples and arsenic-doped samples with different impurity concentrations, and on one *p*-type, indium-doped sample. One-hour anneals for as many as eleven different temperatures, equally spaced on the  $1/T$  scale, were made. Figure 2 summarizes the results for antimony-doped material. Here the fraction of damage not annealed is plotted as

TABLE I. Irradiation received by various samples.

Sample	Total irradiation ( $\gamma$ 's/cm <sup>2</sup> )
EP Sb 15	$9 \times 10^{15}$
EP Sb 6.2	$5 \times 10^{16}$
NC Sb 3.7	$4 \times 10^{16}$
EP Sb 2.3	$3.3 \times 10^{16}$
UM Sb 0.4	$3 \times 10^{15}$
NC As 20	$9 \times 10^{16}$
NC As 5.4	$4 \times 10^{16}$
NC As 2.6	$2.1 \times 10^{16}$
NC Sb 1.4	$5.2 \times 10^{15}$
UM Sb 1.3(A)	$2.1 \times 10^{16}$
UM Sb 1.3(B)	$2.1 \times 10^{16}$
NC In 8.3	$2 \times 10^{17}$

a function of the annealing temperature. The following resistivities are represented in this plot: 15, 6.2, 3.7, 2.3, 1.4, and 0.4 ohm-cm. Table I gives the total amount of irradiation received for these and other specimens. (No evidence for a dependence of annealing on total dose was found.) The important feature shown in Fig. 2 is that the annealing behavior depends markedly on the impurity concentration (as determined from conductivity) throughout the resistivity range.

The results for arsenic-doped material, shown in Fig. 3, were entirely different. The results for three resistivities are shown in the figure: 20, 5.4, and 2.6 ohm-cm. There was an early, apparently impurity-concentration-dependent annealing whose extent ranged from about 15 to about 60% recovery in the three samples. At higher temperature, if the curves for the two lower resistivities (higher impurity concentration) are normalized, they very nearly superimpose. The annealing behavior of NC As 20 was actually rather similar to that for EP Sb 15, which might be expected since in these higher resistivity samples the impurity

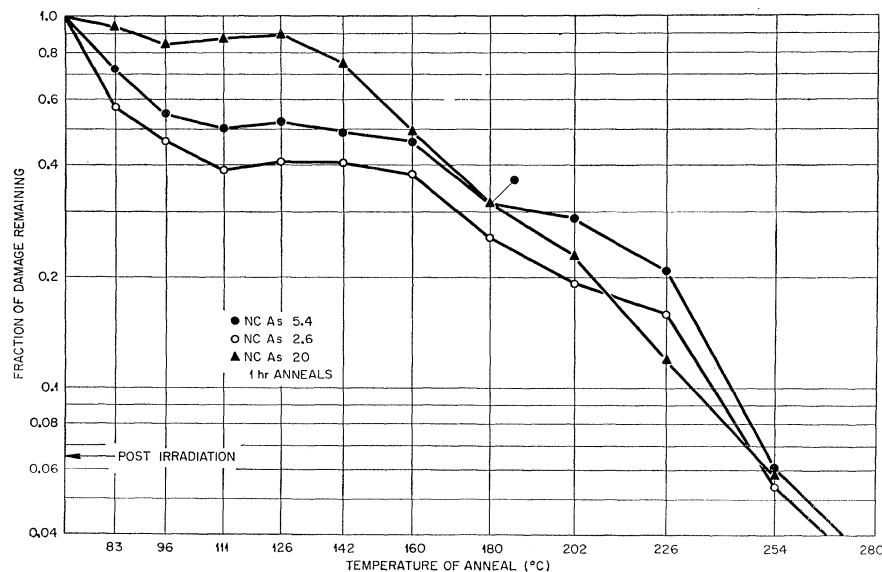


FIG. 3. Fraction of damage remaining following successive 1-hr anneals, arsenic-doped germanium.

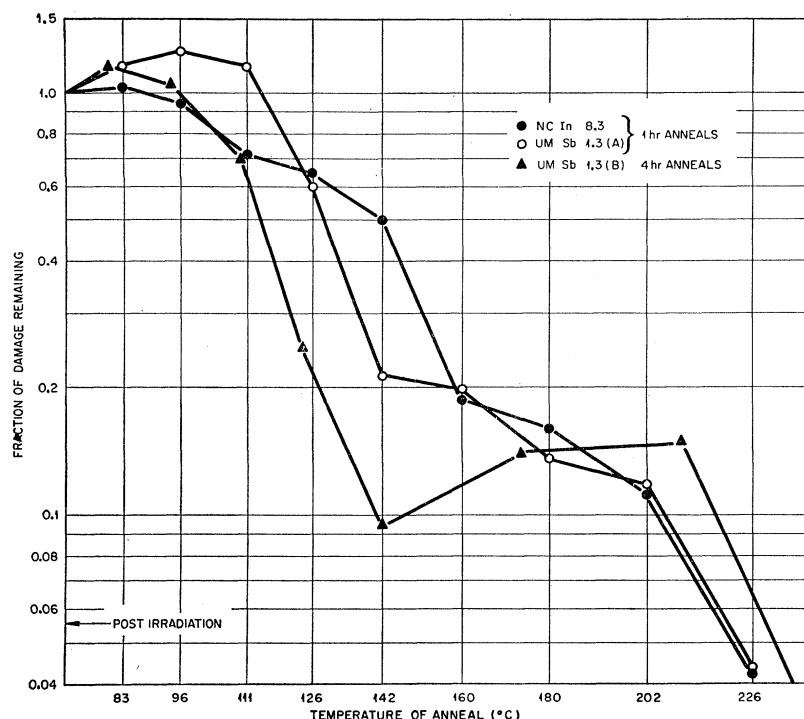


FIG. 4. Fraction of damage remaining following successive anneals for one indium- and two antimony-doped specimens.

concentration was rather low and might, therefore, play a less important role in the annealing process.<sup>12</sup>

The results for two antimony-doped specimens were not included in Fig. 2 in order to avoid confusion. These results, as well as those for the *p*-type sample, are shown in Fig. 4. UM Sb 1.3(A) and UM Sb 1.3(B) were two samples from the same ingot. In contrast to all the other antimony-doped samples, they displayed an early reverse anneal and a sizable amount of damage which remained to rather high temperatures. Note that the annealing time for UM Sb 1.3(B) was 4 hr at each temperature, and some of the annealing temperatures were slightly different from those used with the other specimens. The major fraction of the annealing occurred at a temperature which is consistent with the results shown in Fig. 2. Finally, the results for a single *p*-type specimen, given in Fig. 4, cannot, of course, give much information about the annealing behavior in *p*-type material. The similarity of its annealing behavior to that of UM Sb 1.3(A) at high temperatures is probably coincidental.

Isothermal anneals were made on several specimens. The case in which it might be hoped to gain the most information is the antimony-doped low-resistivity material where the annealing appears to be nearly a single-step process. Figure 5, which is a semilogarithmic plot of the fraction of damage remaining as a function of time, shows the results for four isothermal anneals

on NC Sb 3.7. The curves appear to follow first-order behavior fairly well; thus, first-order rate constants  $k'$  have been assigned to them. If a second-order effect is present, increasing the amount of irradiation should increase the apparent value of  $k'$ . As observed for a difference of a factor of three in the amount of irradiation, only a small difference in  $k'$  is observed, which is in the opposite sense to that expected for a second-order contribution. Figure 6 is a similar plot for 1.4 ohm-cm antimony-doped material. Here the behavior appears first-order after an initial transient. Such a transient is often expected in first-order diffusion-

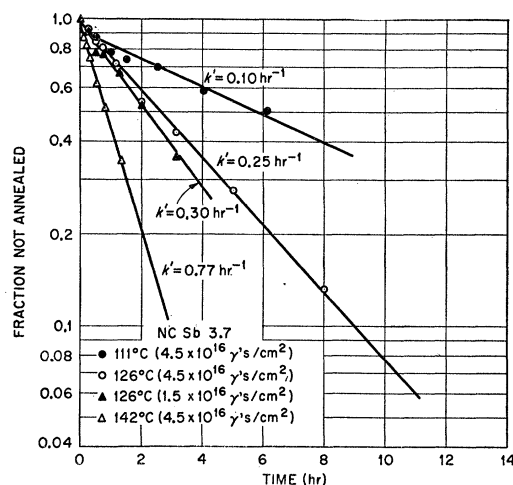


FIG. 5. Isothermal annealing curves for 3.7 ohm-cm, antimony-doped germanium following  $\text{Co}^{60}$  gamma irradiation.

<sup>12</sup> An attempt to correlate annealing temperature with dislocation density was unsuccessful. Samples which, on the basis of etch-pit counting, had large differences in dislocation density, showed little difference in annealing behavior.

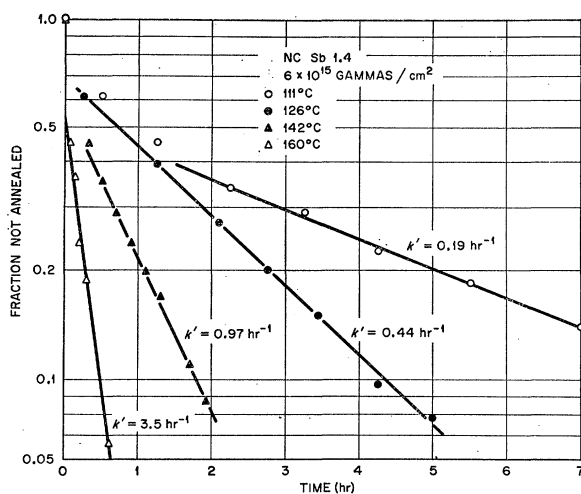


FIG. 6. Isothermal annealing curves for 1.4 ohm-cm, antimony-doped germanium following  $\text{Co}^{60}$  gamma irradiation.

limited processes.<sup>6,13</sup> Figure 7 shows somewhat more complicated behavior for UM Sb 1.3(A) and UM Sb 1.3(B). However, Fig. 4 indicates that these samples retained residual damage following a large amount of annealing at fairly low temperature. This amount should be subtracted from the data of Fig. 7. For UM Sb 1.3(A) the correction was about one-tenth, and for UM Sb 1.3(B) the correction was about two-tenths. These values were subtracted from the results of Fig. 7 to give the data of Fig. 8. Again, except for the anomalous early increase in damage associated with these samples, the behavior appears first-order, and first-order rate constants have been assigned. Again, measurements show that  $k'$  is independent of damage concentration.

Figure 9 shows the result of an attempt to obtain the activation energy assuming first-order kinetics. The difference in values obtained for the three samples is disappointing. Due to the complicated behavior of UM Sb 1.3, the apparent activation energy associated with it is probably incorrect. In all samples there may be competing processes with somewhat different activation energies which might tend to affect the values obtained. Nonetheless, the annealing process seems to be dominated by a first-order process with an activation energy of  $\sim 0.9$  eV.

Due to the complexity of the annealing behavior in arsenic-doped material, one cannot measure an activation energy as in the case of antimony-doped specimens. However, the early anneal is well separated from the remaining portion. Therefore, by first allowing the early anneal to occur, one may investigate the anneal occurring at higher temperatures. Such an attempt is demonstrated in Fig. 10. These isothermal annealing curves were taken following irradiation and heat treatment for one hour at 126°C. On the basis of Fig. 3, nearly all of the early anneal, but almost none of the

later anneal, would have occurred. It is clear from the shape of the curves that the behavior cannot be described by a unique activation energy. Rather, there seems to be a distribution of activation energies. The processes apparently are very nearly first-order, as evidenced by the two sets of data taken at 190°C for different damage concentrations. It would seem unwise to speculate on the nature of this annealing because of the small amount of information available. However, since this anneal does not depend on the defect or impurity concentration, it is evidently not direct vacancy-interstitial recombination; and it must take place at some location other than an impurity center.

## DISCUSSION

Figures 1-3 demonstrate that the annealing process by which lifetime recovers from the effect of irradiation is not a simple one. Furthermore, the presence of trapping levels complicates the analysis of the lifetime data since there are two types of centers present. The recombination behavior is governed in our case by the following equation<sup>1</sup>:

$$\tau = \frac{p_{1r}}{c_{nr}nN_r} + \frac{1}{c_{nr}n} + \frac{N_t p_{1r}}{c_{nr}nN_r p_{1t}} + \frac{N_t}{c_{pr}N_r p_{1t}} + \frac{1}{c_{pt}p_{1t}} + \frac{1}{c_{pr}N_r} \quad (1)$$

In this equation there are two terms,  $N_t/c_{pr}N_r p_{1t}$  and  $1/c_{pt}p_{1t}$ , which display the same temperature dependence. The first term depends on  $N_t$ ; the second does not. Thus, it does not seem possible to determine the annealing kinetics of trapping levels from the present measurements.

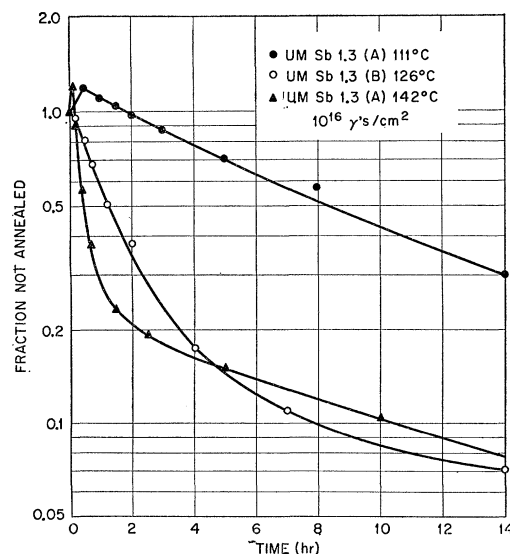


FIG. 7. Isothermal annealing curves for 1.3 ohm-cm, antimony-doped germanium following  $\text{Co}^{60}$  gamma irradiation.

<sup>13</sup> Howard Reiss, J. Appl. Phys. 30, 1141 (1959).

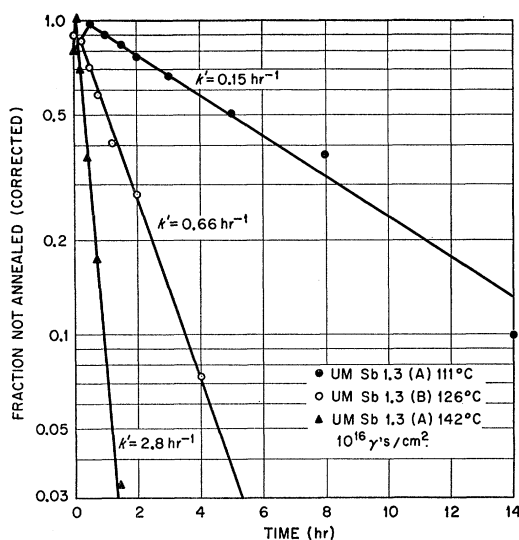


FIG. 8. Corrected isothermal annealing curves. Data of Fig. 7.

In order to explain the annealing data, the defect responsible for recombination is postulated to become mobile in the temperature range in which annealing occurs. Upon coming under the influence of an impurity atom, the isolated defect responsible for recombination becomes ineffective either through recombining with a vacancy or interstitial associated with the impurity or through forming a complex with the impurity. Thus, the annealing behavior of antimony-doped material can be explained.<sup>14</sup> However, this does not account for the more complicated behavior in arsenic-doped germanium.

The difference in atomic radii between antimony and arsenic might reasonably be expected to be somehow responsible for the difference in observed annealing behavior. The covalent radii of germanium, antimony, and arsenic are 1.22, 1.41, and 1.21 Å, respectively.<sup>15</sup> However, the antimony and arsenic atoms carry unit positive charge, decreasing their size. On the basis of arguments given by Pauling,<sup>16</sup> the covalent radii for the antimony and arsenic atoms in the germanium lattice are approximately 1.39 and 1.19 Å, respectively. Thus, it would seem that there is a positive lattice strain produced by the antimony atom which is not present in the case of arsenic. An interstitial would avoid an antimony atom because its presence would add to the strain present in the region of the antimony atom. However, a vacancy would find it energetically favorable to be in the region of the large antimony atom. Furthermore, a vacancy is expected to be nega-

tively charged and, thus, would be attracted to the antimony atom. This negative charge agrees with the fact that electron capture is the limiting process in recombination, as seen from the fact that  $c_{nr}$  is the important capture probability in the recombination equation.<sup>1</sup> On the basis of these arguments, the recombination centers are postulated to be vacancies.

Hopefully, the data of Fig. 9 could be used to check this conclusion. The activation energy for motion has been determined<sup>17</sup> as 1.0 ev. However, the data are not sufficiently accurate to be conclusive.

If the above arguments are correct, the annealing of the arsenic-doped samples should be impurity-concentration independent and should be the same as for antimony-doped samples with sufficiently low antimony concentration. This is approximately true except for the initial concentration-dependent anneal observed in arsenic-doped specimens. Possibly there was a small number of interstitial-arsenic atoms which recombined with part of the vacancies, or a small fraction of the arsenic atoms might have had interstitials associated with them (either initially or as a result of irradiation) with which the vacancies could recombine.

A brief statement regarding the nature of the trapping centers is appropriate. While trapping occurs near room temperature in arsenic-doped germanium, it does not in antimony-doped material. A logical explanation would be that the trapping level in arsenic-doped germanium is due to an impurity-imperfection complex. This could be, for instance, an interstitial-arsenic pair. An interstitial-antimony pair would not be expected to occur due to the large size of the antimony atom. The trapping level was assigned the position of 0.10 ev

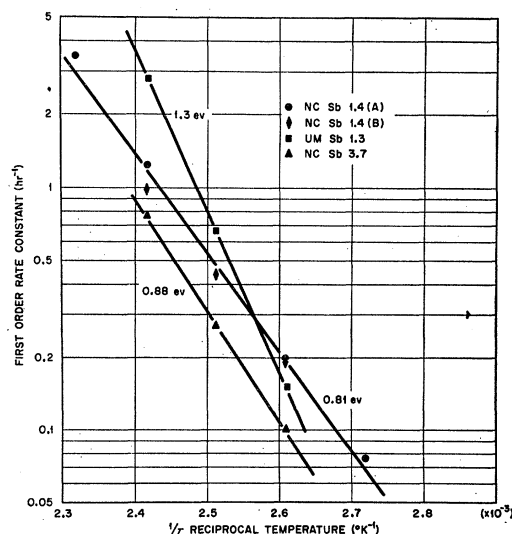


FIG. 9. First-order rate constants as a function of reciprocal temperature. Apparent activation energies are indicated.

<sup>14</sup> Although there is a clear association between the rate of annealing and antimony concentration, attempts to obtain a quantitative relationship were unsuccessful. This is presumably due to the effect of other impurities on the carrier concentration (our measure of the amount of antimony present).

<sup>15</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948), p. 165.

<sup>16</sup> Reference 15, p. 169.

<sup>17</sup> H. Letaw, Jr., W. M. Portnoy, and L. Slifkin, *Phys. Rev.* **102**, 636 (1956).

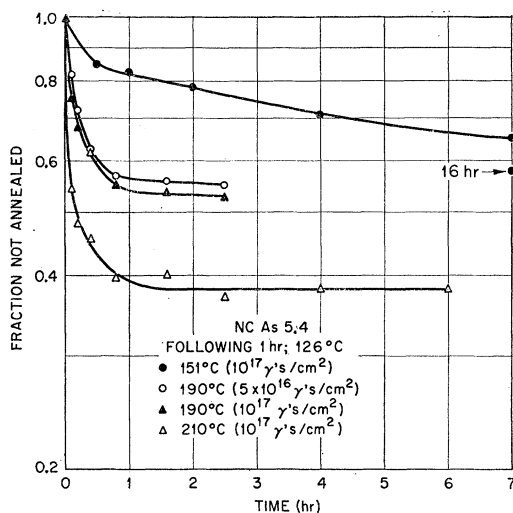


Fig. 10. Isothermal annealing curves for 5.4 ohm-cm, arsenic-doped germanium following  $\text{Co}^{60}$  gamma irradiation and 1 hr at  $126^\circ\text{C}$ .

above the valence band,<sup>18</sup> but this estimate involves a greater uncertainty than that involved in the determination of the position of the recombination center.<sup>1</sup>

An attempt has been made to explain the annealing at higher temperatures on the basis of the annealing of vacancies. An obvious possibility is to ascribe the lower temperature anneal seen by Brown, Augustyniak, and Waite<sup>4</sup> to interstitial migration. The less rapid anneal and, also, the trapping levels present in the case of arsenic doping could be explained on the basis of interstitials associating themselves with arsenic atoms instead of being completely annealed. If the annealing process occurring near  $50^\circ\text{C}$  is, indeed, due to interstitial migration, then there may well be some vacancy-interstitial recombination. Whether or not this occurs could probably be determined by investigating the dependence of the annealing on the defect concentration. The various annealing results seem to indicate that neither the vacancy nor the interstitial is a positively-charged donor. On the basis of the data of Brown, Augustyniak, and Waite<sup>4</sup> and Brown, Fletcher, and Wright,<sup>5</sup> in no temperature range is there any significant annealing which produces a decrease in electron concentration. If the interstitial were a positively charged donor, then at the time of its anneal the magnitude of the change in carrier concentration should actually increase. Brown, Augustyniak, and Waite, in Figs. 8 and 9 of their paper, show that, for arsenic-doped material, the annealing of mobility proceeds along an entirely different path than the carrier concentration. In antimony-doped material, the two properties anneal nearly together. This seems

consistent with the idea that the early (approximately  $50^\circ\text{C}$ ) anneal is associated with interstitial motion and that, in the case of arsenic-doped material, at least part of the interstitials associate themselves with arsenic atoms. In antimony-doped material, this association would not be expected to occur because of the lattice strain an antimony-interstitial pair would produce. If the interstitial is an acceptor, it is negatively charged; and each time an interstitial associates itself with an arsenic atom, two charged-scattering centers are removed, thus increasing the mobility. The notion that this mobility increase for arsenic-doped material might be caused by the association of a defect with an arsenic atom was mentioned by Brown, Augustyniak, and Waite.

Brown, Fletcher, and Wright<sup>5</sup> performed annealing experiments on neutron-irradiated germanium in which they observed the restoration of conductivity due to annealing in the temperature range 160 to  $300^\circ\text{C}$ . These data were re-analyzed by Waite,<sup>6</sup> who included some more accurate data of Augustyniak. Augustyniak's measurements were made on arsenic-doped material, as were probably Brown, Fletcher, and Wright's.<sup>19</sup> Brown, Augustyniak, and Waite present some of these data in Fig. 2 of their paper. It was found that these data agree surprisingly well with lifetime data for arsenic-doped material shown in Fig. 10. Figure 11 contains the data given in Fig. 10 as well as data of Brown, Fletcher, and Wright and of Augustyniak. The data are plotted in the manner used by Brown, Augustyniak, and Waite. Considering the different properties employed for indices of annealing, the agreement between the conductivity and lifetime data is remarkable. The resistivity of the samples from which

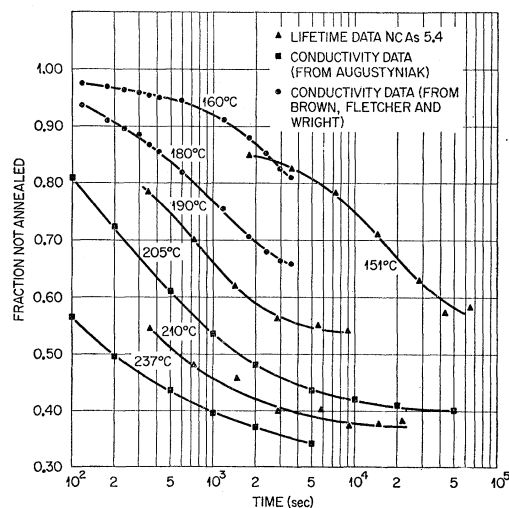


Fig. 11. Comparison of isothermal anneals performed on arsenic-doped germanium using lifetime and conductivity data following  $\text{Co}^{60}$  gamma irradiation and electron irradiation, respectively. Conductivity data from references 5 and 6.

<sup>18</sup> The previous<sup>1</sup> assignment of 0.17 eV was an error caused by adding the correction for the temperature variation of the density-of-states function to the observed slope, rather than subtracting it.

<sup>19</sup> W. M. Augustyniak (private communication).

the conductivity data were obtained was<sup>6,19</sup> 0.7 ohm-cm (before irradiation), as compared with the 5.4 ohm-cm specimen used for lifetime measurements. The results agree with the observation previously made that this annealing process is not dependent upon impurity concentration. NC As 5.4 had a pre-anneal treatment of one hour at 126°C. In the case of the conductivity samples with much higher impurity concentrations, the early lower-temperature anneal would probably have occurred in a relatively short time at room temperature and would not have been observed. The dose used for conductivity changes was very large compared with those used for lifetime changes. Their initial concentration of bombardment-induced defects was<sup>6</sup>  $\sim 10^{15}$  cm<sup>-3</sup>, while the value in the present case was  $\sim 2 \times 10^{13}$  cm<sup>-3</sup>. The agreement between the two types of data further substantiates the fact that this anneal is defect-concentration independent.

It seems unlikely that the agreement<sup>20</sup> of the two sets of data shown in Fig. 11 is fortuitous. On the basis

<sup>20</sup> One must not assume from these data that the recovery of lifetime and conductivity go together in the lower-temperature range or in antimony-doped material.

of this agreement, the center responsible for recombination in arsenic-doped material after the early anneal had occurred is felt to be the same center responsible for carrier removal. Therefore, it was possible to count the number of recombination levels on the basis of Hall measurements and, thus, determine the electron-capture probability for the recombination level. The value obtained is  $(2.0 \pm 0.4) \times 10^{-11}$  cm<sup>3</sup> sec<sup>-1</sup>. Any inaccuracy in the position of the recombination level would have a large effect on this value. However, the estimated error does not include any such uncertainty. The cross section is approximately equal to the capture probability divided by the mean-thermal velocity,  $\langle v \rangle$ . Using a value for the mean thermal velocity of electrons in germanium at 300°K of  $3.1 \times 10^7$  cm sec<sup>-1</sup>, the electron capture cross section was found to be approximately  $7 \times 10^{-19}$  cm<sup>2</sup>.

#### ACKNOWLEDGMENT

We wish to thank S. Othmer, a student under the cooperative plan of Virginia Polytechnic Institute, who assisted in much of the experimental work

### Spin-Lattice Relaxation Time of Samarium Ethyl Sulfate\*

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(Received December 15, 1961)

The spin-lattice relaxation time  $T_1$  of  $\text{Sm}^{3+}$  in the ethyl sulfate is computed. It is shown that  $T_1$  in the direct-process region should exhibit a large anisotropy with respect to the direction of the external magnetic field. The necessary Zeeman admixture of excited levels into the ground level is shown to be much smaller when the external field is parallel rather than perpendicular to the symmetry axis. This is because, on the one hand, the levels connected by a parallel field lie in the next  $J$  multiplet, some 1100 cm<sup>-1</sup> away. On the other hand, a perpendicular field can connect the ground state with a level within the ground multiplet, only 53.6 cm<sup>-1</sup> away. This is shown to be a general result for ions with small  $J$  values in crystals of moderately high symmetry.

THE theory of the spin-lattice relaxation time  $T_1$  for rare-earth salts has been given previously<sup>1</sup> but was restricted to orbit-lattice transitions solely between ground multiplet states. It was pointed out that  $T_1$  in the direct process region could vary markedly with the direction of the applied magnetic field, and a specific case, dysprosium ethyl sulfate, was examined at some length. In this paper we extend the theory to cover cases when intermultiplet transitions are important. Such a condition will arise, for example, for  $\text{Sm}^{3+}$  in the ethyl sulfate. Rather than treat an abstract case, we shall restrict our attention to samarium ethyl

sulfate, and indicate when necessary how to extend the treatment to other salts.

The configuration for  $\text{Sm}^{3+}$  is  $4f^5$  and the lowest term value is  $^6H$ . As Sm is in the first half of the rare-earth series,  $J = \frac{5}{2}$  for ground multiplet, and the first excited multiplet is a  $J = \frac{7}{2}$  level at about 1100 cm<sup>-1</sup>. The local symmetry in the ethyl sulfate is  $C_{3h}$  and, as Elliott and Stevens<sup>2</sup> have shown, this implies that an expansion of the static crystalline field in the spherical harmonics  $Y_n^m$  need only retain terms with  $n=2, 4$ , and 6 and  $m=0, \pm 6$ . Optical measurements<sup>3</sup> indicate the lowest level to be a  $|J = \frac{5}{2}, J_z = \pm \frac{1}{2}\rangle$  with a  $|J = \frac{5}{2}, J_z = \pm \frac{3}{2}\rangle$

\* This research was supported by the Advanced Research Projects Agency, Department of Defense.

<sup>1</sup> R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

<sup>2</sup> R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A215**, 437 (1952); **A218**, 553 (1953); **A219**, 387 (1953).

<sup>3</sup> H. Lammerman, Z. Physik **150**, 551 (1958).