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Effect of Minority Impurities on Impurity Conduction in *p*-Type Germanium[†][*]

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Hall coefficient R and resistivity ρ of various p-type germanium samples which contained the same concentration of acceptors N_A but different amounts of compensating donors N_D have been measured between 300°K and 1.3°K. The process of impurity conduction at low impurity concentrations differs from that at high concentrations in that it requires the presence of empty majority centers. As in the case of n-type Ge, the two different impurity conduction processes could be distinguished by observing the change of ρ resulting from a change in the degree of compensation in the temperature range of impurity conduction. At large impurity concentrations ($N_A=2.4\times10^{17}$/cc) the resistivity is independent of temperature only if the concentration of mobile carriers is sufficiently large. The resistivity increases with a finite activation energy in strongly compensated samples.

I. INTRODUCTION

It has been emphasized by several authors[1] that at small impurity concentrations ($N<2\times10^{16}$/cc in Ge) impurity conduction[2,3] is not possible unless compensating impurities produce empty majority centers. The reason for this is that an electron exchange interaction between occupied impurity centers which are separated by more than a few "radii" of the ground-state wave function of an impurity can only yield an exchange of carriers but no transport of charge. One expects that if compensators are added, the resistivity ρ of impurity conduction first decreases because there are more empty centers into which carriers can jump. But at higher degrees of compensation, ρ should increase because there will be a decreasing number of mobile carriers occupying majority centers. In the case of complete compensation, impurity conduction again vanishes because all donors are empty and all acceptors are occupied with electrons.

At large impurity concentrations ($N>10^{17}$/cc in Ge) on the other hand, the localization of the carriers around individual impurities is sufficiently removed so that they can migrate through the crystal without the presence of empty centers and hence of compensators. On the basis of this one expects, in the high-N range, the resistivity ρ of impurity conduction to be finite for zero compensation, and to increase continuously until it becomes infinite for complete compensation.

The initial decrease of ρ in the low-N range and the increase of ρ in the high-N range upon adding compensating impurities has already been observed in n-type germanium.[4] The two different processes for impurity conduction could be distinguished in this way.

The present paper reports measurements of the effect of compensation on impurity conduction in p-type germanium at low and at high acceptor concentrations. They were performed to investigate whether the same criterion can be used to distinguish the two impurity conduction processes in p-type germanium.

II. PREPARATION OF SPECIMENS

p-type germanium containing various degrees of compensation were prepared in two different ways. In one the crystals were grown[5] from melts which contained pure germanium and zone-refined InSb. Because of the larger segregation coefficient[6] of Sb as compared to that of In in Ge, an additional amount of In-doped Ge had to be added to obtain crystals with the desired excess of In.

Other samples were prepared by irradiating pure Ge with thermal neutrons.[7] The samples were exposed[8] in a facility that provides a cadmium ratio of 3.2, a thermal neutron flux of 1.3×10^{13} neutrons/cm^2/sec, and a fast (>0.1 ev, <1 Mev) neutron flux of 2.9×10^{12} neutrons/cm^2/sec. After waiting 3 months, i.e., about 8 half-lives of the longer living Ge^{71}, the specimens were annealed at 450°C for 24 hours to heal the damaging effect of the high-energy particles. The capture cross sections and the abundances of the Ge^{70} and Ge^{74} isotopes yield a value of 3 for the ratio of the Ga (acceptor) to As (donor) concentrations produced by transmutation.

III. RESULTS AND DISCUSSION

In order to observe the effect of compensation on impurity conduction, samples will be compared which have the same concentration of acceptors N_A but different amounts of compensating donors N_D, i.e., dif-

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[1] P. Aigrain, Physica **20**, 978 (1954); W. Schottky, Manuscript of Zurich Seminar, 1955 (unpublished); E. M. Conwell, Phys. Rev. **103**, 51 (1956); N. F. Mott, Can J. Phys. **34**, 1356 (1956).

[2] C. S. Hung and J. R. Gliessman, Phys. Rev. **79**, 726 (1950); **96**, 1226 (1954); C. S. Hung, Phys. Rev. **79**, 727 (1950).

[3] H. Fritzsche, Phys. Rev. **99**, 406 (1955).

[4] H. Fritzsche, J. Phys. Chem. Solids **6**, 69 (1958).

[5] L. Roth, Purdue University Quarterly Report, October–December, 1956 (unpublished).

[6] J. A. Burton, Physica **20**, 845 (1954).

[7] K. Lark-Horovitz, Elec. Eng. **68**, 1047 (1949); Cleland, Lark-Horovitz, and Pigg, Phys. Rev. **78**, 814 (1950).

[8] We are very grateful to J. H. Crawford, Jr., and J. W. Cleland for irradiating these specimens in the Oak Ridge National Laboratory reactor.

TABLE I. R and ρ at 290°K and 77°K.

Sample	298°K R (cm^3 coul^{-1})	 ρ (ohm-cm)	77°K R (cm^3 coul^{-1})	 ρ (ohm-cm)
a	1200	0.484	1110	0.0865
b[a]	1380	0.590	1390	0.137
c[b]	2880	1.25	2820	0.250
d	25	0.029	27	0.024
e[a]	43	0.051	59	0.056
f[b]	122	0.123	220	0.154
g[b]	225	0.264	460	0.51

[a] Neutron-irradiated specimens; sample *e* was measured by C. S. Hung and J. R. Gliessman, Phys. Rev. **96**, 1226 (1958).
[b] InSb added to the melt.

TABLE II. Sample properties.

Sample	N_A (cm^{-3})	$K=N_D/N_A$	ϵ_3[a] (10^{-3} ev)	ρ at 2.5°K (ohm-cm)
a	6.1×10^{15}	0.05	1.6	1.3×10^{6}
b	6.8×10^{15}	0.33	0.56	2.2×10^{3}
c	6.5×10^{15}	0.6	0.58	3.0×10^{4}
d	2.5×10^{17}	0	0	0.03
e	2.3×10^{17}	0.33	0	0.09
f	2.4×10^{17}	0.7	0.22	2.35
g	2.4×10^{17}	0.8	0.38	49

[a] For the definition of ϵ_3 see reference 11.

ferent degrees of compensation $K=N_D/N_A$. Three samples of the low-N range having approximately $N_A=6.5\times10^{15}$/cc were selected and four samples of the high-N range with $N_A=2.4\times10^{17}$/cc.

Table I lists the Hall coefficient R measured in a magnetic field of 600 gauss and the resistivity ρ at 298°K and 77°K. The acceptor concentration N_A and the degree of compensation K of these samples are given in Table II. The values of N_A and K of the doubly-doped samples were calculated[9] from the ionized impurity scattering at 77°K using the Brooks-Herring formula.[10] In the case of the neutron-irradiated samples, the values of K obtained from the mobility data could be compared with the values calculated more accurately from the scattering cross sections and abundances of the two germanium isotopes. The comparison showed an agreement of the K values to within $\pm10\%$ in the low-N range. At large impurity densities the values of K quoted in Table II for the samples f and g have significance only in their relative magnitudes.

Figures 1 and 2 show the results of the Hall and resistivity measurements between 300°K and 1.3°K. One observes the sudden change of slope of the resistivity curves at the onset of impurity conduction. The maxima in the Hall curves occur at the temperatures at which the two competing conduction processes, valence band conduction predominant at higher temperatures, and impurity conduction predominant at low temperatures, are of equal magnitude.

Comparing the resistivities due to impurity conduction at a fixed temperature, say 2.5°K (see last column of Table II), one observes the expected minimum of ρ at small N_A, and the continuous increase of ρ at large N_A, as K increases. This qualitative result is unaffected by small differences in N_A within the two groups of samples because of the large resistivity changes resulting from the changes in compensation.

The activation energies ϵ_3 determined[11] from the slopes of the resistivity curves at the lowest temperatures are listed in Table II. The value of ϵ_3 decreases in the low-N range from $\epsilon_3=1.6\times10^{-3}$ ev to $\epsilon_3=0.56\times10^{-3}$ ev as the compensation is raised from $K=0.05$ to $K=0.33$. There is almost no further change of ϵ_3 after increasing the compensation to $K=0.6$. Approximately the same value of $\epsilon_3=(5.5\pm0.5)\times10^{-4}$ ev has been found in the case of many other samples in the range of concentrations $7\times10^{14}<N_A<2\times10^{16}$/cc and the range of compensations $0.3<K<0.8$. Even the samples of the high-N range seem to approach this value at large K.

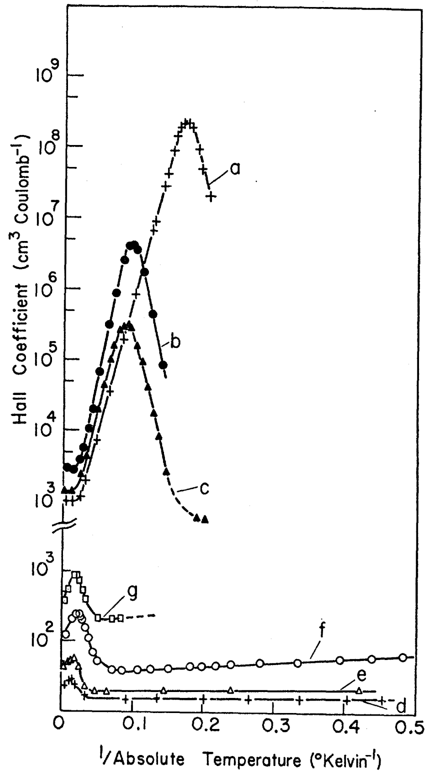

FIG. 1. Effect of different degrees of compensation $K=N_D/N_A$ on the Hall coefficient of p-type Ge. The upper three curves were measured on samples with $N_A=6.5\times10^{15}$/cc, the lower four curves on samples with $N_A=2.5\times10^{17}$/cc. Table II lists the values of K for each sample.

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

[10] H. Brooks, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1956), Vol. 7, p. 87.

[11] The temperature dependence of the conductivity σ is approximated by a sum of exponential terms $\sigma=\Sigma_{i=1}^{3}C_i\exp(-\epsilon_i/kT)$, in which the last term represents σ in the low-temperature limit. For details see references 3 and 4.

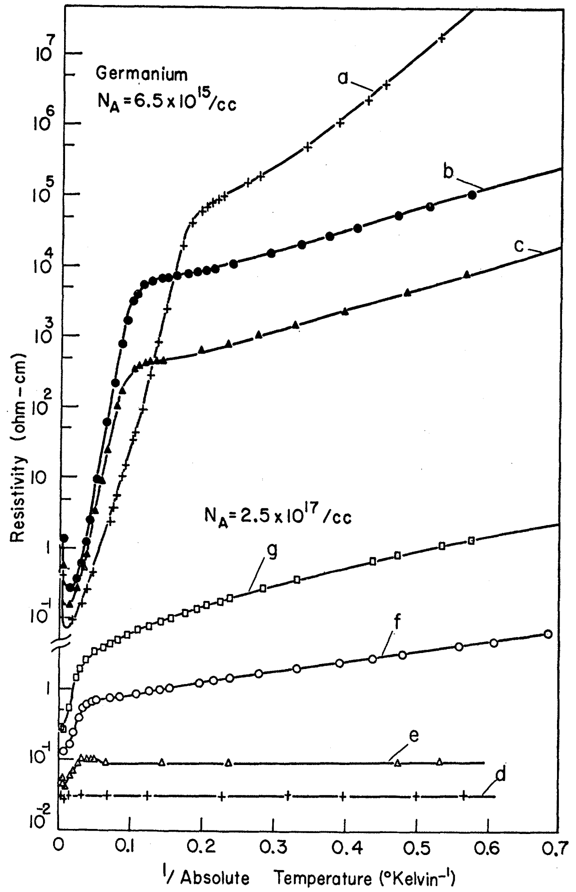

FIG. 2. Effect of different degrees of compensation $K = N_D/N_A$ on the resistivity of *p*-type Ge. The lettering of the samples agrees with that of Fig. 1 and of the tables.

The activation energy ϵ_3 has been interpreted by Mott[1] as being due to the Coulomb repulsion between the charge carriers and the charged compensating impurities. Comparing ϵ_3 of sample *a* with the value obtained from Mott's model, using the statistical calculation of Price,[12] one finds that the experimentally observed value is larger than the calculated value by approximately a factor of two. Mott's model can in its present form not be compared with the strongly compensated samples *b* and *c*, because in these almost every acceptor is a nearest neighbor of a donor so that a distinction between free states and trap states becomes meaningless. At larger degrees of compensation the value of ϵ_3 was found to be nearly the same in a wide range of impurity concentrations. This might be an indication of a different process which gives rise to a thermally activated impurity conduction.

The resistivity curves of the strongly compensated samples *f* and *g* of the high-*N* range seem to show the presence of an impurity ionization energy between about 300°K and 50°K which decreases with decreasing *K* (or increasing concentration of mobile holes) until it vanishes at $K=0$. It seems as if bound states can exist even at these large acceptor concentrations, at which the overlap of the individual acceptor wave functions is substantial, provided the concentration of mobile carriers is small. This indicates that, as Lehman and James[13] pointed out, the screening effect of the mobile charges is important for reducing the energy difference between the various impurity centers.

The Hall coefficients remain positive in the low-temperature range. At temperatures below the Hall maximum the Hall coefficient usually reaches a value which is lower by a factor between 1.5 and 2 than that at room temperature. The Hall curve of sample *f* continues to rise at the lowest temperatures. Its slope is only about one-half the slope of the corresponding resistivity curve.

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[12] P. J. Price, IBM J. Research Develop. **2**, 123 (1958).

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