Germanium doped with antimony in the range of 1 to $2 \times 10^{17}$ atoms/cm$^3$ exhibits a temperature independent resistivity for temperatures less than $10^6$K. As acceptor states are introduced by irradiation with fast neutrons, it is found that the low temperature resistivity exhibits an activation energy $\varepsilon_2$. Since the magnitude of $\varepsilon_2$ depends upon the distribution and the number of occupied donors, this parameter is useful for studying the thermal stability of the defects that are introduced by irradiation. It is found in these highly doped materials that the motion of charged defects to form neutral complexes does not seem to involve the neutral donors.

It is well-known that the low temperature resistivity of germanium is strongly dependent upon the concentration of the dopant. Figure 1 presents resistivity data on four samples of antimony doped with germanium. The room temperature resistivities, Hall coefficients, donor concentrations, and the average separation between donors is given in Table I for these samples. For temperatures below about $10^6$K, the resistivity...
of samples F1 and SM1 is independent of temperature. If the low temperature resistivity is described by the equation \( \rho = \rho(\infty) \exp \left( \frac{\varepsilon_2}{kT} \right) \), the activation energy \( \varepsilon_2 \) of samples El and L1 is 0.62 and 0.08 milli-electron volts, respectively.

![Figure 1. Variation of resistivity with reciprocal temperature for the specimens listed in Table I.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity (Room Temperature) (( \Omega \text{ cm} ))</th>
<th>Hall Coefficient (Room Temperature) (( \text{cm}^3/\text{coulomb} ))</th>
<th>Donor Concentration (( 10^{17} \text{cm}^{-3} ))</th>
<th>Average Donor d(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM1</td>
<td>0.016</td>
<td>28.0</td>
<td>2.2</td>
<td>103</td>
</tr>
<tr>
<td>F1</td>
<td>0.020</td>
<td>36.4</td>
<td>1.7</td>
<td>112</td>
</tr>
<tr>
<td>L1</td>
<td>0.029</td>
<td>58.6</td>
<td>1.1</td>
<td>131</td>
</tr>
<tr>
<td>El</td>
<td>0.037</td>
<td>84.0</td>
<td>0.74</td>
<td>147</td>
</tr>
</tbody>
</table>

A completely satisfactory theory of this thermally activated conduction has not been developed. Fritzsche\(^{(1)}\) first suggested that \( \varepsilon_2 \) is to be associated with the energy to put a second electron onto a neutral donor site. Mott and Twose\(^{(2)}\) consider that the critical parameter is the magnitude of the overlap integral associated with electrons on two different sites. As the average separation of the impurities decreases, it is supposed that the magnitude of the overlap energy increases to such an extent that a long-range order is established. It is possible, then, for the lowest energy state of the system to be nonconducting. Separated
from it by a small energy decreasing with increasing overlap. As the concentration of impurities further increases, the energy between the non-conducting and conducting states decreases and becomes zero. It seems reasonable to associate the state having a zero activation energy with a system that shows no temperature dependence of the conductivity at low temperatures, but still exhibits a thermal activation energy at higher temperatures (Samples F1 and SM1). Consistent with this view is the constancy of the Hall coefficient at the low temperatures (figure 2). Nishimura has recently calculated the magnitude of $\epsilon_2$ for a simple model that assumes that the ground state of the donor is hydrogenic and that a band at higher energies results from the interaction between states of negatively charged donors.

Figure 2. Variation of Hall coefficient with reciprocal temperature for the specimens listed in Table I.

Davis and Compton have studied the dependence of $\epsilon_2$ upon the degree of compensation of the sample. An increase in the compensation may be viewed in a qualitative sense as merely reducing the average electron overlap of the occupied donors. Thus, $\epsilon_2$ would be expected to increase with increasing compensation as the number of neutral donors is decreased. Data indicating that this is indeed the case are given for samples F1 and SM1 in Figure 3. The theoretical expression derived by Nishimura for the compensation dependence of $\epsilon_2$ does not quantitatively predict the proper variation. This is not altogether surprising since the field of the ionized donors and acceptors was omitted in the treat-
ment of the lattice potential. Similarly, deviations of the donor wave functions from spherical symmetry were neglected. It is believed, however, that the ideas developed by Fritzsche, Mott and Twose, and Nishimura correctly describe the physical origin of the process giving rise to the thermally activated process described by the energy $\epsilon_2$.

Since the parameters associated with the low temperature conduction process, namely $\epsilon_2$ and the value of the intercept of the low temperature resistivity curve at $1/T = 0$, $\rho(0)$, depend upon the distribution and number of neutral donors, they can provide additional information about the stability and nature of radiation induced defects. This paper describes the results of the thermal annealing of fast neutron induced changes in the electrical properties of samples of germanium that contain $2.2 \times 10^{17}$ cm$^{-3}$ antimony donors (Sample SM1). The irradiation introduces acceptors (of density $N_A$) which have energy levels deep in the forbidden gap, thereby reducing the concentration of electrons free to conduct to $n = N_D(1-K)$ electrons which are condensed onto the broadened donor ground state levels at temperatures below 10$^6$K. A set of anneals offered the possibility of changing the distribution of compensating defects without changing their total number, and therefore the possibility of observing the influence of the distribution of the compensating defects on the impurity conduction parameters.

The samples were irradiated at ambient with neutrons of energy
exceeding 10 Kev to an integrated flux of $\sim 4 \times 10^{16}$/cm$^2$. Thermal neutrons were removed by enclosing the samples in a cadmium foil shield. Since the irradiations were performed in the "Lazy Susan" position of a Triga Mark II Experimental reactor at a depth of 6" in the graphite reflector, rather than at the core, the energy spectrum is somewhat degraded from a fission spectrum. This will tend to reduce the importance of large damage clusters$^{(5)}$ which have been shown to electrically resemble insulating voids. The high doping and consequent large carrier concentration furthermore will lead to a short Debye screening length$^{(5)}$ of about 150 Å at 300°K, thus reducing the size of the space charge region surrounding larger damage clusters. The compensation after irradiation was determined from the measured values of the Hall coefficient at 0°C carrier concentration to about 56% of its initial value, corresponding to a value of $K = 0.44$. The mobility at 0°C was reduced from 1700 cm$^2$/volt sec to 1250 cm$^2$/volt sec. This is consistent with an increase in charged center scattering, as given by the Brooks-Herring formula,$^{(6)}$ of $N_A = K N_D$ additional charged centers. Although this agreement does not necessarily imply the absence of radiation induced scattering other than that from charged centers, it is likely, in view of the probable unimportance of large insulating voids, that charged center scattering accounts for the major part of the mobility change.

Following irradiation, the samples were annealed at temperatures between 100°C and 380°C at intervals of 10°C. The samples were wrapped in platinum foil, placed in a metal container sealed in air, and immersed in an oil bath for 45 minutes at each temperature. Electrical contacts
were made with Cerroseal 35 solder which was removed with aqua regia before each anneal. The Hall constant $R_H$ and the resistivity $\rho$ at 0°C and 78°C were measured after each anneal. Complete resistivity vs $1/T$ data were taken after selected anneals. The annealing data are presented in terms of the fraction unannealed $f$

$$f = \frac{\text{value after irradiation} - \text{value after anneal}}{\text{value after irradiation} - \text{value before irradiation}}$$

of the carrier concentration ($1/R_H$) and the reciprocal of the mobility at 78°C. It is presumed that changes in the latter quantity, $1/\mu = \rho/R_H$, are proportional to changes in the concentration of charged centers. The annealing of the impurity conduction (resistivity from 2° to 10°K) is represented by the fraction remaining $f$ of the activation energy $\varepsilon_2$ and the resistivity intercept $\rho(\infty)$. These data are shown in Figures 4 and 5. Measurements at 0°C indicated a close similarity to the 78°C data.

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**Figure 4.** Isochronal annealing of the 78°C carrier concentration (the squares) and the reciprocal mobility, presumed proportional to the charged scattering center concentration (the circles).

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**Figure 5.** Isochronal annealing of the impurity conduction parameters; the activation energy $\varepsilon_2$ (the squares) and the high temperature intercept $\rho(\infty)$ (the circles). The triangles are the fraction unannealed of the resistivity at 4.2°C, which, by virtue of the constancy of $\varepsilon_2$, is similar to the anneal of $\rho(\infty)$. 
The major features of these data are the lack of major annealing below 300°C of all quantities except the scattering center concentration, the gradual annealing and then distinct annealing stage at 1/μ at 275°C, and the failure of the carrier concentration to completely anneal. The observations are to be contrasted with the results obtained on the annealing of n-type germanium that has been irradiated with Co⁶⁰ gamma rays. (7-9) Annealing of the damage introduced by room temperature gamma ray irradiation of antimony doped germanium indicates a substantial anneal of the carrier concentration at about 157°C with a nearly complete anneal by 277°C. (7) An inverse relationship exists between the recovery of damage and the concentration of antimony following gamma irradiations at 77°K, (8) with the recovery occurring at a lower temperature and with a more unique activation energy for crystals with $1.445 \times 10^{14}$ than for crystals with $1.074 \times 10^{15}$ Sb atoms/cm³. These comparisons suggest that two factors may be responsible for the differences observed in the present experiment. First, the nature of the damage is certainly different for the neutron irradiation than for the gamma irradiation. Second and perhaps more important, the very high antimony content present in the crystals of this experiment would tend to result in a more complete complexing of the interstitials with the impurities forming interstitial antimony or a substitutional antimony-interstitial germanium and vacancy-antimony pairs. Low temperature annealing observed in lightly doped samples has been interpreted as resulting from the motion of individual vacancies or the breakup of impurity interstitial-vacancy complexes. (9,10) The lack of a complete anneal of the carrier concentration in the present case appears
consistent with the observation of Bertolotti, et al.\(^{(11)}\) that remnants of neutron-induced damage regions remain in germanium after an anneal of 12 hours at 460°C.

It is clear that the anneal of the impurity conduction parameters more nearly resembles that of the 78°K carrier concentration than of the scattering center concentration. In particular, the impurity conduction parameters do not reflect the gradual anneal of \(1/\mu\) which occurs between 110°C and 250°C nor the initial drop in the 275°C \(1/\mu\) annealing stage. It seems likely that this anneal of \(1/\mu\) results from a redistribution of charged defects and involves the pairing of oppositely charged species, without reducing the number of deep acceptor states available. Furthermore, it seems unlikely that the pairing involves a significant number of neutral donors, since an accompanying change in \(\varepsilon_2\) does not occur.

Although a detailed interpretation of the annealing is not possible, it is suggested that the sharp annealing stage at 310°C is more likely the breakup of some complex of simple defects with the abundant antimony than the breakup of disordered regions. The damage regions presumably have a broad distribution of sizes and breakup temperatures, which should lead to a relatively featureless anneal. Gradual breakup of the damage regions, we speculate, may occur in the range 110° to 250°, with charged decay products complexing with the ionized antimony, thereby reducing the charged scattering center concentration. That such complexing with some fraction of the \(K_{ND}\) ionized donors in the range 110° to 250°C should not affect \(\varepsilon_2\) and \(\rho(\infty)\) is consistent with the view that the \(\varepsilon_2\) conduction process does not depend on the presence of unoccupied donor ground state.
levels, and supports the contention that the impurity conduction parameters, at least for concentrations near the metallic transition, are only slightly affected by the distribution of compensating defects. Thus, the complexing of the acceptors does not measurably affect the overlap of the occupied donors. The observation that $\epsilon_2$ recovers suggests that the irradiation and anneal have not altered the average distribution of the antimony in any substantial fashion. It should be noted that this is not inconsistent with the observation that the carrier concentration has not completely recovered, since brief initial irradiations did not increase $\epsilon_2$ from zero, although the low temperature Hall coefficient indicated a decrease in the concentration of carriers in the impurity band.

The complex which decays at $310°C$ could possibly be the strongly bound antimony-divacancy. The remaining deep states which do not anneal by $380°C$ are most probably associated with larger damaged regions.

Although the nature of the annealing process in highly doped materials that have been irradiated with neutrons is substantially different from the processes observed for more pure material that has been gamma ray irradiated, there is little evidence that any redistribution of donors occurs as a result of the irradiation.
References
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5