Compensation Dependence of Impurity Conduction in Antimony-Doped Germanium*

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A study has been made of the compensation dependence of impurity conduction in n-type germanium containing between 7×10^{15} and 2×10^{17} antimony atoms cm^{-3}, the compensation being changed by fast-neutron irradiation. Activation energies ϵ_1, ϵ_2, and ϵ_3, characteristic of the resistivity-temperature curves, change continuously with increasing compensation. The energies ϵ_1 and ϵ_2 increase monotonically with compensation, while ϵ_3 passes through a minimum value. The compensation dependence of ϵ_2 is in qualitative agreement with the suggestions that this activation energy is associated with the thermal excitation of electrons from the donor ground state to a band that arises from the interaction of negatively charged donors. For small donor concentrations, the value of the compensation at which ϵ_3 is a minimum is 0.5, in agreement with the Miller-Abrahams theory. At higher donor concentrations, this minimum occurs at smaller compensations. It is suggested that this occurs because the effective compensation at low temperatures is greater than that determined at room temperature, the increase arising because electrons on neutral donors are lost not only to acceptor sites but also to the negatively charged donor band.

I. INTRODUCTION

IMPURITY conduction in germanium is observed in crystals containing a high concentration of donor impurities at temperatures sufficiently low that most electrons are frozen out of the conduction band. For very high impurity concentrations the resistivity and Hall constant are temperature-independent, corresponding to the existence of an impurity band which may overlap the conduction band. At lower concentrations the resistivity-temperature curves exhibit one or more activation energies which are sensitive functions both of the donor concentration and of the compensation. The Hall constant then passes through one or more maxima as a function of temperature.

Fritzsche[1–7] has made extensive studies of the impurity conduction processes. His observations and deductions, along with those of other workers, may be summarized as follows:

(1) The conductivity can in general be expressed by

$$\sigma=\sum_{i=1}^{3}\sigma_i^{(0)}\exp[-\epsilon_i/kT].$$

ϵ_i is the activation energy of the ith conduction process and $\sigma_i^{(0)}$ is the extrapolated value of σ_i for $1/T\to0$. ϵ_1 is the familiar donor ionization energy and is observed in all samples with donor concentrations less than 10^{18} cm^{-3}. The decrease of ϵ_1 with increasing donor concentration, associated with the eventual formation of an impurity band, is well known. ϵ_1 is also observed to increase with compensation. ϵ_2 is an activation energy which occurs only in specimens in the so-called "intermediate concentration range" ($2\times10^{17}>N_D>2\times10^{16}$ Sb atoms cm^{-3}). It increases sharply with decreasing donor concentration and is a sensitive function of applied stress.[6] These observations led Fritzsche to suggest that its primary dependence is on the overlap between wave functions of neighboring donor states. However, no single mechanism has been demonstrated for conduction in this concentration range. The activation energy denoted by ϵ_3 is the most prominent in the conductivity-temperature curves of specimens with an even lower concentration of impurities (the "low concentration" range) and is successfully interpreted as the energy associated with the transition of an electron from an occupied to an unoccupied donor site. Compensation is thus an essential feature for the ϵ_3-impurity conduction mechanism. Although the transition is considered to take place by tunneling, an activation energy still exists because of the need to overcome the Coulomb barriers associated with the compensating impurities. For concentrations such that the resonance energy of the electron exchange process is less than that associated with the Coulomb field (i.e., $N_D<5\times10^{15}$ Sb atoms cm^{-3}), the theories of Miller and Abrahams[8] and others[7,9] correctly predict the dependence of ϵ_3 on donor separation and compensation. In this concentration range ϵ_3 increases with donor concentration and has a minimum value for a given donor concentration when the compensation is one-half. The coefficient $\rho_3^{(0)}=1/\sigma_3^{(0)}$ can also be reasonably well estimated on this model.

(2) In the low concentration range (when only ϵ_3 is observed) the Hall constant passes through a single maximum value near the temperature at which the

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conduction via the impurity levels equals that in the conduction band. In the intermediate concentration range the behavior is more complicated. Two maxima in the Hall constant versus reciprocal temperature curve are generally observed. At temperatures lower than that at which the second maximum occurs the Hall constant generally exhibits an activation energy which is about one-half of that occurring in the equivalent resistivity curve. No change in the sign of the Hall constant has been observed. Hung and Glissman[10] interpreted the behavior of the Hall constant for samples with intermediate donor concentrations in terms of a two-band model. Holstein[11] has developed a theory of the Hall constant applicable to ac measurements on highly compensated material.

(3) The effect of stress on impurity conduction processes is most significant in the intermediate impurity concentration range where it is manifested by a change in ϵ_2. Fritzsche[6] has shown that the sign of the change in ϵ_2 is dependent on the size of the valley-orbit splitting of the donor-impurity element used. For example, the effect of a [111] compression on germanium doped with antimony (valley-orbit splitting $\sim$0.57 meV) is to increase ϵ_2, whereas, the effect on germanium doped with arsenic (valley-orbit splitting $\sim$4.15 meV) is to decrease it. Fritzsche successfully interprets these results by showing that, with stress, the increase of effective Bohr radius (and hence overlap) of donors with large valley-orbit splitting more than compensates for the decrease of overlap which occurs for all donors as a result of the change in shape in the wave functions. The latter arises from the reduced contribution to the wave functions from three of the four conduction-band valleys.

(4) The magnetoresistance associated with impurity conduction has been studied by several workers. In the low-impurity-concentration range, Sladek and Keyes[12] have found a positive magnetoresistance associated with a decrease in size of the overlapping wave functions. In the intermediate impurity-concentration range Sadasiv[13] has also found an increase in ϵ_2 with magnetic field. Degenerate samples showed a negative magnetoresistance[14] whose temperature dependence[15] suggests the existence of an antiferromagnetic interaction between localized electron spins.[16] Yamanouchi[17] has measured the magnetoresistance in both the low and the intermediate concentration range and has found that in the former the main effect is an increase in the pre-exponential constant $\rho_3^{(0)}$ while in the latter it is an increase in ϵ_2 (in agreement with Sadasiv). Mikoshiba's theory[18,19] of magnetoresistance in the low concentration range shows that a contribution from a field-induced change in phase difference between wave functions on neighboring donors is as important as the shrinkage of the individual wave functions.

(5) The frequency dependence of impurity conductivity has been studied by Pollak and Geballe[20] between 10^2 and 10^5 cps. They find an increased contribution to the conduction arising from polarization effects.

(6) Dobrego and Ryvkin[21] have observed a negative photoconductivity associated with impurity conduction. This has been shown[22] to arise from an effective decrease in the compensation produced by trapping of the photoexcited carriers.

(7) Additional information on the interactions between donors at overlap concentrations has been obtained by measurement of the temperature dependence of the magnetic susceptibility[23] and by nuclear-magnetic-resonance studies.[24]

The main feature of impurity conduction which is, as yet, unresolved, is that of the mechanisms responsible for conduction in the intermediate concentration range and in particular the process which gives rise to the activation energy ϵ_2. In order to help to decide between various proposed models,[2,25,26] the compensation dependence of impurity conduction has been studied, with particular emphasis being placed on the behavior of samples in this intermediate concentration range. The difficulty of obtaining specimens of exactly the same donor concentration but with various compensations has been overcome by progressively changing the compensation in a sample of fixed antimony concentration by irradiating with fast neutrons.[27,28] The position and origin of the energy levels associated with the introduced damage are not known in detail. Different techniques of analysis by various investigators have led to different conclusions. However, it is known that the predominant effect of the interstitial-vacancy–type damage produced is that of the introduction of vacant sites which trap electrons. The energy distribution in the forbidden gap of these and other levels should be unimportant as long

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as the Fermi level stays reasonably close to the Sb donor level. The highest level found in neutron-irradiated germanium is a donor lying ~0.2 eV below the conduction band. Evidence for localized disordered regions has also been obtained, but again the predominant effect at low temperatures is a reduction in the number of electrons at Sb donor sites.

The two main advantages of this method of varying the compensation are as follows: (1) Measurements are made on the same specimen, thereby assuring that the donor concentration remains exactly the same. (2) Very good control over the number of acceptors introduced is achieved. By annealing out some of the defects, reversibility of the induced compensation is possible.

II. EXPERIMENTAL DETAILS

The specimens, which, with one exception, had six arms for conductivity and Hall leads, were ultrasonically cut from 1-mm-thick germanium slices. They were 2 cm long and 3 mm wide. No differences were found between samples whose surfaces had been etched in CP 4 and those which were left with a 400-grit finish, although surface conduction would probably be important for resistivities somewhat higher than those measured in this investigation. Contacts were made using Cerroseal 35 solder. The specimens were glued down with GE 7031 to a $\frac{1}{2}$-mil Mylar sheet which in turn was glued onto the copper specimen holder. In later measurements, to avoid possible strain caused by differential expansion, the specimens were glued at one end only. A helium-gas heat-exchange system was built into a liquid-helium cryostat in order that good temperature stability and control could be obtained between 1.5 and 77°K. A Minneapolis-Honeywell germanium thermometer was incorporated into the specimen holder. Precautions were taken to avoid any radiation falling on the specimens.

The neutron irradiations were made at room temperature in a Triga Mark II experimental nuclear reactor. Slow neutrons were absorbed by a cadmium shield which surrounded the specimens. Before each irradiation, however, it was found necessary to remove completely the solder used for contacts in order to avoid long-lived radioactivity. Some room-temperature reverse annealing[28] of the defects was observed but it was sufficiently slow so as not to interfere with the measurements.

TABLE I. Room-temperature (R.T.) resistivities, Hall coefficients, donor concentrations and the average separation between donors (given by $4\pi d^3 N_D/3=1$) of the specimens measured.

Code	Resistivity $\rho_{\text{R.T.}}$ (Ω cm)	Hall coefficient $R_{\text{R.T.}}$ (cm³/Coulomb)	Donor concentration N_D (cm^{-3})	Average donor separation d (Å)
$F1$	0.020	36.4	1.7×10^{17}	112
$L1$	0.029	58.6	1.1×10^{17}	131
$E1$	0.037	84.0	7.4×10^{16}	147
$L2$	0.040	89.0	7.0×10^{16}	150
$F2$	0.048	116	5.4×10^{16}	164
$L3$	0.058	138	4.5×10^{16}	174
$F3$	0.076	179	3.5×10^{16}	190
$F4$	0.088	213	2.9×10^{16}	201
$E2$	0.095	250	2.5×10^{16}	212
$E3$	0.312	930	6.7×10^{15}	328

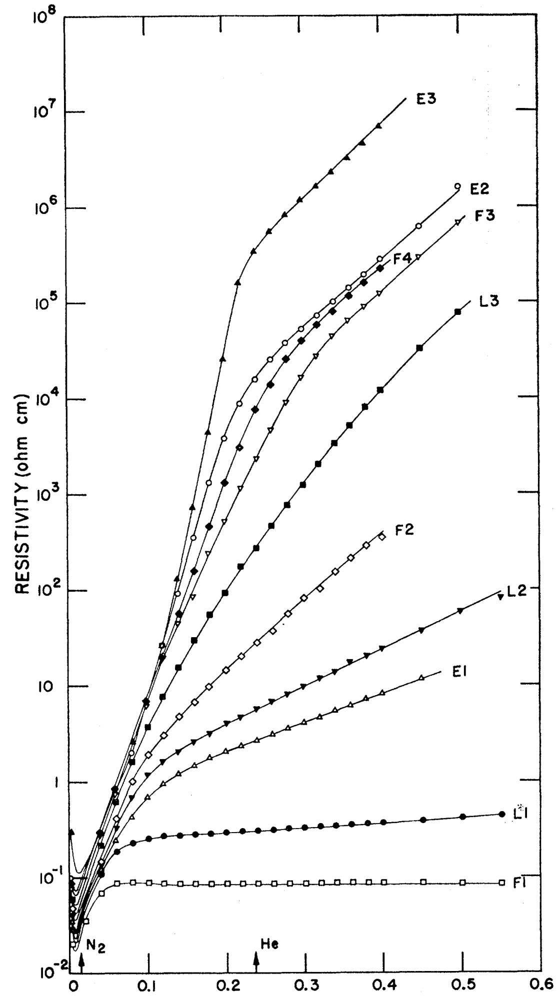

FIG. 1. Variation of resistivity with reciprocal temperature for the specimens listed in Table I.

The conductivity and Hall voltages were measured on a Leeds and Northrup potentiometer, a General Radio electrometer or a Cary 35 vibrating reed electrometer. The electric field was never allowed to exceed 300 mV/cm and normal precautions were taken to avoid errors due to end contact injection, heating, thermal emf's, etc. The Hall effect was measured in a field of 7000 G provided by a Varian 4-in. magnet.

III. EXPERIMENTAL RESULTS

The specimens measured were all antimony doped and are listed in Table I[29] with their room-temperature

[29] Samples with the code letters L and F were cut from slices kindly supplied by Miss Roth, Physics Department, Purdue University and H. Fritzsche, Institute for the Study of Metals, University of Chicago, respectively.

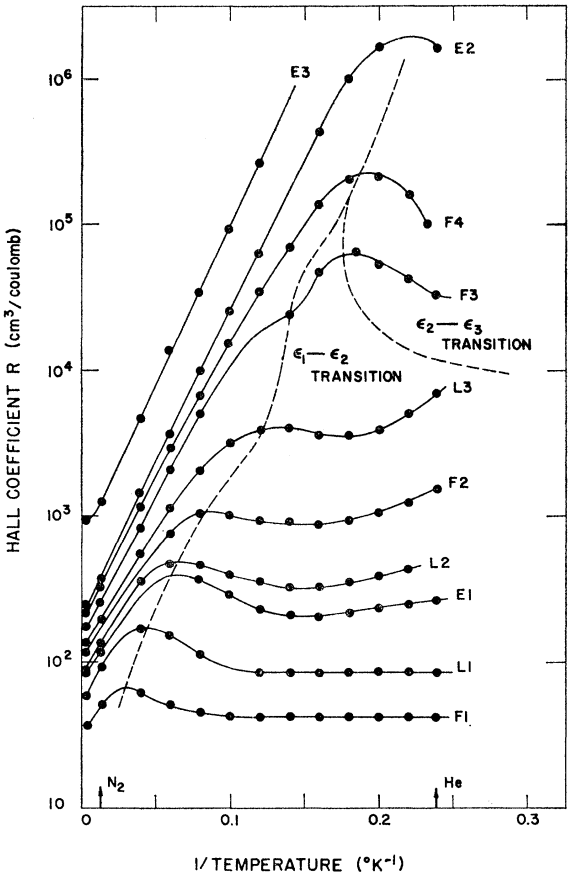

FIG. 2. Variation of Hall coefficient with reciprocal temperature for the specimens listed in Table I. Dotted lines, see text.

resistivities, Hall coefficients, and donor concentrations. The average separation between donors has been obtained using the relation $4\pi d^3 N_D/3=1$. Figures 1 and 2 show the resistivity and Hall coefficient of these samples as a function of temperature. The activation energies associated with impurity conduction processes can be clearly seen in the resistivity curves. The seemingly more complex behavior of the Hall coefficients arises from the following feature: namely, that a maximum in the Hall curves corresponds to a knee or change of slope in the resistivity curves. Thus, for specimens $E2$ and $F4$, the single maximum in the Hall curves occurs at about the same temperature at which the activation energy associated with the resistivity curves changes from ϵ_1 to ϵ_3. For specimen $F3$, ϵ_1, ϵ_2, and ϵ_3 are all distinguishable. The maximum in the Hall curve for this specimen occurs at the same temperature as the ϵ_2-ϵ_3 transition, whereas the inflection on the left of the maximum corresponds to the ϵ_1-ϵ_2 transition. The remainder of the Hall curves show a single maximum corresponding to the ϵ_1-ϵ_2 transition: The temperature required for observation of the ϵ_3 conduction mechanism rapidly decreases as the donor concentration is increased. For specimen $F1$, no activation energy in the ρ or R curve is observed below 10°K indicating that the critical donor concentration for the formation of an impurity band has been exceeded. However, the Hall curve for this specimen still passes through a maximum corresponding to the disappearance of the ϵ_1 mechanism in the resistivity curve.

The variation of ϵ_1, ϵ_2, and ϵ_3 with average donor separation is shown in Fig. 3. A similar plot has been obtained by Fritzsche.[6] The values of ϵ_1 in specimens with high donor concentrations are subject to scatter because of the small temperature range over which the resistivity curves are linear. As $d\rightarrow\infty$, the activation energy ϵ_1 approaches the low-concentration antimony ionization energy of about 10 meV. For $d>300$ Å other workers have found the variation of ϵ_3 with d to be given correctly by Miller and Abrahams' theory.[8] The model is that of an electron tunneling from an occupied donor site to an unoccupied site in the presence of the Coulomb fields arising from compensating acceptors and ionized donors. Because of the difficulty of determining small compensation values experimentally, the compensation $K=N_A/N_D$ is normally used as a variable parameter in the theory in order to fit the data. Specimen $E3$ appears to have a compensation of about 0.04.

For $d<300$ Å the tunneling theory is not expected to be applicable. In fact, as the donor separation is further reduced, ϵ_3 decreases and approaches ϵ_2 at $d\sim150$ Å. ϵ_2 is seen only in specimens which have donor concentrations lying between 2×10^{16} and 10^{17} antimony atoms

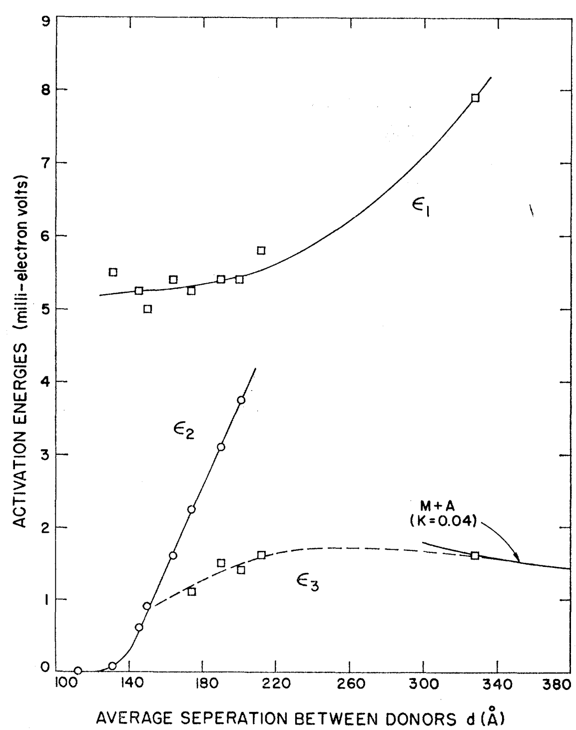

FIG. 3. Variation of ϵ_1, ϵ_2, ϵ_3 with d, the average donor separation. $M+A$ refers to the Miller and Abrahams theory for ϵ_3 with a compensation $K=0.04$.

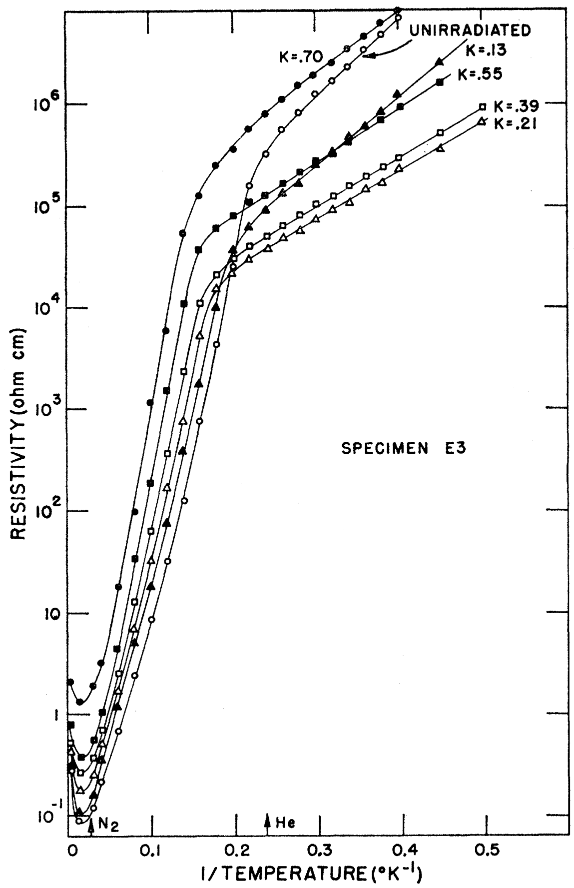

FIG. 4. Variation of resistivity with reciprocal temperature of specimen $E3$ for various values of the compensation.

cm^{-3}. For concentrations greater than about $10^{17}\ \mathrm{cm}^{-3}$, $\epsilon_2=0$. For concentrations $2\times10^{16}<N_D<5\times10^{16}$, ϵ_2 has to be obtained by subtraction of $[\sigma_1^{(0)}\exp(-\epsilon_1/kT)+\sigma_3^{(0)}\exp(-\epsilon_3/kT)]$ from the total conductivity curve. For $N_D<2\times10^{16}\ \mathrm{cm}^{-3}$ the subtraction process becomes uncertain but ϵ_2 is evidently approaching ϵ_1.

A. Determination of the Compensation after a Given Irradiation

The amount of compensation introduced by the fast-neutron irradiations was determined from the change in the room-temperature Hall coefficient. Because of the high level of doping, the intrinsic contribution to the number of free carriers was negligible in all the samples. The R versus $1/T$ curves showed that some carrier freeze-out was present even at room temperature, but the error introduced by not accounting for this is small. This will be clear later when it is shown that the slope of the Hall curves at room temperature does not change significantly with compensation. If the room-temperature Hall coefficient changes from R_i to R_f, assuming no change in the donor concentration, the new compensation is given by

$$K_f=1-R_i(1-K_i)/R_f,$$

where K_i is the initial compensation. For the samples used in this investigation K_i was clearly only a few percent. In samples with low donor concentration this could be seen from the behavior of the Hall constant with temperature. For higher donor concentrations K_i is not expected to be much larger. Some variation is expected between material from various sources but, without information on this, K_i has been taken as 0.025 in all samples. Choosing a slightly different value would not greatly affect the calculated values of K_f, especially for high values of the latter.

Another procedure for determining the compensation would be to calculate the number of defects (and hence acceptor levels) introduced by the irradiation. However three factors made this method impractical. First, the reactor's fast-neutron flux was not known with sufficient accuracy; second, the number of secondary defects created after the primary collision could not be calculated with certainty; third, annealing processes occurring after the irradiation could not easily be accounted for.

Two other methods which are frequently used to obtain values for the compensation cannot be usefully employed for samples with donor concentrations greater than about 5×10^{15} Sb atoms cm^{-3}. The first is to fit the Hall coefficient versus $1/T$ curves to the relationships,[30]

$$R=1/ne,$$

where n is determined by

$$n(n+N_A)/(N_D-N_A-n)=(2\pi m^*kT/h^2)^{3/2}\exp(-\epsilon_1/kT).$$

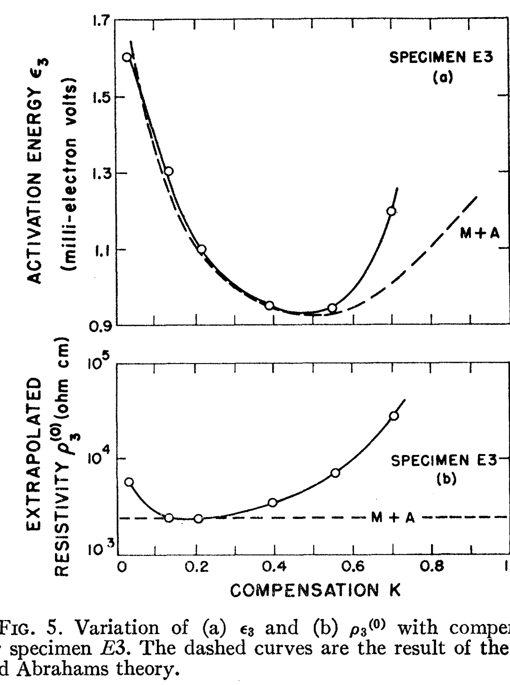

FIG. 5. Variation of (a) ϵ_3 and (b) $\rho_3^{(0)}$ with compensation for specimen $E3$. The dashed curves are the result of the Miller and Abrahams theory.

[30] See H. Brooks, Advan. Electron. Electron Phys. **7**, 87 (1956).

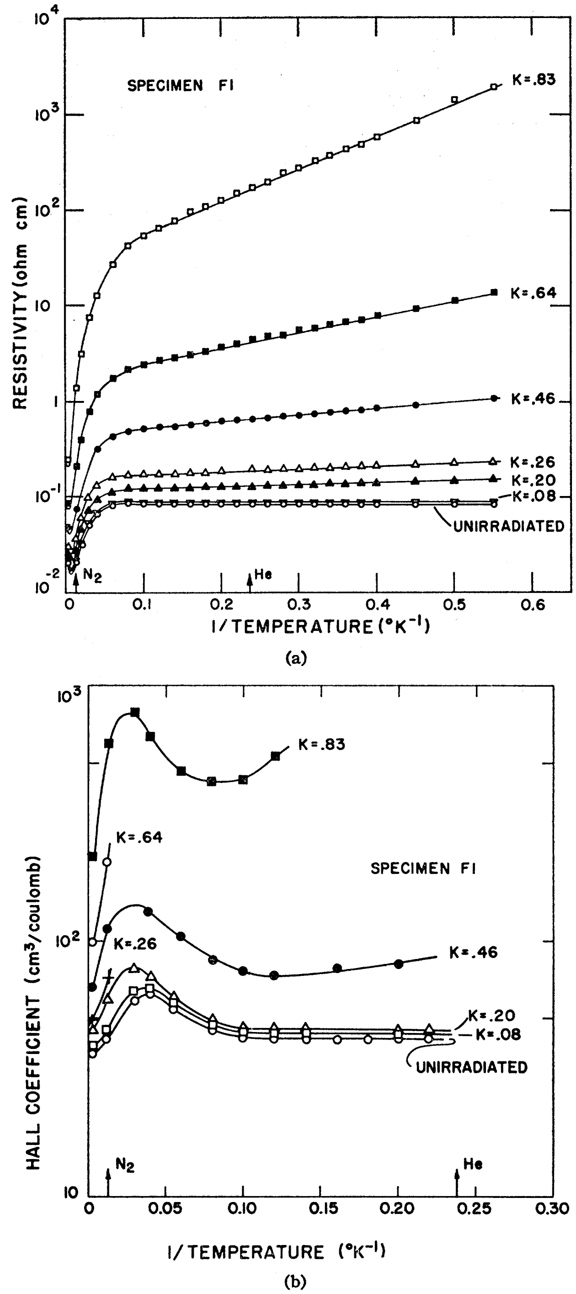

FIG. 6. Variation of (a) resistivity and (b) Hall coefficient with reciprocal temperature of specimen $F1$ for various values of the compensation.

The critical part of the curves for fitting purposes is the nonlinear region. However, it was found that in this region agreement could not be obtained for accepted (or even reasonable) values of the electron effective mass. The second method which is often used to obtain compensation values is that of fitting the mobility versus temperature curves to the Brooks-Herring formula[30] appropriate to ionized-impurity scattering. Again, uncertainties in this method when the donor concentration is high rendered it unsuitable for use on the data presented here.

B. The Effect of Compensation on Specimen $E3$

Specimen $E3$ was the only sample measured which had a sufficiently low concentration of donors for the Miller and Abrahams theory of impurity conduction to be applicable. In view of the good agreement with theory obtained by Fritzsche and Cuevas[4] on a p-type specimen whose compensation was changed by transmutation of Ge^{70} to Ga^{71}, it seemed desirable to make similar measurements using the present technique of radiation damage to change K. In addition, the previous experimental work determined ϵ_3 for values of K between 0.4 and 0.9 only. Figure 4 shows the resistivity of $E3$ as a function of $1/T$ for various values of the compensation. Note that the ϵ_2 conduction process does not occur in this sample. The effect of increasing the compensation is first to reduce ϵ_3 and then to increase it as is shown in Fig. 5(a). Figure 5(b) shows the variation with compensation of $\rho_3^{(0)}$. Also shown in these figures are the results of the Miller and Abrahams theory. Good agreement for ϵ_3 versus K is obtained for $K<0.55$ but no compensation dependence of $\rho_3^{(0)}$ is predicted.

C. The Effect of Compensation on Specimens $F1$ and $L1$

Specimen $F1$ is so highly doped ($N_D=1.7\times10^{17}$ Sb atoms cm^{-3}) that before irradiation no activation energy is observed in the resistivity and Hall curves below 10°K [Fig. 6(a) and 6(b)]. However, after the compensation has been increased by irradiation to above 10%, an activation energy, presumably that associated with the ϵ_2 conduction process, appears. As the compensation is increased further the resistivity at low temperatures rises in a striking manner until at $K=0.83$, it has increased by over four orders of magnitude at 2°K. The corresponding change in ϵ_2 is shown in Fig. 7(a). No ϵ_3 conduction process occurs even at the highest value of compensation reached. Figure 7(b) shows the variation of $\rho_2^{(0)}$ with compensation.

Figures 8(a) and 8(b) show the results of a similar experiment on specimen $L1$. This specimen showed an activation energy before the compensation was increased by irradiation, but the results are qualitatively the same as for $F1$.

D. The Effect of Compensation on Specimens $L2$ and $F2$

Specimens $L2$ and $F2$ show more complicated behaviors than the aforementioned samples with higher donor concentration. In addition to the increase in ϵ_2 with compensation, a new activation energy, assumed to be ϵ_3, appears in the curves. Generally ϵ_2 has then to be obtained by subtraction. Figure 9 shows the resistivity versus reciprocal-temperature plots for specimen $F2$.[31]

The corresponding variations of ϵ_2, ϵ_3, $\rho_2^{(0)}$, and $\rho_3^{(0)}$ with compensation are shown in Fig. 10. Because the variation of ϵ_2 with K is in the opposite direction to that of ϵ_3 [Fig. 10(a)], the resistivity versus $1/T$ curves exhibit peculiar behavior and in particular the resistivity at low temperature oscillates up and down as the compensation is increased. ϵ_3 passes through a minimum value but not at $K=0.5$ as was the case for specimen $E3$ [see Fig. 5(a)]. Similar results for specimen $L2$, also in this intermediate concentration range, are shown in Fig. 11.

E. The Effect of Compensation on Specimens L3, F3, F4, and E2

When the donor concentration is sufficiently low for the uncompensated specimen to show clearly the ϵ_2 and ϵ_3 conduction processes, the effect of compensation is to drive ϵ_2 rapidly towards ϵ_1 leaving the ϵ_3 process to control the resistivity. Specimens $L3$, $F3$, and $F4$ are in this concentration range. Specimen $E2$, with a slightly higher donor concentration, showed no ϵ_2 region. The resistivity curves for $F3$ and $F4$ are shown in Figs. 12 and 13, respectively. Figure 14 shows the variation of ϵ_2, ϵ_3, and $\rho_3^{(0)}$ with compensation for both $L3$ and $F3$. Figure 15 shows similar results for $F4$ and $E2$. Due to uncertainty in the subtraction process used to obtain the contribution to the conduction by the ϵ_2 mechanism, the values of $\rho_2^{(0)}$ are not presented. In all cases ϵ_3 passes through a minimum at a value of $K<0.5$.

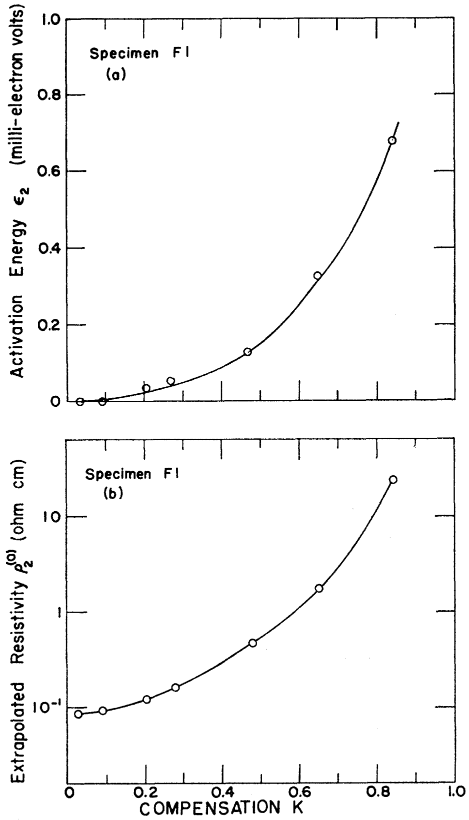

FIG. 7. Variation of (a) ϵ_2 and (b) $\rho_2^{(0)}$ with compensation for specimen $F1$.

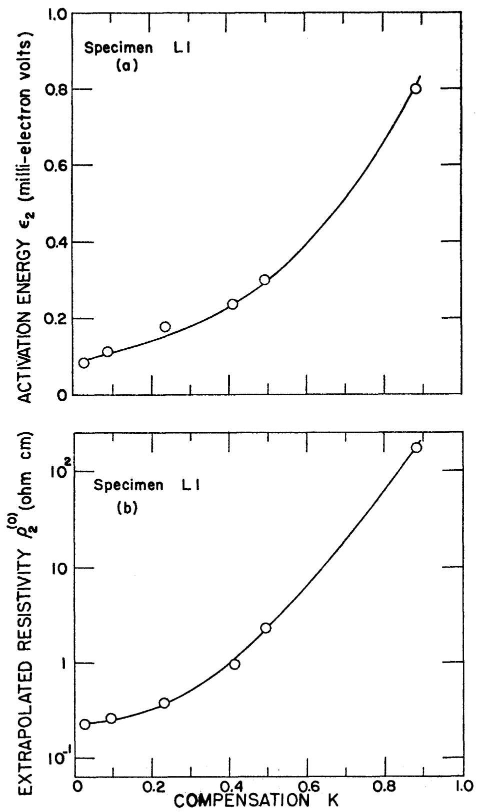

FIG. 8. Variation of (a) ϵ_2 and (b) $\rho_2^{(0)}$ with compensation for specimen $L1$.

IV. DISCUSSION

For the unirradiated samples, the variations with average donor separation of the activation energies obtained from the resistivity plots have been presented in Fig. 3. Several features of these curves have been discussed before and by other workers. For a given donor concentration, the effect of increasing the compensation is to increase ϵ_1 and ϵ_2 monotonically; ϵ_3 passes through a minimum value at $K\leq 0.5$. The quantitative behavior depends strongly on the donor concentration. The following discussion is divided into the detailed behavior of ϵ_1, ϵ_2, and ϵ_3 as a function of compensation and donor concentration.

[31] As for most other specimens, the Hall coefficient was also measured as a function of compensation, but over a smaller temperature range. Because no features other than the increase in ϵ_1 and the shift of the maximum to higher temperature occurred, the results are not presented here.

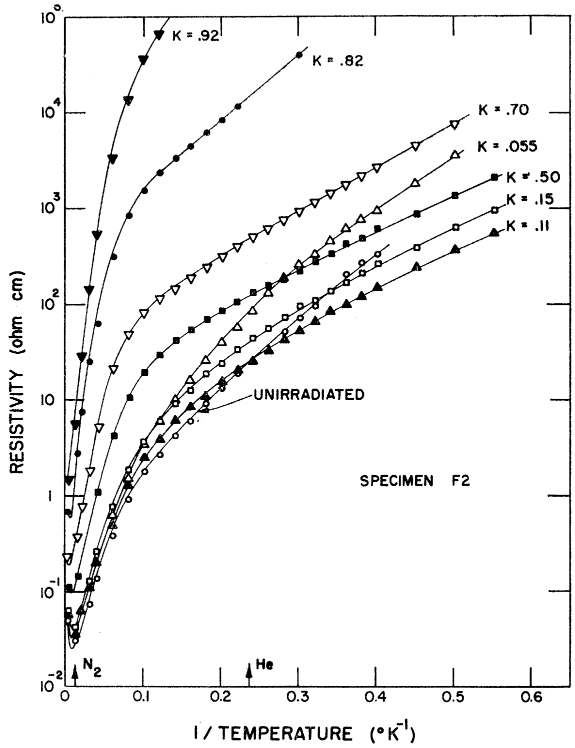

FIG. 9. Variation of resistivity with reciprocal temperature of specimen $F2$ for various values of the compensation.

A. The Activation Energy ϵ_1

The well-known decrease of the donor ionization energy ϵ_1 with increasing donor concentration has been attributed[32] to three effects: first, the increased potential energy of attraction between electrons and ionized donors; second, the increased screening[33] of the ionized centers by free electrons; and third, a change in the dielectric constant giving rise to a greater polarization and a lowering of the conduction band with increasing donor concentration.

At a given temperature and donor concentration, the effect of increasing the compensation will be to increase the numbers of ionized donors and therefore the average energy of attraction. However, the screening effect around each ion will be reduced due to the smaller number of free electrons. Experimentally, with increasing compensation, ϵ_1 is observed to rise slowly at first and then more rapidly as K approaches 1. This is seen in both the resistivity and Hall curves. As the polarization effect mentioned above is probably not so important as the other two effects, the increase with compensation of ϵ_1, which is observed in all specimens, suggests that the screening effect is dominant in determining the donor ionization energy for highly doped specimens.

[32] See P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).

[33] G. W. Lehman and H. M. James, Phys. Rev. **100**, 1698 (1955).

A decrease of ϵ_1 to zero is anticipated when d is of the order of an effective Bohr radius but the shift of the onset of impurity conduction processes to higher temperatures as the donor concentration is increased precludes the possibility of observing this directly in resistivity or Hall-effect measurements.

B. The Activation Energy ϵ_2

A completely satisfactory theory has not been evolved for the intermediate range in which ϵ_2 is prominent.

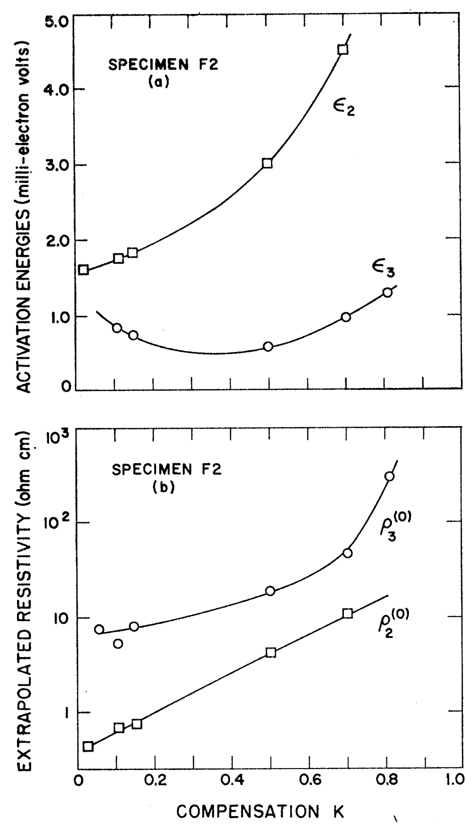

FIG. 10. Variation of (a) ϵ_2 and ϵ_3, and (b) $\rho_2^{(0)}$ and $\rho_3^{(0)}$ with compensation for specimen $F2$.

Fritzsche[2] first suggested that ϵ_2 may be associated with energy required to put a second electron onto a neutral donor site. Mott and Twose[7] have discussed the transition from a nonconducting state to the metallic state. state. The authors point out that as the distance between impurities decreases, the magnitude of the overlap integral for electrons on two different sites may increase to such a magnitude that a long-range order (perhaps antiferromagnetic) may exist. Under these conditions, it is possible that the lowest energy state of the system will be nonconducting but separated from this by a small energy will be a conducting state which can be reached by thermal excitation from the ground state. It seems reasonable to associate ϵ_2 with this excitation energy. The energy separation between these states depends upon the overlap and decreases with increased overlap. As the concentration increases, the energy between the two states decreases and becomes zero. It is not unreasonable to associate this state with a system which shows no temperature dependence of the conductivity at low temperature but still exhibits an ϵ_1 at higher temperatures.

A theory based on Fritzsche's suggestion for the ϵ_2 mechanism has been developed by Mikoshiba.[34] He considers a band formed by negatively charged donors, ϵ_2 then being the energy gap between the neutral-donor ground state and the bottom of this band. The problem of calculating the interaction energy is similar to that of the hydrogen molecule. He obtains

$$\epsilon_2 = \epsilon_1 - (ne^2s^2/\kappa_0 a)[1+(sd/a)]\exp[-(sd/a)],$$

where s is a screening parameter, n is the number of nearest neighbors, and a is the effective Bohr radius of

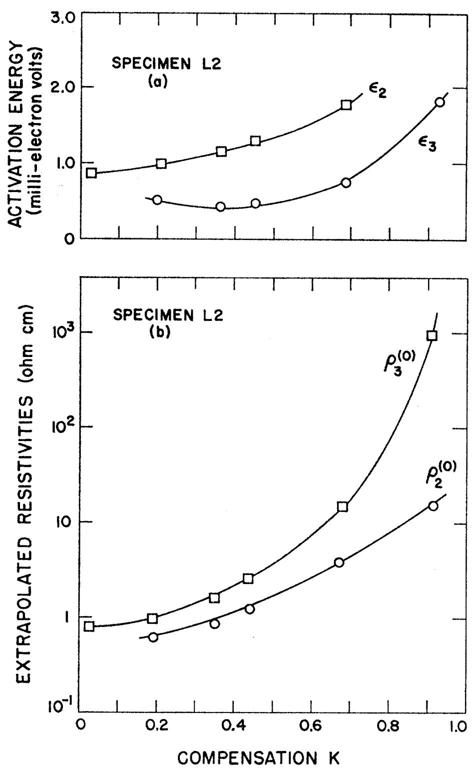

FIG. 11. Variation of (a) ϵ_2 and ϵ_3, and (b) $\rho_2^{(0)}$ and $\rho_3^{(0)}$ with compensation for specimen $L2$.

the N_D^- state. Taking[34] $s=0.7$ and $n=2$, a fit with the experimental results presented here is obtained with $a=32$ Å.

Mycieleski[26] proposes that ϵ_2 may be due to a hopping over the Coulomb barrier separating an occupied donor site and an unoccupied one. He suggests that tunneling through this barrier (which is the process considered by Miller and Abrahams in their calculation of ϵ_3—see below) may not always occur because of the possible incoherence between the initial- and final-state wave functions arising from carrier-phonon interaction. The expression of ϵ_2 obtained by Mycieleski is

$$\epsilon_2 = \epsilon_1 - (3e^2/\kappa_0 d).$$

A best fit to the experimental results on this theory is obtained by taking $d=0.87N_D^{-1/3}$ and $\epsilon_1 \sim 12.6$ meV. This value of ϵ_1 is considerably higher than the experimental value. Since d is essentially unaffected by changes in compensation, this expression for ϵ_2 indicates that the changes in ϵ_2 with compensation are determined by changes in ϵ_1.

Nishimura[35] has calculated ϵ_2 using a hydrogenic model for the donor-ground state and an exponential-type wave function to describe the behavior of an electron in a weakly bound negative donor-ion state. A band results from the interaction between the states of the negatively charged donors. The value of ϵ_2 (in meV) becomes

$$\epsilon_2 = [4.54 - 4.43\times 10^{-17} N_D(1-K)],$$

where N_D is the donor concentration. The theory was developed for small compensation whereby the potential

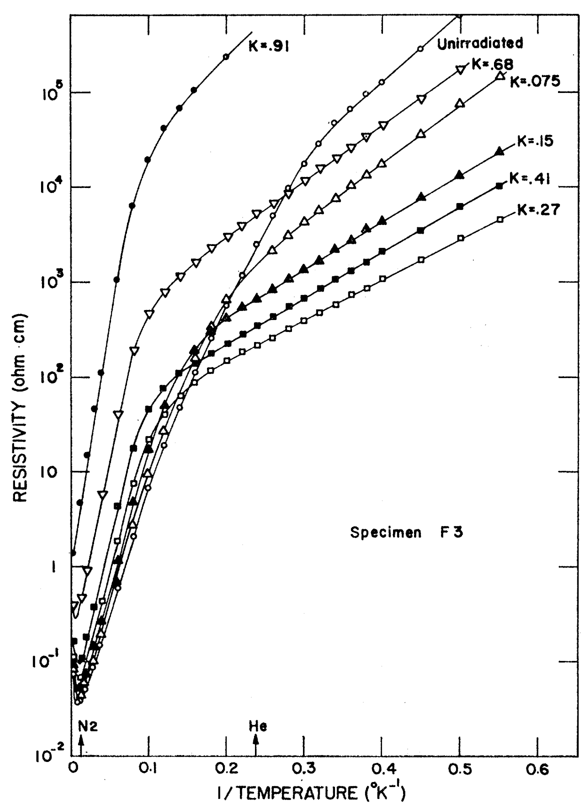

FIG. 12. Variation of resistivity with reciprocal temperature of specimen $F3$ for various values of the compensation.

[34] See F. H. Pollak, Phys. Rev. 138, A618 (1965).

[35] H. Nishimura, Phys. Rev. 138, A815 (1965).

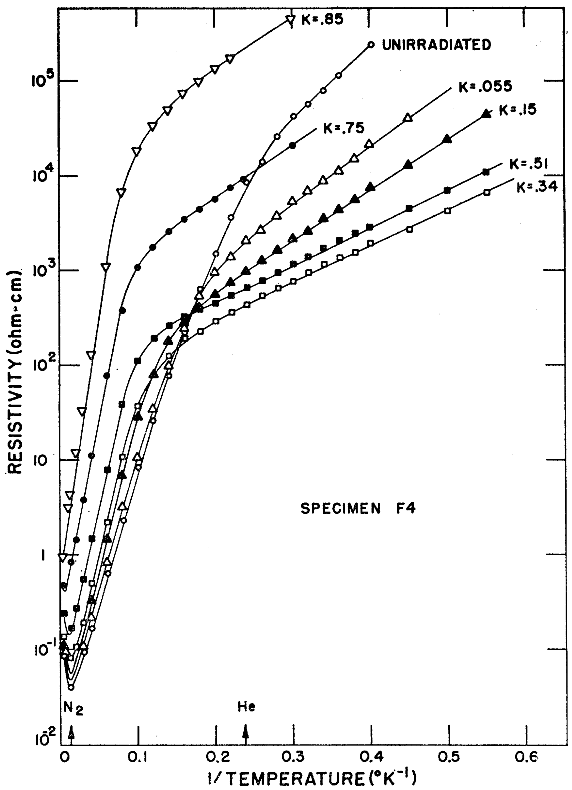

FIG. 13. Variation of resistivity with reciprocal temperature of specimen $F4$ for various values of the compensation.

fluctuations due to ionized donors and acceptors is neglected.

Frood[25] has proposed that the interaction among donor excited states becomes sufficiently great at large concentrations that a dielectric catastrophe occurs. Conduction then takes place in a band, formed by overlap of the excited states of the donors. This band lies in the tail of the conduction band. ϵ_2 is presumed to arise from excitation from the donor ground state into this band. Results of the stress measurements[6,34] and the studies of impurity conduction with other impurities, both donor and acceptor, suggest that this probably is not the mechanism. In addition no ϵ_1 is expected on this model.

With the exception of Nishimura's expression, no explicit dependence of ϵ_2 upon compensation has been considered in the above theories. Since ϵ_2 depends upon the overlap between neighboring donor wave functions, it is tempting to suggest that the effect of increasing the compensation is essentially equivalent to decreasing the donor concentration. The increased average separation between neutral donors at a compensation K is $d'=d(1-K)^{-1/3}$ where d is the average donor separation in the uncompensated sample. Thus, a sample with donor concentration N_D and compensation of 0.5 would have the same ϵ_2 as a sample with donor concentration $N_D/2$ and compensation of zero.

This simple view leads to a linear variation of ϵ_2 with K. Figure 16 shows that this is not in agreement with the data. In all specimens the variation of ϵ_2 with K is almost linear on a log plot. Specimens $F1$ and $L1$ appear to lie in a class of their own. When uncompensated, these specimens had ϵ_2 values which lay off the extrapolated ϵ_2 versus d line (see Fig. 3); presumably the interaction between neighboring wave functions is of a different magnitude in these specimens than in the remainder. The slopes of the other log ϵ_2 versus K lines increase monotonically with decreasing donor concentration.

Evidently the effect of compensation on ϵ_2 involves more than an increase in the average separation between neutral donors. Inclusion of the field of the ionized donors and acceptors in the treatment of the lattice potential and the associated change in the donor wave functions from spherical symmetry is almost certainly necessary. Qualitatively, the positive (negative) field of the ionized donors (acceptors) tends to increase the overlap between two nearby neutral donors and to alter the spherical distribution of the wave function. The rate of change of ϵ_2 with respect to K might be less than would be expected on the basis of a simple increase in average donor separation. This is indeed the case.

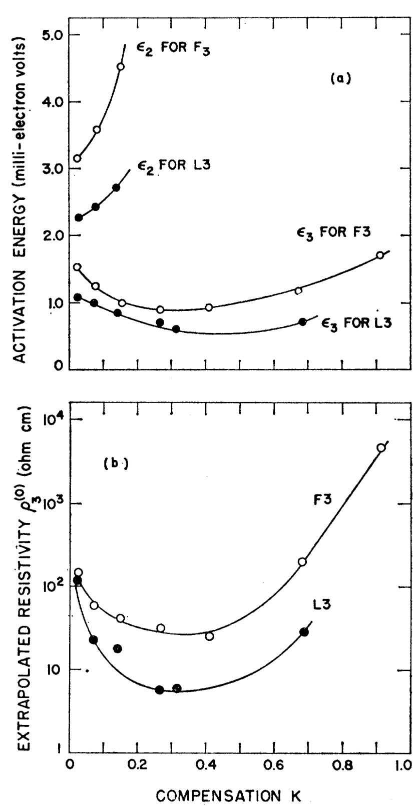

FIG. 14. Variation of (a) ϵ_2 and ϵ_3, and (b) $\rho_3^{(0)}$ as a function of compensation for specimens $L3$ and $F3$.

C. The Activation Energy ε_3

In samples of relatively low donor concentration the variation of ϵ_3 with d is correctly given by the Miller and Abrahams theory.[8] For low values of compensation K they obtain

$$\epsilon_3 = e^2(4\pi N_D/3)^{1/3}(1-1.35K^{1/3})/\kappa_0.$$

It is worth noting that if N_A/N_D is substituted for K and if the factor 1.35 is replaced by 2 the above equation becomes

$$\epsilon_3 = e^2(1/d - 2/A)/\kappa_0,$$

which is the expression obtained by Mott.[7] d and A are the average separations between donors and acceptors, respectively. When K is small, d is also the average separation between a donor and a neighboring acceptor because an acceptor does not go into the random array of impurities in any way different than does a donor. The first term in Mott's expression is simply the energy required to remove the carrier[36] from its trapped site out of the field of a compensating acceptor to which it is attracted. The second term suggests that the carriers, in order to be mobile in the crystal, need not go beyond half the average distance between acceptors.

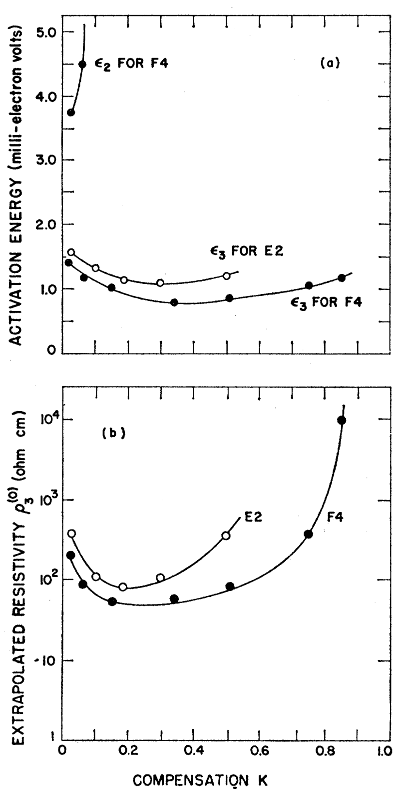

FIG. 15. Variation of (a) ϵ_2 and ϵ_3, and (b) $\rho_3^{(0)}$ as a function of compensation for specimens $F4$ and $E2$.

[36] At low K this will be a hole on a donor site.

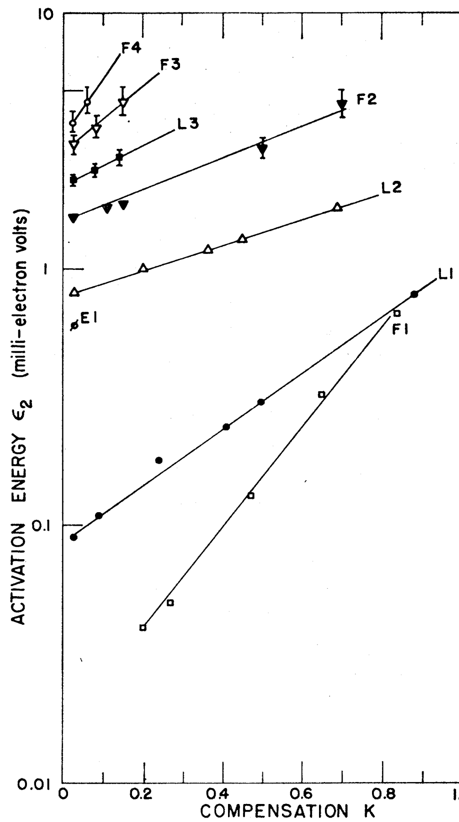

FIG. 16. Variation of ϵ_2 with compensation K for the specimens listed in Table I. Specimen $E1$ was not measured as a function of compensation.

Figure 3 shows that in the intermediate concentration range ϵ_3 decreases with increasing donor concentration. This behavior has not previously been discussed. Two features seem significant: (i) The maximum in ϵ_3 occurs at a value of d not too much below the limit of validity of the Miller-Abrahams theory. (ii) the decrease of ϵ_3 with decreasing d appears when the ϵ_2 conduction process is manifested. If the ϵ_2 process is associated with the transfer of electrons to a band formed from negatively charged donor states, as discussed above, there must be an accompanying effect on ϵ_3 for those samples in which both processes are operative. In fact, the effect is almost equivalent to simply increasing the compensation in the sample; the only difference being that an electron is transferred into a delocalized state rather than to a neutral acceptor. Thus the number of positively charged donor sites N_D^+ will be increased from N_A to N_A+N_D', where N_D' is the number of donor sites which have lost their electrons to the N_D^- band formed from negatively charged donor sites. The effective compensation $K_{\rm eff}$ will be related to the actual compensation K by

$$K_{\rm eff} = (N_A+N_D')/N_D = K + (N_D'/N_D).$$

If 12% of the donor sites lose their electrons to the band, ϵ_3 would be reduced by about a factor of 2. Of course, as ϵ_2 becomes smaller a larger number of donor sites are expected to lose their electrons to the N_D^- band. The Miller-Abrahams theory for ϵ_3 may well be applicable at lower values of d than expected if the effective increase in compensation could be accounted for quantitatively.

The variation of ϵ_3 with compensation has been shown for the various specimens in Figs. 5, 10, 11, 14, and 15. Specimen $E3$ is the only one expected to lie in the concentration range of the Miller-Abrahams theory. As K is increased this theory predicts a minimum of ϵ_3 when K reaches 0.5. This can be visualized by considering the resistivity which, in the appropriate temperature range, is given by $\rho=\rho_0 \exp\epsilon_3/kT$. Noting that the variation of ρ with K is essentially controlled by the exponential term, a minimum in ϵ_3 can be predicted from a minimum in ρ; the latter occurs because at a low K there are only a few vacant sites to which electrons can jump while at high K there are only a few electrons. The theory fits the measured values of ϵ_3 for specimen $E3$ [see Fig. 5(a)] up to $K=0.55$ beyond which the experimental curve lies above the theory. A similar deviation has been observed by Fritzsche and Cuevas[4] at $K=0.7$. The lower value of K reported here at which theory and experiment disagree could suggest that the technique of irradiation damage used to change the compensation may be suspicious at high K values. One possible reason for this could be interference from deep donor levels introduced by the irradiations, which become important when the Fermi level is sufficiently low. However, this cannot be concluded on the basis of the one result.

As the donor concentration is increased, the minimum in ϵ_3 shifts to lower K values. A simple explanation for this follows from the above discussion of ϵ_3 in the intermediate concentration range where it was suggested that the presence of donors that have lost electrons to a band leads to an effective increase in the compensation. Thus, if the minimum in ϵ_3 occurs where the effective compensation is 0.5, as predicted on the Miller-Abrahams theory, then it will occur at a measured compensation of less than 0.5. For the case considered above of 12% of the donors losing their electrons to a band formed from negatively charged donors, a minimum in ϵ_3 is expected at a value of $K=0.38$.

Interpretation of the variation of $\rho_2^{(0)}$ and $\rho_3^{(0)}$ with compensation has not been attempted. Theoretically it is much more difficult to calculate the magnitude of the resistivity than the activation energy associated with an impurity conduction process. This is clear from the Miller-Abrahams theory which, in the low concentration range, correctly predicts ϵ_3 but results in an independence of $\rho_3^{(0)}$ with compensation [see Fig. 5(b)]. Mott's trapping model predicts a compensation dependence of $\rho_3^{(0)}$ which has the same sign as found here for low K values in specimen $E3$ but there is disagreement quantitatively. It is not clear how to calculate $\rho_2^{(0)}$ on Fritzsche's model of ϵ_2. In addition, if the technique of irradiation damage used here to change K results in the production of localized regions of disorder, a calculation of the resistivity in both the ϵ_2 and ϵ_3 regions would be even more difficult.

V. SUMMARY

The present experiments provide data on the compensation dependence of the activation energies for conduction ϵ_1, ϵ_2, and ϵ_3 of n-type germanium containing between 7×10^{15} and 2×10^{17} antimony atoms cm^{-3}. ϵ_1 and ϵ_2 are found to increase monotonically with increasing compensation. An initial decrease in ϵ_3 with increasing compensations is followed by an increase as K approaches unity.

The compensation dependence of ϵ_2 is in qualitative agreement with the suggestions that this activation energy is associated with the thermal excitation of electrons from the donor ground state to a band which arises from the interaction of negatively charged donors. It is believed that quantitative agreement is absent because of the neglect of the potential arising from the ionized donors and acceptors. These data however do not necessarily rule out other mechanisms.

The value of the compensation for which ϵ_3 is a minimum is about 0.5 for a donor concentration of 6.7×10^{15} cm^{-3}. This is as predicted by Miller and Abrahams. At higher concentrations of donors, the minimum occurs at lower values of compensation. It is suggested that this departure from the Miller-Abrahams theory for ϵ_3 may be associated with the same mechanism that gives rise to ϵ_2. As an increased number of electrons are ionized into the band formed from negatively charged donors, the actual compensation will apear to be greater than the compensation determined from the high-temperature Hall effect. Thus the minimum in ϵ_3 will occur at compensations which appear to be less than one-half.

ACKNOWLEDGMENTS

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